673. *The Mechanism of Hydrolysis of Acid Chlorides. Part V.* The Effect of Solvent and Hydroxyl Ions on the Rate of Solvolysis of Substituted Benzoyl Chlorides.*

By D. A. BROWN and R. F. HUDSON.

Studies of the effect of solvent composition and added hydroxide ions on the rate of hydrolysis of substituted benzoyl chlorides show that a change in mechanism from S_N2 to S_N1 occurs in the following order :

$$(S_N2) - 2 : 4 : 6\text{-}(NO_2)_3 \simeq p\text{-}NO_2 > H > p\text{-}CH_3O \gg 2 : 4 : 6\text{-}(CH_3)_3 - (S_N1)$$
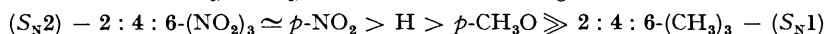
The nature of solvation of the transition state in aqueous mixtures is discussed, and the change in rate of S_N1 solvolysis with changes in solvent composition is attributed entirely to changes in entropy of solvation.

The observed increases in activation energy with water content are shown to be due to the gradually changing structure of the transition state, and not directly to changes in the structure of the solvent.

PREVIOUS papers have dealt with the effect of substitution on the rate of hydrolysis of benzoyl chloride in media of low and high water content, and the considerable change in rate order has been discussed in terms of a gradual change in mechanism from a bimolecular

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* Part IV, *J.*, 1953, 888.

(S_N2) to a unimolecular ionisation process (S_N1). The effect of increasing the water content of the medium on the rate of hydrolysis in the case of the unsubstituted chloride at various temperatures is in agreement with this interpretation, for a considerable increase in activation energy is observed.

To broaden the investigations, it was decided to investigate the variations in E and k with changes in solvent composition for several substituted chlorides containing strong electron-donating and electron-attracting groups and to compare the effects with the corresponding behaviour of well-established S_N1 reactions.

EXPERIMENTAL

Purification of Materials.—Acetone, benzoyl chloride and p-nitrobenzoyl chloride were all purified as described by Hudson and Wardill (*J.*, 1950, 1729). p-Methoxybenzoyl chloride was purified by distillation twice under reduced pressure; it had b. p. 145°/14 mm. 2 : 4 : 6-Trinitrobenzoyl chloride was prepared from 2 : 4 : 6-trinitrobenzoic acid by means of thionyl chloride, and purified by repeated recrystallisation from light petroleum; it had m. p. 158°.

2 : 4 : 6-Trimethylbenzoyl chloride was prepared from mesitylene by bromination, conversion of the product into the acid *via* the Grignard reagent by means of carbon dioxide, and treatment of the acid as usual; the chloride was purified by distillation under reduced pressure, and then had b. p. 118°/18 mm. 2 : 4 : 6-Trimethylbenzyl chloride was prepared by treating mesitylene with formaldehyde and concentrated hydrochloric acid, and similarly purified; it had b. p. 130°/22 mm., m. p. 37°.

TABLE 1. *Effect of* OH^- *on the solvolysis of* p-*methoxybenzoyl chloride.*

Solvent composition : 75% aqueous acetone by volume. Temperature of reaction medium : 0·2°.
Initial concn. of chloride (a) : $2·424 \times 10^{-3}$ mole/l. Initial concn. of NaOH (b) : $5·790 \times 10^{-3}$ mole/l.
Mean $k_2 = 0·40(4) \pm 0·015$ l. mole^{-1} sec.$^{-1}$.

Time, secs.	No. of drops of HCl	Reaction, %	10^3x, mole/l.	$10^3 (a - x)$, mole/l.	$10^3 (b - 2x)$, mole/l.	k_2
69	4	14·0	0·3402	2·084	5·109	0·350
79	5	17·5	0·4253	1·999	4·939	0·405
96	6	21·1	0·5103	1·914	4·769	0·417
132	7	24·6	0·5954	1·829	4·699	0·460
150	9	29·8	0·7654	1·659	4·259	0·397
196	10	35·1	0·8505	1·574	4·089	0·396
256	12	42·1	1·021	1·403	3·749	0·402
369	15	52·6	1·276	1·148	3·238	0·410
541	18	63·2	1·530	0·8937	2·729	0·406
705	20	70·2	1·701	0·7230	2·388	0·398
925	22	77·2	1·871	0·5530	2·048	0·409

TABLE 2. *The effect of solvent and temperature on the rate of hydrolysis of benzoyl chloride in dioxan–water mixtures.*

Temp.	% H_2O (v/v)	N_{H_2O} †	Concn. of chloride, mole l.$^{-1}$	10^5k_1, sec.$^{-1}$	10^5k_1, mean	Temp.	% H_2O (v/v)	N_{H_2O} †	Concn. of chloride, mole l.$^{-1}$	10^5k_1, sec.$^{-1}$	10^5k_1, mean
15°	5 *	—	0·0217	3·81	3·90	25°	15	0·4630	—	—	36·8 ‡
			0·0201	3·98		35	,,	—	—	—	77·4 ‡
25	,,	0·2000	0·0253	7·80	7·71	15	20	—	0·0271	24·13	24·27
35	,,	—	0·0217	7·62		15	,,	0·5500	0·0280	24·41	
			0·0285	14·61	14·8	25	,,	—	—	—	56·0 ‡
			0·0276	14·98		35	—	—	—	—	122·0 ‡
15	10 *	—	0·0208	10·51	10·60	15	33⅓	—	0·0219	60·01	60·1
			0·0219	10·69					0·0206	60·19	
25	,,	0·3520	0·0250	21·19	21·40	25	,,	0·7096	—	—	144·0 ‡
			0·0261	21·61		35	,,	—	—	—	323·0 ‡
35	,,	—	0·0201	41·81	41·80	15	50	0·8301	0·0256	261·2	260·6
			0·0215	41·79		25	,,	—	0·0217	260·0	
15	15	—	0·0289	17·01	17·10				—	—	>600·0 ‡
			0·0297	17·19							

* Results obtained by acidimetric titration method. † N_{H_2O} = mole-fraction of H_2O.
‡ These rate values were obtained by J. Wardill.

Rate Measurement.—Three different methods were employed, depending on the rate of the reaction and the accuracy required. The experiments with benzoyl chloride in water–dioxan mixtures utilised the conductivity method described by Archer and Hudson (*J.*, 1950, 3259)

since the activation energies were required with the maximum accuracy. In most cases, the rate was followed electrometrically by the balancing-cell method used by Hudson and Wardill (*loc. cit.*). The method was improved by the following modifications. Only a small volume (5 ml.) of acetone was used as solvent for the chloride before initiating the reaction, because it was found that the addition of this amount to the acetone–water mixture at the same temperature produced no appreciable temperature change in the resulting reaction medium. The concentration of acid liberated on completion of reaction was measured either by direct balancing of the reaction and titration cells, or by volumetric and/or gravimetric analysis. In all experiments the temperature of the reaction mixture was measured by means of a calibrated " thermistor " resistance, in order to detect very small temperature changes.

Reaction with 2 : 4 : 6-trinitrobenzoyl chloride was so slow that the rate was followed by titration of liberated hydrogen chloride after removal of the unhydrolysed chloride by ether-extraction (Olivier and Berger, *Rec. Trav. chim.*, 1926, **45**, 452). Direct titration of the mixture in acetone, with lacmoid as indicator, which was used for following the rate of hydrolysis of 2 : 4 : 6-trimethylbenzyl chloride, could not be employed for the trinitrobenzoyl chloride because sodium hydroxide reacts with 2 : 4 : 6-trinitrobenzoic acid non-stoicheiometrically.

Evaluation of Rate Constants.—Except in the experiments in alkaline solution, the rate constant k_1 was evaluated graphically by applying the first-order rate equation. In the presence of hydroxide ions, the rate is given by $dx/dt = k_1(a - x) + k_2(a - x)(b - 2x)$, where a and b are the initial concentrations of chloride and hydroxide respectively. Integration leads to the general equation

$$t[k_1 + k_2(b - 2a)] = \ln[a/(a - x)] - \ln\{(k_1 + k_2b)/[k_1 + k_2(b - 2x)]\}$$

As the value of k_1 is known from the neutral hydrolysis, the bimolecular rate constant for the hydroxide reaction k_2 may be obtained by successive approximations. This yields more accurate values than the graphical determination of the initial rate previously employed (Hudson and Wardill, *loc. cit.*), and the results of a typical experiment are given in Table 1.

DISCUSSION

An ionisation reaction (S_N1) is characterised by (*a*) the lack of bond formation between two dissimilar molecules and (*b*) considerable separation of charge in one particular bond only. Consequently, the transition states in these reactions are similar in structure, and it is not surprising, therefore, that the rates of solvolysis are related uniformly to the solvating power of the solvent (Grunwald and Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846). This mechanism in general is associated with high activation energies, which are found to be approximately constant for several alkyl halides in alcohol, water, and mixed solvents. The considerable changes in velocity constant with solvent are therefore due almost entirely to changes in the collision frequency.

Similarly the heats of solvation of salts in water and the alcohols are very similar (Mischenko, *Acta Physicochim. U.R.S.S.*, 1935, **3**, 693). The free energy of solvation changes considerably with the polarity of solvent, so that ion solvation is controlled mainly by the entropy change. The similarity of salt ionisation and S_N1 solvolysis is shown by the following comparison. The difference in ΔF of solvation of KCl and NaCl in water and methyl alcohol is approximately 7·5 cal./mole (Latimer and Slansky, *J. Amer. Chem. Soc.*, 1940, **62**, 2020). This would account for a rate ratio of *ca.* 10^5 compared with the observed value of $0·4 \times 10^5$ for the solvolysis of *tert.*-butyl chloride (Olsen and Halford, *ibid.*, 1937, **59**, 2644). It seems highly probable, therefore, that the change in velocity of an S_N1 reaction may be attributed almost entirely to changes in entropy of solvation.

Consider a similar reaction which is proceeding by a bimolecular S_N2 mechanism : the influence of the nucleophilic reagent A is to decrease the activation energy by partial bond formation, and by reduced extension of R–X : A + R–X $\longrightarrow$ A–R–X. For a given increase in the polarity of the solvent, the change in $-\Delta F_s$ will be greater for the ionisation process than for the S_N2 process, the charge distribution being assumed to be smaller and less localised in the latter case, irrespective of the nature of the solvent forces (see below). This condition is expressed in Hughes and Ingold's generalisation that solvation influences S_N1 to a greater extent than S_N2 reactions (*J.*, 1935, 244).

The greater value of $-\Delta F_s$ tends to promote the S_N1 mechanism, involving a decrease in the energy contribution from the partially formed bond, with a consequent increase in

E^*. Simultaneously, the contribution to the entropy decrease due to the interaction of the attacking molecule and the central carbon atom is reduced, so that the resultant increase in activation entropy is due to two inter-related effects. According to this view, the increases in E with solvent polarity are caused by changes in transition-state structure, and not by changes in the structure of the solvent only. These energy changes have been attributed to the increased force necessary to remove a solvent molecule from the pseudo-crystalline structure of the more polar liquid (Pearson, *J. Chem. Phys.*, 1952, **20**, 1478). Clearly, this effect would be greater in S_N1 reactions, which are controlled entirely by solvent action, *i.e.*, in cases where the actual changes in E^* are negligible.

The experimental activation energies given in Tables 3 and 4, and related to water content in Fig. 1, show that the change is less in the hydrolysis of p-methoxybenzoyl chloride, which tends to react by the S_N1 mechanism, than in that of the corresponding nitro-compound. The presence of a strongly electron-attracting group in the latter

FIG. 1.

Benzoyl chlorides in acetone–water.
tert.-Butyl chloride in methanol–water.
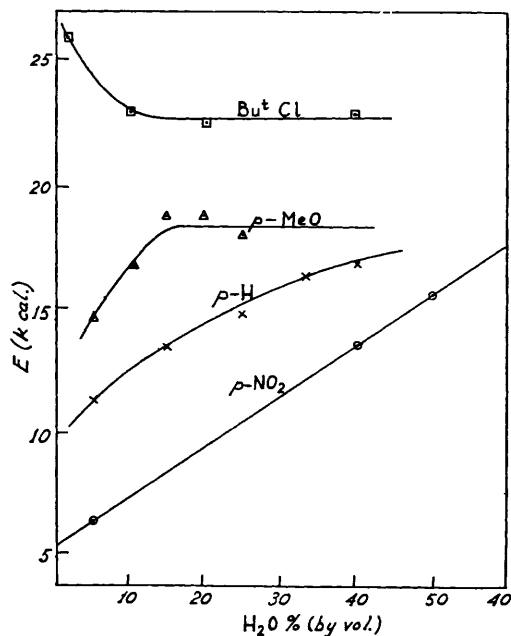
promotes the S_N2 mechanism, so that a considerable change in transition-state structure is produced by increasing the ionising power of the medium in order to promote the S_N1 mechanism.

TABLE 3. *The effect of solvent on Arrhenius parameters for the hydrolysis of benzoyl chloride.*

% Water (v/v)	N_{H_2O}	$10^5 k_1$, sec.$^{-1}$	E_{15-25}	log P_{25}	E_{25-35}	log P_{35}
5	0·2000	7·71	11·6	4·387	11·9	4·613
10	0·3520	21·40	12·0	5·132	12·2	5·278
15	0·4630	36·8	13·1	6·176	13·6	6·539
20	0·5500	56·0	14·3	7·238	14·2	7·166
33⅓	0·7096	144·0	14·9	8·088	14·8	8·109
50	0·8301	>600	—	—	—	—

The Nature of the Solvation.—The energy and entropy changes of reactions leading to pseudo-ionic transition states have recently been interpreted by Pearson (*loc. cit.*) in terms of Kirkwood's theory of dipole interaction (*J. Chem. Phys.*, 1934, **2**, 351). According to this treatment, which assumes a Born changing process, the free energy of a dipole of moment μ and radius r in a liquid of dielectric constant D is given by

$$-\Delta F = kT \ln x = \mu^2(D-1)/r^3(2D+1)$$

TABLE 4. *The effect of solvent on the rate of hydrolysis of substituted benzoyl chlorides.*

Temp.	% H_2O (v/v)	Concn. of chloride	$10^4 k_1$, sec.$^{-1}$	$10^4 k_1$, mean	E	log PZ
			p-Nitrobenzoyl chloride.			
0°	5	—	—	5·86 *	—	—
15	,,	—	—	12·3 *	6·67	2·12
25	,,	—	—	16·9 *	—	—
0	15	0·00219	12·55 }	12·65	,.	,,
		0·00258	12·76 }			
,,	20	0·00228	16·12 }	16·20	—	—
		0·00289	16·28 }			
,,	25	0·00356	20·50 }	20·32	—	—
		0·00187	20·15 }			
0	40	0·00371	48·96 }	50·16	—	—
		0·00320	51·37 }			
— 9·9	,,	0·00251	19·95	—	—	—
−10·1	,,	0·00221	18·84	—	13·7	8·65
−11·7	,,	0·00219	15·90	—	—	—
−15·6	,,	0·00312	10·64	—	—	—
			2 : 4 : 6-Trinitrobenzoyl chloride.			
0	10	0·0115	0·3908 }	0·4017	—	—
		0·0107	0·4127 }			
20·1	,,	0·0119	2·2776 }	2·82	15·5	6·81
		0·0121	2·865 }			
0	20	0·0101	0·7711 }	0·733	—	—
	20	0·0120	0·6950 }			
,,	30	0·0109	0·9826 }	1·029	—	—
		0·0121	1·075 }			
			p-Methoxybenzoyl chloride.			
25	5	—	—	0·292 *	14·7	5·89
35	,,	—	—	0·654 *	—	—
0	10	0·0275	0·1271 }	0·128	16·8	8·56
		0·0270	0·1289 }			
15	,,	0·0281	0·647 }	0·639	17·7	—
		0·0219	0·631 }			
25	,,	0·0210	1·79 }	1·80	—	—
		0·0320	1·81 }			
0	15	0·0212	0·415 }	0·429	18·9	10·77
		0·0272	0·443 }			
15	,,	0·0251	2·62 }	2·63	—	—
		0·0201	2·65 }			
0	20	0·0195	1·259 }	1·252	18·9	11·24
		0·0310	1·244 }			
12	,,	0·0197	4·946 }	4·940	—	—
		0·0215	4·933 }			
0	25	0·00415	2·820	—	—	10·87
— 4·65	,,	0·00519	1·303	—	18·0	—
−12·46	,,	0·00301	0·535	—	—	—
−13·9	,,	0·00356	0·4950	—	—	—
0	30	0·00391	7·12 }	7·03	—	—
,,	,,	0·00410	6·93 }			
			2 : 4 : 6-Trimethylbenzoyl chloride.			
0·2	5	0·00195	15·84	—	—	—
— 3·5	,,	0·00221	8·861	—	—	—
— 7·1	,,	0·00250	5·041	—	22·0	14·78
−10·75	,,	0·00181	2·890	—	—	—
— 8·8	10	0·00270	71·29	—	—	—
−10·75	,,	0·00219	50·30	—	—	—
−12·2	10	0·00250	42·18	—	24·0	17·67
−16·1	,,	0·00210	18·84	—	—	—
−19·2	,,	0·00310	10·87	—	—	—
			2 : 4 : 6-Trimethylbenzyl chloride.			
30·0	25	0·0215	0·1308 }	0·1342	—	—
		0·0192	0·1376 }			
20·4	50	0·0105	105·5 }	103·2	—	—
—	—	0·0112	101·1 }			

* Values taken from Part III.

Results in the concentration range 0·01—0·03N were obtained by acidimetric titration method.
Results in the 0·002—0·005N concentration range were obtained by the electrometric method.

By differentiation with respect to temperature, an equation for the entropy change is obtained which, combined with the above equation, leads to an expression for the heat of solvation. These expressions may be combined with the general equation of the absolute rate theory

$$k = \left(\frac{kT}{h}\right)e^{-\Delta F/RT} = \left(\frac{kT}{h}\right)e^{\Delta S/R}e^{-\Delta H/RT}$$

to give corresponding relations for heat and entropy of activation :

and

$$\left[\frac{\partial \Delta F^*}{\partial T}\right] = -\Delta S^* = \frac{3D}{(2D+1)^2} \cdot \left[\frac{d \ln D}{dT}\right]_p \cdot \Sigma\frac{\mu^2}{r^3}$$

$$-\Delta H = \left[\left(\frac{D-1}{2D+1}\right) + \frac{3DT}{(2D+1)^2}\left(\frac{d \ln D}{dT}\right)_p\right] \cdot \Sigma\frac{\mu^2}{r^3}$$

where $\Sigma\frac{\mu^2}{r^3}$ refers to the difference in $\frac{\mu^2}{r^3}$ for reactants and transition state. Assuming a likely value for this factor representing the increase in polarity of the transition state, we reach the following conclusions : (a) $(-\Delta F)$ increases regularly with dielectric constant; (b) $(-\Delta H)$ is approximately constant for most polar liquids; (c) the change in $(-\Delta F)$ is due almost entirely to changes in $(-\Delta S)$.

Conclusions (b) and (c) are in qualitative agreement with data on the ionisation of salts and solvolysis of alkyl halides already considered, although the magnitude of the calculated values, a likely value for $\Sigma\frac{\mu^2}{r^3}$ being assumed, is much less than experimentally observed in these reactions. In addition, a uniform relation between ΔF and D is not observed in the case of ionisation S_N1 reactions as shown by the following values for the solvolysis of *tert.*-butyl chloride (see values listed by Grunwald and Winstein, *loc. cit.*).

Solvent	D	E	K	Solvent	D	E	K
Acetic acid ...	7·1	26·43	$2 \cdot 1 \times 10^{-7}$	Water	80	22·6	$3 \cdot 3 \times 10^{-2}$
Ethyl alcohol	25	26·0	$9 \cdot 7 \times 10^{-8}$	48·6% H_2O in dioxan	34	22·8	$1 \cdot 81 \times 10^{-4}$
Methyl alcohol	32·5	25·0	$8 \cdot 2 \times 10^{-7}$	80% aqueous acetone}	33·4	22·6	$1 \cdot 94 \times 10^{-6}$
Formic acid ...	47	22·9	$1 \cdot 1 \times 10^{-3}$	(v/v)			

Owing to the inadequacy of this treatment, the solvation process can probably be treated more satisfactorily, as in the case of the ionisation of salts, by considering an inner solvation shell to be formed by co-ordination of a definite number of solvent molecules surrounded by an outer layer in which solvent molecules are mobile. It is solvation due to the solvent molecules in this outer shell only which can be treated by the above method, and, as shown by Eley and Evans (*Trans. Faraday Soc.*, 1938, **34**, 1093), the contribution of this energy is less than that of the co-ordination energy. The latter is given approximately by $E = \mu_1\mu_2/(r_1 + r_2)^3$ for interaction of two dipoles μ_1 and μ_2 of radii r_1 and r_2, or more closely by $z_1z_2e^2/(r_1 + r_2)^3$ where z_1 and z_2 represent the fractional charges in the interacting atoms of the two dipoles and r_1 and r_2 are the effective radii. Thus, in the case of hydroxylic liquids solvation is due largely to the interaction of oxygen and hydrogen atoms of the hydroxyl group with ion or dipole, and consequently the interaction distance $r_1 + r_2$ is probably equal to $\frac{1}{2}r_{OH} + \frac{1}{2}r_{CCl}$ and not to the average radii of the two interacting molecules. Consequently, the co-ordination energy of water and the alcohols is very similar, with the result that the total heat of solvation is approximately constant.

Similarly, the large entropy decreases (the magnitude of which, as already mentioned, cannot be explained by entropy of Born changing) are due primarily to co-ordination of the inner shell resulting in reduced rotation (libration) of the dipoles. The small entropy changes in the case of water and other associated liquids are attributed to the pseudo-crystalline structure of the liquids, as shown by the low entropies of fusion of water and alcohols. Thus solvation of a large dipole or ion pair by several water molecules which become firmly bound may cause a considerable difference in solvation entropy on change of the solvent from water to an organic liquid (*e.g.*, acetone or dioxan).

In spite of the formal complexity of the solvation process in binary liquid mixtures, the variation in reaction velocity with changes in solvent composition may be represented simply in terms of this specific solvation. In general, the free energy of solvation of the transition state by one liquid will be much greater than that by less polar liquids, so that a stoicheiometric relation between reaction velocity and concentration of the more polar component is to be expected. Thus in aqueous mixtures, the specific solvation will be due only to water molecules over a wide range of solvent composition. This explains the considerable effect of small quantities of water and alcohol in a solvent of low polarity on

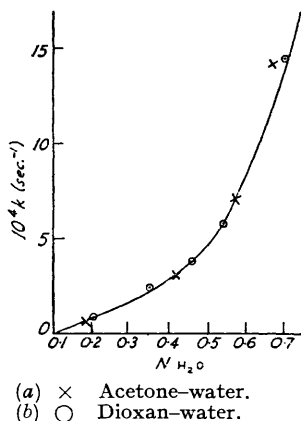FIG. 2. *Reaction rate vs. mole fraction (benzoyl chloride).*

(a) × Acetone–water.
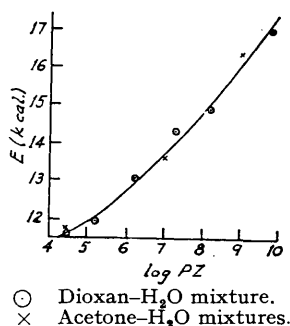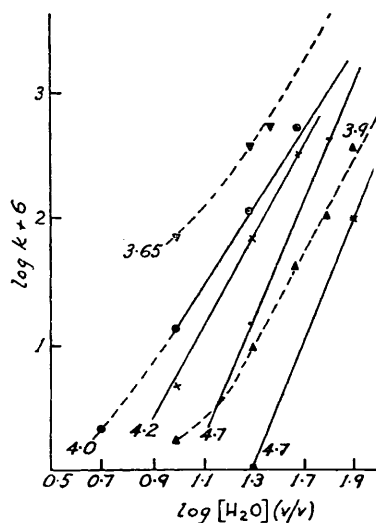(b) ○ Dioxan–water.

FIG. 3. *E vs. log PZ.*

⊙ Dioxan–H_2O mixture.
× Acetone–H_2O mixtures.

FIG. 4. *Log k vs. log [H_2O] for S_N1 reactions in mixed solvents.*

△ Bu^vCl at 25° in EtOH–H_2O mixtures.
● CHPhMeCl at 50° in acetone–water.
× Ph_2·CHCl at 25° in acetone–water.
⊙ Bu^tBr at 25° in acetone–water.
▽ Bu^tBr at 25° in EtOH–H_2O.
＊ Bu^tCl in 80% acetone–water and 50% dioxan–H_2O.
– – – – Conditions with varying E.

conductivity (Hartley and Evans, *Phil. Mag.*, 1935, **15**, 610), rate of reaction (Farinacci and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 3542; Swain and Eddy, *ibid.*, 1948, **70**, 119), and other kinetic phenomena, although the effect on dielectric constant is small.

In Fig. 2 the velocity constants at 25° measured in dioxan– and acetone–water mixtures are plotted against the mole-fraction of water, and shown to be independent of the second component of the mixture. This may be attributed to the specific solvation of the transition state by water molecules, supported by the observation that an identical E–log *PZ* relation is obtained with both mixtures (Fig. 3).

On this basis, ionisation will occur only when the transition state is surrounded by a critical number of water molecules. A random distribution of molecules in the solvent being assumed, the probability P_1 of a water molecule's being adjacent to an RX molecule is given by n_1v_1/V, where n_1 is the number of water molecules of volume v_1 in a volume V

of solvent containing one RX molecule. This volume is composed only of water and inert solvent molecules if the concentration of RX is low so that $V \simeq n_1 v_1 + n_2 v_2$ and $P_n \simeq n_1 v_1/(n_1 v_1 + n_2 v_1) \equiv$ volume ratio of water in the solvent.

For the simultaneous arrangement of n water molecules around the central RX molecule, the probability $P_n = (v/V)^n$ Thus, for these reactions, $\log P_n = n \log (v_1/V)$.

A relation of this type would be expected to hold approximately except in regions of low and high water content. In the first case solvation by the second component may become important with a consequent rise in E (see Fig. 1), and in the second case the uniform distribution of water molecules is destroyed by clusters which are formed because the association energy of water molecules is greater than that between water and solvent. The available data, given in Fig. 4, show that a linear relation between $\log k$ and $\log v_1/V$ is obeyed over a considerable range of solvent composition for several S_N1 reactions, and from the slope of the graphs values of 4 ± 0.5 are obtained for n.
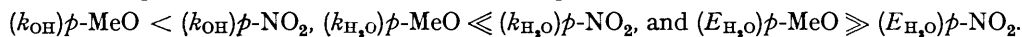
The Influence of Hydroxyl Ions.—As hydroxyl ions increase the rate of S_N2 reactions considerably, but have little or no effect on S_N1 reactions, the ratio of the rate constants for alkaline and neutral reactions has been widely used as a semi-quantitative measure of the bimolecular reaction (Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603). Thus values of 10^4—10^5 are obtained for this ratio for S_N2 reactions, whereas in S_N1–S_N2 intermediate cases values of 10^2—10^3 have been recorded. Previous results (Part I) have shown that this ratio (k_{OH}/k_{H_2O}) for unsubstituted benzoyl chloride in 50% aqueous acetone is approximately 600, thus supporting the contention that benzoyl chloride reacts by a mechanism between the S_N2 and the S_N1 mechanism in highly aqueous media.

It was surpising to find that the ratio is of the order of 10^4 for both the *p*-nitro- and the *p*-methoxy-compound in 25% aqueous acetone (Table 5), the value for the former being approximately twice the latter. This difference is in agreement with the greater tendency of the *p*-methoxybenzoyl chloride to react by the S_N1 mechanism but is much smaller than predicted. As the choice of solvent is arbitrary, it is instructive to consider the effect of varying the solvent on the rate ratio. As the effect of water concentration is large in the case of the *p*-methoxy-compound and small in the case of the *p*-nitro-compound, the following order would be expected as the water concentration decreases : $(k_{OH}/k_{H_2O})p$-MeO $> (k_{OH}/k_{H_2O})p$-NO$_2$.

TABLE 5. *The effect of* OH$^-$ *on the rate of hydrolysis of* p-*nitro- and* p-*methoxybenzoyl chloride.*

$10^3 \times$ Concn. of : chloride	OH	k_2, l. mole^{-1} sec.$^{-1}$	Mean	$10^3 \times$ Concn. of : chloride	OH$^-$	k_2, l. mole^{-1} sec.$^{-1}$	Mean
p-Nitrobenzoyl chloride at 0·2° in 25% H$_2$O–COMe$_2$ (v/v)				*p*-Methoxybenzoyl chloride at 0·2° in 25% H$_2$O–COMe$_2$ (v/v)			
1·654	3·528	6·632		2·424	5·790	0·404	
1·587	,,	6·955	6·816	2·612	,,	0·408	0·405
1·496	,,	6·862		2·548	,,	0·403	
1·150	2·612	7·135		1·768	3·925	0·408	
1·091	,,	6·764	6·884	1·652	,,	0·405	0·408
1·262	,,	6·754		1·852	,,	0·410	
1·042	2·201	6·684		1·067	2·238	0·403	
0·982	,,	6·508	6·593	0·981	,,	0·410	0·408
0·957	,,	6·587		0·892	,,	0·411	

This suggests that the S_N2 tendency is greater in the case of the *p*-methoxy-compound if the hydroxide-ion effect is taken as a criterion. This is not so, however, as shown by the following absolute rates and activation energies :

$(k_{OH})p$-MeO $< (k_{OH})p$-NO$_2$, $(k_{H_2O})p$-MeO $\ll (k_{H_2O})p$-NO$_2$, and $(E_{H_2O})p$-MeO $\gg (E_{H_2O})p$-NO$_2$.

This anomaly shows that the values of k_{OH}/k_{H_2O} have no simple fundamental significance when compared for reactions in a particular solvent. In the present case it follows that the reaction with hydroxyl ions is less sensitive to substitution than the reaction with water molecules, which appears to be the reverse of Hinshelwood, Laidler, and Timm's generalisation (*J.*, 1938, 848). Their predictions only hold, however, for a series of compounds with similar transition states, whereas the structures of the solvolytic transition

states of the *p*-nitro- and the *p*-methoxy-compound differ considerably (Brown and Hudson, *J.*, 1953, 883).

TABLE 6. *The effect of* OH⁻ *on the rate of hydrolysis of* 2 : 4 : 6-*trimethyl-benzoyl and -benzyl chloride.*

	$10^3 \times$ Concn. of :				10^4k_1, sec.⁻¹
	chloride	OH⁻	10^4k_1, sec.⁻¹	Mean	(solvolysis)
2 : 4 : 6-Trimethylbenzoyl chloride at $\{$	1·873	1·800	15·36		
0·2° in 5% H₂O–COMe₂ (v/v) $\{$	1·724	,,	15·70 $\}$	15·36	15·84
	1·931	,,	15·01		
2 : 4 : 6-Trimethylbenzyl chloride at $\{$	19·73	27·11	105·3 $\}$	104·1	103·2
20·4° in 50% H₂O–COMe₂ $\{$	18·12	,,	102·9		
			10^3k_2,		
			1. mole⁻¹/sec.⁻¹	Mean	
2 : 4 : 6-Trimethylbenzyl chloride at $\{$	16·25	13·12	4·257 $\}$	4·306	0·134
30·0° in 25% H₂O–COMe₂ $\{$	15·17	,,	4·356		

The abnormally high value of k_{OH}/k_{H_2O} for the *p*-methoxy-compound in solvents of low water content may be due to repression of the electromeric effect, which is brought into play by the charge separation in the C–Cl bond and tends to reduce the rate of the solvolysis, by the strongly nucleophilic hydroxyl ion. In comparison, a water molecule is weakly nucleophilic, so that the influence is greater and the bond-breaking process becomes more dominant.

Increasing the water content has a considerable effect on the rate ratio for *p*-methoxy-benzoyl chloride and almost no effect on that for the *p*-nitrobenzoyl chloride. Thus in media of high water content, $(k_{OH}/k_{H_2O})p$-MeO $\ll (k_{OH}/k_{H_2O})p$-NO₂. This is in agreement with the relative rates of the *p*-methoxy- and the unsubstituted chloride, and the high activation energy of the hydrolysis of *p*-methoxybenzoyl chloride, and supports the contention that a gradual change from an S_N2 to an S_N1 mechanism is produced by increasing the polarity of the solvent.

Finally, it is observed that an accumulation of electron-releasing groups in the benzene nucleus causes the hydrolysis to proceed by the ionisation mechanism even in solvents of low water content. Thus addition of hydroxyl ions has no effect on the rate of hydrolysis of 2 : 4 : 6-trimethylbenzoyl chloride in 95% aqueous acetone (Table 6). This acid chloride reacts much faster than the corresponding benzyl chloride, the rate of which is increased by the addition of hydroxyl ions in 25% aqueous acetone.

This supports the conclusion that, under suitable conditions, acid chlorides may be hydrolysed by the S_N1 mechanism at a much greater rate than the corresponding benzyl chlorides, and that this mechanism is very sensitive to substituent and solvent changes.

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