mixture up to 90 °C. Some H_2O and all the product thiane distilled too. A small amount of H_2O was added to the distillate, and the mixture was extracted five times with CH_2Cl_2. The organics were back-extracted with one portion of H_2O and dried over $MgSO_4$. Removal of the drying agent and solvent gave a 67% yield of thiane after distillation.

References and Notes

(1) This work was supported by the National Science Foundation, Grant No. CHE-75-05006.

(2) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 1st ed, Pergamon Press, Elmsford, N.Y., 1959, pp 112–119.

(3) For a review, see J. B. Lambert and S. I. Featherman, *Chem. Rev.*, **75**, 611 (1975).

(4) The negative sign for thiane has now been proved unambiguously; A. Fava and G. Barbarella, unpublished results. We wish to thank Professor Fava and Dr. Barbarella for making these data available to us before publication.

(5) S. A. Khan, J. B. Lambert, O. Hernandez, and F. A. Carey, *J. Am. Chem. Soc.*, **97**, 1468 (1975).

(6) E. Campaigne, N. F. Chamberlain, and B. E. Edwards, *J. Org. Chem.*, **27**, 135 (1962).

(7) E. L. Eliel, V. S. Rao, and F. G. Riddell, *J. Am. Chem. Soc.*, **98**, 3583 (1976); E. L. Eliel, V. S. Rao, F. W. Vierhapper, and G. Zúñiga Juaristi, *Tetrahedron Lett.*, 4339 (1975); G. Barbarella and A. Fava have also called attention to this anomaly.

(8) J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Am. Chem. Soc.*, **89**, 5921 (1967).

(9) R. Lett and A. Marquet, *Tetrahedron*, **30**, 3379 (1974).

(10) L. Canuel and M. St-Jacques, *J. Org. Chem.*, **41**, 1380 (1976).

(11) J. B. Lambert, H. F. Shurvell, L. Verbit, R. G. Cooks, and G. F. Stout, "Organic Structural Analysis", Macmillan, New York, N.Y., 1976, p 34.

(12) P. Albriktsen, *Acta Chem. Scand.*, **29A**, 824 (1975).

(13) L. Phillips and V. Wray, *J. Chem. Soc., Perkin Trans. 2*, 223 (1972); J. B. Lambert and L. G. Greifenstein, *J. Am. Chem. Soc.*, **96**, 5120 (1974).

(14) E. L. Eliel, W. F. Bailey, L. D. Kopp, R. L. Willer, D. M. Grant, R. Bertrand, K. A. Christensen, D. K. Dalling, M. W. Duch, E. Wenkert, F. M. Schell, and D. W. Cochran, *J. Am. Chem. Soc.*, **97**, 332 (1975).

(15) J. A. Pople, *J. Chem. Phys.*, **37**, 60 (1962).

(16) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969, p 81.

(17) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(18) J. B. Lambert, *J. Am. Chem. Soc.*, **89**, 1836 (1967).

(19) See ref 9–15 of J. B. Lambert, D. A. Netzel, H.-n. Sun, and K. K. Lilianstrom, *J. Am. Chem. Soc.*, **98**, 3778 (1976).

(20) J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).

Halogen Order in the Kinetics of Bromination of Poly(methylbenzenes) in 90% Aqueous Acetic Acid

R. M. Keefer* and L. J. Andrews

Contribution from the Department of Chemistry, University of California, Davis, California 95616.

Received November 1, 1976

Abstract: The results of earlier kinetic studies by the authors of the bromination of poly(alkylbenzenes) in aqueous acetic acid have been accounted for by rate laws which contain terms higher than first order in halogen. On the basis of observations made in the investigation of acetanilide bromination Schubert and Dial recently proposed that the rate behavior attributed to second and higher orders in halogen can, in fact, be explained solely in terms of a reaction first order in halogen, the first step of which is subject to reversal as bromide ion accumulates in the medium. The applicability of this explanation to poly(alkylbenzene) bromination has now been tested through investigating the influence of added sodium bromide and sodium perchlorate on the rates of bromination of mesitylene, pentamethylbenzene, and pentamethylbenzene-*1*-d_1 in 90% aqueous acetic acid. The results show clearly that for these reactions the explanation of Schubert and Dial does not apply.

Rate laws reported[1] for aromatic bromination in the absence of added bromide ion often include terms higher than first order in bromine, as in eq 1.

$$-\mathrm{d}[\mathrm{ArH}]/\mathrm{d}t = k_{\mathrm{I}}[\mathrm{ArH}][\mathrm{Br_2}] + k_{\mathrm{II}}[\mathrm{ArH}][\mathrm{Br_2}]^2 \qquad (1)$$

This has been attributed to the existence of activated complexes in which more than one halogen molecule is incorporated. Recently it was observed that the rate constants for bromination of acetanilide in 50% acetic acid, calculated on the assumption that the reaction is first order in bromine, are subject to pronounced depression with time.[2] This depression, substantially greater than can be ascribed to the complication of tribromide formation, has been shown not to be associated with reaction orders higher than one in halogen. Rather it is a consequence of the increasing reversibility in the first step of the reaction (see eq 2-4) as bromide ion accumulates in the medium.

$$\mathrm{ArH} + \mathrm{Br_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ArHBr^+} + \mathrm{Br^-} \qquad (2)$$

$$\mathrm{ArHBr^+} + \mathrm{B}_i \xrightarrow{k_i} \mathrm{ArBr} + \mathrm{HB}_i{}^+ \qquad (3)$$

$$-\mathrm{d}[\mathrm{ArH}]/\mathrm{d}t = \frac{k_1k_2[\mathrm{ArH}][\mathrm{Br_2}]}{k_{-1}[\mathrm{Br^-}] + k_2},\ k_2 = \Sigma k_i[\mathrm{B}_i] \qquad (4)$$

Sigma complexes ($\mathrm{ArHBr^+}$) are also reported to form reversibly in the bromination of certain highly hindered substrates in acetic acid.[3]

The results of earlier kinetic studies of electrophilic halogenation of poly(methylbenzenes) conducted by the authors and their associates have been interpreted on the premise that there are terms in the rate law higher than first in halogen.[4] These studies were conducted using relatively low initial bromine concentrations so that the bromide ion concentration during a rate run was always small. Under these conditions there was no evidence for a reversible first step as shown in eq 2. Because of the outcome of the studies of acetanilide bromination, the earlier kinetic investigation, specifically that concerning the bromination of mesitylene and pentamethylbenzene in 90% aqueous acetic acid,[4b] has now been extended. The additional results indicate that at the bromine concentrations employed, rate law 1 correctly applies. Even with substantial amounts of bromide ion initially present in the medium no definitive evidence of reaction reversibility as depicted in eq 2 has been obtained.

Experimental Section

Reagents and Solvents. Sodium bromide, Mallinckrodt Analytical Reagent grade, was dried for 24 h at 120 °C. Sodium perchlorate ($NaClO_4{\cdot}H_2O$), G. F. Smith Reagent grade, was dehydrated by

Table I. Rate Constants for Bromination of Mesitylene and Pentamethylbenzene in 90% Aqueous Acetic Acid (25.1 °C)[a]

$10^3[\text{Mes}]_i$, mol/L	$10^3[\text{Br}_2]_i$, mol/L	$10^3[\text{NaBr}]$, mol/L	k_0/Mes, L mol^{-1} s^{-1}	k_1, L mol^{-1} s^{-1}
28.29	0.23	500.0	0.0313	1.94
28.29	0.23	250.0	0.0345	1.17
28.24	3.02	100.2	0.0430	0.675
28.24	0.186	50.0	0.0578	0.489
28.24	0.186	30.00	0.0751	0.419
28.24	0.186	20.00	0.0885	0.362
5.65	0.201	8.01	0.1305	0.298
		$M_{\text{NaClO}_4} + M_{\text{NaBr}} = 0.100$		
28.24	3.02	100.2	0.0430	0.675
28.35	0.203	80.1	0.0533	0.665
28.35	0.203	50.1	0.0800	0.654
28.35	0.203	30.0	0.1250	0.663
28.35	0.203	20.0	0.1824	0.707
5.67	0.222	20.0	0.182	0.705
5.67	0.222	12.0	0.260	0.710
5.67	0.222	6.00	0.373	0.70
28.24	0.186	50.1[b]	0.0590	0.483
		$M_{\text{NaClO}_4} + M_{\text{NaBr}} = 0.500$		
28.29	0.23	500.0	0.0313	1.94
28.29	0.23	250.0	0.0715	2.25
5.65	0.23	125.0	0.1524	2.48
5.65	0.23	62.5	0.309	2.67
5.66	0.18	50.0	0.358	2.55
5.65	0.23	31.25	0.548	2.64
		$M_{\text{NaClO}_4} + M_{\text{NaBr}} = 0.500$		
$10^3[\text{PMB}]$, mol/L	$10^3[\text{Br}_2]_i$, mol/L	$10^3[\text{NaBr}]$, mol/L	k_0/PMB	k_1
10.0	0.21–0.23	500.0	0.105 ± 0.001	6.51
10.0	0.21–0.23	250.0	0.258 ± 0.006	8.16
5.00	0.214	125.0	0.579 ± 0.002	9.42
2.50	0.214	62.5	1.173 ± 0.010	10.13
$10^3[\text{dPMB}]$, mol/L				$k_{\text{ArH}}/k_{\text{ArD}}$
10.05	0.23	500.00	0.101	1.04
10.05	0.23	250.0	0.246	1.05
2.51	0.20–0.23	125.0	0.539	1.07
2.51	0.189	62.5	1.120	1.04

[a] Mes = mesitylene; dPMB = pentamethylbenzene-*l*-d_1; PMB = pentamethylbenzene. [b] NaOAc used instead of NaClO_4 to keep total salt concentration equal to 0.100.

heating for 48 h at 120 °C. Sodium acetate, Baker and Adamson Anhydrous Reagent grade, was dried for 24 h at 120 °C, and Mallinckrodt Analytical Reagent grade bromine and acetic acid were used without further treatment. Pentamethylbenzene, Eastman Organic Chemicals, mp 51.0–52.2 °C, was recrystallized from ethanol. Pentamethylbenzene-*l*-d_1, prepared as described previously,[5] was found to be 87 atom % labeled at the unsubstituted ring position both by mass spectrometric and NMR analysis. Mesitylene, Chemical Samples Co., 99.7%, was used without further purification.

Rate Measurements. The solvent, 90% aqueous acetic acid, was prepared by mixing nine volumes of acetic acid with one volume of water. The procedures used previously for studying the rates of aromatic hydrocarbon brominations in acetic acid[4a] were adapted, with minor revision, to the present study. The disappearance of bromine from the solutions was followed by observing changes in absorbance of the reaction mixtures at 320 nm and/or 290 nm, using 1-cm glass-stoppered cells and 90% aqueous acetic acid as the blank. The initial concentrations of sodium bromide (6×10^{-3} M or greater) and aromatic hydrocarbon (2.5×10^{-3} M or greater) were generally in large excess of the initial bromine concentration.

Equilibrium Constant for Tribromide Ion Formation. To determine the effect of added salts on the equilibrium constant for tribromide ion formation in 90% acetic acid a series of solutions in this solvent were prepared which varied in the concentrations of sodium bromide (0.0025–0.0250 M) and bromine (1.5×10^{-4}–6.0×10^{-4} M). The solutions also contained varying amounts of sodium perchlorate. Absorbances of these solutions were recorded at 340, 350, and 360 nm, a region in which the absorbance of tribromide ion is much more intense than that of free bromine. The molar absorptivity of tribromide ion at these wavelengths was calculated from the absorbance of a solution containing 3.03×10^{-4} M bromine and 0.500 M sodium bromide. The molar absorptives of Br_3^-, after a small correction for uncomplexed bromine, were 2224 (340 nm), 1388 (350 nm), and 984 (360 nm). The equilibrium constants, K (eq 8), for tribromide ion formation in 90% acetic acid (shown in parentheses) vary with total salt concentrations of the medium, $M_{\text{NaBr}} + M_{\text{NaClO}_4}$, in the following order at 25.0 °C: 0.500 M (122 ± 1.0), 0.280 M (132 ± 1.5), 0.100 M (147 ± 2), 0.050 M (147 ± 3), 0.015 M (155), 0.006 M (160).

The details of the procedures used were much the same as those described in a previous investigation of tribromide formation in acetic acid.[6]

Results

Rates of Bromination of Mesitylene and Pentamethylbenzene in 90% Acetic Acid. In all runs conducted sodium bromide and the aromatic substrate were initially in sufficient excess of bromine that the bromide and hydrocarbon concentrations were essentially constant throughout the reactions. In all cases free bromine concentration was low enough so that the contribution to the rate law of a term second order in bromine was anticipated to be negligible (cf. ref 4b). Under these conditions the rate of disappearance of bromine (as determined spectrophotometrically) is, in fact, first order in total bromine concentration, $[\text{Br}_2]_\text{T}$.

$$[\text{Br}_2]_\text{T} = [\text{Br}_2] + [\text{Br}_3^-] \tag{5}$$

First-order rate constants, k_0, were calculated from the slopes of plots of $-\ln (D - D_\infty)$ vs. time, where D is the absorbance of the reaction mixture at time t and D_∞ is the absorbance after at least 10 half-lives,

$$-\text{d}[\text{Br}_2]_\text{T}/\text{d}t = k_0[\text{Br}_2]_\text{T} \tag{6}$$

The plots obtained for reactions followed at 320 nm were linear throughout 2 half-lives. In some runs later phases of reaction were followed by shifting to a wavelength of 290 nm. The plots for such runs were linear throughout 5 half-lives. The k_0 values for duplicate runs were in agreement within 1 to 2%. Values obtained for $k_0/[\text{ArH}]$ are shown in the fourth column of Table I. In the fifth column of Table I values of k_1 (see eq 7 and 8) are listed,

$$\text{d}[\text{ArBr}]/\text{d}t = -\text{d}[\text{Br}_2]_\text{T}/\text{d}t = k_1[\text{ArH}][\text{Br}_2] \tag{7}$$

$$k_1 = (1 + K[\text{Br}^-])(k_0/[\text{ArH}])$$

$$K = [\text{Br}_3^-]/[\text{Br}_2][\text{Br}^-] \tag{8}$$

In the first set of rate runs on mesitylene, the results of which are summarized in Table I, the sodium bromide concentration of the reaction mixture was varied from 0.008 to 0.500 M. Although the values of $k_0/[\text{Mes}]$ show a marked decrease in value with increasing sodium bromide concentration, the k_1 values (corrected for Br_3^-) show an increase in value with increasing sodium bromide concentration. This increase in k_1 with increasing sodium bromide concentration is probably due to a salt effect. Such an effect would mask any small decrease in k_1 values resulting from the reversibility of the first step (eq 2) of the proposed reaction mechanism.

To explore the possibility of such masking, a second set of runs on mesitylene was conducted in which the sodium bromide concentration was varied while keeping the total salt concentration constant at 0.100 M through the addition of an appropriate amount of sodium perchlorate. Under these conditions the calculated values of k_1 for mesitylene are observed to decrease slightly (0.71 to 0.67) as the bromide content of the medium increases from 0.006 to 0.100 M. Certainly the results of this set of runs do not provide convincing evidence that k_1 is subject to variation with bromide because of reversibility of the first step of the reaction (eq 2).

It is interesting to note that when sodium acetate, rather than sodium perchlorate, is used to fix the total salt concentration of the medium, it does not noticeably influence the ionic strength of the medium (cf. k_1 values for reaction at $[\mathrm{NaBr}]_i = 0.050$ M in the first and second sets of runs summarized in Table I). Presumably sodium acetate is a highly associated salt in acetic acid.

In the third set of runs on mesitylene the total salt concentration of the media was fixed at 0.500 M through addition of sodium perchlorate. At higher bromide concentrations the calculated k_1 values diminish appreciably as sodium perchlorate is replaced by sodium bromide, a fact which might be ascribed to differences in the effect of the two salts on the activated complex, or to reversibility, or to a combination of the two effects.

In the fourth set of runs summarized in Table I, the aromatic substrate was pentamethylbenzene and the total concentration of added salts, sodium bromide and sodium perchlorate, was fixed at 0.500 M. Again k_1 values diminish, but not precipitously, with increasing bromide concentration of the medium and somewhat more noticeably than in the reactions of mesitylene. If this decrease is a reflection of the increasing influence of the rate of proton loss from the σ complex (eq 3) on the overall rate, it can be anticipated that k_1 values for pentamethylbenzene should be larger than those for pentamethylbenzene-*1*-d_1. The k_1 values for a series of runs with the deuterated substrate (see the fifth set of runs in Table I) are in fact somewhat less (of the order of 5%) than those for the corresponding runs with pentamethylbenzene. These kinetic isotope effects are similar to those obtained for bromination of pentamethylbenzene in acetic acid,[7] and they show no dependence on the sodium bromide concentration from 0.0625 to 0.500 M. If the formation of the σ complex is rate determining, the change in hybridization at the reaction site would lead to a kinetic isotope effect[8] of less than one. On the other hand if the rate of loss of the proton is rate determining, the kinetic isotope effect would be much larger than one. Thus the small kinetic isotope effect of 1.05 is in accord with the two-step mechanism if the second step makes only a small contribution to the overall rate of the reaction. Therefore the observed decrease in k_1 values with increasing sodium bromide concentration (total salt concentration = 0.500 M) must be due primarily to differences in the effects of sodium perchlorate and sodium bromide on the activity coefficients of the reactants and the activated complex.

If bromide ion and the solvent both function as bases in eq 3, the rate of the reaction would be given by eq 9.

$$\frac{d(\mathrm{ArBr})}{dt} = \frac{k_1(\mathrm{ArH})(\mathrm{Br_2})}{k_{-1}(\mathrm{Br^-}) + k_2 + k_2'(\mathrm{Br^-})} \times [k_2 + k_2'(\mathrm{Br^-})] \quad (9)$$

If $k_2'(\mathrm{Br^-})$ were much greater than k_2, the rate of reaction would not be altered by an increase in sodium bromide concentration. In view of the large corrections required for tribromide ion formation and the large salt effects encountered, it is not possible to reach a definitive conclusion about the relative abilities of bromide ion and solvent to function as bases in the bromination of mesitylene.

It is interesting to note that a plot of the logarithms of k_1 values for mesitylene (Table I) vs. the square roots of the total salt concentrations of the medium is linear up to 0.100 M salt concentration. A single line accommodates the points both for runs in which the salt was sodium bromide and for runs in which NaBr-$\mathrm{NaClO_4}$ mixtures were used. Above 0.100 M salt concentration deviations from linearity occur which become more marked when sodium bromide is the added salt. The extrapolated value of k_1 at zero sodium bromide concentration is 0.221 L $\mathrm{mol^{-1}\,s^{-1}}$. This value is in reasonable agreement with a value of $k_0/(\mathrm{Mes}) = 0.264$ L $\mathrm{mol^{-1}\,s^{-1}}$ obtained for a rate run in 10-cm cells at 25.3 ± 0.3 °C using 0.0095 M mesitylene and 1.9×10^{-4} M bromine with no added salts (the first-order plot was linear to 70% reaction).

The results of this investigation of the reaction of bromine with mesitylene or with pentamethylbenzene under conditions such that the rate is first order in bromine provide no evidence of a decrease in rate (after correction for tribromide formation and specific salt effects) with increasing sodium bromide concentration. Thus it is evident that the earlier investigations[4] at higher bromine concentrations cannot be interpreted by eq 4 unless terms of higher order than one in bromine are included. For example, for a rate run in which initial mesitylene and bromine concentrations were 0.019 and 0.00567 M and there were no added salts the calculated initial rate using eq 7 with $k_1 = 0.264$ L $\mathrm{mol^{-1}\,s^{-1}}$ is 2.84×10^{-5} mol $\mathrm{L^{-1}\,s^{-1}}$. The observed initial rate[4b] was about ten times faster (27×10^{-5} mol $\mathrm{L^{-1}\,s^{-1}}$).

Acknowledgments. The authors wish to thank Paul Bruins and Sheldon Ball for the mass spectrographic and NMR analyses and Professor Robert K. Brinton for assistance in interpreting the mass spectral data.

References and Notes

(1) (a) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution", Butterworths, London, 1959, Chapter 9; (b) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds", Elsevier, Amsterdam, 1965, Chapter 5; (c) E. Baciocchi and G. Illuminati, *Prog. Phys. Org. Chem.*, **5**, 9 (1967).
(2) W. M. Schubert and J. L. Dial, *J. Am. Chem. Soc.*, **97**, 3877 (1975).
(3) (a) P. C. Myhre, G. S. Owen, and L. L. James, *J. Am. Chem. Soc.*, **90**, 2115 (1968); (b) H. J. Reich and D. J. Cram, *ibid.*, **91**, 3505 (1969).
(4) (a) R. M. Keefer, A. Ottenberg, and L. J. Andrews, *J. Am. Chem. Soc.*, **78**, 255 (1956); (b) R. M. Keefer and L. J. Andrews, *ibid.*, **78**, 3637 (1956); (c) L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 1412 (1957); (d) R. M. Keefer and L. J. Andrews, *J. Org. Chem.*, **31**, 541 (1966).
(5) R. Josephson, R. M. Keefer, and L. J. Andrews, *J. Am. Chem. Soc.*, **83**, 3562 (1961).
(6) T. W. Nakagawa, L. J. Andrews, and R. M. Keefer, *J. Phys. Chem.*, **61**, 1007 (1957).
(7) E. Baciocchi, G. Illuminati, G. Sleiter, and F. Stegel, *J. Am. Chem. Soc.*, **89**, 125 (1967).
(8) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).