



Ethereal oxygen influences on solvomercuration and hydrogenation reactions
by Steven Ben Glancy

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemistry

Montana State University

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Abstract:

Influences of the ethereal oxygen on the reactivity of cis-8-oxabicyclo[4.3.0]non-3-ene in solvomercuration and catalytic hydrogenation reactions are examined. The solvomercuration rate enhancement observed for this compound, compared to its carbon analog, is examined using the law of increasing electron demand. The rate decrease observed with the substitution of a vinyl proton with a methyl group is discussed in relation to the present solvomercuration model. The results presented indicate that changes in solvomercuration rate are due to changes in the rate of the solvolysis step and not the stability of the mercurinium ion intermediate.

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These results also show that due to the size of cis-8-oxabicyclo[4.3.0]nonane, unlike THF, it inhibits both cyclohexene adsorption as well as hydrogen adsorption.

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Steven Ben Glancy

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of

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MONTANA STATE UNIVERSITY
Bozeman, Montana

December 1983

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APPROVAL

of a thesis submitted by

Steven Ben Glancy

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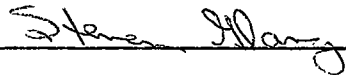
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to
my wife and friend

VITA

Steven Ben Glancy, the only son of Jack and Carleen Glancy, was born on December 15, 1953, in Adrian, Michigan. After living in California until the age of 11, he moved with his family to Jackson, Mississippi. After graduating from Callaway High School in June 1972, he moved to Billings, Montana with his mother and two of his sisters. After receiving a Bachelor of Science degree in chemistry in June 1977 from Eastern Montana College he pursued graduate studies in chemistry at Montana State University. On March 20, 1982 he married Vickie Leigh Nelson.

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ABSTRACT

Influences of the ethereal oxygen on the reactivity of cis-8-oxabicyclo[4.3.0]non-3-ene in solvomercuration and catalytic hydrogenation reactions are examined. The solvomercuration rate enhancement observed for this compound, compared to its carbon analog, is examined using the law of increasing electron demand. The rate decrease observed with the substitution of a vinyl proton with a methyl group is discussed in relation to the present solvomercuration model. The results presented indicate that changes in solvomercuration rate are due to changes in the rate of the solvolysis step and not the stability of the mercurinium ion intermediate.

The influence of the ethereal oxygen on the catalytic hydrogenation of cis-8-oxabicyclo[4.3.0]non-3-ene over 5% Pt on alumina is examined using tetrahydrofuran (THF) as a model. The results presented indicate that the oxygen atom of both compounds inhibits the adsorption of hydrogen. These results also show that due to the size of cis-8-oxabicyclo[4.3.0]nonane, unlike THF, it inhibits both cyclohexene adsorption as well as hydrogen adsorption.

INTRODUCTION

Heteroatom Effects in Directing Organic Reactions

Our lab has been, and continues to be, interested in the effects of heteroatoms on the structure and reactivity of molecules. It has been shown that heteroatoms can influence the reactivity of molecules in ionic reactions through inductive and dipolar effects and by participation, when stereochemistry allows. In reactions where the lone pair electrons can interact with the active reagent, heteroatoms can compete with a double bond for the reagent, as in the case of catalytic hydrogenation. Determining the type of interaction a heteroatom is exerting during a reaction is often difficult and of the three heteroatoms, oxygen, nitrogen, and sulfur, of particular interest to our program the effects produced by oxygen appear to be the most subtle.

The most-widely used approach in the elucidation of heteroatom effects has involved the determination of relative and/or absolute reaction kinetics. Investigators have rationalized the effect of a remote oxygen on the solvolysis rate of a molecule in terms of the interaction between the incipient carbonium ion in the transition state and the oxygen induced dipole, and/or oxygen's lone pair

electrons. Oxygen's effect on the rate of solvolysis has been shown to be dependent on its position in the molecule, relative to the carbon on which the positive charge will form, and the stereochemistry of the molecule. These factors have been illustrated by Tarbell and Hazen in the solvolysis of the arenesulfonates of cyclohexane, tetrahydropyran, and tetrahydrofuran.¹ The oxygen-induced dipole was thought to destabilize the incipient carbonium ion in the transition state, resulting in a decrease in the rate of solvolysis beyond the expected decrease for inductive effects alone. The results shown in Table 1 also illustrate that when stereochemistry permits, as in the case of 3-tetrahydropyranyl brosylate, oxygen can participate in the reaction to stabilize the carbonium ion. The proposed participation, shown in figure 1, has been suggested as the reason for the unexpectedly high rate of solvolysis found for this compound.

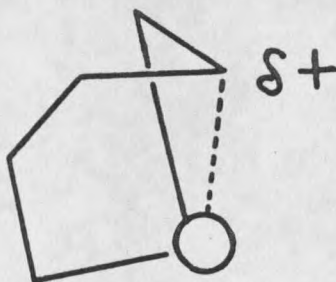
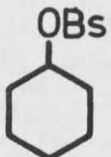
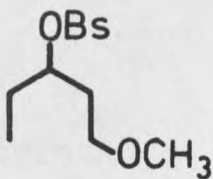
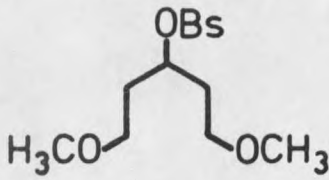
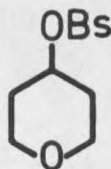
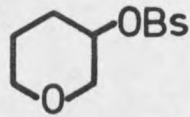
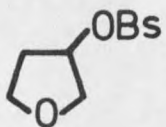


Figure 1. Oxygen Participation in Carbonium ion Stability.

Table 1
Acetolysis of Arenesulfonates.

compounds	rate $\times 10^5 \text{ sec}^{-1}$
	45.2
	35.1
	8.20
	1.40
	2.47
	0.55

The 24-fold increase in rate of solvolysis of the endo isomer of 9-oxabicyclo[4.2.1]nonan-2-yl compared to the exo isomer was rationalized by Paquette in terms of the oxygen participation shown in Figure 2.² The rate increase due to the stabilization of the incipient carbonium ion in the transition state by oxygen participation has been shown to be less than the rate increase due to participation by other heteroatoms. For example, Wilder found the solvolysis rate ratio of the endo/exo isomers of 4-oxatricyclo[5.2.1.0^{2,6}]dec-8-yl brosylates to be 50:1³ while the ratio for the sulfur analog was 1000:1.⁴ Although Wilder felt the rate ratio alone was insufficient evidence for oxygen participation, the rearrangement outlined in Figure 3 gave support to the proposed participation. It was rationalized that the oxygen had stabilized the carbonium ion intermediate long enough for the rearrangement to occur, whereas with the carbon analog the solvolysis of the carbonium ion was too fast for any rearrangements to occur.

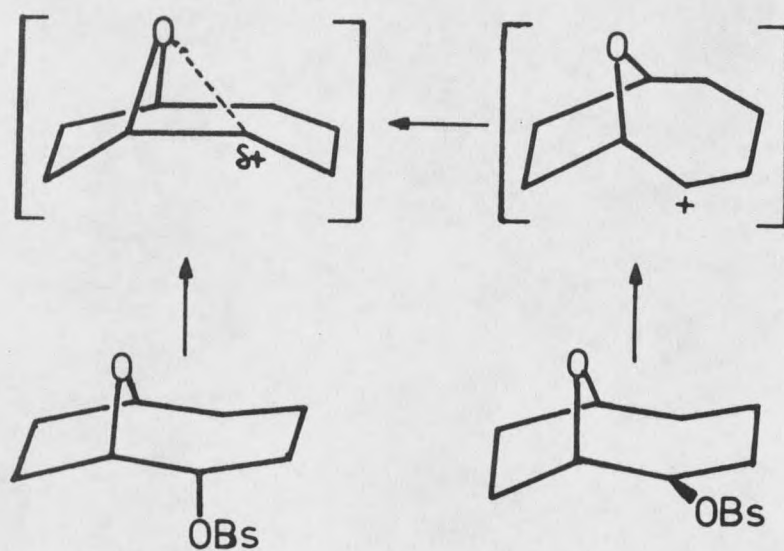


Figure 2. Rationale for the 24-fold increase in solvolysis rate.

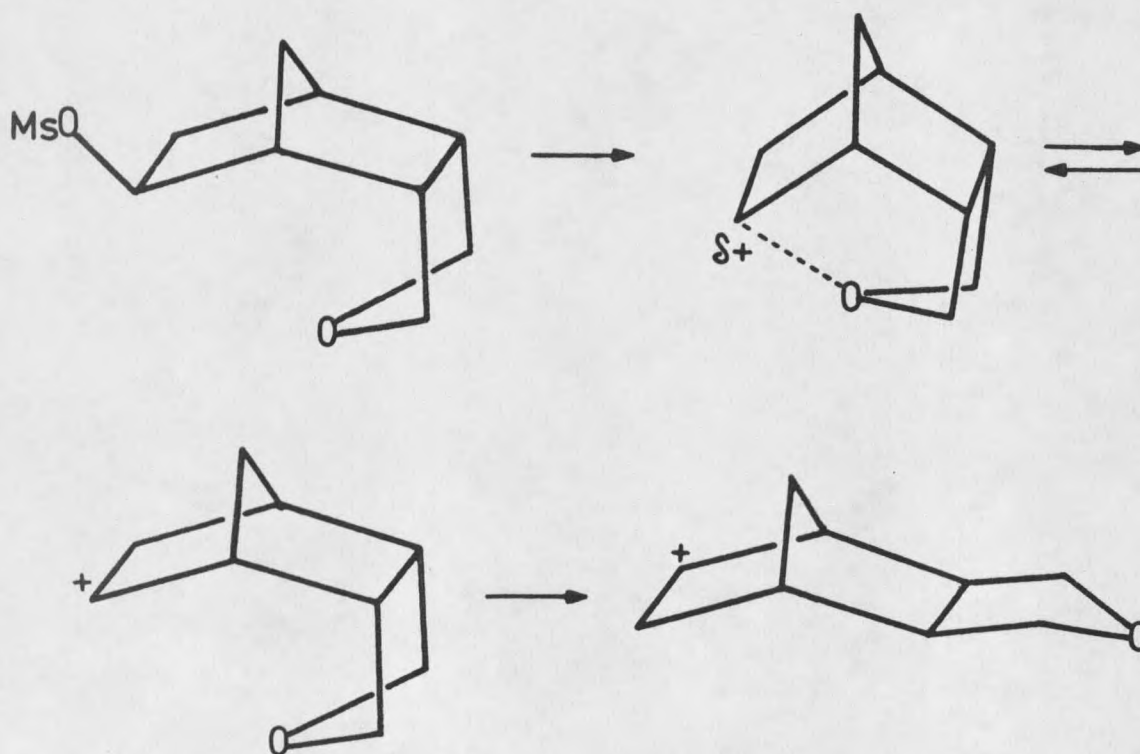
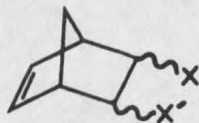


Figure 3. Rearrangement due to oxygen participation.

Some investigators insist that at least an order of magnitude difference in rates is required before heteroatom participation can be considered a contributing factor in the rate increase. Since the heteroatom electronic effects may not be identical for the stereoisomers used in the test for heteroatom participation, it would be difficult to isolate participation from electronic differences for small rate enhancements. In the investigation of the effects of remote substituents on the addition of 2,4-dinitrobenzenesulfonyl chloride to norbornene, Kwart and Miller observed that the electronic effects of substituents are not the same for the exo and endo isomers of norbornene, as the results shown in Table 2 indicate.⁵ Likewise, Kwart found the electronic effects of substituents in the axial position to be different from those at the equatorial position of mono- and disubstituted cyclohexenes.

Gassman used the method of "increasing electron demand" to determine the relative ability of the carbon-carbon bond of an epoxide, a cyclopropyl group, and a pi-bond to stabilize the carbonium ion formed during the solvolysis of the compounds shown in Table 3.⁶ This method is based on the assumption that if the electron demand of the incipient carbonium ion in the transition state is satisfied by the electron density "donated" by substituents on the carbon atom, then a remote functional group will not participate in

Table 2
Addition of 2,4-Dinitrobenzenesulfonyl chloride to
Norbornenes.



X		X'	Relative rates
exo	CH ₂ CH ₂ CH ₂	(cis)	139
	H	H	100
exo	CH ₃	H	98.3
endo	CH ₃	H	66.5
exo	COOH	COOH (cis)	0.637
endo	COOH	COOH (cis)	1.50
exo	$\begin{array}{c} \text{-C-O-C-} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$	(cis)	0.0501
endo	$\begin{array}{c} \text{-C-O-C-} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$	(cis)	0.000893

the reaction. The relative ability of a functional group to participate in a reaction was determined by comparing the ratio of the rate when the electron demand was satisfied by substituents on the carbon atom to the ratio when the electron demand was satisfied by a remote functional group participation. Gassman found that the electron demand of a tertiary carbonium ion was low enough that the functional group under investigation did not participate, while a secondary carbonium ion possessed a high enough electron demand to promote participation. By examining the "alpha-methyl/hydrogen" ratio the problem of changing electronic effects with changes in the stereochemistry of the molecule was avoided.

Peterson found that inductive effects from a methoxy group influenced the rate of addition of trifluoroacetic acid to a double bond over a span of eleven methylene carbons.⁷ The inductive effects were found to decrease linearly with the number of methylene groups at a rate of 0.64 per methylene carbon. Table 4 shows the relative rates of addition of trifluoroacetic acid found by Peterson for three compounds related to our work. In a related study, investigating the electron withdrawing effects of an ether linkage and acetal groups on the oxidation of alkene with permanganate ion and osmium tetroxide, Henbest⁸ observed the results shown in Table 5.

Table 3
Oxygen's inductive effects
on carbon-carbon bond participation.

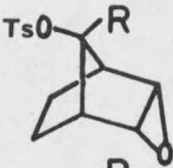
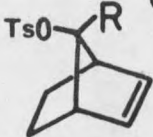
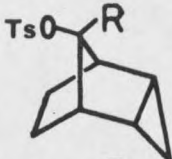
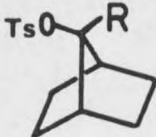
compound	relative (Me/H) ratio
	10^8
	10^{11}
	10^{14}
	1

Table 4
Addition of Trifluoroacetic Acid.

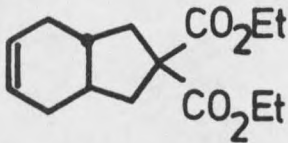
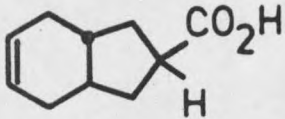
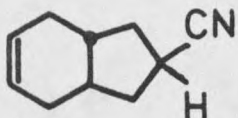
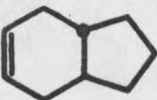
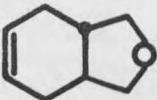
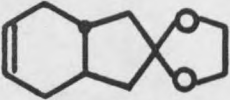
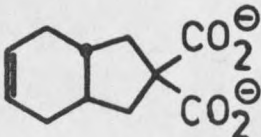
compound	relative rate
	1.0
	122
	30
	152

Table 5
Electronic effects on oxidation with KMnO_4 and OsO_4 .

compound	relative rate	
	KMnO_4	OsO_4
	1.0	1.0
	1.6	0.35
	1.29	0.28
	0.9	----

In the investigation of heteroatom effects, our lab previously used solvomercuration as the model for the ionic reaction and catalytic hydrogenation as the model reaction for the nonionic competition reaction. At this point it is of interest to discuss some of the characteristics of these two reactions. For the sake of uniformity the reactions will be discussed separately, starting with the solvomercuration reaction.

Oxygen Effects in Solvomercuration

When the solvomercuration reaction is carried out in aqueous perchloric acid solution, Halpern and Tinker found the rate law shown in Equation 1.⁹

$$\text{rate} = k [\text{Hg}^{+2}] [>\text{C}=\text{C}<] \quad (1)$$

There was an excellent correlation between $\log(k)$ and Taft's σ^* for substituted olefins. The observed ρ^* value of -3.3 indicated a transition state with considerable carbonium ion character. Although they could not disprove the existence of a mercurinium ion intermediate, they found no evidence for it. Under the conditions used by Tinker, it is believed the reaction species is solvated Hg^{+2} and not $\text{Hg}(\text{OAc})^{+1}$ as found by other workers using a 50% water/tetrahydrofuran ($\text{H}_2\text{O}/\text{THF}$) mixture or methanol (MeOH), for which there is evidence for a mercurinium ion intermediate. Some of the results found by Halpern and Tinker are shown in Table 6.

Table 6
Rate constant for solvomercuration with Hg^{+2} .

compounds	rate $\times 10^{-3} \text{M}^{-1} \text{sec}^{-1}$
Ethylene	5.1
Propylene	100
1-butene	80
isobutene	>1000
cis-2-butene	5.8
trans-2-butene	1.7
cyclohexene	5.0

It has been shown by a number of investigators that when the solvomercuration reaction is carried out with mercuric acetate in H_2O/THF or $MeOH$, the mercurinium ion intermediate has little carbonium ion character, and that most of the charge remains on the mercury.^{10,11,15,17,63} Yet, the relative reactivity of substituted olefins was rationalized in terms of the stability of the mercurinium ion intermediate.^{10,18,64} Brown found the reactivity for substituted olefins to follow the trend:¹⁰ terminal disubstituted > terminal monosubstituted > internal trisubstituted > internal disubstituted > internal tetrasubstituted. Any additional branching, even on remote carbons, resulted in a decreased reaction rate. However, a significant deviation from the carbonium ion stabilization trend was observed with the relative solvomercuration rate of styrene compared to alpha-methylstyrene, as shown in Table 7 with other examples of the relative rates found by Brown. It was suggested that the low reaction rate for styrene was due to steric hindrance and the lower ground state energy of the double bond when conjugated to a benzene ring, but the enhanced rate for the methylstyrene was unexplained.

Table 7
Relative rate of solvomercuration with $\text{Hg}(\text{OAc})^{+1}$.

compound	relative rates
cyclohexene	1
1-pentene	6.6
1-Hexene	4.8
2-methyl-1-pentene	48
cis-2-pentene	0.56
trans-2-pentene	0.17
2-methyl-2-pentene	1.24
cyclopentene	0.78
1-methylcyclopentene	1.86
norbornene	3.7
bicyclo[2.2.2]octene	0.01
styrene	0.28
alpha-methylstyrene	1.18
cis-propenylbenzene	<0.02

The lack of a carbonium ion in the mercurinium ion intermediate has been shown by Bach and Richter in the investigation of the oxymercuration of cis- and trans-di-tert-butylethylene.¹¹ The results shown in Figure 4 reveal that the oxymercuration of cis-di-tert-butylethylene gave only the stereospecific trans addition without carbon-carbon bond rotation, despite the 10.2 kcal/mole higher strain energy compared to the cis isomer.¹² These results also show the first case of the solvomercuration reaction resulting in cis addition for an unstrained open chain.

Bach found only the expected solvomercuration products and none of the rearrangement products found with the bromination of trans-di-tert-butylethylene in methanol,

where an appreciable charge develops on the carbon atoms.^{13,14} This observation was rationalized in terms of a bridged mercurinium ion intermediate with little charge on the carbon atoms.

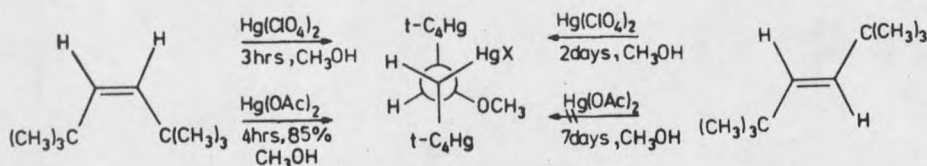


Figure 4. Oxymercuration of cis- and trans-di-tert-butylethylene.

The solvomercuration reaction characteristics, found by most investigators using H_2O/THF and $MeOH$, are summed up in the following way by Waters and Kiefer in their study of the methoxymercuration of allenes¹⁵:

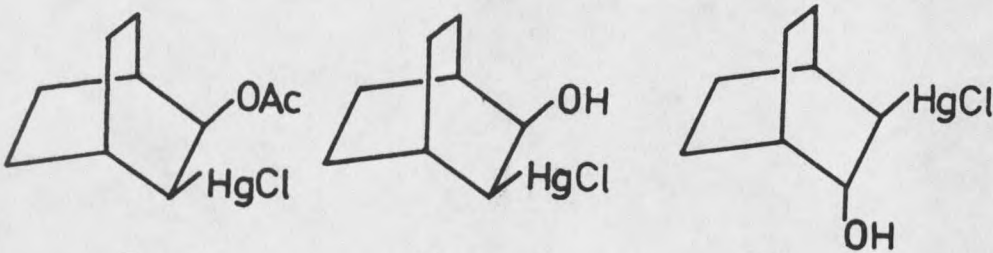
1. The mercurinium ion is reversibly formed, prior to the rate-limiting step, and is not subject to important steric control;
2. The opening of the mercurinium ion by solvent is both rate and product determining and is stereospecifically trans;
3. The rate of the latter step is remarkably sensitive to steric influence of substituents on the opposite end of the allenic system, implying that the central

carbon atom has acquired a good deal of trigonal character.

The only area of disagreement is with regard to the structure of the mercurinium ion intermediate. Bach suggested that the mercurinium ion intermediate for di-*t*-butylethylene had to be planar, based on theoretical calculations.¹¹ Brown, on the other hand, declines to say whether the intermediate is a bridged mercurinium ion or not.¹⁰

The solvomercuration of most olefins occurs via trans attack of the mercurinium ion by solvent. One exception to this observation is norbornene, which results only in cis addition.¹⁶ In the investigation of solvomercuration of bicyclo[2.2.2]oct-2-ene, Traylor found the solvent attack on the mercurinium ion occurred both cis and trans, with the ratio being dependent on the nucleophilicity of the solvent.¹⁷ The results shown in Table 8 reveal that in nucleophilic solvents, trans addition is favored, whereas cis addition is favored in solvents of poor nucleophilicity. Traylor rationalized these results in terms of the ring opening of the mercurinium ion in competition with the trans attack by the solvent. As in the norbornene system, no rearrangement products were detected, indicating little carbonium ion character in the intermediate.

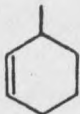
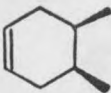
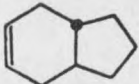
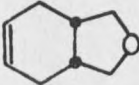
Table 8
Solvent effects on solvomercuration of
Bicyclo[2.2.2]octene.

					
I II III					
Solvent	[Hg (OAc) ₂]	[NaOAc]	I	II	III
water	0.1 [*]	0	0	50	50
water-acetone	0.67	0	0	60	40
water-acetone	0.09	0	Tr	60	40
water-acetone	0.1	0.139	75	0	25
acetic acid	0.3	0	100	0	0

* Hg (OTos) (OH)

The results shown in Table 9 were obtained by Otzenberger in the investigation of heteroatom effects on the solvomercuration reaction.¹⁸ These results reveal that the ethereal oxygen in cis- and trans-8-oxabicyclo-[4.3.0]non-3-ene has a rate enhancing effect on this reaction. The rate increase for the cis-isomer was attributed to oxygen participation similar to that shown in Figure 5. The rate increase found for the trans isomer, which is not capable of participation, was attributed to induced strain from the shorter C-O-C bond lengths and larger C-O-C bond angle compared to the carbon analog.

Table 9
Oxygen effect in solvomercuration.

compound	relative rate
	1.0
	0.36
	0.09
	0.11
	0.15
	0.81
	0.40
	0.35

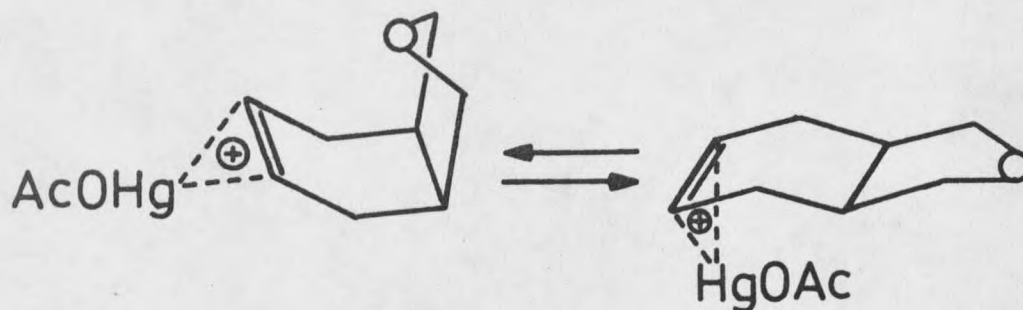


Figure 5. Oxygen participation in solvomercuration.

The stereochemistry of solvomercuration resulted in the hydroxyl group being syn to the ring juncture in the cis-oxabicyclononene, with a syn/anti ratio of 3:1. However, Otzenberger found the stereochemistry of epoxidation for this compound gave a syn/anti ratio of 1:4, as shown in Figure 6. This then indicates that, in the absence of electronic effects, attack anti to the ring juncture is the less sterically hindered direction of approach for epoxidation, while the solvent attack syn to the ring juncture was the less hindered direction in the solvomercuration reaction. Based on NMR results, Otzenberger found the open conformation to be more stable than the folded conformation.

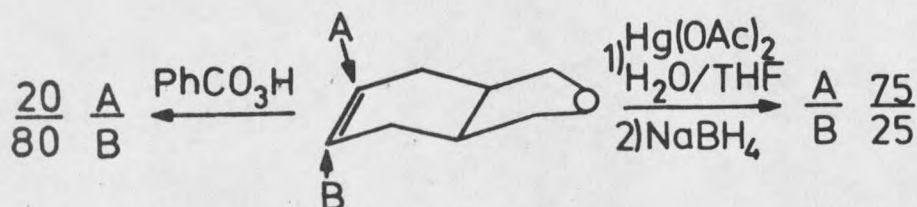


Figure 6. Stereochemistry of epoxidation and solvomercuration.

The stereochemistry of epoxidation was used by Cope and Gleason to assign the conformation of cis-bicyclo[4.2.0]oct-3-ene¹⁹ and by Hallageas and Casadevall to assign the conformation of cis-bicyclo[4.3.0]non-3-ene.²⁰ Both groups found the folded conformation to be preferred over the open by a ratio of about 87:14. The proposed conformation assignments were based on the rationale that if the open conformers were preferred the syn to anti ratio would have been 50:50.

The stereochemistry and reaction rate of epoxidation with peroxy acids has been shown by several investigators to be sterically sensitive and to be influenced by electronic effects. It has been reported that vinyl alkyl substituents result in an enhanced rate of epoxidation.^{21,22} Henbest rationalized the directive effects of a remote nitrile substituent in terms of the dipole-dipole interaction between the nitrile and the transition state of the olefin-peroxy acid.²³ However, Rickborn and Lwo have

reported that steric interaction with remote alkyl substituents have a rate retarding effect on the epoxidation reaction.²⁴

The results shown in Table 10 compare the relative rates of epoxidation found by Rickborn with the relative rates of solvomercuration found by Otzenberger. Rickborn rationalized the decrease in the relative rate in terms of the steric interaction between the peroxy acid and the remote substituents. The proposed reason for the relatively high solvomercuration rate of the cis-oxabicyclononene was, as mentioned earlier, due to oxygen participation in the transition state of the mercurinium ion formation. However, two major inconsistencies are revealed in the comparison of these two sets of data. The relative rate of the trans-oxabicyclonon-3-ene is higher than expected for the mercuration reaction and lower than expected for the epoxidation reaction, based on steric effects alone. The sterically sensitive step in the solvomercuration reaction is the addition of solvent. The solvomercuration stereochemistry found by Otzenberger would then indicate that the side of the double bond cis to the ring junction is the less hindered direction of approach. However, the stereochemistry of the epoxidation reaction indicates that the less hindered direction of approach is the side of the double bond trans to the ring juncture. From these

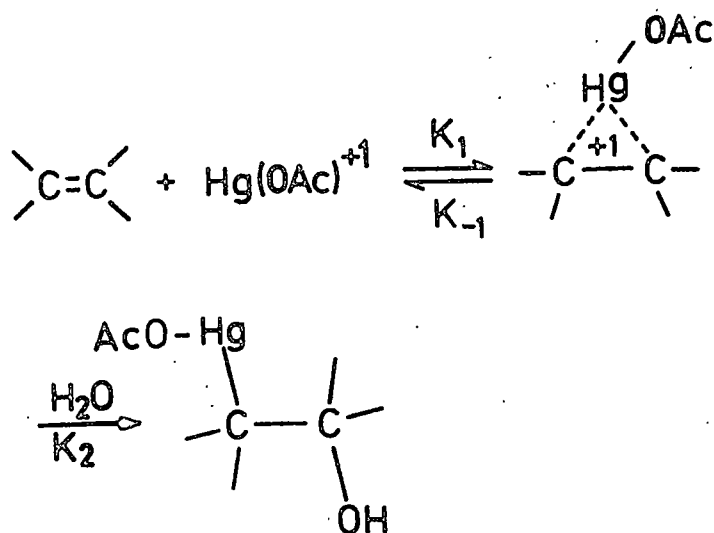
observations it is logical to conclude that more than just steric factors are involved in both the epoxidation and solvomercuration reactions. Although these discrepancies are small compared to the heteroatom effects found in solvolysis reactions, they do raise questions about the effects produced by the ethereal oxygen and the kinetics of solvomercuration in general.

Table 10
The comparison between relative rates of epoxidation and solvomercuration.

cyclohexene	relative rate	
	epoxidation	mercuration
3-methyl	0.94	0.36
trans-4,5-dimethyl	0.79	-----
cis-4,5-dimethyl	0.46	0.09
cis-4,5-(-CH ₂ -O-CH ₂ -)	0.50	0.81
trans-4,5-(CH ₂ -O-CH ₂ -)	0.29	0.40
cis-4,5-(CH ₂ -CH ₂ -CH ₂ -)	----	0.11
trans-4,5-(CH ₂ -CH ₂ -CH ₂ -)	----	0.15

It has been shown by a number of investigators that the rate limiting step in the solvomercuration reaction is not the formation of the mercurinium ion intermediate, but rather the solvolysis of the intermediate. It is believed that the mercurinium ion intermediate forms at a preequilibrium rate and that the rate constants have the

relationship shown in Figure 7. The sequence of the rate constants for the solvomercurcation reaction are based on the observed stereochemistry of solvent addition, the relative reaction rates, and the observed reaction kinetics.



$$K_{-1} > K_1 \gg K_2$$

Figure 7. Mechanism of solvomercurcation reaction.

Based on the relationship of the rate constants, it is logical to conclude that decreasing only the energy of the transition state for the formation of the intermediate would lead to an increase in both k_1 and k_{-1} which would not effect the reaction rate significantly. Likewise, if only the energy of the intermediate were decreased, it follows then that k_{-1} will decrease, resulting in a higher

concentration of the intermediate; but k_2 will also decrease which would be a rate decreasing effect. However, if the energy of the transition state of the solvolysis step were decreased, there would be an increase in k_2 resulting in an overall rate increase.

The energy of the three species of this reaction, the two transition states and the intermediate, are interrelated. Since the first transition state involves the formation of a partial positive charge on the olefinic carbon atoms and the intermediate contains the positive charge, decreasing the energy of the first transition state will result in a more stable intermediate. However, the transition state of the solvolysis step involves the interaction of the positively charged intermediate and solvent. It then follows that the more charge on the carbon atoms in the intermediate the lower the energy of the transition state for the solvolysis reaction will be, due to the higher electrophile-nucleophile interaction energy. Even though most investigators acknowledge that the solvolysis step is rate determining,^{10,11,15,17,64} it has been proposed by a number of investigators that stabilizing the charge in the intermediate results in an enhanced rate.^{10,16,18}

The stabilization of the charge in the intermediate can be accomplished by induction, delocalization, and

participation. It is of interest to discuss each of these methods separately since their effects on the overall rate may not be the same.

The effects of inductively stabilizing the intermediate can be illustrated by the relative rates for a series of compounds from Table 7. The relative rates for the pentene series are typical of the reactivities found for various alkyl substitutions on the double bond.

Based on the generally accepted assumption that the intermediate is a three-atom bridged, positively charged ion with most of the charge on the mercury atom,^{25,26} the little charge that forms on the carbon atoms should be shared equally between symmetrical olefinic carbons. It follows then that if the rate depends on the stability of the intermediate then the relative rate for 2-pentene would be higher than that of 1-pentene, as the reactivity trend for the bromination reaction, shown in Table 11, illustrates. However, the relative solvomercuration rate for 1-pentene is 6.6 compared to 0.56 for 2-pentene which is opposite to the expected relative stability trend of the mercurinium ion intermediate, based on the bromination reaction. An even larger reaction rate difference occurs between 2-methyl-1-pentene and 2-methyl-2-pentene with relative rates of 48 and 1.24 respectively, and again the rate enhancement is in the opposite direction of the intermediate

stabilization. These observations contradict the hypotheses that the reactivity trend found by Brown was due to the relative stability of the mercurinium ion intermediate.

Table 11
Relative reactivity of alkenes toward
bromination.²⁷

Alkene	Relative reactivity
1-butene	1.00
cis-2-butene	27
trans-2-butene	17.5
2-methyl-2-butene	13700
2,3-dimethyl-2-butene	190000

The effects of stabilizing the intermediate through delocalization are illustrated by the relative rates of styrene and methylstyrene. The ability of a benzene ring to stabilize a carbonium ion is comparable to that of three methyl groups and yet the relative rate for styrene is 0.28. As mentioned earlier, Brown rationalized the low relative rate in terms of a decrease in the ground energy of the double bond and the steric effects of the benzene ring. However, the problem with the proposed rationalization can be seen with the relative rate of 1.18 for alpha-methylstyrene. If anything, the steric effects have increased with the addition of a methyl group and it is doubtful the ground state energy of the double bond could explain the rate increase.

The objective of this research is in two parts. We wish to revise the present solvomercuration reaction model in order to explain the discrepancies mentioned above. This research is also to determine the role the ethereal oxygen plays in the relative reaction rate of the 8-oxabicyclo[4.3.0]non-3-ene system.

Oxygen Effects in Hydrogenation

The catalytic hydrogenation of olefins has been studied by a number of investigators using a variety of reaction conditions and instrumentation techniques. It has been shown that the reaction solvent, hydrogen pressure, substrate concentration, catalyst metal, the metal to support ratio, the pretreatment of the catalyst, and even the sequence in which the olefin and hydrogen are added to the catalyst has an effect on the reaction rate and/or the change in the reaction rate with time (rate-profile). As a necessary prelude to the examination of the effects oxygen has on the reaction rate, it became obvious that additional understanding of the simple alkene reduction process was required.²⁸

It has been well documented that pretreatment of catalyst can have a significant effect on the reaction rate of catalytic hydrogenation, prompting a number of proposed explanations. Glassl et al. used electron microscopy to

investigate the effects of platinum catalyst sintering under argon, oxygen, and hydrogen atmospheres on the metal particle size distribution.²⁹ The metal particles produced by some pretreatment procedures were found to be unstable, as the particle size distribution was prone to change during the hydrogenolysis of methyl cyclopentane. Glassl found an alternating treatment with hydrogen at 510° K and oxygen at 720° K produced the most stable catalyst. The particle size distribution of some platinum catalysts was found to affect the proportion of 2-methylpentane, 3-methylpentane, and n-hexane produced in the hydrogenolysis of methylcyclopentane.³⁰

Antonucci et al. investigated the effect of metal dispersion on the catalytic hydrogenation of benzene over platinum on alumina catalyst.³¹ As the catalyst was diluted with alumina, the specific activity of the platinum catalyst increased, with reference to the metal content, up to a dilution factor of 50:1. These results led Antonucci to propose that the hydrogenation of benzene occurs on both the metal aggregates as well as the support. Since the specific activity of the catalyst remained constant beyond the 50:1 ratio it was rationalized that the adsorbed hydrogen did not migrate beyond a certain point around the metal particle.

The interparticulate mobility of atomic hydrogen adsorbed onto platinum on alumina was demonstrated by

Bianchi et al.³² It was shown that methanol was produced when hydrogen was allowed to flow over a mixture of platinum on alumina and methoxylated silica aerogel. Without the platinum metal no reaction occurred. Although the half-life of the process was on the order of hours, depending on the packing of the particles, it clearly demonstrated that active hydrogen could travel from one catalyst particle to another.

Augustine and Warner found that when the catalyst was presaturated with olefin there was an initial reaction delay and a larger degree of curvature in the rate-profile for the hydrogenation reaction.³³ It was proposed that the delay was due to the time required for the hydrogen to remove adsorbed oxygen from the catalyst surface. Although the presaturation of platinum catalyst with either hydrogen or olefin made no difference in the outcome of the reaction, initial treatment of palladium catalyst with an olefin resulted in a change in its reaction characteristics. By using a quantitative single cycle hydrogenation technique, Augustine was able to show that platinum on silica was able to store more hydrogen than the catalyst had sites. These results were rationalized in terms of hydrogen "spillover", where the adsorbed hydrogen migrated to the support where it was stored. Once the concentration of the adsorbed hydrogen on the metal decreased, the hydrogen migrated back to the reaction sites.

Further evidence for hydrogen migration and subsequent spillover onto the support of platinum catalyst was found by Sheng and Gay using PNMR.³⁴ The resonance line for adsorbed hydrogen was found to be as much as 60 ppm upfield of TMS. The position of this line was found to be a function of hydrogen coverage and metal dispersion. These results were interpreted in terms of spin pairing in the platinum crystallites, due to a quasi covalent bond formation between adsorbed hydrogen and the platinum metal. The broad line width of adsorbed hydrogen illustrated the mobility of adsorbed hydrogen on the platinum surface at room temperature. Evidence for hydrogen spillover was based on the dependence of the SiOH relaxation time on the concentration of adsorbed hydrogen.

The exchange rate of deuterium with the protons from hydroxyl groups chemisorbed on alumina in the presence of Rhodium particles has been made by Cavanagh and Yates using infrared spectroscopy.³⁵ Near 300° K, the exchange rate was found to be rapid and was shown to decrease when carbon monoxide was chemisorbed on the Rh catalyst. The decrease in the exchange rate was rationalized as being due to adsorption site blockage.

Gallezot and Bergeret used radial electron distribution to examine the effects of adsorbed hydrogen and benzene on the platinum crystallites of Y zeolite⁷² supported catalyst.³⁶ The crystal surface structure was found to be

distorted and the interatomic distances contracted with respect to the normal face center cubic (fcc) structure of bulk platinum when free of adsorbates. When hydrogen was adsorbed onto the platinum the aggregates exhibited normal fcc structure and interatomic distances, which supports the concept of quasi covalent bonds between adsorbed hydrogen and platinum as proposed by Sheng. However, when the benzene was adsorbed onto the platinum the structure was still distorted and contracted, indicating the benzene overlayer coordinates the surface atoms less efficiently than dissociated hydrogen. When both benzene and hydrogen were adsorbed onto the platinum surface, Gallezot found that benzene covers only a fraction of the metal surface even with an excess of benzene, contrary to the assumption made by most investigators.

Comparisons of olefin adsorbtivities are usually based on the absolute and relative competitive reaction rates. The models used in the comparisons are based on the assumption that most of the catalyst surface is covered with olefin, leaving only a fraction of the surface for hydrogen adsorption. The mechanism shown in Figure 8 was proposed by Polanyi and Horiuti in 1934³⁷ and is considered valid today. The only changes made in the mechanism has been the reversibility of the various reaction steps.

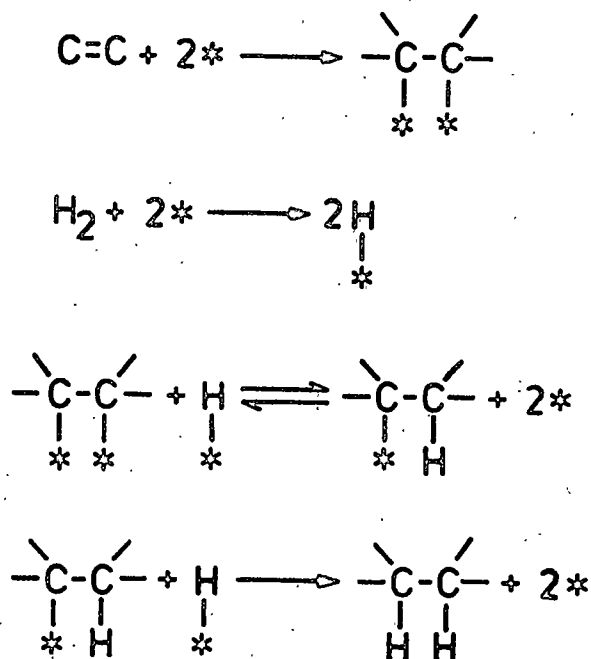


Figure 8. Hydrogenation mechanism.

In the catalytic hydrogenation of various olefins over supported platinum catalyst and under approximately one atmosphere of hydrogen pressure, Hussey et al. found the rate to be proportional to the hydrogen pressure and catalyst weight and independent of substrate concentration throughout the reaction.³⁸ The adsorption of molecular hydrogen was found to be irreversible in the presence of olefin, as was found by previous investigators, despite the rapid formation of HD from H₂ and D₂ at 195° K in the absences of olefin.^{39,40} It was proposed that the proton and deuterium scrambling found when D₂ was used, instead of hydrogen, had occurred on catalyst sites not used in the

hydrogenation reaction. Thus, the desorption of olefin in the Polanyi mechanism was proposed as irreversible. Hussey proposed the addition of the first hydrogen atom is highly reversible and the addition of the second hydrogen atom irreversible, due to the low adsorbtivity of alkanes. The activation energies for cyclohexene and cycloheptene were 5.7 Kcal/mole and 6.5 Kcal/mole, although no single rate limiting step was proposed.

Hussey et al. found the hydrogenation rate over palladium catalyst to be pore diffusion controlled, base on the reaction orders shown in Table 12.⁴¹ It was proposed that the hydrogenation reaction occurred in the larger pore, which contained both adsorbed hydrogen and olefin. While the isomerization reaction, for which palladium is notorious, occurred in the hydrogen-deficient smaller pores. Hussey found that for a particular hydrogen pressure these results could be accommodated by the form of the Langmuir-Hinshelwood shown in Equation 2, but not the simpler form shown in Equation 3. Equation 2 allows for the competitive adsorption between hydrogen and alkene while equation 3 assumes that hydrogen does not interfere with the chemisorption of alkene.

$$\text{rate} = k K_{\text{sub}} [\text{sub}] / (1 + K_{\text{sub}} [\text{sub}] + K_{\text{H}} [\text{H}_2]) \quad (2)$$

$$\text{rate} = k K_{\text{sub}} [\text{sub}] / (1 + K_{\text{sub}} [\text{sub}]) \quad (3)$$

where k is the overall rate constant under a particular set of conditions. K_{sub} and $[\text{sub}]$ is the adsorbtivity coefficient and concentration of the alkene. K_{H} and $[\text{H}_2]$ is the adsorbtivity coefficient and concentration of the hydrogen.

Table 12
Reaction orders for palladium catalyst.

rate = $k [\text{cycloalkene}]^m [\text{P}(\text{H}_2)]^n$		
cycloalkene	m	n
bicyclo[2.2.1]heptene	0.20	1
cyclopentene	0.26	0.57
cyclohexene	0.34	0.45
cycloheptene	0.27	0.43
cyclooctene	0.23	0.23

In the investigation of the hydrogenation of cyclohexene Madon et al. used the turn-over rate (N) of the platinum catalyst as defined by moles substrate/site-sec,⁴² where the number of sites was determined by the oxygen titration technique.⁴³ The value of N was found to be independent of particle size, for 1 to 7 nm particles, and of the nature of the support, with SiO_2 , neu- Al_2O_3 , and gamma- Al_2O_3 . The reaction rate was found to be proportional to the hydrogen pressure and catalyst weight. However, contrary to Hussey's

findings for platinum catalyst, Madon found the rate to be dependent on the cyclohexene concentration, as the concentration approached zero. The pseudo first order rate constant was found to be independent of solvent type, as long as the hydrogen solubility was used in the rate expression and not the activity of hydrogen.

Baltzly showed that in aqueous methanolic and aqueous acetic acid solutions the rate of catalytic hydrogenation of a variety of substrates became independent of substrate concentration, beyond a certain concentration limit, and hydrogen pressure, above 3 atmospheres.⁴⁴ It was found that as the water content of the solvent increased, the substrate concentration limit, above which the reaction order was zero, decreased.^{45,46} Baltzly proposed this to mean that the substrate adsorption was proportional to the activity of the substrate and inversely proportional the substrate solubility. With reference to the acidity of the solvent, platinum on carbon was found to be highly sensitive to acidity, while palladium on carbon was relatively insensitive. Baltzly found two types of contaminants in cyclohexene, which had different effects on the rate of hydrogenation of cyclohexene. The first type resulted in a reduced rate of hydrogenation without increasing the degree of curvature in the rate-profile. The second type of contaminant decreased the rate and increased the degree of curvature in the rate-profile. Reactions with either type

of contaminant were discarded. The effects of cyclohexene contamination were significantly decreased by fractional distillation followed by a filtration through alumina just prior to the hydrogenation experiment.

The hydrogenation of compounds with a single reducible group usually give reaction orders which are either positive or zero, whereas compounds with two reducible groups result in a reaction with a negative reaction order in substrate concentration. For example, the reaction order for 1,3-butadiene was found to -0.7 on platinum catalyst⁴⁷ and -2 on copper catalyst and at low hydrogen pressures⁴⁸. The reaction order of 1,4-cyclohexanedione was found to be -0.6 with only one carbonyl group being reduced.⁴⁹ Compounds containing two functional groups with different reactivities can also result in negative reaction orders. For example, 2-cyclohexenone gave a reaction order of -1.4 , even though the double bond selectivity was about 90%.⁵⁰ The reaction order of acetophenone was found to be -0.3 , indicating the benzene rings were competing with the carbonyl group for surface sites.⁵¹ However, the reaction order of 3,4-dihydro-2H-pyran, which is capable of adsorption via oxygen's lone pair electrons, was found to have the same reaction order as cyclohexene with a value of 1.

The effect of oxygen, nitrogen, and sulfur on the relative rate of hydrogenation of cis- and trans-8-heterobicyclo[4.3.0]non-3-ene has been examined by

Theodore.⁵² The results shown in Table 13 indicate that nitrogen and sulfur not only inhibited the reduction of cyclohexene, under competitive conditions, they also produced self inhibition as indicated by the low relative rate. As a means of comparing the relative amount of substrate adsorbed onto the catalyst Theodore determined the relative competitive and noncompetitive catalyst affinities, shown in Table 14, under "static" conditions. The relative affinities likewise illustrates that nitrogen is capable of inhibiting the adsorption of cyclohexene. The relative affinity of the oxabicyclononene indicates that the oxygen atom is capable of inhibiting the adsorption of cyclohexene more so than the bicyclononene. However, the relative competitive and noncompetitive rates indicates the bicyclononene has more of an inhibiting effect than does the oxabicyclononene.

The most extensive investigations of hydrogenation inhibitions have been conducted by Maxted et al.⁵³ and Baltzly.⁵⁴ Both investigators used the decrease in the initial rate as a means of comparing the relative catalyst toxicity of various inhibitors. Maxted used equation 4 as the standard model for quantitatively comparing relative poisoning strengths, while Baltzly applied the

Table 13
Relative rates of hydrogenation.

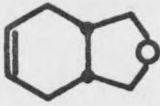
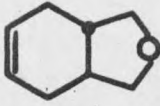
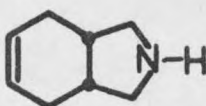
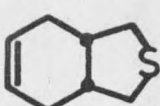
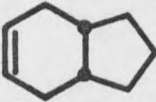
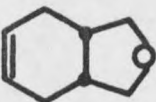
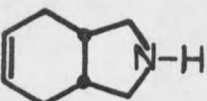
compound	competitive	non-competitive
	1.00	1.00
	6.59	.78
	1.33	.55
	4.92	.13
	23.63	.0039
	?	-----

Table 14
Relative platinum affinities.

compound	competitive	non-competitive
	1.00	1.00
	.88	.75
	3.36	.13
	40.20	4.22

Langmuir-Hinshelwood type kinetics (Equation 5) to reactions that had a sufficient amount of inhibitor added to reduce the initial rate by one half (half poison). Under the conditions of half poison, Baltzly proposed that equation 6 was valid and could be used to compare relative adsorbtivities of inhibitors.

$$k_p/k_o = 1 - AC_i \quad (4)$$

where: k_p = the inhibited initial rate
 k_o = the standard initial rate
 A = the poisoning coefficient
 and C_i = the inhibitor concentration

rate =

$$\frac{akWK_s[\text{sub}]K(H_2)P(H_2)}{(1+K_s[\text{sub}]+K_{\text{sol}}[\text{sol}]+K_{\text{inh}}[\text{inh}]+K_{\text{pro}}[\text{pro}])(1+K(H_2)P(H_2))} \quad (5)$$

Where a = the reaction parameter constant
 k = the rate constant
 W = the catalyst weight
 K = the adsorbtivity coefficients for the product, substrate, solvent, inhibitor, and hydrogen
 P = the partial pressure of hydrogen
 K_{pro} was assumed equal to zero for alkane products

$$k_p/k_o = 0.5 = K_s[\text{sub}] / (K_s[\text{sub}] + K_{\text{inh}}[\text{inh}]) \quad (6)$$

Maxted and Evans observed that the relative catalyst poisoning ability of thiols and dialkyl sulfide increased with chain length,^{55,56} although nonlinearly. It was proposed that the sulfur atom was bound to a particular platinum atom, while the rest of the molecule was free to

move about the surface of the catalyst. This freedom of movement resulted in the alkyl portion of the molecule blocking adjacent catalyst sites. However, due to the increased apparent surface area requirement, the larger inhibitors were exposed to stronger forces tending to remove them from the catalyst surface. Based on the calculations from known atomic dimensions, methyl sulfide could block as many as nine catalyst sites. Yet the relative catalyst toxicity of methyl sulfide, compared to hydrogen sulfide, was found to be 7.1, based on the solution concentration. The relative toxicity of methyl sulfide, as measured by surface concentration, was found to be nine compared to hydrogen sulfide,⁵⁷ indicating the methyl sulfide was less efficiently adsorbed onto the catalyst. Baltzly, likewise, found that large inhibitors had a higher apparent toxicity than smaller inhibitors, but the larger inhibitors were less efficiently adsorbed than the smaller inhibitors.

Of particular interest to the present work is the observation Baltzly made with regard to the relative inhibition of nitrobenzene compared to acetophenone. Baltzly found that a much larger fraction of the catalyst surface had to be occupied by an inhibitor in order to decrease the rate of reduction of nitrobenzene to the same comparable decrease in the rate of acetophenone. The two following conclusions were proposed:

1. Reduction of acetophenone requires complete planar adsorption, whereas with nitrobenzene, approach of the oxygen atoms to the surface suffices for primary attachment.
2. The more strongly adsorbed substrate may be able to nudge aside single particles of inhibitor.

The former conclusion is supported by the investigation by Garrison on the ejection of benzene and pyridine from a nickel surface by energetic argon bombardment.⁵⁸ Mass spectra of the ejectected species revealed that benzene desorbed from the nickel surface intact, whereas the desorption of pyridine resulted in fragmentation products. Based on classical dynamic calculations, it was proposed that pyridine bonds to the nickel surface through the nitrogen atom, resulting in the pyridine being vertical rather than horizontal as found for benzene.

Baltzly noted that some of the inhibitors investigated did not fit the theoretical poisoning curve at all, while other inhibitors only fit approximately. Thus, attempts to calculate the relative adsorbitivity coefficients of the inhibitors at various degrees of inhibition, using equation 6, resulted in different values for the coefficients, which are supposed to be constant. Some of the discrepancies in the values of the relative adsorbitivity coefficients can be traced to the basic assumption of substrate coverage of

catalyst made in the Langmuir-Hinshelwood adsorption isotherms. There is ample evidence in the literature that all active catalyst sites are not equivalent as the Langmuir-Hinshelwood kinetics assume.⁵⁹ However, the Langmuir-Hinshelwood is still one of the most widely used model in the investigations of adsorptivities because of the ease with which it can be applied.

Another potential source of error in the calculated relative adsorptivity coefficients is the assumption made by most of the investigators working on the kinetics of catalytic hydrogenation reaction. Hussey assumed the catalyst to be almost completely covered by substrate in the application of equation 2. Likewise, Baltzly and Maxted assumed that the catalyst is almost completely covered by substrate; thus the addition of any inhibitor would result in only the inhibition of substrate adsorption. However, as mentioned earlier, Gallezot found that benzene covered only a fraction of the catalyst surface, with the rest of the surface being covered with hydrogen. If the substrate does adsorb onto only a fraction of the catalyst surface, then there is the possibility that an inhibitor could adsorb onto those catalyst sites not used for substrate adsorption. The reverse of this hypothesis was observed by Baltzly in the investigation of the inhibition of nitrobenzene mentioned earlier.

Since those sites not used for substrate adsorption are used for hydrogen adsorption, the inhibitor would then inhibit hydrogen adsorption. However, Baltzly would not have been able to detect hydrogen inhibition directly since only the initial rates were measured and not the degree of curvature. Both hydrogen and substrate inhibition would result in a decrease in the initial rate, but only substrate inhibition would result in an increase in the degree of curvature in the rate profile, for a given pressure, based on the Langmuir-Hinshelwood equation.

This hypothesis may explain the results found by Theodore for the oxabicyclononene. Most of the inhibition investigations conducted by Baltzly and Maxted centered around potent catalyst poisons. A mild inhibitor, such as THF, could be used to probe the adsorption inhibition of hydrogen, to gain further insight into the oxygen effect observed by Theodore for the oxabicyclononene.

RESULTS AND DISCUSSION

Preparation of Substrates

Otzenberger used cis- and trans-8-oxabicyclo[4.3.0]non-3-ene as the model compounds in the investigation of heteroatom effects on the solvomercuration reaction. Theodore expanded the number of model compounds to the cis-8-heterobicyclo[4.3.0]non-3-ene series, where the heteroatoms were oxygen, nitrogen, and sulfur, for the investigation of the heteroatom effects in the catalytic hydrogenation reaction. This investigation, as a bridge between the two previous studies, centered around cis-8-oxabicyclo[4.3.0]non-3-ene as a model. The supporting compounds synthesized for this investigation are shown in Figure 9.

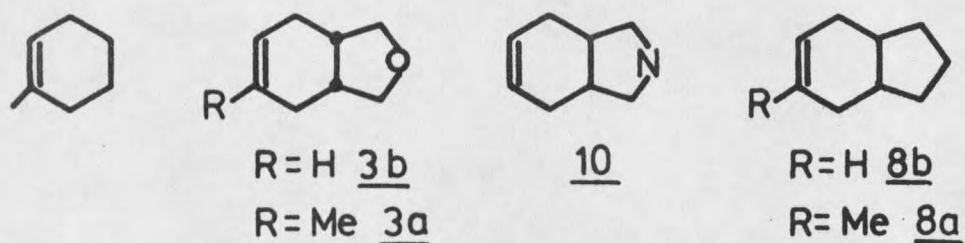


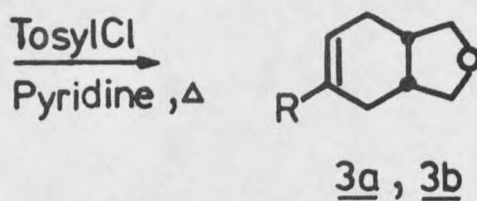
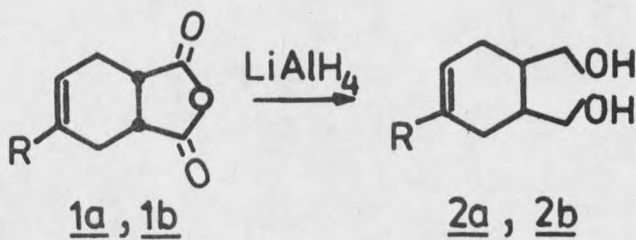
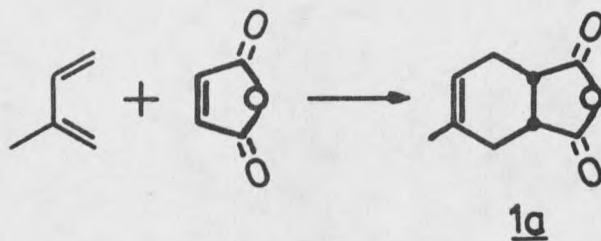
Figure 9. The major compounds prepared for this study.

The various compounds were prepared according to the reaction schemes shown in Figures 10-13. The Diels-Alder

reaction of isoprene with maleic anhydride resulted in the anhydride (1a). Lithium aluminum hydride reduction of the anhydrides (1a) and (1b) to the diols (2a) and (2b), followed by cyclization resulted in 3-methyl-8-oxabicyclo[4,3,0]non-3-ene (3a) and 8-oxabicyclo[4.3.0]non-3-ene (3b) (Figure 10). Conversion of 2a and 2b to the ditosylates (4a) and (4b) (Figure 11) followed by cyanide displacement gave the diacetonitriles (5a) and (5b). The hydrolysis of the diacetonitriles to the diacetic acids (6a) and (6b) was followed by the Ruzicka cyclization to the ketones (7a) and (7b), and Wolff-Kishner reduction of the carbonyl groups gave 8a and 8b.

Preparation of 1-methylcyclohexene was carried out by the reaction of cyclohexanone with methyl Grignard followed by dehydration with sulfuric acid (Figure 12).

Cis-8-azabicyclo[4.3.0]non-3-ene 10 was prepared (Figure 13) in one step by lithium aluminum hydride reduction of commercially available cis-1,2,3,6-tetrahydrophthalimide 11.



$\text{R} = \text{H}$ b

$\text{R} = \text{Me}$ a

Figure 10. Synthesis of cis-8-oxabicyclo[4.3.0]non-3-ene and 3-methyl-cis-8-oxabicyclo[4.3.0]non-3-ene.

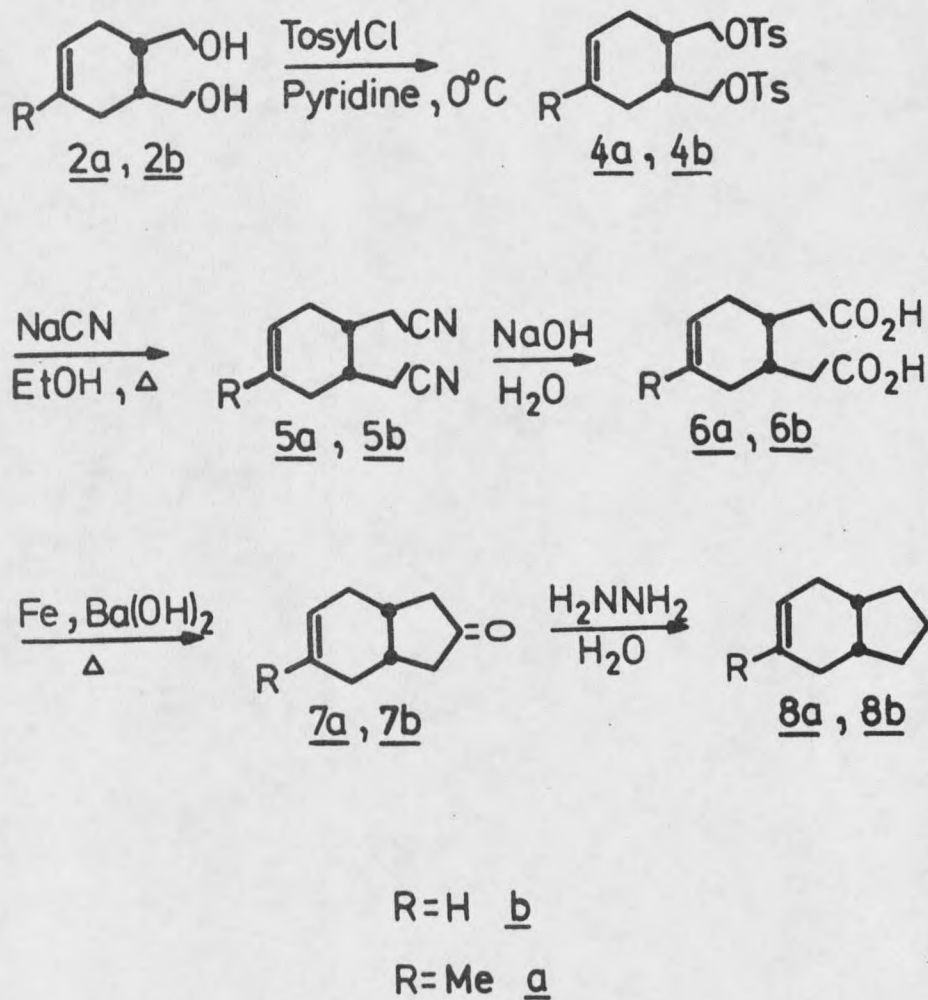


Figure 11. Synthesis of *cis*-bicyclo[4.3.0]non-3-ene and 3-methyl-*cis*-bicyclo[4.3.0]non-3-ene.

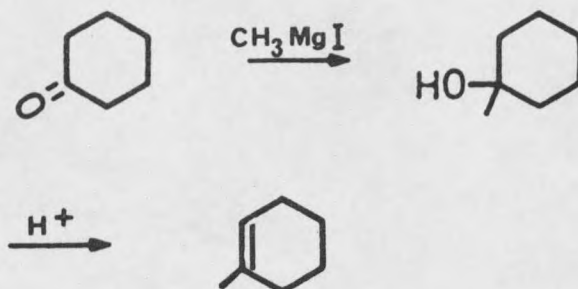


Figure 12. Preparation of 1-methyl-1-cyclohexene.

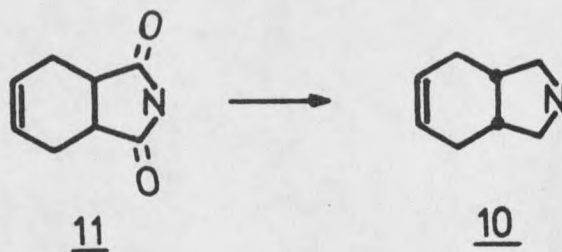


Figure 13. Preparation of cis-8-azabicyclo[4.3.0]non-3-ene.

Solvomercuration

Since the rate limiting step in the solvomercuration reaction is the solvolysis of the mercurinium ion intermediate, it is reasonable to assume, initially, that any rate enhancing effects are due to an increase in the rate of this step. A close examination of the relative rates shown in table 7 and the general reactivity sequence found by Brown indicates that the reaction rate increases when the electron demand is increased for one of the olefinic carbon atoms and decreased for the other. The

effect of making the olefinic carbon atoms electronically dissimilar would be to decrease the electron density of the P-orbital of the carbon atom with the lower electron demand and increase the electron density in the P-orbital of the other carbon atom. A decrease in the P-orbital electron density will increase the electrophile-nucleophile interaction energy between the mercurinium ion intermediate and solvent, resulting in a higher solvolysis rate.

The above rationale is supported by both the Markovnikov nature of this reaction and the rates obtained by Tinker. The increase in the charge on the carbon atoms resulting from using Hg^{+2} , compared to $\text{Hg}(\text{OAc})^{+1}$, results in a 1000 fold increase in the reaction rate. Likewise, the stereospecific Markovnikov addition resulting from solvomercuration indicates that the incoming solvent molecule "seeks-out" the olefinic carbon atom with the lower P-orbital electron density.

As a test for the above rationale, the compounds whose relative reaction rates are known were divided into five categories based on the position of allylic substituents, for which the following are the model compounds: propene, cis-2-butene, iso-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene. The total energy and the pi-orbital electron density of the $+1$ ion of the model compounds were then calculated using CNDO, the results of which are shown

in Table 15. As the plot of relative rate of the sample compounds vs. energy increase, from the neutral molecule to the +1 ion of the model compounds, shown in Figure 14, clearly illustrates there is No consistent relationship. However, a plot of the relative rate vs. the smaller P-orbital electron density of the olefinic carbon atoms, shown in Figure 15, clearly reveals that as the electron density decreases, the relative reaction rate increases.

Table 15
Electron density and energy increase for the
+1 ion and neutral molecules.

		electron		
olefin		density*		energy**
category	model	C1	C2	0 - +1
1,1-disubstituted	isobutene	.130	.523	1.23
monosubstituted	propene	.144	.459	1.33
trisubstituted	2-methyl- 2-butene	.369	.472	1.11
cis-1,2- disubstituted	cis-2-butene	.389	.379	1.20
tetrasubstituted	2,3-dimethyl- 2-butene	.440	.444	1.05

* Electron densities of the +1 ions with C₁ being the more substituted carbon atom.

** Energy difference, in atomic units, between the neutral molecule and the +1 ion.

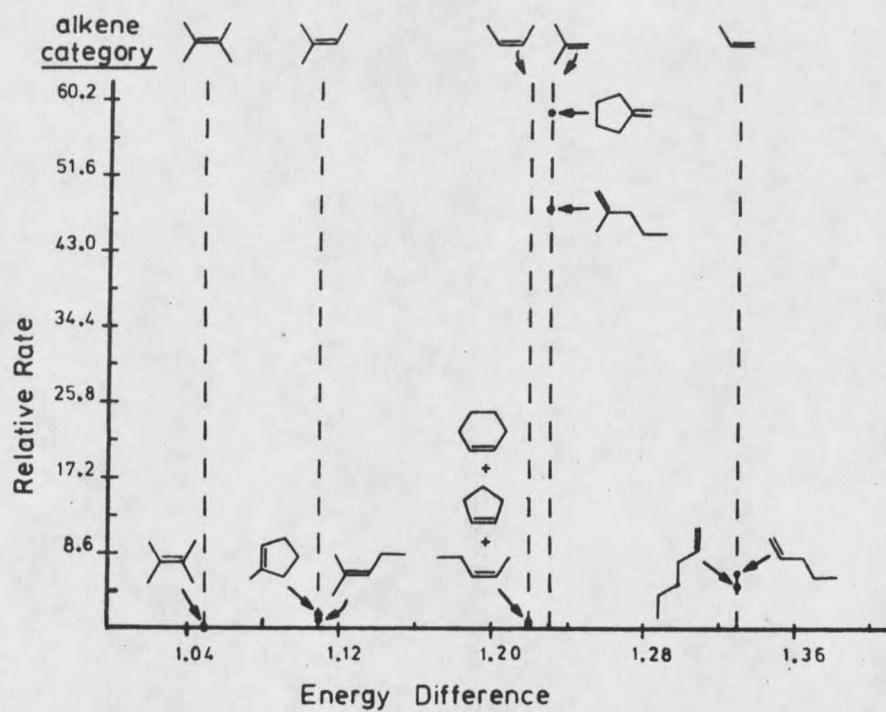


Figure 14. Effect of energy on solvomercuration rate.

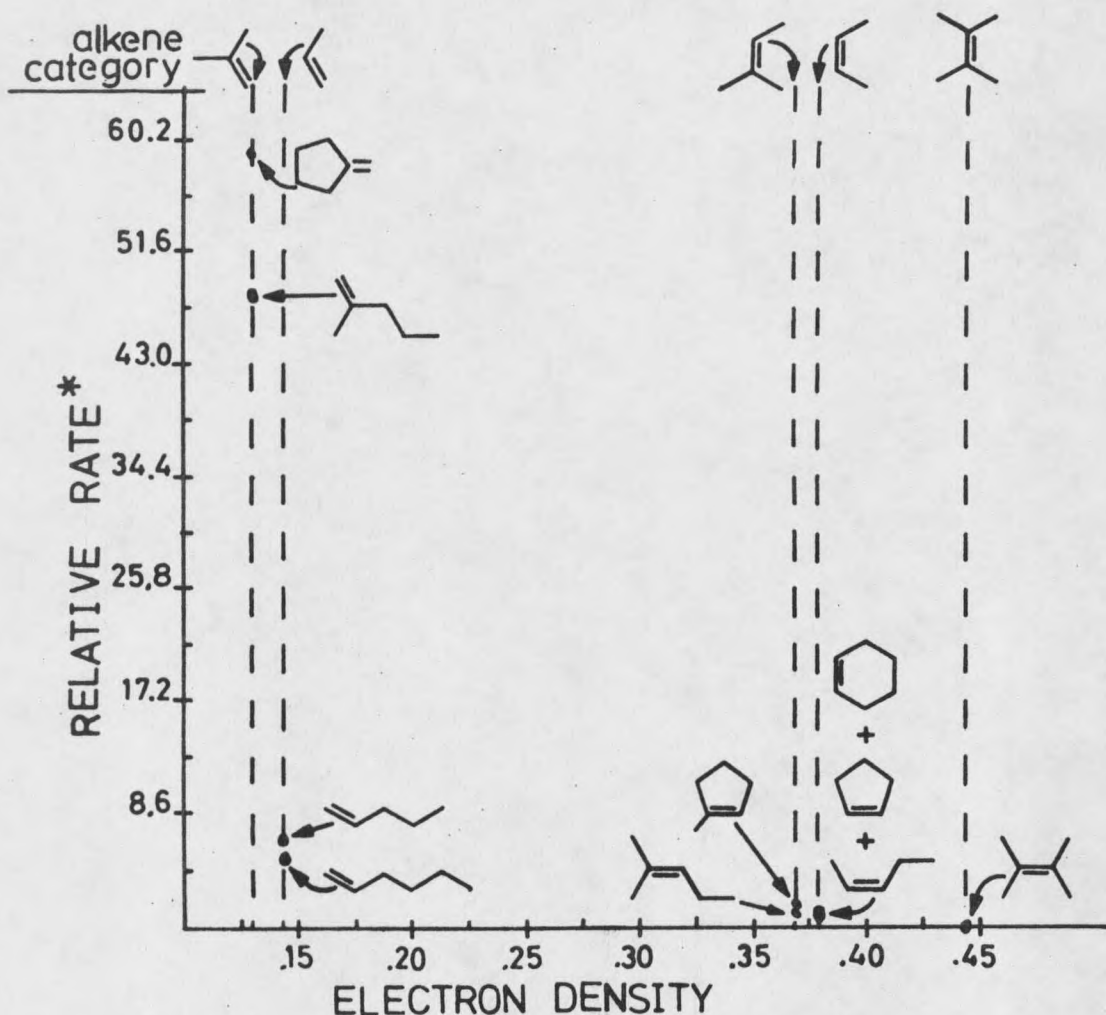


Figure 15. Effect of electron density on solvomercuration rate.

Under this model, conjugating the olefin with benzene would result in a rate decrease, due to an increase in the total electron density of the double bond in the mercurinium ion intermediate. It would also follow that if the electron demand of the olefinic carbon atom to which the benzene ring is attached were decreased, the degree of delocalization would likewise decrease, resulting in a rate increase.

The advantage of this solvomercuration model over the previous one, where the rate enhancements were attributed to the intermediate stability, is in its consistency with known kinetic data. Under this model, substituents which effect the rate are rationalized in terms of their influence on the rate determining solvolysis step, rather than on the "fast" intermediate formation step.

Based on this model, an alternate hypothesis for the rate enhancement observed by Otzenberger for cis- and trans-8-oxabicyclo[4.3.0]non-3-ene, compared to the carbon analog, would be that the electron density in the mercurinium ion intermediate had been lowered. This would then indicate that the ethereal oxygen influenced the reaction rate by induction rather than participation. The potential for the ethereal oxygen atom of these molecules to electronically influence the mercurinium ion intermediate is illustrated by the relatively low epoxidation rate and high permanganate oxidation rate for the cis-8-oxabicyclonon-3-ene, as discussed earlier.

A viable test to determine whether or not the ethereal oxygen is influencing the rate of solvomercuration by induction would be to compare the relative rate of cis-8-oxabicyclo[4.3.0]non-3-ene with its 3-methyl derivative. The electron donating ability of a methyl group placed on the double bond would counter the electron

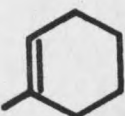
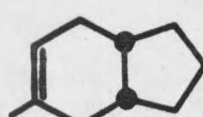
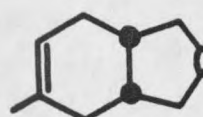
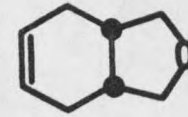
withdrawing effects of a ether linkage three carbon atoms away. Since a trisubstituted olefin normally results in a higher solvomercuration rate than an internal disubstituted olefin, a reverse in the relative rate sequence would clearly indicate the oxygen atom is decreasing the electron density of the reaction center. If on the other hand the addition of a vinyl methyl group results in a further rate enhancement, then the effects of the oxygen atom may be steric in nature.

The decrease in the relative solvomercuration rate, shown in Table 16, when a vinyl methyl group was added to the oxabicyclononene does in fact indicate that the oxygen effect on the solvomercuration reaction is electronic in nature rather than steric. Further evidence against steric and participation arguments for the rate enhancement has been independently observed in our laboratory⁶⁰ by examining the stereochemistry of solvomercuration and epoxidation of the propellene shown in Figure 16. The lack of stereochemical preference in both the epoxidation and solvomercuration reaction of the propellene indicates that the oxygen atom does not directly participate in either reaction.⁶⁰



Figure 16. Stereochemistry of epoxidation and solvomercuration.

Table 16
The vinyl methyl effect.

compounds	relative rate (R=Me/R=H)
 / 	1.29 ($\pm$.07)
 / 	1.40 ($\pm$.36)
 / 	0.67 ($\pm$.16)

The unexpectedly low Me/H rate ratio found for cyclohexene, with a value of 1.3 instead of 2 as found by other workers⁶¹, may be due to the solvent effects. Most solvomercuration studies, by other investigators, have been carried out in H₂O/THF solvent; however, this investigation was conducted in MeOH. The ionic strength of the solvent has

been shown to effect the absolute rate of solvomercuration, but little work has been done with regard to solvent effects on the relative rates.¹⁰

From these results we tentatively conclude that, contrary to published rationalizations, changes in the rate of solvomercuration are in fact due to influences on the electronic and steric parameters of the solvolysis step. Results in the literature clearly indicate that the rate of formation of the mercurinium ion intermediate is both fast and sterically insensitive. Since the "polarization" of the electron density of the pi-bond, in the mercurinium ion intermediate, will follow the same trend as the carbonium ion stability, it is possible that the ρ^* value obtained by Tinker was not an indication of the degree of carbonium ion character formed in the transition state for the mercurinium ion intermediate; but rather the electronic effects on the solvolysis step. As a test to determine whether the ρ^* value found by Tinker is due to stabilization of the incipient charge in the transition state or is due to the increase in the solvolysis rate, experiments should be carried out to find the ρ^* value for HgOAc^{+1} in THF/ H_2O , which has been shown to produce little carbonium ion character.

The solvomercuration reaction has an unusual mechanism for an organic process, in that few reactions occur in which

the formation of a charged species is not the rate limiting step. As such, care must be taken to avoid confusing cause and effect relationships of this reaction with those of a "typical" solvolysis reaction. Other studies in our laboratory are investigating these facets of this reaction in more detail.

Hydrogenation at One Atmosphere

The apparatus used in this study was designed and built in our laboratory; the methodology, however, has been used by other investigators.⁶² The major components of the apparatus, shown in Figure 17, are a reaction flask, an electrolysis cell, a current integrator, an 8080 based microcomputer equipped with a real time clock, and a mercury manometer-switch. A more complete diagram of the apparatus is shown in Appendix B. Although the methodology used in this study had a lot of potential, a number of technical flaws became evident after the data had been analyzed. The next few paragraphs describe some of the problems with the above design.

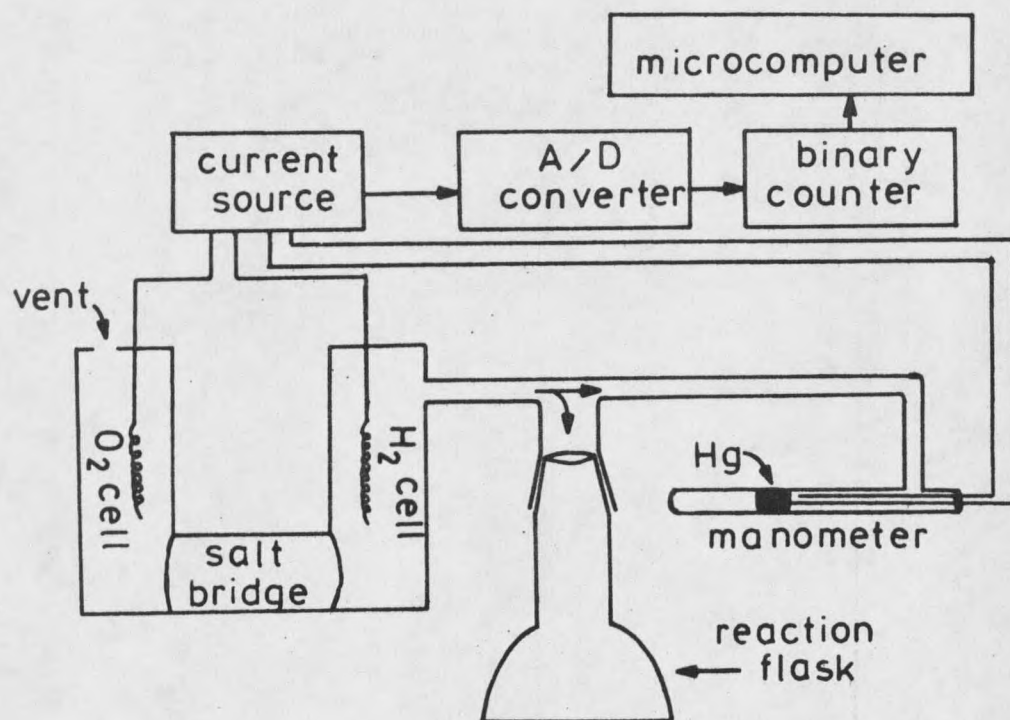


Figure 17. One atmosphere hydrogenator.

Although the salt bridge, separating the hydrogen cell from the oxygen cell of the electrolysis chamber, was necessary to maintain constant pressure in the reaction flask the small bore connecting the hydrogen cell to the salt bridge limited the rate of hydrogen production. This then set a limit on the amount of catalyst we could use in the reaction to about 2 mg. Because of the small amount of catalyst any variation in particle size and loss from it sticking to the sides of the flask resulted in significant reaction rate changes.

The horizontal mercury manometer, shown in Appendix B, used in this apparatus offered better sensitivity than a

vertical design. However, due to the small amount of mercury used in this manometer, any oxidation of the mercury decreased the sensitivity to the point where the pressure differential between the electrolysis cells broke the seal between the salt bridge and the plexiglass.

The binary counters used for the current integrator, as shown in Appendix B, were effected by the voltage spikes in the power supply caused by the constant temperature bath. These aberrations in the data could have been eliminated by adding filtering capacitors to the circuit power supply had the cause been detected sooner than it was.

The computer program, shown in Appendix B, collected the data, made a rough plot, calculated the linear regression, and printed the moles of hydrogen consumed and the time intervals. The lack of mass storage on the microcomputer caused a considerable lag between the time the data were collected and a complete analysis was conducted. The inconsistencies in the reaction data were not detected until a sufficient number of reactions had been carried out under a variety of conditions.

The design flaws described above makes direct comparisons of the absolute rates impossible; however, the trends in the rate profiles and induction periods are intact. A comparison of the results obtained from the reactions conducted at one atmosphere with the results from

the medium pressure reactions, to be discussed later, reveals a consistency between the results.

The general reaction parameters used during this set of experiments are as follows:

1. The catalyst was used as purchased without pretreatment.
2. The catalyst was added to a solution of substrate, in either ethanol (EtOH) or cyclohexane, before the introduction of hydrogen. Hydrogen was then allowed to flow over the reaction mixture to remove the air from the system.
3. The solution was stirred instead of shaken, which was one reason for the inconsistency in the data. The data collection was started as soon as the stirrer was turned on so that the delay period could be measured.

The graph shown in Figure 18 illustrates the typical reaction delay and rate profile our lab found for cycloheptene in EtOH. Augustine et al.³³ proposed the delay in the initial reaction and the curvature was due to the time required for hydrogen to remove oxygen from the catalyst surface.

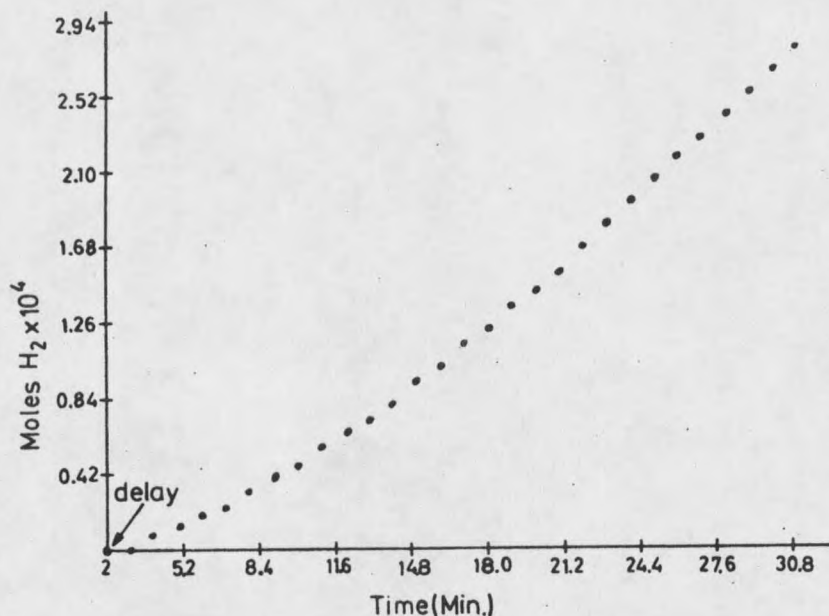


Figure 18. Hydrogenation reaction delay.

The addition of piperidine to the cycloheptene reaction solution resulted in an unexpected decrease in the degree of curvature of the rate profile and an increase in the reaction delay, as shown in Figure 19. A further increase in the reaction delay was observed when *cis*-8-azabicyclo[4.3.0]nonane was used as an inhibitor in the reduction of cycloheptene. In fact the induction period found when the azabicyclo[4.3.0]nonane was used as an inhibitor was only a little shorter than the reaction delay observed when *cis*-8-azabicyclo[4.3.0]non-3-ene was used as the substrate in ethanol, shown in Figure 20.

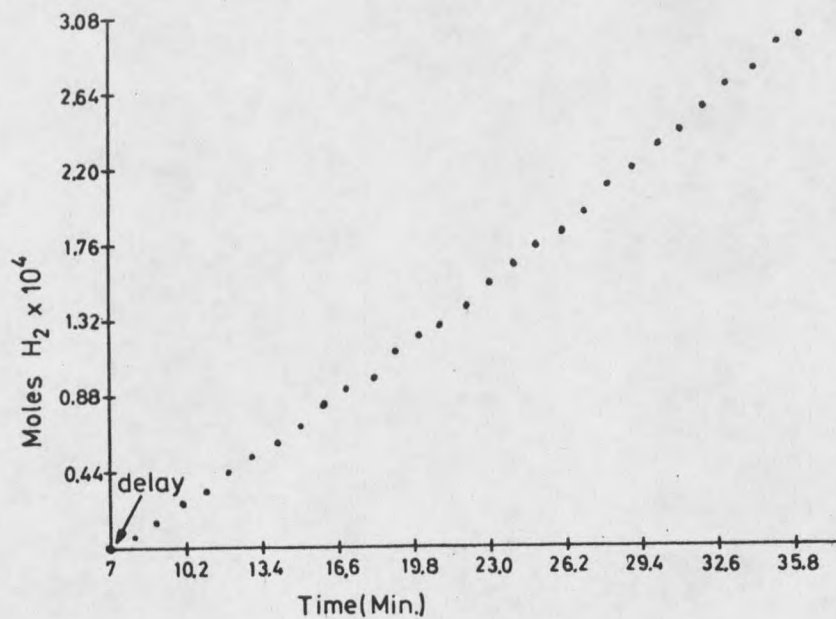


Figure 19. Effect of piperidine.

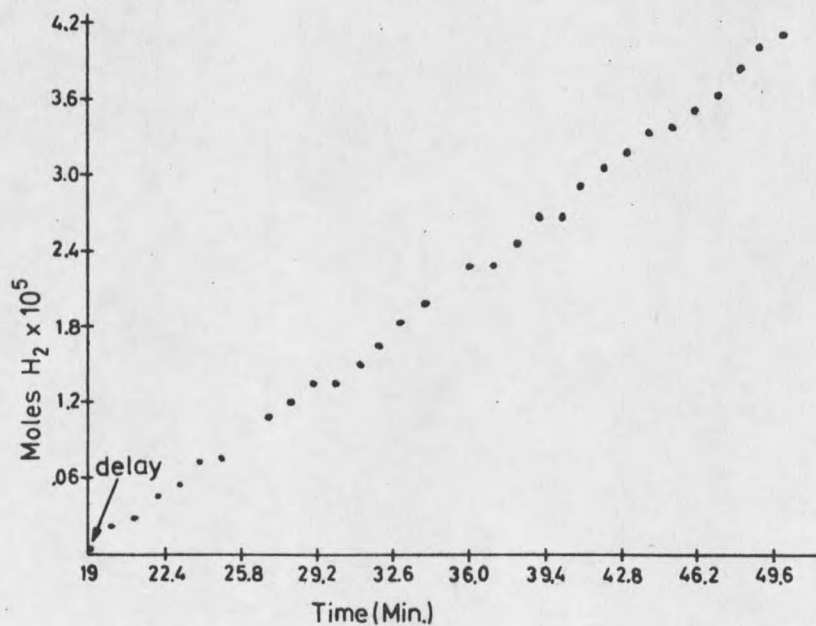


Figure 20. Hydrogenation of *cis*-8-azabicyclo[4.3.0]non-3-ene.

The reaction delay found for *cis*-bicyclo[4.3.0]non-3-ene in EtOH, shown in Figure 21, was about the same as was found for cycloheptene in EtOH. However, the induction period observed for cyclohexene in cyclohexane was smaller than for either cycloheptene or the bicyclo[4.3.0]non-3-ene. With the addition of piperidine to the cyclohexene in cyclohexane solution, a very large induction period was observed. The degree of curvature resulting from the addition of piperidine to the cyclohexene reaction indicated the reaction was almost completely inhibited, as shown in Figure 22.

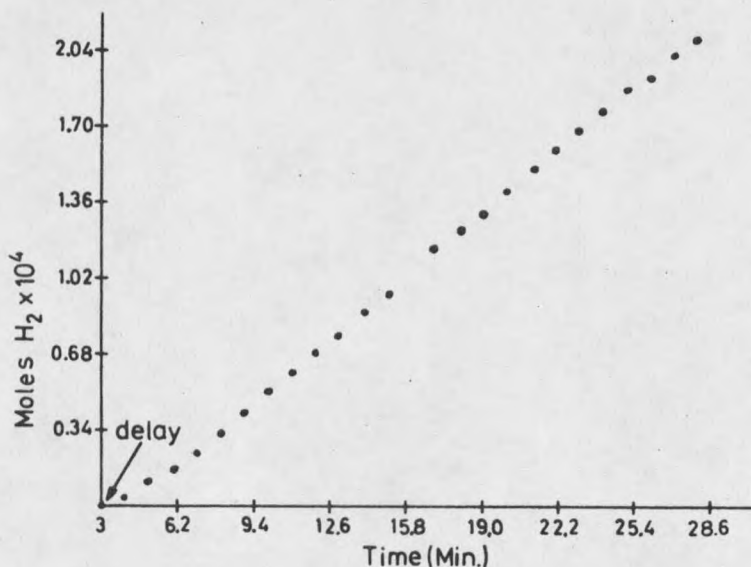


Figure 21. Hydrogenation of *cis*-bicyclo[4.3.0]non-3-ene.

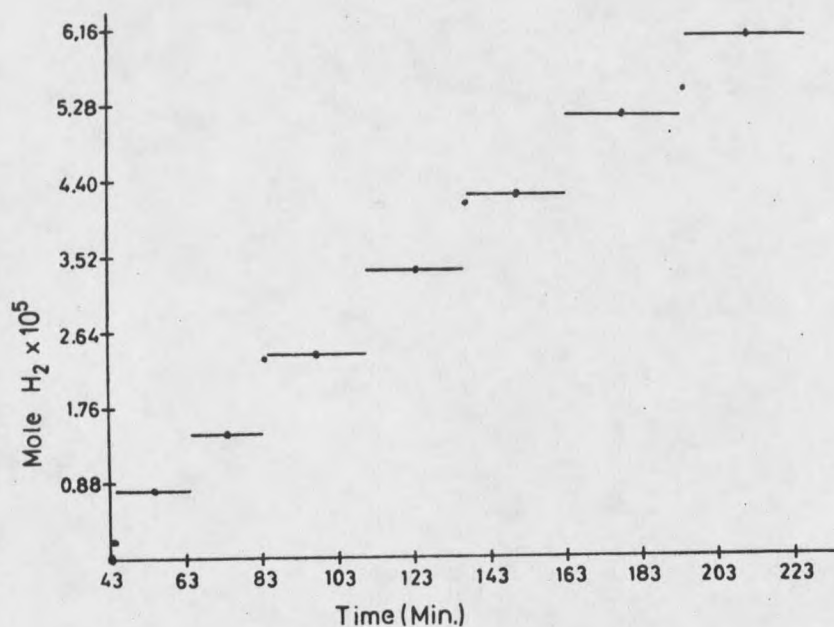


Figure 22. Effect of piperidine on cyclohexene reduction rate.

Although no firm conclusions can be drawn from these results they do raise important questions with regard to the source of the reaction delay and the curvature in the rate profile. If the delay were simply due to adsorbed oxygen on the catalyst surface why would the addition of an inhibitor result in an increase in the induction period? Likewise, why would using cyclohexane instead of EtOH decrease the observed induction period?

Due to the technical problems with this apparatus as well as general problems encountered with one atmosphere hydrogen pressure it was preferable to continue this investigation using a medium pressure apparatus. The rest

of this study was conducted using a modified Parr medium pressure hydrogenation apparatus. This apparatus allowed reactions with up to 60 psi total pressure to be carried out.

Medium pressure hydrogenation study

Briefly, the hydrogenator used in this study, shown in Appendix C, consisted of a medium pressure reactor, a constant temperature water bath for the reaction flask, a pressure sensor with an analog to digital converter, a pressure controller, and a microcomputer. The pressure sensor was a pizo electric crystal based transducer which converted the reactor pressure into an analog voltage that was then converted to a digital value by a computer controlled circuit, shown in Appendix C. The pressure controller, also shown in Appendix C, compared the voltage from the pressure transducer to two "standard" voltages. The relationship between the transducer voltage and the standard voltages was used to turn a solenoid valve on and off. A listing of "initialization", calibration, and stability computer programs are shown in Appendix C.

Initially the medium pressure hydrogenator consisted of the medium pressure reactor, reaction flask, pressure transducer, interface circuit, and the microcomputer. Visible variations in the hydrogen pressure with changes in

room temperature prompted us to enclose the flask in a water jacket. After a series of reactions had been completed, variations in the reaction rate became obvious. The inconsistency in the initial rate was at first attributed to temperature effects on the transducer response, since all the other components were considered temperature stable. However, the rate variations persisted after the transducer was enclosed in a controlled environment. This then led us to believe the differences in the rate were due to variations in the catalyst surface area, since the method of production and stability was an unknown variable.

After a number of reactions had been carried out, under a wide variety of conditions, the pressure controller was installed. Up to this point the operator had to manually repressurize the flask. The pressure controller was connected directly to the transducer, which allowed us to compare the transducer output voltage with the pressure gage at the maximum and minimum pressure settings. The consistency of the pressure span indicated that the rate variations were not due to transient transducer responses.

Shortly after the pressure controller was installed we found it necessary to install a cooling fan to the back of the computer, since the linear regulated power supply increased the computer temperature above the 90°F room temperature. At one point the fan was turned on after a

reaction had been started. This resulted in a substantial decrease in the computer measured pressure span, even though the observed pressure span had not changed, indicating the rate variations were due to fluctuations in the interface circuit calibration. A plot of calibration vs computer temperature, shown in Figure 23, clearly revealed that the variations in the rates were due to changes in the pressure to digital conversion.

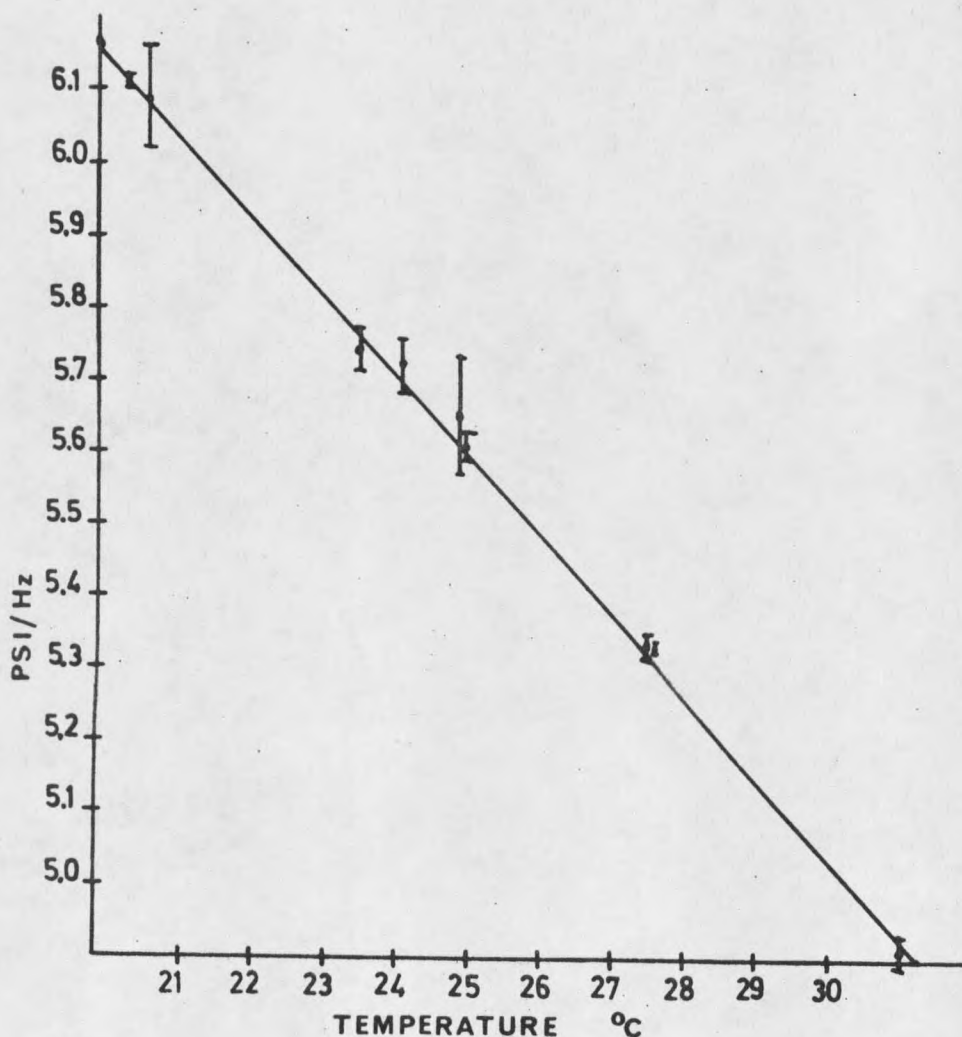


Figure 23. Temperature effect on calibration.

In order to determine which component of the interface circuit was temperature sensitive, the analog portion of the circuit was monitored with a voltmeter and the digital portion with an oscilloscope. By monitoring both parts of the circuit the temperature was found to be due to the voltage to frequency converter (V to F) circuit. After replacing the capacitor in the capacitor-resistor couple, used to adjust the frequency span of the V to F converter, the interface circuit was found to be temperature stable.

The computer program used for collecting the data, listed in Appendix C, carried out the following tasks:

1. It monitored the real time clock in the computer, allowing the data points to be collected at preset time intervals and for a preset period of time.
2. It sent a control code number to the "interface" circuit determining how much the signal from the transducer was to be amplified and/or offset in order to keep it within a measurable voltage range. The code number could be predetermined or computer determined.
3. It stored the data, read as a binary number from the interface circuit, on a floppy disk under a preset format in such a way that it could be recalled with a minimum amount of search time.

Computer programs were build to analyze the data in

three stages. The data were plotted shortly after the reaction was finished to determine if the integrity of the data permitted further analysis. Plots of this type were crude teletype graphs, using the computer programs listed in Appendix C. Once it was determined the data were free of mechanical errors it was plotted with previously collected data, using the computer programs shown in Appendix C, to determine consistency and/or relationships. The final form of analysis involved numerical curve fitting, which was carried out using the computer programs shown in Appendix C.

The reactions carried out at medium pressure (50-55 psi) were under somewhat different conditions from those at one atmosphere. The substrate was still added to the catalyst before hydrogen was admitted to the reaction flask. The catalyst weight used was increased from 2 mg for the one atmosphere to 10 mg. The reaction solution was shaken instead of stirred. The solution volume was increased from the 2 mL used at one atmosphere to 20-50 mL. The larger quantities resulted in a more statistical average of surface area for a given sample of catalyst.

By automating our hydrogenator we were able to collect and manipulate more data than would have been considered practical by other means. The larger number of data points permitted us to examine fine details of the hydrogenation reaction which are masked when only a portion of the

reaction is examined. The results presented here are the "bottom-line" conclusions reached after the examination of about 175 reactions. Although few of the results have the statistical limits given, they are backed by the internal consistency and reaction trends of a large data base.

The reduction of cyclohexene in EtOH at medium pressure, shown in Figure 24, has a significantly different rate profile from those reactions carried out at one atmosphere. Instead of the induction period found at one atmosphere, when the olefin was added to the catalyst first, reactions at medium pressure showed an enhanced initial rate.

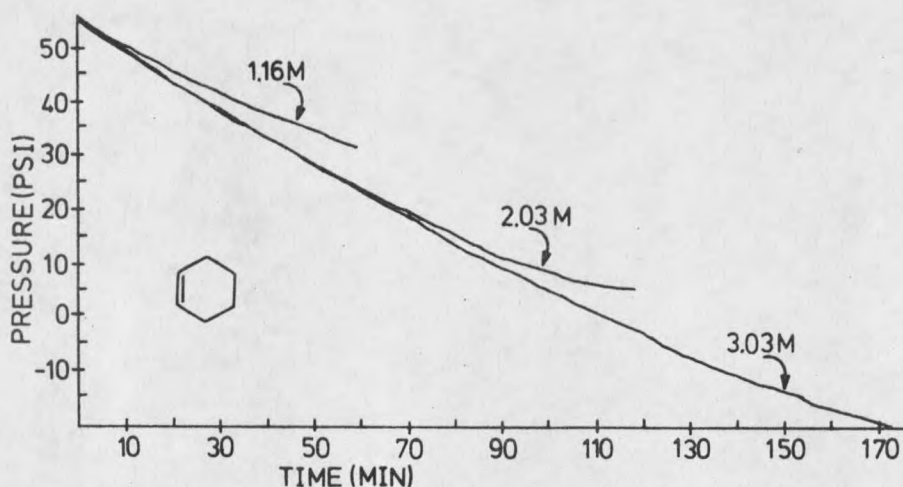


Figure 24. Reduction of cyclohexene in ethanol.

As mentioned earlier most investigators assume that when an inhibitor is added to a hydrogenation solution only the olefin adsorption is inhibited. Then by determining the

inhibitor concentration needed to reduce the initial rate by a predetermined amount, the relative adsorbtivity of the inhibitor is calculated. Based on the Langmuir-Hinshelwood type mechanism, the model used by most investigators, when the substrate adsorption is inhibited the reaction order with respect to substrate concentration should increase, ie. the degree of curvature in the rate profile should increase.

We chose THF as a model for the investigation of the oxygen effects in the hydrogenation of *cis*-8-oxabicyclo[4.3.0]non-3-ene. The results shown in Figure 25 illustrate the effect of adding THF to a reaction solution of cyclohexene in EtOH. As indicated by the decrease in the initial rate the reaction was inhibited; however, the inhibition was not accompanied by an increase in the substrate reaction order. In fact, the degree of curvature in the rate profile did not increase even when the concentration of THF was sufficient to perturb the solvent characteristics, as indicated by the increase in the initial rate with a high THF concentration.

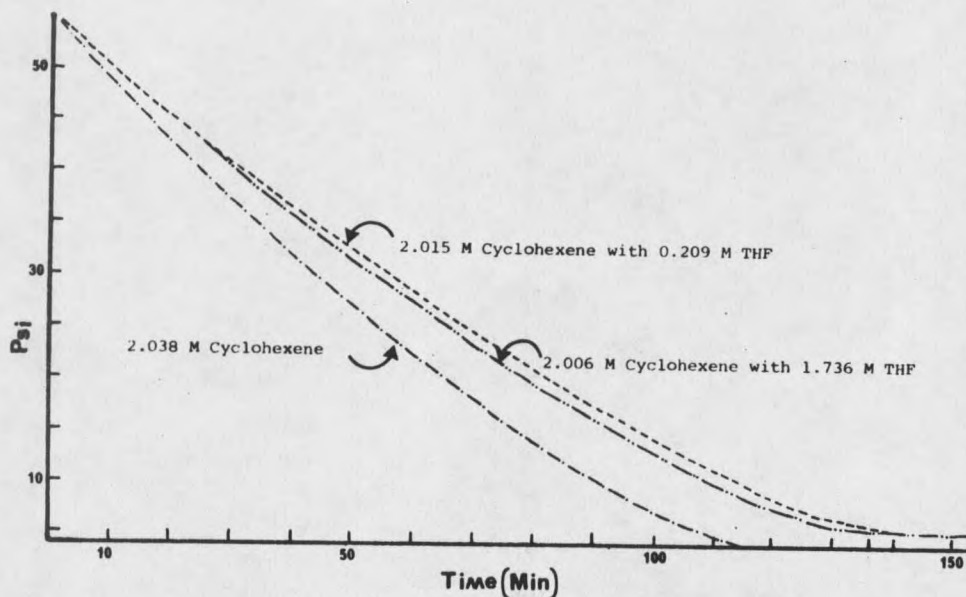


Figure 25. Effect of THF on cyclohexene reduction.

As a probe for characterizing the rate profile we subjected Equation 7 to curve fitting techniques. This equation is a simplified version of the Langmuir-Hinshelwood equation. By setting the hydrogen adsorption isotherm, $K(H_2)P(H_2)/(1+K(H_2)P(H_2))$, equal to a constant, which may not be true even though the pressure was maintained between 50 and 55 psi, and dividing the denominator and numerator of equation 5 (page 40) by the substrate adsorbtivity coefficient, K_s , equation 7 results upon simplification.

$$\text{rate} = [\text{sub}]/\text{min} = K'W[\text{sub}]/(K_{1/\text{sub}} + [\text{sub}] + K_{\text{pro}/\text{sub}}[\text{prod}]) \quad (7)$$

$$\text{Where: } K' = a k P(H_2)K(H_2)/(1 + P(H_2)K(H_2))$$

from equation 5

W = the catalyst weight

$[sub]$ = the substrate concentration

$$K_{1/sub} = (K_{inh} [inh] + K_{sol} [sol] + 1) / K_s$$

from equation 5

$$K_{pro/sub} = (\text{product adsorbitivity coefficient}) / K_s$$

The values of the constants were then determined using an iteration technique, shown in Appendix C, for a "best-fit" between the calculated and observed product concentrations. The interpretation we propose for the value of the constants are as follows:

1. Most investigators have attributed observed rate decreases, from the addition of inhibitors, to an increase in the value of $K_{1/sub}$. In general, the value of $K_{1/sub}$ is used to determine the dependency of the rate on the olefin concentration. The source of the concentration dependency can be from the inhibition substrate adsorption by solvent and/or an added inhibitor or a diffusion limited rate. Baltzly⁵⁴ used this term as a means of comparing the relative adsorbtivities of various inhibitors.
2. Most investigators have assumed the value of $K_{pro/sub}$ to be zero when an alkane product is formed in the hydrogenation reaction. In general this term will be significant only if the rate decreases faster than can

be attributed to changes in the substrate concentration during the course of a reaction. This can be due to the inhibition of substrate adsorption by product formation or a concentration independent decrease in the amount of adsorbed substrate.

Examples of the latter case would be a shift from the initial static to the dynamic reaction catalyst surface coverage by the olefin or a time dependent build up of a substance on the catalyst surface. If the rate decrease is due to the inhibition of substrate adsorption by product formation then $K_{\text{pro/sub}}$ is a true constant. On the other hand $K_{\text{pro/sub}}$ is not a true reaction constant if the rate decrease is due to the difference between the initial and dynamic adsorbed substrate concentration. In those cases where this term is not a true reaction constant the value of $K_{\text{pro/sub}} \times [\text{pro}]$ can be expected to reach a maximum value during the reaction.

3. A change in the value of K' from one reaction to another indicates an olefin concentration independent decrease in the reaction rate, a change in the solvent characteristics, and/or an inhibition of hydrogen adsorption. Since the inhibitors used in this study are "mild", the olefins can compete favorably for the catalyst sites. Any interactions between the

substrate and inhibitor should thus show effects on the concentration dependency of the rate. Most investigators assume that all of the readily available catalyst sites are occupied by substrate, in the absence of any inhibitors, and that only the few remaining sites are used for hydrogen adsorption. Based on this assumption, it has then been proposed that if an inhibitor is added only the olefin adsorption is inhibited. If this assumption is correct then the addition of an inhibitor should result in an increase in the value of $K_{1/sub}$ rather than a decrease in K' .

The computer program built to determine the "best-fit" values of $K_{1/sub}$ and $K_{pro/sub}$ used the root-mean-square (RMS) of the difference between the observed product concentrations and the calculated product concentrations. The calculated product concentrations were derived from the fourth order Runge-Kutta numerical integration of equation 7. The value of the constants were initially iterated in 10% increment. The increment was then decreased and the direction of the increment reversed every time the RMS passed a minimum, until the increment equalled $1 \times 10^{-2}\%$ of the value of the constant.

It became obvious early in analysis of the iteration results that this equation was an inadequate model to

describe the rate profile. The problem was traced to the assumption that the value of $K_{\text{pro/sub}}$ was a constant. A better fit occurred when a limit was placed on the maximum value of $[\text{pro}]$ from equation 7. Once the value of $[\text{pro}]$ reached the allowed limit, $[\text{pro}]_{\text{max}}$, it was held constant.

The best-fit values of $K_{1/\text{sub}}$ and $K_{\text{pro/sub}}$ were determined for each value of $[\text{pro}]_{\text{max}}$. The value of $[\text{pro}]_{\text{max}}$ was set equal to the calculated product concentration at each data point. The effect of the value of $[\text{pro}]_{\text{max}}$ on the RMS, shown in Figure 26, indicates that the olefin concentration independent decrease in the rate occurs only during the first portion of the rate profile.

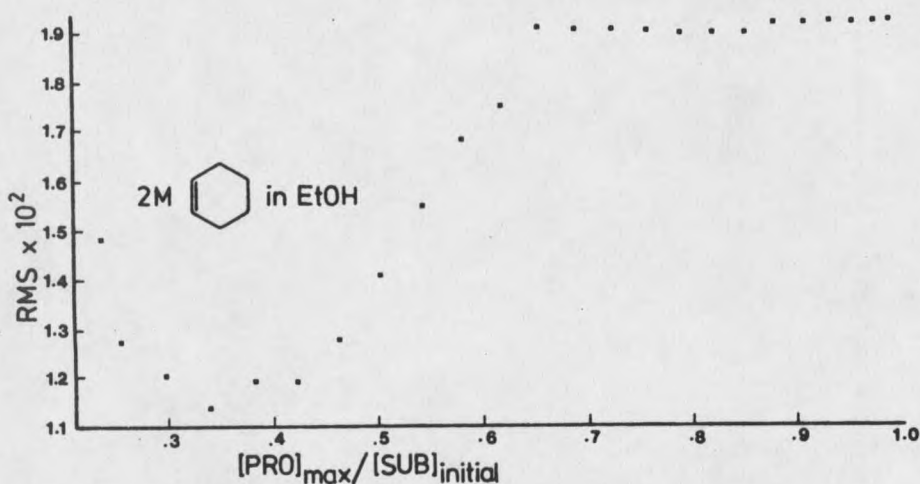


Figure 26. Graph of RMS vs $[\text{pro}]_{\text{max}}/[\text{sub}]_{\text{initial}}$

When interpreting the value of $K_{\text{pro/sub}} \times [\text{pro}]_{\text{max}}$, both its magnitude and the time required for $[\text{pro}]_{\text{max}}$ to be

reached may be significant. These two values can be used to determine if the inhibition is substrate concentration dependent or time dependent. If the inhibition is concentration dependent the relative magnitude of $K_{\text{pro/sub}} \times [\text{pro}]_{\text{max}}$ can be expected to decrease with an increase in the concentration of substrate. However, if the inhibition is concentration independent and time dependent then the relative magnitude can be expected to increase with an increase in the substrate concentration.

The results of the curve-fitting routine, shown in Table 17, reveals an increase in the value of $K_{\text{pro/sub}} \times [\text{pro}]_{\text{max}}$ proportional to the cyclohexene concentration in ethanol. This would then indicate that the rate decrease is independent of the substrate concentration and dependent on time.

Although the degree of inhibition is small, it is still significant and raises the question of its source. At this point two reasons for the rate decrease can be proposed. The substrate may initially be occupying catalyst sites that are simply unaccessible during the reaction. This would be the case if the cyclohexene had diffused into catalyst pores during the initial mixing of the substrate and catalyst in the absence of hydrogen. The second source of the rate reduction could be the slow build-up of a substance on the catalyst surface. The unknown substance would then be

blocking catalyst sites that were initially accessible to cyclohexene.

Table 17
Curve fitting results for cyclohexene in EtOH

[sub]	[THF]	$K' \times 10^2$	K_{sub}^1	K_{inh}^2	$[pro]_{max}$	time ³	RMS ⁴
1.04M	0	2.22	5.86	0.116	0.388M	19 min	0.31
2.03M	0	2.43	7.17	0.189	0.683M	30 min	1.1
3.03M	0	2.32	6.73	0.307	0.719M	33 min	2.1
2.01M	0.21M	1.97	4.20	0.202	0.718M	39 min	1.1
2.01M	1.74M	2.05	6.00	0.206	0.857M	45 min	0.91

1 $K_{sub} = K_1 / sub \times 10^3$

2 $K_{inh} = K_{pro/sub} \times [pro]_{max}$

3 time required for $[pro]_{max}$ to be reached

4 $RMS = RMS \times 10^2$

The effect of adding THF to the reaction solution did not effect the magnitude of the inhibition term as shown in table 17, which was likewise indicated by the lack of an observable increase in the degree of curvature in the graphs shown in figure 25. However, the time required for $[pro]_{max}$ had increased indicating that THF has slowed down the rate at which the substance causing the inhibition is covering the catalyst surface.

The results in table 17 also shows that the THF has decreased the value of K' . As mentioned earlier, the two possible reasons for the decrease in K' are from solvent characteristic perturbation and the inhibition of hydrogen

adsorption. The effects of THF on the solvent characteristics are illustrated by the increase in the K' when the concentration of THF was substantially increased. As discussed earlier, it is possible for molecules that adsorb onto the catalyst via a single atom to occupy portions of the catalyst surface that are not accessible to olefins. It is then reasonable to conclude that the THF had inhibited hydrogen adsorption. Since the catalyst sites not used by substrate are used by hydrogen, any molecule that occupies those sites would decrease the rate of hydrogen adsorption, resulting in a reduced rate.

If THF can adsorb onto the catalyst surface why not EtOH? As the results in Table 18 indicate, EtOH does in fact decrease the value of K' for the reduction of cyclohexene in cyclohexane. As with THF, low concentrations of EtOH decrease the reaction rate, however, as the concentration of EtOH is increased the rate also increases. This indicates that both THF and EtOH are restricted to only a small portion of the catalyst surface and as their concentration increases the solvent perturbation results in a higher reaction rate.

Table 18
Ethanol as an inhibitor in cyclohexane.

[sub]	[inh]	$K' \times 10^2$	K_{inh}^*	$[pro]_{max}$	time**	RMS***
2.02M	0	2.87	0.201	0.411M	16 min	1.8
2.01M	$\frac{0.27M}{THF}$	2.21	0.147	0.464M	22 min	1.5
2.03M	$\frac{0.26M}{EtOH}$	1.88	0.259	0.723M	42 min	0.3

* $K_{inh} = K_{pro/sub} \times [pro]_{max}$

** time required for $[pro]_{max}$ to be reached

*** $RMS = RMS \times 10^2$

Although the value of $K_{pro/sub} \times [pro]_{max}$ remains the same in cyclohexane as it was in EtOH, the time required for $[pro]_{max}$ to be reached had decreased by one half. The effect of THF and EtOH on the time factor indicates that both compounds had reduced the rate of inhibition. However, THF has decrease the magnitude of the inhibition while EtOH increased the magnitude.

The rough correlation between the reaction rate and the inhibition rate strongly suggests a link between the two. Since the above results indicate that both THF and EtOH inhibit hydrogen adsorption it is reasonable to suggest that adsorbed hydrogen is blocking some of the catalyst sites to substrate adsorption. Just as there appears to be limits to

the portions of catalyst THF and EtOH can adsorb onto, there also appears to be limits to the number of sites hydrogen can block, as indicated by the magnitude of $K_{\text{pro/sub}} \times [\text{pro}]_{\text{max}}$.

The reaction delays found when the catalyst was presaturated with olefin and low hydrogen pressure was used support the above hypothesis. When it is considered that piperidine, like THF, is capable of inhibiting hydrogen adsorption, it is then reasonable to conclude that the reaction delay was due to the time required for hydrogen to adsorb onto the catalyst and migrate to the adsorbed substrate. The addition of piperidine to the solution could then inhibit hydrogen adsorption sufficiently enough to increase the time required for the hydrogen to migrate to the active site. At 55 psi of pressure, instead of a reaction delay the hydrogen migration can occur fast enough to compete with cyclohexene adsorption for some of the catalyst sites.

The limit on the number of sites hydrogen migration can compete for would depend not on the amount of substrate in solution, but rather the inhomogeneity of the catalyst. The nonequivalence of catalyst sites has been well established. Thus if the catalyst is saturated with substrate before the introduction of hydrogen it is reasonable to expect that the substrate will not only occupy the sites it strongly

adsorbed onto but the catalyst sites for which it is only weakly adsorbed as well. Then as the amount of hydrogen on the catalyst increases it will replace the substrate on these sites. However, if the catalyst is saturated with hydrogen first then the substrate will adsorb onto only those sites for which it has a high affinity, resulting in a constant adsorbed substrate concentration.

A second plausible explanation for the link between the reaction rate, the inhibition time and the magnitude of $K_{\text{pro/sub}} \times [\text{pro}]_{\text{max}}$ would be one in which the adsorption of substrate is irreversible, as has been suggested by Hussy et al.³⁸ In the absence of a mechanism by which cyclohexene can desorb from the catalyst surface, the substrate could "nudge" its way onto catalyst sites inaccessible under reaction conditions. The enhanced initial rate would then be due to the combined rate of hydrogenation of cyclohexene on the "normal" and the abnormal catalyst sites. The rate reduction would then result from the gradual removal of the cyclohexene from the abnormal catalyst sites.

This rationalization would then suggest that the reaction delay found for the hydrogenation at one atmosphere is unrelated to the rate enhancement found under medium pressure. It does not, however, conflict with the proposed rationale for reduction in the value of K' with the addition of THF or EtOH to the reaction solution.

A potential flaw with the normal/abnormal site rationalization is the linearity between the substrate concentration and the value of $K_{\text{pro/sub}}[\text{pro}]_{\text{max}}$. Even if the abnormal catalyst site are difficult for cyclohexene to access, it is expected that if the substrate concentration were increased the the number of catalyst sites used would increase. This would then result in a decrease in the degree of apparent inhibition. However, if the sites are blocked by adsorbed hydrogen then an increase in the cyclohexene concentration would not effect the relationship between $K_{\text{pro/sub}}[\text{pro}]_{\text{max}}$ and the amount of substrate. However, there is still an unresolvable question as to which model is a true representation of what is occurring on the catalyst surface.

We are now left with the question of whether or not the value of $K_{\text{pro/sub}}x[\text{pro}]_{\text{max}}$ is a true indication of the substrate concentration dependency of the rate during the final portion of the rate profile. Even with the reasonable fit between the calculated and observed product concentrations, shown in Figure 27, there is not a clear indication that THF and EtOH does not interact with the cyclohexene adsorption. As the graph in figure 24 illustrates the most inhibitor sensitive concentration region is from 1 M cyclohexene to completion.

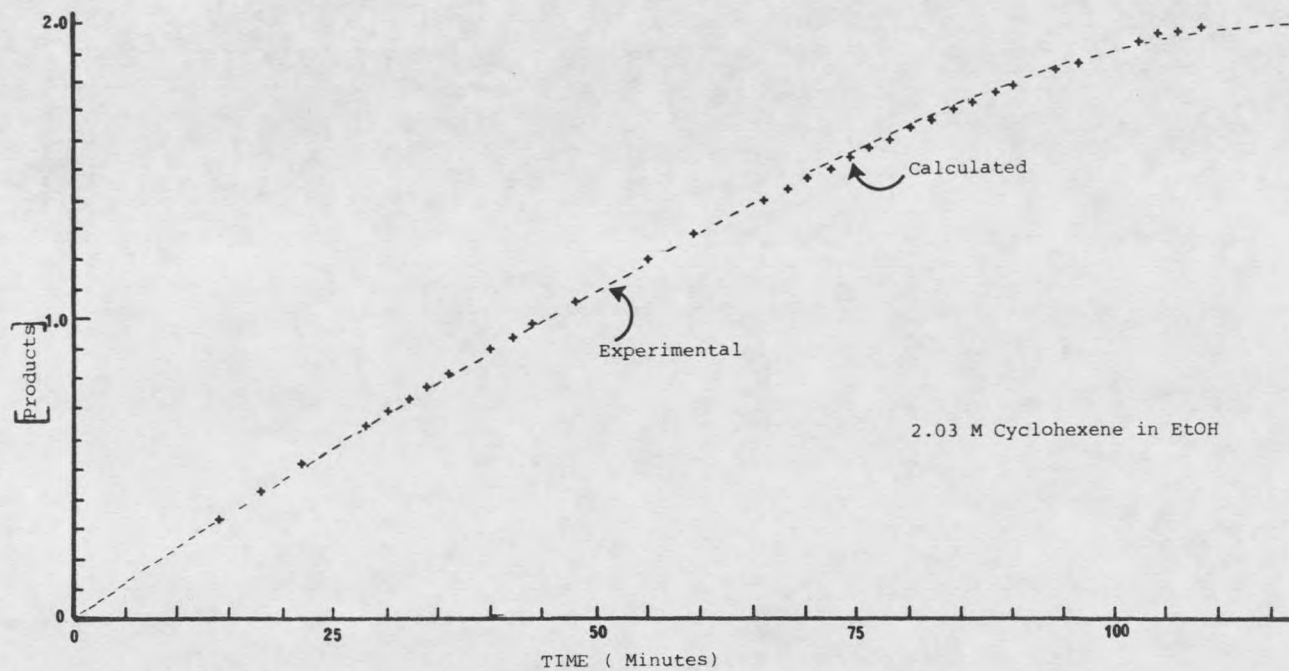


Figure 27. Calculated and Observed Product Concentration

As an alternate means of determining the degree of substrate inhibition by THF and EtOH, the slopes of $\ln(\text{rate})$ vs $\ln([\text{sub}])$ were calculated for a series of reactions in EtOH and cyclohexane. The rates were calculated by determining the slope between every two point interval. Since the maximum value of $[\text{pro}]_{\text{max}}$ was .86 moles/liter, the substrate concentration range chosen as the standard for comparison was from 1 moles/liter to 0.3 moles/liter for initial substrate concentrations of 2 moles/liter.

For the reduction of cyclohexene in EtOH, the reaction order with respect to substrate concentration, the slope shown in Table 19, indicates that the major source of substrate inhibition was due to the solvent. These results also indicate that as an inhibitor, EtOH is stronger than THF. The reason EtOH is a more potent inhibitor may be due to the conformational freedom of the CH_2CH_3 portion of EtOH, based on the conclusion proposed by Maxted et al.^{55,56} with regards to the size effect on thiol inhibitors.

Table 19
Results from $\ln(\text{rate})/\ln([\text{sub}])$ for 2M cyclohexene.

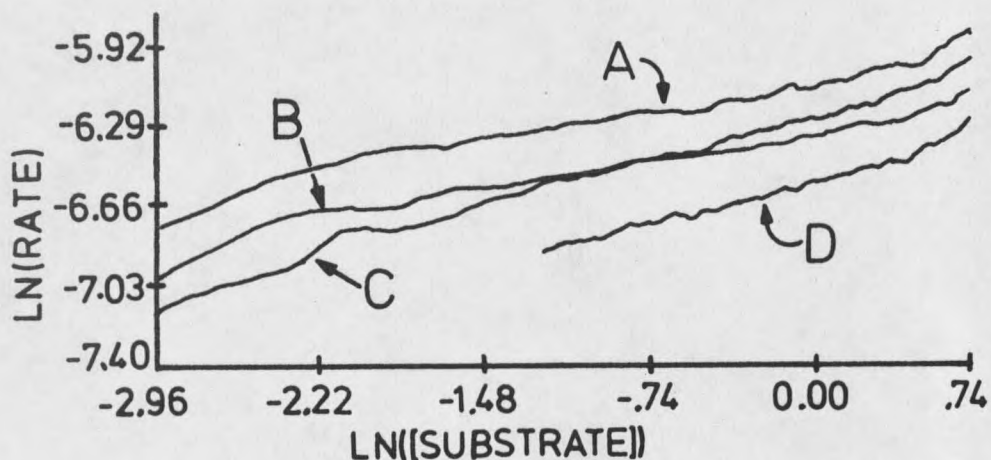
$K' \times 10^2$ *	slope**	y-inter***	[inh]	solvent
2.44 $\pm$.01	.246 $\pm$.008	-6.30 $\pm$.005	0	EtOH
2.85 $\pm$.05	.158 $\pm$.012	-6.14 $\pm$.004	0	C ₆ H ₁₂
1.83	.258	-6.22	.102M/THF	EtOH
1.97	.234	-6.51	.208M/THF	EtOH
2.05	.270	-6.48	1.73 M/THF	EtOH
2.21	.134	-6.37	.269M/THF	C ₆ H ₁₂
2.08	.189	-6.40	.551M/THF	C ₆ H ₁₂
1.86	.251	-6.58	.259M/EtOH	C ₆ H ₁₂

* K' = the initial rate

** slope = the reaction order with respect to substrate

*** y-inter = $\ln(\text{rate constant})$

A comparison of the slopes for EtOH as a solvent and as an inhibitor, shown in Figure 28, supports the conclusion reached earlier that the alcohol is restricted to only a portion of the catalyst surface. Otherwise the reaction order would be significantly higher when EtOH was used as a solvent compared to the low concentration inhibitor. These results also indicate that THF has little effect on the reaction order, as illustrated by the slope of the curves, but decreases the the initial rate significantly, as shown by the shift of the Y-intercept.



A - 2.03 M C1=CCCCC1 in C1=CCCCC1

B - 2.01 M C1=CCCCC1 in C1=CCCCC1 with 0.269 M THF

C - 2.04 M C1=CCCCC1 in EtOH

D - 2.03 M C1=CCCCC1 in C1=CCCCC1 with 0.259 M EtOH

Figure 28. Graph of $\ln(\text{rate})$ vs $\ln([\text{sub}])$ for cyclohexene in cyclohexane

The effect of adding THF to the cyclohexene reaction solution in EtOH, shown in Figure 29, also indicates that only the hydrogen adsorption had been inhibited and not the substrate adsorption. These results also show that even with a 7 fold increase in the THF concentration there is no noticeable increase in the reaction order nor was there a further decrease in the equilibrium reaction rates, as the data in table 19 indicate.

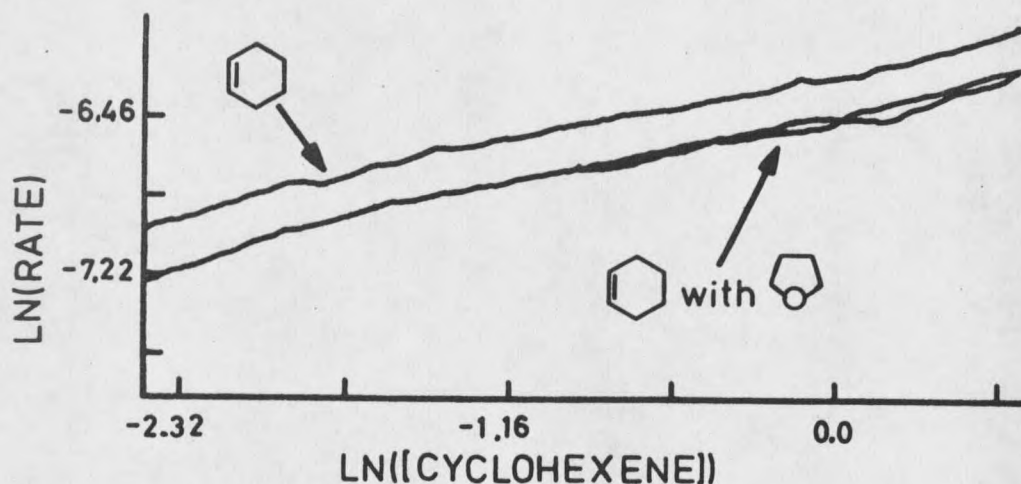


Figure 29. Graph of $\text{Ln}(\text{rate})$ vs $\text{Ln}([\text{sub}])$ for cyclohexene in EtOH

Based on the results above, cis-8-oxabicyclo[4.3.0]nonane should have two effects on the cyclohexene rate profile. Since this compound has only a single atom capable of adsorbing onto the catalyst surface, as did THF, it should be capable of inhibiting hydrogen adsorption resulting in reduced initial rate. The alkyl portion of this molecule is substantially larger than the methyl group on EtOH which should increase the inhibition of substrate adsorption, resulting in a larger slope in the reaction order plot. The graphs shown in Figure 30 illustrates the effect of adding various amounts of the oxabicyclo[4.3.0]nonane to the cyclohexene reaction solution. These results do indicate that the oxabicyclo[4.3.0]nonane is in fact inhibiting the

hydrogenation of cyclohexene, as shown by the decrease in the reaction rate. The lack of an increase in the slope of the $\ln(\text{rate}) - \ln([\text{sub}])$ plot, shown in Figure 31, at low concentrations of the oxabicyclo[4.3.0]nonane indicates that the major contribution to the rate decrease was due to the inhibition of hydrogen adsorption. As the concentration of the oxabicyclo[4.3.0]nonane was increased, the resulting larger slopes in the $\ln - \ln$ plots do indicate that substrate adsorption was being inhibited.

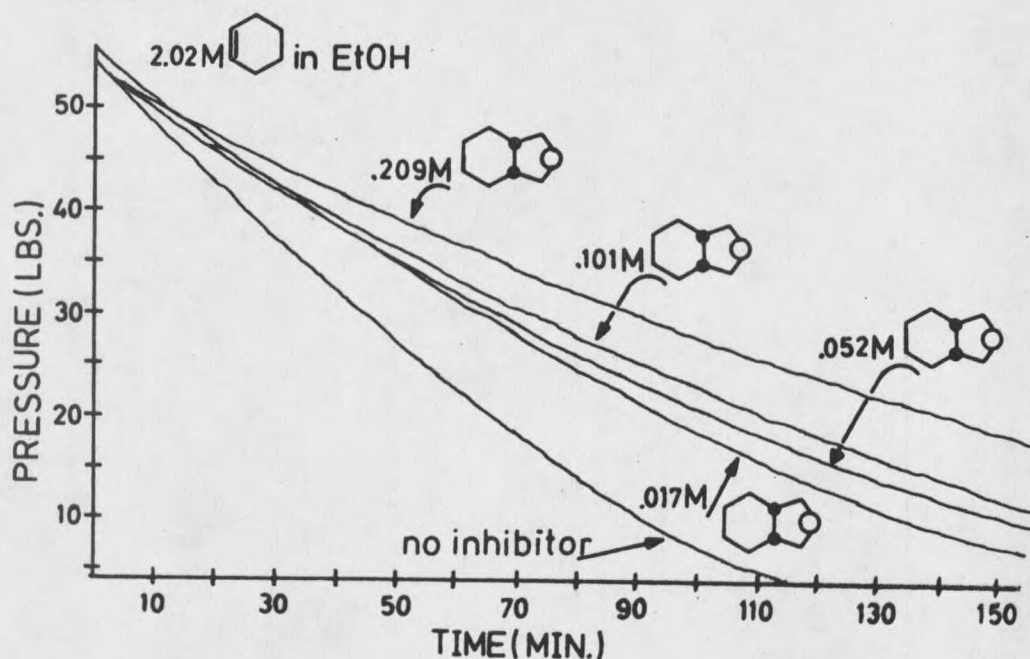


Figure 30. Effect of cis-8-oxabicyclo[4.3.0]nonane on hydrogenation of cyclohexene.

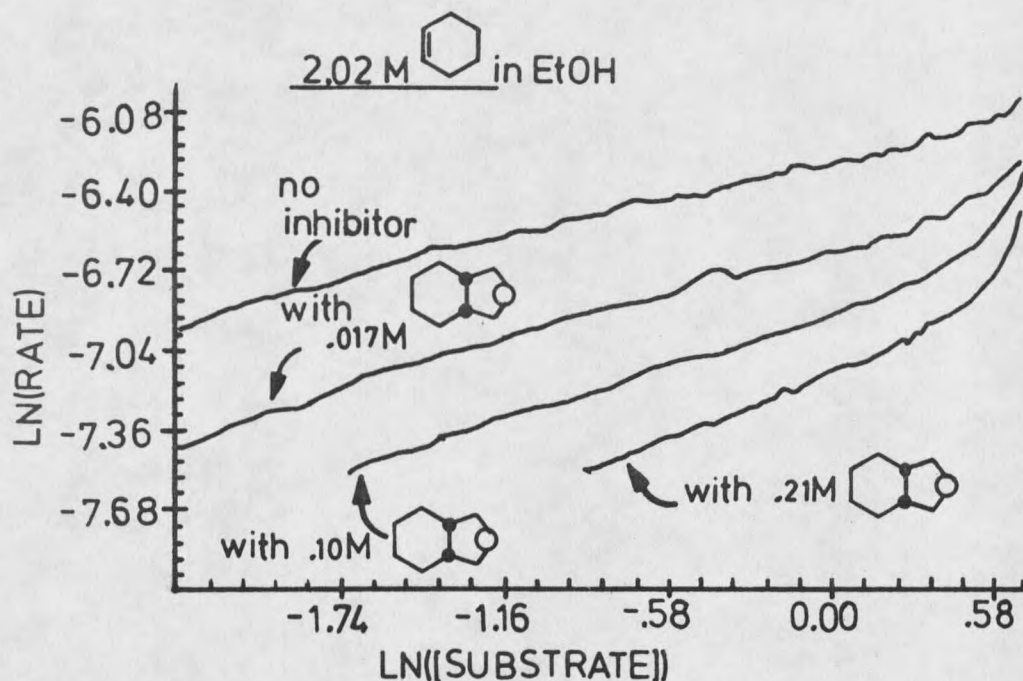


Figure 31. Graph of $\text{Ln}(\text{rate})$ vs $\text{Ln}([\text{sub}])$ for cyclohexene with cis-oxabicyclo[4.3.0]nonane.

In comparing the effects of cis-8-oxabicyclo[4.3.0]nonane and THF on the reduction of cyclohexene, it is of interest to recall the earlier discussion on the inhibitor size effects found by Maxted et al.^{55,56} As the size of the inhibitor increases so does the inhibitor-substrate interaction. A strong interaction between the oxabicyclo[4.3.0]nonane and cyclohexene is illustrated by the inhibitor concentration dependency of the rate. Unlike the inhibitor concentration effects found with THF which reached a maximum degree of inhibition at a low

THF concentration, the reduction rate continued to decrease as the concentration of the oxabicyclo[4.3.0]nonane was increased. Further evidence for a strong inhibitor-substrate interaction is revealed by the increase in the reaction order with respect to substrate concentration with "high" concentrations of cis-8-oxabicyclo[4.3.0]nonane.

Although the curvature in the initial portion of the $\ln-\ln$ plot does not totally disprove the hypothesis that the value of $K_{\text{pro/sub}}$ is due to the inhibition of substrate adsorption by hydrogen, it does support the normal/abnormal site theory. The reaction order with respect to substrate concentration indicates a strong interaction between cyclohexene and the oxabicyclo[4.3.0]nonane. The high initial rate followed by the rapid rate decrease indicates that the cyclohexene had initially adsorbed onto catalyst sites for which there was a strong interaction with the oxabicyclo[4.3.0]nonane. It is then reasonable to conclude that if the adsorbed cyclohexene concentration was the result of an equilibration between the adsorption and desorption of the olefin, there would not have been such a drastic decrease in the initial rate. It appears as though there was a gradual build up of cyclohexene onto the catalyst surface, in the absence of hydrogen.

The graph of pressure vs. time for the catalytic hydrogenation of cis-8-oxabicyclo[4.3.0]non-3-ene, shown in

Figure 32, reveals that the rate decreases with an increase in the substrate concentration. This indicates a negative reaction order with respect to substrate concentration, contrary to the first order found by Geneste et al.⁵⁰ for 3,4-dihydro-2H-pyran. However, the linearity of the pressure drop with time for any particular initial substrate concentration would indicate the reaction kinetics were zero order with respect to substrate concentration. Applying the curve fitting techniques to these reactions results in a value of zero for $K_{1/sub}$ and $K_{pro/sub}$ and a decrease in K' with an increase in the initial substrate concentration.

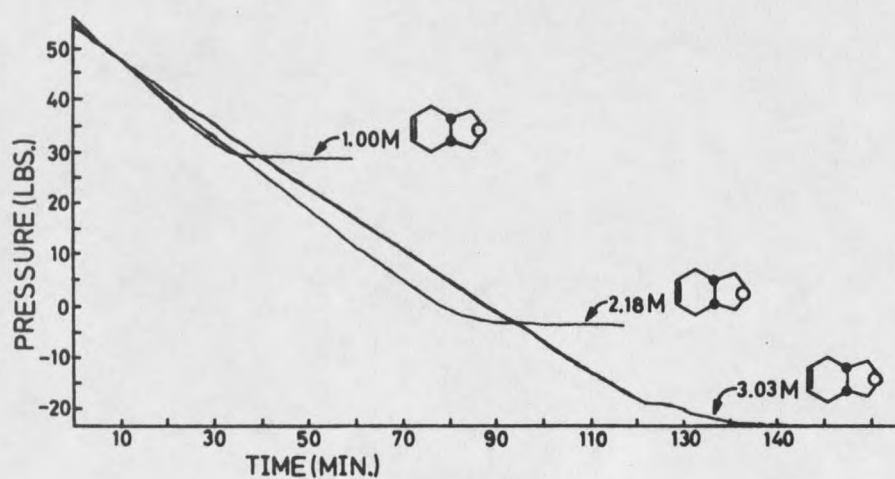


Figure 32. Catalytic hydrogenation of cis-8-oxabicyclo[4.3.0]non-3-ene.

By carrying out the reduction with a solution containing 2M cis-8-oxabicyclo[4.3.0]non-3-ene and 1M of the

cis-oxabicyclo[4.3.0]nonane, shown in Figure 33, it was revealed that the reaction rate had decreased to the rate of the 3M solution. This result illustrates that the oxygen atom was inhibiting the reaction. The zero values for the inhibition terms in the probe equation indicates that the hydrogen adsorption and not the adsorption of olefin was inhibited, since the inhibition of olefin by the ethereal oxygen would have resulted in a reaction order greater than zero.

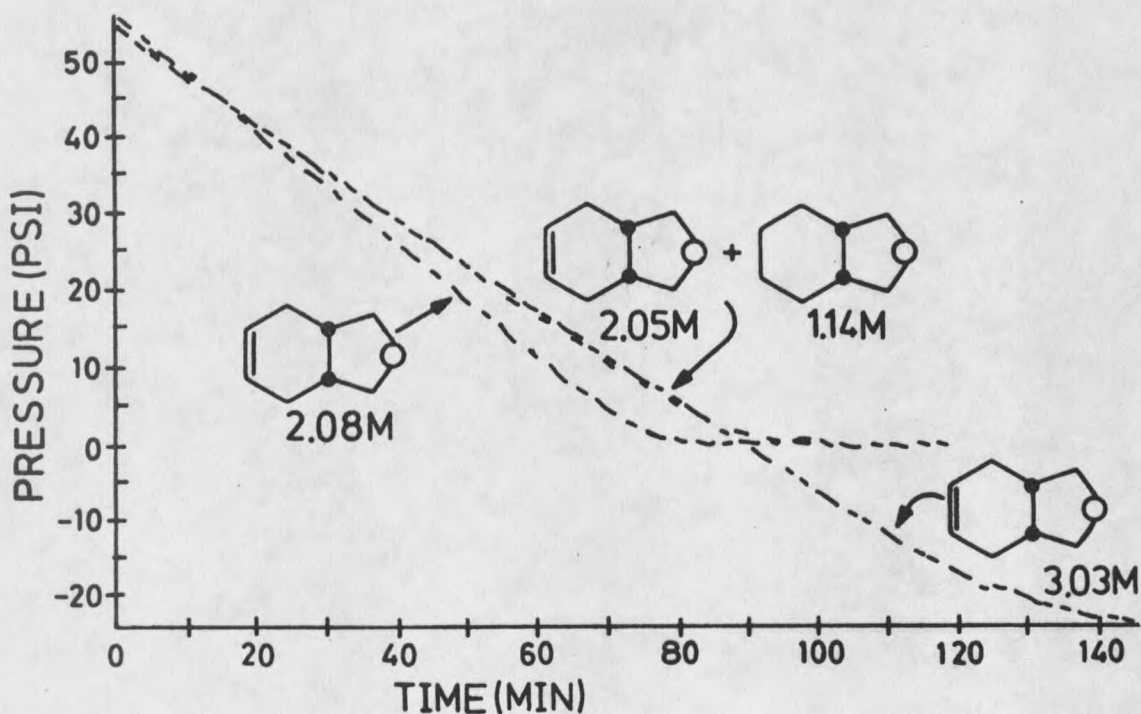
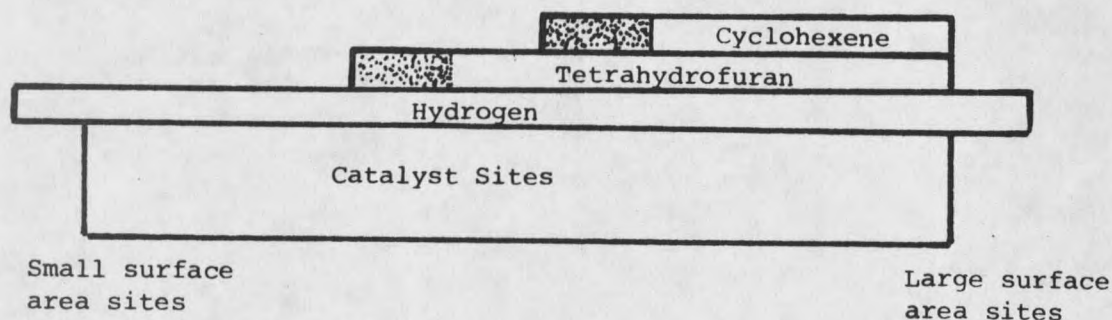
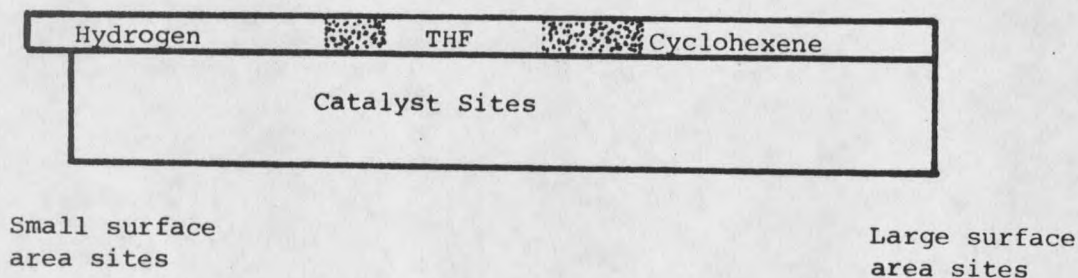


Figure 33. Oxygen effect on the rate.

A model consistent with the available data is presented in Figure 34. This model shows (34a) that for the adsorption of a single species, hydrogen can occupy all of the catalyst sites and can "spill over" to positions on the support. Olefins, on the other hand, are restricted by steric requirements to a portion the of the total catalyst sites. In Figure 34b, the model for the adsorption of a mixture of species clearly distinguishes, in a qualitative sense, different sites for hydrogen and substrate adsorption.



(a)



(b)

Figure 34. Qualitative adsorption model.

In this model, the sites are not totally restrictive of one another; indeed, a large proportion of the sites can be viewed as "intermediate". Using the "competitive" model (34b), inhibitors with a lower steric requirements than the olefin may occupy those sites for which hydrogen would otherwise adsorb. The overall decrease in the initial rate would then be due to the inhibition of both hydrogen and olefin adsorption. This would then indicate that the initial rate alone can not be used to determine the relative adsorbtivities of inhibitors.

SUMMARY

Solvomercuration

These results indicate that the solvomercuration rate effect of vinyl substituents is electronic in nature and due to influences on the rate of solvolysis, not the stability of the mercurinium ion intermediate. It is shown that the energy of the intermediate does not have an appreciable effect on the overall rate of solvomercuration. It is then proposed that the rate enhancing effect of the ethereal oxygen, in cis- and trans-8-oxabicyclo[4.3.0]non-3-ene, found by Otzenberger¹⁸ was due to electronic influences rather than from oxygen participation. This proposal was supported by the rate decrease found when a vinyl proton was substituted by a methyl group.

The most dominant rate effect that remote substituents have on the solvomercuration reaction is due to steric interactions between the incoming solvent molecule and the substituent. As the results obtained by Otzenberger¹⁸ reveal, even though the ethereal oxygen results in an increase in the reaction rate compared to the carbon analog it is still less than that found for cyclohexene. The conformational difference between cis-8-oxabicyclo[4.3.0]non-3-ene and its carbon analog could

have been the reason for the higher rate found for the oxabicyclononene. However, this can be discounted on the basis of the relative rates of the trans isomers and the alph-methyl rate ratios.

As yet a clear comparison between using Hg^{+2} and HgOAc^{+1} has not been made. Further investigations of the solvomercuration reaction should include a determination of Taft's ρ^* value for mercuric acetate. If the ρ^* value is comparable to the value found by Halpern et al.⁹ for Hg^{+2} , then the mechanisms are more than likely the same.

Hydrogenation

From these results it can be concluded that the ethereal oxygen in THF and cis-8-oxabicyclo[4.3.0]non-3-ene can adsorb onto catalyst sites normally used for hydrogen adsorption. This results in a decrease in the rate of hydrogenation without direct competition between the adsorption of the oxygen atom and the olefin. Although the oxygen atom in the oxabicyclo[4.3.0]non-3-ene does not compete directly with cyclohexene, the bulk of the molecule can interact with the olefin adsorption, which is in agreement with the size effects found by Maxted et al. for thiols.^{55,56,57} The implications of these results have an impact on general hydrogenation inhibition studies.

The results from this investigation shows that an inhibitor can inhibit both substrate and hydrogen adsorption. Which of these reactants is inhibited is dependent on the relative size and adsorbtivity of the inhibitor. In order to distinguish between the inhibition of hydrogen adsorption and substrate adsorption, both the initial rate and the substrate concentration dependency of the rate must be examined. It is not possible to distinguish between hydrogen inhibition and substrate inhibition from the initial rate alone.

These result show that an inhibitor can occupy catalyst sites without inhibiting the adsorption of cyclohexene. This would imply that the olefin does not almost completely cover the catalyst surface. Instead a substantial amount of the surface is used for hydrogen adsorption, contrary to the basic assumption of most mathematical models.

The values obtained for $K_{\text{pro/sub}}[\text{pro}]$ can be interpreted in terms of two possible events occurring on the catalyst surface. The rate decrease could be due to the inhibition of substrate adsorption by the migration of adsorbed hydrogen or the presaturation of the catalyst with the irreversibly adsorbed olefin onto sterically unfavorable catalyst sites. Although the available data is insufficient to conclusively distinguish between the hypotheses, the effect of THF and the olefin concentration on the value of

$K_{\text{pro/sub[pro]_{max}}}$ and the time factor does implicate hydrogen migration as the source of the rate decrease.

The least squares curve fitting results show that the magnitude of $K_{\text{pro/sub[pro]_{max}}}$ does not change with the addition of THF to a 2 M cyclohexene solution in EtOH. The decrease in the reaction rate, resulting from addition of THF, should have given the cyclohexene sufficient time to adsorb onto at least some of the less favorable catalytic sites, unless they were blocked. Likewise, an increase in the olefin concentration should have increased the cyclohexene diffusion rate, a first order process, resulting in an increase in the number of olefin useable catalyst sites, unless the sites are blocked.

An extensive investigation of the hydrogen pressure effects on the value of $K_{\text{pro/sub[pro]_{max}}}$ and the time factor would provide the data needed to distinguish between these two hypotheses. The rate of hydrogen migration on the catalyst surface would be influenced by the hydrogen concentration in solution. At low hydrogen pressure it has been shown that a reaction delay occurs, while at high pressure a rate enhancement occurs. At pressures between these two extremes the value of this inhibition term can be expected to decrease proportionally with the hydrogen concentration, if adsorbed hydrogen is the source. If the adsorbed hydrogen is not the source of the inhibition, then

the value of this term will remain constant until the reaction rate decreases to the point where the rate of olefin adsorption is much faster than the overall reaction rate.

Although this investigation covered only a very narrow aspect of catalytic hydrogenation, it has established a methodology for the investigation of hydrogenation inhibition. The methods used in this investigations allowed us to distinguish between the inhibition of hydrogen and olefin adsorption.

EXPERIMENTAL

Reported boiling points and melting points are uncorrected. Nmr spectra were recorded on either a Varian A-60 nmr spectrometer using CCl_4 as a solvent and TMS as an internal standard or a Bruker 250 MHz spectrometer using CDCl_3 as a solvent and an internal standard. Chemical shifts are reported in delta units relative to TMS. Infrared spectra were obtained using a Beckman IR-5 spectrometer. Adsorption frequencies are reported in cm^{-1} . Glc analyses were carried out using a Varian 1400 gas chromatograph using either an 8 foot 15% SE-30 on Chromosorb-W or an 8 foot 10% Apiezon-L on Chromosorb-W column. Mass spectra were obtained using a VG 7070 high resolution mass spectrometer.

Preparation of cis-1,2,3,6-tetrahydrophthalyl alcohol,
(2b):^{66,69}

A solution of cis-1,2,3,6-tetrahydrophthalic anhydride, (1b), (150 g, 1.0 mol) in 800 ml of dry THF was added dropwise to a stirred mixture of lithium aluminum hydride (43.7 g, 1.15 mol) in 250 ml of dry THF. The reaction was conducted in a 5 liter, 3-necked flask equipped with a reflux condenser, addition funnel, and a mechanical stirrer. After the addition was complete the resulting gray mixture was allowed to stir at room temperature for 12 hours, followed by a 6 hour reflux. It was then cooled to room temperature and hydrolyzed by the dropwise addition of 250 ml of saturated Rochelle salt solution. The white mixture was then refluxed for 9 hours. After cooling the mixture was suction filtered and concentrated. Distillation of the viscous liquid gave the colorless diol (109.2 g, 77% yield).

bp_{0.5} 127-130°C Literature⁶⁹ bp_{0.25} 110-111°C

infrared - 3220, 3000, 2860, 1650, 1440, 1180, 1030, 662

nmr - 2.05 (singlet, 6H), 3.53 (multiplet, 4H), 5.28 (triplet, 2H), 5.58 (singlet, 2H)

Preparation of cis-8-oxabicyclo[4.3.0]non-3-ene,
(3b):^{69,67}

A solution of p-toluenesulfonyl chloride (55 g, 0.29 mol) in 100 ml of pyridine was added dropwise to a refluxing

solution of cis-1,2,3,6-tetrahydrophthalyl alcohol (40 g, 0.28 mol) in 100 ml of pyridine. The resulting solution was then allowed to reflux an additional 4 hours after which it was cooled to room temperature and poured into a sulfuric acid ice bath to neutralize the pyridine. The mixture was then extracted with diethyl ether. The extract was dried over anhydrous magnesium sulfate and then stripped of solvent to give a clear yellow solution. Distillation of the crude product gave a clear liquid. An FT nmr spectrum of the product indicated that a trace amount of pyridine was present. Although no pyridine could be detected after the second distillation the compound was distilled again just prior to being used in the catalytic hydrogenation study. The second distillation resulted in 24.2 g of cis-8-oxabicyclonon-3-ene (69% yield).

bp₁₅ 74-75.5°C literature⁶⁹ bp₁₈ 90-93°C

nmr 2.15 (methylene envelope, 4H), 2.42 (2H), 3.53 (quartet, 2H), 3.93 (quartet, 2H), 5.70 (triplet, 2H)

infrared - 3010, 2870, 2660, 1660, 1490, 1440, 1340, 1320, 1300, 1210, 1190, 1120, 1090, 1060, 1020, 970, 950, 900, 884, 850, 717, 653

Preparation of cis-1,2,3,6-tetrahydrophthalyl alcohol - diparatoluenesulfonate, (4b):^{69,20}

A solution of cis-1,2,3,6-tetrahydrophthalyl alcohol (110 g, 0.77 mol) in 300 ml of pyridine was added dropwise

to a stirring solution of p-toluenesulfonyl chloride (385 g, 2.02 mol) in 650 ml of pyridine at 0°C. The mixture was allowed to stir at 0°C for 3 hours before being poured into an ice water bath. The resulting crude solid was collected by suction filtration and recrystallized from methanol, giving 232 g of the crystalline ditosylate (67% yield).

mp 91-92° Literature⁶⁹ mp 97-98°C

nmr - 1.93 (doublets of doublets, 4H), 2.20 (triplet, 2H), 2.47 (sharp singlet, 6H), 3.89 (doublet, 4H), 5.50 (single, 2H), 7.55 (doublet of doublets, 8H)

infrared - 3000, 2900, 2840, 1923, 1600, 1440, 1360, 1290, 1250 1183, 1120, 1095, 960, 910, 813, 760, 660

Preparation of cyclohexene-4-cis-1,2-diacetonitrile,
(5b):^{69,20}

A mixture of cis-1,2,3,6-tetrahydrophthalyl alcohol diparatoluene sulfonate (232 g, .514 mol) and sodium cyanide (75.0 g, 1.53 mol) in 1.5 liters of ethanol was refluxed for 57 hours in a 2000 ml round bottom flask equipped with condenser and mechanical stirrer. After the reflux period the ethanol was removed at reduced pressure. Water (600ml) was then added to dissolve the salts and the mixture was extracted with methylene chloride. Removal of the solvent resulted in a dark brown liquid. After attempts to crystallize the diacetonitrile failed, the mixture was distilled under .5 mmHg pressure using a high temperature

short path distillation apparatus to yield 63.4 grams of crude product, which was used in the next step without further purification.

infrared - 3030, 2900, 2820, 2240, 1660, 1550, 1430, 1370, 1340, 1200, 1180 1100, 1075, 1050, 1060, 870, 847, 758, 667

Preparation of cyclohexene-4-cis-1,2-diacetic acid,
(6b):^{69,20}

A solution of the crude cyclohexene-4-cis-1,2-diacetonitrile (17.0 g, approx. 0.106 moles) in 125 ml of 33% aqueous KOH was refluxed until the evolution of ammonia had ceased (approximately 17 hours). The reaction mixture was cooled in an ice bath and acidified with 125 ml of 85% phosphoric acid. 200 ml of ethanol was added and the inorganic salts were filtered out. The yellow solid which formed after stripping off the ethanol was recrystallized from water to give 13.7 g (65.1% yield) of white crystals.

mp 153-157°C Literature⁶⁹ mp 157-159°C

infrared - 3040, 2900, 1680, 1410, 1270, 1205, 1190, 905, 719, 655

Preparation of cis-bicyclo[4.3.0]non-3-ene-8-one,
(7b):^{69,20,68}

cyclohexene-4-cis-1,2-diacetic acid (11.8 g, .060 mol), 11.8 g of Ba(OH)₂·8H₂O, and 11.8 g of iron powder were

thoroughly mixed in a roundbottom flask and pyrolyzed with an open flame. The crude ketone product that distilled was taken up in diethyl ether and dried over anhydrous potassium carbonate. After the mixture was stripped of solvent, the crude oil was distilled to give a yellow liquid with a boiling point range of 67-91°C at 12 mmHg. Glc analysis of the solution showed that 96.6% of the mixture was the desired product. The result was 3.8 g of the ketone (47% yield).

bp₁₂ 67-91°C Literature⁶⁹ bp₁₃ 115-118°C

infrared - 3030, 2940, 2900, 2840, 1740, 1440, 1410, 1240, 1170, 1140, 1075, 1023, 960, 870, 680, 640

nmr - 2.2 (methylene envelope, 8H), 2.4 (2H), 5.7 (triplet, 2H)

Preparation of cis-bicyclo[4.3.0]non-3-ene, (8b):^{69,20}

A solution of cis-bicyclo[4.3.0]non-3-ene-8-one (3.8 g, 0.028 mol), 5.8 g of potassium hydroxide, 50 ml of diethylene glycol, and 4.7 ml of hydrazine was refluxed for 17 hours. The product, water, and excess hydrazine were distilled until the distillate temperature reached 212°C. The product was then extracted with diethyl ether and dried over anhydrous potassium carbonate. Distillation resulted in 1.55 g of a clear liquid in 45.4% yield.

bp₁₂ 39-40°C Literature⁶⁹ bp₁₉ 73-75°C

infrared - 3020, 2920, 1660, 1460, 1440, 1030, 935, 650

nmr - 1.6 (methylene envelope, 6H), 1.97 (multiplet, 2H), 2.08 (doublet of doublets, 2H), 2.15 (doublet of doublets, 2H), 5.59 (triplet, 2H)

Preparation of 1-methylcyclohexanol:

A solution of methyl iodide (139 g, 1.36 mol) in 360 ml of anhydrous diethyl ether was added dropwise to magnesium turnings (36 g, 1.5 mol) in a 2 liter three neck flask equipped with an addition funnel, mechanical stirrer, and condenser. After the addition was complete the mixture was refluxed for 3 hours. The solution was then cooled via an ice bath followed by the dropwise addition of cyclohexanone (138 g, 1.38 mol) in 250 ml of anhydrous diethyl ether. The solution was refluxed for 12 hours, cooled to room temperature and hydrolyzed by the dropwise addition of 400 ml water followed by 100 ml of acetic acid. The solvent layers were then separated and the aqueous layer was extracted with diethyl ether. The ether fractions were combined, dried over magnesium sulfate, and concentrated to give a light yellow mixture containing 1-methyl-1-cyclohexene, 1-methylcyclohexanol, cyclohexanone, and water, as determined by Glc analysis. This crude mixture was then used in the next step of the synthesis.

Preparation of 1-methylcyclohexene:

The crude product from the above Grignard reaction was

added to 300 ml of 6 M sulfuric acid in an ice water bath. Water and the product were distilled using an oil bath at 141°C. The mixture was extracted with methylene chloride, dried over anhydrous magnesium sulfate, and concentrated. Distillation gave 47.2 g of a clear liquid (36.1% yield from cyclohexanone).

bp₆₄₉ 103-103.5°C

infrared - 3000, 2870, 1710, 1440, 1380, 1340, 1310, 1270, 1160, 1140, 1090, 1050, 1020, 970, 920, 890, 860, 820, 796, 758

nmr - 1.62 (singlet, 7H), 1.90 (methylene envelope, 4H), 5.38 (triplet, 1H)

Preparation of 4-methyl-cis-1,2,3,6-tetrahydrophthalic anhydride, (1a):⁷⁰

A solution of isoprene (75 g, 1.1 mol) in 140 ml of benzene was added dropwise to a stirring solution of maleic anhydride (98.0 g, 1.0 mol) in 500 ml of benzene. The solution was allowed to stir for 23 hours at room temperature. Removal of solvent and recrystallization gave 149 g of white crystals (90% yield).

mp 61.5-62°C literature⁷⁰ mp 78-79°C

infrared - 2900⁷, 1830, 1770, 1690, 1440, 1340, 1240, 1200, 1170, 1090, 1030, 1015, 976, 930, 810, 790, 757, 697

nmr - 1.79 (singlet, 3H), 2.26 (doublet of doublets, 2H), 2.51 (doublet of triplet, 2H), 3.36 (doublet of

triplet, 2H), 5.64 (broad singlet, 1H)

Preparation of 4-methyl-cis-1,2,3,6-tetrahydrophthalyl alcohol, (2a):

A solution of 4-methyl-cis-1,2,3,6-tetrahydrophthalyl anhydride (150 g, 0.90 mol) in 500 ml of dry THF was added dropwise to a stirring mixture of lithium aluminum hydride in (40 g, 1.0 mol) in 1 l of dry THF. The mixture was then refluxed for 16 hours, cooled to room temperature, and hydrolyzed with 200 ml of saturated Rochelle salt solution. After refluxing for 9 hours the product was suction filtered and stripped of solvent. Distillation gave 103 g (70% yield) of a clear viscous liquid. A strong infrared peak at 1750 found in the lower boiling fractions indicated the presence of a carbonyl-containing compound, believed to have been the lactone.

bp₈ 144.5-149.5°C

infrared - 3290, 2860, 1750, 1440, 1380, 1070, 1020, 794

nmr - 1.64 (singlet, 3H), 1.83 (2H), 1.97 (singlet, 4H), 3.52 (doublet, 4H), 5.07 (broad singlet, 2H), 5.30 (broad singlet, 1H)

Preparation of
3-methyl-cis-8-oxabicyclo[4.3.0]non-3-ene, (3a):

A solution of p-toluenesulfonyl chloride (9.24 g, 0.050 mol) in 35 ml of pyridine was added dropwise to a refluxing solution of 4-methyl- cis-1,2,3,6-tetrahydrophthalyl alcohol

(7.00 g, 0.045 mol) in 25 ml of pyridine. The solution was refluxed for 4 hours, poured into a sulfuric acid ice bath, and extracted with methylene chloride. Distillation gave 4.1 g of product in 66% yield.

bp 78-80°C

infrared - 3450, 2900, 1670, 1480, 1555, 1380, 1216, 1160, 1090, 1060, 1000, 943, 905, 889, 840, 800, 787, 755, 690

nmr - 1.67 (singlet, 3H), 2.10 (6H), 3.39 (doublet of doublet, 2H), 3.78 (doublet of doublets, 2H), 5.38 (singlet, 1H)

C₉ H₁₄ O

M/e - calculated 138.1044: found 138.1037 $\pm$.0035

Preparation of 4-methyl-cis-1,2,3,6-tetrahydrophthalyl alcohol-diparatoluenesulfonate, (4a):

A solution of 4-methyl-cis-1,2,3,6-tetrahydrophthalyl alcohol (160 g, 1.0 mol) in 350 ml of pyridine was added dropwise to a stirring solution of p-toluenesulfonyl chloride (400 g, 2.1 mol) in 500 ml of pyridine at 0°C. The solution was stirred at 0°C for 3 hours and poured into 2 l of ice water. The resulting white solid was collected by suction filtration and recrystallized twice from methanol to give 243 g (53% yield) of the ditosylate. The methanol solution from the second recrystallization was concentrated and distilled at 15 mmHg to give a clear liquid with a

boiling point of 78-80°C. However, the solution also contained tosylate which decomposed resulting the loss of the side product believed to be

3-methyl-cis-8-oxabicyclo[4.3.0]non- 3-ene.

mp. 97-99°C

infrared - 2940, 2900, 2840, 1600, 1440, 1360, 1295, 1190, 1180, 1120, 1100, 1020, 1000, 960, 837, 830, 810, 793, 760, 663

nmr - 1.52 (singlet, 3H), 1.66 (doublet of triplet, 2H), 2.09 (multiplet, 4H), 2.45 (sharp singlet, 6H), 3.88 (doublet of doublets, 4H), 5.19 (singlet, 1H), 7.36 (doublet, 4H), 7.75 (doublet, 4H)

Preparation of

1-methyl-1-cyclohexene-cis-4,5-diacetonitrile, (5a):

A solution of 4-methyl-cis-1,2,3,6-tetrahydrophthalyl alcohol- diparatoluenesulfonate (242 g, 0.523 mol), sodium cyanide (54.4 g, 1.11 mol), and ethanol were refluxed for 54 hours. 175 ml of water was added and the ethanol distilled off. The resulting brown liquid was extracted with ether, dried over potassium carbonate and distilled to give 77.9 g of a mixture. The crude product was taken to the next step without further purification.

bp₅ 156-164°C

Preparation of 1-methyl-1-cyclohexene-cis-4,5-diacetic acid, (6a):

A solution of 1-methyl-1-cyclohexene-cis-4,5-diacetonitrile (77.8 g, crude) in 200 ml of 33% aqueous potassium hydroxide was refluxed for approximately 12 hours in a 500 ml round bottom flask equipped with a condenser and magnetic stirrer. The stir bar then broke through the side of the flask allowing the solution to drain into the heating mantle, which increased the heating efficiency. The heating mantle was then extracted with 1.5 l of water followed by an extraction with methylene chloride. The methylene chloride extract contained a small amount of polymer, which was discarded. The aqueous extract was concentrated to 500 ml and acidified with 300 ml of 95% phosphoric acid and ice resulting in a brown precipitate. extracting the diacetic acid with ethanol and recrystallization gave 34.3 g of white crystals (31% yield from the ditosylate).

mp 130.5-131.5°C

infrared - 2900, 1690, 1440, 1410, 1380, 1270, 1210, 1160, 966, 915, 790, 778, 740, 669

nmr - 1.63 (singlet, 3H), 1.80 (doublet of triplet, 2H), 2.15 (triplet, 2H), 2.30 (singlet, 6H), 5.32 (singlet, 1H), 7.26 (singlet, 2H)

C₁₁ H₁₆ O₄

M/e - calculated 212.1048: found 212.10724 $\pm$.0039

Preparation of

3-methyl-cis-bicyclo[4.3.0]non-3-ene-8-one, (7a):

1-methyl-1-cyclohexene-cis-4,5-diacetic acid (32.2 g, 0.152 mol), 32.2 g of iron powder, and 32.2 g of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ were thoroughly mixed in a round bottom flask and pyrolyzed with an open flame. Extraction with methylene chloride resulted in a viscous yellow liquid after concentration. Distillation gave 13.3 g (54% yield) of the ketone.

bp₂₀ 110-115°C

infrared - 2900, 1740, 1450, 1410, 1150, 950, 803

nmr - 1.58 (singlet, 3H), 2.20 (multiplet, 6H), 1.98 (doublet of triplet, 4H), 5.29 (singlet, 1H)

$\text{C}_{10} \text{H}_{14} \text{O}$

M/e - calculated 150.1045: found 150.1040 $\pm$.0039

Preparation of 3-methyl-cis-bicyclo[4.3.0]non-3-ene,

(8a):

A solution of 3-methyl-cis-bicyclo[4.3.0]non-3-ene-8-one (11.3 g, 0.075 mol), 15 g of potassium hydroxide, and 11.0 ml of hydrazine in 125 ml of diethylene glycol was refluxed for 19 hours. The excess hydrazine, water, and product was distilled until the distillate temperature reached 212°C. The product was then extracted with ether and distilled to give 4.30 g (42% yield) of

3-methyl-cis-bicyclo[4.3.0]non-3-ene.

bp₂₀ 58-64°C

infrared - 2900, 1440, 1370, 803, 690

nmr - 1.78 (multiplet, 2H), 2.07 (singlet, 3H), 2.10 (multiplet, 4H), 2.36 (6H), 5.75 (singlet, 1H)

C₁₀ H₁₆

M/e - calculated 136.1252: found 136.1229

Preparation of cis-8-azabicyclo[4.3.0]non-3-ene, 10:⁷¹

A solution of cis-1,2,3,6-tetrahydrophthalimide (40 g, .27 mol) in 300 ml of dry THF was added dropwise to a stirred mixture of lithium aluminum hydride (11 g, .30 mol) in 200 ml of dry THF in a nitrogenous atmosphere. When the addition was complete the mixture was refluxed for 7 hours. The reaction mixture was cooled to room temperature and hydrolyzed with 90% aqueous THF solution followed by 50 ml of water. Filtration and removal of the solvent gave a clear liquid. Distillation gave 3.75 g (10% yield) of the colorless amine.

bp₁₂ 84.5-86.5°C Literature⁷¹ bp₁₂ 106-112°C

infrared - 3280, 2980, 2860, 2820, 1630, 1530, 1440, 1420, 1090, 950, 660

nmr - 2.075 (6H), 2.73 (4H), 3.05 (1H), 5.63 (triplet, 2H)

Sample procedure for Methoxymercuration study:

A 25.0 ml stock solution containing cyclohexene (0.421 g, 5.12 mmol), 1-methylcyclohexene (0.493 g, 5.13 mmol), and diglyme (0.767 g, 5.72 mmol) in methanol was divided into four 4.00 ml aliquots, which were placed in separate test tubes. A sample of the remaining stock solution (3.00 ml) was then diluted to 5.00 ml, with methanol, in a volumetric flask. One of the 4 ml stock solution samples (S1) and the diluted sample (S2) was set aside as glc calibration samples. Dry mercuric acetate was then added to each of the 3 reaction solutions (R1 - 0.153 g, 0.480 mmol: R2 - 0.158 g, 0.496 mmol: R3 - 0.153 g, 0.480 mmol). The test tubes were then sealed, placed in a jar with ice water, and shaken for 1 hour. Following reduction with 2.0 ml of 0.5 M sodium borohydride in methanol at 0°C, the samples were analyzed via glc, using a Spectra Physics integrator.

Sample procedure for Hydrogenation study:

Purification of cyclohexene:⁴⁴ The cyclohexene (approximately. 500 ml) was filtered through a 30 x 3.5 cm column of activated basic alumina. The effluent was then distilled using a 90 cm glass packed distillation apparatus with a reflux ratio of 2:1. After discarding the first 50 ml of distillate, a 25 ml sample was collected and filtered through a second column of activated basic alumina (10 X 4 cm). After 5 ml of cyclohexene was discarded, a sample

(approximately. 4 g) was collected and weighed in a 25 ml volumetric flask.

bp₆₃₅ 77.5°C

Purification of ethanol: Absolute ethanol (500 ml) was distilled from sodium ethoxide, discarding the first 100 ml and retaining the next 250 ml. The ethanol was stored for 3 day before a fresh sample was prepared.

bp₆₃₈ 74.5°C

Purification of THF: THF (100 ml) was distilled from lithium aluminum hydride (approximately. 2 g). The rate of distillation was kept very slow to avoid contaminating the distillate with aluminum salts. The dry THF was not stored for any length of time, instead it was promptly weighed in a volumetric flask. Attempts to purify the THF by filtering it through alumina were abandoned, when it was revealed that THF had stripped contaminants from the column, instead of leaving them behind.

Purification of cis-8-oxabicyclo[4.3.0]non-3-ene: The oxabicyclononene had to be distilled three time prior to being used in the hydrogenation study. It was stored under nitrogen and in a freezer. Just before the start of a reaction, the oxabicyclononene was redistilled.

The 5% Pt on alumina and hydrogen was used as purchased, without purification or pretreatment. Any contaminate

and/or peculiarities with these two components was taken as a constant throughout this study.

Procedure: The computer, temperature bath, and pressure controller were turned on. The program diskette was placed in disk drive 1 and an initialized data diskette in drive 2. The computer program "COLLEC" was loaded into memory and started. A sample of freshly prepared cyclohexene (4.138 g, 0.05037 mol) was placed in a 25 ml volumetric flask and diluted with absolute ethanol to approximately 24 ml. The volumetric flask was then placed in a constant temperature bath set at the same temperature as the reaction vessel. After the temperature of the solution equilibrated, it was diluted to 25.00 ml with ethanol. A sample of 5% Pt on alumina (10.00 - 10.99 mg) was weighed out and placed in the reaction flask. A 20.00 ml aliquot of the cyclohexene solution was then pipetted into the flask, which was placed in the hydrogenation. After the flask had been flushed four times with hydrogen, the controller was set for the minimum and maximum pressure range. The pressure was then set at the maximum value for the reaction and the appropriate information was supplied to the computer, which was prompted by questions from the computer to the operator. The hydrogenator shaker was then started at which point the operator could leave.

APPENDICES

APPENDIX A.Atomic coordinates for CNDO/2 calculation.Table 20
Propene coordinates.

atom	X	Y	Z
6	.000000000	.000000000	.000000000
6	1.334999999	.000000000	.000000000
6	-.755000000	1.307698360	.000000000
1	-.484685326	1.875787970	.897452045
1	-.484685326	1.875787970	-.897452045
1	-1.830863393	1.098571702	.000000000
1	1.860048819	-.947213143	.000000000
1	1.860048819	.947213142	.000000000
1	-.525048819	-.947213143	.000000000

Table 21
Iso-butene coordinates.

atom	X	Y	Z
6	1.510000000	.000000000	.000000000
6	2.157220843	1.167617308	.000000000
6	.000000000	.000000000	.000000000
1	-.356822697	-.518144180	-.897452045
1	-.356822697	-.518144180	.897452045
1	-.356822698	1.036288358	.000000000
1	3.240220844	1.167617309	.000000000
1	1.583318281	2.086053397	.000000000
6	2.310178147	-1.280554265	.000000000
1	2.059858868	-1.857731882	.897450000
1	2.059858868	-1.857731882	-.897450000
1	3.378084230	-1.034004689	.000000000

Table 22
2,3-Dimethyl-2-butene coordinates.

atom	X	Y	Z
6	-1.510000000	.000000000	.000000000
6	-2.157220843	1.167617308	.000000000
6	.000000000	.000000000	.000000000
1	.356822697	-.518144180	.897452045
1	.356822697	-.518144180	-.897452045
1	.356822698	1.036288358	.000000000
6	-2.310178147	-1.280554264	.000000000
1	-2.059858867	-1.857731882	-.897450000
1	-2.059858867	-1.857731882	.897450000
1	-3.378084230	-1.034004688	.000000000
6	-1.357042754	2.448169933	.000000000
1	-2.046777902	3.299921907	.000000000
1	-.728544347	2.476198160	.897452044
1	-.728544347	2.476198160	-.897452044
6	-3.667220843	1.167617308	.000000000
1	-4.024043540	2.203905667	.000000000
1	-4.024043540	.649473129	-.897452044
1	-4.024043540	.649473129	.897452044

Table 23
Methyl-2-butene coordinates.

atom	X	Y	Z
6	.000000000	.000000000	.000000000
6	-.647220842	1.167617308	.000000000
6	-.800178146	-1.280554264	.000000000
1	-.549858867	-1.857731882	-.897450000
1	-.549858867	-1.857731882	.897450000
1	-1.868084230	-1.034004688	.000000000
6	.152957247	2.448169933	.000000000
1	-.536777902	3.299921907	.000000000
1	.781455653	2.476198160	.897452044
1	.781455653	2.476198160	-.897452044
6	-2.157220842	1.167617308	.000000000
1	-2.514043540	2.203905667	.000000000
1	-2.514043540	.649473129	-.897452044
1	-2.514043540	.649473129	.897452044
1	1.083000000	.000000000	.000000000

Table 24
Trans-2-butene coordinates.

atom	X	Y	Z
6	.000000000	.000000000	.000000000
6	1.334999999	.000000000	.000000000
6	-.732062527	1.320675758	.000000000
1	-1.358232714	1.381558637	-.897452045
1	-1.358232714	1.381558637	.897452045
1	.001304616	2.135162487	.000000000
6	2.067062525	1.320675758	.000000000
1	3.146411822	1.130357356	.000000000
1	1.786874490	1.883961205	-.897452044
1	1.786874490	1.883961205	.897452044
1	-.525049332	-.947212858	.000000000
1	1.860048818	-.947213143	.000000000

Glc Analysis of Solvomercuration

A solution containing cyclohexene, 1-methylcyclohexene, 3a, 3b, and bis-(2-methoxy ethyl) ether in methanol was used to calibrate the T.C. detector response with concentration. The graphs of peak areas vs. concentrations presented are the results from the average of 3 injection at each concentration.

The 5-microliter samples were injected onto an 8 foot 10% Apiezon-L on chromosorb-W column. The glc parameter were as follows:

1. The filament current was set at 100 ma.
2. The column temperature was programed to increase from 70°C to 150°C at a rate of 8°C min⁻¹.
3. The column head pressure was set at 25psi.

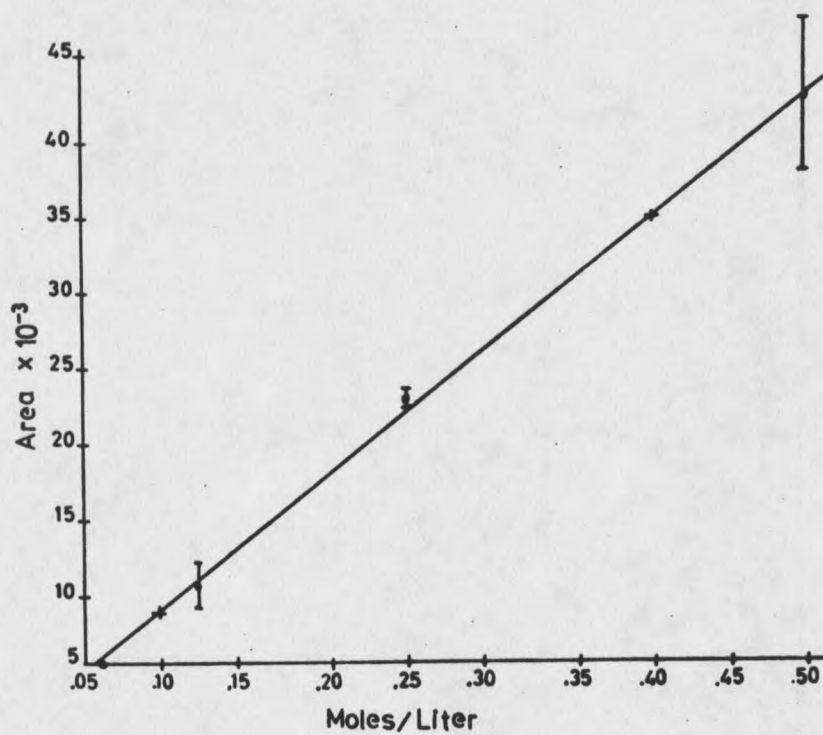


Figure 35. Calibration curve for cyclohexene.

slope = 1.15×10^{-5} moles liter⁻¹ unit-area⁻¹

Y-intercept = $-.00434$ moles liter⁻¹

C.C. = .9993

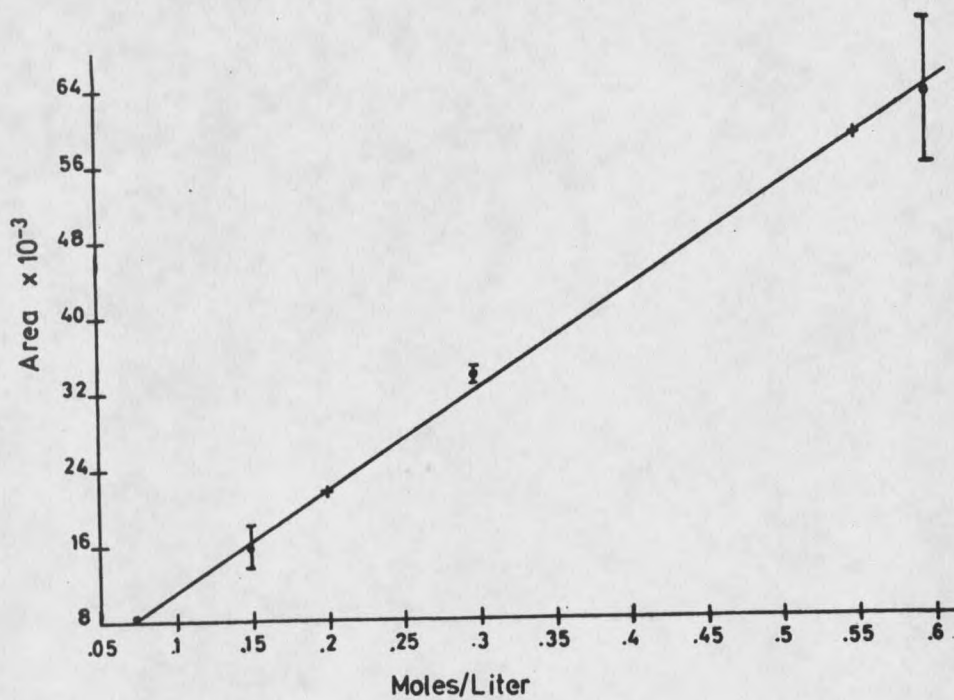


Figure 36. Calibration curve for 1-methylcyclohexene.

slope = 9.94×10^{-6} moles liter⁻¹ unit-area⁻¹

Y-intercept = $-.00530$ moles liter⁻¹

C.C. = .9991

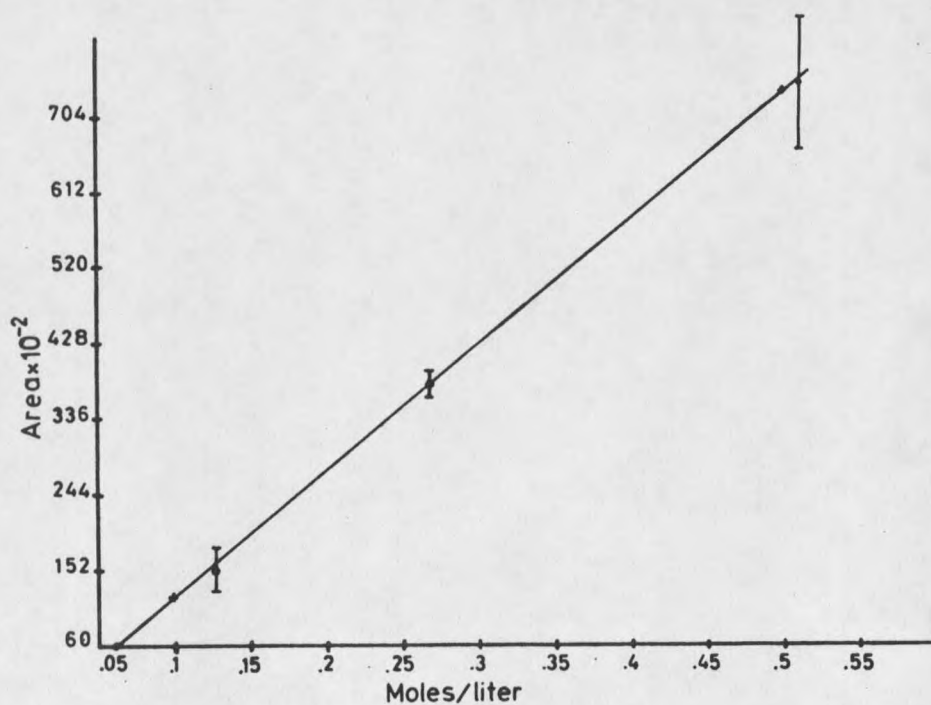


Figure 37. Calibration curve for bis-(2-methoxy ethyl) ether.

slope = 6.47×10^{-6} moles liter $^{-1}$ unit-area $^{-1}$

Y-intercept = .0220 moles liter $^{-1}$

C.C. = .9993

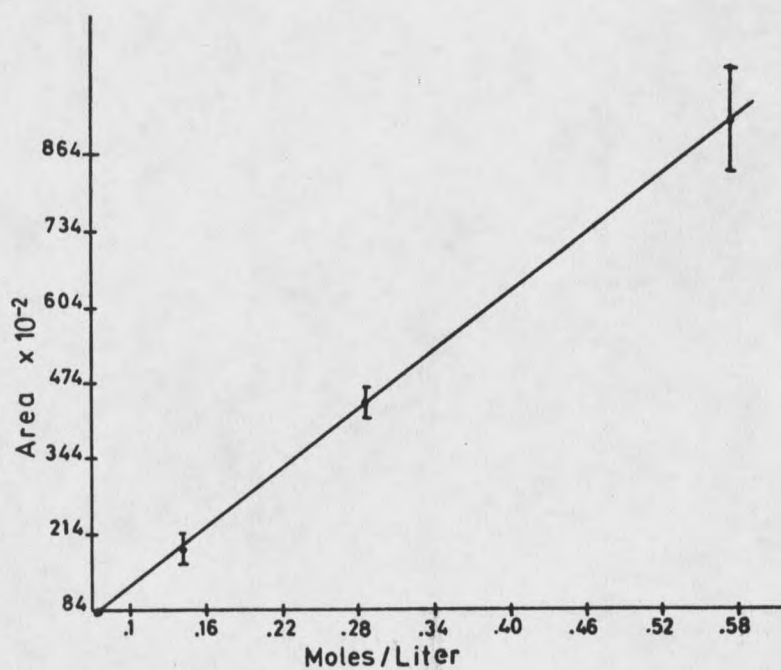


Figure 38. Calibration curve for
cis-8-oxabicyclo[4.3.0]non-3-ene.

slope = 5.97×10^{-6} moles liter⁻¹ unit-area⁻¹

Y-intercept = .0264 moles liter⁻¹

C.C. = .9998

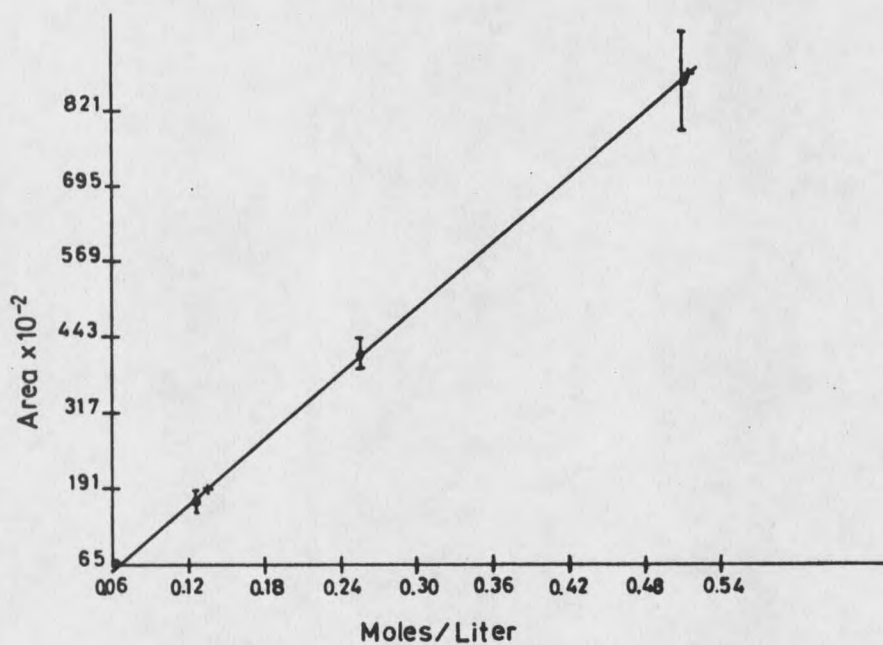


Figure 39. Calibration curve for
3-methyl-cis-8-oxabicyclo[4.3.0]non-3-ene.

slope = 5.47×10^{-6} moles liter⁻¹ unit-area⁻¹

Y-intercept = .0300 moles liter⁻¹

C.C. = .9998

Mathematics of Solvomercuration Study.

Equations

The linear relationship between peak area and substrate concentration allowed us to calibrate the glc detector using two standard solutions with a known concentration ratio. From this two point calibration the relative concentrations of the substrate and the internal standard was determined. The equations and computer program used to determine the relative reaction rate constants are presented on the next few pages.

Equation for calculating the y-intercept/slope (b/k)

$$\frac{b}{k} = \frac{(\text{Area}_2 \times (\text{concentration ratio}) - \text{Area}_1)}{(1 - (\text{concentration ratio}))}$$

Equation for calculating the fraction of substrate remaining after reaction

$$\frac{([\text{substrate}]_i)}{([\text{substrate}]_f)} = \frac{(\text{Area}_{(\text{substrate}) i}^{+b/k})}{(\text{Area}_{(\text{substrate}) f}^{+b/k})}$$

Equation for calculating relative rate constants

$$\frac{k_1}{k_2} = \frac{\text{Ln}([\text{substrate}]_i / [\text{substrate}]_f)}{\text{Ln}([\text{substrate}]_i / [\text{substrate}]_f)}$$

The computer program used.

```

5 REM GLC analysis program for
  solvomercuration study
10 DIM X(3,4)
20 PRINT "How many substrates (2 or
  3)"; INPUT A
30 PRINT "Input name of substrate "
40 PRINT 1; INPUT LINE A$
50 PRINT 2; INPUT LINE B$
60 IF A = 2 THEN 80
70 PRINT 3; INPUT LINE C$
80 PRINT "Input dilution factor for
  standard solution"; INPUT D
90 PRINT "Input average areas
  standard and diluted standard"
100 PRINT "for component"
110 PRINT A$; INPUT A1,A2
120 PRINT B$; INPUT B1,B2
130 IF A = 2 THEN 150
140 PRINT C$; INPUT C1,C2
150 PRINT "STAND"; INPUT S1,S2
160 PRINT "Input the average areas for
  the each of the three reactions"
170 PRINT "for component"
180 PRINT A$; INPUT A3,A4,A5
190 PRINT B$; INPUT B3,B4,B5
200 IF A = 2 THEN 220
210 PRINT C$; INPUT C3,C4,C5
220 PRINT "STAND"; INPUT S3,S4,S5
230 R1 = (A1*D-A2)/(1-D)
240 R2 = (B1*D-B2)/(1-D)
250 IF A = 2 THEN 270
260 R3 = (C1*D-C2)/(1-D)
270 R4 = (S1*D-S2)/(1-D)
280 PRINT "Reaction dilution values"
290 PRINT "for reaction"
300 PRINT 1,2,3
310 X(1,4) = (S3+R4)/(S1+R4)
320 X(2,4) = (S4+R4)/(S1+R4)
330 X(3,4) = (S5+R4)/(S1+R4)
440 X(3,3) = (C5+R3)/(C1+R3)
450 PRINT "Uncorrected concentration
  ratios for reaction"
460 PRINT 1,2,3, "COMPONENT"
470 PRINT X(1,1),X(2,1),X(3,1),A$
480 PRINT X(1,2),X(2,2),X(3,2),B$
490 IF A = 2 THEN 510
500 PRINT X(1,3),X(2,3),X(3,3),C$
510 FOR I = 1 TO 3
520 FOR J = 1 TO A
530 X(I,J) = X(I,J)/X(1,4):NEXT J
540 NEXT I
550 PRINT "Corrected concentration
  ratios for reaction"
560 PRINT 1,2,3
570 FOR I = 1 TO A
580 FOR J = 1 TO 3
590 PRINT X(J,I);
600 NEXT J
610 PRINT
620 NEXT I
630 PRINT "LN("A$")/LN("B$")"
640 X = 0
650 FOR I = 1 TO 3
660 X(1,4) = LN(X(1,1))/LN(X(1,2))
670 X = X+X(1,4)
680 NEXT I
690 X = X/3:S = 0
700 FOR I = 1 TO 3
710 S = (ABS(X(1,4)-X))^2+S
720 NEXT I
730 S = SQR(S/2)
740 PRINT 1,2,3, "AVE", "S.D"
750 PRINT X(1,4),X(2,4),X(3,4),X,S
760 IF A = 2 THEN 900
770 PRINT "LN("C$")/LN("B$")"
780 X = 0
790 FOR I = 1 TO 3
800 X(1,4) = LN(X(1,3))/LN(X(1,2))

```

```
340 PRINTX(1,4),X(2,4),X(3,4)
350 X(1,1) = (A3+R1)/(A1+R1)
360 X(2,1) = (A4+R1)/(A1+R1)
370 X(3,1) = (A5+R1)/(A1+R1)
380 X(1,2) = (B3+R2)/(B1+R2)
390 X(2,2) = (B4+R2)/(B1+R2)
400 X(3,2) = (B5+R2)/(B1+R2)
410 IF A = 2 THEN450
420 X(1,3) = (C3+R3)/(C1+R3)
430 X(2,3) = (C4+R3)/(C1+R3)

810 X = X+X(I,4)
820 NEXT I
830 X = X/3:S = 0
840 FOR I = 1TO3
850 S = (ABS(X(I,4)-X))^2+S
860 NEXT I
870 S = SQR(S/2)
880 PRINT1,2,3,"AVE.", "S.D"
890 PRINTX(1,4),X(2,4),X(3,4),X,S
900 STOP
```

Appendix B

One atmosphere hydrogenation.

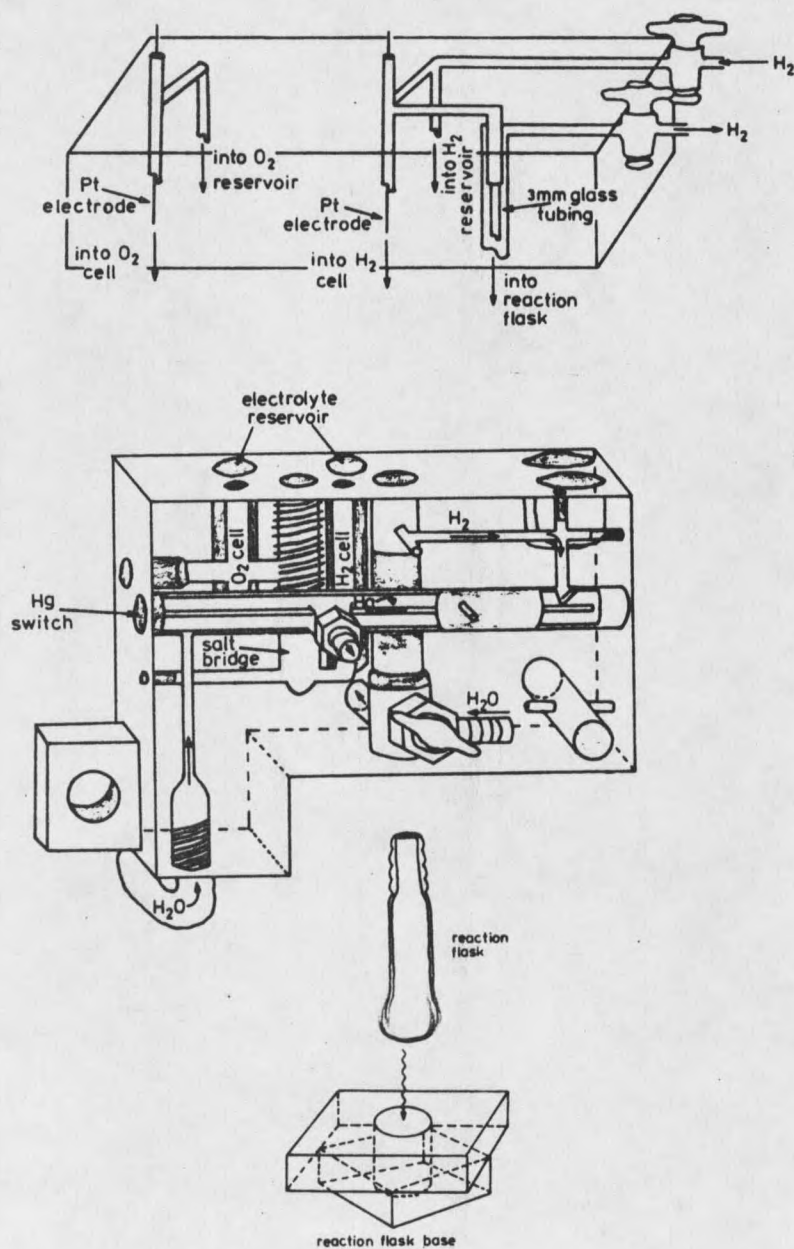


Figure 40. One atmosphere hydrogenator.

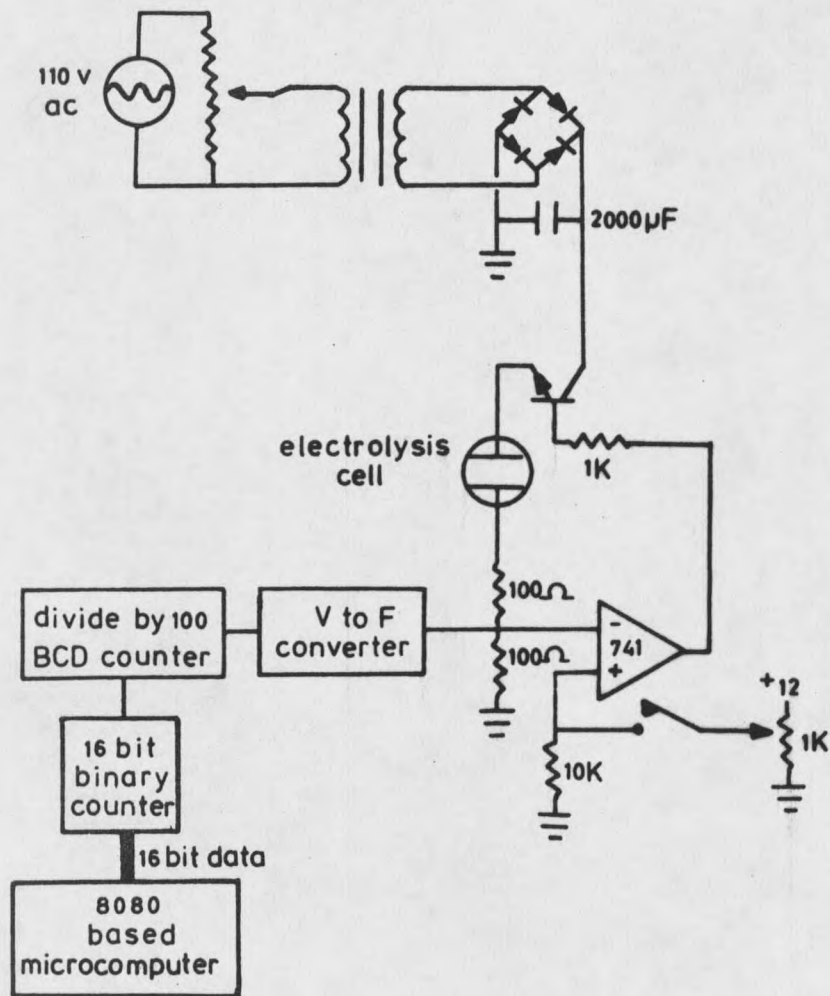


Figure 41. Computer interface circuit.

Data collection program.

```

10 PRINT 'Input run No. and
   Date';
20 INPUT LINE R$:INPUT LINE D$
30 PRINT 'Input substrate';
40 INPUT LINE S$
50 PRINT 'Input amount of
   substrate and amount of
   catalyst';
60 INPUT S,C9
70 PRINT 'Input NO. of Pt.s to
   be taken, Time EST. in hours'
80 PRINT 'and delay before data
   is to be taken';
90 INPUT P,T1,T2
100 T1=T1*60^2:P2=T2*60^2
110 P1=(T1-P2)/P
130 OUT7,154: OUT11,154: OUT6,2:
   OUT10,2
140 DIM A(P),B(P)
200 INPUT Z9:OUT6,2:OUT10,2
210 OUT 6,1:OUT10,1
230 FOR I=1 TO P
240 A=INP(4):B=INP(5)
250 A=B*256+A
260 IF A<P2 THEN 240
265 P9=P2+2*P1:IF A>P9
   THEN 240
290 C=INP(8):D=INP(9)
310 A(I)=A:B(I) =
   (D*256+C)*5.00462E-8
330 P2=P2+P1
340 NEXT I
350 PRINT:PRINT:PRINT R$,S$,D$
360 PRINT 'Substrate =
   'S'moles', 'Catalyst='C9'mg'
390 PRINT:PRINT'Moles H2','sec'
410 FOR I=1 TO P:PRINT
   B(I),A(I),I:NEXT I
440 Z=65/(B(P)-B(1))
450 FOR I=1 TO P:Y=
   INT((B(I)-B(1))*Z+.5)
460 PRINT TAB(Y)'+':NEXT I
461 Z=65/(A(P)-A(1)):FOR I=
   1 TO P: Y=(Z*(A(I)-A(1))+.5)
462 PRINT TAB(Y)'+':NEXT I
490 PRINT'Input portion of graph
   for least squares';
500 INPUT N,M
501 X3=0:Y4=0:Y=0:X=0:
   Y2=0
502 PRINT' NO. of pts. not
   included':INPUT P
503 PRINT 'List pt. NO.':FOR E=
   1 TO P: INPUT P(E): NEXT E
510 FOR I= N TO M
511 FOR E= 1 TO P: IF P(E)=
   I THEN 521:NEXT E
520 Y=Y+B(I):X=X+A(I)
521 NEXT I
550 Y=Y/(M-(N+P)):X =
   X/(M-(N+P))
560 FOR I=N TO M
561 FOR E= 1 TO P: IF P(E)=I
   THEN 591
570 Y1=(B(I)-Y)*(A(I)-X):Y2 =
   Y2+Y1
580 X2=(A(I)-X)*(A(I)-X):Y3 =
   (B(I)-Y)*(B(I)-Y)
590 X3=X3+X2:Y4=Y4+Y3
591 NEXT I
600 S=Y2/Y3:C =
   Y2/(X3^.5*Y4^.5)
610 Y=Y-S*X
620 X3=(X3/(M-(N+P)))^.5:Y4 =
   (Y4/(M-(N+P)))^.5
630 PRINT'Slope =
   'S,'Y-Intercept='Y
640 PRINT' CORRELATION COEFFICIENT
   ='C,'X-Devi='X3' Y-Devi='Y4
650 END

```

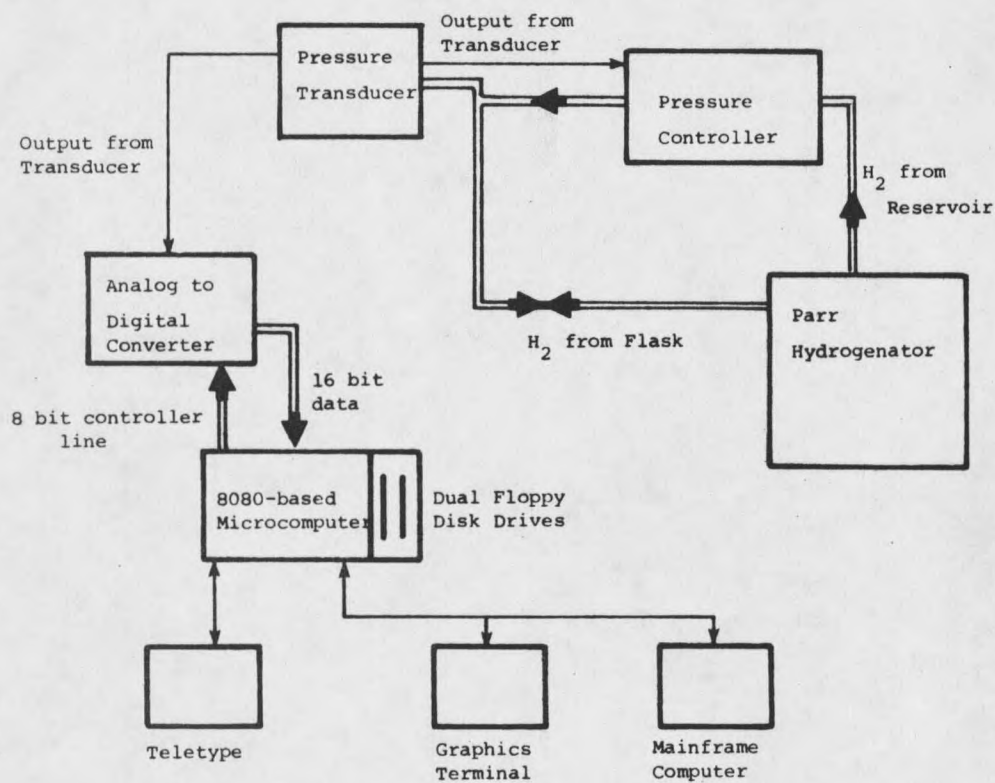
Appendix CMedium pressure hydrogenation.

Figure 42. Medium pressure hydrogenator.

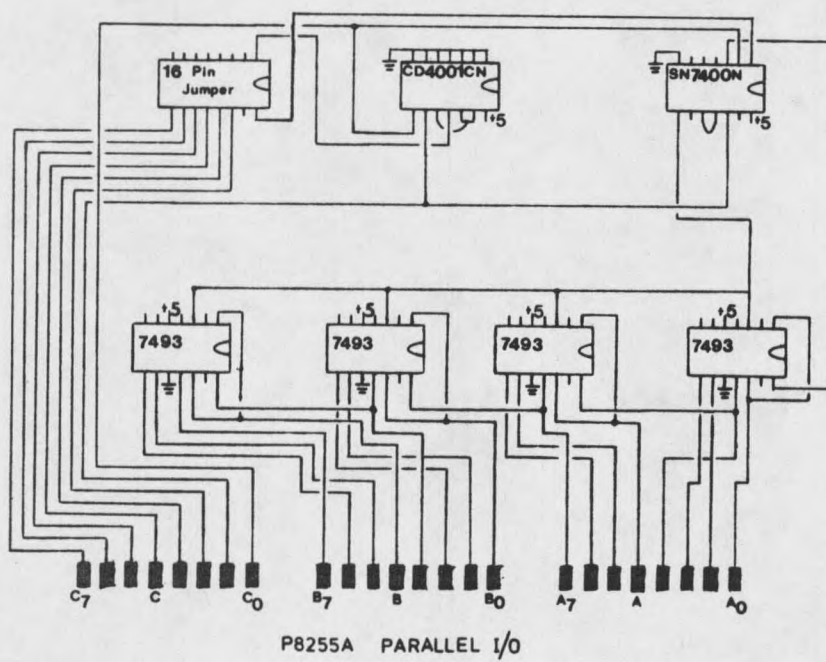
Circuits for hydrogenator

Figure 43. Digital counter circuit.

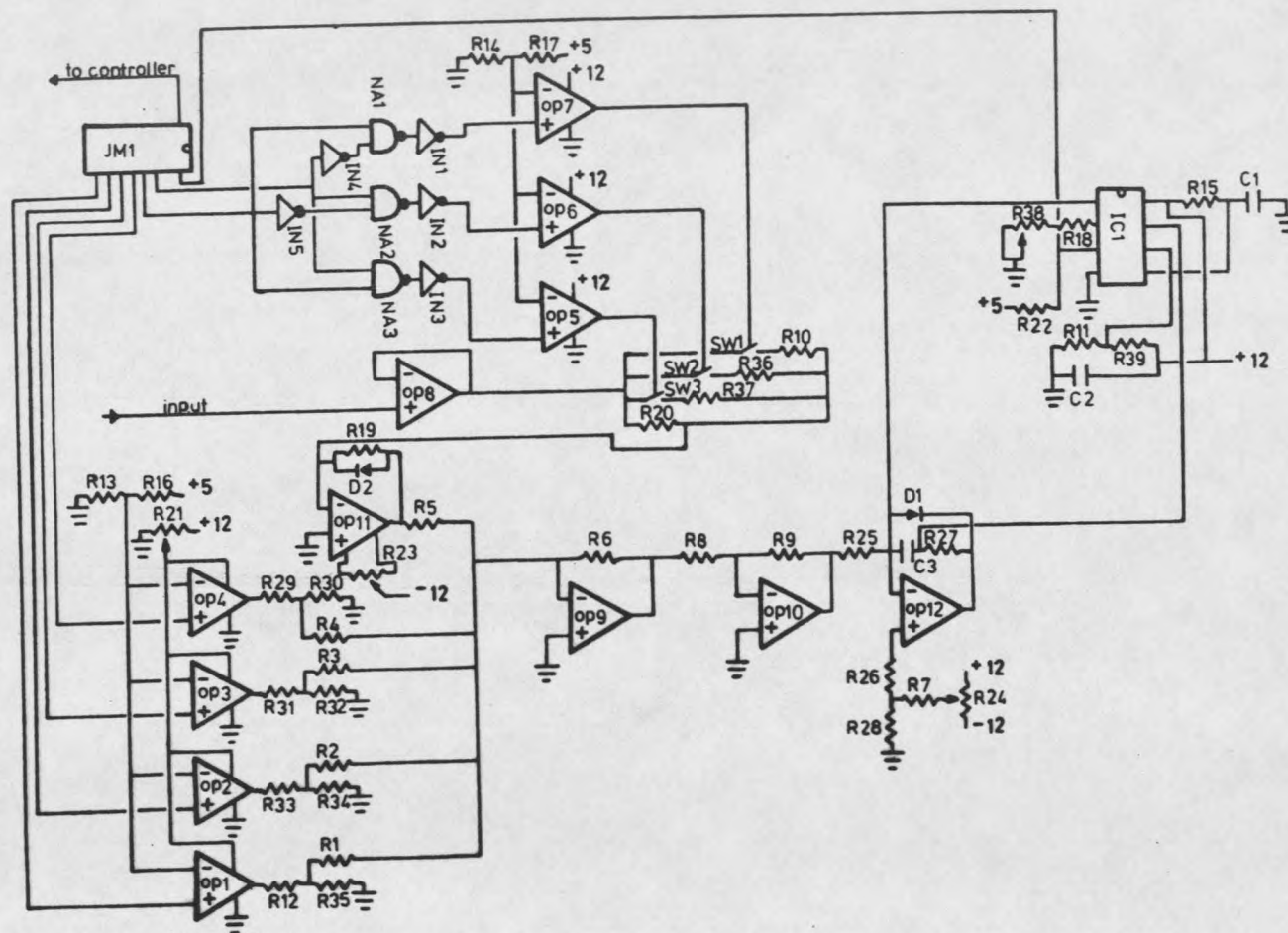


Figure 44. Analog to digital converter circuit.

R1 - R7	120K	R8 - R11	10K
R12 - R15	6.8K	R16 - R18	12K
R19 - R20	1 M	R21 - R22	1K
R23 - R24	25K	R25 - R26	100K
R27 - R28	100 Ohm	R29	9.5K
R30	300 Ohm	R31	9.2K
R32	800 Ohm	R33	8.4K
R34	1.6K	R35	3.2K
R36	110K	R38	5K
R37	920 Ohm	R39	5.1K
C1 .01 microfarad			
C2 .1 microfarad			
C3 .005 microfarad			
D1 - D2 1N914 diode			
OP1 - OP7	1/4 324 operational amplifier		
OP8 - OP10	741 operational amplifier		
OP11	341 operational amplifier		
OP12	318 operational amplifier		
IC1	4151 voltage to frequency converter		
SW1 - SW3	1/4 4066 bilateral switch		
JM1	16 pin jumper to counter circuit		
IN1 - IN5	1/6 7404 inverter buffer		
NA1 - NA3	1/4 7400 NAND gate		

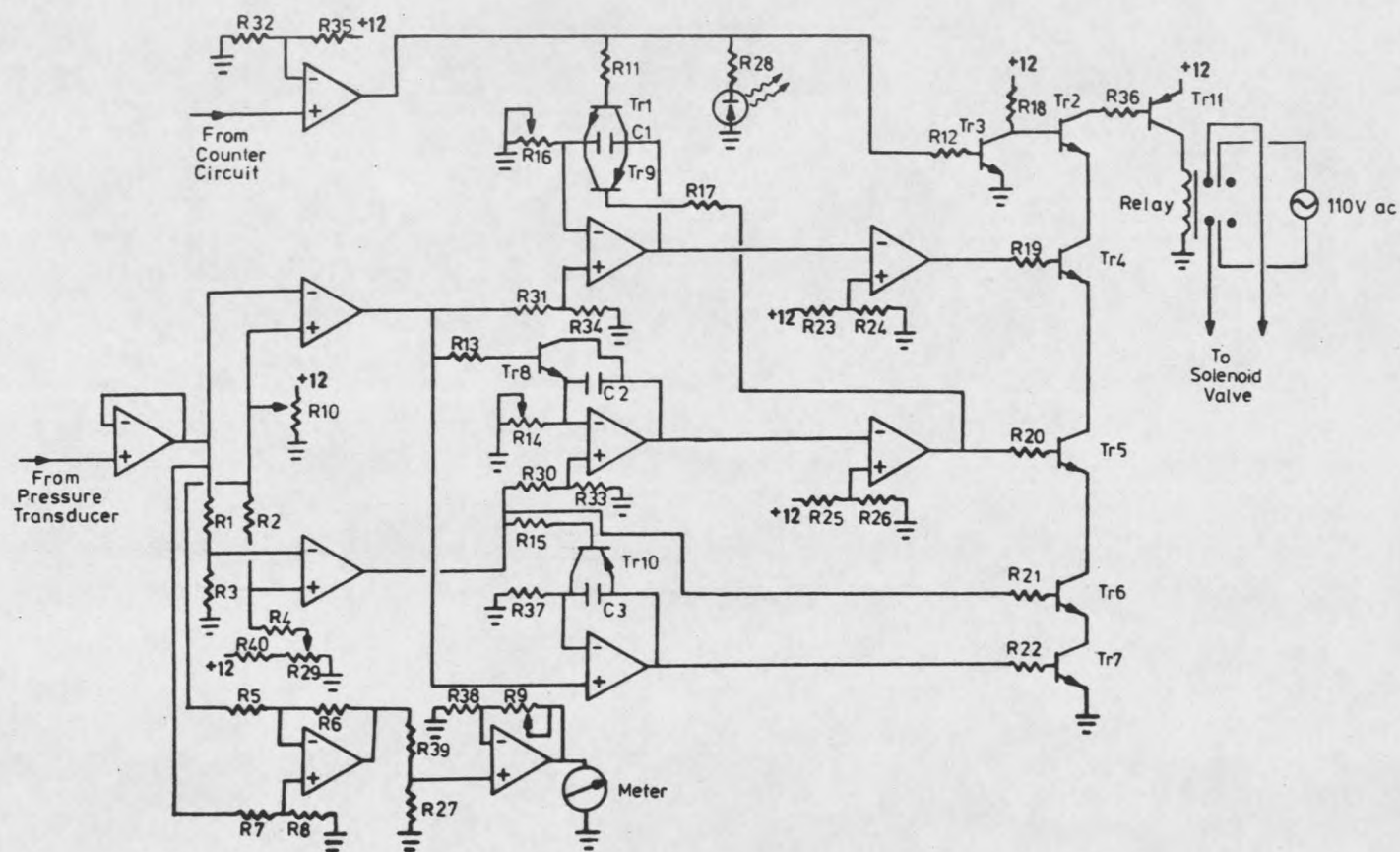


Figure 45. Pressure Controller.

R1 - R8	120K	R9 - R12	10K
R13 - R22, R27	1K	R23 - R26	8.2K
R28 - R29	5K	R30 - R32	6.8K
R33 - R35	680 Ohm	R36	920 Ohm
R37	56 Ohm	R38	380 Ohm
R39	500 Ohm	R40	22K
Tr1 - Tr8	417801	NPN transistor	
Tr9	417295	PNP transistor	
Tr10	25B263	PNP transistor	
Tr11	Tip32	PNP transistor	
C1	500 microfarad		
C2	1000 microfarad		
C3	220 microfarad		

ALL operational amplifiers are 1/4 324

Preliminary computer programs.

Data disk initialization program

```

1 REM Data disk initialization
  program for hydrogenation study
5 PRINT "Input disk #";
6 INPUT X
10 DIM A(31),B(31),C(31),D(31),E(31)
11 E(1) = X
12 !WD2,0,R,E
20 FOR I = 1 TO 31
30 A(I) = I*5
40 B(I) = I*5+155
50 C(I) = I*5+310
60 D(I) = I*5+465
70 NEXT I
80 !WD2,1,R,A
90 !WD2,2,R,B
100 !WD2,3,R,C
110 !WD2,4,R,D
120 END

```

Transducer calibration program

```

10 REM Calibration program for
  hydrogenator
20 PRINT "Input the number of points
  you wish to collect"; INPUT A
25 X = 0: Y = 0: Z = 0: X1 = 0: Y1 = 0
30 DIM X(A), Y(A)
40 PRINT "Input the gage pressure for
  each point"
50 POUT 43,146: POUT 42,210
60 FOR I = 1 TO A
70 INPUT Y(I)
80 POUT 43,146: POUT 42,210
90 SWAP OFF
100 POUT 42,210: POUT 42,209: WAIT 32:
    POUT 42,208: PIN 40,B: PIN 41,C
110 SWAP ON
120 X(I) = B+255*C
125 X = X+X(I): Y = Y+Y(I)
    :X1 = X1+X(I)*X(I)
    :Y1 = Y1+Y(I)*Y(I)
    :Z = Z+X(I)*Y(I)
130 NEXT I
140 S = (A*Z-X*Y)/(A*X1-X*X)
150 I = Y/A-S*X/A
160 R = (A*Z-X*Y)/((ABS((A*X1-X*X)
    *(A*Y1-Y*Y)))^5)
170 PRINT "LBS. = "S"*Hz+"I,"Corr.
    Coef. = "R

```

Computer program to test circuit reproducibility

```

1 REM Hydrogenator stability test
2 X3 = 0: X2 = 0: X = 0: X1 = 1
3 DIM A(1100)
4 FOR I1 = 1 TO 100
5 FOR I = 1 TO I1: WAIT 16
6 POUT 43,146: POUT 42,210
10 POUT 42,210: POUT 42,209: WAIT 32:
21 IF 255*B+A() THEN 24
22 X1 = X1-1: X3 = X3+1
24 NEXT I
25 PRINT: NEXT I1
26 FOR J = 1 TO X1-1: X2 = X2 +
    (ABS(X/(X1-1)-A(1)))^2: NEXT I
27 X2 = (X2/(X1-2))^5

```

```

      POUT42,208
20 PIN40,A: PIN41,B: PRINT255*B+A;: X
   = X+255*B+A: A(X1) = 255*B+A: X1 =
   X1+1
      28 PRINT"S.D. = "X2,"AVE. =
      "X/(X1-1),X2*(X1-1)*100/X" =
      S.D.*100/AVE", " NO.ZEROS = "X3
      30 STOP

```

Data collection programs.COLLECT

```

1 REM hydrogenation data collection
  program
5 REC71,A:IF A = 0 THEN 86
6 PRINT"How many reactions are to be
  run on this sample";:INPUTS
7 PASS70,S:PASS71,S-1:PRINT"Input ID
  no. for each reaction"
8 DIMA(4,S),B(4),E(S),F(S)
9 FOR I = 1TOS: PRINTI;: INPUTLINEA$:
  ALTERA$TOB: FOR J = 1T04:A(J,I) =
  B(J):NEXT J:NEXT I
10 FOR I = 1TOS:FOR J = 1T04:
  PASSI+71+(J-1)*5,A(J,I): NEXT J:
  NEXT I
17 PRINT"INPUT DATE";:INPUTD:PASS91,D
18 PRINT"The reactions will be
  carried out in the sequence they
  are given in."
19 PRINT"Input reaction time and pt.
  interval for each RX."
20 FOR I = 1TOS: PRINTI;:
  INPUTE(I),F(I): PASSI+91,E(I):
  PASSI+96,F(I): NEXT I
60 PRINT"Input catalyst, amount of
  catalyst, compound, amount of
  compound, "
70 PRINT"solvent, amount of solvent,
  temp, and starting pressure (one
  line)."
80 INPUT A$
81 !WD1,559,A,A$: A = LEN(A$):
  PASS102,A
82 POUT43,146: POUT42,210:
  PRINT"Input test pressure (gage
  pressure)";: INPUT M1: Z5 = 1:
  I = 1: N1 = 0: GOTO220
83 N1 = M1-B(1): PASS103,N1:
  PRINTM1B(1): Z5 = 0
84 PRINT"Type 1 then return to
  start";: INPUT AB
85 STIME0,0: SWITCH
86 CLEAR

88 DIMZ(4): FOR I = 1T04:
  REC71+S+((I-1)*5),Z(I): NEXT I
89 B$ = "": FOR I = 1T04: B$ =
  B$+CHR$(Z(I)): NEXT I: SWITCH:
  PRINT B$: SWITCH
90 !RD1,559,R,A$: REC102,A: A$ =
  LEFT$(A$,A): A$ = B$+A$
91 RECS+91,T: RECS+96,G: D1 = 0:
  REC91,D
92 C$ = NUM$(S)+"-": REC70,S: C$ =
  C$+NUM$(S): A$ = A$+C$
121 REC103,N1: Z5 = 0
130 T = INT(T/G+.5)
140 T1 = T+2
150 DIMA(T1),B(T1),C(31),D(31)
160 A(1) = LEN(A$): B(1) = D:
  A(2) = T
180 FOR I = 3TOT1
190 RTIMEIN,M
200 IF N = D1 THEN 215
210 GOTO190
215 POUT43,146: POUT42,210
216 SWAP OFF
220 POUT42,210: POUT42,209: WAIT32:
  POUT42,208: PIN40,A: PIN41,B
225 SWAP ON
240 B(1) = A+B*256: A(1) = N
260 B(1) = INT((B(1)*5.09323E-3+N1)
  *100+.5)/100
265 IF Z5 = 1 THEN 83
270 D1 = N+G: NEXT I
285 X = 528: B(2) = 4
290 !WD1,X,R,A$: J = 1: X = X+1
291 J = 1: X = 529
300 FOR I = 1TOT1
310 C(J) = A(I): D(J) = B(I)
320 IF J = >31 THEN 340
330 J = J+1: NEXT I
340 !WD1,X,A,C: X = X+1
350 !WD1,X,R,D: X = X+1
351 J = 0
360 IF I < T1 THEN 330

```

```

87 REC70,S: REC71,S1: PASS71,S1-1: 400 CHA TRANS
   S = S-S1                          401 STOP

```

TRANSfer

```

5 REM This program transfers
  hydrogenation data from disk
  1 to disk 2
6 CLEAR
10 DIM A(31),B(31),C(31)
11 X = 528
20 !RD1,X,R,A$
30 !RD2,0,R,A
40 B$ = LEFT$(A$,1)
50 B = VAL(B$)
60 IF A(1) = B THEN 90
65 SWITCH
70 PRINT "This is the wrong data disk.
  Please insert the correct disk"
80 PRINT "and type 1 then return";
  INPUT Z$
85 SWITCH
90 B$ = MID$(A$,3,2)
100 B = VAL(B$)
110 B$ = MID$(A$,2,1)
120 IF B$ = "A" THEN 190
130 IF B$ = "B" THEN 200
140 IF B$ = "C" THEN 210
150 IF B$ = "D" THEN 220
155 SWITCH
160 PRINT "You have assigned an
  incorrect data code letter. Do
  you wish to change it";
180 INPUT LINE Z$: IF Z$ = "YES"
  THEN 320
185 STOP
190 Y = 1: GOTO 230
200 Y = 2: GOTO 230
210 Y = 3: GOTO 230
220 Y = 4: IF B > 18 THEN 360
230 !RD2,Y,R,A: Y = A(B)
240 !RD1,X,R,A$: X = X+1
250 !WD2,Y,R,A$: Y = Y+1
260 FOR I = 1 TO 4
270 !RD1,X,R,B
280 !WD2,Y,R,B
290 Y = Y+1: X = X+1
300 NEXT I
310 GOTO 370
320 INPUT B$: C$ = B$+RIGHT$(A$,3)
335 PRINT C$
336 PRINT "Is this correct"; INPUT
  Z$: IF Z$ = "NO" THEN 320
337 SWITCH
340 !WD1,X,R,A$
350 CLEAR: GOTO 10
360 PRINT "This disk is saturated
  please change the code and use
  another disk"
365 SWITCH: PRINT "done"
366 SWITCH: STOP
370 REC71,A: IF A < 0 THEN 365
371 CLEAR: CHA COLLEC

```

Preliminary analysis programs.QUICK plotting program

```

5 REM Quick plot program for
hydrogenation data
10 PRINT"Input NO. of files to be
outputted"; INPUT A
11 DIM J(5)
15 DIM A1(31), B1(31), C1(31), D1(31),
E1(120,1), F1(120,1),
A(5,A), B(120), O(120)
160 PRINT"Input RX ID. NO. if the
reaction is a continuation end
the id. no. with (')"
161 PRINT"If the reaction is a
competition end the ID NO.
with (*)"
170 FOR I = 1 TO A: PRINT I;: INPUT LINE
A$: ALTER A$ TO J
180 FOR J = 1 TO J(O): A(J,I) = J(J):
NEXT J: A(O,I) = J(O): NEXT I
190 FOR A1 = 1 TO A: IF A(5,A1) = 39
THEN 240
195 GOSUB 2000
200 FOR I = 1 TO N: B(I) = F1(I,1):
NEXT I
210 GOSUB 700
220 FOR I = 1 TO N: B(I) = E1(I,1):
NEXT I
230 GOSUB 710
240 NEXT A1
245 STOP
701 PRINT: PRINT
700 REM PLOT 705 PRINT: PRINT A$:
705 PRINT A$: PRINT
710 FOR I = 1 TO N: O(I) = B(I): NEXT I
711 T = 0
712 FOR I = 1 TO N: IF O(I) < T THEN 714
713 T = O(I)
714 NEXT I
715 B = T
716 FOR I = 1 TO N
717 IF O(I) > B THEN 719
718 B = O(I): NEXT I
720 FOR I = 1 TO N
770 PRINT"-----^-----+-----"
780 FOR I = 1 TO N: PRINT
TAB(ABS(O(I))) "I: NEXT I
785 PRINT"Y MAX-MIN = "TB,"X MAX =
"E1(N,0)
790 RETURN
2000 REM DATA INPUT
2020 Y = 0: N = 0
2030 X = A(2,A1)-64
2040 !RD2,X,R,A1
2050 X = VAL(CHR$(A(3,A1)) +
CHR$(A(4,A1)))
2060 X = A1(X)
2061 !RD2,X,R,A$: X = X+1
2070 !RD2,X,R,A1: X = X+1
2080 !RD2,X,R,B1: X = X+1
2090 !RD2,X,R,C1: X = X+1
2100 !RD2,X,R,D1: N = N+A1(2)
2110 FOR I = 3 TO 31
2120 E1(I-2+60*Y,0) = A1(I):
E1(I-2+60*Y,1) = B1(I): NEXT I
2130 FOR I = 1 TO 31
2140 E1(29+I+60*Y,0) = C1(I):
E1(29+I+60*Y,1) = D1(I): NEXT I
2145 IF A1+1 > A THEN 2165
2150 IF A(5,A1+1) <> 39 THEN 2165
2160 A1 = A1+1: Y = Y+1: GOTO 2030
2165 !MF1: !MF2
2170 FOR I = 1 TO N: F1(I,0) = E1(I,0):
F1(I,1) = E1(I,1): NEXT I
2180 FOR I = 1 TO N-1
2190 IF E1(I,1) > E1(I+1,1) THEN 2320
2200 X = -2*E1(I,1)+E1(I+1,1)+
E1(I-1,1): I = I+1
2300 FOR J = 1 TO N: E1(J,1) =
E1(J,1)-X: NEXT J
2310 GOTO 2180
2320 NEXT I
2330 FOR I = 3 TO N-1
2340 IF E1(I,1)-3*(E1(I+1,1)+E1(I-1,1)) >
2350 X = 2*E1(I,1)-E1(I+1,1)-
E1(I-1,1): I = I+1

```

```

730 O(I) = INT((O(I)-B)*78/(T-B)):NEXT I 2360 FOR J = ITON: E1(J,I) =
740 B1 = (T-B)/15.6                      E1(J,I)+X: NEXT J
750 PRINTB,"                               "B+14*B1 2370 GOTO2330
760 PRINT"-----+-----+-----+----- 2380 NEXT I
      +-----+-----+-----+----- 2390 REM DATA ADJUSTED
      +-----+-----+";               2395 RETURN

```

multiple PLOtting program for TTY

```

1 REM Multiple hydrogenation data      "CHR$(13);
  plotting program for TTY              440 FOR I1 = 1TOB
10 READ B                               450 FOR I2 = 1TOT(0,I1)
20 PRINT: PRINT: PRINT:                460 IF T(I2,I1)<(I1)THEN480
  PRINT"RxNo", "MgCat", "[Sub]",       470 PRINT TAB(P(I2,I1))I1 CHR$(13);
  "[Inh]", "No."                       475 GOTO 490
30 DIMA(31), B(31), C(31), D(31),     480 NEXT I2
  J(5), T(60,B), P(60,B)              490 NEXT I1
40 FOR I = 1TOB                         500 PRINT
50 READ A$,C,S,T                       510 NEXT I
60 ALTERA$TOJ                          520 STOP
70 PRINT A$,C,S,T,I                    1000 REM INPUT ROUTINE
80 GOSUB1000                           1001 ALTER JTOA$
90 NEXT I                              1002 FOR I8 = 0TO4
100 X = 6                              1003 !RD2,I8,R,A
110 FOR I = 1TOB                       1005 FOR I9 = 1TO31
120 IF T(2,I)>= XTHEN140                1007 X = A(I9)
130 X = T(2,I)                         1008 !RD2,X,R,B$
140 NEXT I                             1009 IF LEFT$(B$,4) =
150 X1 = 0                             LEFT$(A$,4)THEN1020
160 FOR I = 1TOB                       1011 NEXT I9
170 FOR I1 = 1TOT(0,I)                 1013 NEXT I8
175 IF T(I1,I)<= X1THEN185              1015 PRINT"Data not on this disk
180 X1 = T(I1,I)                        insert different disk type
185 NEXT I1                             return";INPUTA1$
190 NEXT I                              1017 GOTO1001
195 X2 = 0                              1020 X = X+1: K = 1: N = 0
200 FOR I = 1TOB                       1040 !RD2,X,R,A: X = X+1
210 FOR I1 = 1TOT(0,I)                 1045 !RD2,X,R,B: X = X+1
220 IF P(I1,I)<= X2THEN240              1050 !RD2,X,R,C: X = X+1
230 X2 = P(I1,I)                       1060 !RD2,X,R,D: X = X+1
240 NEXT I1                             1063 N = N+A(2)
250 NEXT I                              1070 FOR J = 3TO31: P(K,I) = B(J):
260 X3 = X2                             T(K,I) = A(J): K = K+1: NEXT J
270 FOR I = 1TOB                       1080 FOR J = 1TO31: P(K,I) = D(J):
280 FOR I1 = 1TOT(0,I)                 T(K,I) = C(J): K = K+1: NEXT J
290 IF P(I1,I)>= X3THEN310              1090 IF J(5)<39THEN1120
300 X3 = P(I1,I)                       1100 J(5) = 0: X = X+1
310 NEXT I1                             1110 GOTO1040
320 NEXT I                              1120 FOR J = 2TON

```

```

330 S1 = (72/(X2-X3))
340 PRINT: PRINT "Lbs./Interval =
      "1/S1
350 FOR I = 1 TO 8
360 FOR I1 = 1 TO 10(I)
370 P(I1,I) = INT((P(I1,I)-X3)*S1+6)
380 NEXT I1
390 NEXT I
400 PRINT: PRINT TAB(5)X3 CHR$(13);
      PRINT TAB(72)X2
410 PRINT TAB(6)"v____^____^____^
      ^____^____^____^____^
      ^____^____^____^____^_v"
420 FOR I = 0 TO X1 STEP X
430 PRINT CHR$(13); PRINT TAB(5)":
1130 IF P(J-1,I)+1>P(J,I) THEN 1160
1140 X = P(J,I)-P(J-1,I)+P(J-2,I)-
      P(J-1,I)
1150 FOR J1 = J TO N: P(J1,I) =
      P(J1,I)-X: NEXT J1
1160 NEXT J
1165 FOR J = 2 TO N
1166 IF P(J-1,I)-5<P(J,I) THEN 1180
1167 X = P(J,I)-P(J-1,I)+P(J-2,I)-
      P(J-1,I)
1170 FOR J1 = J TO N: P(J1,I) =
      P(J1,I)-X: NEXT J1
1180 NEXT J
1190 T(0,I) = N
1210 RETURN

```

Final analysis programs.General data transfer program

```

1 REM data correction program
  (general read write data program)
19 DATA STOP,0
20 REM A$ = REACTION ID S9 =
  SUBSTRATE CONCENTRATION CO = MG
  CATALYST 'REACTION'
21 REM C1 = MG CATALYST OF 'REACTION
  STANDARD' D = DISK DRIVE NUMBER
22 REM B$ = 'YES' IF STANDARD IS TO
  BE USED FOR NEXT REACTION
32 DIM A(31), B(31), C(31), D(31),
  J(6), J1(5), T(120), T1(120),
  P(120), S(1)
33 S(0) = 24.519
40 READ A$, S9: IF A$ = "STOP"
  THEN 290
45 PRINT A$
50 ALTER A$ TO J
60 IF J(5) > 83 THEN 300
70 IF B$ = "YES" THEN 90
80 READ CO,A$,C1,D,B$
82 PRINT A$
85 ALTER A$ TO J1
86 GOTO 100
90 READ CO,B$: GOTO 150
100 D$ = "J1"
110 GOSUB 1000
120 N = 7: N1 = 1
130 GOSUB 2000
140 S(1) = S/CO
150 S1 = S(1)*CO
160 D$ = "J": D = 2
170 GOSUB 1000
180 P = P(1)
190 FOR I = 1 TO N3
200 P(I) = P-P(1): NEXT I
220 GOSUB 3000
230 S = S1/S
235 PRINT S,S1,S(1)
240 FOR I = 1 TO N3
250 P(I) = P(I)*S
1140 !RDD,X,R,D: X = X+1
1150 N3 = N3+A(2): A6 = A(1):
  A7 = B(1)
1160 FOR J = 3 TO 31: P(K) = B(J):
  T1(K) = A(J): K = K+1: NEXT J
1170 FOR J = 1 TO 31: P(K) = D(J):
  T1(K) = C(J): K = K+1: NEXT J
1180 IF J$(1) < " " THEN 1210
1190 J$ = " ": X = X+1
1200 GOTO 1110
1210 FOR J = 2 TO N3
1220 IF P(J-1)+.5>P(J) THEN 1250
1230 X = P(J)-P(J-1)+P(J-2)-P(J-1)
1240 FOR J1 = J TO N3: P(J1) = P(J1)-X:
  NEXT J1
1250 NEXT J
1260 FOR I = 1 TO N3: T(I) = T1(I):
  NEXT I
1270 RETURN
2000 REM PRESSURE TO PRODUCT
  CONVERSION
2010 P = P(1)
2020 FOR I = 1 TO N
2030 P(I) = (P-P(1))/S(0)
2040 NEXT I
2050 GOSUB 3000
2060 RETURN
3000 REM LINEAR REGRESSION
3010 X = 0: Y = 0: X1 = 0:
  Y1 = 0: Z = 0
3015 N2 = N-N1+1
3020 FOR I = 1 TO N
3030 X = X+T(I): Y = Y+P(I): X1 =
  X1+T(I)*T(I): Y1 = Y1+P(I)*P(I):
  Z = Z+T(I)*P(I): NEXT I
3040 S = (Z-X*Y/N2)/(X1-X*X/N2)
3050 RETURN
4000 REM WRITE SUBPROGRAM FOR DISK
  DRIVE 1
4001 SWAP OFF
4010 A9 = INT((N3/30+.5)*2)

```

```

260 P(1) = 55-P(1)*S(0)
262 NEXT I
265 IF (P(1)-P(N3))/S(0) <=
    S9+.05*S9 THEN 270
266 PRINT"The final product
    concentration is higher than the
    substrate concentration"
267 PRINT(P(1)-P(N3))/S(0) = CAL
    PRODUCT",S9" = SUBSTRATE CON.":
    GOTO280
270 GOSUB4000
280 GOTO40
290 STOP
300 REM COMPLETION REACTION
    CORRECTION
310 D$ = "J": D = 2
320 GOSUB 1000
325 IF J(5)<>67 THEN 360
330 S = S9/(P(1)-P(N3)): P = P(1)
340 FOR I = 1TON3: P(I) =
    (P-P(I))*S: P(I) = 55-P(I)*S(0)
350 NEXT I
360 GOSUB 4000
370 GOTO 40
1000 REM DISK INPUT PROGRAM
1001 A$ = ""
1010 IF D$ = "J1" THEN 1018
1012 ALTERJTOA$
1013 J$ = MID$(A$,6,1)
1016 GOTO1022
1018 ALTER J1TOA$
1019 J$ = MID$(A$,6,1)
1022 FOR I = 0TO4
1024 !RDD,I,R,A
1026 FOR I1 = 1TO31: X = A(I1)
1027 IF X<3 THEN 1034
1029 IF X>559 THEN 1034
1030 !RDD,X,R,C$
1032 IF LEFT$(C$,4) = LEFT$(A$,4)
    THEN 1090
1034 NEXT I1: NEXT I
1036 PRINT"Data not on disk"D
1038 D = INT((D+1)/D+.1)
1040 GOTO 1010
1090 K = 1: N3 = 0
1100 !RDD,X,R,A$: X = X+1
1110 !RDD,X,R,A: X = X+1
1120 !RDD,X,R,B: X = X+1
1130 !RDD,X,R,C: X = X+1
4020 A8 = (N3/30)*2
4030 IF A8>A9 THEN 4060
4040 B(2) = A9+1
4050 GOTO4070
4060 B(2) = A9+3
4070 I2 = 0
4071 FOR I = 0TO3
4080 !RD1,I,R,A
4090 FOR I1 = 1TO31
4095 IF I2 = A(I1) THEN 4100
4096 I2 = A(I1)
4100 IF A(I1) = 0 THEN 4135
4101 !RD1,A(I1), R,E$
4102 IF LEFT$(E$,4) < LEFT$(A3,4)
    THEN 4110
4103 X = A(I1): A$ = LEFT$(A3,A6)
4104 GOTO4170
4110 NEXT I1
4120 NEXT I
4130 GOTO4300
4135 A(I1-1) = I2
4140 IF A(I1-1)+B(2)>559 THEN 4300
4150 A(I1) = B(2)+A(I1-1)
4155 !WD1,I,R,A
4160 X = A(I1-1): A$ = LEFT$(A3,A6)
4170 K = 1: A(2) = N3: A(1) = A6:
    B(1) = A7
4180 FOR J = 3TO31: B(J) = P(K):
    A(J) = T1(K): K = K+1: NEXT J
4190 FOR J = 1TO31: D(J) = P(K):
    C(J) = T1(K): K = K+1: NEXT J
4200 !WD1,X,R,A$: X = X+1
4210 !WD1,X,R,A: X = X+1
4220 !WD1,X,R,B: X = X+1
4230 !WD1,X,R,C: X = X+1
4240 !WD1,X,R,D: X = X+1
4250 IF K>N3 THEN 4320
4260 FOR J = 1TO31: A(J) = T1(K):
    B(J) = P(K): K = K+1
4262 IF K>N3 THEN 4270
4264 NEXT J
4270 !WD1,X,R,A: X = X+1
4280 !WD1,X,R,A: X = X+1
4290 GOTO4250
4300 PRINT"data disk full insert new
    disk then type return.";
4310 INPUTZ$: GOTO4070
4320 SWAP ON
4330 RETURN

```

Alternate subroutines for transfers

4000 REM Data transfer program to Honeywell 66	4000 REM Data transfer program to VAX
4005 SI034,250,39	4005 SI034,250,39
4010 A\$ = LEFT\$(A\$,78)	4010 A\$ = LEFT\$(A\$,78)
4030 PRINT A\$ CHR\$(13);	4030 PRINT A\$ CHR\$(13);
4040 PRINTS9,C0,N3CHR\$(13);	4040 PRINTS9,C0,N3+.1CHR\$(13);
4060 P1 = P(1)	4060 P1 = P(1)
4070 FOR I = 1TON3:P(1) = (P1-P(I))/S(0)	4070 FOR I = 1TON3:P(1) = (P1-P(I))/S(0)
4080 PRINT T1(I),P(1)CHR\$(13);	4075 T1(I) = T1(I)+.1
4090 NEXT I	4080 PRINT T1(I),P(1)CHR\$(13);
4092 PRINT CHR\$(13);	4090 NEXT I
4095 SI034,250,0	4092 PRINT CHR\$(13);
4110 RETURN	4095 SI034,250,0
	4110 RETURN

Curve fitting program for Vax 11 computer

```

C LEAST SQUARES CURVE FITTING PROGRAM FOR VAX
  FUNCTION F1(CON,SUBS,PROD,KSUB,KPROD,PROD2)
  REAL KSUB,KPROD
  F1=CON*(SUBS-PROD)/(KSUB+(SUBS-PROD)+KPROD*PROD2)
  END
  SUBROUTINE INTEGRATION(A,B,C,D,E,F,G,H)
  DIMENSION B(120),C(120,2),D(1),G(2,2)
  INTEGER H,F
  C A=RMS:B=TIME:C=PRODUCT:D=RATE CON=E=SUBSTRATE:F=NUMBER POINTS
  C G=INHIBITION CONSTANTS:H=K(PROD) CUT OFF POINT
    A=0
    K9=0
    C(1,2)=C(1,1)
    D(1)=2,F
    T=B(1)-B(1-1)
    K9=K9+1
    IF(1.LE.H)GOTO100
    J3=H
    J2=0
    GOTO101
  0100 J3=I-1
    J2=1
  0101 P0=C(J3,2)
    R1=T*F1(D,E,C(I-1,2),G(1,1),G(1,2),P0)
    P0=C(J3,2)+R1*J2/2
    R2=T*F1(D,E,C(I-1,2)+R1/2,G(1,1),G(1,2),P0)

```

```

P0=C(J3,2)+R2*J2/2
R3=T*F1(D,E,C(I-1,2)+R2/2,G(1,1),G(1,2),P0)
P0=C(J3,2)+R3*J2
R4=T*F1(D,E,C(I-1,2)+R3,G(1,1),G(1,2),P0)
C(I,2)=C(I-1,2)+(R1+R2*2+R3*2+R4)/6
0102 A=A+(C(I,2)-C(I,1))*2
A=(A/(F-1))*5
END
PROGRAM A
DIMENSION R(3),K(1),K1(2),X(2),K2(2,2),M(5,25,50),T(120)
1,P(120,2),K3(3,2),M2(25)
REAL K,K1,K2,M,K3
INTEGER CUT
CHARACTER*(78)REACTION,REACT*(78)
BIG=1
0127 READ(7,1)REACTION
REACT='STOP'
IF(REACTION.EQ.REACT)GOTO128
WRITE(8,5)REACTION
READ(7,2)SUB,CATA,RNUM
NUM=RNUM
DO 100 I=1,NUM
READ(7,3)T(I),P(I,1)
IT=T(I)
T(I)=IT
0100 CONTINUE
V=0
Y=0
V1=0
Y1=0
Z=0
D01011=1,7
V=V+T(I)
Y=Y+P(I,1)
V1=V1+T(I)*T(I)
Y1=Y1+P(I,1)*P(I,1)
0101 Z=Z+T(I)*P(I,1)
K(1)=(Z-V*Y/7)/(V1-V*V/7)
M9=0
0121 M9=M9+1
IF(M9,GE.2)GOTO122
FIRST=0
IRMAX=10
DO 102 IRATE=1,IRMAX
K(1)=K(1)+K(1)*.01*FIRST
FIRST=1
ICUTOFF=0
DO 102 CUT=NUM,10,-2
ICUTOFF=ICUTOFF+1
D0104 ITERATE =1,2
K1(1)=.3

```

```

      K1(2)=.3
      X(1)=1
      X(2)=1
      IF(ITERATE.EQ.2)GOTO106
      K2(1,2)=.1
      K2(2,2)=.1
      K2(1,1)=4
      K2(2,1)=4
      GOTO 105
0106 K2(1,2)=4
      K2(2,2)=4
      K2(1,1)=.1
      K2(2,1)=.1
0105 CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
      R(3)=RMS
      K2(1,1)=K2(2,1)+K2(2,1)*K1(1)
      CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
      K2(1,1)=K2(2,1)
      R(1)=RMS
      K2(1,2)=K2(2,2)+K2(2,2)*K1(2)
      CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
      K2(1,2)=K2(2,2)
      R(2)=RMS
      X(1)=SIGN(X(1),X(1)*(R(3)-R(1)))
      X(2)=SIGN(X(2),X(2)*(R(3)-R(2)))
0107 CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
      R(3)=RMS
      DO 108 I=1,2
      K2(1,I)=K2(2,I)+K2(2,I)*X(1)*K1(1)
      CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
      R(1)=RMS
0108 K2(1,I)=K2(2,I)
      X8=0
      DO 109 I=1,2
      K2(2,I)=K2(2,I)+K2(2,I)*X(1)*K1(1)
      K2(1,I)=K2(2,I)
      X(1)=SIGN(X(1),X(1)*(R(3)-R(1)))
      SIG=SIGN(SIG,R(3)-R(1))
      IF(SIG.GE.0)GOTO110
      K1(1)=K1(1)/2
0110 IF (K1(1).GE.0.01)GOTO111
      K1(1)=.001
      X8=X8+1
      GOTO109
0111 IF (K2(1,I).LE.100)GOTO112
      K1(I)=.001
      X8=X8+1
      GOTO109
0112 IF(K2(1,I).GE.0.0001)GOTO109
      K1(I)=.001
      X8=X8+1

```

```

0109 CONTINUE
      IF(X8.LT.2)GOTO107
      CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
      K3(3,ITERATE)=RMS
      K3(1,ITERATE)=K2(2,1)
0104 K3(2,ITERATE)=K2(2,2)
      IF(K3(3,1).GT.K3(3,2))GOTO114
      M(1,IRATE,ICUTOFF)=K3(3,1)
      M(2,IRATE,ICUTOFF)=K3(2,1)
      M(3,IRATE,ICUTOFF)=K3(1,1)
      GOTO115
0114 M(1,IRATE,ICUTOFF)=K3(3,2)
      M(2,IRATE,ICUTOFF)=K3(2,2)
      M(3,IRATE,ICUTOFF)=K3(1,2)
0115 M(4,IRATE,ICUTOFF)=K(1)
      M(5,IRATE,ICUTOFF)=CUT
      WRITE(8,9)M(1,IRATE,ICUTOFF)
      1,M(2,IRATE,ICUTOFF)
      2,M(3,IRATE,ICUTOFF)
      3,M(4,IRATE,ICUTOFF)
      4,M(5,IRATE,ICUTOFF)
0102 CONTINUE
      D0117 I=1,IRMAX
      V=M(1,I,1)
      D0116J=1,ICUTOFF
      IF(V.LT.M(1,I,J))GOTO116
      V=M(1,I,J)
      M2(I)=J
0116 CONTINUE
0117 CONTINUE
      X4=0
      MIN1=M2(1)
      MIN2=M2(2)
      X2=SIGN(BIG,(M(1,1,MIN1)-M(1,2,MIN2)))
      D0119 I=2,IRMAX
      MIN1=M2(I-1)
      MIN2=M2(I)
      SIG=SIGN(BIG,M(1,I-1,MIN1)-M(1,I,MIN2))
      IF(SIG.EQ.X2)GOTO119
      X4=X4+1
      MIN1=M2(I-1)
      MIN2=M2(I)
      X2=SIGN(BIG,M(1,I-1,MIN1)-M(1,I,MIN2))
0119 CONTINUE
      IF(X4.GT.0)GOTO122
      IF(X2.LT.0)GOTO121
0122 WRITE(6,5)REACTION
      WRITE(6,6)
      D0123 I=1,IRMAX
0123 WRITE(6,7)M(1,I,M2(I)),M(2,I,M2(I)),M(3,I,M2(I))
      1,M(4,I,M2(I)),M(5,I,M2(I))

```

```

0009 FORMAT(/,3X,'DATA',G,',',G,',',G,',',G,',',G)
      GOTO127
0001 FORMAT(1A)
0002 FORMAT(3G)
0003 FORMAT(2G)
0005 FORMAT(/,/,/,3X,1A78)
0006 FORMAT(/,/,8X,'RMS',8X,'K(PROD/SUB)',5X,'K(1/SUB)',7X,'KRATE',8X,
      1'CUT OFF')
0007 FORMAT(/,3X,5G)
0128 CALL EXIT
      END

```

Curve fitting program for Honeywell 66

```

C LEAST SQUARES CURVE FITTING PROGRAM FOR HONEYWELL
      FUNCTION F1(CON,SUBS,PROD,KSUB,KPROD,PROD2)
      REAL KSUB,KPROD
      F1=CON*(SUBS-PROD)/(KSUB+(SUBS-PROD)+KPROD*PROD2)
      END
      SUBROUTINE INTEGRATION(A,B,C,D,E,F,G,H)
      DIMENSION B(120),C(120,2),D(1),G(2,2)
      INTEGER H,F
C A=RMS:B=TIME:C=PRODUCT:D=RATE CON=E=SUBSTRATE:F=NUMBER POINTS
C G=INHIBITION CONSTANTS:H=K(PROD) CUT OFF POINT
      A=K9=0
      C(1,2)=C(1,1)
      D(1)=2,F
      T=B(1)-B(1-1)
      K9=K9+1
      IF(1.LE.H)GOTO100
      J3=H
      J2=0
      GOTO101
0100 J3=J3-1
      J2=1
0101 P0=C(J3,2)
      R1=T*F1(D,E,C(1-1,2),G(1,1),G(1,2),P0)
      P0=C(J3,2)+R1*J2/2
      R2=T*F1(D,E,C(1-1,2)+R1/2,G(1,1),G(1,2),P0)
      P0=C(J3,2)+R2*J2/2
      R3=T*F1(D,E,C(1-1,2)+R2/2,G(1,1),G(1,2),P0)
      P0=C(J3,2)+R3*J2
      R4=T*F1(D,E,C(1-1,2)+R3,G(1,1),G(1,2),P0)
      C(1,2)=C(1-1,2)+(R1+R2*2+R3*2+R4)/6
0102 A=A+(C(1,2)-C(1,1))*2
      A=(A/(F-1))*5
      END
      PROGRAM A
      DIMENSION R(3),K(1),K1(2),X(2),K2(2,2),M(5,25,50),T(120)

```

```

1,P(120,2),K3(3,2),M2(25)
REAL K,K1,K2,M,K3
INTEGER CUT
CHARACTER*(78)REACTION,REACT*(78)
BIG=1
0127 READ(101,1)REACTION
    REACT="STOP"
    IF(REACTION.EQ.REACT)GOTO128
    WRITE(109,10)REACTION
0010 FORMAT(/,3X,"DATA",A78)
    READ(101,2)SUB,CATA,NUM
    DO 100 I=1,NUM
0100 READ(101,3)T(I),P(I,1)
    V=Y=V1=Y1=Z=0
    D01011=1,7
    V=V+T(I)
    Y=Y+P(I,1)
    V1=V1+T(I)*T(I)
    Y1=Y1+P(I,1)*P(I,1)
0101 Z=Z+T(I)*P(I,1)
    K(1)=(Z-V*Y/7)/(V1-V*V/7)
    M9=0
0121 M9=M9+1
    IF(M9.GE.2)GOTO122
    FIRST=0
    IRMAX=10
    DO 102 IRATE=1,IRMAX
    K(1)=K(1)+K(1)*.01*FIRST
    FIRST=1
    ICUTOFF=0
    DO 102 CUT=NUM,10,-2
    ICUTOFF=ICUTOFF+1
    D0104 ITERATE =1,2
    K1(1)=K1(2)=.3
    X(1)=X(2)=1
    IF(ITERATE.EQ.2)GOTO106
    K2(1,2)=K2(2,2)=.1
    K2(1,1)=K2(2,1)=4
    GOTO 105
0106 K2(1,2)=K2(2,2)=4
    K2(1,1)=K2(2,1)=.1
0105 CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
    R(3)=RMS
    K2(1,1)=K2(2,1)+K2(2,1)*K1(1)
    CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
    K2(1,1)=K2(2,1)
    R(1)=RMS
    K2(1,2)=K2(2,2)+K2(2,2)*K1(2)
    CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
    K2(1,2)=K2(2,2)
    R(2)=RMS

```

```

      X(1)=SIGN(X(1),X(1)*(R(3)-R(1)))
      X(2)=SIGN(X(2),X(2)*(R(3)-R(2)))
0107 CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
      R(3)=RMS
      DO 108 I=1,2
      K2(1,I)=K2(2,I)+K2(2,I)*X(I)*K1(I)
      CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
      R(1)=RMS
0108 K2(1,I)=K2(2,I)
      X8=0
      DO 109 I=1,2
      K2(2,I)=K2(2,I)+K2(2,I)*X(I)*K1(I)
      K2(1,I)=K2(2,I)
      X(I)=SIGN(X(I),X(I)*(R(3)-R(1)))
      SIG=SIGN(BIG,R(3)-R(1))
      IF(SIG.GE.0)GOTO110
      K1(I)=K1(I)/2
0110 IF (K1(I).GE.0.01)GOTO111
      K1(I)=.001
      X8=X8+1
      GOTO109
0111 IF (K2(1,I).LE.100)GOTO112
      K1(I)=.001
      X8=X8+1
      GOTO109
0112 IF(K2(1,I).GE.0.001)GOTO109
      K1(I)=.001
      X8=X8+1
0109 CONTINUE
      IF(X8.LT.2)GOTO107
      CALL INTEGRATION(RMS,T,P,K,SUB,NUM,K2,CUT)
      K3(3,ITERATE)=RMS
      K3(1,ITERATE)=K2(2,1)
0104 K3(2,ITERATE)=K2(2,2)
      IF(K3(3,1).GT.K3(3,2))GOTO114
      M(1,IRATE,ICUTOFF)=K3(3,1)
      M(2,IRATE,ICUTOFF)=K3(2,1)
      M(3,IRATE,ICUTOFF)=K3(1,1)
      GOTO115
0114 M(1,IRATE,ICUTOFF)=K3(3,2)
      M(2,IRATE,ICUTOFF)=K3(2,2)
      M(3,IRATE,ICUTOFF)=K3(1,2)
0115 M(4,IRATE,ICUTOFF)=K(1)
      M(5,IRATE,ICUTOFF)=CUT
      WRITE(109,9)M(1,IRATE,ICUTOFF),I=1,5
0009 FORMAT(/,3X,"DATA",6,"",6,"",6,"",6,"",6,"",6)
0102 CONTINUE
      DO117 I=1,IRMAX
      V=M(1,I,1)
      DO116J=1,ICUTOFF
      IF(V.LT.M(1,I,J))GOTO116

```

```

      V=M(1,I,J)
      M2(I)=J
0116 CONTINUE
0117 CONTINUE
      X4=0
      MIN1=M2(1)
      MIN2=M2(2)
      X2=SIGN(BIG,(M(1,1,MIN1)-M(1,2,MIN2)))
      DO119 I=2,IRMAX
      MIN1=M2(I-1)
      MIN2=M2(I)
      SIG=SIGN(BIG,M(1,I-1,MIN1)-M(1,I,MIN2))
      IF(SIG.EQ.X2)GOTO119
      X4=X4+1
      MIN1=M2(I-1)
      MIN2=M2(I)
      X2=SIGN(BIG,M(1,I-1,MIN1)-M(1,I,MIN2))
0119 CONTINUE
      IF(X4.GT.0)GOTO122
      IF(X2.LT.0)GOTO121
0122 WRITE(107,5)REACTION
      WRITE(107,6)
      DO123 I=1,IRMAX
0123 WRITE(107,7)M(J,I,M2(I)),J=1,5
      GOTO127
0001 FORMAT(1A)
0002 FORMAT(3G)
0003 FORMAT(2G)
0005 FORMAT(/,/ ,/,3X,1A78)
0006 FORMAT(/,/ ,8X,"RMS",8X,"K(PROD/SUB)",5X,"K(1/SUB)",7X,"KRATE",8X,
1" CUT OFF")
0007 FORMAT(/,3X,6,4X,6,4X,6,4X,6,4X,6)
0128 CALL EXIT
      END

```

General plotting programs for TTY and plotter

1 REM TTY plotting program for calculated and observed [pro] vrs time	K(pro/sub) = "K(3) 2035 PRINT " K(pro/sub)*[PRODUCT] (FINAL) = "P(CD,1)*K(3)
10 DATA STOP	2040 X = 0
15 DIMA(31), B(31), C(31), D(31), K(3), T(120), P(120,1), J(5)	2050 FOR J = 1TON
20 REM READ RX.ID,Substrate concentration, Krate,K(1/sub), K(pr/sub, CUTOFF PT.	2060 IF P(J,1)< = XTHEN2080 2070 X = P(J,1)
25 PRINT"INPUT THE CONVERSION FACTOR";: INPUTQ9	2080 IF P(J,0)< = XTHEN2100 2090 X = P(J,0)
30 READ A\$	2100 NEXT J 2110 X1 = X 2120 FOR J = 1TON

```

40 IF A$ = "STOP" THEN 900
45 ALTER A$ TO J
50 READ S, K(1), K(2), K(3), C0
60 GOSUB 1000
70 GOSUB 4000
80 GOSUB 2000
90 GOTO 30
900 STOP
1000 REM INPUT ROUTINE
1001 X = J(2) - 64
1010 X1 = VAL(CHR$(J(3)) + CHR$(J(4)))
1020 !RD2, X, R, A
1030 X = A(X1) + 1: K = 1: N = 0
1040 !RD2, X, R, A: X = X + 1
1045 !RD2, X, R, B: X = X + 1
1050 !RD2, X, R, C: X = X + 1
1060 !RD2, X, R, D: X = X + 1
1063 N = N + A(2)
1070 FOR J = 3 TO 31: P(K, 0) = B(J):
    T(K) = A(J): K = K + 1: NEXT J
1080 FOR J = 1 TO 31: P(K, 0) = D(J):
    T(K) = C(J): K = K + 1: NEXT J
1090 IF J(5) > 39 THEN 1120
1100 J(5) = 0: X = X + 1
1110 GOTO 1040
1120 FOR J = 2 TO N
1130 IF P(J-1, 0) + 1 > P(J, 0) THEN 1160
1140 X = P(J, 0) - P(J-1, 0) +
    P(J-2, 0) - P(J-1, 0)
1150 FOR J1 = J TO N: P(J1, 0) =
    P(J1, 0) - X: NEXT J1
1160 NEXT J
1165 FOR J = 2 TO N
1166 IF P(J-1, 0) - 5 < P(J, 0) THEN 1180
1167 X = P(J, 0) - P(J-1, 0) + P(J-2, 0) -
    P(J-1, 0)
1170 FOR J1 = J TO N: P(J1, 0) =
    P(J1, 0) - X: NEXT J1
1180 NEXT J
1190 P = P(1, 0)
1200 FOR J = 1 TO N: P(J, 0) =
    (P - P(J, 0)) / Q9: NEXT J
1210 RETURN
2000 REM PLOT ROUTINE
2001 PRINT: PRINT: PRINT A$: PRINT:
    PRINT "***** = CALCULATED",
    "+++++ = OBSERVED"
2010 PRINT "RMS = " R
2020 PRINT "K(rate) = " K(1) "
    K(1/substrate) = "K(2) "
2130 IF P(J, 1) = X THEN 2150
2140 X1 = P(J, 1)
2150 IF P(J, 0) = X1 THEN 2170
2160 X1 = P(J, 0)
2170 NEXT J
2180 S1 = 72 / (X - X1)
2190 FOR J = 1 TO N
2200 P(J, 1) = INT((P(J, 1) - X1) * S1 + 6):
    P(J, 0) = INT((P(J, 0) - X1) * S1 + 6)
2210 NEXT J
2220 PRINT "[PRODUCT] / MARK = " 1 / S1
2225 PRINT
2230 PRINT TAB(6) X1 CHR$(13);:
    PRINT TAB(7) X;
2240 PRINT TAB(6) "v ____ ^ ____ ^ ____
    ^ ____ ^ ____ ^ ____ ^ ____ ^ ____
    ^ ____ ^ ____ ^ ____ ^ ____ ^ ____ ^ ____ v"
2250 FOR J = 1 TO N
2260 PRINT T(J) CHR$(13);: PRINT
    TAB(5) "": CHR$(13);: PRINT
    TAB(P(J, 1)) " " CHR$(13);
2270 PRINT TAB(P(J, 0)) " + "
2280 NEXT J
2290 RETURN
4000 REM 4th Order Runge-Kutta
4001 DEF FNA(A) = K(1) * (S - A) / (K(2) +
    (S - A) * K(3) * P0)
4002 J9 = 1: J8 = 2: Z8 = 1
4010 R = 0: K9 = 0: P(J9, 1) = P(J9, 0)
4020 FOR J7 = J8 TO N STEP 28
4030 T = T(J7) - T(J7 - 28): K9 = K9 + 1
4040 IF J7 <= C0 THEN 4070
4050 J3 = C0: J2 = 0
4060 GOTO 4080
4070 J3 = J7 - 28: J2 = 1
4080 P0 = P(J3, 1)
4090 J1 = T * FNA(P(J7 - 28, 1))
4100 P0 = P(J3, 1) + J2 * J1 / 2
4110 J6 = T * FNA(P(J7 - 28, 1) + J1 / 2)
4120 P0 = P(J3, 1) + J2 * J6 / 2
4130 J5 = T * FNA(P(J7 - 28, 1) + J6 / 2)
4140 P0 = P(J3, 1) + J2 * J5
4150 J4 = T * FNA(P(J7 - 28, 1) + J5)
4160 P(J7, 1) = P(J7 - 28, 1) +
    (J1 + J6 * 2 + J5 * 2 + J4) / 6
4170 R = R + (ABS(P(J7, 1) - P(J7, 0))) ^ 2
4180 NEXT J7
4190 R = (R / K9) ^ .5
4200 RETURN

```

```

1 REM TTY plotting program for
  weighted difference between
  observed and calculated [product]
10 DATA STOP
15 DIM A(31), B(31), C(31), D(31),
  K(3), T(120), P(120,1), J(5)
20 REM READ RX.ID, Substrate
  concentration, Krate, K(1/sub),
  K(pr/sub, CUTOFF PT.
25 PRINT "INPUT THE CONVERSION
  FACTOR";: INPUT Q9
30 READ A$
40 IF A$ = "STOP" THEN 900
45 ALTER A$ TO J
50 READS, K(1), K(2), K(3), CO
60 GOSUB 1000
70 GOSUB 4000
80 GOSUB 2000
90 GOTO 30
900 STOP
1000 REM INPUT ROUTINE
1001 X = J(2) - 64
1010 X1 = VAL(CHR$(J(3)) + CHR$(J(4)))
1020 !RD2, X, R, A
1030 X = A(X1) + 1: K = 1: N = 0
1040 !RD2, X, R, A: X = X + 1
1045 !RD2, X, R, B: X = X + 1
1050 !RD2, X, R, C: X = X + 1
1060 !RD2, X, R, D: X = X + 1
1063 N = N + A(2)
1070 FOR J = 3 TO 31: P(K,0) = B(J):
  T(K) = A(J): K = K + 1: NEXT J
1080 FOR J = 1 TO 31: P(K,0) = D(J):
  T(K) = C(J): K = K + 1: NEXT J
1090 IF J(5) < 39 THEN 1120
1100 J(5) = 0: X = X + 1
1110 GOTO 1040
1120 FOR J = 2 TO N
1130 IF P(J-1,0) + 1 > P(J,0) THEN 1160
1140 X = P(J,0) - P(J-1,0) + P(J-2,0) -
  P(J-1,0)
1150 FOR J1 = J TO N: P(J1,0) =
  P(J1,0) - X: NEXT J1
1160 NEXT J
1165 FOR J = 2 TO N
1166 IF P(J-1,0) - 5 < P(J,0) THEN 1180
1167 X = P(J,0) - P(J-1,0) + P(J-2,0) -
  P(J-1,0)
1170 FOR J1 = J TO N: P(J1,0) =
  P(J1,0) - X: NEXT J1
2015 FOR J = 1 TO N: P(J,0) =
  (P(J,0) - P(J,1)) / P(J,0): NEXT J
2020 PRINT "K(rate) = " K(1) "
  K(1/substrate) = " K(2) "
  K(pro/sub) = " K(3) "
2035 PRINT " K(pro/sub) * [PRODUCT]
  (FINAL) = " P(CO,1) * K(3)
2040 X = 0
2050 FOR J = 3 TO N
2080 IF P(J,0) <= X THEN 2100
2090 X = P(J,0)
2100 NEXT J
2110 X1 = X
2120 FOR J = 3 TO N
2150 IF P(J,0) >= X1 THEN 2170
2160 X1 = P(J,0)
2170 NEXT J
2180 S1 = 72 / (X - X1)
2190 FOR J = 1 TO N
2200 P(J,0) = INT((P(J,0) - X1) * S1 + 6)
2210 NEXT J
2220 PRINT "[PRODUCT] / MARK = " 1 / S1
2225 PRINT
2230 PRINT TAB(6) X1 CHR$(13);:
  PRINT TAB(71) X;
2240 PRINT TAB(6) "v____^____^____^
  ^____^____^____^____^____^
  ^____^____^____^____^____^____v"
2250 FOR J = 3 TO N
2260 PRINT T(J) CHR$(13);: PRINT
  TAB(5) " : " CHR$(13);: PRINT
  TAB(P(J,0)) " * " CHR$(13);
2270 PRINT
2280 NEXT J
2290 RETURN
4000 REM 4th Order Runge-Kutta
4001 DEF FNA(A) = K(1) * (S - A) / (K(2) +
  (S - A) + K(3) * P0)
4002 J9 = 1: J8 = 2: Z8 = 1
4010 R = 0: K9 = 0: P(J9,1) = P(J9,0)
4020 FOR J7 = J8 TO N STEP 28
4030 T = T(J7) - T(J7 - 28): K9 = K9 + 1
4040 IF J7 <= CO THEN 4070
4050 J3 = CO: J2 = 0
4060 GOTO 4080
4070 J3 = J7 - 28: J2 = 1
4080 P0 = P(J3,1)
4090 J1 = T * FNA(P(J7 - 28,1))
4100 P0 = P(J3,1) + J2 * J1 / 2
4110 J6 = T * FNA(P(J7 - 28,1) + J1 / 2)

```

```

1180 NEXT J
1190 P = P(1,0)
1200 FOR J = 1 TO N: P(J,0) =
      (P-P(J,0))/Q9: NEXT J
1210 RETURN
2000 REM PLOT ROUTINE
2001 PRINT: PRINT: PRINT$:
      PRINT"CALCULATED FRACTIONAL
      ERROR"
2010 PRINT "RMS = "R

```

```

4120 P0 = P(J3,1)+J2*J6/2
4130 J5 = T*FNA(P(J7-Z8,1)+J6/2)
4140 P0 = P(J3,1)+J2*J5
4150 J4 = T*FNA(P(J7-Z8,1)+J5)
4160 P(J7,1) = P(J7-Z8,1)+
      (J1+J6*2+J5*2+J4)/6
4170 R = R+(ABS(P(J7,1)-P(J7,0)))^2
4180 NEXT J7
4190 R = (R/K9)^.5
4200 RETURN

```

```

1 REM General plotting program for
  hewlett packard 2647A plotter
10 PRINT" Type LIST for the commands"
20 PRINT" COMMAND";: INPUT Z$
30 Z$ = LEFT$(Z$,3)
40 IF Z$ = "PTP" THEN 2000
50 IF Z$ = "PLP" THEN 2500
55 IF Z$ = "LTP" THEN 2500
60 IF Z$ = "CON" THEN 2500
70 IF Z$ = "RAT" THEN 2500
80 IF Z$ = "LRA" THEN 2500
90 IF Z$ = "CAL" THEN 2500
110 IF Z$ = "INP" THEN 1000
120 IF Z$ = "LIS" THEN 180
130 IF Z$ < "AB0" THEN 140
131 PRINT CHR$(27)"*dA"
132 GOTO 20
140 IF Z$ = "ST0" THEN 320
150 IF Z$ < "PRI" THEN 160
151 PRINT CHR$(27)"&p5d5u0C"
152 INPUT Z$
153 PRINT CHR$(27)"*dA"
154 GOTO 20
160 PRINT"INVALID COMMAND!"
170 GOTO 20
180 PRINT"This is a list of
  commands:"
190 PRINT "PTP -will plot the true
  pressure for the reactions"
200 PRINT"PLP -will plot the linked
  pressure for the reaction"
205 PRINT"LTP -will plot both the
  true pressure and linked pressure"
210 PRINT"CON -will plot substrate
  concentration vrs. time"
220 PRINT "RAT -will plot rate vrs.
  time"
230 PRINT"LRA -will plot Ln(rate)
  vrs. Ln(con)"

```

```

3020 FOR I = 1 TO P(0,1)
3030 Y(I,2) = P(I,1): X(I,2) = T(I,1):
      NEXT I
3040 GOSUB 7000
3050 Y(0,0) = 1
3060 GOTO 20
3500 REM**PLOT [SUBSTRATE] VRS. TIME**
3510 FOR I = 1 TO P(0,0)
3520 FOR I1 = 1 TO P(0,1)
3530 Y(I1,I) = S(I)-(P(I,1)-
      Y(I1,I))/K(I)
3540 NEXT I1
3550 NEXT I
3560 Y$ = "[SUBSTRATE] (MOLES/LIT)"
3580 IF Z$ = "RAT" THEN 4000
3590 IF Z$ = "LRA" THEN 4500
3600 GOSUB 7000
3610 GOTO 20
4000 REM*** RATE VRS. TIME ***
4010 FOR I = 1 TO P(0,0)
4020 Y(0,I) = 0
4030 FOR I1 = 1 TO P(0,1)-1
4040 Y(0,I) = Y(0,I)+1
4050 Y(I1,I) = (Y(I1,I)-Y(I1+1,I)) /
      ((X(I1,I)-X(I1+1,I))*M(I))
4060 X(I1,I) = (X(I1,I)+X(I1+1,I))/2
4065 Y(I1,I) = Y(I1,I)*1E3
4070 NEXT I1
4080 NEXT I
4090 Y$ = "RATE (MOLES/LITER-MG-MIN)
      *10^3"
4100 GOSUB 7000
4110 GOTO 20
4500 REM** LN(RATE) VRS. LN(CON) **
4510 FOR I = 1 TO P(0,0)
4520 FOR I1 = 1 TO P(0,1): X(I1,I) =
      Y(I1,I): NEXT I1
4530 Y(0,I) = 0
4540 FOR I1 = 1 TO P(0,1)-1

```

```

240 PRINT"CAL -will plot calculated data and observed data"
260 PRINT"INPUT -will allow you to input reaction data"
270 PRINT"LIST -will print this list of commands"
280 PRINT"PRINT -will transfer the screen to the printer"
290 PRINT"ABORT -will clear the screen for another plot"
300 PRINT"STOP -will terminate this program"
310 GOTO20
320 STOP
1000 REM*** INPUT ROUTINE *****
1001 PASS1,25
1010 CLEAR
1014 REC1,25: 25 = 25+1
1015 24 = 0
1020 PRINT "Input the number of reactions to be inputted (5 max)"; INPUT I
1021 IF I>1 THEN 1023
1022 I1 = 2: GOTO1030
1023 I1 = 1
1030 DIM A(31), B(31), C(31), D(31), P(60,I1), T(60,I1), X(60,I1), Y(60,I1), K(I1), S(I1), M(I1), J(5,I1)
1035 DIM L(I1)
1040 PRINT"Input reaction ID., conversion constant, substrate concentration"
1050 PRINT"and milligrams of catalyst."
1060 FOR I1 = 1 TO I: INPUT A$, K(I1), S(I1), M(I1)
1070 J(0,I1) = LEN(A$)
1080 FOR I2 = 1 TO J(0,I1)
1090 J(I2,I1) = ASCII(MID$(A$,I2,1)): NEXT I2
1095 X = 1
1100 !RDX,0,R,A
1110 IF A(1) = VAL(MID$(A$,1,1)) THEN 1140
1115 X = 2
1120 !RDX,0,R,A
1130 IF A(1) = VAL(MID$(A$,1,1)) THEN 1140
1135 PRINT"INSERT PROPER DISK TYPE RETURN"; INPUT LINE$

4550 Y(0,I) = Y(0,I)+1
4560 Y(I1,I) = (Y(I1,I)-Y(I1+1,I)) / ((T(I1,I)-T(I1+1,I))*M(I1))
4561 Y(I1,I) = ABS(Y(I1,I))
4570 X(I1,I) = (X(I1,I)+X(I1+1,I))/2
4580 Y(I1,I) = LN(Y(I1,I)): X(I1,I) = LN(X(I1,I))
4581 IF ABS(Y(I1,I)) = 9 THEN 4600
4590 NEXT I1
4600 NEXT I
4610 Y$ = "LN(RATE)": X$ = "LN([SUBSTRATE])"
4620 GOSUB7000
4630 GOTO20
5000 REM** CALCULATED AND OBSERVED VRS. TIME **
5001 FOR I = 1 TO J(0,I): Y(I,1) = (P(I,1)-Y(I,1))/K(I): NEXT I
5010 PRINT"INPUT KR, K(1/SUB), K(PR/SUB), AND CUTOFF PT."
5020 A$ = "": FOR I = 1 TO J(0,I): A$ = A$+CHR$(J(I,1)): NEXT I
5030 PRINTA$; INPUT K1,K2,K3,C1
5040 DEF FNA(A) = K1*(S(1)-A) / (K2+(S(1)-A)+K3*A1)
5050 R = 0: K9 = 0: Y(1,2) = Y(1,1): X(1,2) = X(1,1)
5055 Y(0,0) = 2: Y(0,2) = Y(0,1)
5060 FOR I = 1 TO J(0,I): I1 = I-1
5070 T = X(I,1)-X(I-1,1): X(I,2) = X(I,1): K9 = K9+1
5080 IF I < C1 THEN 5110
5090 I2 = C1: I3 = 0
5100 GOTO5120
5110 I2 = I1: I3 = 1
5120 A1 = Y(I2,2)
5130 J1 = T*FNA(Y(I1,2))
5140 A1 = Y(I2,2)+I3*J1/2
5150 J2 = T*FNA(Y(I1,2)+J1/2)
5160 A1 = Y(I2,2)+I3*J2/2
5170 J3 = T*FNA(Y(I1,2)+J2/2)
5180 A1 = Y(I2,2)+I3*J3
5190 J4 = T*FNA(Y(I1,2)+J3)
5200 Y(I,2) = Y(I1,2) + (J1+J2*2+J3*2+J4)/6
5210 R = R+(ABS(Y(I,1)-Y(I,2)))^2
5220 NEXT I
5230 R = (R/K9)^.5
5231 PRINT"RMS = ";R
5240 Y$ = "[PRODUCT]": X$ = "TIME (MIN)"

```

```

1136 GOTO1070
1140 X1 = J(2,11)-64
1150 !RDX,X1,R,A
1160 X2 = VAL (MID$(A$,3,2))
1170 X2 = A(X2)+1
1175 X3 = 1
1180 !RDX,X2,R,A: X2 = X2+1
1190 !RDX,X2,R,B: X2 = X2+1
1200 !RDX,X2,R,C: X2 = X2+1
1210 !RDX,X2,R,D: X2 = X2+1
1220 FOR I2 = 3 TO 31
1230 P(X3,I1) = B(I2): T(X3,I1) =
    A(I2): X3 = X3+1: NEXT I2
1240 FOR I2 = 1 TO 31: P(X3,I1) = D(I2):
    T(X3,I1) = C(I2)
1250 X3 = X3+1: NEXT I2
1260 X2 = X2+1
1270 IF MID$(A$,5,1) = "" THEN 1180
1275 P(0,I1) = X3-1
1280 NEXT I1
1285 P(0,0) = 1
1290 GOTO20
2000 REM** TRUE PRESSURE VRS. TIME **
2010 Y(0,0) = P(0,0)
2020 FOR I = 1 TO 10: Y(0,I) = P(0,I)
2030 Y(0,1) = P(0,1)
2040 FOR I1 = 1 TO 10: Y(I1,I) = P(I1,I)
2050 Y(I1,1) = P(I1,1)
2060 X(I1,I) = T(I1,I)
2070 NEXT I1
2080 NEXT I
2090 Y$ = "PRESSURE (LBS.): X$ =
    "TIME (MIN)"
2100 GOSUB7000
2110 GOTO20
2500 REM*** PLOT LINKED PRESSURE ***
2510 Y(0,0) = P(0,0)
2520 FOR I = 1 TO 10: Y(0,I) = P(0,I)
2530 Y(0,1) = P(0,1)
2540 FOR I1 = 1 TO 10: Y(I1,I) = P(I1,I)
2550 Y(I1,1) = P(I1,1)
2560 X(I1,I) = T(I1,I)
2565 NEXT I1
2570 FOR I1 = 2 TO 10: Y(I1,I) = Y(I1-1,I)
2580 IF Y(I1-1,I)+.5 = Y(I1,I)
    THEN 2660
2590 X = Y(I1,I)-Y(I1-1,I)
2600 X1 = Y(I1-2,I)-Y(I1-1,I)
2610 X2 = Y(I1,I)-Y(I1+1,I)
2620 X = X+(X1+X2)/2
2630 FOR I2 = 1 TO 10: Y(I2,I) =
    Y(I2-1,I)
5250 GOSUB7000
5260 GOTO20
7000 REM** PLOT ROUTINE **
7010 Z4 = Z4+1
7020 PRINT: PRINT: PRINT: PRINT:
    PRINT" PLOT"Z4;"-";Z5
7030 Y = Y(1,1): Y1 = Y: X = X(1,1):
    X1 = X
7040 FOR I = 1 TO 10: Y(I,0) =
    Y(I,1)
7050 FOR I1 = 1 TO 10: Y(I1,I) =
    Y(I1,1)
7060 IF Y(I1,I) THEN 7080
7070 Y = Y(I1,I)
7080 IF Y1<Y(I1,I) THEN 7100
7090 Y1 = Y(I1,I)
7100 IF X<X(I1,I) THEN 7120
7110 X = X(I1,I)
7120 IF X1<X(I1,I) THEN 7140
7130 X1 = X(I1,I)
7140 NEXT I1
7150 NEXT I
7160 Y1 = Y1-Y1*.01:
    X1 = X1-X1*.01
7170 PRINTZ$
7180 A$ = ""
7190 FOR I = 1 TO 10: Y(I,0) =
    Y(I,1)
7199 IF J(0,1) = 0 THEN 7220
7200 FOR I1 = 1 TO 10: A$ =
    A$+CHR$(J(I1,I)): NEXT I1
7210 A$ = A$+" "
7220 NEXT I
7230 PRINTA$
7240 PRINT"INPUT LINE TYPE (1-9)".
7250 FOR I = 1 TO 10: PRINTI:
    INPUTL(I): NEXT I
7260 SI044,250,0
7270 IF LEFT$(X$,1)<"T" THEN 7310
7280 IF X>130 THEN 7300
7290 P = 5: Q = 1: GOTO7320
7300 P = 10: Q = 2: GOTO7320
7310 P = (X-X1)/10: Q = P/5
7320 IF LEFT$(Y$,1)<"P" THEN 7340
7330 R = 5: S = 1: GOTO7370
7340 IF LEFT$(Y$,1)<"I" THEN 7360
7350 R = INT(Y)/20: S = R/5: GOTO7365
7360 R = (Y-Y1)/10: S = R/5
7365 P = (INT(P*100+.5))/100: R =
    (INT(R*100+.5))/100
7370 H = 2: I = 1: J = 2: L = X1: M =
    X: N = Y1: O = Y: T = 0
7380 PRINT CHR$(27)"*ad"H"i"j"
    J"j"L"i" M"m"N"n"O"o"

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2640 Y(12,I) = Y(12,I)-X
2650 NEXT I2
2660 NEXT I1
2661 IF K(I)>0 THEN 2670
2662 K(I) = (Y(1,I)-Y(Y(0,I),I))/S(I)
2670 NEXT I
2675 Y$ = "PRESSURE (LBS.)": X$ =
      "TIME (MIN)"
2680 IF Z$ = "LTP" THEN 3000
2690 IF Z$ = "CON" THEN 3500
2700 IF Z$ = "RAT" THEN 3500
2710 IF Z$ = "LRA" THEN 3500
2715 IF Z$ = "CAL" THEN 5000
2730 GOSUB7000
2740 GOTO20
3000 REM*CONTINUOUS AND TRUE PRESSURE*
3010 Y(0,0) = 2: Y(0,2) = Y(0,1)
      P"p"q"q"R"r"S"s"T"tOwgC"
7385 FOR J = 1TO250: A = A*1: NEXT J
7390 FOR I = 1TOY(0,0)
7400 PRINTCHR$(27)"a"L(I)
      "K"Y(0,I)"uA"
7420 FOR I1 = 1TOY(0,I): PRINTX(I1,I),
      Y(I1,I): NEXT I1
7440 NEXT I
7445 PRINTCHR$(27)"aB"
7450 PRINT CHR$(27)"m4N": PRINT
      CHR$(27)"*dsk19,2550"Y$
7460 PRINT CHR$(27)"m1N": PRINT
      CHR$(27)"*dk264,190" X$
      "24;"-" ;25
7580 PRINT CHR$(27)"dT"
7590 SI044,250,39
7600 RETURN

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