port. Purity of the sample as checked by vpc was 99%. The ir spectrum confirmed the structure by comparison with the ir spectrum of compound IV:[1] ir ν (film) 2945, 2840, 1740, 1460, 1425, 1190, 1040, 965, and a weak 663-cm^{-1} band (C-S-C) (lit.[22] 658 cm^{-1}); nmr ($CDCl_3$) δ 1.25 (t, 3 H, J = 7.3 Hz, OCH_2CH_3), 2.75 (m, 8 H, methylene ring protons), 3.35 (s, 2 H, NCH_2CO_2Et), and 4.18 ppm (m, 2 H, J = 7.3 Hz, OCH_2CH_3).

Thiomorpholine was prepared by the $LiAlH_4$ reduction of thiomorpholin-3-one (Aldrich). A 105-g (0.896 mol) sample of thiomorpholin-3-one was slowly shaken into an ether solution of 48.5 g (1.28 mol) of $LiAlH_4$ (Ventron). After the excess $LiAlH_4$ was decomposed and the solid was filtered, the solution was rotary evaporated and vacuum distilled to yield 14.0 g (14.6% yield) of thiomorpholine, bp 82–83° (2.9 mm).

Compound II, bp 51° (0.2 mm), was prepared by adding $BrCH_2CO_2Et$ (0.302 mol) (Aldrich) to an excess of 4-methylpiperidine (0.510 mol) (Aldrich) dissolved in CH_3CO_2Et. Fractional distillation of the mother liquor produced a 75% yield of product. Preparative gas chromatographic analysis as previously described for compound I produced 7.2 ml of product of 99.7% purity. The ir spectrum compared favorably with that for compound III:[1] ir ν (film) 2940, 2820, 1740, 1460, 1380, 1190, 990, and 830 cm^{-1}; nmr ($CDCl_3$) δ 1.30 (m, 11 H, ring hydrogens and methyl hydrogens), 2.70 (m, 4 H, ring hydrogens adjacent to nitrogen, 3.35 (s, 2 H, NCH_2CO_2Et) and 4.25 (m, 4 H, J = 7.0 Hz, OCH_2CH_3).

Kinetic Procedure.—Initial concentration for the amines and $BrCH_2CO_2Et$ was 0.0500 M. Three independent samples of each compound were prepared and studied at the same time. Sample preparations and potentiomatic titrations were similar to the procedures as reported in the previous study.[1]

Reaction Products *via* Tlc.—In order to establish that two products were formed in the quaternization of I, a 50-ml sample of 0.0500 M reaction solution was heated at 60° for 427 hr. After removal of the solvent the product was recrystallized into fine white crystals from a solvent of ethyl acetate and ether (2:1) containing a small amount of methanol. The crystals (60-μg spots) were chromatographed on 4 × 7$^3/_4$ in. glass plates coated with Silicar TLC 7G (Mallinckrodt). The mobile phase was absolute CH_3OH, and the plates were developed in an I_2 chamber. The R_f values for the two compounds were 0.64 ± 0.03 and 0.57 ± 0.02 (average and average deviation for two plates containing three spots per plate).

A similar tlc analysis was made from the reaction product of II. However, only one compound was resolved with R_f value of 0.51 ± 0.03.

Registry No.—Compound I, 39981-80-1; compound II, 39981-81-2; ethyl bromoacetate, 105-36-2; thiomorpholine, 123-90-0; thiomorpholin-3-one, 20196-21-8; 4-methylpiperidine, 626-58-4.

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[22] E. A. Allen, N. P. Johnson, O. T. Rosevear, and W. Wilkinson, *J. Chem. Soc. A*, 2137 (1970).

Reaction Kinetics of 2-Thiophenesulfonyl Chloride with Anilines in Methanol

A. ARCORIA,* E. MACCARONE, G. MUSUMARRA, AND G. A. TOMASELLI

Institute of Industrial Chemistry of the University, Viale Andrea Doria, 8-95125 Catania, Italy

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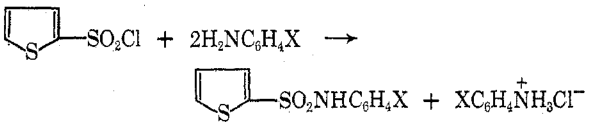
The reaction rate constants of 2-thiophenesulfonyl chloride with some substituted anilines have been measured in methanol at different temperatures. The reaction is second order overall and pseudo first order with respect to each reactant. The rate constants value is greater with electron-donating substituents, while it is lower with electron-withdrawing groups. The activation parameters and the slopes of the Hammett (−2.25) and Brønsted (0.53) plots are similar to those of the reaction of benzenesulfonyl chloride with anilines, showing that the reaction mechanism is the same for the two substrates, although 2-thiophenesulfonyl chloride reacts more slowly. The Tommila equation points out that the sulfur atom, the reaction center, is less positively charged, and thus less reactive toward nucleophiles, than that of benzenesulfonyl chloride.

Previously the mechanism of the reaction of 2-thenoyl chloride with some meta- and para-substituted anilines was investigated.[1] Following this research we report in this paper the kinetics of the reaction of 2-thiophenesulfonyl chloride with a series of substituted anilines to verify the reactivity in comparison with the analogous reaction of benzenesulfonyl chloride, which have been widely studied recently.[2-7]

The reaction between 2-thiophenesulfonyl chloride and aniline in methanol takes place quantitatively according to eq 1.


(1)

X = H, m-CH_3, p-CH_3, m-OCH_3, p-OCH_3, m-Cl, p-Cl

The rate of reaction 1 was measured by continuous titration of the acid produced (see Experimental Section).

We found that the reaction of 2-thiophenesulfonyl chloride with anilines follows second-order kinetics, first order with respect to each reactant.

By the comparison of the slopes of the Hammett and Brønsted plots it seems that the reaction mechanism is the same as for benzenesulfonyl chloride and anilines,[2] although the rates observed with 2-thiophenesulfonyl chloride are lower, probably because of the thiophene conjugative effect on the sulfonyl group which also makes the sulfur atom less electrophilic than that of benzenesulfonyl chloride as the Tommila equation shows.

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[1] A. Arcoria, S. Fisichella, G. Scarlata, and D. Sciotto, *J. Org. Chem.*, **38**, 32 (1973).

[2] O. Rogne, *J. Chem. Soc. B*, 1855 (1971).

[3] L. M. Litvinenko and V. A. Savelova, *Zh. Obshch. Khim.*, **38**, 747 (1968); *Chem. Abstr.*, **69**, 76142 (1968).

[4] L. M. Litvinenko, A. F. Popov, and L. I. Sorokina, *Ukr. Khim. Zh.*, **34**, 595 (1968); *Chem. Abstr.*, **69**, 95598 (1968).

[5] Ya. P. Berkman, G. A. Zemlyakova, and N. P. Lushina, *Ukr. Khim. Zh.*, **34**, 601 (1968); *Chem. Abstr.*, **69**, 95597 (1968).

[6] L. V. Kuritsyn, *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, **12**, 1037 (1969); *Chem. Abstr.*, **72**, 30895 (1970).

[7] E. Ciuffarin, L. Senatore, and M. Isola, *J. Chem. Soc., Perkin Trans. 2*, 468 (1972).

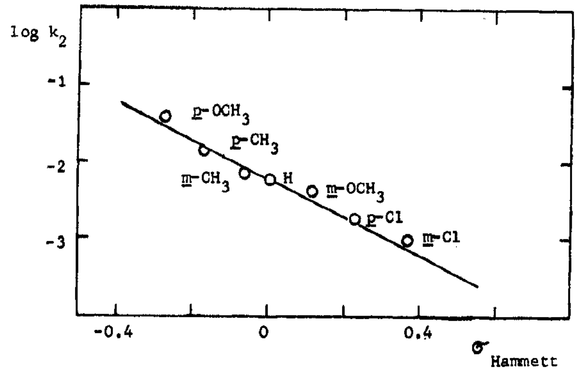

Figure 1.—Hammett plot for the reaction of 2-thiophenesulfonyl chloride with substituted anilines in methanol at 25°.

Results and Discussion

The reaction of 2-thiophenesulfonyl chloride with a large excess of aniline in methanol is pseudo first order with respect to 2-thophenesulfonyl chloride.

The plot of pseudo-first-order rate constants at 25° against aniline concentration is linear (Table I), showing that the reaction is first order also with respect to aniline and that the rate constants do not change appreciably with the dilution.

Table I

Rate Constants for the Reaction of 2-Thiophenesulfonyl Chloride with Aniline in Methanol at 25°

No.	Initial concn of reagents, mol l.$^{-1}$ Sulfonyl chloride	Aniline	$k_1 \times 10^4$, sec^{-1}	$k_2 \times 10^3$, l. mol^{-1} sec^{-1}
1	0.00158	0.0390	2.14	5.49
2	0.00308	0.0915	5.29	5.78
3	0.00393	0.127	7.28	5.73
4	0.00467	0.143	7.83	5.48

The kinetics of the reaction is thus as expected from eq 1 with the rate law eq 2.

$$\text{rate} = k_2[C_4H_3SSO_2Cl][H_2NC_6H_4X] \qquad (2)$$

The reaction was studied at different temperatures; the second-order overall rate constants, obtained by dividing the first-order observed rate constants by aniline concentration, are reported in Table II.

This assumption results in little error since k_{solv} is negligible[8] (eq 3).

$$k_{\text{obsd}} = k_{\text{solv}} + k_2[\text{aniline}] \qquad (3)$$

The activation parameters are listed in Table III, together with the standard deviations (*s*) and the linear correlation coefficients (*r*).

Small amounts of water in methanol have no effect on the observed first-order rate constants, since duplicate runs in methanol containing 2% water gave only slightly higher rate constants.

It was not possible to consider the *m*- and *p*-nitroaniline rate constants, because, with these scarcely reactive anilines, apparently there is competition with solvolysis reactions.

Table II shows that electron-donating substituents in aniline increase the rate, while electron-withdrawing groups decrease the rate.

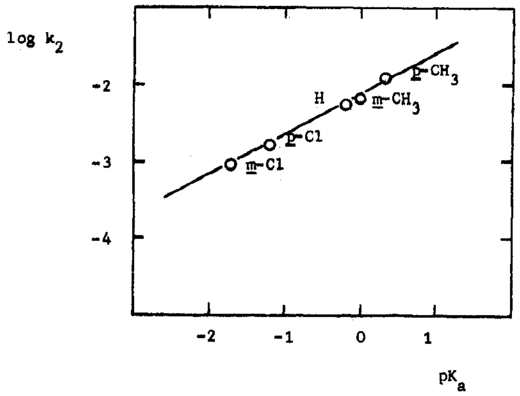

Figure 2.—Plot of log k_2 at 25° for the reaction of 2-thiophenesulfonyl chloride with substituted anilines in methanol against the pK_a of protonated anilines in methanol at 25° (Brønsted plot).

Figure 1, in which the Hammett plot is reported, shows that the reaction rate depends on the electron density on the nitrogen atom of aniline. The sensitivity of the rates to substituents in the aniline (ρ −2.25) is comparable with that found for other analogous reactions.[2,9] Moreover, we found that the activation energies (Table III) are linearly correlated with the substituent constants; in fact, the substituent of larger electronic availability and the more reactive (*p*-OCH_3) shows the lowest activation energy, while, on the contrary, the most deactivating substituent (*m*-Cl) shows the highest E_a.

The large negative entropies of activation are as expected for bimolecular reactions with a highly polar transition state.[10]

The slope of the Brønsted plot (Figure 2), obtained using the pK_a values of anilines calculated in methanol,[11] gives the reaction sensitivity to the basicity of the nucleophile and is related to the relative amount of bond formation in the transition state.[12]

The value obtained (β 0.53) can be ascribed to the partial formation of the sulfur–nitrogen bond in the transition state;[13] this value is comparable with that calculated by us from Rogne data[2] using the pK_a values of anilines in methanol, for the reaction of benzenesulfonyl chloride with anilines (β 0.52).

The reaction rate constants ratio of benzenesulfonyl chloride and 2-thiophenesulfonyl chloride with anilines ($k_{PhSO_2Cl}/k_{ThSO_2Cl} = 13.5 \pm 1.5$) is higher than that of benzoyl chloride and thenoyl chloride ($k_{PhCOCl}/k_{ThCOCl} = 2.5 \pm 0.5$) with anilines.[1]

The lower reaction rate of 2-thiophenesulfonyl chloride with respect to benzenesulfonyl chloride can be ascribed to the greater conjugative effect of the thiophene ring system on the sulfonyl group, which makes the sulfur atom less reactive toward nucleophiles. The Tommila equation[14] points out that

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[8] O. Rogne, *J. Chem. Soc. B*, 727 (1970).

[9] E. Ciuffarin and L. Senatore, *J. Chem. Soc. B*, 1680 (1970).

[10] A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, Chapter 7.

[11] M. Kilpatrick and C. A. Aremberg, *J. Amer. Chem. Soc.*, **75**, 3812 (1953).

[12] J. E. Leffler and F. Grunwald, "Rates and Equilibria of Organic Reaction," Wiley, New York, N. Y., 1963, pp 238–242; R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

[13] L. T. Stangeland, L. Senatore, and E. Ciuffarin, *J. Chem. Soc., Perkin Trans.*, **2**, 852 (1972).

[14] E. Tommila and T. Vihavainen, *Acta Chem. Scand.*, **22**, 3224 (1968).

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF 2-THIOPHENESULFONYL CHLORIDE WITH META- AND PARA-SUBSTITUTED ANILINES IN METHANOL

Registry no.	No.	Substituent	pK_a (25°) Water[a]	pK_a (25°) Methanol[b]	$k_2 \times 10^3$, l. mol^{-1} sec^{-1} 15°	25°	35°	40°	45°
62-53-3	1	H	4.596	−0.195	2.616	5.620	11.05		20.80
108-44-1	2	*m*-CH_3	4.712	−0.0079	3.608	6.901	15.18		25.52
106-49-0	3	*p*-CH_3	5.084	0.3426	6.705	13.52	26.38		45.32
536-90-3	4	*m*-OCH_3	4.200		1.747	4.035	7.336		15.72
104-94-9	5	*p*-OCH_3	5.357		18.98	32.82	56.54	69.81	87.30
108-42-9	6	*m*-Cl	3.521	−1.727		0.9739	2.441	3.294	4.892
106-47-8	7	*p*-Cl	3.982	−1.199	0.6325	1.794	3.746		6.789

[a] P. D. Bolton and F. M. Hall, *Aust. J. Chem.*, **20**, 1797 (1967); **21**, 939 (1968); *J. Chem. Soc. B*, 259 (1969). [b] M. Kilpatrick and C. A. Aremberg, *J. Amer. Chem. Soc.*, **75**, 3812 (1953).

TABLE III

ACTIVATION PARAMETERS FOR THE REACTION RATES IN TABLE II

Substituent	E_A, kcal mol^{-1}	*s*	*r*	ΔS^* at 25°, cal mol^{-1} °K^{-1}	Log *A*
H	12.50	0.03	0.9999	−28.70	6.95
m-CH_3	12.08	0.12	0.9980	−30.10	6.76
p-CH_3	11.61	0.06	0.9995	−29.95	6.68
m-OCH_3	13.02	0.11	0.9984	−27.69	7.18
p-OCH_3	9.28	0.03	0.9996	−36.03	5.35
m-Cl	15.00	0.15	0.9978	−23.70	8.05
p-Cl	14.29	0.22	0.9950	−25.16	7.73

the reaction center is less positively charged in the thiophene derivative. This is depicted in eq 4 below

$$\ln \frac{k_s}{k_u} = -\frac{e_x \delta e_s}{RTr_1} + \frac{e_y \delta e_s}{RT}\left(\frac{1}{r_0} - \frac{1}{r_2}\right) - \frac{\Delta W}{RT} \qquad (4)$$

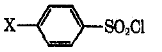
where k_s = the rate constant of the substituted compound, k_u = the rate constant of the unsubstituted compound, e_x, e_y, e_s = the effective electric charge on the attacking agent, on the leaving group, and on the atom reaction center, respectively, δe_s = the positive or negative incremental change in charge e_s by the substituent introduced in the substrate molecule, r_0 = the distance S–Y in the unperturbed substrate molecule, r_1 and r_2 = the distances X–S and S–Y in the transition state, and $\Delta W/RT$ is the nonelectrostatic part of ln (k_s/k_u) in the reaction

$$X + S\overset{r_0}{—}Y \longrightarrow X\overset{r_1}{—}S\overset{r_2}{—}Y \longrightarrow \text{products}$$

where S is the center of the reaction, X is the attacking agent, and Y is the leaving group.

In Table IV the ratio ln (k_s/k_u) at 25° for the reaction of some benzenesulfonyl chloride derivatives[2] and 2-thiophenesulfonyl chloride with aniline are reported.

TABLE IV

Sulfonyl chloride	X	ln (k_s/k_u)[a]
	*p*-NO_2	1.81
	H	0.00
	p-CH_3	−0.37
	p-OCH_3	−0.91
		−2.50

[a] k_u = reaction rate constant of benzenesulfonyl chloride with aniline.

According to eq 4, since e_x is negative, the term $-e_x/RTr_1$ is positive. Thus, if the increment δe_s is positive, and if the term $-e_x\delta e_s/RTr_1$ is greater than the terms $e_y\delta e_s/RT(1/r_0 - 1/r_2)$ and $\Delta W/RT$, ln (k_s/k_u) is positive; if the increment δe_s is negative, also ln (k_s/k_u) is negative, which is in accordance with the experimental results (Table IV).

The ln (k_s/k_u) value for 2-thiophenesulfonyl chloride (−2.50) is more negative than that of benzenesulfonyl chloride, showing that the reaction center in the thiophene derivative is less positively charged.

Experimental Section

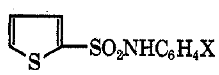
Materials.—2-Thiophenesulfonyl chloride was obtained according to the Hartough procedure,[15] bp 92–93° (1 mm), mp 32–33° from petroleum ether (bp 30–60°).

The various anilines are commercial products which were purified to constant melting point or boiling point by recrystallization or distillation. Methanol containing ~0.04% water (Carlo Erba) was used throughout.

All the sulfonanilides were synthesized by adding to a solution containing 0.065 mol of aniline in methanol (50 ml) 0.030 mol of 2-thiophenesulfonyl chloride in methanol (10 ml). The reaction was kept until completion; then the methanol was evaporated and the residue was treated with aqueous 40% sodium hydroxide and extracted twice with ether or filtered. The aqueous layer was acidified and the precipitate was filtered off, washed, and crystallized. In all cases the yield was ~95% in agreement with eq 1. The physical constants of sulfonanilides are reported in Table V.

TABLE V

PHYSICAL CONSTANTS OF 2-THIOPHENESULFONANILIDES[a]



No.	Registry no.	X	Mp, °C	Formula
1	39810-46-3	H[b]	99–100	
2	39810-47-4	*m*-CH_3[c]	88–89	$C_{11}H_{11}NO_2S_2$
3	39810-48-5	*p*-CH_3[c]	115	$C_{11}H_{11}NO_2S_2$
4	39810-49-6	*m*-OCH_3[c]	72–73	$C_{11}H_{11}NO_3S_2$
5	39810-50-9	*p*-OCH_3[c]	104	$C_{11}H_{11}NO_3S_2$
6	39810-51-0	*m*-Cl[c]	114	$C_{10}H_8ClNO_2S_2$
7	39810-52-1	*p*-Cl[c]	115	$C_{10}H_8ClNO_2S_2$

[a] All the compounds were crystallized from aqueous ethanol. [b] L. Weitz, *Ber.*, **17**, 799 (1884); A. P. Terent'ev and G. M. Kadatskiĭ, *Zhr. Obshch. Khim.*, **22**, 153 (1952); *Chem. Abstr.*, **46**, 11178 (1952). [c] Satisfactory combustion analytical data for C, H, N (±0.2%) were provided for these compounds: Ed.

Kinetic Procedure.—Rate measurements were done by a pH meter Jonosis type pH-Q_3 by titration of the acid produced with 0.1 *N* sodium hydroxide. The pH meter was standardized before each run with a buffer. The electrode was combined (glass, saturated calomel) type Ingold. The reaction vessel was sur-

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(15) H. D. Hartough, "Thiophene and Its Derivatives," Interscience, New York, N. Y., 1952, p 513.

rounded by a jacket for circulation of water at constant temperature (±0.05°) 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 ±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^*, were computed for 25° by eq 5.[16]

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

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.

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[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

KEITH YATES,* ROBERT S. MCDONALD, AND STANLEY A. SHAPIRO

Department of Chemistry, University of Toronto, Toronto M5S 1A1, Ontario, Canada

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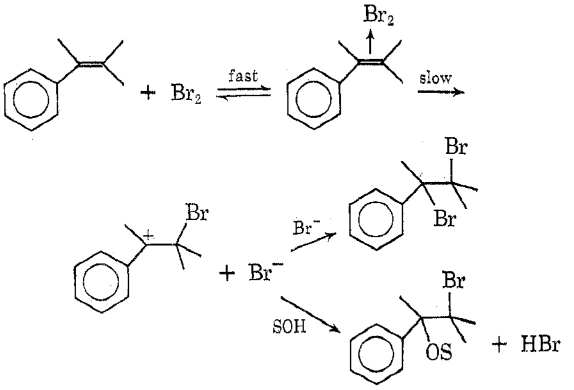
The rates of bromination of several ring-substituted styrenes have been measured as a function of temperature under both dominant second-order (k_2) and dominant third-order (k_3) conditions in acetic acid. The k_2 process is enthalpy controlled, while k_3 is entropy controlled. The ρ values (*vs.* σ^+) 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 equation[1] (1). Thus bromination

$$-\mathrm{d}[\mathrm{Br_2}]/\mathrm{d}t = [\text{olefin}](k_2[\mathrm{Br_2}] + k_3[\mathrm{Br_2}]^2 + k_{\mathrm{Br^-}}[\mathrm{Br_2}][\mathrm{Br^-}]) \qquad (1)$$

(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 $k_{\mathrm{Br^-}}$) is only important in the presence of significant bromide concentrations and has been ascribed to either a bromide ion catalyzed AdE3 process[2] 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 regiospecificity[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 intermediate[13] (eq 2). However, much



(2)

less is known[15] about the corresponding higher order process (k_3) which becomes important at higher bromine concentrations ($\gtrsim 10^{-2}$ M), mainly because the observed rates are very high under these conditions. Nonetheless, many early kinetic studies[1,14] 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

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

[2] N. Kanyaev, *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 ion[9] 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).