Kinetics of the Reaction of Benzenesulfonyl Chloride with Substituted **Benzoate Ions in Methanol**

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The rate constants and activation parameters for the reaction of benzenesulfonyl chloride with substituted benzoate ions have been measured in methanol. The reaction is second order overall and first order with respect to each reactant. The rate constants are greater with electron-donating substituents while they are lower with electron-withdrawing groups. The substituent effects are correlated by Hammett (ρ -0.35) and Brønsted (β 0.35) equations, respectively, and the results compared with the corresponding data for the reaction of benzenesulfonyl chloride with substituted anilines and related reactions. The kinetic results are interpreted in terms of a synchronous direct bimolecular nucleophilic displacement mechanism.

A number of studies have been made on the kinetics of the reaction of picryl chloride with anilines.¹⁻⁵ Ryan and Humffray,⁴ on one hand, reported the kinetics of picryl chloride with substituted phenoxide ions and anilines, respectively, while Mohanty and Nayak,⁵ on the other, reported the kinetics of the same compound with substituted benzoate ions, thus providing a comparison of this compound with oxygen and nitrogen nucleophiles. We report here a similar study involving the reaction of another activated halide, this time at a tetracoordinate sulfur in the side chain of an aromatic ring, with substituted benzoate ions in methanol with a view to comparing its reaction with that of the anilines on one hand and also with those of the reactions of picryl chloride and benzoate ions and anilines, respectively, on the other.

The reaction of benzenesulfonyl chloride with substituted benzoate ions in methanol takes place quantitatively according to eq 1. The reaction is second order overall,



 $X = H, m-CH_3, p-CH_3, p-OCH_3, p-OCH_3, p-Cl, m-Br, p-Br, m-NO_2, p-NO_2$

first order with respect to each reactant, and was followed by titrating the chloride ion produced by Volhard's method (see Experimental Section).

Results and Discussion

The reaction kinetics of benzenesulfonyl chloride with a large excess of the benzoate ion in methanol is pseudo first order with respect to benzenesulfonyl chloride. The plot of pseudo-first-order rate constant against benzoate ion concentration is linear, showing that the reaction is first order also with respect to the benzoate ion.

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

$$rate = k_2 [C_6 H_5 SO_2 Cl] [-OOCC_6 H_4 X]$$
(2)

Table I.	Second-Order	Rate	Constants	for the	Reaction		
of	Benzenesulfony	l Chlo	ride with	Substitu	ited		
Benzoate Ions in Methanol							

no.	substituent	$10^{3}k_{2}, \text{ L mol}^{-1} \text{ s}^{-1}$			
		$25 \degree C$	30 °C	35 °C	
1	Н	5.18	7.18	9.97	
2	m-CH ₃	5,33	8.40	11.67	
3	<i>p-</i> CH,	5.75	8.69	12.50	
4	m-OCH,	4.56	6.58	9.50	
5	p-OCH ₁	6.58	9,87	13.18	
6	p-Cl	4.27	6.38	9.32	
7	m-Br	3.80	5.92	8.06	
8	<i>p</i> -Br	4.07	6.10	8.89	
9	m-NO,	2.91	4.67	7.53	
10	p-NO ₂	2.78	4.30	6.76	

studied at different temperatures; the second-order overall rate constants, obtained by dividing the first-order rate constant by the benzoate ion concentration, are reported in Table I. Table I shows that electron-donating substituents in the benzoate ion increase the rate, while electron-withdrawing groups decrease it. A comparison of these results with those of the same compound with substituted anilines⁶ shows that the benzoates react more slowly than the anilines; they are weaker nucleophiles than anilines.

The activation parameters are listed in Table II, together with the linear correlation coefficients (r). In this reaction series, it has been found that the activation energies do not show a regular variation with substituents in the benzoate ion but that the changes in rate are due to changes in both ΔH^* and ΔS^* , with these two quantities varying in a parallel fashion such that a plot of ΔH^* against ΔS^* is linear. Thus they obey the isokinetic relationship, the isokinetic temperature being 337 K (r = 0.998). This linear relationship shown by the majority of the substituents is indicative of a single mechanism.⁴

The entropies of activation are negative, as expected for bimolecular reactions. The average value is -106 J mol⁻¹ K^{-1} . Comparing this with the average value of -146 J mol^{-1} K^{-1} (calculated from Rogne data⁶) for the reaction of benzenesulfonyl chloride with the substituted anilines, one notes a large difference. This difference could be attributed to a greater solvent participation in the transition state of the reaction of benzenesulfonyl chloride with aniline than with benzoate ion. In the aniline series, the transition state involves much greater charge separation than exists in the reactants, resulting in loss of freedom of solvent and a consequent decrease in entropy. In the

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 no.	substituent	E_{a} , ^b kJ mol ⁻¹	r	$\Delta H^{\pm}, a, b$ kJ mol ⁻¹	$\Delta S^{\ddagger,a,c}$ J mol ⁻¹ K ⁻¹	log A	
1	H	50.3	0.9974	47.8	134	6.53	
2	m-CH ₃	59.2	0.9999	56.7	105	8.13	
3	p-CH,	59.1	0.9998	56.6	104	8.13	
4	m-OCH,	55.5	0.9986	53.1	118	7.40	
5	p-OCH,	52.3	0.9997	49.8	125	7.00	
6	p-Cl	59.0	0.9986	56.5	107	7.98	
7	m-Br	57.5	0.9994	55.1	113	7.68	
8	<i>p</i> -Br	59.1	0.9998	56.6	107	7.98	
9	m-NO	72.9	0.9986	70.4	65	10.25	
10	p-NO,	67.6	0.9977	65.2	83	9.30	

Table II. Activation Parameters for the Reaction Rates in Table I

^a At 25 °C. ^b Estimated error ca. ± 2 kJ mol⁻¹. ^c Estimated error ca. ± 6 J mol⁻¹ K⁻¹.



Figure 1. Hammett plot for the reaction of benzenesulfonyl chloride with substituted benzoate ions in methanol at 25 °C.

benzoate ion on the other hand, there is already a formal charge on the oxygen atom, and the change from reactants to transition state involves only the spreading of an already existing charge. There will thus be less loss of freedom of solvent here than in the aniline series, hence the smaller decrease in entropy. The activation energies, on the other hand, are larger in the benzoate ion series than in the aniline series, average values being 59 and 47 kJ mol⁻¹, respectively. This can be accounted for, in part at least, by differences in the energy required for rehybridization of the oxygen or nitrogen as the case may be and by the differences in stabilization by solvation.

Figure 1, in which the Hammett plot is reported, shows that the reaction rate depends on the electron density on the oxygen atom of the benzoate ion. The sensitivity of the rate to substituents in the benzoate ion (ρ -0.35, r = (0.997) is comparatively smaller than that in aniline⁶ (ρ -2.15) with the same substrate in methanol. This is as expected; the reaction constant, which is a measure of the change in charge at the reaction center, is related to the extent of bond formation and bond breaking in the transition state.⁸ The more negative ρ is, the more will bond breaking have proceeded relative to bond making.

A similar result is also obtained in the comparison of the reactions of picryl chloride with benzoate ions,5 for which ρ is -1.05, and with anilines,⁴ for which ρ is -4.70, both in alcohol-water medium. The relatively higher values of ρ for the latter substrate are due to the nature of the transition state in nucleophilic aromatic substitution where there is a substantial charge development on the aryl





Figure 2. Plot of log k_2 at 25 °C for the reaction of benzene-sulfonyl chloride with substituted benzoate ions in methanol against the pK_a of the corresponding benzoic acids in water at 25 °C (Brønsted plot)

carbon due to the great electron withdrawal to the ring.

The Brønsted plot (Figure 2), obtained by using the pK_a values of the corresponding conjugate acids in water, is linear, verifying that the reaction rate depends on the basicity of the nucleophilic reagent. The slope (β 0.35, r = 0.974) is related to the degree of S-O bond formation in the transition state.⁹⁻¹¹

The kinetics, products, stoichiometry, and activation parameters of the reaction of benzenesulfonyl chloride with benzoate ions are consistent with the mechanism of a bimolecular nucleophilic substitution on sulfur. A nucleophilic substitution on sulfur can conceivably take place by a synchronous direct displacement or via an intermediate complex. One way of distinguishing between the two mechanisms is by a study of the element effect¹² which relates the relative rates for different leaving groups to the strength of the bond which is broken. By such a study, Ciuffarin et al.¹³ have postulated that the reactions of benzenesulfonyl chloride with oxygen and nitrogen nu-

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cleophiles follow an SAN mechanism with bond making as the rate-limiting step. Another way is by recourse to the Brønsted coefficients 14,15 for the nucleophile and for the leaving group, which have been related to the amount of bond formation and bond breaking, respectively, in the transition state. In this connection, the small (β 0.35) nucleophilic Brønsted coefficient obtained for the reaction of the substrate with benzoate ions should be considered as indicating little bond formation $^{16-18}$ in the transition state. Since this value is less than that for the anilines⁶ $(\beta 0.75)$ with the same substrate in the same solvent medium, we should assume a lesser degree of bond making with oxygen nucleophiles than with nitrogen bases. This behavior is in some way similar to that found for acyltransfer reactions¹⁹ studied by Fersht and Jencks, who infer that these reactions are coupled in such a way that a given degree of bond formation is accompanied by a similar amount of bond cleavage and that there is no indication of a tendency for a large amount of bond formation to be accompanied by much less bond breaking or vice versa. They suggest that the data are consistent both with a direct displacement or with an intermediate complex mechanism where bond formation is rate determining and remark that it is more meaningful to consider these reactions in terms of "early" or "late" transition states than in terms of relative amounts of bond formation and cleavage.

From the foregoing, we would expect the small nucleophilic Brønsted coefficient obtained for the reaction to be coupled with a correspondingly small leaving-group Brønsted coefficient. Even if we assume the value of -0.6reported by Vizgert²⁰ for the leaving-group Brønsted coefficient at sulfonyl sulfur, it would seem that a synchronous direct displacement mechanism is to be favored here because the "fairly" large Brønsted coefficient for the leaving group has to be coupled with the small Brønsted coefficient for the nucleophile.

Experimental Section

Materials. The socium benzoates were prepared from the corresponding benzoic acids by dissolving the acid in each case

in methanol and titrating it against a methanolic solution of sodium hydroxide, the end point being determined by an indicator. The solution was then concentrated and the sodium salt filtered off. Any excess acid was removed by washing with chloroform. The salt was then recrystallized from methanol and dried to constant weight at 100-110 °C.

The benzenesulfonyl chloride (Koch-Light grade) was repurified by distillation under reduced pressure; bp 80 °C (17 mmHg.).

Kinetic Procedure. In a typical kinetic run, the reaction was started by addition of a solution (50 mL) of ca. 0.02 mol of benzenesulfonyl chloride to a methanol solution (100 mL) containing ca. 0.1 mol of the benzoate ion. The reagents were mixed at the temperature of the experiment. The container was immediately stoppered, shaken, and placed in a constant-temperature bath (± 0.01 °C). At the initial time, the reagent concentrations were ca. $0.007 \text{ mol } L^{-1}$ for benzenesulfonyl chloride and ca. 0.07-0.14 mol L⁻¹ for the various benzoates. The reaction was then monitored by pipetting 5-mL aliquots at suitable intervals into 10 mL of 5% nitric acid and titrating the chloride ion by Volhard's method. All operations after the stoppage of the reaction were performed at 0 °C in order to prevent the hydrolysis of the unchanged benzenesulfonyl chloride. It was shown by control experiments that under such conditions the hydrolysis of benzenesulfonyl chloride was less than 2%. The observed pseudo-first-order rate constants were calculated from slopes of conventional plots of log (a - x) against time by using the least-squares method. In all cases, the reaction followed the pseudo-first-order kinetics well to at least 70% completion. The second-order rate constants k_2 were obtained by dividing the pseudo-first-order rate constants by the benzoate concentration. All rates were run in duplicate. The rate constants were reproducible to within $\pm 3\%$.

The activation energies and log A values were computed from the rate constants at three different temperatures by the method of least squares with the Arrhenius equation, the plot of log k_2 against 1/T being linear in all cases.

The Brønsted and Hammett slopes, their standard deviations, and the correlation coefficients were calculated by a least-squares treatment of log k_2 against pK_a or σ .

Product Analysis. Qualitative and quantitative product analyses were done by GLC by comparison of retention times and peak areas for the final reaction mixtures with methanolic solutions of the corresponding sulfobenzoates. For each of the pure isolated products, the GLC showed only a single peak. In the quantitative analysis, the sulfonyl chloride concentrations were about 5 times that used in the kinetic runs.

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Registry No. Benzenesulfonyl chloride, 98-09-9; sodium benzoate, 532-32-1; sodium 3-methylbenzoate, 17264-86-7; sodium 4-methylbenzoate, 17264-54-9; sodium 3-methoxybenzoate, 17264-90-3; sodium 4-methoxybenzoate, 536-45-8; sodium 4-chlorobenzoate, 3686-66-6; sodium 3-bromobenzoate, 17264-87-8; sodium 4-bromobenzoate, 2532-15-2; sodium 3-nitrobenzoate, 827-95-2; sodium 4-nitrobenzoate, 847-57-2.

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