A STUDY OF THE BROMINATION OF

ALKENES IN CARBON TETRACHLORIDE

by

Gary D. Frederick

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Charles G. Gebelein   May 28, 1971
Advisor   Date

Frank Altoona   June 2, 1971
Dean of the Graduate School   Date

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ABSTRACT

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The mechanism of the bromination of alkenes has generally been believed to proceed through a bromonium ion intermediate. In recent years a bromine-alkene charge transfer complex has been suggested as an equilibrium step preceding the bromonium ion formation. This study was an attempt to test the hypothesis that a charge transfer complex is a necessary step in the bromination of alkenes. A nonpolar solvent, carbon tetrachloride, was used here to minimize effects due to solvent complexation.

Individual bromination kinetic runs, competitive brominations, and iodine-alkene complexation experiments were conducted to test this hypothesis. The kinetic runs were followed by measuring the bromine absorbance with time using a Cary 14 spectrophotometer at approximately $23^{\circ}C$ and concentration ranges of 10^{-3} to 10^{-2} molarity. The competitive reactions were conducted at $25^{\circ}C$ at concentrations of 10^{-2} to 10^{-1} molarity. The final reaction mixtures were analyzed by gas-liquid chromatography. Iodine-alkene complexation constants were determined in

carbon tetrachloride using the Benesi-Hildebrand method.
Reproducibility of alkene bromination was shown to be
possible in carefully purified carbon tetrachloride if
impurities and light are excluded.

The kinetic data for the bromination of E-3-hexene,
Z-3-hexene, and E-4-octene were shown to be first order in
alkene and second order in bromine. The apparent third
order rate constants were shown to increase with increasing
initial relative bromine concentration and to decrease with
decreasing initial relative bromine concentration. These
trends were shown to support the complexation hypothesis and
are consistent with predictions made using an equation
derived using the steady state-equilibrium approximation.

The kinetic results clearly show that Z-3-hexene
has a greater relative reactivity than E-4-octene. Under
competitive conditions the relative reactivity of Z-3-hexene
was much greater than predicted from the kinetic studies.
This enhanced reactivity was shown to be consistent with a
charge transfer complex formation, assuming that the
Z-3-hexene complexes with bromine to a greater extent than
does E-4-octene. This assumption is in accord with the
iodine-alkene complexation data.

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

History

The bromination of alkenes has long been used as a qualitative test for unsaturation and more recently a quantitative method has been developed.[1,2] Solvents such as water, acetic acid, and carbon tetrachloride are used to dilute the solutions in order to minimize substitution reactions. Carbon tetrachloride is the most common of these solvents for the qualitative test because bromine and most alkenes have good solubilities and hydrogen bromide is insoluble. The rapid disappearance of the bromine color without the evolution of hydrogen bromide is taken as a positive test for the presence of unsaturation. Carbon tetrachloride is also one of the best solvents for the synthesis of dibromides.[3]

Until now, most of the kinetic studies on alkene brominations had been done in hydroxylic solvents such as water, acetic acid, and alcohols. Little work had been done in nonpolar aprotic solvents such as carbon tetrachloride. The reasons are that the kinetics are difficult to reproduce, the mechanisms are complicated, and heterogeneous reactions may occur on the glass surfaces of the reaction vessels.[1,3,4] The presence of impurities could account for some of these

problems. The kinetic studies in polar solvents are generally reproducible and show second or third order behavior depending on the temperature, solvent, alkene, and concentration as noted in Table 1.

TABLE 1

REACTION ORDERS IN POLAR SOLVENTS

Solvent	Alkene	Concentration Range (moles/l)	T($^\circ$C)	Order	Ref
Methanol	Stilbene	10^{-3}-10^{-2}	0	2nd	5
Methanol	Aliphatic	10^{-3}-10^{-2}	25	2nd	6
Methanol and Water	Aromatic and Aliphatic	10^{-3}-10^{-2}	25	2nd	7
Water	$RCH=CH_2$ and $RCH=CHCO_2Et$	10^{-2}	25	2nd	8
Acetic Acid	Aliphatic	10^{-3}	24	2nd	9
Acetic Acid	Styrenes and Stilbenes	10^{-2}	25	2nd & 3rd	10
Acetic Acid	Unsaturated Ketones	10^{-2}	24	3rd	11
Acetic Acid	Substituted Styrenes	10^{-3}-10^{-2}	25.3	2nd	12 13
Acetic Acid	Substituted Styrenes	10^{-4}	25	2nd	14

The mechanism of bromination of alkenes in nonpolar solvents, such as carbon tetrachloride, has been considered analogous to the reaction in polar solvents which is summarized in Figure 1. The first step consists of the rapid

formation of the alkene-bromine charge transfer
complex (I).[4,15,16] Dubois and Garnier have attempted to
demonstrate complex formation during bromination by
spectroscopic techniques at low temperatures.[17,18] Analogies
can be drawn to the alkene-iodine and alkene-silver salt
complexation.[19,20,21,22,23]
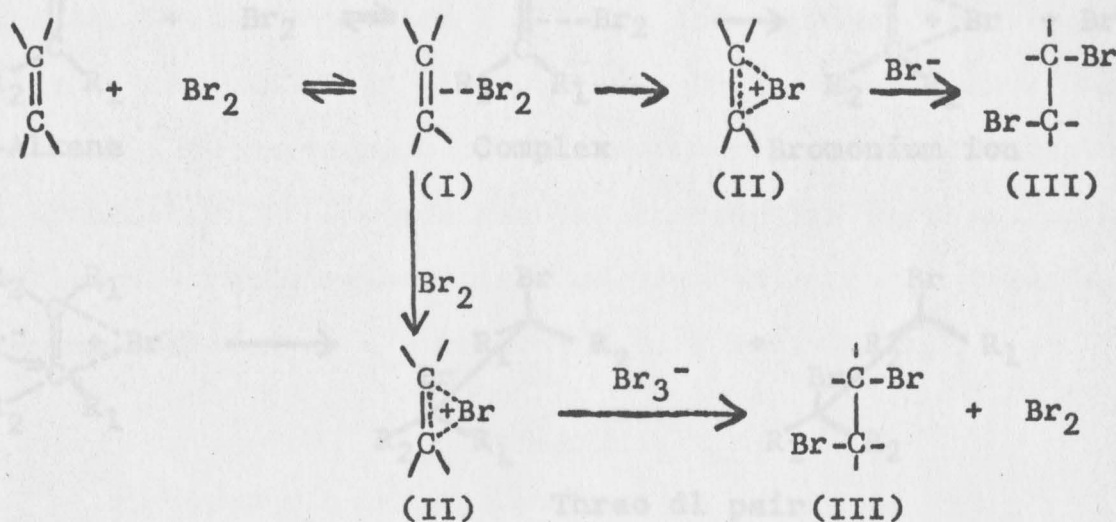
Fig. 1. The Mechanism of the Bromination
of Alkenes in Polar Solvents Involving a Charge
Transfer Complex and a Bromonium Ion.

The second step of the mechanism is the breakdown
of the charge transfer complex to the bromonium ion (II)
and the bromide ion or to the bromonium ion (II) and the
tribromide ion with the assistance of another bromine
molecule. This step in the mechanism has had wide acceptance
with little supporting evidence.[4] Fahey and Schneider cite
three types of supporting data; (1) stereochemistry,
(2) relative reactivity of alkenes, and (3) nuclear magnetic
studies of bridged halonium ions.[24] The stereochemistry of

alkene bromination is predominantly trans as shown in Figure 2.[25,26,27,28,29,30] The bromonium ion would hinder cis-addition. In his review Banthrope points out that the complex could cause the same steric hindrance.[31]

Z-Alkene + Br_2 ⇌ Complex → Bromonium ion

Br^- ··· + Br → Threo dl pair

E-Alkene + Br_2 ⇌ Complex → Bromonium ion

Br^- ··· + Br → Erythro dl pair
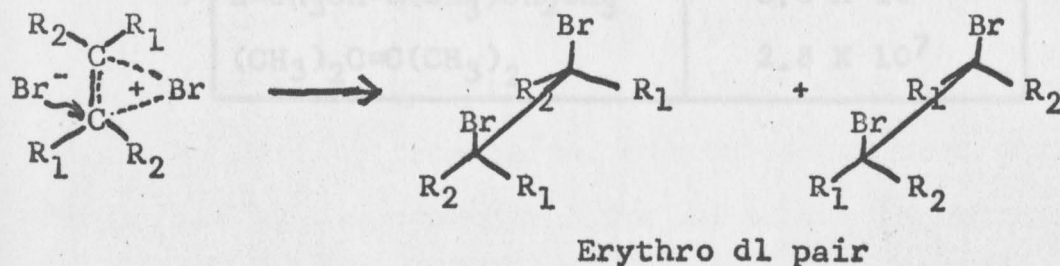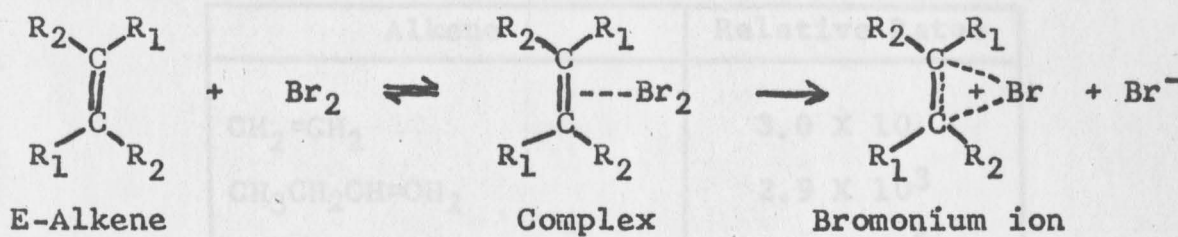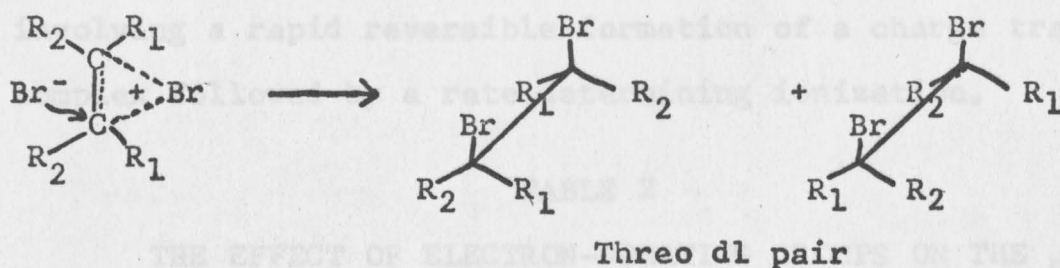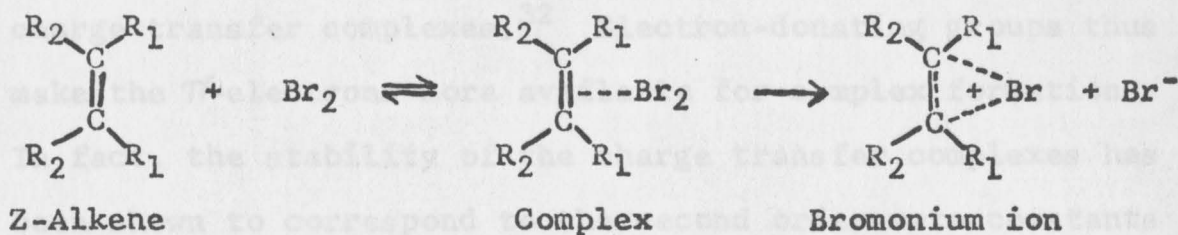
Fig. 2. Trans Bromination

Second, electron-donating groups enhance the rate of bromination as shown in Table 2.[6] The increased rate of addition is presumed to result from bromonium ion stabilization by electron-donating groups. Taft σ^* values have been shown to correlate with enhanced stability of charge transfer complexes.[32] Electron-donating groups thus make the π-electrons more available for complex formation. In fact, the stability of the charge transfer complexes has been shown to correspond to the second order rate constants of bromination.[16] Dubois has interpreted his work as involving a rapid reversible formation of a charge transfer complex followed by a rate determining ionization.

TABLE 2

THE EFFECT OF ELECTRON-DONATING GROUPS ON THE
RATE OF ALKENE BROMINATIONS IN METHANOL AT 25°C[6]

Alkene	Relative Rates
$CH_2=CH_2$	3.0×10
$CH_3CH_2CH=CH_2$	2.9×10^3
$Z-CH_3CH_2CH=CHCH_3$	1.3×10^5
$Z-CH_3CH=C(CH_3)CH_2CH_3$	3.6×10^6
$(CH_3)_2C=C(CH_3)_2$	2.8×10^7

In support of bromonium ions Olah and coworkers have shown bridged halonium ions using nuclear magnetic resonance.[33,34,35] However, the polar conditions used are extremes compared to those used for bromination in carbon tetrachloride. Dubois and Garnier used the Grunwald-Winstein relationship, $\log(k/k_0) = m_s Y$, in an attempt to indicate the possibility of bromonium ion formation. A slope, m_s, of 1.16 was obtained which indicated an $S_N 1$, bromonium ion intermediate, opposed to an $S_N 2$ mechanism shown in Figure 3. Polar hydroxylic solvents such as water, methanol, ethanol, 1-propanol, 1-butanol, and acetic acid were used.[17]
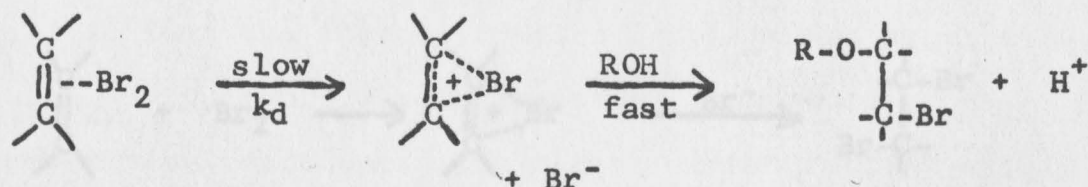
S_N 1 Type Mechanism
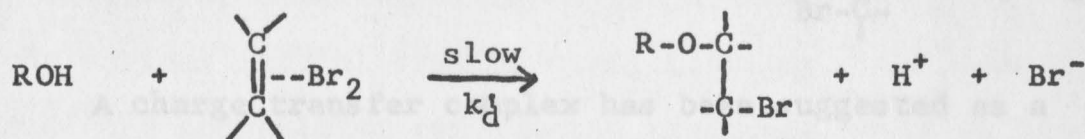
S_N 2 Type Mechanism

Fig. 3. S_N 1 and S_N 2 Type Bromination Mechanisms

Banthrope suggests that the bromonium ion intermediate may not be correct because the dibromide products continue to predominate at low concentrations of anions in hydroxylic polar solvents.[31] If transient bromonium ions were present, the anions could not compete with the solvent in the

subsequent nucleophilic attack that completes the addition.
The charge transfer complex was suggested as the intermediate
which causes discrimination in the nucleophilic attack.

Statement of the Problem

Although the bromination of alkenes has been
extensively studied several years, the mechanism continues
to be controversial. The generally accepted mechanism
consists of a rate-determining formation of a bromonium ion
intermediate which is subsequently attacked by a nucleophilic
bromide or tribromide anion. This mechanism is consistent
with the observed kinetics and products.[29,36,37,38]

$$\text{C=C} + Br_2 \longrightarrow \left[\text{C}\overset{+}{\cdots}Br\right] \xrightarrow{Br^-} \begin{array}{c} -\overset{|}{C}-Br \\ Br-\overset{|}{C}- \end{array}$$

$$\xrightarrow{Br_3^-} \begin{array}{c} -\overset{|}{C}-Br \\ Br-\overset{|}{C}- \end{array} + Br_2$$

A charge transfer complex has been suggested as a
precursor to this bromonium ion.[4,15,16,18,39,40] This
complex formation is presumed to be rapid and the subsequent
bromonium ion formation would be slow. This mechanism is
equally consistent with the kinetic studies and product

$$\text{C=C} + Br_2 \rightleftharpoons \text{C=C} \cdots Br_2 \longrightarrow \left[\text{C}\overset{+}{\cdots}Br\right] \longrightarrow$$

analyses. The direct attack of bromine on the charge transfer
complex has been suggested also.[3,15,17,39] This study is an

attempt to test the hypothesis that the charge transfer complex is an intermediate in the bromination mechanism.

A nonpolar aprotic solvent was used to favor alkene-bromine complexation and to minimize the ionic tendency of the reaction. Carbon tetrachloride, a readily available bromination solvent was chosen for this purpose. Kinetic studies were made on the addition of bromine to Z-3-hexene, E-3-hexene, and E-4-octene in this solvent. Reproducibility in such studies was difficult for previous investigators. Therefore, a secondary experimental objective was to demonstrate that the kinetics could be reproduced. The kinetic data and resulting rate expression were to be used to test the charge transfer complexation hypothesis.

A pair of these alkenes was brominated using competitive reactions. The alkene concentrations were held constant while the bromine concentrations were varied. The relative bromination rates of the alkenes were determined at the various initial bromine concentrations. The combined data of the competitive and kinetic reactions could be used to test the hypothesis.

Relative complexation tendencies of the alkenes were estimated by the evaluation of the equilibrium constants of iodine-alkene complexes in carbon tetrachloride. The direct determination of the bromine-alkene complexation constants was impossible due to the fast rate of addition. Iodine, which adds slowly and reversibly to alkenes, was expected to complex similar to bromine. These values could

be used to confirm the conclusions obtained from the kinetic
and competitive data.

CHAPTER II

EXPERIMENTAL

Chemicals and Purification

The chemicals used in this study are listed in
Table 3 along with the source and the claimed purity. The
alkene purities were confirmed by gas-liquid chromatography,
nuclear magnetic resonance, and mass spectrometry. The
purities of the n-pentane, 1-bromopentane, and the specially
purified carbon tetrachloride were ascertained by gas-liquid
chromatography. The observed melting point of the free
radical inhibitor, 2,6-di-tertiary butyl-4-methyl phenol,
was in agreement with the literature value.[41]

Since reproducibility of the experimental work in
carbon tetrachloride was of first concern, all impurities
had to be removed from the solvent. The following procedure
was used.[42] Technical grade carbon tetrachloride was stirred
with twenty per cent aqueous sodium hydroxide solution
overnight or longer. The solutions were separated and the
carbon tetrachloride layer was washed four times with equal
volumes of distilled water. After drying overnight with
anhydrous magnesium sulfate, the solvent was filtered into a
clean, dry one liter 24/40 standard joint flask. This flask
was connected to a distillation apparatus consisting of a
heating mantle, vigreux column, thermometer, condenser,

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TABLE 3

SOURCE AND CLAIMED PURITY OF
THE CHEMICALS USED IN THIS STUDY

Chemical	Source	Claimed Purity
Carbon Tetrachloride	Fisher Scientific	Technical
n-Pentane	Phillips Petroleum	99%
Bromine	Baker and Adamson	99.5%
Iodine	Fisher Scientific	99.99%
Cyclohexene	Chemical Samples	99%
E-3-Hexene	Chemical Samples	99%
Z-3-Hexene	Chemical Samples	96%
E-4-Octene	Chemical Samples	99%
1-Bromopentane	Matheson Coleman and Bell	Red Label
2,6-di-tertiary butyl-4-methyl phenol	Dupont	----

vacuum adapter with a drying tube attached and a receiving flask. Silicon grease was not used on the joint between the condenser and the vacuum adapter and the joint between the vacuum adapter and the receiving flask in order to prevent contamination. The carbon tetrachloride was distilled slowly at 75-76°C and the middle ninety per cent fraction was collected in a clean, dry brown storage bottle.

The final purification step consisted of refluxing a portion of the carbon tetrachloride from the brown storage bottle with phosphorus pentoxide overnight or longer in a clean, dry flask which was part of a second distillation apparatus that was identical to the one described above. The solvent then was distilled slowly at 75-76°C. The middle eighty per cent fraction was collected into a clean, dry receiving flask which was stoppered with a drying tube upon completion of the distillation. The solvent was used the same day as the final purification.

Glassware

All glassware was cleaned and dried thoroughly. Initially all flasks, distilling equipment, pipettes, etc., were washed with soap, rinsed thoroughly with distilled water and dried in an oven at 110°C. After this initial washing the distillation equipment, excluding the distilling and receiving flasks, was not cleaned or dried. The reaction flasks were rinsed with carbon tetrachloride, then distilled water, and finally dried overnight in an oven at 110°C.

The 1-cm quartz cells used in the Cary 14 were
rinsed thoroughly with carbon tetrachloride and stored in a
desiccator containing calcium chloride.

Molar Absorptivity Determinations

Since kinetic data of the bromination reactions were
to be obtained by following the bromine absorbance decrease
with time using the Cary 14 spectrophotometer, the molar
absorptivities were determined with the Beer-Lambert
equation. After determining the wavelength of maximum
absorption, λ_{max}, for bromine in carbon tetrachloride, the
absorbance of known concentrations of bromine in carbon
tetrachloride were measured using 1-cm quartz cells with
pure solvent as a reference. The molar absorptivity, ε_{max},
at λ_{max} was computed from equation (1) using a least squares

$$(\Delta A/\Delta c)/d = \varepsilon_{max} \tag{1}$$

regression analysis. The term ΔA is the change of the
absorbance for a difference in concentration, Δc, using a
path length, d, of one centimeter.

Molar absorptivities were also determined for iodine
in n-pentane and carbon tetrachloride using the method just
described. All determined values are listed in Table 4.

TABLE 4

WAVELENGTHS OF MAXIMUM ABSORPTION, MOLAR
ABSORPTIVITIES AND STANDARD DEVIATIONS FOR BROMINE
AND IODINE IN n-PENTANE AND(OR) CARBON TETRACHLORIDE

Absorbing Molecule	Solvent	λ_{max} (mμ)	ε_{max} (1/mole-cm)	σ
Bromine	CCl$_4$	415	205.9	3.3
Bromine	CCl$_4$	480*	123	4
Iodine	CCl$_4$	517	935	12
Iodine	n-pentane	523	903	19
Iodine	n-pentane	295	95.0	3.2

* This determination is on the shoulder of the
415 mμ peak.

Kinetic Run Procedures

The reaction solutions were prepared by diluting
one milliliter of a stock bromine solution to 250 milliliters
in a clean, dry volumetric flask. Aliquots of this diluted
solution were transferred to fifty or one hundred milliliter
volumetric flasks which were then covered with aluminum
foil. The alkene stock solutions were prepared in ten
milliliter volumetric flasks to minimize weighing errors
due to alkene evaporation. After weighing the alkene on a
Mettler balance, the flasks were immediately filled to the
marks with purified carbon tetrachloride and stoppered.

The diluted bromine and stock alkene solutions were
allowed to come to thermal equilibrium in the room containing
the Cary 14 before mixing them together. Immediately prior
to mixing the alkene and bromine solutions, the Cary 14 was

zeroed at 415 mμ using carbon tetrachloride in the sample
and reference cells. The initial bromine concentrations
were determined spectroscopically on the diluted solutions.
Corrections were made for the subsequent dilution with the
alkene stock solutions. The initial alkene concentrations
were calculated from the dilution factors.

To minimize light induced free radical substitution
or addition and to favor electrophilic addition, the room
in which the Cary 14 was located was darkened and the
reaction flasks were wrapped with aluminum foil. A one
milliliter aliquot of the alkene stock solution was added
to the bromine solution and a stopwatch started as the first
drops of alkene solution were added. The addition took
about five seconds. The flask was immediately stoppered,
completely covered with aluminum foil and shaken to mix
completely. Samples were removed from the reaction flask
by pouring into the 1-cm quartz cell starting within two
minutes of the initial mixing and continuing for
approximately twenty minutes. The absorbance of each sample
was determined immediately in the Cary 14 and the quartz
cell was emptied and air dried between determinations. A
fresh sample was used for each reading to guard against
errors in the initial or subsequent readings and to minimize
the effect of light catalysis. Room temperature was recorded
during the reactions. In several cases, the solution
temperatures were also determined to ascertain that they were
the same as the room temperature. Several kinetic runs were

conducted in which 2,6-di-tertiary butyl-4-methyl phenol, a free radical inhibitor, was present in concentrations of 1.1×10^{-3} or 2.7×10^{-3} molarity. These reactions were kinetic runs 3, 25, and 52.

The data of the kinetic runs are summarized in Tables 5, 6, and 7. The full experimental results of each kinetic run are in the Appendix in Tables 13-30. The initial bromine and alkene concentrations are b and a, respectively. The bromine concentrations at various times, t, in seconds are symbolized b-x. The third order rate constants at various times, the least squares average third order rate constants, and the standard deviations are k_3, $\bar{k}_3$, and δ, respectively. All concentrations and all third order rate constants have units of moles per liter and liters^2/moles^2/second, respectively.

TABLE 5

SUMMARY OF KINETIC RUNS, INITIAL CONCENTRATIONS,
LEAST SQUARES AVERAGE THIRD ORDER RATE CONSTANTS AND
STANDARD DEVIATIONS FOR THE BROMINATION OF Z-3-HEXENE

Kinetic Run	10^3b	10^3a	$\bar{k}_3$	σ	$100\sigma/\bar{k}_3$	Table in Appendix
1	8.88	9.07	45.7	1.4	3.1	13
2	8.88	7.04	48.8	1.4	2.9	13
3	8.93	7.04	65.2	1.7	2.6	13
4	8.91	4.85	50.8	0.8	1.6	14
5	9.00	2.97	57.8	0.9	1.6	14
6	8.70	3.15	47.3	1.7	3.6	14
7	6.81	9.98	49.0	0.8	1.6	15
8	6.81	9.11	47.3	0.9	1.9	15
9	6.81	6.95	43.1	0.6	1.4	15
10	7.03	5.14	47.5	0.7	1.5	15
11	4.48	10.00	39.7	0.5	1.3	16
12	4.52	9.08	43.9	0.7	1.6	16
13	4.45	6.94	49.4	0.5	1.0	16
14	4.50	5.14	48.6	0.6	1.2	16
15	4.69	3.04	51.8	0.9	1.7	17
16	4.57	3.04	54.2	0.8	1.5	17
17	4.69	1.89	50.9	0.9	1.8	17
18	4.57	1.91	47.6	1.0	2.1	17
19	3.65	8.69	38.4	0.8	2.1	18
20	3.65	6.85	39.2	1.0	2.6	18
21	3.66	5.00	45.1	0.7	1.6	18
22	3.69	2.03	44.9	2.3	5.1	18

TABLE 6

SUMMARY OF KINETIC RUNS, INITIAL CONCENTRATIONS,
LEAST SQUARES AVERAGE THIRD ORDER RATE CONSTANTS AND
STANDARD DEVIATIONS FOR THE BROMINATION OF E-4-OCTENE

Kinetic Run	10^3b	10^3a	$\bar{k}_3$	σ	$100\sigma/\bar{k}_3$	Table in Appendix
23	8.89	9.88	35.2	0.7	2.0	19
24	8.89	6.98	34.6	0.7	2.0	19
25	8.93	7.01	44.8	0.8	1.8	19

TABLE 7

SUMMARY OF KINETIC RUNS, INITIAL CONCENTRATIONS,
LEAST SQUARES AVERAGE THIRD ORDER RATE CONSTANTS AND
STANDARD DEVIATIONS FOR THE BROMINATION OF E-3-HEXENE

Kinetic Run	$10^3 b$	$10^3 a$	$\bar{k}_3$	σ	$100\sigma/\bar{k}_3$	Table in Appendix
26	9.59	4.83	56.1	1.6	2.9	20
27	9.43	4.72	70.8	2.0	2.8	20
28	9.40	4.66	63.0	1.8	2.8	20
29	9.24	9.31	93.7	1.3	1.4	21
30	9.28	9.08	66.6	3.3	5.0	21
31	9.28	7.06	76.7	1.2	1.6	21
32	9.23	4.85	69.3	0.5	0.7	22
33	9.23	2.95	80.3	0.4	0.5	22
34	9.11	9.99	59.0	1.9	3.3	23
35	9.05	4.61	66.4	0.6	0.9	23
36	9.11	1.97	67.4	0.4	0.6	23
37	8.72	4.23	62.1	3.8	6.1	24
38	7.89	7.93	71.5	0.9	1.3	24
39	6.83	4.72	46.9	1.7	3.6	24
40	4.88	10.10	51.2	1.1	2.2	25
41	4.70	9.01	52.2	1.7	3.2	25
42	4.70	7.10	52.9	0.8	1.5	25
43	4.88	4.74	64.8	0.4	0.6	25
44	4.81	4.66	72.7	2.5	3.4	26
45	4.86	3.06	73.8	0.7	0.9	26
46	4.76	4.83	64.4	3.0	4.7	26
47	4.89	3.15	65.9	0.8	1.2	27
48	4.93	1.96	64.1	1.6	2.5	27
49	4.86	1.91	67.4	0.8	1.2	27
50	4.31	4.61	62.0	0.7	1.1	28
51	3.73	8.74	48.8	0.5	1.0	28
52	3.68	8.70	53.0	0.8	1.5	28
53	3.73	6.87	53.7	1.0	1.9	29
54	3.73	5.00	49.8	1.3	2.6	29
55	3.73	1.98	49.7	3.6	7.2	29
56	2.55	4.34	52.5	1.3	2.5	30
57	2.04	4.28	46.0	2.4	5.2	30

Interfering Specie Experiment

Yates and Wright reached an erroneous conclusion
that the bromination of substituted styrenes followed second
and third order kinetics because they did not account for
the absorption of the tribromide anion in their studies.[12]
Subsequent work by Pincock and Yates showed that these
reactions followed simple second order kinetics when
measurements were made at a wavelength at which the
tribromide anion did not absorb.[13] We conducted an
experiment to test a similar possibility in this research.
The Beer-Lambert law was shown to apply at 415 mμ and 480 mμ
for bromine absorption in carbon tetrachloride. The
tribromide anion would not absorb at 480 mμ. Equation (2)
would hold if no tribromide anion is present. In this

$$A_{415_t}/A_{415_o} = A_{480_t}/A_{480_o} \tag{2}$$

equation A_{415_o}, A_{415_t}, A_{480_o}, and A_{480_t} are the absorbances
of bromine at 415 mμ or 480 mμ and at times zero and t,
respectively. Kinetic run 6 was used for the study and the
results are illustrated in Figure 4.
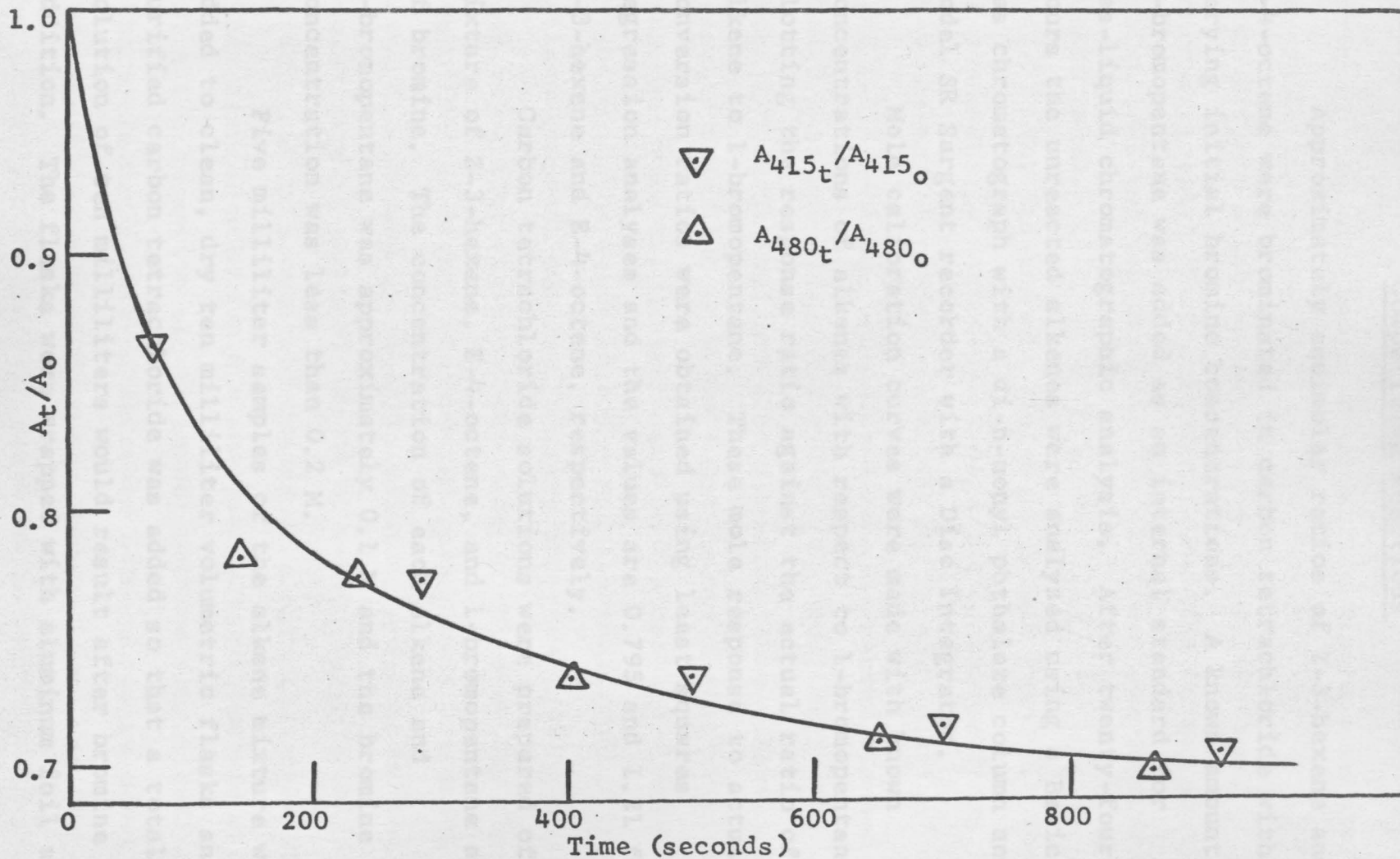
Fig. 4. A Study to Show the Absence of
the Tribromide Anion in the Kinetic Studies.

Competitive Reactions

Approximately equimolar ratios of Z-3-hexene and E-4-octene were brominated in carbon tetrachloride with varying initial bromine concentrations. A known amount of 1-bromopentane was added as an internal standard for gas-liquid chromatographic analysis. After twenty-four hours the unreacted alkenes were analyzed using a Basic Carle gas chromatograph with a di-n-nonyl phthalate column and a Model SR Sargent recorder with a Disc integrator.

Mole calibration curves were made with known concentrations of alkenes with respect to 1-bromopentane by plotting the response ratio against the actual ratio of alkene to 1-bromopentane. These mole response to actual conversion ratios were obtained using least squares regression analyses and the values are 0.795 and 1.21 for Z-3-hexene and E-4-octene, respectively.

Carbon tetrachloride solutions were prepared of a mixture of Z-3-hexene, E-4-octene, and 1-bromopentane and of bromine. The concentration of each alkene and 1-bromopentane was approximately 0.1 M and the bromine concentration was less than 0.2 M.

Five milliliter samples of the alkene mixture were added to clean, dry ten milliliter volumetric flasks and purified carbon tetrachloride was added so that a total solution of ten milliliters would result after bromine addition. The flasks were wrapped with aluminum foil and

the bromine solution was added in a darkened room to minimize
free radical reactions. The reaction flasks were stored
overnight in a constant temperature water bath at 25°C. The
next day the solutions were analyzed by gas-liquid
chromatography. Each solution, including unreacted alkene
solutions, was analyzed five to six times and an average
value taken.

The results are listed in Tables 8 and 9. The
experimentally determined Z-3-hexene/1-bromopentane, the
E-4-octene/1-bromopentane remaining in the reaction solutions
and the Z-3-hexene reacted/E-4-octene reacted are Z-3-H/1-B,
E-4-O/1-B, and d(Z-3-H)/d(E-4-O), respectively. The
standard deviations are also given in these tables. In the
results described in Table 9 the relative reactivities
analyses were calculated based on a stock and control
solution. The stock solution was the undiluted
alkene-internal standard mixture and gas-liquid
chromatography analyses were made in the same day that the
reaction was begun. In the same experiment a bromine free
control solution was made by diluting a sample of the stock
solution with an equal amount of carbon tetrachloride and
placing it in a constant temperature bath overnight at 25°C.
This control solution was analyzed after twenty-four hours.
With the exception of the lowest bromine concentration,
there are negligible differences between the relative
reactivities computed from the analyses based on the stock
or control solution. The relative reactivity data of

Table 8 were computed from the stock solution analyses which were made at the start of the reaction.

TABLE 8

COMPETITIVE REACTIONS OF Z-3-HEXENE AND
E-4-OCTENE WITH LIMITED AMOUNTS OF BROMINE AT 25°C

Initial Bromine (molarity)	$\frac{\text{Z-3-H}}{\text{1-B}}$	σ	$\frac{\text{E-4-O}}{\text{1-B}}$	σ	$\frac{d(\text{Z-3-H})}{d(\text{E-4-O})}$ [a]
0.119	0.283	0.021	0.508	0.015	1.55
0.098	0.365	0.034	0.605	0.020	1.76
0.078	0.522	0.010	0.683	0.015	1.68
0.055	0.569	0.006	0.800	0.007	2.87
0.033	0.698	0.008	0.844	0.007	2.84
0.022	0.781	0.028	0.881	0.023	3.33
[b] 0	0.931	0.050	0.926	0.031	----

[a] This column is based on the stock solution of the original mixture.

[b] This is the analysis of the stock solution.

TABLE 9

COMPETITIVE REACTIONS OF Z-3-HEXENE AND E-4-OCTENE WITH LIMITED AMOUNTS OF BROMINE AT 25°C

Initial Bromine (molarity)	$\frac{Z-3-H}{1-B}$	σ	$\frac{E-4-O}{1-B}$	σ	$\frac{d(Z-3-H)}{d(E-4-O)}$ [a]	$\frac{d(Z-3-H)}{d(E-4-O)}$ [b]
0.117	0.350	0.011	0.512	0.016	1.77	1.74
0.097	0.444	0.015	0.611	0.012	2.03	1.97
0.078	0.595	0.014	0.692	0.006	2.08	2.00
0.058	0.684	0.031	0.771	0.025	2.56	2.39
0.039	0.801	0.045	0.857	0.032	4.04	3.33
0.023	0.911	0.042	0.923	0.039	43.3	7.41
0 [c]	1.111	0.011	0.950	0.023	----	----
0 [d]	1.084	0.042	0.927	0.055	----	----

[a]This column is based on the stock solution.

[b]This column is based on the control solution.

[c]This is the analysis of the stock solution.

[d]This is the analysis of the control solution.

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Iodine Complexation with Alkenes

The relative complexation tendencies of the alkenes were estimated by determining the alkene-iodine equilibrium constants. The decrease of the iodine absorption peak could not be used because the complex absorbs in the same region.[43] The Benesi-Hildebrand method was applied to the charge-transfer band of the alkene-iodine complexes at 300 mμ using equation (3).[20,44] In equation (3) i is the

$$id/A = 1/K_N(\epsilon_c + \epsilon_i)N_o + 1/(\epsilon_c + \epsilon_i) \quad (3)$$

initial iodine concentration in moles per liter; A is the absorbance of the complex at λ_{max} of the complex; d is the cell thickness; K_N is the equilibrium constant of the complex in reciprocal mole fraction units; ϵ_c and ϵ_i are the molar absorptivities of complex and iodine at λ_{max} of the complex; N_o is the mole fraction of the alkene. Plots of id/A versus $1/N_o$ give an ordinate intercept of $1/(\epsilon_c + \epsilon_i)$ where $1/N_o$ has a value of one and a slope of $1/K_N(\epsilon_c + \epsilon_i)$.

Stock solutions of iodine and alkene were prepared and were covered with aluminum foil while they equilibrated to room temperature. Measured quantities of the iodine solution and the alkene solutions were mixed in clean, dry ten milliliter flasks which were covered with aluminum foil. The resulting concentrations for iodine ranged from 10^{-4} to 10^{-3} M. The mole fraction of the alkenes ranged from 0.02 to 0.6. Within two minutes samples were transferred to a 1-cm quartz cell and a rapid scan was taken with the Cary 14

spectrophotometer of the λ_{max} region of the complex using pure solvent as the reference. Each complex had a λ_{max} near 300 mμ. The absorbance of the complex did not change appreciably during the time the readings were taken as was also shown by other investigators.[23]

Table 10 lists the alkene-iodine equilibrium constants in reciprocal mole fraction units, K_N, and liters per mole, K_C. These were calculated from the slope and intercept with the least squares regression analysis. The equilibrium constants for cyclohexene and iodine in Table 10 compare well with the value 3.30 obtained by Traynham and Olechowski in 2,2,4-trimethylpentane.[20] The complexation constant of E-3-hexene was not determined because there was insufficient sample.

TABLE 10

ALKENE-IODINE COMPLEXATION CONSTANTS

Alkene	Solvent	Temp. (^{o}C)	λ_{max} (mμ)	ε_c (l./mole/cm)	K_N (1/mole fraction)	K_C (l./mole)
Cyclohexene	n-Pentane	23 ± 1	298	1.36×10^4	4.24	0.442
Cyclohexene	CCl$_4$	24 ± 1	302	1.50×10^4	4.12	0.308
Z-3-Hexene	CCl$_4$	24 ± 1	302	1.04×10^4	4.48	0.292
E-4-Octene	CCl$_4$	24 ± 1	305	1.17×10^4	2.02	0.201

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CHAPTER III

RESULTS AND CONCLUSIONS

Reproducibility

The reproducibility of the kinetic data for bromination in carbon tetrachloride had to be shown before the data could be used to test the hypothesis that complexation is a necessary step in the bromination of alkenes. In addition it was necessary to ascertain that a free radical reaction was not occurring. The reaction data fit third order kinetic plots well and such plots are used in Figures 5-9 to confirm these facts. Equations 4 and 5 show the form for stoichiometric and nonstoichiometric third order expressions, respectively. In these equations k_3, a,

$$k_3 t = \tfrac{1}{2}(a-x)^{-2} - \tfrac{1}{2}a^{-2} \tag{4}$$

$$k_3 t = 1/(a-b)\left[x/b(b-x) + 1/(a-b)\ln\left[a(b-x)/b(a-x)\right]\right] \tag{5}$$

b, x, and t represent the third order rate constant, initial alkene concentration, initial bromine concentration, product concentration, and time, respectively.

Figures 5, 6, and 7 show third order plots of pairs of reactions for the bromination of E-3-hexene, Z-3-hexene, and E-4-octene, respectively. The right term of equations 4 and 5 is plotted against time. In each case one reaction of the pair contained a free radical inhibitor, 2,6-di-tertiary butyl-4-methyl phenol, and in all three cases

the inhibited reaction has either the same or faster rate than the uninhibited reaction. The increased rate of reaction for the inhibited kinetic runs 3 and 25 can be attributed to a slight increase in solvent polarity caused by inhibitor. This increased polarity should increase the rate of reaction in an electrophilic type reaction. The concentration of the free radical inhibitor in each case was nearly three times that in kinetic run 52 which has essentially the same reaction rate as kinetic run 51. These kinetic run pairs indicate that the free radical reactions are not important in our systems.

Figures 5, 8, and 9 show pairs of reactions for the bromination of E-3-hexene in carbon tetrachloride. Each pair has nearly the same concentrations and the rates are within experimental error. These reaction pairs show that reproducibility of the bromination of alkenes in carbon tetrachloride can be achieved under carefully controlled reaction conditions.

The kinetic reactions were conducted in two sizes of volumetric flasks which have different volume to surface area ratios. Reaction pair 44 and 46 shown in Figure 9 is an example. The reproducible rates indicate that surface catalyzed reactions are not important.
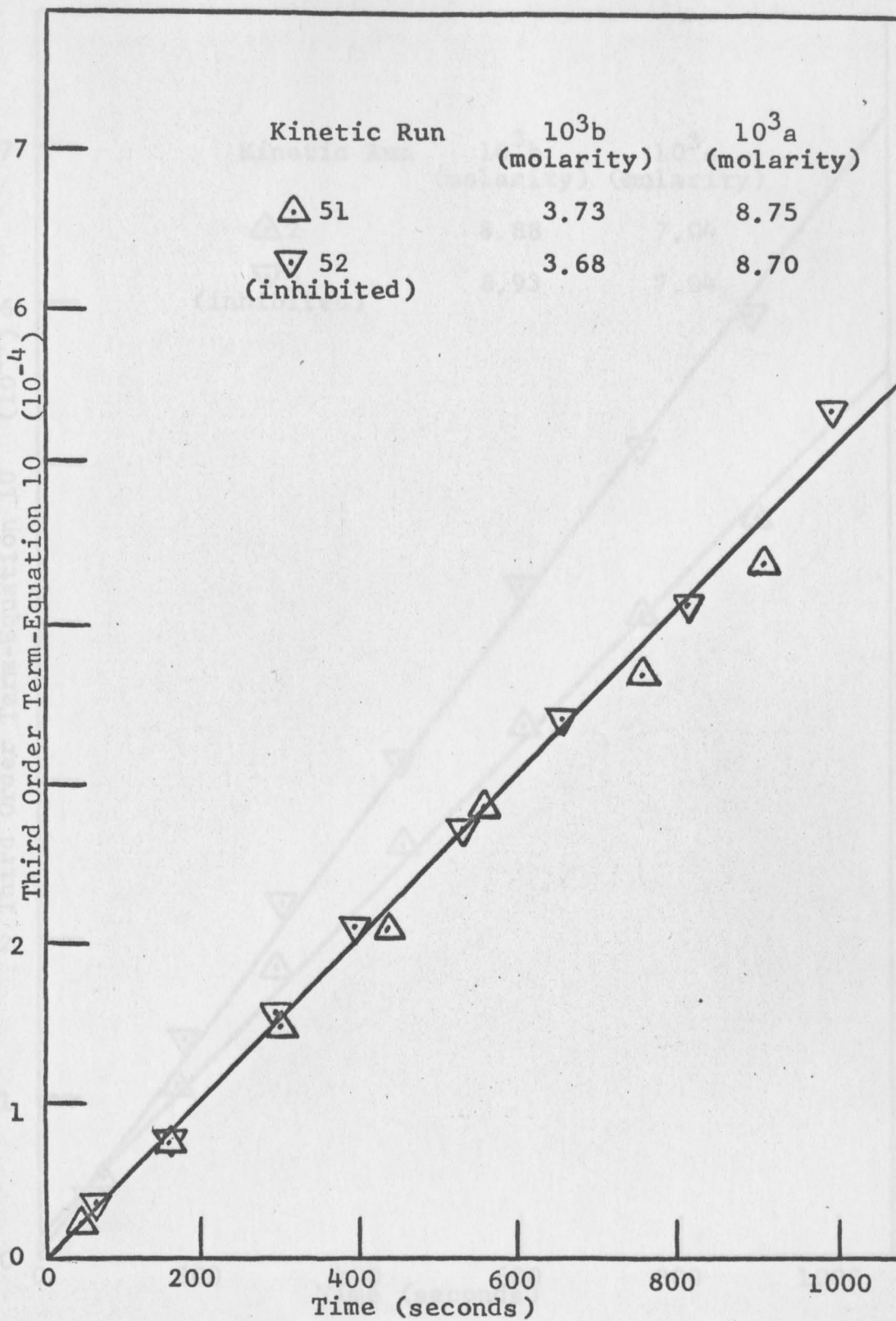
Fig. 5. Third Order Plot for Inhibited
and Uninhibited Bromination of E-3-Hexene
in Carbon Tetrachloride.
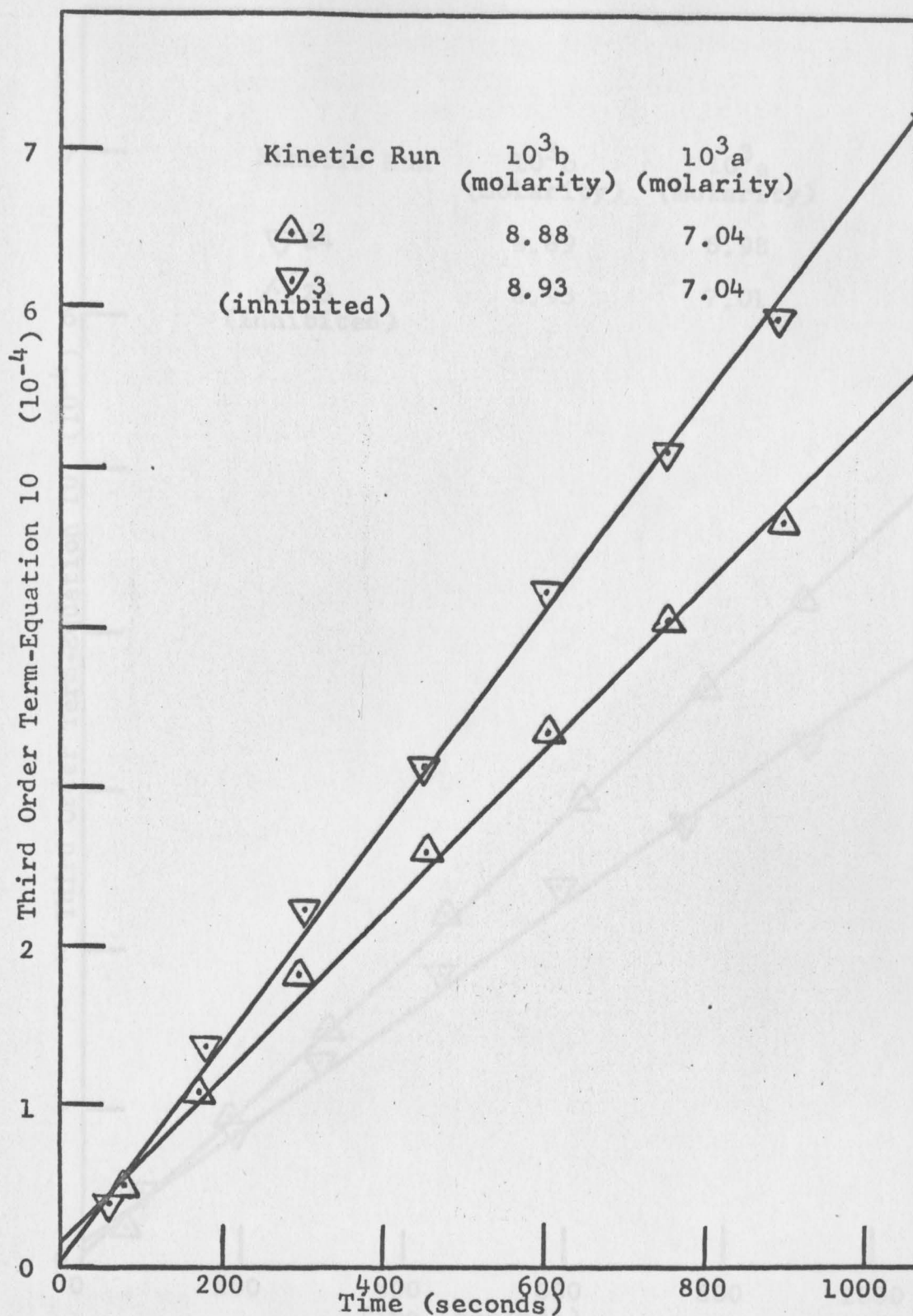
Fig. 6. Third Order Plot for Inhibited
and Uninhibited Bromination of Z-3-Hexene
in Carbon Tetrachloride.
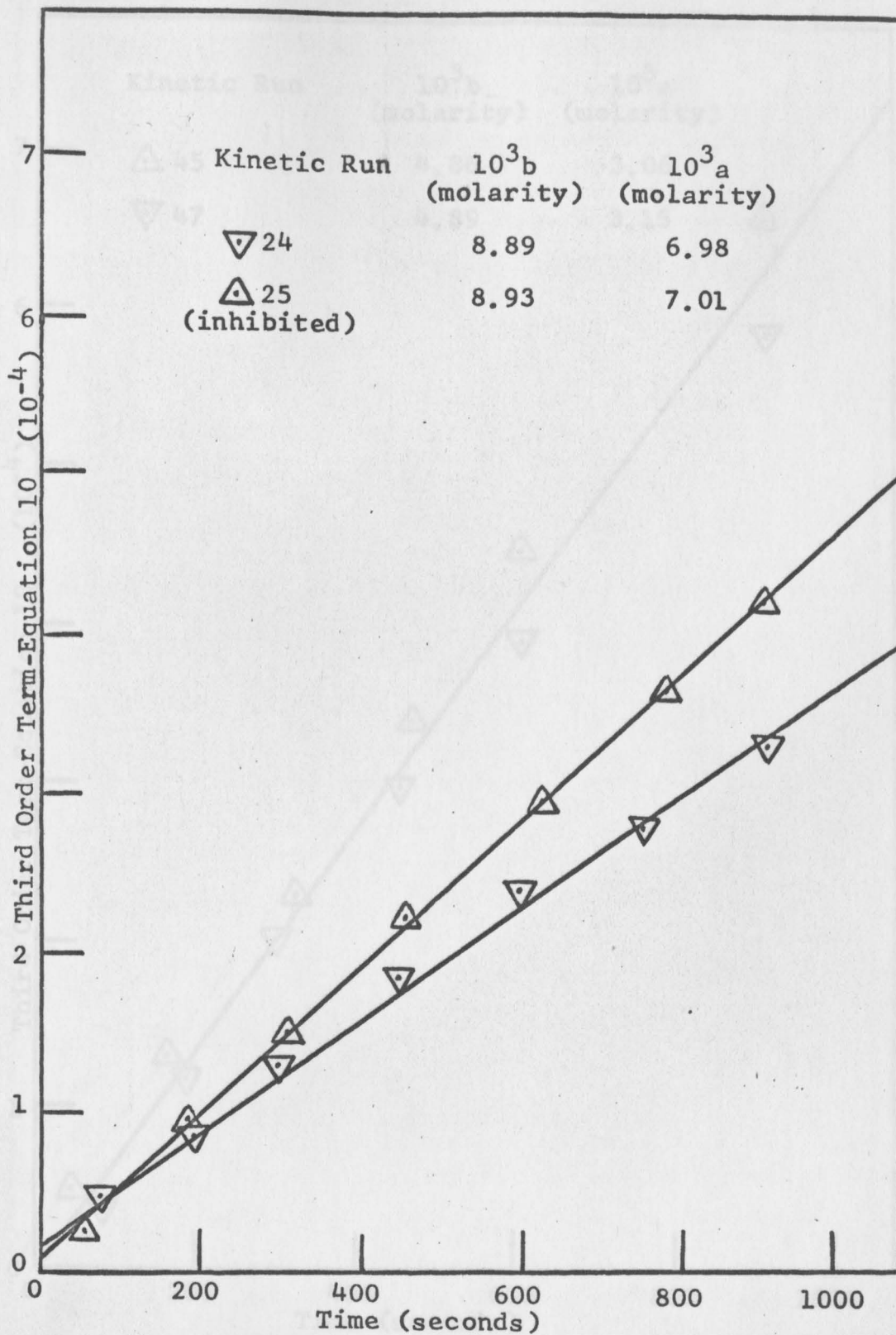
Fig. 7. Third Order Plot for Inhibited and Uninhibited Bromination of E-4-Octene in Carbon Tetrachloride.
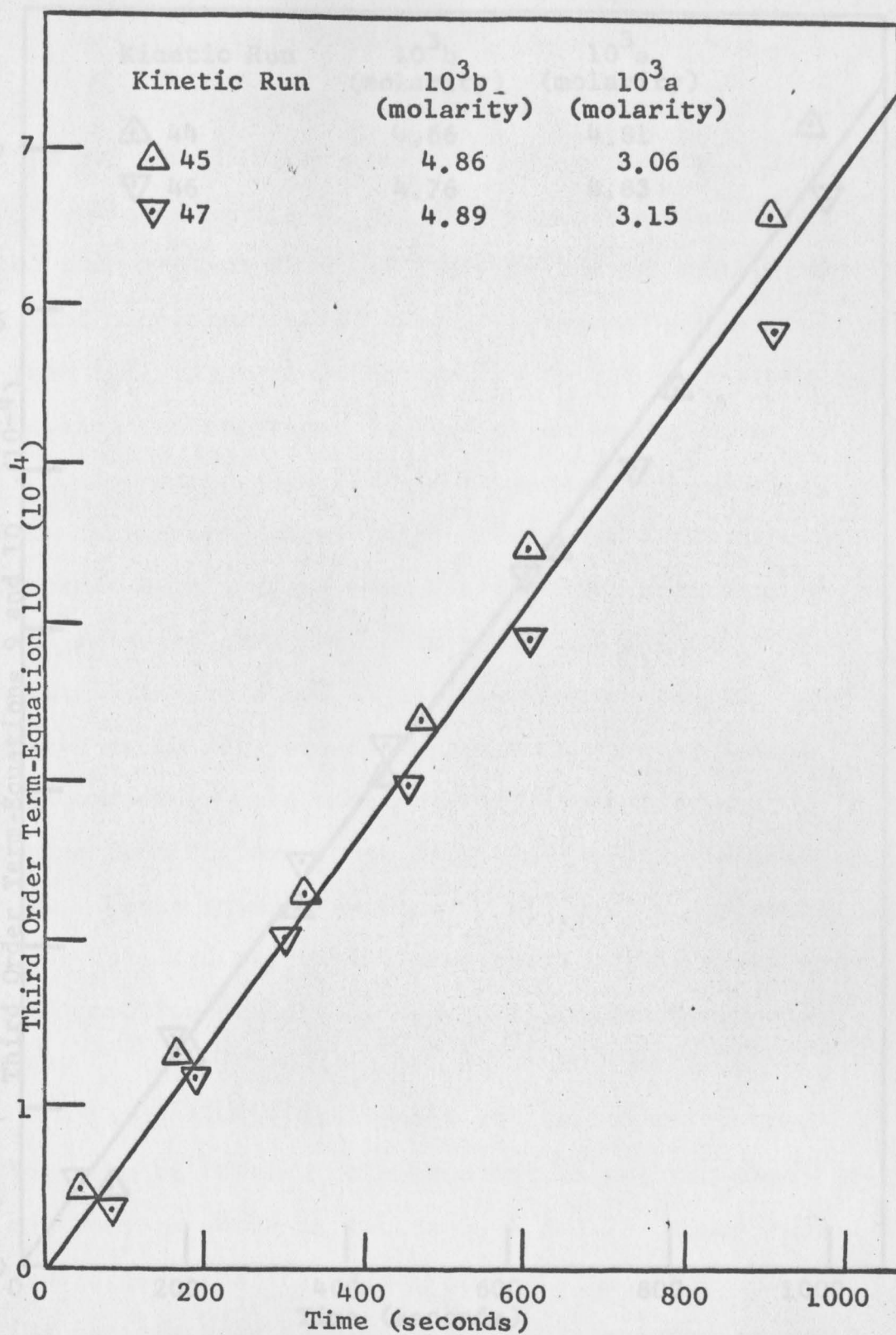
Fig. 8. Reproducibility Using Third Order Plots of the Bromination of E-3-Hexene in Carbon Tetrachloride.

Kinetic Run	$10^3 b$ (molarity)	$10^3 a$ (molarity)
△ 44	4.66	4.81
▽ 46	4.76	4.83

Third Order Term-Equations 9 and 10 (10^{-4})

Time (seconds)
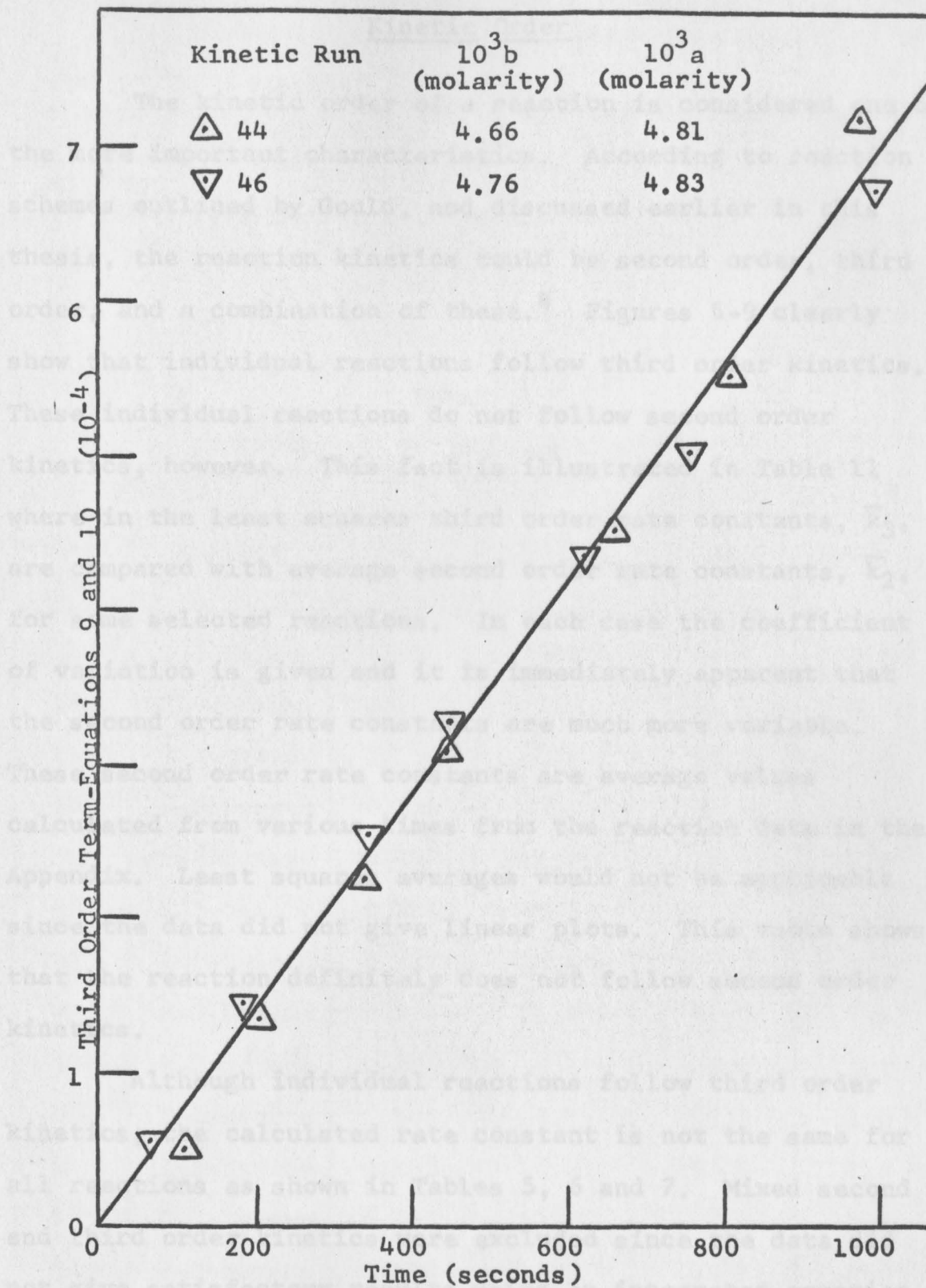
Fig. 9. Reproducibility Using Third Order
Plots of the Bromination of E-3-Hexene in
Carbon Tetrachloride.

Kinetic Order

The kinetic order of a reaction is considered one of the more important characteristics. According to reaction schemes outlined by Gould, and discussed earlier in this thesis, the reaction kinetics could be second order, third order, and a combination of these.[4] Figures 5-9 clearly show that individual reactions follow third order kinetics. These individual reactions do not follow second order kinetics, however. This fact is illustrated in Table 11 where in the least squares third order rate constants, $\bar{k}_3$, are compared with average second order rate constants, $\bar{k}_2$, for some selected reactions. In each case the coefficient of variation is given and it is immediately apparent that the second order rate constants are much more variable. These second order rate constants are average values calculated from various times from the reaction data in the Appendix. Least squares averages would not be applicable since the data did not give linear plots. This table shows that the reaction definitely does not follow second order kinetics.

Although individual reactions follow third order kinetics, the calculated rate constant is not the same for all reactions as shown in Tables 5, 6 and 7. Mixed second and third order kinetics were excluded since the data did not give satisfactory results using an integrated equation obtained by Yates and coworkers based on equation (6).[45]

$$dx/dt = k_2(a-x)(b-x) + k_3(a-x)(b-x)^2 \qquad (6)$$

The terms a-x, b-x, x, k_2 and k_3 are the concentrations of alkene, bromine and products at time t and the second and third order rate constants, respectively.

TABLE 11

COMPARISON OF CALCULATED AVERAGE
SECOND AND THIRD ORDER RATE CONSTANTS

Kinetic Run	Alkene	$\bar{k}_2$	$100\delta/\bar{k}_2$	$\bar{k}_3$	$100\delta/\bar{k}_3$
3	Z-3-hexene	0.404	23.3	69.3	4.6
15	Z-3-hexene	0.211	8.4	51.8	1.7
21	Z-3-hexene	0.136	8.8	45.1	1.6
30	E-3-hexene	0.354	25.1	66.6	5.0
31	E-3-hexene	0.467	21.9	76.7	1.6
38	E-3-hexene	0.369	28.5	71.5	1.3
45	E-3-hexene	0.322	18.4	73.8	0.9
47	E-3-hexene	0.256	11.5	65.9	1.2
50	E-3-hexene	0.196	9.1	62.0	1.1
51	E-3-hexene	0.141	18.3	48.8	1.0
52	E-3-hexene	0.143	16.5	53.0	1.5
54	E-3-hexene	0.161	13.1	49.8	1.3
56	E-3-hexene	0.110	13.9	52.5	2.5

The reactions did not follow first order kinetics.
The fact that the specific third order rate constants vary
signifies that other factors are involved which are not
considered in simple kinetics. Most of the more
complicated kinetic schemes involve complexation and these
are discussed in the following sections.

The Effect of Complexation on Kinetics

If the reaction mechanism does involve complexation,
the observed third order rate constants would be a
combination of second order rate constants, equlibrium
constants and possibly some concentration terms. This
observed third order rate constant would more appropriately
be termed apparent third order rate constant. Apparent
third order rate constants could very well vary with
concentration. A similar effect was observed by Ross and
Kuntz for the reaction of 2,4-dinitrochlorobenzene with
aniline.[46] In that study the increased concentrations of
aniline increases the complexation of the
2,4-dinitrochlorobenzene and caused the apparent second
order rate constant to decrease. Since our rate constants
do vary, it is reasonable to assume that these are apparent
rate constants that vary with complexation.

The bromination of alkenes could follow a general mechanism illustrated by equations (7) and (8). The terms

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \tag{7}$$

$$C + B \xrightarrow{k} P \tag{8}$$

A, B, C, P, k_1, k_{-1}, and k are the concentrations of alkene, bromine, complex, product, and the various rate constants, respectively. Since previous workers have considered the charge transfer complex in equations (7) and (8) as a transient intermediate, a steady state assumption is reasonable as shown in equation (9).[17,18] The terms a, b,

$$dc/dt = k_1(a-x-c)(b-x-c) - k_{-1}c - kc(b-x-c) = 0 \tag{9}$$

x, c, k_1, k_{-1}, and k are the initial alkene concentration, the initial bromine concentration, the product and complex concentration at time t and the various rate constants, respectively. Solving equation (9) for the complex, c, yields equation (10). The equilibrium constant, K, is the

$$c = K(a-x-c)(b-x-c)/\left[1 + \frac{k}{k_{-1}}(b-x-c)\right] \tag{10}$$

ratio of k_1/k_{-1}. If the rate determining step is equation (8), then equation (11) is applicable. If we

$$dx/dt = kCB = kK(a-x-c)(b-x-c)^2/\left[1 + \frac{k}{k_{-1}}(b-x-c)\right] \tag{11}$$

assume $k \ll k_1$, k_{-1} then k/k_{-1} becomes negligibly small and the second term in the denominator of equation (11) can be neglected. This leads directly to equation (12).

$$dx/dt = kK \left[(a-c)-x\right] \left[(b-c)-x\right]^2 \qquad (12)$$

Equation (12) is an example of the steady state-equilibrium approximation in reaction kinetics which was discussed by Pyun in his review.[47] Equation (12) integrates to equation (13).

$$kKt = x/(a-b)(b-c)(b-c-x) + 1/(a-b)^2 \ln\left[\frac{(a-c)(b-c-x)}{(b-c)(a-c-x)}\right] \qquad (13)$$

If equation (5) used in the calculation of the apparent third order rate constants is recalled, a comparison can be made between equations (5) and (13). In this case the apparent third order constant, k_3, is equal to kK. Note also that equation (13) contains complex concentration terms which would cause the kK combination "constant" to vary. It is instructive to determine how the "kK" (or k_3) would vary with the relative initial concentrations of alkene and bromine. Table 12 summarizes how the concentration of the complex would affect each term in equation (13) and the apparent third order rate constant. The ratio of initial bromine to initial alkene, b/a, in column one is given as greater or less than one. Regardless of the b/a ratio the complex causes term I of equation (13) to increase and term II of equation (13) to decrease. In column two the complex concentration causes term I to increase in magnitude due to a decrease in the denominator while the complex concentration causes the log term of term II to decrease.

Column three shows that term I of equation (13) would decrease and term II would increase, respectively, if the concentration of the complex was not taken into consideration. Column four shows the relative signs of terms I and II which are dependent only on the ratio b/a. Column five shows the net effect on the apparent third order rate constants. It is immediately evident that the apparent third order rate constant increases as b/a becomes greater than one and decreases as b/a becomes less than one. This variation in the apparent third order rate constant is due to the concentration of the complex.

TABLE 12

EFFECT OF RELATIVE BROMINE AND ALKENE
CONCENTRATIONS ON THE APPARENT THIRD
ORDER RATE CONSTANT, kK, FROM EQUATION (13)

Ratio b/a	Effect of Complex on		Effect of Ignoring Complex on		Sign of		Net Effect on kK
	term I	term II	term I	term II	term I	term II	
>1	inc.	dec.	dec.	inc.	-	+	inc.
<1	inc.	dec.	dec.	inc.	+	-	dec.

As noted previously the observed third order rate constants vary. This variation is not, however, random as can be seen in Figures 10 and 11. In Figures 10 and 11 the observed third order rate constants are plotted against the bromine reaction fraction for the bromination of Z-3-hexene and E-3-hexene, respectively. In both cases it is immediately apparent that the observed third order rate constant increases as the bromine fraction increases. In both cases a least squares regression line was fitted to the data. For Z-3-hexene, Figure 10, this line has a slope of -22.64 and an intercept of 58.05 when the bromine reaction fraction is one. The standard deviation of this line is 3.44. In Figure 11 the corresponding line for E-3-hexene has a slope of -43.22 and an intercept of 82.48 at a bromine reaction fraction of one. The standard deviation of this line is 6.26.

Although there is considerable experimental scatter in both Figures 10 and 11, particularly for the E-3-hexene data, none of the data exceeds the ninety-five per cent confidence limit. Regardless of the experimental scatter there is no question that the apparent third order rate constant increases with increased relative bromine concentration. This experimental observation is in accord with the predictions of equation (13) summarized in Table 12. This leads to the conclusion that the deviations of the apparent third order rate constants is due to complex formation.
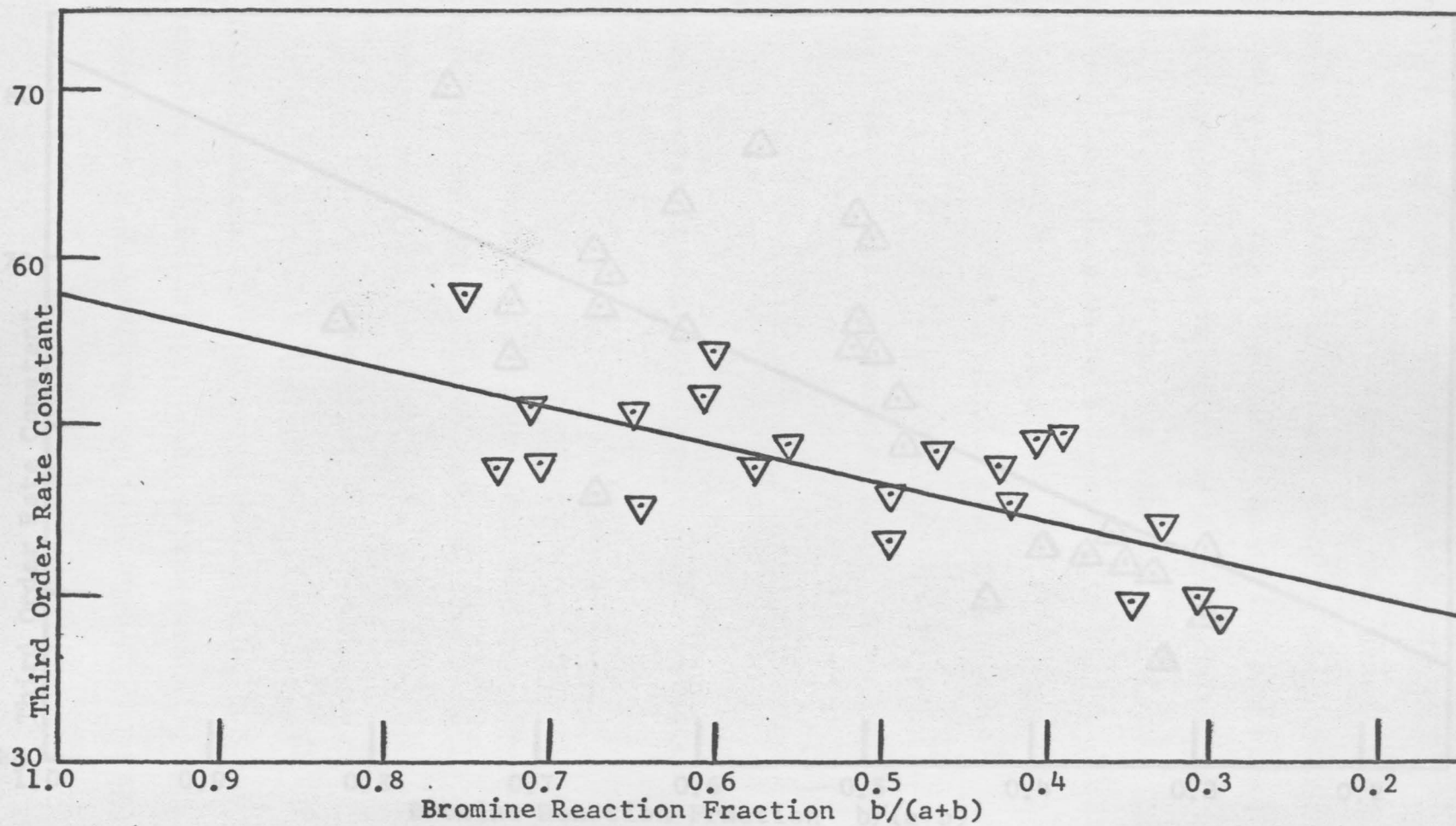
Fig. 10. Effect of the Bromine Reaction
Fraction on the Apparent Third Order Rate
Constant for the Bromination of Z-3-hexene
in Carbon Tetrachloride.
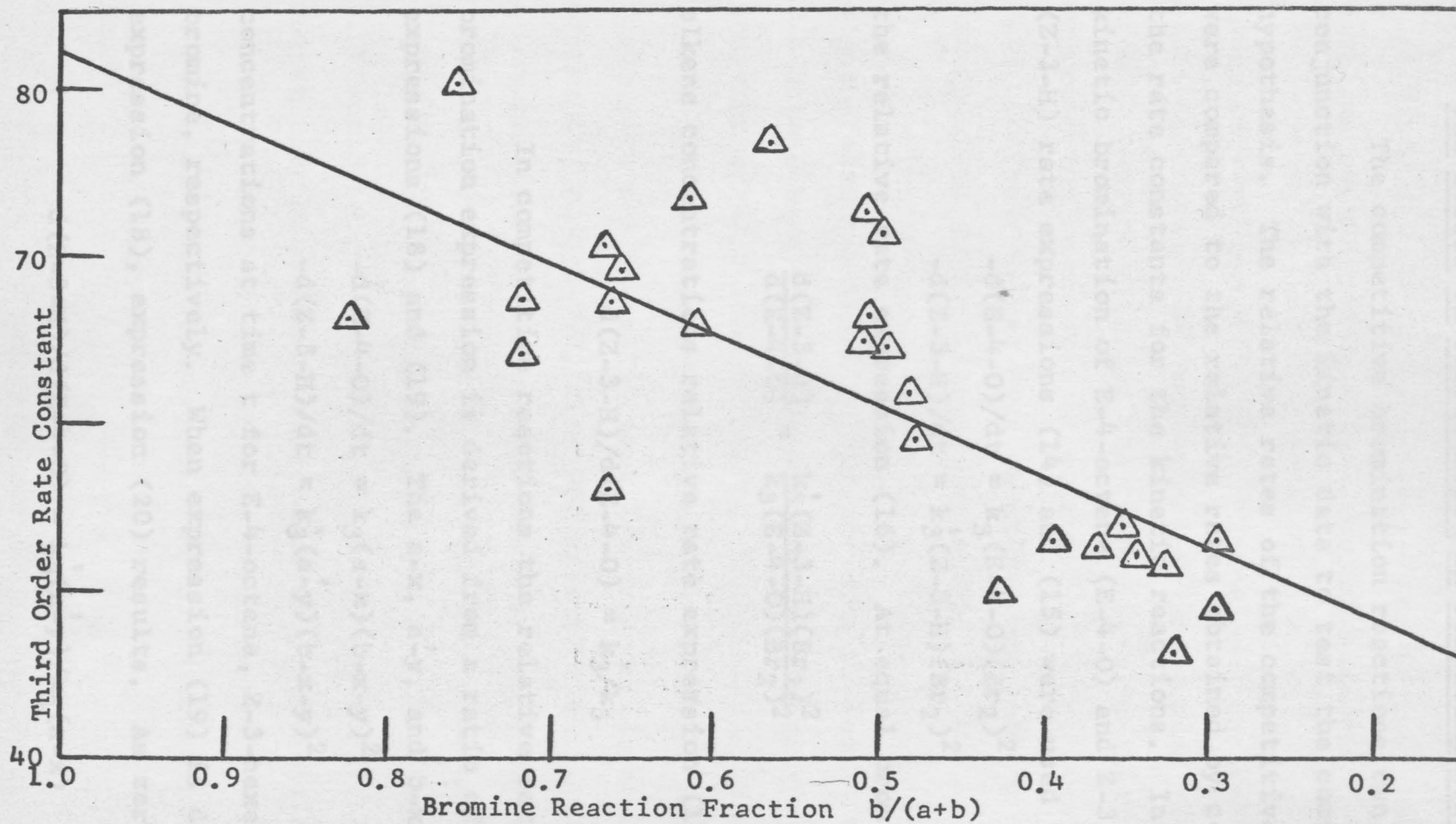
Fig. 11. Effect of the Bromine Reaction Fraction on the Apparent Third Order Rate Constant for the Bromination of E-3-hexene in Carbon Tetrachloride.

The Effect of Complexation on Competing Reactions

The competitive bromination reactions can be used in conjunction with the kinetic data to test the complexation hypothesis. The relative rates of the competitive reactions were compared to the relative rates obtained by comparing the rate constants for the kinetic reactions. In the kinetic bromination of E-4-octene (E-4-O) and Z-3-hexene (Z-3-H) rate expressions (14) and (15) were used to obtain

$$-d(E\text{-}4\text{-}O)/dt = k_3(E\text{-}4\text{-}O)(Br_2)^2 \qquad (14)$$

$$-d(Z\text{-}3\text{-}H)/dt = k_3'(Z\text{-}3\text{-}H)(Br_2)^2 \qquad (15)$$

the relative rate expression (16). At equal bromine and

$$\frac{d(Z\text{-}3\text{-}H)}{d(E\text{-}4\text{-}O)} = \frac{k_3'(Z\text{-}3\text{-}H)(Br_2)^2}{k_3(E\text{-}4\text{-}O)(Br_2)^2} \qquad (16)$$

alkene concentrations relative rate expression (17) results.

$$d(Z\text{-}3\text{-}H)/d(E\text{-}4\text{-}O) = k_3'/k_3 \qquad (17)$$

In competitive reactions the relative rates of bromination expression is derived from a ratio of expressions (18) and (19). The a-x, a'-y, and b-x-y are the

$$-d(E\text{-}4\text{-}O)/dt = k_3(a\text{-}x)(b\text{-}x\text{-}y)^2 \qquad (18)$$

$$-d(Z\text{-}3\text{-}H)/dt = k_3'(a'\text{-}y)(b\text{-}x\text{-}y)^2 \qquad (19)$$

concentrations at time t for E-4-octene, Z-3-hexene, and bromine, respectively. When expression (19) is divided by expression (18), expression (20) results. As zero initial

$$d(Z\text{-}3\text{-}H)/d(E\text{-}4\text{-}O) = k_3'(a'\text{-}y)/k_3(a\text{-}x) \qquad (20)$$

bromine concentration is approached, x and y become
negligible and when the concentrations of the alkenes are
equal we obtain the relative rate expression (21) which is

$$d(Z-3-H)/d(E-4-O) = k_3'/k_3 \qquad (21)$$

identical with equation (17). Therefore, the relative rates
of bromination of Z-3-hexene and E-4-octene at zero initial
bromine concentration in the competitive reactions should
approach the same ratio as obtained with the kinetic study
rate constants unless some other factors such as complexation
are involved in the kinetic mechanism.

Kinetic runs 1 and 2 of Z-3-hexene which have
concentrations similar to kinetic runs 23 and 24 of
E-4-octene have an average apparent third order rate
constant of 47.8 $l^2 mole^{-2} sec^{-1}$. Kinetic runs 23 and 24 have
an average third order rate constant of 34.9 $l^2 mole^{-2} sec^{-1}$.
These give a k_3'/k_3 ratio of 1.37. Figure 12 shows a plot
of the log of $d(Z-3-H)/d(E-4-O)$ against the initial bromine
concentrations of the competitive reaction studies in
Tables 8 and 9. A least squares regression line has been
fitted to the data with an intercept of 5.06. This value of
5.06 would be the relative reactivity based on the
competitive reactions. This value is substantially greater
than 1.37 obtained from kinetic measurements. This deviation
is consistent with complexation as an intermediate step in
the reaction mechanism.

Fig. 12. Relative reactivities of bromination
of Z-3-hexene compared to E-4-octene at
varying initial bromine concentrations.

In the previous section on the effect of complexation on kinetics a steady state-equilibrium approximation with a complex as an intermediate was shown to be consistent with the observed kinetics. If the same approximation is made in competitive reactions, the relative concentrations of the complex would be determined by the relative complexation constants of the alkenes with bromine. The subsequent formation of product from the complex would depend primarily on the concentration of the complex at low bromine concentrations since the alkene with the larger complexation tendency for the bromine would capture the major portion of the bromine molecules. Therefore, if Z-3-hexene has a larger alkene-bromine complexation constant than E-4-octene, the relative reactivity of Z-3-hexene compared to E-4-octene would be greater than the ratio of 1.37 derived from the kinetic rates. The ratio of iodine complexation equilibrium constants for Z-3-hexene/E-4-octene is 2.21 based on the reciprocal mole fraction data of Table 10. Muhs and Weiss have found ratios of the complexation constants of Z-3-hexene/E-3-hexene and Z-2-butene/E-2-butene with silver nitrate to be 3.9.[48] The complexation data of Muhs and Weiss and of this study are consistent with the hypothesis that the complexation is a necessary step in the reaction mechanism of the bromination of alkenes in carbon tetrachloride.

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The Effect of Complexation on Relative Reactivity Rankings

Figure 13 illustrates the relative reactivity rankings which are E-3-hexene > Z-3-hexene > E-4-hexene. In equation (13) the apparent third order rate constant, k_3, was shown to be a product of the equilibrium constant of complexation, K, and the specific rate constant of product formation from the complex, k. Considering the relative magnitudes of the apparent third order rate constants and the complexation constants, K, the relative magnitudes of k can be suggested. The relative magnitudes of the alkene-iodine and the alkene-silver salt complexation constants from this study and the literature can be used to evaluate the relative ranking of the alkene-bromine complexation constants.[22,48,49] On this basis the relative ranking of the equilibrium constants are Z-3-hexene > E-3-hexene > E-4-octene. Knowing both the relative magnitudes of K and k_3 the relative ranking of k can be deduced in which E-3-hexene > Z-3-hexene and E-4-octene. The relative ranking of Z-3-hexene and E-4-octene can not be known for certain as the absolute ratio of the equilibrium constants are not known. Both of these trends in K and k can be explained by steric hindrance considerations.

In complex formation with Z-3-hexene the bromine can attack near the side of the double bond on which the two hydrogens are bonded and thereby minimizing the steric interference of the ethyl groups. In complex formation with

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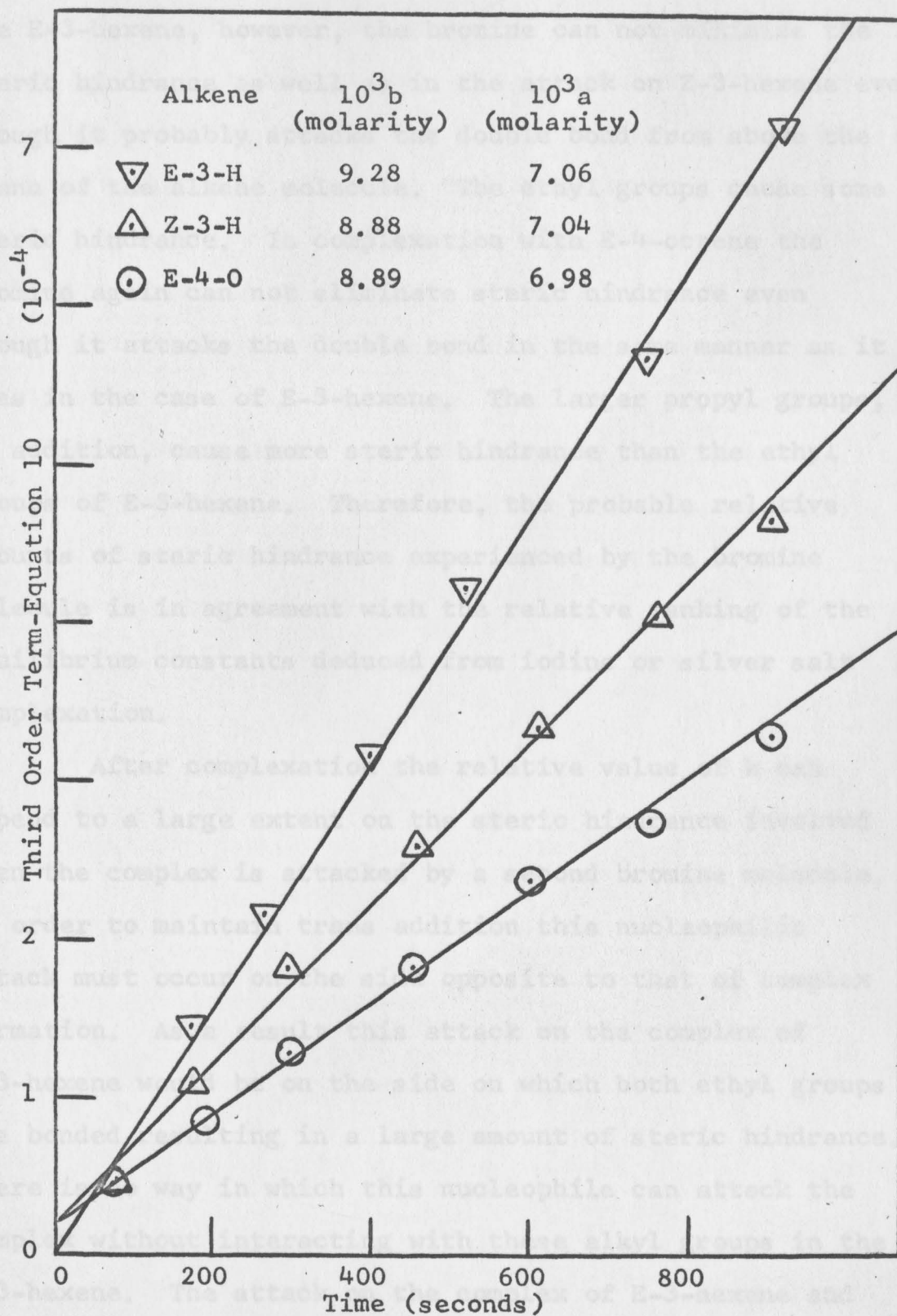
Fig. 13. Comparison of the Third Order
Reactions of E-3-Hexene, Z-3-Hexene, and
E-4-Octene.

the E-3-hexene, however, the bromine can not minimize the steric hindrance as well as in the attack on Z-3-hexene even though it probably attacks the double bond from above the plane of the alkene molecule. The ethyl groups cause some steric hindrance. In complexation with E-4-octene the bromine again can not eliminate steric hindrance even though it attacks the double bond in the same manner as it does in the case of E-3-hexene. The larger propyl groups, in addition, cause more steric hindrance than the ethyl groups of E-3-hexene. Therefore, the probable relative amounts of steric hindrance experienced by the bromine molecule is in agreement with the relative ranking of the equilibrium constants deduced from iodine or silver salt complexation.

After complexation the relative value of k can depend to a large extent on the steric hindrance involved when the complex is attacked by a second bromine molecule. In order to maintain trans addition this nucleophilic attack must occur on the side opposite to that of complex formation. As a result this attack on the complex of Z-3-hexene would be on the side on which both ethyl groups are bonded resulting in a large amount of steric hindrance. There is no way in which this nucleophile can attack the complex without interacting with these alkyl groups in the Z-3-hexene. The attack on the complex of E-3-hexene and E-4-octene would result in less steric hindrance than that

for Z-3-hexene because alkyl groups do not interfere directly. The propyl groups, being larger than the ethyl group would be expected to cause a slightly larger steric hindrance, however. These steric considerations are in accord with the relative ranking of k and are consistent with the formation of a charge transfer complex.

The observed concentration variation in the apparent third order rate, the deviations from the predicted behavior in competitive bromination studies and the relative reactivity rankings are all consistent with the hypothesis that a charge transfer complex is an essential intermediate in the bromination of alkenes.

CHAPTER IV

SUMMARY

Reproducible kinetic data for the bromination of alkenes in carbon tetrachloride was shown to be possible if carefully purified solvent was used and if impurities and light were excluded from the reaction. Third order plots for replicate runs gave a single line within experimental error. In addition, reactions which were run in the presence of a free radical inhibitor did not differ significantly from those in which the inhibitor was absent. This indicates that the reactions studied in this research did not involve a free radical mechanism.

The kinetic data for Z-3-hexene, E-3-hexene, and E-4-octene brominations in carbon tetrachloride follow third order kinetics (first order in alkene and second order in bromine). However, the apparent third order rate constants decrease as the initial fraction of bromine decreases and increases as the fraction increases. This is believed due to a larger percentage of the total bromine molecules being complexed with the alkenes as the bromine concentration decreases at constant alkene concentrations. This decrease in uncomplexed bromine would cause a deviation from simple concentration considerations since free bromine molecules are required for the nucleophilic attack on the

charge transfer complex. Thus, the decrease in the apparent third order rate constant is consistent with predictions based on a charge transfer complex. In addition, an equation was derived using the steady state-equilibrium approximation for the reaction sequence involving the complex. This equation predicts the observed variation of the apparent rate constant with bromine (or alkene) concentration.

For the competitive bromination reactions in carbon tetrachloride the relative reactivity of Z-3-hexene to E-4-octene, at zero bromine concentration, is much larger than the relative reactivity determined from the individual kinetic runs. In the competitive reactions the bromine molecules would tend to form the more stable charge transfer complex, which would be the more favorable thermodynamic step, regardless of the apparent reactivity on a kinetic basis. If Z-3-hexene has a greater complexation tendency than E-4-octene, the apparent reactivity compared to E-4-octene in the competitive brominations would increase beyond that predicted by the kinetic data. Alkene-iodine complexation of the same two alkenes in carbon tetrachloride support these conclusions since the Z-3-hexene complexes more.

A relative reactivity ranking of E-3-hexene, Z-3-hexene, and E-4-octene (fastest to slowest) was observed in this study. The smaller reactivity of E-4-octene can be attributed to greater steric hindrance by the larger alkyl

groups during complexation and during the nucleophilic attack on the charge transfer complex compared to that in E-3-hexene and Z-3-hexene brominations. The steric hindrance by adjacent alkyl groups in the nucleophilic attack on the Z-3-hexene-bromine complex is suggested to cause a larger amount of steric hindrance in the bromination of the Z-3-hexene than in the bromination of E-3-hexene even though the Z-3-hexene complexes to the greater extent because of a lack of steric hindrance, in the alkene.

APPENDIX

Experimental Data for Individual Kinetic Runs

(Tables 13-30 are included and are described
in the List of Tables on pages ix and x.)

TABLE 13

KINETIC STUDIES OF THE BROMINATION OF Z-3-HEXENE
AT 8.9×10^{-3} M BROMINE AND HIGH ALKENE CONCENTRATIONS

Kinetic Run 1 $(23.0-23.2^{\circ}C)$ $a = 0.00907$ M			Kinetic Run 2 $(23.1-23.3^{\circ}C)$ $a = 0.00704$ M			Kinetic Run 3[j] $(22.8-23.0^{\circ}C)$ $a = 0.00704$ M		
t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3
0	8.88	----	0	8.88	----	0	8.93	----
70	6.90	58.2	75	7.01	67.0	55	7.38	69.0
190	5.06	67.5	170	5.93	63.1	180	5.59	75.0
305	4.53	57.2	295	5.12	61.1	305	4.83	72.4
450	4.00	53.5	455	4.57	57.0	450	4.32	69.4
595	3.59	52.5	605	4.20	55.5	605	3.91	69.8
740	3.31	50.9	755	3.94	53.5	755	3.68	67.3
900	3.13	47.5	900	3.76	51.6	895	3.49	66.3
1200	2.78	46.3	1200	3.49	48.6	1190	3.20	65.3

[j]Approximately 2.7×10^{-3} M free radical inhibitor present.

TABLE 14

KINETIC STUDIES OF THE BROMINATION OF Z-3-HEXENE
AT 8.9 X 10⁻³ M BROMINE AND LOW ALKENE CONCENTRATIONS

Kinetic Run 4 (22.1°C) a = 0.00485 M			Kinetic Run 5 (22.1°C) a = 0.00297 M			Kinetic Run 6 (22.4-22.5°C) a = 0.00315 M		
t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3
0	8.91	----	0	9.00	----	0	8.70	----
60	7.44	91.7	90	7.84	78.5	65	7.54	108.6
180	6.63	61.4	180	7.35	69.7	285	6.75	60.0
300	6.05	58.0	300	6.96	64.9	500	6.41	49.6
445	5.70	52.1	445	6.72	58.3	700	6.27	42.0
600	5.42	48.8	595	6.59	51.7	920	6.18	35.4
740	5.26	45.4	745	6.49	47.0	1220	6.13	28.4
905	5.15	41.1	890	6.46	41.4			
1140	5.00	37.7	1140	6.41	34.8			

TABLE 15

KINETIC STUDIES OF THE BROMINATION OF Z-3-HEXENE
AT 6.8 X 10^{-3} M BROMINE AND HIGH ALKENE CONCENTRATIONS

Kinetic Run 7 (20.8-23.0°C) a = 0.00998 M			Kinetic Run 8 (23.0°C) a = 0.00911 M			Kinetic Run 9 (21.0-23.0°C) a = 0.00695 M			Kinetic Run 10 (24.6-25.3°C) a = 0.00514 M		
t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3
0	6.81	----	0	6.81	----	0	6.81	----	0	7.03	----
65	5.50	57.9	70	5.58	54.8	70	5.91	49.7	175	5.42	57.3
195	4.17	57.0	200	4.32	55.7	190	4.92	50.7	290	4.92	54.4
300	3.54	57.3	305	3.76	54.2	315	4.38	47.4	445	4.45	52.6
460	2.99	54.9	460	3.22	52.8	455	3.94	45.6	590	4.14	51.7
620	2.64	52.7	605	2.89	50.9	625	3.52	46.0	740	3.90	50.5
750	2.44	50.7	760	2.63	49.7	745	3.32	44.9	925	3.68	49.2
910	2.21	50.3	905	2.42	49.3	890	3.11	44.3	1220	3.41	47.9
1205	1.91	49.2	1200	2.14	47.1	1150	2.84	42.9			

TABLE 16

KINETIC STUDIES OF THE BROMINATION OF Z-3-HEXENE
AT 4.5×10^{-3} M BROMINE AND HIGH ALKENE CONCENTRATIONS

Kinetic Run 11 (22.0-23.3°C) a = 0.01000 M			Kinetic Run 12 (23.3-23.5°C) a = 0.00908 M			Kinetic Run 13 (21.0°C) a = 0.00694 M			Kinetic Run 14 (20.9-21.0°C) a = 0.00514 M		
t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3
0	4.48	----	0	4.52	----	0	4.45	----	0	4.50	----
65	3.58	90.9	65	3.92	55.9	70	3.91	66.7	65	4.03	81.3
190	3.31	44.6	190	3.29	50.3	160	3.51	58.9	155	3.80	55.2
305	2.90	43.7	300	2.93	48.0	310	3.02	56.5	255	3.47	56.9
455	2.54	42.7	450	2.53	48.5	480	2.69	52.4	475	3.04	52.8
605	2.29	40.8	600	2.27	47.0	590	2.52	50.7	605	2.86	51.0
750	2.04	42.1	750	2.06	46.6	755	2.28	51.1	750	2.67	50.9
900	1.91	40.3	900	1.92	44.6	900	2.13	50.0	895	2.54	49.1
1205	1.64	40.0	1200	1.67	44.0				1195	2.28	49.3

TABLE 17

KINETIC STUDIES OF THE BROMINATION OF Z-3-HEXENE
AT 4.6×10^{-3} M BROMINE AND LOW ALKENE CONCENTRATIONS

Kinetic Run 15
(22.9-23.0°C)
a = 0.00304 M

Kinetic Run 16
(18.0-19.0°C
a = 0.00304 M

Kinetic Run 17
(22.7-22.9°C)
a = 0.00189 M

Kinetic Run 18
(22.7-22.9°C)
a = 0.00191 M

t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3
0	4.69	----	0	4.57	----	0	4.69	----	0	4.57	----
95	4.42	46.4	90	4.41	30.8	85	4.54	45.4	90	4.53	12.4
205	4.11	53.4	210	4.14	38.2	190	4.39	45.0	275	4.24	35.7
290	3.92	54.8	370	3.77	48.5	290	4.22	50.7	460	3.94	48.4
475	3.65	52.6	560	3.49	50.3	455	4.02	51.4	665	3.75	50.2
600	3.46	54.4	745	3.29	50.1	595	3.90	51.1	830	3.63	50.2
755	3.36	49.9	905	3.12	52.1	750	3.75	53.0	1020	3.55	48.0
900	3.20	52.3	1260	2.86	53.5	905	3.67	51.2	1200	3.47	47.0
1240	2.96	51.9				1200	3.54	49.5			

TABLE 18

KINETIC STUDIES OF THE BROMINATION OF Z-3-HEXENE
AT 3.7 X 10^{-3} M BROMINE AND VARIOUS ALKENE CONCENTRATIONS

Kinetic Run 19 (23.0°C) a = 0.00869 M			Kinetic Run 20 (23.0°C) a = 0.00685 M			Kinetic Run 21 (21.4-23.0°C a = 0.00500 M			Kinetic Run 22 (21.0-21.4°C) a = 0.00203 M		
t	10^3(b-x)	k_3	t	10^3(b-x)	k_3	t	10^3(b-x)	k_3	t	10^3(b-x)	k_3
0	3.65	----	0	3.65	----	0	3.66	----	0	3.69	----
75	3.26	51.7	75	3.05	110.0	75	3.46	43.5	75	3.56	67.2
205	2.82	47.6	165	3.05	50.5	195	3.20	42.8	150	3.49	54.6
305	2.58	46.2	300	2.78	45.0	295	3.00	44.2	310	3.28	59.8
455	2.30	44.7	465	2.50	43.7	450	2.81	40.8	460	3.16	56.6
595	2.13	42.4	600	2.30	44.5	605	2.56	44.5	610	3.07	52.8
750	1.97	40.9	750	2.16	42.6	760	2.38	45.3	895	2.99	43.3
900	1.86	38.7	900	2.03	41.8	905	2.25	45.7	1135	2.84	47.0
1205	1.61	39.3	1205	1.85	39.0	1210	2.05	44.5			

TABLE 19

KINETIC STUDIES OF THE BROMINATION OF E-4-OCTENE AT 8.9×10^{-3} M BROMINE AND HIGH ALKENE CONCENTRATIONS

Kinetic Run 23
(23.3-24.1°C)
a = 0.00988 M

Kinetic Run 24
(23.3-23.4°C)
a = 0.00698 M

Kinetic Run 25[j]
(23.0°C)
a = 0.00701 M

t	$10^3(b-x)$	k_3
0	8.89	----
65	7.14	47.6
185	5.63	44.6
305	4.83	42.6
485	4.15	39.7
600	3.81	39.3
755	3.53	37.0
900	3.27	36.9
1190	2.92	35.3

t	$10^3(b-x)$	k_3
0	8.89	----
75	7.16	60.1
190	6.29	44.9
295	5.68	43.2
450	5.12	40.6
600	4.73	39.6
750	4.50	36.8
900	4.25	36.7
1245	3.87	35.3

t	$10^3(b-x)$	k_3
0	8.93	----
55	7.77	47.6
185	6.16	51.0
305	5.44	49.2
455	4.84	48.7
625	4.42	47.0
775	4.13	46.7
895	3.93	46.8
1200	3.64	44.2

[j]Approximately 2.7×10^{-3} M free radical inhibitor present.

TABLE 20

KINETIC STUDIES OF THE BROMINATION OF E-3-HEXENE
AT 9.5×10^{-3} M BROMINE AND LOW ALKENE CONCENTRATIONS

Kinetic Run 26
(21.0-21.3°C)
a = 0.00483 M

Kinetic Run 27
(21.9-22.4°C)
a = 0.00472 M

Kinetic Run 28
(20.0-20.5°C)
a = 0.00466 M

t	$10^3(b-x)$	k_3
0	9.59	----
65	7.52	122
180	6.78	78.6
290	6.28	71.4
390	5.92	72.0
520	5.75	63.2
725	5.51	57.4
1015	5.37	48.0
1235	5.39	38.3

t	$10^3(b-x)$	k_3
0	9.43	----
45	8.31	77.3
220	6.74	63.2
305	6.00	82.7
420	5.72	77.1
605	5.37	76.5
750	5.27	69.4
905	5.12	70.3

t	$10^3(b-x)$	k_3
0	9.40	----
60	7.97	82.8
185	6.64	81.8
315	6.00	81.1
465	5.74	69.6
595	5.55	65.5
745	5.37	63.7
905	5.33	54.9
1250	5.21	46.2

TABLE 21

KINETIC STUDIES OF THE BROMINATION OF E-3-HEXENE
AT 9.2×10^{-3} M BROMINE AND HIGH ALKENE CONCENTRATIONS

Kinetic Run 29 (24.0°C) a = 0.00931 M

Kinetic Run 30 (23.0-23.5°C) a = 0.00908 M

Kinetic Run 31 (23.0-23.5°C) a = 0.00706 M

t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3
0	9.24	----	0	9.28	----	0	9.28	----
65	6.81	76.4	65	7.05	67.0	65	7.20	76.6
165	5.14	79.4	255	5.44	44.8	175	5.65	83.3
310	3.94	85.1	355	4.01	74.2	265	5.03	81.9
450	3.36	85.5	455	3.71	70.6	400	4.47	79.0
600	2.88	90.8	605	3.30	69.2	520	4.07	81.2
755	2.55	94.1	755	2.94	72.6	750	3.71	75.6
920	2.26	100.1	895	2.82	67.3	920	3.46	77.4
1205	1.88	112.6	1205	2.53	63.8	1200	3.20	77.4

TABLE 22

KINETIC STUDIES OF THE BROMINATION OF E-3-HEXENE
AT 9.2×10^{-3} M BROMINE AND LOW ALKENE CONCENTRATIONS

Kinetic Run 32 (22.9-23.0°C) a = 0.00485 M			Kinetic Run 33 (22.0-22.9°C) a = 0.00295 M		
t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3
0	9.23	----	0	9.23	----
75	7.77	67.2	60	8.45	65.8
180	6.63	72.7	170	7.46	81.3
300	6.00	71.4	275	7.04	80.3
410	5.67	68.4	490	6.63	79.4
600	5.39	60.2	595	6.58	71.8
780	5.20	55.8	890	6.44	65.2
1030	5.09	47.6	1250	6.38	54.7
1200	4.99	45.9			

TABLE 23

KINETIC STUDIES OF THE BROMINATION OF E-3-HEXENE
AT 9.1×10^{-3} M BROMINE AND VARIOUS ALKENE CONCENTRATIONS

Kinetic Run 34 (24.6-25.0°C) a = 0.00999 M			Kinetic Run 35 (20.0-20.1°C) a = 0.00461 M			Kinetic Run 36 (24.7-25.0°C) a = 0.00197 M		
t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3
0	9.11	----	0	9.05	----	0	9.11	----
55	7.11	63.3	65	7.47	96.8	70	8.46	74.5
135	5.59	65.3	155	6.73	76.6	170	7.99	68.7
240	4.53	66.4	273	6.09	73.0	325	7.59	68.5
365	3.84	65.4	435	5.63	67.6	520	7.52	48.8
475	3.44	64.1	595	5.38	62.9	750	7.49	35.7
605	3.06	64.7	705	5.28	58.0	1200	7.46	23.6
725	2.86	62.4	890	5.14	53.7			
905	2.64	59.0	1230	4.98	47.1			
1220	2.27	59.0						

TABLE 24

KINETIC STUDIES OF THE BROMINATION OF E-3-HEXENE
AT VARIOUS BROMINE AND ALKENE CONCENTRATIONS

Kinetic Run 37
(24.8-25.0°C)
a = 0.00423 M

Kinetic Run 38
(23.8-24.0°C)
a = 0.00793 M

Kinetic Run 39
(24.8-24.9°C)
a = 0.00422 M

t	10^3(b-x)	k_3	t	10^3(b-x)	k_3	t	10^3(b-x)	k_3
0	8.72	----	0	7.89	----	0	6.83	----
60	7.82	58.8	65	6.13	81.8	65	6.23	55.5
180	6.52	74.5	170	4.85	78.0	175	5.47	60.1
275	6.00	76.1	300	4.03	76.0	285	5.06	56.7
410	5.63	71.3	455	3.47	73.7	405	4.73	55.1
610	5.28	68.4	620	3.11	70.5	545	4.39	56.5
750	5.13	66.1	750	2.85	71.4	700	4.22	51.8
900	5.03	62.6	905	2.60	72.9	885	4.04	48.8
1200	4.83	62.4	1200	2.30	72.1	1160	3.82	46.6

TABLE 25

KINETIC STUDIES OF THE BROMINATION OF E-3-HEXENE AT 4.8×10^{-3} M BROMINE AND VARIOUS ALKENE CONCENTRATIONS

Kinetic Run 40
(24.2-24.6°C)
a = 0.01010 M

t	$10^3(b-x)$	k_3
0	4.88	----
95	3.86	59.7
205	3.22	56.7
340	2.67	57.1
460	2.33	57.6
665	2.02	53.5
915	1.68	54.2
1210	1.48	50.7

Kinetic Run 41
(22.2-22.5°C)
a = 0.00901 M

t	$10^3(b-x)$	k_3
0	4.70	----
60	4.28	39.7
165	3.39	60.6
305	2.79	60.6
445	2.40	60.4
600	2.14	58.0
920	1.81	52.7
1200	1.57	52.0

Kinetic Run 42
(21.1-22.3°C)
a = 0.00710 M

t	$10^3(b-x)$	k_3
0	4.70	----
70	4.09	66.3
190	3.54	57.2
285	3.15	59.2
420	2.79	58.3
605	2.44	57.4
935	2.08	53.4
1195	1.85	53.4

Kinetic Run 43
(24.6°C)
a = 0.00474 M

t	$10^3(b-x)$	k_3
0	4.88	----
70	4.53	50.2
170	4.03	59.4
300	3.56	64.1

TABLE 26

KINETIC STUDIES OF THE BROMINATION OF E-3-HEXENE
AT 4.8 X 10^{-3} M BROMINE AND LOW ALKENE CONCENTRATIONS

Kinetic Run 44
(22.2-22.8°C)
a = 0.00466 M

t	10^3(b-x)	k_3
0	4.81	----
110	4.30	46.5
205	3.77	65.2
340	3.37	66.6
445	3.10	68.9
660	2.76	67.8
815	2.57	67.6
975	2.34	73.4
1190	2.19	71.5

Kinetic Run 45
(23.0-23.5°C)
a = 0.00306 M

t	10^3(b-x)	k_3
0	4.86	----
60	4.51	80.2
175	4.10	76.5
330	3.78	69.7
475	3.50	71.8
605	3.30	73.6
900	3.01	73.3
1205	2.78	74.2

Kinetic Run 46[j]
(21.0°C)
a = 0.00483 M

t	10^3(b-x)	k_3
0	4.76	----
70	4.32	72.7
190	3.74	73.9
350	3.27	71.6
455	3.04	71.2
625	2.77	69.5
765	2.64	65.4
995	2.38	66.9
1215	2.24	64.2

[j]May be contaminated
with stopcock grease.

TABLE 27

KINETIC STUDIES OF THE BROMINATION OF E-3-HEXENE
AT 4.9×10^{-3} M BROMINE AND LOW ALKENE CONCENTRATIONS

Kinetic Run 47
(21.5-21.7°C)
a = 0.00315 M

Kinetic Run 48
(21.2-21.5°C)
a = 0.00196 M

Kinetic Run 49
(23.2-23.3°C)
a = 0.00191 M

t	10^3(b-x)	k_3
0	4.89	----
85	4.63	44.2
195	4.21	61.4
305	3.87	68.7
450	3.62	66.2
605	3.41	65.0
910	3.10	64.6
1200	2.88	65.7

t	10^3(b-x)	k_3
0	4.93	----
70	4.75	60.6
185	4.45	69.8
305	4.24	68.8
460	4.04	67.9
605	3.85	71.9
945	3.66	64.2
1195	3.54	63.8

t	10^3(b-x)	k_3
0	4.86	----
65	4.70	60.4
180	4.37	78.7
330	4.17	67.5
480	3.97	69.4
610	3.85	68.3
940	3.61	67.4
1215	3.53	61.3

TABLE 28

KINETIC STUDIES OF THE BROMINATION OF E-3-HEXENE
AT LOW BROMINE AND VARIOUS ALKENE CONCENTRATIONS

Kinetic Run 50
(20.1-20.3°C)
a = 0.00461 M

t	10^3(b-x)	k_3
0	4.31	----
60	4.27	7.1
190	3.67	50.2
310	3.26	59.7
430	3.06	56.4
550	2.82	59.9
755	2.55	60.8
900	2.39	61.3
1220	2.21	55.6

Kinetic Run 51
(21.9-22.0°C)
a = 0.00870 M

t	10^3(b-x)	k_3
0	3.68	----
45	3.47	51.3
155	3.02	49.0
295	2.59	49.5
430	2.31	48.7
560	2.04	51.2
750	1.84	48.7
900	1.69	48.5
1200	1.45	49.0

Kinetic Run 52[j]
(20.4-21.0°C)
a = 0.00870 M

t	10^3(b-x)	k_3
0	3.68	----
65	3.32	53.7
160	2.99	47.3
290	2.53	53.3
390	2.29	53.5
525	2.07	51.9
650	1.89	52.3
985	1.52	54.3
1190	1.39	52.7

[j]Approximately
1.1 X 10^{-3} free
radical inhibitor
present

TABLE 29

KINETIC STUDIES OF THE BROMINATION OF E-3-HEXENE
AT 3.7×10^{-3} M BROMINE AND VARIOUS ALKENE CONCENTRATIONS

Kinetic Run 53 (22.5-23.4°C) a = 0.00687 M			Kinetic Run 54 (26.1-26.2°C) a = 0.00500 M			Kinetic Run 55 (28.0°C) a = 0.00198 M		
t	10^3(b-x)	k_3	t	10^3(b-x)	k_3	t	10^3(b-x)	k_3
0	3.73	----	0	3.73	----	0	3.73	----
34	3.56	40.7	45	3.61	40.6	150	3.49	11.9
150	3.05	61.9	145	3.26	55.6	245	3.37	31.6
290	2.67	58.5	255	2.99	57.0	360	3.23	41.5
400	2.47	56.0	380	2.77	54.6	470	3.08	52.0
510	2.25	57.6	475	2.65	52.8	735	2.87	56.1
600	2.13	56.9	600	2.53	49.6	945	2.79	51.7
750	1.99	54.0	690	2.37	53.6	1240	2.70	48.2
900	1.81	56.0	870	2.20	52.8	1420	2.73	48.2
1195	1.63	53.0	1205	2.01	48.7	1800	2.53	46.5
						2410	2.34	49.6

TABLE 30

KINETIC STUDIES OF THE BROMINATION OF E-3-HEXENE
AT LOW BROMINE AND LOW ALKENE CONCENTRATIONS

Kinetic Run 56
(21.0-21.1°C)
a = 0.00434 M

Kinetic Run 57
(20.0-20.5°C)
a = 0.00428 M

t	$10^3(b-x)$	k_3	t	$10^3(b-x)$	k_3
0	2.55	----	0	2.04	----
80	2.35	98	210	1.93	30.6
185	2.31	53.0	400	1.80	39.0
310	2.14	59.4	605	1.67	44.6
545	1.97	52.5	810	1.55	47.1
775	1.81	52.6	1005	1.48	42.0
1000	1.67	54.0	1220	1.43	43.3
1200	1.60	51.2	1500	1.31	47.1
1420	1.50	52.2	2100	1.17	46.7
1680	1.41	52.1	2700	1.07	44.5
2110	1.27	53.5			

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