2-butenes are fully consistent with formation of strongly bridged bromonium ion intermediates of the type originally postulated by Roberts and Kimball.[14] The nature of the bromine participation in such intermediates is clearly quite different from any participation which may be present in the intermediates formed by bromine addition to phenyl-substituted olefins such as styrenes or stilbenes.

Experimental Section

Materials. Lithium perchlorate, lithium bromide, and sodium acetate were the best commercial grades available and were dried before use over P_2O_5 at 140° (0.1 mm) for 48 hr. Acetic acid (C.I.L. Glacial) was purified by refluxing for 48 hr with a calculated 2% excess of acetic anhydride, followed by fractionation through a 75-cm column packed with glass helices. The fraction boiling at 118.1° was collected and stored in an automatic buret fitted with drying tube. Only samples with minimum melting point of 15.58° were used in reactions. The other solvents were purified by standard methods[29] and fractionally distilled before use. Pure samples of the olefins were prepared or obtained as described previously.[28]

Product Analysis. Details of the addition procedures used have also been given previously.[28] Products of reactions in acetic acid, acetic anhydride, and dioxane were isolated by the extraction procedure described previously.[28] Products of reactions in dichloromethane, tetrachloroethane, and nitrobenzene were obtained by direct evaporation of the solvent. Providing these evaporations were carried out at room temperature for a minimum length of time analysis of the concentrates gave results within 1–2% of those obtained by direct glpc analysis of the reaction solutions.

Determination of percentage compositions of product mixtures was carried out either by nmr analysis as described previously or by calibrated glpc analysis, or by both methods. The results obtained by each method were found to be in good agreement and were individually reproducible to within ±1% for most reaction mixtures. Product structures were determined as described previously.[28]

Acknowledgments. The continued financial support of the National Research Council and awards of Studentships to J. H. R. are gratefully acknowledged. We also wish to thank Professor George H. Schmid for several valuable discussions.

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[29] (29) See Weissberger, *et al.*, footnote *a*, Table III.

Polar Additions to the Styrene and 2-Butene Systems. III. Kinetics and Linear Free Energy Relationships

John H. Rolston and Keith Yates

Contribution from the Department of Chemistry, University of Toronto, Toronto, Canada. *Received October 5, 1968*

Abstract: The rates of bromination of styrene and its six side-chain methyl-substituted derivatives have been measured in acetic acid using a potentiometric method. The observed rate constants (which are composites of the molecular bromine and tribromide ion processes) show no simple dependence on the number of methyl groups attached to the double bond, unlike similar reactions of the ethylene system. This plus the fact that α-methyl substitution gives significant rate enhancements, whereas β substitution produces little or no effect, is taken as evidence for an unsymmetrical charge distribution at the transition state for bromine additions to styrene systems. The rates of bromination of eight *meta*- and *para*-substituted styrenes have also been investigated under similar conditions and the separated rate constants for bromine and tribromide ion attack have been obtained from a study of the dependence of k_{obsd} on added bromide, and measurement of the tribromide formation constant. Both sets of rate constants give better correlations against σ^+ than σ, with $\rho_{Br_2} = -4.21$ and $\rho_{Br_3^-} = -2.02$. The magnitude of the former ρ value is taken as evidence for a transition state in which a substantial charge is developed at C_α, similar to that expected for a benzylic type carbonium ion. The latter ρ value is interpreted in terms of an electrophilic attack by tribromide ion in which much less cationic charge is developed on C_α at the transition state, rather than in terms of a kinetically equivalent bromide ion catalyzed attack of molecular bromine. This conclusion is based on consideration of the relationship between the kinetics and observed product distribution. A simple mechanistic scheme is developed which is consistent with both the observed kinetics and product distribution.

Kinetic studies of the polar addition of bromine to olefins in both aqueous and organic solvents have shown that there are several paths available for the reaction.[1,2] These include both first- and second-order bromine processes, as well as the kinetic equivalent of a bromide ion catalyzed addition of molecular bromine. It has been shown[3,4] that high kinetic orders with respect to bromine are generally confined to the more concentrated bromine solutions, and that these processes become less important kinetically as the temperature is raised and as the solvent becomes more polar, *e.g.*, as water is added to acetic acid.[5]

Additions of bromine to some unsaturated compounds, particularly vinyl and allyl halides, in the presence of halide ions follow a kinetic equation involving the concentration of olefins and bromine and halide ion.[2] The effectiveness of this "halide ion catalyzed process" appears to be sensitive to olefin structure

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[1] (1) B. E. Swedlund and P. W. Robertson, *J. Chem. Soc.*, 630 (1947).

[2] (2) K. Nozaki and R. A. Ogg, Jr., *J. Am. Chem. Soc.*, **64**, 697, 704, 709 (1942).

[3] (3) I. Ting and P. W. Robertson, *J. Chem. Soc.*, 628 (1947).

[4] (4) P. W. Robertson, N. T. Clare, K. J. McNaught, and G. W. Paul, *ibid.*, 335 (1937),

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and to the solvent. For example, added bromide ions accelerate the addition of bromine to many olefins in acetic acid,[6] whereas additions in methanol[7] and in water[8] are generally inhibited. Kanyaev's results[8] indicate that the "halide ion catalyzed process" becomes kinetically more important for less reactive olefin systems, although some doubt has been cast[9] on this conclusion. Other authors[9,10] have interpreted kinetic terms involving the bromide ion concentration as arising from direct electrophilic attack by tribromide ions, which would be kinetically indistinguishable from a bromide ion catalyzed addition of molecular bromine.

The relationship between the kinetics of bromination and the distribution of product between dibromide and solvent-incorporated product has been investigated[8,9] for a wide range of olefins. Such studies can be valuable in considering possible alternative reaction mechanisms, but further systematic studies of this type are needed to test suggested mechanistic schemes.[8,9,11] Structure reactivity relationships[10,12] have already shown that electron-donating substituents increase the rate of bromination, in accord with generally established electrophilic nature of these additions. However further work is needed in this area also, to identify the separate structural dependence of the various possible modes of reaction.

In the present investigation, detailed kinetic studies of the addition of bromine to a variety of styrene derivatives have been carried out to complement our previous investigations[13,14] of product distributions and stereochemistry, and to throw further light on the detailed mechanisms, particularly the nature of the reaction intermediates.

Results and Discussion

Rates of Bromination of Side-Chain-Substituted Styrenes. The rates of bromine addition to 15 substituted styrenes in acetic acid were investigated by means of a potentiometric method based on the rate of change of the bromine–bromide redox potential. The kinetics of these additions are known[5,10] to exhibit both first- and second-order dependence on bromine, but a recent spectrophotometric study[10] of the rates of brominations of some ring-substituted styrenes in acetic acid showed that the second-order bromine term only becomes significant in the concentration range 10^{-2}–10^{-3} M bromine. The presently used potentiometric method is capable of following the reactions at much lower initial bromine concentrations ($\sim 10^{-4}$ M) than this, where the second-order term in bromine would not be expected to contribute to the over-all rate of reaction. The excellent linearity of all plots of observed potential against time found in the present study fully substantiates this assumption. A typical set of results is shown in Figure 1 where the linearity extends over some 45–50 mV, corresponding to consumption of better than 95% of the initial bromine. The observed rate constant, k_{obsd}, is a composite second-order rate constant involving two competing processes (*i.e.*, bromination by molecular bromine and by the tribromide ion or its kinetic equivalent) since the potentiometric method requires the presence of a large and effectively constant bromide concentration ([LiBr] = 0.1 M).

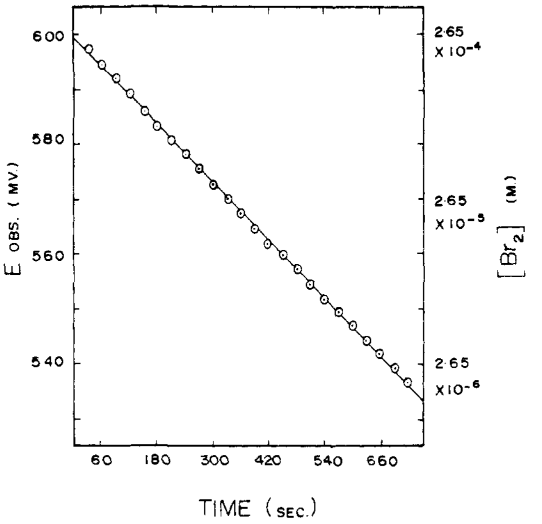

Figure 1. Plot of observed potential *vs.* time for the reaction of 3-chlorostyrene with bromine at 25°; $[Br_2]_0 = 2.65 \times 10^{-4}$ M; $[\text{styrene}]_{\text{av}} = 9.78 \times 10^{-3}$ M; [LiBr] = 0.1 M; slope 8.71×10^{-2} mV sec^{-1}.

The rates of bromination of styrene and its seven side-chain methyl-substituted derivatives were measured under pseudo-first-order conditions ([olefin] = 10^{-2} M) and the observed second-order rate constants are given in Table I. These results show that styrenes with α-methyl substituents are substantially more reactive than those with only β-methyl groups. For example, α-methylstyrene is at least 60 times more reactive than either *cis*- or *trans*-β-methylstyrene. The fact that the α-methylstyrenes which also have β-methyl groups show less of an increase in rate can be attributed to steric effects as the reaction center becomes more crowded. Steric effects have been noted previously[14] for α-methylstyrenes, whereas β-methyl substitution alone has little effect on the rate. It is clear that there is no simple relationship between the number of methyl groups and the rate of bromine addition, in sharp contrast to the effects of methyl substitution on the rate of bromination of ethylene in methanol[15,16] ([NaBr] = 0.2 M) and the rate of epoxidation of ethylene by peracetic acid[17] as shown in Figure 2. The reported data for the ethylene derivatives yield remarkably linear relationships when plotted simply against the number of methyl groups attached to the double bond, indicating highly symmetrical charge distributions at the transition states of these two reactions.[18,19] Similar effects have been noted for the ionic chlorination of substituted ethylenes.[20] On the other hand, the results of substitution on the styrene

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(7) P. D. Bartlett and D. S. Tarbell, *J. Am. Chem. Soc.*, **58**, 466 (1936).

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(9) J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 3260 (1963).

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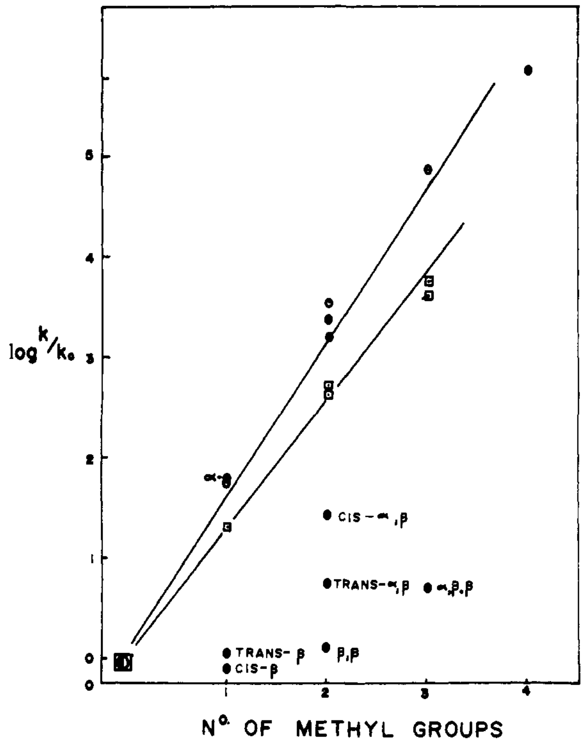

Figure 2. Comparison of rate dependence of bromination of styrene (●), bromination of ethylene[15,16] (○), and epoxidation of ethylene[17] (□), on methyl substitution.

system show that the transition state for bromination must have a highly unsymmetrical charge distribution with most of the positive charge being located on C_α. This resembles the effect of substitution on the acid-catalyzed hydration of ethylene,[18] where the rate-determining step involves proton addition to give a classical carbonium ion, with the charge being effectively localized on only one carbon of the original double bond.[21] The effects observed in the present study provide further support for the previously stated idea[13,14,22] of a benzylic carbonium ion intermediate for bromine addition to the styrene system, and are inconsistent with an even approximately symmetrical charge distribution, such as would be expected for a cyclic bromonium ion.[23]

Since the rate constants for bromination of both styrenes and ethylenes in Figure 2 are composites of two kinetic terms, some ambiguity exists as to the charge distributions in the transition states for the competing molecular bromine and tribromide ion processes. It was therefore desirable to separate the rate constants for bromine additions to typical styrenes so that the structural dependence of each contributing process could be examined individually. This required a knowledge of the bromide–tribromide ion equilibrium constant.

Table I. Effect of Side-Chain Methyl Substitution on the Rate of Bromination of Sytrene in Acetic Acid[a] at 25°

Substitution	k_{obsd}[b]	Substitution	k_{obsd}
None	11.2 ± 0.1[c]	β,β	14.7 ± 0.2
α	680 ± 20	*cis*-α,β	300 ± 20
trans-β	12.3 ± 0.8	*trans*-α,β	61.7 ± 0.4
cis-β	8.89 ± 0.1	α,β,β	56 ± 0.3

[a] 0.1 *M* LiBr added. [b] In l. mole^{-1} sec^{-1}. [c] Mean deviation based on at least three runs.

Table II. Formation Constants for Tribromide Ion in Acetic Acid at 25°

[LiClO$_4$], *M*	ε_{Br_2}[a]	$\varepsilon_{Br_3^-}$[a]	K_f[b]
0	189	777	92 ± 2
0.05	181	757	103 ± 1
0.10	179	736	136 ± 3

[a] Measured at 390 mμ. [b] In l. mol^{-1}.

Table III. Effect of Ring Substitution on the Rate of Bromination of Styrene in Acetic Acid[a] at 25°

Substituent	k_{obsd}[b]	σ[c]	σ^+[d]
4-Fluoro	14.5 ± 0.1	0.071	−0.073
Hydrogen	11.2 ± 0.2	0.000	0.000
4-Chloro	3.26 ± 0.01	0.235	0.114
4-Bromo	3.60 ± 0.01	0.241	0.150
3-Chloro	0.672 ± 0.01	0.382	0.399
3,4-Dichloro	0.439 ± 0.004	0.572[e]	0.476[f]
3-Nitro	0.140 ± 0.001	0.719	0.674
4-Nitro	0.083 ± 0.002	0.787	0.790

[a] With [LiBr] = 0.1 *M*. [b] In l. mol^{-1} sec^{-1}. [c] Taken from ref 31. [d] Taken from ref 32. [e] Based on p*K* value of 3,4-dichlorobenzoic acid. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths & Co. (Publishers), Ltd., London, 1965, pp 526, 530. This value is 0.927 of the sum of the 3-chloro and 4-chloro σ values. [f] Estimated as 0.927 ($\sigma^+_{3\text{-Cl}} + \sigma^+_{4\text{-Cl}}$).

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

$$K_f = \frac{[Br_3^-]}{[Br_2][Br^-]}$$

The Bromide–Tribromide Equilibrium. Although several values of the tribromide formation constant, K_f, have been reported[24] for acetic acid–water solutions, it was necessary to redetermine the constant under the exact conditions used for kinetic measurements. Values of K_f were determined spectrophotometrically using the absorbance of solutions of known concentration of bromine and bromide at 390 mμ.[25] Application of the criterion suggested by Person[26] to the data showed that the observed equilibrium constant can be considered reliable and that tribromide ion is being formed in the solutions used. It is interesting to compare the value of K_f obtained (92 ± 2 l. mol^{-1}) using lithium bromide as the source of bromide ion, with the values of 125 and 53 ± 2 l. mol^{-1} reported by Keefer and Andrews[24] using hydrogen bromide and sodium bromide, respectively. This marked dependence of K_f on the source of bromide ion shows that the trihalide ion stability depends on the nature of its counterion. This is not

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(21) P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *J. Am. Chem. Soc.*, **79**, 3274 (1957).

(22) R. J. Fahey and H.-J. Schneider, *ibid.*, **90**, 4429 (1968).

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Table IV. Rate Data for the Bromination of 3-Chlorostyrene

[LiBr],[a] M	dE_{obsd}/dt, mV sec^{-1}	[Styrene] × 10^3, M	k_{obsd}[b] × 10^1, l. mol^{-1} sec^{-1}	$(1 + K_f[LiBr])k_{obsd}$
0.10	9.05	9.87	6.7	6.85
	8.71	9.78		
0.09	9.26	9.89	6.98	6.51
	9.33	9.89		
0.08	9.46	9.91	7.08	6.03
	9.38	9.86		
0.06	9.62	9.84	7.23	5.02
	9.59	9.89		
0.05	9.64	9.86	7.40	4.55
	10.0	9.89		
0.03	10.2	9.85	7.80	4.44
	10.5	9.90		
0.02	10.8	9.89	8.14	2.77
	10.8	9.88		
0.01	12.0	9.86	8.98	2.04
	11.9	9.85		

[a] $LiClO_4$ added to give total salt concentration of 0.1 M. [b] Mean of two runs.

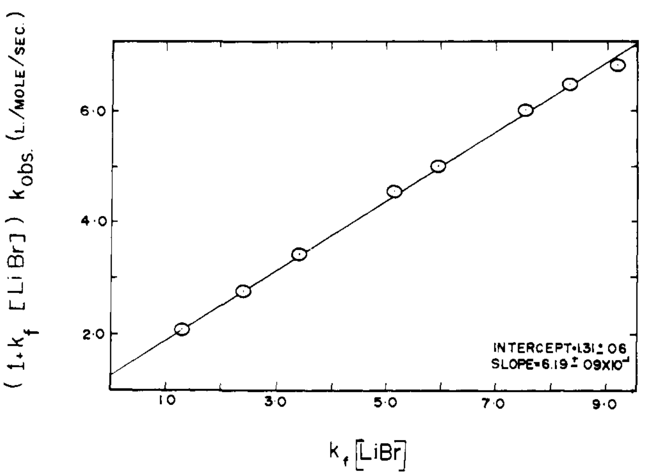

Figure 3. Plot of $(1 + K_f[LiBr])k_{obsd}$ *vs.* $K_f[LiBr]$ for separation of rate constants k_2 (intercept) and $k_{Br_3^-}$ (slope) for bromination of 3-chlorostyrene at 25°.

surprising in anhydrous acetic acid, since little dissociation[27] of either added electrolytes or trihalide ion pairs is to be expected. Even in aqueous solution the formation constant shows a slight dependence on the counterion.[28] Since the ratio of tribromide to molecular bromine is of critical importance in the analysis of the kinetic data, the effect of added $LiClO_4$ on the equilibrium constant was also investigated. The data are summarized in Table II. The value of K_f increases with added $LiClO_4$, similar to the effect noted[29] in aqueous solution with increasing ionic strength. In aqueous media the increase in the apparent equilibrium constant with added electrolytes presumably reflects an increase in the bromine activity coefficient. Superimposed upon this in acetic acid would be the effect of added $LiClO_4$ on the ion-pair dissociation constant of LiBr. Thus by using concentrations instead of activities to obtain an apparent equilibrium constant it is not surprising there is some variation in the magnitude of K_f with the medium. Additional values of K_f were obtained where necessary by interpolation from a linear plot of K_f *vs.* the square of the LiBr concentration.

Kinetics of Bromination of Ring-Substituted Styrenes. The rates of bromination of eight *meta-* and *para-*substituted styrenes[30] were first measured in acetic acid with added LiBr (0.1 M) with the initial $[Br_2] = 5 \times 10^{-4}$ M. The rate constants (k_{obsd}) obtained under these conditions are given in Table III. These rates [log $(k/k_{styrene})$] were found to correlate reasonably well ($r = 0.987$) with σ substituent constants[31] ($\rho = -2.85$), but considerably better ($r = 0.996$) with the σ^+ scale,[32] yielding a ρ value of similar magnitude (−2.65). The fact that the 4-fluoro derivative reacts faster than the parent styrene is also more in accord with the σ^+ scale. These results are consistent with an electrophilic attack in which significant conjugation with phenyl is developed at the transition state. The above ρ values can be compared directly with the value obtained by Dubois[12] (−4.30) for analogous brominations in methanol in the presence of bromide ([NaBr] = 0.2 M). This considerably more negative value shows that substituent effects on the composite rate of bromination are much more pronounced in methanol than in acetic acid. However more mechanistic significance could be attached to ρ values based on the separated rate constants rather than these composite values.

The rate equation for bromination in acetic acid in the presence of bromide ion is given by

$$-\frac{d[Br_2]_a}{dt} = k_2[Br_2][S] + k_2'[Br_2][Br^-][S] + k_3[Br_2]^2[S] \quad (1)$$

where $[Br_2]_a$ is the total analytical bromine concentration. At low bromine concentrations, the third term can be neglected, and this equation rearranges to

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(27) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 (1956); I. M. Kolthoff and S. Bruckenstein, *ibid.*, **78**, 1 (1956).

(28) D. B. Scaife and H. J. V. Tyrrell, *J. Chem. Soc.*, 386 (1958).

(29) R. O. Griffith, A. McKeown, and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

(30) Separation of rate constants was not attempted for any of the previously studied side-chain-substituted styrenes since some of their observed rates are near to the limit which is accurately measurable with the present method.

(31) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

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Table V. Rate Dependence on Bromide Concentration at Constant Ionic Strength

[LiBr],[a] M	k_{obsd}[b]							
	4-Fluoro × 10^{-1}	Styrene × 10^{-1}	4-Chloro × 10^0	4-Bromo × 10^0	3-Chloro × 10^1	3,4-Dichloro × 10^1	3-Nitro × 10^1	4-Nitro × 10^2
0.100	1.45	1.11	3.26	3.60	6.72	4.39	1.40	8.28
0.090	1.53	1.18	3.42	3.62	6.98	4.42	1.39	7.92
0.080	1.62	...	3.55	3.60	7.08	4.49	1.36	8.01
0.075	...	1.24	...	...	...	...	...	...
0.060	1.88	1.40	3.88	4.07	7.23	4.59	1.36	8.11
0.050	2.06	1.56	4.20	4.12	7.39	4.64	1.36	7.80
0.040	...	1.73	...	...	...	...	...	...
0.030	2.73	...	5.08	5.14	7.81	4.81	1.29	7.59
0.025	...	2.30	...	...	...	...	...	...
0.020	3.51	2.55	6.14	5.81	8.14	4.87	1.22	6.88
0.010	5.04	3.58	7.62	7.29	8.98	4.95	1.13	6.18
k_2	108 ± 1.0[c]	77 ± 1.0	15.6 ± 0.3	13.7 ± 0.2	1.3 ± 0.06	0.65 ± 0.03	0.067 ± 0.07	0.031 ± 0.03
$k_{Br_3^-}$	4.1 ± 0.2[d]	3.8 ± 0.2	1.95 ± 0.05	2.40 ± 0.03	0.619 ± 0.01	0.420 ± 0.005	0.147 ± 0.001	0.087 ± 0.001

[a] $LiClO_4$ added to give total salt concentration of 0.1 M. [b] Observed second-order rate constants in l. mole^{-1} sec^{-1} reported as means of at least two runs. Mean deviation ±0.67% based on all runs. [c] Standard deviation of least-squares intercept. [d] Standard deviation of least-squares slope.

$$\frac{1}{[S]}\frac{d[Br_2]_a}{dt} = (k_2 + k_2'[Br^-])[Br_2] \tag{2}$$

Taking into account the tribromide equilibrium the total bromine is given by $[Br_2]_a = [Br_2] + [Br_3^-] = [Br_2]\cdot(1 + K_f[Br^-])$ but the reaction is followed by measuring free bromine. Therefore eq 2 becomes

$$-\frac{1}{[S]}\frac{d[Br_2]}{dt} = \frac{(k_2 + k_2'[Br^-])[Br_2]}{1 + K_f[Br^-]}$$

$$= k_{obsd}[Br_2] \tag{3}$$

where [S] is effectively constant, being present in large excess. Thus the observed second-order rate constant in eq 3 can be expressed

$$(1 + K_f[Br^-])k_{obsd} = k_2 + k_2'[Br^-] \tag{4a}$$

$$= k_2 + k_{Br_3^-}K_f[Br^-] \tag{4b}$$

These alternatives arise because the second term can be expressed either in terms of a bromide ion catalyzed addition of molecular bromine with rate constant k_2' as in (4a) or in terms of a direct attack by tribromide as in (4b) with rate constant $k_{Br_3^-}$. Using either of these kinetically equivalent formulations the separated rate constants can be obtained from a study of the variation of k_{obsd} with added bromide. Since k_2' is easily derivable from $k_{Br_3^-}$, eq 4b was arbitrarily chosen to separate the rate constants. The rates of bromination of the eight phenyl-substituted styrenes were studied as a function of added LiBr, with $LiClO_4$ added to maintain constant ionic strength. Detailed rate data obtained for 3-chlorostyrene are given as an example in Table IV and more abbreviated results are given for the other styrenes in Table V. The separated rate constants were obtained from plots of $(1 + K_f[LiBr])k_{obsd}$ against K_f[LiBr], similar to that shown in Figure 3. The excellent linearity of these plots establishes that the kinetics given in eq 2–4 are being followed by each styrene over the range studied. The values of k_2 and $k_{Br_3^-}$ obtained from the slopes and intercepts of these plots for each of the eight substituted styrenes are also listed in Table V.

Each set of rate constants correlates well against the σ^+ substituent constants as shown in Figure 4. The most striking feature of these plots is the large difference in slope. The ρ value for the molecular bromine process is −4.21 while that for the tribromide process is only −2.02, showing that the former process is more than 100 times as sensitive to the effects of ring substituents. It is also significant that both k_2 ($r = 0.998$) and $k_{Br_3^-}$ ($r = 0.995$) give much better correlations against σ^+ than against σ, where the plots show some scatter ($r = 0.983$ and 0.988, respectively). This is taken as further evidence for an unsymmetrical charge distribution in the transition state for each process, with most of the charge being developed at C_α in direct conjugation with phenyl. For the molecular bromine process this closely parallels the charge distribution in the transition state for the solvolysis of phenyldimethyl-

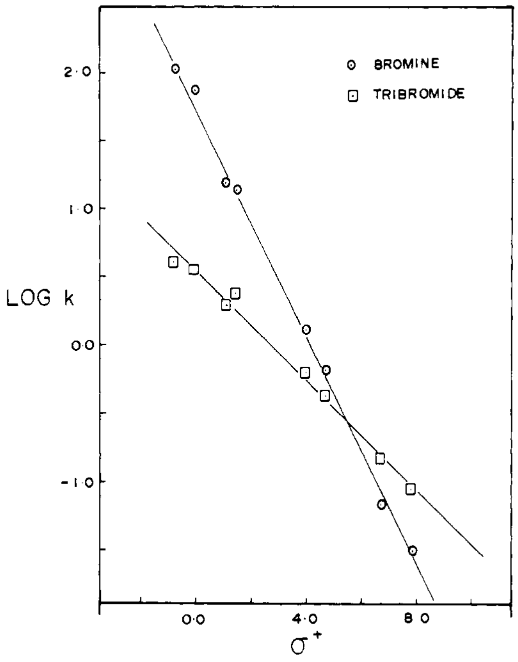
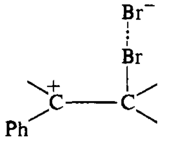


Figure 4. Plot of separated rate constants for bromination of substituted styrenes against σ^+.

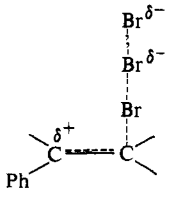
Table VI. Rate Dependence on Bromide Concentration with No Added KiClO$_4$

[LiBr], *M*	k_{obsd} Styrene × 10^{-1}	3-Chloro × 10^1	3,4-Dichloro × 10^1	3-Nitro × 10^1	K_f[LiBr]
0.10	1.11	6.81	4.31	1.43	9.20
0.09	1.06	7.11	...	1.36	8.28
0.08	1.06	6.94	4.20	1.35	7.36
0.06	1.04	6.73	4.09	1.27	5.52
0.05	1.02	6.35	4.02	1.26	4.60
0.03	1.02	6.13	3.65	1.09	2.76
0.02	1.04	5.70	...	1.05	1.84
0.01	1.11	4.59	2.89	0.96	0.92
k_2	8.9	0.23	0.089	0.012	
$k_{Br_3^-}$	10.9	0.74	0.470	0.153	

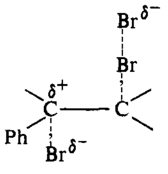
carbinyl chlorides studied by Brown,[33] who found a ρ value of −4.54 against σ^+ for the reaction in 90% aqueous acetone. This suggests that in the transition state I for the molecular bromine process the positive charge is almost fully developed at C_α with little significant delocalization onto C_β or bromine. However, a weak electrostatic interaction[14] between C_α and bromine can not be ruled out.



I



II



III

The lower demand on the substituent in the tribromide process shows that much less charge is being developed at C_α in the transition state. This is consistent with the decreased electrophilicity of tribromide ion, compared with bromine, and the fact that two bromine–bromine bonds are being broken. This would be expected to result in a less fully developed charge at C_α as shown in II. However the same ρ value[34] is equally consistent with a transition state such as III for the kinetically equivalent bromide ion catalyzed process, which would also be expected to result in less fully developed charge at C_α. The difficult question of which of these processes is more probable will be discussed in a later section.

It is interesting to note that a ρ value of −2.24 has been reported previously[11] for bromination of styrenes in acetic acid. This involved a study of only deactivated styrenes, with no added salts, and the ρ was based on the σ scale. Since no bromide was added to the system this value refers to the molecular bromine process only but it is quite different in magnitude from the ρ value obtained for the similar process in the present investigation. Since even small concentrations of LiClO$_4$ are known to have pronounced effects on some reactions,[35] separation of rate constants was repeated for four of the substituted styrenes in the absence of LiClO$_4$. The rate constants obtained as before are given in Table VI. Plots of these separated rate constants against σ^+ again gave excellent linearity, with $\rho_{Br_2} = -4.26$ and $\rho_{Br_3^-} = -2.78$. It is clear from this that the presence of LiClO$_4$ does not have sufficient effect on the mechanism of the molecular bromine process to explain the large difference between the present ρ_{Br_2} value and that reported earlier using pure acetic acid as solvent.

It has been noted in the present study that the σ^+ substituent constants generally give much better correlations than the σ constants. If the previously reported data[10] for pure acetic acid are replotted against the σ^+ constants a definite curvature occurs, as shown in Figure 5. This type of behavior has been used as a method[36] of indicating a change of mechanism in a reaction series. For the present bromine additions this change of mechanism can be associated with two possible methods of stabilization of the positive charge, *i.e.*, delocalization into the phenyl ring and participation by neighboring bromine. It is therefore possible that the transition states for the molecular bromine process in pure acetic acid can vary as the reactivity of the olefin is changed.

Highly deactivated styrenes (*i.e.*, nitrostyrenes) may not easily permit dispersal of a charge developed on the α-carbon which is similar in magnitude to that observed for the solvolysis of the phenyldimethylcarbinyl chlorides[33] and thus may require significant neighboring bromine participation. This would reduce the rate dependence on ring substitution. In support of this idea, the ρ value for the bromination of 3-fluoro-, 3-chloro-, 3-bromo-, and 3,4-dichlorostyrenes in pure acetic acid using the σ^+ scale is about −4.5 (see Figure 5). In contrast that based upon the 3-nitro- and 4-nitrostyrenes alone is about −2.0. Hence, the charge distribution in the transition state can vary with the styrene reactivity.

With the addition of electrolytes to acetic acid the medium could be altered sufficiently so that this second mode of stabilization, *i.e.*, by neighboring bromine, is no longer as necessary. Thus the ρ value in the presence of added electrolyte remains high (−4.26) throughout the full range of styrene reactivity, as shown in Figure 4.

That added electrolytes do affect the molecular bromine process can be seen from a comparison of the data

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(33) Y. Okamoto, T. Inukai, and H. C. Brown, *J. Am. Chem. Soc.*, **80**, 4972 (1958).

(34) It could be argued that this lower ρ value should be associated with neighboring bromine participation and charge delocalization in the side chain, whichever process ($k_{Br_3^-}$ or k_2') is actually involved. However this is not consistent with the observed effects of side chain methyl substitution discussed previously. Under the conditions used to obtain these composite rate constants approximately 80% of total reaction is proceeding by way of the $k_{Br_3^-}$ (or k_2') process.

(35) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).

(36) P. R. Wells, *Chem. Rev.*, 63, 171 (1963).

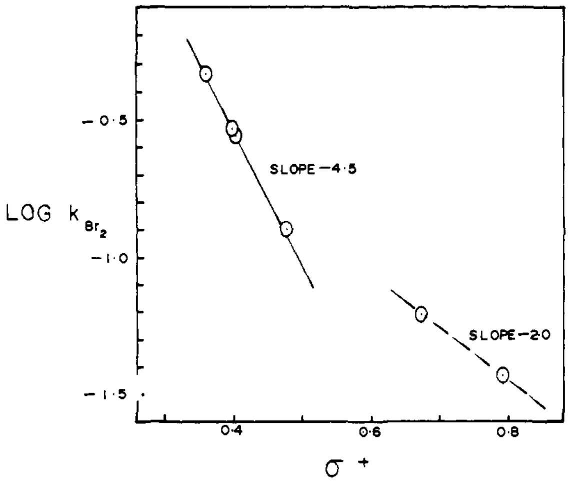

Figure 5. Plot of rate constants *vs.* σ^+ for bromination of substituted styrenes (by molecular bromine only) in pure anhydrous acetic acid at 25° (rate data taken from ref 10).

in Tables V and VI. where the addition of $LiClO_4$ results in roughly sevenfold increases in rate. This type of positive salt effect has been reported previously[37,38] and is to be expected since the transition state of the molecular bromine process involves an increased charge separation over that in the initial state. In contrast, the tribromide process shows a small negative salt effect. A similar decrease in rate with increasing ionic strength has been observed in an earlier study.[2] Some degree of caution is warranted in the interpretation of this effect, since one set of tribromide ion rate constants was not obtained at constant ionic strength, but if this negative salt effect were real it would suggest that the transition state for the tribromide ion process is less polar than the initial state.

The Relative Reactivities of Br_2 and Br_3^-. The relative reactivities of these reagents have been investigated by both Bell[9] and Kanyaev[8] for brominations in aqueous media. Their results cover a wide range of olefin reactivities and appear to yield opposite conclusions. Kanyaev reports that $k_{Br_3^-}/k_{Br_2}$ decreases steadily with increasing reactivity of the olefin, while Bell's results show no general relation between $k_{Br_3^-}/k_{Br_2}$ and reactivity. In view of these conflicting views it was of interest to compare the reactivity ratios for the present series of structurally related styrenes. The reactivity ratios, $k_{Br_3^-}/k_{Br_2}$ can easily be obtained from the rate constants separated at both constant and varying ionic strength which are given in Tables V and VI. Since the two rate processes show opposite salt effects it is only strictly valid to compare rate ratios obtained at constant ionic strength, but nonetheless both sets of reactivity ratios decrease smoothly as styrene reactivity increases, which is in accord with Kanyaev's results. However Bell's results were based on a much wider structural range than either the present limited set of *meta-* and *para-*substituted styrenes or the olefins investigated by Kanyaev.

The higher reactivity of the tribromide ion than molecular bromine toward the more deactivated styrenes is difficult to understand in terms of the general accepted mechanism for halogen addition.[11] Both Br_2 and Br_3^- are considered to form a highly reactive intermediate, usually taken to be some type of carbonium ion, in the rate-determining step of the reaction. Subsequent rapid reaction of this intermediate with either a solvent molecule or a bromide ion leads to products. This mechanism supposes that both the bromine molecule and the tribromide ion attack the olefinic bond in an electrophilic manner to give the same cationic intermediate. However, it is hardly likely in this case that the negatively charged tribromide ion could behave as a more powerful electrophile than a bromine molecule. Hence, such a mechanism[39] fails to accommodate the observed fact that $k_{Br_3^-}/k_{Br_2}$ is greater than unity for the most deactivated styrenes.

Table VII. Product Ratios for Selected Styrenes in Acetic Acid at 25° with [LiBr] = 0.10 *M*

	Dibromide/acetoxy bromide ratios				
		Obsd[a]			
Styrene	Predicted	A	B	α	β[b]
Styrene	11.3	5.3	5.6	0.86	0.68
3-Chloro	30.0	14.4	...	0.94	0.72
3-Nitro	132	26.8	...	0.96	0.87

[a] Taken from ref 14. [b] Calculated from results in ref 14.

Two further kinetic schemes have been proposed. The scheme proposed by Kanyaev,[8] for aqueous brominations, is one in which dibromide is assumed to arise only from attack of the tribromide ion, and bromohydrin only by attack of molecular bromine. If this mechanism were operative in acetic acid the ratio of dibromide (SBr_2) to acetoxy bromide (S(OAc)Br) would be governed by the ratio of the rates for the two brominating species.

$$\frac{[SBr_2]}{[S(OAc)Br]} = \frac{k_{Br_3^-}[Br_3^-]}{k_{Br_2}[Br_2]} = \frac{K_f k_{Br_3^-}[Br^-]}{k_{Br_2}}$$

This hypothesis is kinetically equivalent to a second scheme proposed by Hine[11] in which an addition complex of bromine and olefin is formed in an equilibrium step, and then reacts with either bromide ion or solvent in the rate-determining step. Again, the product ratio would be given by the above expression.

In an attempt to assess the applicability of these schemes the ratio of dibromide to acetoxy bromide was calculated from the preceding expression using the rate constants separated without attempting to maintain constant ionic strength. The value of K_f was taken as 92.1/mol with a bromide ion concentration of 0.10 *M*. The calculated product ratios are compared in Table VII with those obtained experimentally under the same conditions. It is clear from Table VII that the predicted ratios do not agree with the observed ratios,[14] although they do suggest that a progressively larger amount of dibromide is to be expected as the styrene reactivity decreases. This parallels the trend in the observed product ratio using procedure A in which microdrops of neat bromine were added to a quantity of olefin dissolved in 50 ml of solvent. In procedure B the olefin

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(37) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 2838 (1950).

(38) P. W. Robertson, R. M. Dixon, W. G. M. Goodwin, I. R. MacDonald, and J. F. Scaife, *ibid.*, 294 (1949).

(39) This mechanism is also inconsistent with the large difference found between ρ_{Br_2} and $\rho_{Br_3^-}$ in the present work.

and bromine solutions were simultaneously added to a small volume of the solvent. However, the over-all poor agreement between the predicted and observed product ratios shows that the reaction schemes of Hine and Kanyaev are not generally applicable to the bromination of styrenes in acetic acid.

The results are also inconsistent with a bromide ion catalyzed addition of molecular bromine being responsible for the $k_{Br_3^-}$ (or k_2') term,[40] since such a process alone would be expected to give exclusively dibromide. In addition the competing uncatalyzed bromine process (k_{Br_2} term) is known[13,14] to give predominantly dibromide. Thus a combination of these two processes would be predicted to give even higher dibromide/acetoxy bromide ratios than those calculated in Table VII.

All the experimental facts can be accommodated by a modification of a reaction scheme recently proposed by Bell[42] in which two distinct carbonium ion type intermediates (such as I and II) are formed in competing reactions of the bromine molecule and the tribromide ion with the olefin. According to such a scheme the product ratio would not be related directly to the relative reactivities of Br_2 and Br_3^- but would depend upon the competition of a bromide ion with a solvent molecule for each of the intermediates. Such a scheme, formulated below, places no restriction on the relative reactivities of the two brominating agents.

$$\mathrm{S + Br_2} \xrightarrow{k_{Br_2}} \mathrm{R} \xrightarrow{\text{fast}} \beta\mathrm{SBr_2} + (1-\beta)\mathrm{S(OAc)Br}$$

$$\mathrm{S + Br_3^-} \xrightarrow{k_{Br_3^-}} \mathrm{R'} \xrightarrow{\text{fast}} \alpha\mathrm{SBr_2} + (1-\alpha)\mathrm{S(OAc)Br}$$

This scheme differs from that proposed by Bell in that the intermediate R is not assumed to react exclusively with solvent. This is known to be the case from our previous results which can be used to obtain values for β. The product distribution is now given by

$$\frac{[\mathrm{SBr_2}]}{[\mathrm{S(OAc)Br}]} = \frac{\beta k_{Br_2} + \alpha k_{Br_3^-} K_f[\mathrm{Br^-}]}{(1-\beta)k_{Br_2} + (1-\alpha)k_{Br_3^-} K_f[\mathrm{Br^-}]}$$

From the observed product ratios, values of α can now be calculated for styrene and 3-chloro- and 3-nitrostyrenes. These are also given in Table VII, and show that the fraction of each intermediate diverted to give solvent-incorporated product varies in a similar way with olefin reactivity. This is reasonable, as is the fact that the intermediate formed from tribromide attack gives much less solvent-incorporated product. This would be expected from the much smaller ρ value for this process, which indicates that R′ would be a much weaker electrophile than R toward the weakly nucleophilic acetic acid molecules.

Experimental Section

Reagents. Acetic acid, lithium bromide, and lithium perchlorate were obtained and purified as reported previously.[14] Pure samples of the styrenes were obtained or prepared as described previously.[13] Bromine solutions (~5 × 10^{-4} *M*) in acetic acid were prepared immediately before use and aliquots standardized against sodium thiosulfate using the "dead-stop" technique.[43] Thiosulfate solutions (4 × 10^{-3} *M*) prepared using reagent grade thiosulfate and conductivity water were standardized against potassium iodate.[44]

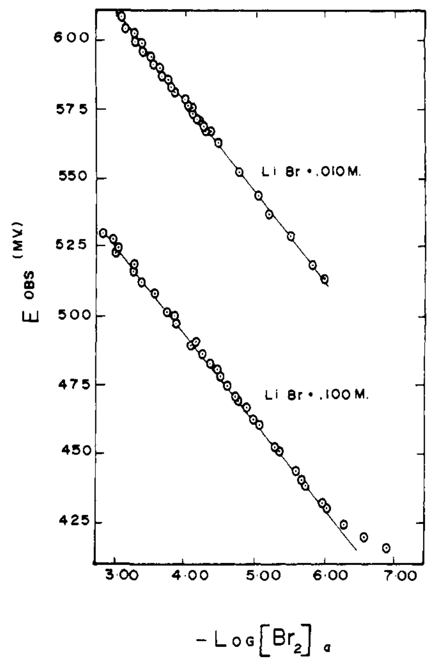

Figure 6. Verification of the Nernst equation for low concentrations of bromine in anhydrous acetic acid.

Apparatus. Potentials were measured with a calibrated precision pH meter (Beckman Model 1019) fitted with a platinum indicating electrode and modified calomel reference electrode. The indicating electrode was made from a cylinder (1 cm diameter by 2 cm) of platinum gauze fused to a platinum rod which was sealed into a tube connected to a standard taper glass stopper. The electrode was cleaned periodically by immersion in boiling nitric acid, followed by washing in distilled water and heating to redness in a bunsen flame. When not in use the electrode was stored in 0.2 *M* bromine in acetic acid saturated with LiBr. A commercial fiber junction calomel electrode (Beckman No. 39170) was modified for use in anhydrous acetic acid solutions by dismantling the electrode and replacing the internal element by a J-shaped glass element made from 2 mm internal diameter glass tubing. A fresh calomel paste, made from mercury and mercurous chloride and moistened with an electrolyte solution[27] of acetic acid saturated with NaCl and $NaClO_4$, was placed on top of a mercury pool in the bottom of the element. The element was resealed to the external tube and filled with the above electrolyte solution. Reference electrodes prepared in this manner gave steady, drift-free potentials in acetic acid for periods of several months. When not in use the tip of the electrode was kept immersed in a solution of the electrolyte. Both electrodes were fitted with shielded cables.

A cylindrical glass jar (200 ml) fitted with four standard taper joints was used as reaction vessel. The electrodes were inserted through two of the joints and a high speed stirrer (1500 rpm) through a third. The remaining inlet was used to inject reagent solutions under pressure from calibrated pipets. The mixing time was about 5 sec. The whole vessel was shielded by means of a grounded wire cage.

Kinetic Measurements. A solution of bromine (5 × 10^{-4} *M*) in acetic acid containing lithium bromide and perchlorate (total electrolyte 0.1 *M*) was placed in the reaction vessel, thermally equilibrated, and the initial potential observed. The reaction was started by injecting a known small volume of olefin (0.08 *M*) in acetic acid and the composite second-order rate constant (k_{obsd}) was then determined from the rate of change of the observed potential in mV sec^{-1}. The potential of the reaction cell, amplified by the pH meter, was fed into a variable-speed recorder and an adjustable "back-off" potential (Zero Displacement Accessory,

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(40) This is in contrast with recent results on the kinetics of bromination of methylphenylacetylene.[41]

(41) J. A. Pincock and K. Yates, *J. Am. Chem. Soc.*, **90**, 5643 (1968).

(42) R. P. Bell and M. Pring, *J. Chem. Soc.*, *B*, 1119 (1966).

(43) C. W. Foulk and A. T. Bawden, *J. Am. Chem. Soc.*, **48**, 2045 (1926); N. H. Furman and E. B. Wilson, *ibid.*, **50**, 277 (1928).

(44) A. I. Vogel, "Quantitative Inorganic Analysis," 2nd ed, Longmans, Green, and Co., London, 1951, pp 334, 361.

Sargent) was used to adjust the recorder input so as to give an 80–100 mV full-scale deflection. Linear variations in potential were observed over 45–50 mV corresponding to better than 95% reaction, after which the potential fell more slowly. Initial bromine concentrations were determined independently by iodimetry. The recorder time scale was checked by stopwatch during or immediately following a kinetic run.

Verification of the Nernst Equation. Since the Nernst equation is used in the treatment of the kinetic data it was of critical importance to test its applicability to the anhydrous acetic acid–electrolyte solutions used.

A fresh solution of bromine (10^{-3} *M*) was prepared and analyzed. Two reaction vessels were filled with this solution and thermostated at 25°. Two calibration curves were constructed by adding sufficient salts to give the required excess of lithium bromide, *i.e.*, 0.01 and 0.10 *M*. Lithium perchlorate was added to the former solution to maintain a constant ionic strength of 0.10 *M* and the potential between the platinum gauze and the modified calomel electrode was measured in each case. More dilute bromine solutions were obtained by removing accurately measured volumes and replacing them with equal volumes of a thermostated acetic acid solution containing the same concentration of the salts. The two calibration curves corresponding to the limit of the lithium bromide concentrations used during the kinetic runs are shown in Figure 6. The expected linear relationship between the observed potential (E_{obsd}) and the logarithm of the analytical bromine concentration extends over a range of bromine concentrations from 10^{-3} to 10^{-6} *M*. Below this region the observed potential decreased more slowly than expected.

The observed potential of aqueous bromine–bromide solutions has been found not to obey the expected linear relation below 10^{-7} *M* bromine.[45] A calomel reference electrode was also used by these investigators. Recently, Bell[42] has reported that the potentiometric method will give the expected linear relations as low as 10^{-9} *M* bromine in aqueous solution if a glass electrode is used as the reference. The higher resistance of this electrode reduces the current following in the reaction cell and therefore minimizes any polarization of the electrodes. Such effects account for the more limited range of linearity observed with the calomel reference electrode in the present medium. For this reason the kinetic studies were confined to bromine concentrations in the region 10^{-3} to 10^{-6} *M*.

An attempt was made to determine the response of the electrode system. as measured by the magnitude of the potential change for a tenfold decrease in bromine concentration, for various ratios of added $LiClO_4$ and LiBr. This was done for 13 different solutions with $LiClO_4$/LiBr ratios ranging from 0.0 to 9.0. There was no evidence of a systematic change in the electrode response with the various salt ratios used and a mean value of 31.0 ± 0.6 mV per power of ten bromine concentration was obtained. This is about 5% higher than the theoretical value of 29.58 mV generally used for aqueous solutions but is in excellent agreement with previously reported[27] values measured in acetic acid. The empirically determined value of 0.0310/2303 was used in place of the factor $(RT)/(2F)$ of the Nernst equation which appears in the next section.

Treatment of Data. The observed potential of the reaction cell is related to the concentration of free bromine by the following form of the Nernst equation

$$E_{\text{obsd}} = E_0 + \frac{RT}{2F}\ln\frac{a_{\text{Br}_2}}{(a_{\text{Br}^-})^2} + E_{\text{lj}}$$

where E_0 is the standard potential of the Pt|Br_2, Br^- half-cell referred to the modified calomel electrode and E_{lj} is the unknown liquid junction potential, which is assumed to be constant during a kinetic run. With a large and effectively constant bromide concentration (0.01–0.10 *M*) and a very low bromine concentration (5×10^{-4} *M*) eq 1 can be written as

$$\begin{aligned} E_{\text{obsd}} &= \left[E_0 + E_{\text{lj}} + \frac{RT}{2F}\ln\frac{a_{\text{Br}_2}}{(a_{\text{Br}^-})^2}\right] + \frac{RT}{2F}\ln\,[\text{Br}_2] \\ &= E_0' + \frac{RT}{2F}\ln\,[\text{Br}_2] \end{aligned}$$

where E_0' is constant. Therefore

$$\frac{dE_{\text{obsd}}}{dt} = \frac{RT}{2F}\frac{d\ln\,[\text{Br}_2]}{dt}$$

and from eq 3 (Results and Discussion), we have

$$-\frac{1}{[\text{S}]}\frac{d\ln\,[\text{Br}_2]}{dt} = k_{\text{obsd}}$$

hence

$$\begin{aligned} k_{\text{obsd}} &= -\frac{1}{[\text{S}]}\frac{2F}{RT}\frac{dE_{\text{obsd}}}{dt} \\ &= -\frac{74.29}{[\text{S}]}\frac{dE_{\text{obsd}}}{dt} \end{aligned}$$

Therefore k_{obsd} can be obtained from the slope of E_{obsd} *vs.* time, taking [S] to be the average styrene concentration during the run. In a typical run $[\text{S}]_{\text{initial}} = 1.0 \times 10^{-2}$ *M* and $[\text{S}]_{\text{final}} = 9.95 \times 10^{-3}$ *M* so that very little error is introduced by using an average concentration.

Acknowledgments. The continued financial support of the National Research Council and awards of Studentships to J. H. R. are gratefully acknowledged.

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[45] W. C. Purdy, E. A. Burns, and L. B. Rogers, *Anal. Chem.*, **27**, 1988 (1955).