

184. *Organosilicon Compounds. Part XX.\* Medium Effects in the Reaction between Trimethylsilylmethylbenzoate Ions and Hydroxide Ion.*

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The reaction between *o*-, *m*-, and *p*-trimethylsilylmethylbenzoate ions and alkali-metal hydroxides in water and in aqueous methanol has been studied kinetically over a wide range of ionic strength. Even at the high salt concentrations involved (up to 1M) the salt-effects are consistent with the Brönsted-Bjerrum theory for reaction between two negative ions.

WE have studied the alkaline cleavage of *o*-, *m*-, and *p*-trimethylsilylmethylbenzoic acids in the hope of obtaining more information about the mechanism of cleavage of C-Si bonds. Whilst this hope was not realised, the results provide a picture of medium effects in reactions between ions at a time when the theory of these effects is under review.<sup>1</sup>

*Salt Effects.*—For all three isomers, increase in the concentration of sodium hydroxide causes marked increase in the specific rate constant,  $k_s$  (the observed first-order rate constant divided by the alkali concentration), as Table 1 shows.

TABLE 1. *Reactions in water at 49.7° of trimethylsilylmethylbenzoate ions.*

<i>para</i> -Ion <sup>a</sup>				<i>meta</i> -Ion <sup>b</sup>				<i>ortho</i> -Ion <sup>b</sup>			
[NaOH]	$10^2 k_s$ , <sup>c</sup>	[NaOH]	$10^2 k_s$ , <sup>c</sup>	[NaOH]	$10^4 k_s$ , <sup>c</sup>	[NaOH]	$10^4 k_s$ , <sup>c</sup>	[NaOH]	$10^4 k_s$ , <sup>c</sup>	[NaOH]	$10^4 k_s$ , <sup>c</sup>
0.983	6.80	0.102	4.43	1.025	6.99	1.025	12.0	1.025	12.0	1.025	12.0
0.788	6.30	0.0760	4.25	0.530	5.63	0.530	9.25	0.530	9.25	0.530	9.25
0.592	5.95	0.0525	3.91	0.282	4.70	0.282	7.28	0.282	7.28	0.282	7.28
0.396	5.48	0.0294	3.61	0.158	3.89	0.158	5.83	0.158	5.83	0.158	5.83
0.200	4.82	0.0150	3.35								

<sup>a</sup>  $2.5 \times 10^{-3}$ M. <sup>b</sup>  $2.5 \times 10^{-2}$ M. <sup>c</sup> In min.<sup>-1</sup> mole<sup>-1</sup> l.

The values for the *para*-isomer extend to sufficiently low salt concentrations to provide a test of the Brönsted-Bjerrum theory of salt effects.<sup>2</sup> According to this the rate of a reaction between two ions, A and B, is given by  $k = k_0 f_A f_B / f_{\ddagger}$ , where  $k_0$  is the rate constant at infinite dilution and  $f_A$ ,  $f_B$ , and  $f_{\ddagger}$  are the activity coefficients of A, B, and the transition state, respectively. The activity coefficient,  $f_i$ , of an ion, *i*, is given by  $-\log f_i = Z_i^2 \alpha \mu^{1/2} / (1 + \beta d_i \mu^{1/2})$  where  $Z_i$  is the charge on the ion,  $d_i$  the distance of closest approach of another ion to the *i*-th ion, and  $\beta$  and  $\alpha$  are constants (which for water at 49.7° have values of  $0.334 \times 10^8$  and 0.503, respectively<sup>3</sup>). When  $Z_A = Z_B = -1$ , and the charge on the transition state is consequently  $-2$ , the reaction rate is given by

$$\log k = \log k_0 - \frac{\alpha \mu^{1/2}}{1 + \beta d_A \mu^{1/2}} - \frac{\alpha \mu^{1/2}}{1 + \beta d_B \mu^{1/2}} + \frac{4 \alpha \mu^{1/2}}{1 + \beta d_{\ddagger} \mu^{1/2}} \quad \dots \quad (1)$$

and a mean value,  $d$ , being adopted for the distance of closest approach,  $\log k = \log k_0 + 2 \alpha \mu^{1/2} / (1 + \beta d \mu^{1/2})$ .

As required, the variation in the rate of reaction,  $k_s$ , of the *para*-isomer with sodium hydroxide can be expressed by an equation,  $\log k_s = \log k_0 + 1.06 / (C + 1/\mu^{1/2})$ , as shown by the fair constancy of  $\log k_0$  [ $= \log k_s - 1.06 / (1.55 + 1/\mu^{1/2})$ ] in Table 2. The value of the constant  $C$  corresponds to the reasonable figure of 4.6 Å for the mean distance of closest approach of the ions. The success of this treatment indicates that there are no complications from ion-association even at the highest salt concentrations.

The rates of reaction of the *ortho*- and the *meta*-isomer increase more rapidly with

\* Part XIX, *J.*, 1957, 498.

<sup>1</sup> Harty and Rollefson, *J. Amer. Chem. Soc.*, 1954, **76**, 4811, and references therein.

<sup>2</sup> Frost and Pearson, "Kinetics and Mechanism," John Wiley and Sons Inc., New York, 1953, p. 138.

<sup>3</sup> Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955, pp. 228, 491.

increasing alkali concentration than does that of the *para*-isomer. The data extend over a very limited range of concentration, but in both cases an equation of form  $\log k_a = \log k_0 + 1.06/(C + 1/\mu^{\ddagger})$  can be derived with moderate success, as Table 3 shows. The values for the mean distance of closest approach of the ions (1.8 and 2.4 Å, respectively, for the *ortho*- and the *meta*-isomer) are rather low.

TABLE 2.

10[NaOH] .....	9.83	7.88	5.92	3.96	2.00	1.02	0.760	0.525	0.294	0.150
10 $\mu^*$ .....	9.86	7.90	5.95	3.98	2.02	1.05	0.785	0.550	0.319	0.175
$-\log k_a$ .....	1.167	1.20	1.225	1.26	1.32	1.35	1.37	1.41	1.44	1.47
$1.06/(1.55 + 1/\mu^{\ddagger})$	0.415	0.396	0.372	0.338	0.285	0.228	0.207	0.182	0.149	0.116
$-\log k_0$ .....	1.58	1.60	1.60	1.60	1.58	1.58	1.59	1.59	1.59	1.59

\* Includes the concentration of sodium *p*-trimethylsilylmethylbenzoate ( $2.5 \times 10^{-3}M$ ).

The results emphasise that in examining effects of structural change on the rate of reaction between ions, rate constants cannot safely be compared at a fixed ionic strength but must be extrapolated to infinite dilution. Thus the relative reactivities of the *para*- and the *ortho*-isomer above are 58 : 1 at a salt concentration of 1.05M, 85 : 1 at a salt concentration of 0.18M, and 100 : 1 at infinite dilution, the derived  $\log k_0$  values being used.

TABLE 3.

	<i>ortho</i> -Ion				<i>meta</i> -Ion			
[NaOH] .....	1.025	0.530	0.282	0.158	1.025	0.530	0.282	0.158
$\mu^a$ .....	1.050	0.555	0.307	0.183	1.050	0.555	0.307	0.183
$-\log k_a$ .....	2.921	3.034	3.138	3.234	3.156	3.250	3.326	3.410
$1.06/(C + 1/\mu^{\ddagger})^b$ .....	0.672	0.555	0.443	0.363	0.594	0.500	0.407	0.338
$-\log k_0$ .....	3.593	3.589	3.581	3.597	3.750	3.750	3.735	3.748

<sup>a</sup> Includes the concentration of the sodium salt of the organosilicon acid (0.025M). <sup>b</sup>  $C = 0.59$  and 0.80, respectively, for the *ortho*- and the *meta*-isomer.

*Specific Salt Effects.*—At high ionic strengths, salt effects frequently depend upon the nature as well as the concentration of the salts present.<sup>1</sup> In the reaction of the *p*-trimethylsilylmethylbenzoate ion, sodium chloride has a markedly smaller effect than sodium hydroxide. Thus at a sodium hydroxide concentration of 0.0294M the presence of 0.0614M-sodium chloride increases  $k_a$  (at 49.7°) from 3.6 to  $4.0 \times 10^{-2}$  min.<sup>-1</sup> mole<sup>-1</sup> l. whereas in 0.0908M-sodium hydroxide  $k_a$  is *ca.*  $4.4 \times 10^{-2}$  min.<sup>-1</sup> mole<sup>-1</sup> l. Again, in the presence of 0.833M-alkali and 0.491M-sodium chloride  $k_a = 6.6 \times 10^{-2}$  min.<sup>-1</sup> mole<sup>-1</sup> l., whereas in 1.324M-alkali  $k_a = ca. 7.8 \times 10^{-2}$  min.<sup>-1</sup> mole<sup>-1</sup> l. (by extrapolation).

TABLE 4. Reaction of the *para*-ion and various alkalis in water (49.7°).

10 <sup>2</sup> [NaOH] .....	98.3	78.8	59.2	39.2	20.0	10.2	7.60	5.25	2.94	1.50
10 <sup>2</sup> $k_a$ (min. <sup>-1</sup> mole <sup>-1</sup> l.)	6.80	6.30	5.95	5.48	4.82	4.43	4.25	3.91	3.61	3.35
* 10 <sup>2</sup> $k_a$ (min. <sup>-1</sup> mole <sup>-1</sup> l.)	10.22	9.28	8.67	7.86	6.62	5.76	5.38	4.77	4.17	3.72
10 <sup>2</sup> [KOH] .....	98.3	78.8	59.2	39.6	20.0	10.2	5.25			
10 <sup>2</sup> $k_a$ (min. <sup>-1</sup> mole <sup>-1</sup> l.)	7.70	6.96	6.57	5.76	4.97	4.64	4.12			
* 10 <sup>2</sup> $k_a$ (min. <sup>-1</sup> mole <sup>-1</sup> l.)	10.20	9.37	8.96	7.83	6.53	5.81	4.78			
10 <sup>2</sup> [LiOH] .....	106.3	85.1	63.9	42.7	21.5	10.9				
10 <sup>2</sup> $k_a$ (min. <sup>-1</sup> mole <sup>-1</sup> l.)	5.49	5.30	5.05	5.06	4.68	4.32				
* 10 <sup>2</sup> $k_a$ (min. <sup>-1</sup> mole <sup>-1</sup> l.)	9.97	9.34	8.55	8.00	6.71	5.74				

\* Activity coefficients  $\gamma_{\pm}$  at 25° have been used since those of lithium hydroxide are not known at higher temperatures.

A more interesting aspect of specific salt effects is revealed by the rates of reaction of the *p*-benzoate with sodium, lithium, and potassium hydroxides. The specific rates depend on which alkali is present, as Table 4 reveals; *e.g.*, at 1M-alkali the reaction with

<sup>1</sup> Harned and Swindells, *J. Amer. Chem. Soc.*, 1926, **48**, 126.

<sup>2</sup> Conway, "Electrochemical Data," Elsevier Publishing Co., 1952, pp. 87, 88.

potassium hydroxide is *ca.* 1.5 times as fast as that with lithium hydroxide. If the specific rates are referred to mean activities instead of concentrations of alkalis (*i.e.*,  $k_a = k_s/f_{\text{MOH}}$ , where  $f_{\text{MOH}}$  is the mean activity coefficient of the alkali) then the specific rates,  $k_a$ , at a particular alkali concentration are reasonably independent of which alkali is present.

Since, say, the first term on the right-hand side of equation (1) refers to variation of the activity coefficient of hydroxide ion with ionic strength, we have  $\log k_a = \log k_0 + 3\alpha\mu^\ddagger/(1 + \beta d'\mu^\ddagger)$  where  $d'$  is now the mean distance of closest approach of carboxylate ion and of the transition state, and would be expected to be rather larger than  $d$ , above, which includes the closest approach distance for hydroxide ion.

A plot of  $\log k_a$  against  $1/(C + 1/\mu^\ddagger)$  (where  $C = 1.7$ , corresponding to a mean distance of closest approach of the ions of 5.1 Å) is, as required, a straight line of slope 1.60 (*i.e.*,  $3\alpha$ ), as revealed by the constancy of  $\log k_0$  in Table 5;  $\log k_0$  has the same value as when derived from specific rate constants,  $k_s$ , above. This plot covers all three alkalis, and it is thus clear that specific effects of the cations are exerted solely on the activity coefficient of the hydroxide ion, the ratio of the activity coefficients of the carboxylate ion and the transition state being independent of the nature of the cation.

TABLE 5.

[MOH]	1.6		KOH		NaOH		LiOH			
	$1.7 + 1/\mu^\ddagger$	$-\log k_a$	$-\log k_0$	$-\log k_a$	$-\log k_0$	[MOH]	$1.7 + 1/\mu^\ddagger$	$-\log k_a$	$-\log k_0$	
0.983	0.592	0.993	1.585	0.991	1.583	1.063	0.600	1.000	1.600	
0.788	0.566	1.028	1.594	1.033	1.599	0.851	0.576	1.030	1.606	
0.592	0.534	1.048	1.582	1.062	1.596	0.639	0.523	1.068	1.591	
0.396	0.486	1.106	1.592	1.105	1.591	0.427	0.494	1.097	1.591	
0.200	0.408	1.185	1.593	1.179	1.587	0.215	0.416	1.173	1.589	
0.102	0.334	1.236	1.570	1.255	1.589	0.109	0.339	1.241	1.580	
0.0760	0.269	1.321	1.590	1.270	1.574	—	—	—	—	
0.0525	—	—	—	1.321	1.590	—	—	—	—	
0.0294	—	—	—	1.380	1.599	—	—	—	—	
0.0150	—	—	—	1.429	1.602	—	—	—	—	

*Change of Solvent.*—Equation (1) for salt effects can be applied with fair success to the cleavage of the *p*-carboxylate ion by sodium hydroxide in 5% (w/w) of water in methanol. (Most of the alkali will be present as methoxide ion.) In methanol at 50° (dielectric constant, 30.4) a plot of  $\log k_a$  against  $1/(C + 1/\mu^\ddagger)$  should have a slope of 3.7. The values of  $\log k_0$  derived from the equation  $\log k_a = \log k_0 + 3.7/(2.8 + 1/\mu^\ddagger)$  are reasonably constant as Table 6 shows. The value, 2.8, of  $C$  corresponds to a mean distance of closest

TABLE 6. Cleavage of the para-ion in 5% (w/w) water-methanol (49.7°).

[NaOH]	1.023	0.869	0.767	0.630	0.526	0.396	0.262	0.130
<sup>a</sup> $-\log k_a$	2.493	2.520	2.548	2.585	2.597	2.652	2.728	2.810
<sup>b</sup> $3.7/(2.8 + 1/\mu^\ddagger)$	0.977	0.955	0.943	0.914	0.888	0.844	0.781	0.670
$-\log k_0$	3.470	3.475	3.491	3.499	3.485	3.496	3.509	3.480

<sup>a</sup>  $k_a$  in  $\text{min.}^{-1} \text{mole}^{-1} \text{l.}$  <sup>b</sup> The concn. of sodium trimethylsilylmethylbenzoate ( $2.5 \times 10^{-3}\text{M}$ ) is taken into account.

approach of the ions of 5.5 Å (since  $\beta = 0.507 \times 10^8$ ) in good agreement with the figures of 4.5 Å for the reaction in aqueous solution where the alkali is all present as hydroxide ion. If the derived value of  $\log k_0$  is correct then the presence of 1M-alkali causes a 10-fold rate increase in the specific rate constant.

The effect on  $k_a$  (at 49.7°) of change of solvent from water to 39% (w/w) of water in methanol is shown in Table 7 for all three isomers at the same sodium hydroxide concentration (0.98M), along with the accompanying changes in the energy and entropy factors of the Arrhenius equation. The rate is decreased in all three cases, more for the *meta*-compound than for the other two. (It is clear from the discussion above that the rate

ratios would be substantially different at infinite dilution.) Such a decrease in rate on going to a less polar medium is expected for a reaction between ions of like charge.<sup>7</sup>

For uncharged benzyltrimethylsilanes increase in activation energy caused by structural change is accompanied by increase in the log *A* factor, while in the case of the carboxylate ions increase in *E* between *para*- and *ortho*- and *meta*-isomers is accompanied by decrease

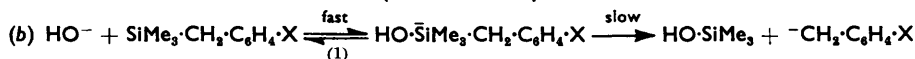
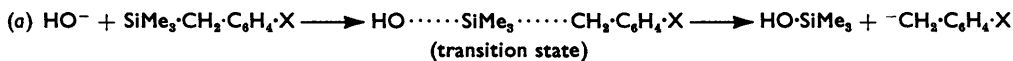
TABLE 7.

Ion	<i>para</i>		<i>ortho</i>		<i>meta</i>	
	100	39	100	39	100	39
Water (wt.-%) .....	100	39	100	39	100	39
10 <sup>4</sup> <i>k</i> <sub>s</sub> (min. <sup>-1</sup> mole <sup>-1</sup> l.) .....	680	94	11.9	1.39	6.9	0.59(5)
Rate ratio .....	7.2	1	8.6	1	11.6	1
<i>E</i> (kcal.) .....	19.6	20.6	21.2	22.4	21.9	22.9
log <i>A</i> * .....	12.05	12.15	11.45	11.3	11.7	11.3

\* Based on time (min.).

in log *A*. This is because of direct interaction between the negative charges on the reactants,<sup>7</sup> which will be least important for the *para*-compound since the charges will be furthest apart in the transition state. This interaction, operating through both *E* and log *A*, along with the larger inductive effect from the *ortho*-position, is sufficient to account for the low reactivity of the *ortho*-compound compared with the *para*-isomer.

*The Mechanism of the Cleavage.*—The kinetics of the reactions between neutral benzyltrimethylsilanes and sodium hydroxide are consistent with either of the two mechanisms below, of which (a) involves synchronous attack of hydroxide ion and separation of the benzyl ion, and (b) initial formation of a quinquevalent silicon intermediate.<sup>6</sup> (In both cases the benzyl anion will react rapidly with solvent.)



At first sight, when X = CO<sub>2</sub><sup>-</sup>, the close agreement of the salt effects with those expected for reaction between two negative ions seem to rule out mechanism (b), since the rate-determining step in this involves a doubly-charged reactant and a doubly-charged transition state and will not be much affected by ionic-strength changes. However, the salt effects are determined by change from the original ground state (*i.e.*, separate negative ions) to this doubly-charged transition state, and thus will be the same in mechanisms (b) and (a). Similar conclusions can be reached by considering the effect on the overall rate of variation in the equilibrium constant of step (1) with ionic strength.

#### EXPERIMENTAL

For reactions in water the acids were dissolved in a slight excess of aqueous alkali and a suitable volume of this solution was added to more concentrated alkali to initiate reaction. The reactions were followed spectrophotometrically as previously described.<sup>6</sup>

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<sup>6</sup> Eaborn and Parker, *J.*, 1955, 126.

<sup>7</sup> Frost and Pearson, *op. cit.*, p. 133.