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Kinetic Evidence for Complex Formation in Alkene Bromination[1]

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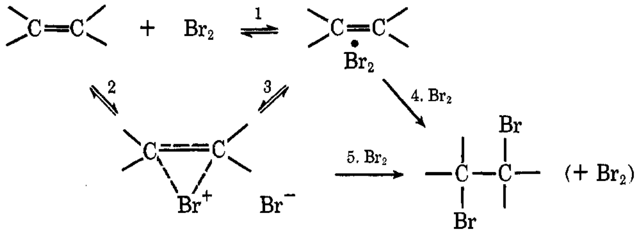
Kinetic and competitive bromination studies on simple alkenes in carbon tetrachloride support the hypothesis that complexation is an essential step in alkene bromination. The kinetic data were reproducible and showed that the reaction was first order in alkene and second order in bromine. These reaction rates were not retarded by a free-radical inhibitor. The observed reactivity order was (fastest to slowest) (*E*)-3-hexene:(*Z*)-3-hexene:(*E*)-4-octene. While the individual reaction rates were reproducible, the apparent third-order rate constants varied systematically with the alkene–bromine composition and were higher at higher bromine fractions. These results are consistent with predictions based on a kinetic model involving the formation of a bromine–alkene complex as the first step. Subsequent steps could involve the direct attack of a second bromine molecule on this complex or the formation of bromonium ions. Under competitive conditions, the relative reactivity of (*Z*)-3-hexene compared to (*E*)-4-octene was much greater than predicted from the kinetic studies. This enhanced reactivity is consistent with complex formation assuming that the (*Z*)-3-hexene complexes form more readily than the (*E*)-4-octene. This assumption is in agreement with the observed iodine–alkene complexation data.

The mechanism of alkene bromination has long been postulated to proceed *via* a bromonium ion intermediate.[2] This mechanism does account for the stereochemistry of addition[3] and the relative reactivity of various alkenes with bromine.[4,5] In addition, halonium ions have been observed experimentally in highly polar media.[6] Mechanisms involving charge-transfer complexes between the bromine and the alkene have also been advanced and these can account for much of the known experimental data.[7-13] However, there is little direct experimental data to support the hypothesis that the bromine–alkene complex plays an essential role in these mechanisms. While some evidence for the formation of such complexes has been claimed by spectroscopic[9,10] and flow techniques,[11] the complex need not lead directly to product, as outlined in Scheme I. Only routes 1–4 and 1–3–5 directly involve the complex in the reaction. Route 2–5 would circumvent this complex and in route 1–2–5 the complex is not an essential step in the reaction.

SCHEME I

GENERALIZED SUMMARY OF ALKENE BROMINATION REACTION MECHANISMS FOR SECOND- OR THIRD-ORDER REACTIONS



This investigation was conducted to see whether any kinetic evidence could be found that would support or reject a hypothesis that charge-transfer complexation is an essential step in alkene bromination. These kinetic studies were run in a nonpolar solvent, CCl_4, in order to minimize complex formation between bromine and the solvent, to restrict the complexation to the alkene and bromine, and to avoid mixed products due to solvent attack. Competitive bromination of pairs of alkenes were also studied in CCl_4 for direct comparison against these kinetic results.

Experimental Section

Materials.—Cyclohexene, (*E*)-3-hexene, (*Z*)-3-hexene, and (*E*)-4-octene were purchased from Chemical Samples Co.

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[1] Presented in part at the Third Northeast Regional Meeting of the American Chemical Society, Buffalo, N. Y., Oct 11, 1971. Based, in part, on the Master's Thesis of G. D. F., Youngstown State University, June 1971.

[2] P. B. D. de la Mare and R. Boulton, "Electrophilic Addition to Unsaturated Systems," Elsevier, New York, N. Y., 1966.

[3] R. C. Fahey in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience, New York, N. Y., 1968, p 237.

[4] J. E. Dubois, F. Garnier, and H. Viellard, *Tetrahedron Lett.*, 1227 (1965), and references cited therein.

[5] S. V. Anantakrishnan and C. K. Ingold, *J. Chem. Soc.*, 984, 1396 (1935).

[6] J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Amer. Chem. Soc.*, **92**, 4025 (1970), and references cited therein.

[7] D. V. Banthorpe, *Chem. Rev.*, **70**, 295 (1970).

[8] F. C. Fahey and H. J. Schneider, *J. Amer. Chem. Soc.*, **90**, 4429 (1968).

[9] R. E. Buckles and J. P. Yuk, *ibid.*, **75**, 5048 (1953).

[10] J. E. Dubois and F. Garnier, *Tetrahedron Lett.*, 3961 (1965); 3047 (1966); *Spectrochim. Acta, Part A*, **23**, 2279 (1967).

[11] G. Heublein and R. Rauscher, *Tetrahedron*, **25**, 3999 (1969).

[12] G. Heublein, *Z. Chem.*, **9**, 281 (1969).

[13] R. E. Buckles, J. L. Miller, and R. J. Thurmaier, *J. Org. Chem.*, **32**, 888 (1967), and references cited therein.

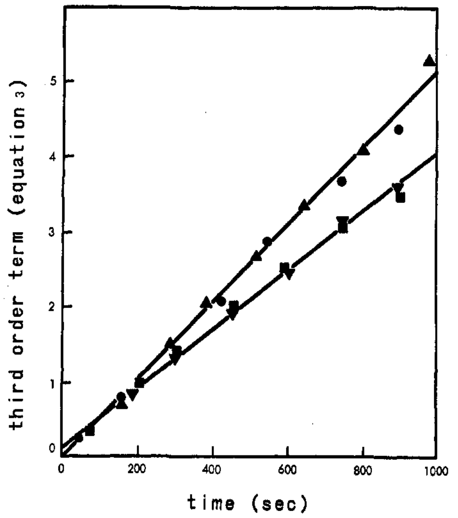

Figure 1.—Third-order plots for the bromination of (*Z*)-3-hexene (kinetic runs 9, ■, and 17, ▼) and of (*E*)-3-hexene (kinetic run 41; ●, uninhibited, and run 42, ▲, inhibited) in carbon tetrachloride.

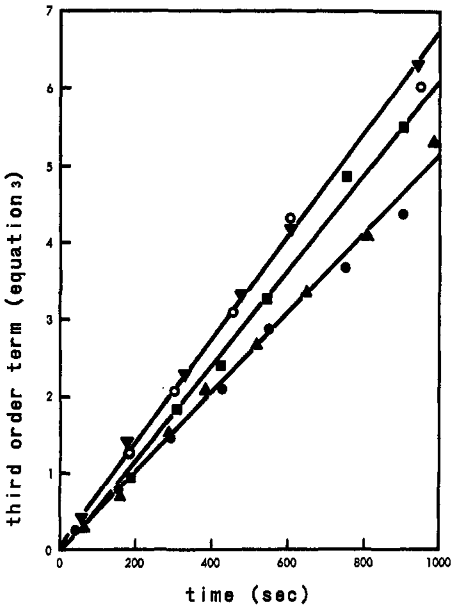

Figure 2.—Effect of the reaction concentration on the apparent third-order rate constants in the bromination of (*E*)-3-hexene in carbon tetrachloride: kinetic runs 38, ○; 39, ▼; 39, 40, ■; 41, ●; 42, ▲.

Since the purity of these alkenes was found to be at least 99% on several columns by glpc and the structures were confirmed by nmr and mass spectroscopy, they were used without further purification. Carbon tetrachloride was purified by a standard procedure[14] and distilled immediately prior to use. The purity was confirmed by glpc and uv. The purity of the 1-bromopentane (MC & B) was also shown to exceed 99% by glpc. The bromine and the iodine used were of the highest analytical reagent grade and were used without further purification.

Glassware.—Initially, all the glassware, including the quartz cells, used in the kinetic and competitive reaction studies were washed thoroughly, rinsed repeatedly with distilled water, dried, rinsed with purified CCl_4, and dried again. After each reaction, the glassware was cleaned by washing in purified CCl_4, drying, and storing in a desiccator. This procedure is essential in order to obtain reproducible kinetic data.

Kinetic Run Procedure.—The reaction rates for the alkene brominations were followed spectrophotometrically with a Cary 14 by determining the absorbance of the bromine solution at 415 mμ (ϵ_{max} 205.9 l./mol-cm) in 1-cm quartz cells. The diluted bromine and alkene solutions, in CCl_4, were allowed to equilibrate thermally in a darkened, controlled-temperature room and were then mixed in a reaction flask that was covered with aluminum foil to exclude light. Aliquots were removed periodically and the bromine absorbance was determined. The first reaction measurement was made within 2 min of mixing; then the reaction was followed for up to 20 min. Fresh aliquots were used for each absorbance determination in order to minimize possible light catalysis. The temperature was recorded during the reaction and had an average standard deviation of 0.14°. The concentrations and apparent third-order rate constants for these kinetic runs are summarized in Tables I [(*Z*)-3-hexene], II [(*E*)-3-hexene], and III [(*E*)-4-octene]. The reported rate constants were computed by the least squares method and the average per cent variance (100 standard deviation/*k*) was 2.17 for these experiments. Examples of individual kinetic runs are shown in Figures 1 and 2 and illustrate the reproducibility of the data.

TABLE I

SUMMARY OF REACTION CONCENTRATIONS AND APPARENT THIRD-ORDER RATE CONSTANTS FOR THE BROMINATION OF (*Z*)-3-HEXENE AT 22.5°

Kinetic run	10^3 $(Br_2)_0$	10^3 $(Alkene)_0$	*k*, $l.^2/mol^2$-sec
1	8.88	9.07	45.7
2	8.88	7.04	48.8
3[a]	8.93	7.04	65.2
4	8.91	4.85	50.8
5	8.70	3.15	47.3
6	6.81	9.98	49.0
7	6.81	9.11	47.3
8	6.81	6.95	43.1
9	4.48	10.00	39.7
10	4.52	9.08	43.9
11	4.45	6.94	49.4
12	4.50	5.14	48.6
13	4.69	3.04	51.8
14	4.57	3.04	54.2
15	4.69	1.89	50.9
16	4.57	1.91	47.6
17	3.65	8.69	38.4
18	3.65	6.85	39.2
19	3.66	5.00	45.1
20	3.69	2.03	44.9

[a] Contains 2.7×10^{-3} *M* 2,6-di-*tert*-butyl-4-methylphenol.

In three experiments, noted in Tables I, II, and III, a substantial quantity of 2,6-di-*tert*-butyl-4-methylphenol was added to the reaction system to test whether a free radical reaction occurred along with (or instead of) the electrophilic addition of bromine. One of these reactions is also shown in Figure 1.

Recently, Pincock and Yates[15] showed that kinetic results for alkene bromination in acetic acid can be erroneous due to tribromide formation if this ion absorbs at the wavelength used for the monitoring. Although tribromide ion formation would not be expected in our solvent, we tested for the presence of an interfering species by making absorbance measurements at both 415 and 480 mμ (ε 123 l./mol-cm) for kinetic run 5, Table I. The same reaction rate was observed, indicating the absence of tribromide or any other interfering species.

Competitive Reactions.—The relative reactivity ratio of (*Z*)-3-hexene to (*E*)-4-octene was determined by the competitive reaction technique in CCl_4 at 25.0°. These reactions were run in flasks wrapped in aluminum foil to exclude light and the thermally equilibrated solutions were mixed in a darkened room to reduce the possiblility of a free radical reaction. All reaction solutions were 0.1 *M* in (*Z*)-3-hexene, (*E*)-4-octene, and 1-bromopentane (internal standard for glpc) and contained varying concentrations of bromine. The unreacted alkene concentrations were determined after 24 hr by glpc using a 5 ft × 0.125 in., 8% dinonyl phthalate on Anakrom ABS 90/100 mesh column at 70°

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[14] J. A. Riddick and E. E. Toops, Jr., "Organic Solvents, Physical Properties and Methods of Purification," Interscience, New York, N. Y., 1955, pp 413–414.

[15] J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 2944 (1970).

TABLE II

SUMMARY OF REACTION CONCENTRATIONS AND APPARENT THIRD-ORDER RATE CONSTANTS FOR THE BROMINATION OF (*E*)-3-HEXENE AT 22.5°

Kinetic run	10^3 $(Br_2)_0$	10^3 $(Alkene)_0$	*k*, l.²/mol²-sec
21	9.43	4.72	70.8
22	9.40	4.66	63.0
23	9.28	9.08	66.6
24	9.23	4.85	69.3
25	9.23	2.95	80.3
26	9.11	9.99	59.0
27	9.05	4.61	66.4
28	9.11	1.97	67.4
29	8.72	4.23	62.1
30	7.89	7.93	71.5
31	4.88	10.10	51.2
32	4.70	9.01	52.2
33	4.70	7.10	52.9
34	4.88	4.74	64.8
35	4.86	3.06	73.8
36	4.76	4.83	64.4
37	4.89	3.15	65.9
38	4.93	1.96	64.1
39	4.86	1.91	67.4
40	4.31	4.61	62.0
41	3.73	8.74	48.8
42[a]	3.68	8.70	53.0
43	3.73	6.87	53.7
44	2.55	4.34	52.5
45	2.04	4.28	46.0

[a] Contains 1.1 × 10^{-3} *M* 2,6-di-*tert*-butyl-4-methylphenol.

TABLE III

SUMMARY OF REACTION CONCENTRATIONS AND APPARENT THIRD-ORDER RATE CONSTANTS FOR THE BROMINATION OF (*E*)-4-OCTENE AT 22.5°

Kinetic run	10^3 $(Br_2)_0$	10^3 $(Alkene)_0$	*k*, l.²/mol²-sec
46	8.89	9.88	35.2
47	8.89	6.98	34.6
48[a]	8.93	7.01	44.8

[a] Contains 2.7 × 10^{-3} *M* 2,6-di-*tert*-butyl-4-methylphenol.

in a Carle Model 6500 gc. Each reacted solution and aliquots of the initial alkene solutions were analyzed five to six times by glpc and the moles of alkene present were computed using calibration curves for each alkene with 1-bromopentane, which served as an internal standard in the glpc studies. The ratio of the moles reacted of each alkene is shown in Figure 3 as a function of the initial bromine concentration. The relative reactivity can be obtained by extrapolating these ratios to zero bromine concentration, and the least squares regression curve is shown in Figure 3.

Iodine–Alkene Complexation.—The equilibrium constants were determined for the complexation of iodine with cyclohexene, (*Z*)-3-hexene, and (*E*)-4-octene in CCl_4 at 25° using a 1-cm quartz cell in the Cary 14 spectrophotometer. The equilibrium constants were computed from eq 1, where the initial iodine concentration is *i*, *d* is the cell thickness, *A* is the absorbance of the complex at λ_{max} of the complex, K_N is the equilibrium constant in reciprocal mole fraction units, ϵ_c and ϵ_i are the molar absorptivities of complex and iodine at λ_{max} for the complex, and N_O is the mole fraction of the alkene.[16]

$$\frac{id}{A} = \frac{1}{K_N(\epsilon_c + \epsilon_i)N_0} + \frac{1}{\epsilon_c + \epsilon_i} \qquad (1)$$

The experimental procedure was similar to that of Traynham and Olechowski.[17] Stock solutions of iodine and alkene were covered with aluminum foil and equilibrated thermally. Aliquots were then mixed in flasks which were wrapped with aluminum foil to exclude light. The resulting reaction solutions ranged from 10^{-4} to 10^{-3} *M* iodine and the mole fraction of alkene ranged from 0.02 to 0.6. Samples were transferred to a 1-cm quartz cell within 2 min of mixing and the absorbance of the complex was measured at the wavelength shown in Table IV. Pure solvent was used as the reference. The absorbance of the complex did not change appreciably during the measurements, as was observed by other investigators.[18]

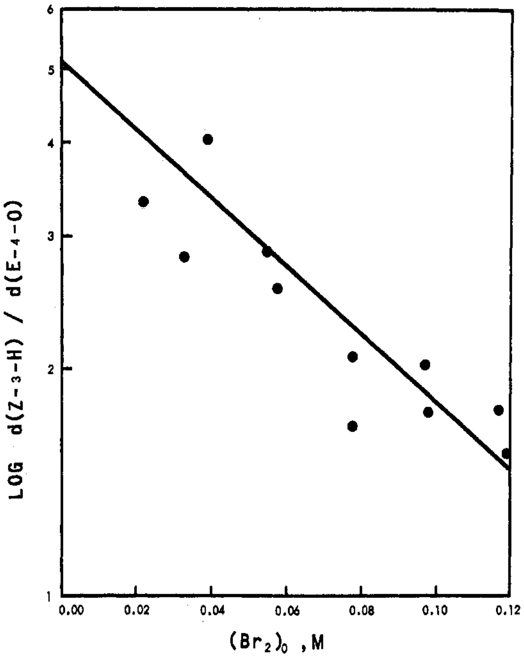

Figure 3.—Relative reactivities in the competitive bromination of (*Z*)-3-hexene [(*Z*)-3-H] and (*E*)-4-octene [(*E*)-4-0] at varying initial bromine concentrations. Initial alkene concentrations were 0.1 *M* in carbon tetrachloride.

TABLE IV

IODINE–ALKENE COMPLEXATION CONSTANTS IN CCl_4 AT 24.0°

Alkene	λ_{max}	10^{-4} ϵ_c, l./mol-cm	K_N[a]	K_C[b]
Cyclohexene	302	1.50	4.12	0.308
(*Z*)-3-Hexene	302	1.04	4.48	0.292
(*E*)-4-Octene	305	1.17	2.02	0.201

[a] Units are reciprocal mole fraction. [b] Units are l./mol.

A plot of *id*/*A* *vs.* 1/N_0 gives a slope of $1/K_N(\epsilon_c + \epsilon_i)$ and an ordinate intercept of $1/(\epsilon_c + \epsilon_i)$, where $1/N_0$ is one. The molar absorptivity of iodine was determined independently to be 95 l./mol-cm at 295 m*M*. Table IV lists the equilibrium constants found in this study along with the observed values of λ_{max} and ϵ_c.

Results and Discussion

The existence of an alkene–bromine complex appears to be well established from the spectroscopic studies of Buckles and Yuk[9] and Dubois and Garnier.[10] Even in the absence of such spectroscopic data such a complex might be anticipated by analogy with iodine–alkene complexation.[17-19] As noted in Scheme I, the existence of a bromine–alkene complex does not necessarily mean that this complex is actually involved in the reaction pathway leading to the dibromide product. If such a complex were involved in the reaction mechanism it should be possible to detect its presence by kinetic and competitive studies, but other com-

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(16) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

(17) J. G. Traynham and J. R. Olechowski, *ibid.*, **81**, 571 (1959).

(18) D. Long and R. W. Neuzil, *Anal. Chem.*, **27**, 1110 (1955).

(19) R. J. Cvetanovic, F. J. Duncan, W. E. Falconer, and W. A. Sunder, *J. Amer. Chem. Soc.*, **88**, 1602 (1966).

plexation reactions (*e.g.*, between bromine and solvent or between bromine and a polar group on the unsaturated compound) could confound these data. In our study we have circumvented this potential problem by using a nonpolar, noncomplexing solvent, CCl_4, and have restricted the unsaturated compound to simple internal alkenes. Although some kinetic measurements have been reported in nonpolar media,[13,20] these reactions often show extensive experimental scatter.[9,13] Part of this experimental problem could be due to trace impurities in the reaction media which would make the media more polar. Bromination reaction rates are known to increase with increasing solvent polarity.[4,13,20] In addition, alkene bromination rates are known to be sensitive to extraneous substances such as acids and halide ions.[2] A third source of experimental scattering would be the presence of a free-radical addition reaction along with the electrophilic bromination reaction.

In our studies, the solvent was purified immediately prior to each kinetic run in order to minimize the first two sources of error. Light was excluded from the reaction system to reduce the possibility of a free-radical reaction. The reactions were observed to follow third-order kinetics, as defined by eq 2 and 3,

$$\frac{dx}{dt} = k(a - x)(b - x)^2 \tag{2}$$

$$kt = \frac{1}{(a - b)}\left[\frac{x}{b(b - x)} + \frac{1}{(a - b)}\ln\left(\frac{a(b - x)}{b(a - x)}\right)\right] \tag{3}$$

where a and b are the initial concentrations of alkene and bromine, respectively, and x is the concentration of dibromide product at time t. Figure 1 illustrates the reproducibility of these third-order reactions for kinetic runs 9–17 and 41–42. Additional indications of reproducibility can be gained from Figure 2 and by comparing other replicate pairs of kinetic runs such as 13–14, 15–16, 21–22, and 38–39. The kinetic data are reproducible when the exact concentration conditions are duplicated. Figure 1 also shows that the reaction rate for (*E*)-3-hexene does not decrease in the presence of a free-radical inhibitor. This point is also illustrated for the other two alkenes in the kinetic pairs 2–3 [(*Z*)-3-hexene] and 47–48 [(*E*)-4-octene]. This data excludes a free-radical reaction as a significant part of this reaction. The increased rate of reaction in the presence of the inhibitor would be expected, since this phenol derivative would increase the polarity of the media.

Although replicate kinetic runs gave reproducible data, the observed rate constant varied widely when the concentrations of reactants changed. This effect can be seen in Figure 2 or in Tables I and II. The data shown in Figure 2 clearly show that the rate of reaction and their rate constants are reproducible for replicate brominations of (*E*)-3-hexene but that these rates change with the concentration. Under these circumstances, the observed specific rate constant for these reactions would be more appropriately termed an apparent third-order rate constant. As will be shown shortly, these apparent rate constants do not fluctuate in a random manner. It is entirely possible that many of the notations about experimental scatter in the literature arise from fluctuations of the apparent rate constant with the reactant concentrations. A similar phenomena was noted in the reaction of *cis*-stilbene with bromine in the presence of tetrabutylammonium tribromide in 1,2-dichloroethane.[13] In this case, the observed third-order rate constant increased with increasing concentration of the tetrabutylammonium tribromide, although no simple relationship was reported. If a bromine–alkene complex is directly involved in the reaction mechanism, the apparent third-order rate constant should fluctuate with the reactant concentrations.

Equations 4 and 5 show a simplified reaction sequence in which a bromine–alkene complex is an essential step.

$$A + Br_2 \rightleftharpoons A\cdot Br_2 \tag{4}$$

$$A\cdot Br_2 + Br_2 \longrightarrow P + Br_2 \tag{5}$$

In these equations, A is the alkene and P is the dibromide product. Equation 4 shows the formation of the bromine–alkene complex as a reversible equilibrium reaction. The rate of formation of charge-transfer complexes is generally considered too fast to be measured by ordinary techniques.[21] This reaction can be defined by an equilibrium constant, K_4, and rate constants k_4, k_{-4} for the forward and reverse reactions, respectively. The reaction of the complex with a second bromine molecule in eq 5 leads irreversibly to product and would be defined by a rate constant k_5. This step would be rate determining and would result in third-order kinetics, as observed. Equation 5 may be a simplification of the actual sequence, which could involve bromonium ion formation, etc., but this is not essential at this point. The sequence shown by eq 4 and 5 can be treated mathematically by the steady state–equilibrium approximation.[22] The rate of reaction, from eq 5, can be expressed by eq 6,

$$\frac{dx}{dt} = k_5c(b - x - c) \tag{6}$$

where a and b are the initial concentrations of alkene and bromine, respectively, x is the concentration of dibromide formed in time t, and c is the concentration of the complex. Using the steady-state assumption, the value of c can be defined by eq 7, which can be combined with eq 6 to produce the modified rate expression shown as eq 8.

$$c = \frac{K_4(a - x - c)(b - x - c)}{1 + \dfrac{k_5(b - x - c)}{k_{-4}}} \tag{7}$$

In order for the steady state–equilibrium assumption to apply, k_5 must be much less than k_4 and k_{-4}.

$$\frac{dx}{dt} = \frac{k_5K_4(a - x - c)(b - x - c)^2}{1 + \dfrac{k_5(b - x - c)}{k_{-4}}} \tag{8}$$

Since complexation is very fast while bromination proceeds at a readily measured rate, this condition appears to be satisfied in the present case. Under these conditions, eq 8 can be approximated by eq 9. The only difference between eq 9 and 2 is that

$$\frac{dx}{dt} = k_5K_4(a - x - c)(b - x - c)^2 \tag{9}$$

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[20] J. G. Hanna and S. Siggia, *Anal. Chem.*, **37**, 690 (1965).

[21] L. S. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964.

[22] C. W. Pyun, *J. Chem. Educ.*, **48**, 194 (1971).

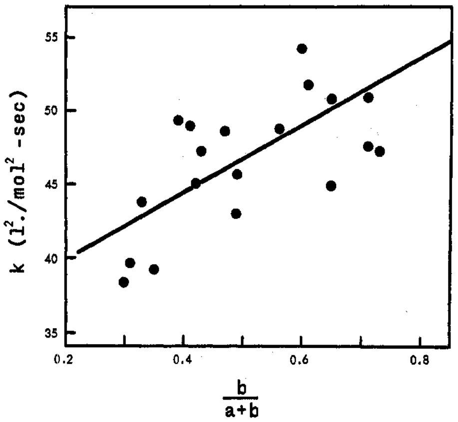

Figure 4.—Effect of the bromine reaction fraction on the apparent third-order rate constant for the bromination of (*Z*)-3-hexene in carbon tetrachloride.

the former contains the concentration of the complex. [Actually the terms $(a - x - c)$ and $(b - x - c)$ are the unreacted and uncomplexed alkene and bromine, respectively.]

Alternatively, eq 9 can be derived from an equilibrium approach. The equilibrium expression for eq 4 can be rearranged to give eq 10, which can be combined

$$c = K_4(a - x - c)(b - x - c) \tag{10}$$

with eq 6 to yield eq 9. Equation 9 contains two variable concentrations, x and c. Although c can be expressed in terms of K_4, a, b, and x, the resulting equation cannot be integrated readily and the value of c cannot be computed since K_4 is unknown. We can, nonetheless, evaluate the effect of the complex if we assume this concentration to be a constant and integrate eq 9 to get eq 11. This approximation would be valid for small changes in concentration.

$$k_5K_4t = \frac{1}{(a - b)}\left[\frac{x}{(b - c)(b - c - x)} + \frac{1}{(a - b)}\ln\left(\frac{(a - c)(b - c - x)}{(b - c)(a - c - x)}\right)\right] \tag{11}$$

The basic difference between eq 3 and 11 is that the latter contains the complex concentration and has a reaction constant that is a product of a rate constant and an equilibrium constant. The apparent third-order rate constants calculated from eq 3 can be considered as arising from eq 11 by ignoring the complex concentration. This neglect of the complex concentration introduces errors into the values of the reacting alkene and bromine and leads to incorrect values of the rate constant. The nature of this error is such that the apparent rate constant calculated from eq 3 will increase at b/a ratios greater than 1 and decrease when b/a is less than 1. This means that the apparent third-order rate constants should vary systematically with the concentrations of the reactants and that k should increase as the ratio of $b/(a + b)$ increases. Figures 4 and 5 show the observed apparent third-order rate constants for the reactions with (*Z*)-3-hexene and (*E*)-3-hexene, respectively, as a function of the fraction of bromine, $b/(a + b)$. In both cases, the observed third-order rate constant increases as the fraction of bromine increases, as predicted by the above analysis. The variation in the observed apparent third-order rate constant is consistent with a complex as an essential step in the reaction mechanism.

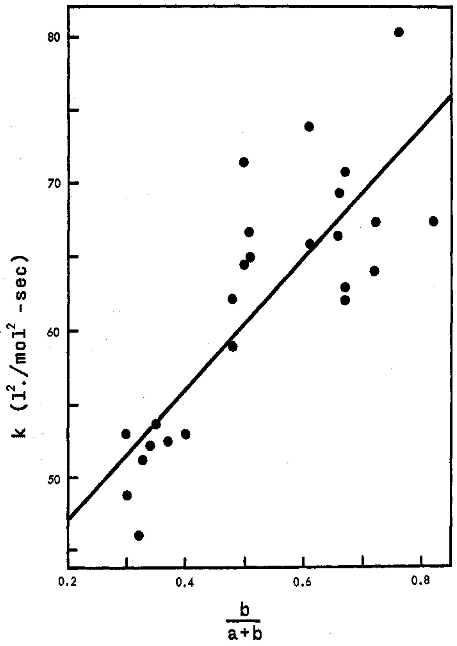

Figure 5.—Effect of the bromine reaction fraction on the apparent third-order rate constant for the bromination of (*E*)-3-hexene in carbon tetrachloride.

There are alternative explanations that do not involve a complex directly. If we consider the series of reactions shown by eq 4, 12, and 13, with k_{13} being

$$\mathrm{A} + \mathrm{Br_2} \rightleftharpoons \mathrm{A{\cdot}Br_2} \tag{4}$$

$$\mathrm{A} + \mathrm{Br_2} \longrightarrow \mathrm{ABr^+Br^-} \tag{12}$$

$$\mathrm{ABr^+Br^-} + \mathrm{Br_2} \longrightarrow \mathrm{P} + \mathrm{Br_2} \tag{13}$$

the rate-determining step, we can derive eq 14. In

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{12}k_{13}(a - x - c)(b - x - c)^2 \tag{14}$$

this sequence, which corresponds to route 1–2–5 in Scheme I, the complex is not directly involved in the reaction path but serves merely to change the concentrations of reactants which are available for reaction. While eq 14 is similar to eq 9, there are important differences. Equation 14 does not contain an equilibrium constant and this will be an important consideration in the competitive reaction data. In addition, eq 12 describes the formation of a bromonium ion. If k_{13} is rate determining, as is necessary for a third-order reaction, this step must be faster than eq 13 and the concentration of the bromonium ion should accumulate during the reaction. This condition appears unreasonable in the nonpolar media used in these studies. If we assume step 12 to be reversible, the resulting rate expression would be eq 15, which is essentially identical

$$\frac{\mathrm{d}x}{\mathrm{d}t} = K_{12}k_{13}(a - x - c - d)(b - x - c - d)^2 \tag{15}$$

with eq 9 except that the equilibrium constant describes the reversible formation of a bromonium ion whose concentration is denoted as d. The magnitude of the change in apparent rate constants shown in Figures 4 and 5 suggests that the concentration of the intermediate (complex and/or bromonium ion) is fairly large, and this requirement does not seem reasonable for a bromonium ion in a nonpolar media. The direct evidence for bromonium ion formation has always been obtained in highly polar solvents.[6] If eq 12 is considered rate determining or if a steady-state assumption is applied to the bromonium ion concentration, second-order kinetics result. An equation similar to eq 14 can also be derived by the unlikely assumption of an intermolecular reaction between the alkene and two molecules of bromine. In general, the observed systematic variation of the apparent third-order rate constants with the reaction composition is inconsistent with mechanisms *not* involving a complex unless unusual assumptions are made.

Other reaction sequences are compatible with the data of Figures 4 and 5. Two such sequences are shown in eq 16, 17, and 18 and in eq 4, 19, and 18. In both cases, the rate-determining step, eq 18, involves the conversion of a 1:2 alkene–bromine complex to product and bromine. The rate expressions which can be derived from these sequences are similar to eq 9 and are consistent with the data of Figures 4 and 5. We have emphasized the sequence of eq 4 and 5 primarily because they are in accord with a 1:1 complex between the alkene and the bromine. There is no evidence to suggest a 1:2 (or higher) complex in these reactions and the 1:1 complex is analogous to the iodine–alkene complexes.[17–19] Even if these 1:2 complexes were assumed, the basic conclusions would be the same as in the treatment leading to eq 9.

$$2\mathrm{Br_2} \rightleftharpoons \mathrm{Br_4} \tag{16}$$

$$\mathrm{A} + \mathrm{Br_4} \rightleftharpoons \mathrm{A\cdot Br_4} \tag{17}$$

$$\mathrm{A\cdot Br_4} \longrightarrow \mathrm{P} + \mathrm{Br_2} \tag{18}$$

$$\mathrm{A} + \mathrm{Br_2} \rightleftharpoons \mathrm{A\cdot Br_2} \tag{4}$$

$$\mathrm{A\cdot Br_2} + \mathrm{Br_2} \rightleftharpoons \mathrm{A\cdot Br_4} \tag{19}$$

$$\mathrm{A\cdot Br_4} \longrightarrow \mathrm{P} + \mathrm{Br_2} \tag{18}$$

The basic conclusion reached from eq 9 and 11 is that the systematic variation in the apparent third-order rate constant is due to complex formation between the alkene and the bromine. Other workers have reported systematic variation of apparent rate constants with concentration and have ascribed this effect to complexation between the reactants. Ross and Kuntz[23] have shown that the apparent second-order rate constant for the aromatic nucleophilic substitution reaction of 2,4-dinitrochlorobenzene with aniline decreases as the aniline concentration increases. Since their studies were made with excess aniline and constant 2,4-dinitrochlorobenzene concentrations, any possible effect of the 2,4-dinitrochlorobenzene concentration on the rate constant could not have been observed. Andrews and Keefer[24] showed that the apparent fourth-order rate constant for the reaction of iodine monochloride with mesitylene or pentamethylbenzene decreased as the concentration of the aromatic compound increased. Their studies used excess aromatic compound and approximately constant ICl concentrations so that effects due to the latter would not be observable. Variation of apparent rate constants with concentration has not been reported previously for alkene bromination, although it is possible that the experimental scatter reported by other workers is due to this effect.[13]

A second method of testing the intermediacy of a bromine–alkene complex involves the competitive reaction technique. In this technique, a pair of alkenes is treated with a limiting amount of bromine and the relative amounts of each alkene that react at infinite dilution of bromine should be equal to the ratio of the rate constants. For the bromination reactions, the relationship derived from eq 2 can be expressed by eq 19, where k and k' are the apparent rate

$$\frac{\mathrm{dA}}{\mathrm{dD}} = \frac{k}{k'} \tag{19}$$

constants for alkenes A and D, respectively, and the alkenes are present in an equimolar ratio. Equation 19 implicitly assumes that no complexation is involved in the reaction and relative reactivity ratio would be the same whether determined by a competitive technique or by a ratio of actual kinetic rate constants.

If a complex is directly involved in the reaction path, the situation becomes more complicated. The basic reactions can be described by eq 20–23. Under com-

$$\mathrm{A} + \mathrm{Br_2} \rightleftharpoons \mathrm{A\cdot Br_2} \tag{20}$$

$$\mathrm{D} + \mathrm{Br_2} \rightleftharpoons \mathrm{D\cdot Br_2} \tag{21}$$

$$\mathrm{A\cdot Br_2} + \mathrm{Br_2} \longrightarrow \mathrm{P_1} + \mathrm{Br_2} \tag{22}$$

$$\mathrm{D\cdot Br_2} + \mathrm{Br_2} \longrightarrow \mathrm{P_2} + \mathrm{Br_2} \tag{23}$$

petitive conditions, most of the bromine would be in the form of a complex due to the high alkene concentrations. The relative concentrations of each complex, $\mathrm{A\cdot Br_2}$ and $\mathrm{D\cdot Br_2}$, would not be the same as in independent kinetic reactions, since these competitive concentrations are established by the competing equilibria in eq 20 and 21. Assuming equimolar alkene concentrations, the bromine would be apportioned in these two complexes according to the ratio of the equilibrium constants as shown in eq 24. Under noncom-

$$\frac{(\mathrm{A\cdot Br_2})}{(\mathrm{D\cdot Br_2})} = \frac{K_{20}}{K_{21}} \tag{24}$$

peting conditions, the relative complex concentrations would be apportioned according to eq 25, where b is

$$\frac{(\mathrm{A\cdot Br_2})}{(\mathrm{D\cdot Br_2})} = \frac{K_{20}(b - c)}{K_{21}(b - e)} \tag{25}$$

the initial bromine concentration and c and e are the $\mathrm{A\cdot Br_2}$ and $\mathrm{D\cdot Br_2}$ concentrations, respectively.

If we assume that the complex is an essential step in the reaction, only complexed alkene can be converted to product. The limited amount of free bromine can either complex with excess free alkene or react with one of the two alkene–bromine complexes. Under these limiting conditions, the relative reactivity would approach the ratio of the equilibrium constants as defined in eq 26. The ratio in eq 19 and 26 should

$$\frac{\mathrm{dA}}{\mathrm{dD}} = \frac{K_{20}}{K_{21}} \tag{26}$$

normally be different if a complex is an essential step in the reaction mechanism.

Figure 3 shows the results of two series of competitive brominations of equimolar solutions of (*Z*)-3-hexene and (*E*)-4-octene. The extrapolated relative reac-

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[23] S. D. Ross and I. Kuntz, *J. Amer. Chem. Soc.*, **76**, 3000 (1954).

[24] L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 1412 (1957).

tivity is approximately 5.0 for the ratio d[(*Z*)-3-hexene]/d[(*E*)-4-octene]. This ratio corresponds to eq 26. The kinetic ratio corresponding to eq 19 can be obtained by dividing the rates of runs 1 and 2 (Table I) by the rates of runs 46 and 47 (Table III). The average kinetic relative reactivity is 1.35 ± 0.06. The competitive relative reactivity ratio is 3.7 times as great as the kinetic ratio. This is consistent with a complex as an essential step providing (*Z*)-3-hexene complexes more readily with bromine than does (*E*)-4-octene.

The use of the apparent third-order rate constants to estimate the relative reactivity of an alkene pair might appear questionable, since these apparent rate constants do vary with concentration. This method is reproducible, if the comparisons are made on the basis of equivalent concentrations. Thus the relative reactivity of (*E*)-3-hexene/(*Z*)-3-hexene is 1.34 ± 0.04 using six matched sets of data from Tables I and II. The pairs used are 23–1; 27–4; 37–13,14; 38,39–15,16; 41,42–17; and 43–18 and these sets comprise a wide concentration range. The individual *k* values vary but the ratios are constant.

No direct determinations of the equilibrium constants for bromine–alkene complexation are available. Normally, *Z* alkenes complex more extensively than *E* alkenes. The ratio of the equilibrium constants for *Z* alkene/*E* alkene has been reported as approximately 3–4 with $AgNO_3$[25–27] and 1.3–4.6 with I_2.[18,19,28] The magnitude of the $AgBF_4$–cyclohexene equilibrium constant has been reported to vary from 0.5 to 280 depending on the solvent.[29] In our studies we determined the iodine–alkene complexation constant for (*Z*)-3-hexene, (*E*)-4-octene, and cyclohexene in CCl_4 at 24° and these are summarized in Table IV. The equilibrium constant for cyclohexene in CCl_4 agrees reasonably well with values reported in nonpolar hydrocarbon solutions.[17,28] The *Z*/*E* complexation ratio was found to be in the range 1.5–2.2, showing that the (*Z*)-3-hexene does complex more extensively with iodine than does the (*E*)-4-octene. Since these data are on the same alkenes, in the same solvent, and use a related compound, iodine, as the complexing agent, it seems reasonable to expect the bromine–alkene complexation constant ratio to be similar. The greater electronegativity of bromine might increase the magnitude of the constants and could effect the ratio, but this change would not be expected to invert the ratio and make the *E* alkene complex more.

Our data and the literature data indicated that the *Z* alkene should complex more than the corresponding *E* alkene with bromine. An enhanced relative reactivity ratio in the competitive reaction studies is completely in accord with these complexation tendencies. This shift of the relative reactivity ratio in the direction corresponding to the complexation constant ratio is consistent with the hypothesis that a complex is an intermediate in the reaction path leading to product. If the complex is not directly involved, the individual rate expressions would be described by eq 14 and the relative reactivity ratio would contain only rate constants, as in eq 19. Since no equilibrium constant appears here, the two techniques for accessing relative reactivity should lead to the same ratio. Since they do not, we must reject the alternative hypothesis that the complex does not participate in the reaction as outlined in Scheme I, route 1–2–5. Our data do not distinguish between routes 1–4 and 1–3–5, since both would be affected by the complex in similar ways.

The presence of a bromine–alkene complex can account for the stereospecific trans addition of bromine to alkenes, especially in a third-order reaction. The stereochemistry of bromine addition has been studied by other workers and has been shown to depend on the structure of the alkene, the solvent, the concentration of the reactants, and the presence of halide ions.[8,13,30–32] Bromination becomes less stereospecific with increasing solvent polarity.[8,30,31] One possible explanation for this fact could be a shift of the reaction pathway from route 1–4 of Scheme I to route 1–3–5 due to solvent-assisted conversion of the complex to the bromonium ion. The resulting bromonium ion might be more readily susceptible to cis attack than the complex or might be in equilibrium with an open-chain bromocarbonium ion. This possible shift in reaction pathway could also account for the observed[2] shift from third-order to second-order kinetics with increasing solvent polarity. Similar decreases in reaction order with increasing solvent polarity have been observed in the electrophilic iodination of aromatic compounds by iodine monochloride.[24] The results of the present study are consistent with either route 1–4 or route 1–3–5 of Scheme I but there would appear to be no compelling reason to assume the existence of a bromonium ion in the bromination of alkenes in carbon tetrachloride.

Registry No.—(*Z*)-3-Hexene, 7642-09-3; (*E*)-3-hexene, 13269-52-8; (*E*)-4-octene, 14850-23-8; cyclohexene, 110-83-8.

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(25) F. R. Hepner, K. N. Trueblood, and H. J. Lucas, *J. Amer. Chem. Soc.*, **74**, 1333 (1952).

(26) M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962).

(27) R. J. Cvetanovic, F. J. Duncan, W. E. Falconer, and R. S. Irwin, *ibid.*, **87**, 1827 (1965).

(28) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 458 (1952).

(29) J. Solodar and J. P. Petrovich, *Inorg. Chem.*, **10**, 395 (1971).

(30) R. E. Buckles, J. M. Bader and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962).

(31) J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469, 1477, 1483 (1969).

(32) V. L. Heasley, G. E. Heasley, S. K. Taylor, and C. L. Frye, *J. Org. Chem.*, **35**, 2967 (1970).