more recently,[38] adapted to equilibrium potentiometric titrations.

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Registry No. 1 (isomer 1), 88454-79-9; 1 (isomer 2), 88495-25-4; 1·Ca, 88455-06-5; **4**, 88454-80-2; **6**, 88454-81-3; **7**, 88454-82-4; **8**, 76777-45-2; **9**, 26549-65-5; **10**, 88454-83-5; **11**, 88454-84-6; 11-diol, 88475-83-6; 11 (dibromo derivative), 88454-85-7; **12**, 57207-20-2; **13**, 88454-86-8; **14**, 61759-30-6; **15**, 88454-87-9; **16**, 88454-88-0; **17**, 88454-89-1; **18**, 88495-26-5; **19**, 76980-05-7; **20**, 88454-90-4; **20** (diiodide derivative), 88454-91-5; **21**, 88454-92-6; **22**, 88475-84-7; **23**, 17401-06-8; **24**, 88454-93-7; **24** (chloride derivative), 54533-84-5; **25**, 88454-94-8; **25** mono-Othp ether, 88454-95-9; 25-diol, 88454-96-0; **25** (dichloride derivative), 88454-97-1; **26**, 88454-98-2; **27**, 88454-99-3; **27** (diacid derivative), 88455-00-9; **27** (diacid chloride derivative), 88455-01-0; **28**, 88455-02-1; **28**-diol, 88455-03-2; **29**, 88455-04-3; **30**, 88455-05-4; **31**, 83458-45-1; **32**, 83458-46-2; 7-phenyl-3,6-dioxaheptanol, 2050-25-1; 1-chloro-7-phenyl-3,6-dioxaheptane, 64352-98-3; lithioacetylide, 1111-64-4; octylamine, 111-86-4; diethylene glycol, 111-46-6; benzyl bromide, 100-39-0; 1-dodecyne, 765-03-7; 1-bromodecane, 112-29-8; diethyl tartrate, 87-91-2; dioctylamine, 1120-48-5.

Nonlinear Least-Squares Method of Separating the Second- and Third-Order Rate Constants for the Ionic Bromination of Alkenes in CCl_4 at 25 °C[†]

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A nonlinear least-squares method of obtaining reliable values of both the second- and third-order rate constants for electrophilic addition of bromine to alkenes when $[\text{alkene}]_0 \gg [Br_2]_0$ is described. The kinetics of the reaction must be followed to at least 80% completion for this method to be successful. The method is applied to the bromination of (*Z*)-2-butene and 2-methyl-2-butene in CCl_4 at 25 °C. For (*Z*)-2-butene $k_2 = (8.9 \pm 0.3) \times 10^{-4}$ $M^{-1}\ s^{-1}$ and $k_3 = 4.0 \pm 0.6\ M^{-2}\ s^{-1}$ while for 2-methyl-2-butene $k_2 = (6 \pm 2) \times 10^{-3}\ M^{-1}\ s^{-1}$ and $k_3 = 240 \pm 40\ M^{-2}$ s^{-1}.

The general rate law for the ionic bromination of alkenes is generally accepted to be as shown in eq 1.[1] This rate

$$-d[Br_2]/dt = (k_2[Br_2] + k_3[Br_2]^2 + k'_{Br_3^-}[Br_3^-])[\text{alkene}] \tag{1}$$

law contains terms that account for first- and second-order dependences on bromine and an additional term for bromide ion participation.

On the basis of existing literature,[2,3] bromination in a nonpolar solvent such as CCl_4 should display third-order kinetics exclusively, i.e., the k_3 process. The $k_{Br_3^-}$ process is not expected to be in operation, especially in the absence of added bromide ion. The k_2 process is favored only under conditions of low bromine concentration in polar solvents. It has been proposed that a solvent molecule participates in the rate-determining transition state of the k_2 process. Nonpolar solvents cannot participate in that fashion, hence a second molecule of bromine is thought to act as a replacement, giving rise to an observed second-order dependance on bromine.

Recently, it has been shown that both the k_2 and the k_3 processes occur in CCl_4.[4] However it is difficult to obtain values of both k_2 and k_3. We present a method of obtaining reliable values of both k_2 and k_3 from bromine absorbance–time data in CCl_4 at 25 °C.

Results and Discussion

The rates of bromination were followed by monitoring the decrease in absorbance of bromine at 415 ± 1 nm under conditions of at least a 20-fold excess of alkene by means of either a Pye Unicam SP 1800 or Cary 16 UV/vis spectrophotometer. The rates of bromination were unaffected by addition of up to 10^{-3} M cyclohexene epoxide.[5] Purging the CCl_4 solutions with oxygen and nitrogen had no effect on the kinetic results compared to those obtained without purging. The results are all consistent with an ionic reaction.[1,5]

The results of analysis of typical absorbance vs. time data for the addition of bromine to (*Z*)-2-butene in CCl_4 at 25 °C by means of a pseudo-first-order (P1O) and a pseudo-second-order (P2O) rate law are shown in Figures 1 and 2, respectively. While the P2O analysis gives the better correlation coefficient, both Figures 1 and 2 shown definite curvature. The P1O plot shows greater curvature than the P2O plot, indicating that the second-order dependence on bromine is the more important process. However, the first-order dependence on bromine cannot be ignored. Thus the experimental rate law does not have either a simple first- or second-order dependence on bromine.

Under conditions of excess alkene, a combined first- and second-order dependence on bromine of the rate of reaction can be expressed as eq 2 where $k_2' = k_2[\text{alkene}]$ and

$$-d[Br_2]/dt = k_2'[Br_2] + k_3'[Br_2]^2 \tag{2}$$

[†] Abstracted from the Ph.D. Thesis of B.T., University of Toronto, 1984.

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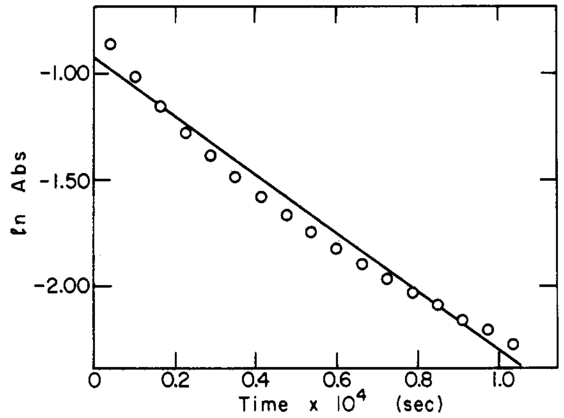

Figure 1. Pesudo-first-order analysis of absorbance vs. time data for addition of bromine to (*Z*)-2-butene in CCl_4 at 25 °C.

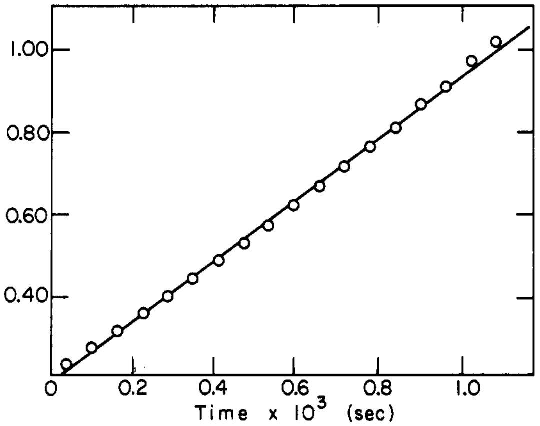

Figure 2. Pseudo-second-order analysis of absorbance vs. time data for the addition of bromine to (*Z*)-2-butene in CCl_4 at 25 °C.

$k_3' = k_3$[alkene]. Integration yields the nonlinear equation 3 with respect to time. In order to obtain k_2' and k_3' from

$$1/[Br_2]_t = (1/[Br_2]_0)e^{k_2't} + (k_3'/k_2')(e^{k_2't} - 1) \quad (3)$$

data that are characterized by eq 1, a nonlinear least-square analysis was adopted. Equation 3 can be rewritten as follows:

$$1/[Br_2]_t = A_3e^{A_1t} + A_2(e^{A_1t} - 1) \quad (4)$$

where

$$A_1 = k_2' \qquad A_2 = k_3'/k_2' \qquad A_3 = 1/[Br_2]_0$$

A general-purpose curve fitting subroutine was modified so that unique values of $[Br_2]_0$, k_2', and k_3', which yield the best fit of equation 4 to the experimental absorbance against time data could be determined. This procedure will be referred to as FIT analysis.[6]

This requires a subroutine FUNCTN containing the equation Q to be fitted (eq 4) and another, FDERIV, which

$$Q = 1/[Br_2]_t$$

$$dQ/dA_3 = e^{A_1t}$$

$$dQ/dA_2 = e^{A_1t} - 1$$

$$dQ/dA_1 = (A_2 + A_3)te^{A_1t}$$

computes the value of the derivatives of eq 4 with respect to each coefficient in it, which are used in the fitting process (gradient search process). The difference d (actually a weighted sum over *i* of d$(i)^2$) is calculated in a subroutine FCHISQ, and a matrix inversion subroutine MATINV is also required. The procedure is iterative insofar as several passes through the program are made until the change in d from the previous pass is negligible, the calculated coefficient values A_1, A_2, and A_3 being essentially unchanged (convergence). Then,

$$k_2' = A_1$$

$$k_3' = A_1A_2$$

$$[Br_2]_0 = 1/A_3$$

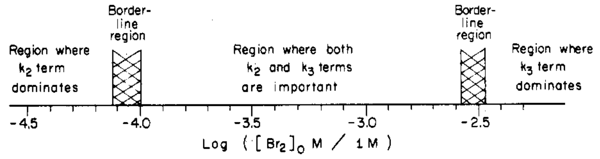

Figure 3. Relative importance of second- and third-order rate processes on initial bromine concentration for the addition of bromine to (*Z*)-2-butene in CCl_4 at 25 °C.

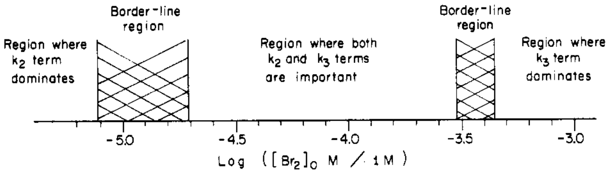

Figure 4. Relative importance of second- and third-order rate processes on initial bromine concentration for the addition of bromine to 2-methyl-2-butene in CCl_4 at 25 °C.

Table I. Values of k_2 and k_3 Obtained by FIT Analysis of the Reaction of Bromine and (*Z*)-2-Butene and 2-Methyl-2-butene in CCl_4 at 25 °C

alkene	N^a	k_2, M^{-1} s^{-1}	k_3, M^{-2} s^{-1}
(*Z*)-2-butene	46	$(8.9 \pm 0.3) \times 10^{-4}$	4.0 ± 0.6
2-methyl-2-butene	6	$(6 \pm 2) \times 10^{-3}$	240 ± 40

^{a} Number of kinetic runs.

The FIT procedure was applied to the absorbance–time data for the bromination of (*Z*)-2-butene and 2-methyl-2-butene in CCl_4 at 25 °C. The initial guess coefficients used were those obtained from the results of P1O and P2O analysis of the data. The values of k_2 and k_3 obtained by the FIT analysis are given in Table I.

Once values of k_2 and k_3 are obtained, it is possible to verify their values by studing the reaction at initial bromine concentrations under which either the k_2 or k_3 process dominates. These regions can be determined by using eq 3 and the FIT values of k_2 and k_3 to generate values of $[Br_2]_t$ and *t* at various initial bromine concentrations $[Br_2]_0$. For each $[Br_2]_0$, 12 pairs of $[Br_2]_t$ and *t* were generated and the total time was chosen to achieve an 80–82% decrease in $[Br_2]_0$. These synthetic data were then subject to P1O and P2O analysis, and the resulting plots were checked for curvature. The results for (*Z*)-2-butene are shown in Figure 3 and for 2-methyl-2-butene in Figure 4.

As illustrated in Figure 3, the rate of bromination of (*Z*)-2-butene will exhibit pure first-order bromine dependence for $[Br_2]_0 < 10^{-4}$ M while a second-order dependence on bromine is found for $[Br_2]_0 > 3 \times 10^{-3}$ M. The rate of reaction for $[Br_2]_0$ between 10^{-4} M and 3×10^{-3} M will exhibit a mixed dependence on bromine. For the rate of bromination of 2-methyl-2-butene, the regions of first-order and second-order dependence on bromine are both lower by a factor of 10 than the corresponding regions for (*Z*)-2-butene. These regions are independent of the initial concentration of alkene as long as $[\text{alkene}]_0 \gg [Br_2]_0$. A

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[6] For a listing of the program, see: Toyonaga, B. Ph.D. Thesis, University of Toronto, 1984.

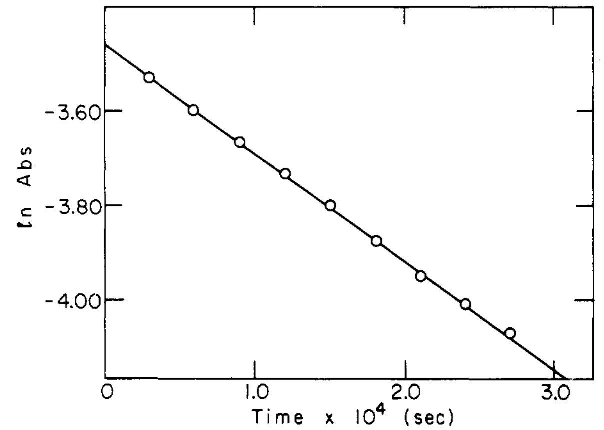

Figure 5. Pseudo-first-order analysis of absorbance vs. time data for addition of bromine (1.48×10^{-5} M) to 2-methyl-2-butene (0.0030 M) in CCl_4 at 25 °C.

40-fold increase in initial concentration of (*Z*)-2-butene (from 0.015 to 0.600 M) at a constant $[Br_2]_0$ concentration (1.0×10^{-4} M) does not affect the curvature of the plots of either a P1O or P2O analysis. Therefore the concentration ranges of bromine in which either the k_2 or k_3 process is dominent is independent of $[\text{alkene}]_0$ as long as $[\text{alkene}]_0 \gg [Br_2]_0$.

The rate of bromination of 2-methyl-2-butene was measured at low bromine concentration where according to Figure 4 first-order dependence on Br_2 is expected. Thus P1O analysis of the absorbance vs. time data for $[Br_2]_0 = 1.48 \times 10^{-5}$ M and $[\text{alkene}]_0 = 0.0030$ M gives the linear plot shown in Figure 5. The value of k_2 obtained from this plot ($k_2 = (7.8 \pm 0.1) \times 10^{-3}$ M^{-1} s^{-1}) is in good agreement with the average value determined by the FIT method (Table I).

The rate of bromination of 2-methyl-2-butene was also measured at bromine concentrations where second-order dominance of bromine concentration is predicted [(1.14 to 3.96) $\times 10^{-3}$ M]. The stopped flow technique was used to measure the rate of bromine disappearance. Analysis of the absorbance–time data by the P2O method gave linear plots. The average value of k_3 (330 ± 20 M^{-2} s^{-1}) for 21 runs is in reasonable agreement with the value of k_3 obtained by the FIT method (Table I).

Fukuzumi and Kochi reported values of k_2 and k_3 for the bromination of 2-methyl-2-butene in CCl_4 at 25 °C.[4] Our value of k_3 agrees well with theirs, but our value of k_2 differs by a factor of 40. We believe that this difference is due to two factors. First, values of $[Br_2]_0$ were not varied enough, and second, Kochi followed the rates of reaction to only 15% completion. Such short reaction times make it difficult to obtain reliable values of both k_2 and k_3. Thus it frequently occurs that P1O or P2O analysis of absorbance–time data can give reasonably linear plots at $[Br_2]_0$ where both the k_2 and k_3 processes are kinetically important. This is particularly true if the reaction is not followed to sufficiently high conversion. This conclusion is reached by analysis of synthetic data generated by the use of eq 3 for various values of the k_3'/k_2' ratio and t at an initial bromine concentration of 2.36×10^{-3} M. The tables of synthetic data, values of calculated k_3'/k_2' ratios, and figures of P1O and P2O analyses of the data are in the supplementary material (see paragraph at end of paper).

To obtain values of both k_2 and k_3, the following steps are recommended. First follow the reaction to at least 80% completion. Second vary $[Br_2]_0$ over a sufficiently wide range to discover where P1O and/or P2O analysis of the data give nonlinear plots. Third analyze the data of the nonlinear plots by the FIT procedure. It is important to find the range of $[Br_2]_0$ where P1O and P2O give nonlinear plots because this is where both the $k_2[Br_2]$ and the k_3 process contribute significantly to the overall rate. Within this range of $[Br_2]_0$, the FIT procedure will give the best values of k_2 and k_3.

Experimental Section

CCl_4. Approximately 1% by weight of P_2O_5 was added to ACS-Grade CCl_4. The mixture was heated under reflux for 12 h under an argon atmosphere. The CCl_4 was then distilled from the P_2O_5. A 3% (by volume) prerun was discarded and the distillate collected, bp 76.6 ± 0.1 °C (lit.[7] bp 76.8 (°C). The CCl_4 was redistilled until the P_2O_5 remained unchanged by the reflux process. This was typically three cycles. The final distillate was stored in a flask equipped with a stopcock containing a side arm. This type of flask allows access to the solvent by pipet under an argon atmosphere.

Bromine was obtained from Alfa Products (99.998%) and used without further purification.

(*Z*)-2-Butene was obtained from Matheson (99.9%) and used without further purification.

2-Methyl-2-butene was obtained from Chemical Samples Co. GLC analysis of the alkene on a 20% bb'ODPN on 80–100 mesh Chrom P indicated a purity of 99.9%. The alkene was used without further purification.

Kinetic Procedure. Conventional Technique. A measured volume of a bromine solution, prepared by weight and temperature equilibrated, was added quickly by using a transfer pipet (equipped with a plunger mechanism) to a 1-cm (3.2 mL) or 10-cm (8.0 mL volume) UV cell that contained an equivalent volume of the alkene solution. Bromine absorbance vs. time data were collected by using a Unicam AR25 linear recorder.

Stopped Flow Techniques. A Cantech Scientific Ltd. TD1 Model IIa instrument was used. Reagent solutions were placed into separate derive syringes of the instrument and allowed to come to thermal equilibrium with the system. Actuation of a pneumatic piston drove the syringe plungers simultaneously, resulting in the rapid mixing of the solutions into a cell equipped to allow transmittance measurements to be made. A monochromatic light source and photomultiplier detector were used. The photomultiplier output was fed into a logrithmic amplifier that was connected to a storage oscilloscope. Polaroid photographs were taken of the displayed absorbance vs. time traces.

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Registry No. (*Z*)-2-Butene, 590-18-1; 2-methyl-2-butene, 513-35-9.

Supplementary Material Available: Tables containing synthetic data, k_3'/k_2' ratio, and figures of P1O and P2O analysis of synthetic data (10 pages). Ordering information is given on any current masthead page.

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