

rounded by a jacket for circulation of water at constant temperature ($\pm 0.05^\circ$) and mounted on a magnetic stirrer.

In a typical run a solution of ca. 0.01 mol of aniline in methanol (90 ml) was placed in the reaction vessel. The reaction was started by adding a solution of ca. 0.0003 mol of 2-thiophenesulfonyl chloride in methanol (10 ml). At the initial time, the reagents concentrations were ca. 0.003 mol/l. for 2-thiophenesulfonyl chloride and ca. 0.08–0.16 mol/l. for the various anilines.

The observed pseudo-first-order rate constants were calculated from conventional plots of $\log(a-x)$ against time from the slope obtained using the least squares method. The correlation coefficients were always 0.995. In all cases the reaction follows the pseudo-first-order kinetics well to at least 70% completion. All rates were run in duplicate. The experimental data are well reproducible within $\pm 4\%$.

The second-order rate constants were obtained by dividing the pseudo-first-order rate constants by the aniline concentration.

The activation energies and $\log A$ values were calculated in the usual way from an Arrhenius plot by the least squares method.

The entropies of activation, ΔS^\ddagger , were computed for 25° by eq 5.¹⁶

$$\Delta S^\ddagger = 4.576 (\log A - \log T) - 49.21 \quad (\text{cal/mol}^\circ\text{K}) \quad (5)$$

Registry No.—2-Thiophenesulfonyl chloride, 16629-19-9.

Acknowledgment.—The authors are grateful to the Consiglio Nazionale delle Ricerche (C. N. R.) for the financial support.

(16) M. Simonetta, "Chimica Fisica," Vol. I, Manfredi, Ed., Milano, 1966, p 278.

Kinetics and Mechanisms of Electrophilic Addition. I. A Comparison of Second- and Third-Order Brominations

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The rates of bromination of several ring-substituted styrenes have been measured as a function of temperature under both dominant second-order (k_2) and dominant third-order (k_3) conditions in acetic acid. The k_2 process is enthalpy controlled, while k_3 is entropy controlled. The ρ values (*vs.* σ^+) for each process are nonetheless very similar (for k_2 , $\rho = -4.8$; for k_3 , $\rho = -4.6$) suggesting that similar cationic intermediates are involved. This is supported by product analysis, which shows virtually identical dibromide-acetoxybromide distribution under either k_2 or k_3 conditions. The most probable mechanism of the k_3 process is proposed.

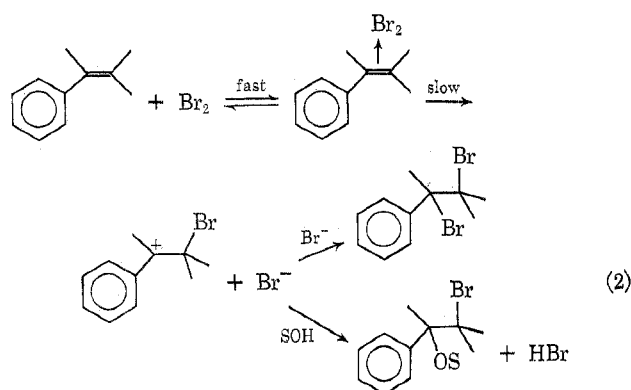
The rates of bromine addition to typical olefins (or acetylenes) in polar solvents can be described by the general rate equation¹ (1). Thus bromination

$$-d[\text{Br}_2]/dt = [\text{olefin}](k_2[\text{Br}_2] + k_3[\text{Br}_2]^2 + k_{\text{Br}^-}[\text{Br}_2][\text{Br}^-]) \quad (1)$$

(to give dibromides and solvent-incorporated products) can arise from one or more of several competing mechanistic pathways, depending on the reaction conditions.

The last term (involving k_{Br^-}) is only important in the presence of significant bromide concentrations and has been ascribed to either a bromide ion catalyzed ADE3 process² or to a kinetically equivalent ADE2 mechanism^{3,4} involving tribromide as the electrophile. In the absence of bromide, and at low bromine concentrations ($< 10^{-3} M$), only the first term (involving k_2) is important. This simple second-order process has been the most widely investigated mechanistically. Based on a combination of kinetic studies,⁴⁻⁷ product regioselectivity^{8,9} and stereochemistry,¹⁰ and spectral evidence,^{11,12} this mechanism of bromination of styrenes can be formulated as an ADE2 reaction proceeding

through a bromine-olefin charge-transfer complex to give an essentially open (or at most a weakly bridged) carbonium ion intermediate¹³ (eq 2). However, much



less is known¹⁵ about the corresponding higher order process (k_3) which becomes important at higher bromine concentrations ($\geq 10^{-2} M$), mainly because the observed rates are very high under these conditions. Nonetheless, many early kinetic studies¹⁴ and most preparative brominations have been carried out under conditions where this process would have been significant or even predominant. It is therefore important to determine and compare the characteristics

(1) I. K. Walker and P. W. Robertson, *J. Chem. Soc.*, 1515 (1939); I. Ting and P. W. Robertson, *ibid.*, 628 (1947).

(2) N. Kanyayev, *J. Gen. Chem. USSR*, **29**, 825 (1959); J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970).

(3) J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 3260 (1963); R. P. Bell and M. Pring, *J. Chem. Soc. B*, 1119 (1966).

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

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

(6) K. Yates and W. V. Wright, *ibid.*, **45**, 167 (1967).

(7) C. Gebelein and G. D. Frederick, *J. Org. Chem.*, **37**, 2211 (1972).

(8) A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).

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

(10) These product analyses have been carried out under conditions where the k_2 process is predominant.⁹

(11) J. E. Dubois and F. Garnier, *J. Chim. Phys.*, **63**, 351 (1966); *Spectrochim. Acta*, **23A**, 2279 (1967).

(12) J. E. Dubois and F. Garnier, *Tetrahedron Lett.*, 3961 (1965).

(13) For additions to simple alkenes such as 2-butenes, this intermediate is, on the contrary, a more or less symmetrically bridged cyclic bromonium ion⁹ of the type first proposed by Roberts and Kimball.¹⁴

(14) I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, **59**, 947 (1937).

(15) (a) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, Amsterdam, 1966. See also B. E. Swedlund and P. W. Robertson, *J. Chem. Soc.*, 630 (1947). (b) The corresponding second- and third-order processes in aromatic bromination have been studied by R. M. Keefer and R. J. Andrews, *J. Amer. Chem. Soc.*, **78**, 255, 3637 (1956), and U. P. Zimmerman and E. Berliner, *ibid.*, **84**, 3953 (1962).

TABLE I
SECOND-ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE
BROMINATION OF STYRENES IN ACETIC ACID

Substituent	n^a	$t, ^\circ\text{C}$	$k_2, M^{-1}\text{sec}^{-1}$	$\Delta H^\ddagger,^b$ kcal mol $^{-1}$	$\Delta S^\ddagger,^b$ cal deg mol $^{-1}$
4-NO $_2^c$	2	25.0	3.58×10^{-3}	9.0	-39.5
	2	45.0	9.95×10^{-3}		
3-NO $_2^c$	2	25.0	9.61×10^{-3}	8.5 ± 1.1^d	-34.8 ± 3.6^d
	3,4-di-Cl c	3	25.0		
1		29.0	1.21×10^{-1}		
3	33.0	1.52×10^{-1}			
3	40.0	1.94×10^{-1}			
2	45.0	2.30×10^{-1}			
3-Cl c	3	25.0	2.15×10^{-1}		
	2	25.1	2.53		
4-Br c	2	18.0	11.0	4.7 ± 0.7	-37.6 ± 2.3
	3	25.0	14.3		
H c	2	34.9	18.2		
	3	25.1	25.3		
4-F c	3	25.1	25.3		
4-Me c	4	25.1	1.07×10^3		

^a Number of kinetic runs. ^b Errors quoted are standard deviations. ^c Data from ref 5. ^d Values corrected from those previously reported incorrectly for this compound in ref 5. ^e This work. Registry numbers are, respectively, 2039-82-9, 100-42-5, 405-99-2, and 622-97-9.

of the k_3 (or termolecular) bromination process with those of the simpler k_2 (or bimolecular) process.

The main objective of the present study was to use the stopped-flow technique to study the rates of the k_3 process for ring-substituted styrenes and to compare its structure-reactivity dependence with that of the k_2 process. Secondary aims were to compare the activation parameters and product distributions for the two parallel bromination processes.

Results and Discussion

Rate Constants.—A previously reported correlation⁵ of $\log k$ vs. σ^+ for bromination of styrenes in acetic acid ($\rho = -4.7$, $r = 0.997$) was based largely on deactivated styrenes, because of the high rates of bromination of the more activated compounds. This linear free-energy relationship has now been extended, using stopped-flow measurements, by determining several second-order bromination rate constants for more reactive olefins, also in acetic acid. These new values are listed in Table I, along with those reported previously. One value of k_2 previously reported incorrectly⁵ (for 3,4-dichlorostyrene) has been corrected. These rate constants now extend over about six powers of ten in reactivity. The present values of k_2 for the eight substituted styrenes, listed in Table II, also correlate well¹⁶ with σ^+ ($\rho = -4.8$, $r = 0.997$). Considerably more scatter is obtained by plotting these $\log k_2$ values vs. σ ($\rho = -5.3$, $r = 0.985$).

Values of the third-order rate constants (k_3) for bromination of seven of the eight substituted styrenes have also been determined in acetic acid and are reported in Table III. Correlation of these $\log k_3$ values with σ^+ again gives significantly less scatter ($\rho = -4.6$, $r = 0.995$) than a corresponding plot vs. σ ($\rho = -5.0$, $r = 0.988$). The values of k_3 obtained at 25°

(16) The point for the 4-methyl compound is significantly off the line. The reasons for this are not understood. In a similar correlation of bromination rates in methanol by Dubois and coworkers,¹⁸ albeit using global rate constants, the point for 4-methyl does not deviate. This suggests that the present deviation is not mechanistically significant. The present correlation is significantly improved by omitting the 4-methyl point ($\rho = -4.6$, $r = 0.9996$).

TABLE II
LINEAR FREE-ENERGY RELATIONSHIPS FOR SECOND- AND THIRD-
ORDER BROMINATIONS OF STYRENES IN ACETIC ACID AT 25°

Substituent	Log k_2^a	Log k_3^b	σ^c	σ^+^d
4-NO $_2$	-2.45		0.778	0.790
3-NO $_2$	-2.02	1.12	0.710	0.674
3,4-Cl $_2$	-1.08	2.12	0.572 e	0.476 e
3-Cl	-0.67	2.49	0.373	0.399
4-Br	+0.40	3.585	0.232	0.150
H	+1.155	4.39	0	0
4-F	+1.40	4.63	0.062	-0.073
4-Me	+3.03	5.69	-0.170	-0.311
	k_2 vs. σ	k_2 vs. σ^+	k_3 vs. σ	k_3 vs. σ^+
ρ values	-5.29	-4.83	-4.98	-4.63
	0.985	0.997	0.988	0.9995

^a Units in $M^{-1}\text{sec}^{-1}$. ^b Units in $M^{-2}\text{sec}^{-1}$. ^c From D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958). ^d From ref 25. ^e From ref 4. ^f Correlation coefficient.

are also listed in Table II with the corresponding values of k_2 for comparison.¹⁷

The large negative ρ value previously reported^{4,5,18} for the k_2 process, the correlation with σ^+ rather than σ , the nonstereospecific nature of the addition to the analogous *cis*- and *trans*-1-phenylpropenes,^{9,19} and the completely regiospecific mode of addition^{6,9} (in the Markovnikov sense) for the solvent-incorporated products have all been interpreted in terms of a transition state leading to an essentially open α -phenyl-carbonium ion intermediate. The very similar behavior of the rate constants for the k_3 process in the ρ - σ^+ relationship²⁰ points to a transition state for the termolecular bromination having a very similar struc-

(17) Comparison of the expected rates of these competing bimolecular and termolecular brominations shows that, in general, the first would dominate the observed rate for bromine concentrations $< 5 \times 10^{-3} M$, whereas the second would be predominant at $[\text{Br}_2] > 10^{-2} M$.

(18) J. E. Dubois and A. Schwarz, *Tetrahedron Lett.*, 2167 (1964).

(19) R. C. Fahey and H. J. Schneider, *J. Amer. Chem. Soc.*, **90**, 4429 (1967).

(20) It is reassuring that a linear free-energy relationship is also obeyed for the termolecular process, despite a previous report⁶ that the k_3 process did not follow the Hammett equation very well. However this was based on an attempted separation of the k_2 and k_3 rate constants in a bromine concentration region where the k_3 process was a minor contributor to the overall rate.

TABLE III
THIRD-ORDER RATE CONSTANTS AND ACTIVATION
PARAMETERS FOR THE BROMINATION OF
STYRENES IN ACETIC ACID

Substituent	n^a	t , °C	k_2 , M^{-2} sec^{-1}	$\Delta H^\ddagger,^b$ kcal mol^{-1}	$\Delta S^\ddagger,^b$ cal deg mol^{-1}		
3-NO ₂	2	18.3	12.6	0.87	-50.5		
		25.0	(13.3) ^c				
3,4-Cl ₂	4	45.0	15.6	0.93 ± 0.24	-45.8 ± 0.8		
		17.9	1.15 × 10 ²				
		25.0	1.13 × 10 ²				
		31.9	1.25 × 10 ²				
		39.1	1.40 × 10 ²				
3-Cl	3	25.1	3.09 × 10 ²	0.01 ± 0.28	-38.5 ± 0.9		
		4-Br	4			25.1	3.85 × 10 ²
		H	4			18.5	2.30 × 10 ⁴
4-F	2	25.0	2.44 × 10 ⁴	1.14 ± 0.36	-33.5 ± 1.2		
		35.1	2.41 × 10 ⁴				
		45.1	2.53 × 10 ⁴				
		45.1	2.53 × 10 ⁴				
4-F	3	16.9	4.19 × 10 ⁴	1.14 ± 0.36	-33.5 ± 1.2		
		24.9	4.25 × 10 ⁴				
		34.9	4.65 × 10 ⁴				
4-Me ^d	1	25.1	4.9 × 10 ⁶	1.14 ± 0.36	-33.5 ± 1.2		
		45.1	5.38 × 10 ⁴				

^a Number of kinetic runs. ^b Errors quoted are standard deviations. ^c Value estimated from rate constants at other temperatures. ^d This compound reacts at a rate near the limit of the stopped-flow apparatus. Estimated error in this single determination is ~10%.

ture and charge development to that for the bimolecular process, at least as far as the cationic portion is concerned.

Activation Parameters.—Values of k_2 and k_3 measured at various temperatures are reported in Tables I and III, respectively, for several of the substituted styrenes, along with the activation parameters calculated from these data by standard methods.²¹ It can be seen from Table I that ΔS^\ddagger is essentially independent of structure for the bimolecular process ($\Delta S^\ddagger \sim -37 \pm 3$ cal deg mol⁻¹)²² with structural effects on rate being reflected in the ΔH^\ddagger values. Thus electron-withdrawing groups retard the bimolecular electrophilic addition reaction by increasing ΔH^\ddagger significantly.

In contrast, the ΔH^\ddagger values for the third-order process are very low and essentially independent of structure ($\Delta H^\ddagger_{\text{ave}} \approx 0.7$ kcal mol⁻¹), while the large unfavorable negative ΔS^\ddagger values dominate the reaction rate. In fact the k_3 series is essentially isoenthalpic while the second-order rates appear to form an isentropic series. Such large negative values of ΔS^\ddagger (-34 to -51 cal deg mol⁻¹) have previously been observed²⁴ for the third-order bromination of acetylenes and are not unexpected for a highly polarized termolecular transition state. Very low values of ΔH^\ddagger for the k_3 process were suggested by early workers,¹ who observed temperature coefficients for the rate of this process which were very close to zero or even negative.

(21) J. F. Bunnett, in "Technique of Organic Chemistry," Vol. VIII, part 1, S. L. Friess, E. S. Lewis and A. Weissberger, Ed., Interscience, New York, N. Y., 1961, p 199.

(22) These values are significantly more negative than those reported²³ for the second-order brominations of symmetrically substituted dialkyl- and diphenylethylenes, where $\Delta S^\ddagger \approx -24$ cal deg mol⁻¹. This may indicate more charge development and increased solvent restriction in the styrene transition states.

(23) K. Yates and R. S. McDonald, *J. Amer. Chem. Soc.*, **93**, 6297 (1971).

(24) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970).

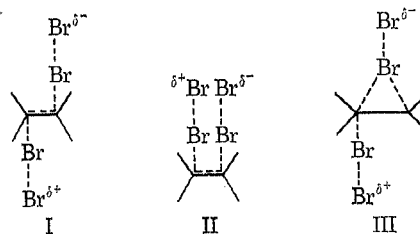
These workers^{1,15a} further suggested that this was indicative of an initial preequilibrium step, followed by rate-determining attack of a third molecule.

Product Distributions.—The products of bromine addition to styrene and to 3,4-dichlorostyrene in acetic acid were analyzed first under conditions where the second-order process dominates the rate and then where the third-order process is predominant. Both processes give a mixture of 1,2-dibromophenylethanes (dibromides) and 1-acetoxy-2-bromophenylethanes (acetoxybromides). The ratio of dibromide to acetoxybromide for bromination of styrene under k_2 conditions ($[\text{Br}_2]_0 < 10^{-3} M$) was 79:21 and under k_3 conditions ($[\text{Br}_2]_0 \geq 10^{-2} M$) was 83:17. For 3,4-dichlorostyrene the corresponding product ratios were 77:23 under k_2 conditions and 78:22 under k_3 conditions. These nearly identical product distributions again imply that very similar intermediates and product-determining steps are involved in the two processes. Although no stereochemical information can be obtained from styrene additions, it has been previously shown⁹ that product stereoselectivity is essentially independent of bromine concentration for bromine additions to *cis*- and *trans*-1-phenylpropenes in acetic acid. Thus it seems reasonable that each process (k_2 and k_3) gives almost identical product distribution and stereochemistry.

Proposed Mechanism of Third-Order Bromination.—

The above results for analogous k_2 and k_3 brominations may now be discussed in terms of possible mechanisms for the latter process. Firstly, the very similar ρ - σ^+ correlations point to considerable positive charge development on the α carbon at the k_3 transition state and are also similar to those typically observed in S_N1 type solvolyses (*e.g.*, cumyl chloride solvolysis in ethanol has $\rho = -4.67$).²⁵ This is also supported by the observed regiospecificity of the solvent-incorporated products in the k_3 process. Similarly the identical stereoselectivity observed under either k_2 or k_3 conditions points to a similar degree of openness in the product-determining carbonium ion intermediates.

These kinetic and product results do not support transition states¹⁴ in which both nucleophilic and electrophilic bromine attack occurs at the two olefinic carbons, as in structures I–III. It would be expected



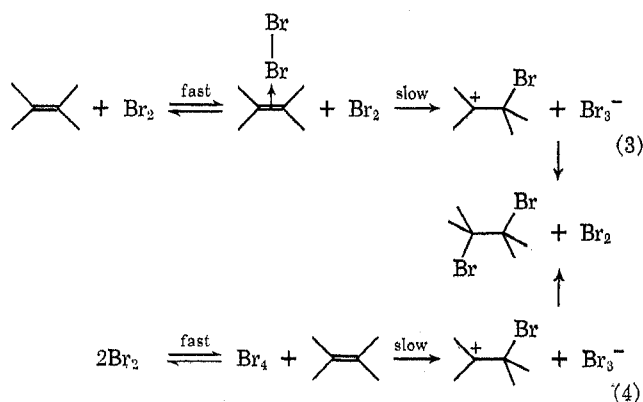
that these AdE3 type transition states would have a considerably different charge distribution²⁶ from that in the k_2 process (which involves an AdE2 mechanism). Further, such transition states would lead to stereospecific (anti from I and III, syn from II) addition for the k_3 process only, whereas both k_2 and k_3 processes show variable stereoselectivity.⁹ In addition, solvent

(25) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(26) For example, the bromide-catalyzed addition of bromine to phenylacetylene, which involves a similar AdE3 process, has a considerably different ρ value from that in the analogous, simple second-order addition, is completely anti stereospecific, and gives no solvent-incorporated products.²⁴

incorporation occurs to the same extent in both processes, whereas I-III would be expected to give no solvent-incorporated products.

A fully synchronous termolecular process is unlikely, and probably few if any truly termolecular processes are known. The very low ΔH^\ddagger values for k_3 are more easily interpreted in terms of an initial pre-equilibrium association, followed by rate-determining attack of a third molecule. However, two kinetically indistinguishable mechanisms of this type have been suggested.^{1,15a} These involve rate-determining bromine attack on a bromine-olefin complex (mechanism 3) or bromination of the olefin by a Br_4 species (mechanism 4). Although 1:1 bromine-olefin com-



plexes have been observed spectroscopically,^{11,12} evidence that these intermediates lie on the reaction coordinate for bromination is largely circumstantial.^{7,11,27} The analogous iodine-olefin complexes are well characterized²⁸ and are known to be formed exothermically. Also, semiempirical MO calculations predict favorable associations between olefins and halogens.²⁹

The kinetic importance of a Br_4 species is difficult to assess. While such species are believed to be present in the pure solid and liquid phases of halogens,³⁰ there is no evidence for such association in the gas phase or in solution. Even in a solvent as weakly polar as acetic acid, bromine-solvent interactions would be expected to be stronger than those between Br_2 molecules. Thus, in fact there is no evidence for Br_4 species in solution while good evidence for bromine-olefin complexes does exist.

Evidence has been discussed previously that the bimolecular k_2 process proceeds *via* olefin-bromine charge-transfer-complex formation followed by rate-determining solvent-assisted bromine-bromine bond cleavage. This would occur most readily in solvents capable of solvating an anionic centre. In solvents incapable of such solvent stabilization, the k_3 term becomes predominant even at low $[\text{Br}_2]$. Thus, one may envisage that, in the k_3 process, a bromine molecule is serving the function of catalytically aiding the Br-Br bond cleavage³¹ by forming a charge dispersed tribromide ion. Such a bromine assisted AeE_2 process

would lead to the well-documented tribromide ion³² and a similar cationic intermediate (the β -bromophenylethyl cation) to that involved in the simpler k_2 process.

The characteristics of the k_2 and k_3 bromination processes are summarized in Table IV. A major point of

TABLE IV
CHARACTERISTICS OF k_2 AND k_3 BROMINATION PROCESSES FOR
SUBSTITUTED STYRENES

	k_2	k_3
Rate constants ^a	10^{-2} – $10^3 M^{-1} \text{sec}^{-1}$	10^1 – $10^8 M^{-2} \text{sec}^{-1}$
Region of predominance	$[\text{Br}_2] < 5 \times 10^{-3} M$	$[\text{Br}_2] > 10^{-2} M$
Dibromide: acetoxy-bromide	79:21 ^b	83:17 ^b
	77:23 ^c	78:22 ^c
Stereoselectivity	Anti > syn ^d	Anti > syn ^d
Regioselectivity	Regiospecific (<i>M</i>)	Regiospecific (<i>M</i>)
ρ value (vs. σ^+)	-4.8	-4.6
ΔH^\ddagger range	5–10 kcal	~1 kcal
ΔS^\ddagger range	Ca. -37	-(34–51)

^a In anhydrous acetic acid. ^b For styrene. ^c For 3,4-dichlorostyrene. ^d See ref 9.

difference between the k_2 and k_3 processes is the more negative ΔS^\ddagger range for k_3 . This is understandable in terms of the proposed mechanism, since not only is a third molecule involved, but also the incipient tribromide ion formation probably requires a fairly rigid linear arrangement of the four bromine atoms.

Experimental Section

The sources and purification of the substituted styrenes, bromine, and the solvent, anhydrous acetic acid, have been previously described.⁹

Kinetic Studies.—The second- and third-order rate constants were measured on a Durrum Gibson stopped-flow kinetics spectrophotometer. The output was coupled into a Tektronix storage oscilloscope which was frequently calibrated on the vertical (per cent transmittance) and horizontal (time) axes. The instrument had a mixing time of 2–3 msec and a 2-cm observation cell. The reaction was monitored by observing the decrease in bromine absorbance at 490 nm using a 0.1-mm slit width. The time constant setting was routinely ≤ 0.1 of the time/division setting on the horizontal scope axis. Temperature control was achieved by the use of a Tamson TE-9 constant-temperature circulating bath equipped with a PBC-4 bath cooler. The temperature remained fairly constant ($\pm 0.05^\circ$) during the equilibration period. The instrument was allowed to stabilize and the system equilibrated thermally for 3–4 hr before any kinetic runs were attempted. The flow system was thoroughly flushed with anhydrous acetone and then with anhydrous acetic acid. The 0% and 100% transmittance readings were adjusted on the scope.

One drive and one reservoir syringe was used for the bromine solution and the other pair of syringes for the olefin solution. The system was flushed with a stock bromine solution (in twice the concentration of that of the initial bromine concentration in the kinetic run) until a constant per cent transmittance reading was observed. Knowing the absorbance of the stock bromine solution and the extinction coefficient of bromine at 490 nm, the initial bromine concentration during the kinetic run could be calculated. The stock olefin solution was prepared by weighing an appropriate amount of styrene into a volumetric flask and diluting to the mark with acetic acid. The stock olefin concentration was twice the desired concentration during the kinetic run. To simplify the kinetics, the value of $[\text{olefin}]_0$ was always at least in 20-fold excess over that of $[\text{Br}_2]_0$ so that all runs were

(27) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, p 322.

(28) J. G. Traynham and J. R. Olechowski, *J. Amer. Chem. Soc.*, **81**, 571 (1959).

(29) B. Nelander, *Theor. Chim. Acta*, **25**, 382 (1972).

(30) R. S. Mulliken, *J. Amer. Chem. Soc.*, **72**, 600 (1950).

(31) Thus lowering the enthalpy of activation.

(32) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, p 1142, 1143. E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, **3**, 133 (1961).

pseudo first order in bromine. The flow system was flushed thoroughly with the olefin solution and the scope line normally returned to the 100% transmittance reading previously set. The drive syringes were then filled with the solutions to be mixed and allowed to equilibrate thermally for 30–45 min.

The second-order kinetic runs were carried out using $[\text{Br}_2]_0 < 5 \times 10^{-4} M$ to ensure that only the contribution from the bimolecular process was significant over most of the kinetic run. This necessitated use of the expanded transmittance scales such that the reaction was monitored over the 100–90 or 100–95% transmittance range. The total absorbance change was usually 0.05 absorbance units.

After the equilibration period, a few trial runs were carried out to optimize the extent of reaction followed (usually 2–3 half-lives were recorded). After several reproducible traces were obtained, the stored scope output was erased, the next run stored, and the bath temperature recorded. An infinity trace was recorded after at least 10 half-lives. The absorbance-time data were obtained from a photograph of the oscilloscope trace.

Integration of the second-order rate expression for the bromination of an olefin (under pseudo-first-order conditions) gives a linear relationship between $\log(A - A_\infty)$ and time, with k_2 being obtained from the slope of the line. The kinetic plots normally were good straight lines at $[\text{Br}_2] \leq 3 \times 10^{-4} M$ over 75% reaction. The occasional problem of a varying infinity value was surmounted by the use of the Guggenheim method.³³ The k_2 values were calculated using the average olefin concentration during the run; even using as low as a 20-fold excess of olefin, this would introduce an error of only 2.5% in k_2 .

The third-order rate constants were measured by an analogous method. To ensure that the k_3 process was predominant, the initial $[\text{Br}_2]$ was $\approx 1.2 \times 10^{-2} M$ and was monitored down to $\approx 6 \times 10^{-3} M$. This corresponded to an absorbance change from 1.5 to 0.7 units. At this lower concentration, the k_2 term began to contribute significantly to the observed rate. The reaction was followed using the expanded scale attachment such that full scale corresponding to 0–10 or 0–20% T. Again the extent of reaction followed was optimized, the run recorded and an infinity value taken on the 100–0% transmittance scale. Operation of the instrument was carried out as previously described and absorbance-time data during the run was obtained in an exactly analogous manner to above.

Integration of the third-order rate expression for the bromination of an olefin (under pseudo-second-order conditions) gives a linear relationship between $(A - A_\infty)^{-1}$ and time, with k_3 being obtained from the slope of the straight line. Some initial curvature in the plots for the reactive styrenes at very short reaction times (≤ 3 msec) was taken to be indicative of incomplete mixing. Some curvature at longer reaction times, and hence at lower bromine concentrations, was routinely encountered and taken to be due to the increasing relative importance of the second-order process.

Two methods were used to calculate the third-order rate constants. For those olefins where the k_2 values were not determined in the same series of runs (for all styrenes except the 4-bromo- and 4-methyl-substituted compounds), the k_3 values were calculated from the slopes of the visibly linear portions of the $(A - A_\infty)^{-1}$ vs. t plots. For the other two substrates, two series of runs at 25° were carried out, one set under predominant k_2 and the other under predominant k_3 conditions. At least two different initial olefin concentrations were used for each set. A nonlinear least-squares regression analysis was then performed on

each pair of k_2 - k_3 runs by an iterative technique, minimizing the variance for the two runs. Thus one set of "best" k_2 and k_3 values could be determined, the second-order contribution having been eliminated from the k_3 process and vice versa. This technique was also carried out for styrene and the 4-fluorostyrene but the rate constants quoted for these compounds are from a subsequent variable temperature series of runs. The "pure" k_3 values generally corresponded to within 5–10% of those calculated from the nonlinear correlations. Thus an estimated error of 10% in the k_3 values appears reasonable for these rapid reactions, which require the use of expanded oscilloscope scales and are complicated by competing rate processes.

Duplicate traces were normally recorded for each kinetic run and usually two–four different initial olefin concentrations were used. The errors in the quoted rate constants were generally ≤ 6 –7%.

For the styrenes for which activation parameters were required, rate constants were measured at three–four temperatures in the 17–45° range. Plots of $\log k/T$ vs. $1/T$ yielded straight lines with ΔH^\ddagger being obtained from the slope and ΔS^\ddagger from the intercept. Each individually determined rate constant was included in the correlation, since small temperature fluctuations did occur on the duplicate runs and the same number of runs was usually not carried out at each temperature.

All final calculations of the rate constants and activation parameters were performed on a computer or a desk top programmable calculator using a linear least-squares regression program.

Product Studies.—The product runs were under second-order bromination conditions were carried out by the slow, dropwise addition of an equivalent amount of bromine in 20 ml of acetic acid to a stirred solution of 1.0 g of the styrene in 20 ml of solvent. The reaction was protected from light in an aluminum foil wrapped flask and each drop of bromine solution added was allowed to react completely before another drop was added. After the addition was complete, the solution was stirred for 1 hr and poured into a separatory funnel containing 50 ml each of pentane and water. Any excess bromine was destroyed by the addition of a crystal of $\text{Na}_2\text{S}_2\text{O}_3$, the mixture was shaken, and the pentane layer was removed. Successive washings with water, saturated NaHCO_3 solution until neutral, and again with water were followed by drying of the pentane layer with MgSO_4 . The drying agent was removed by filtration and the solution was concentrated on a rotary evaporator.

The product run under third-order bromination conditions was carried out by an analogous slow, dropwise addition of the olefin solution to the stirred, light-protected solution of bromine in acetic acid. After complete addition, the reaction mixture was worked up in exactly the same manner as that described above.

The crude products in CCl_4 solutions were analyzed directly on a Varian T-60 nmr spectrometer. Only two products could be observed from the bromination runs; these were the dibromo- and α -acetoxy- β -bromo adducts which have been previously characterized.⁹ The ratios of the products were determined by repeated integrations in the methylene and methine hydrogen regions of the two compounds. The spectra are well separated in these regions.

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