182. *The Mechanism of Hydrolysis of Acid Chlorides. Part IV.* Salt Effects.*

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The effect of salts on the rate of hydrolysis of benzoyl chloride has been studied in acetone–water mixtures containing 5—33·3 vol. % of water, at 25°. It is found that common-ion salts have no effect on the velocity of reaction, whereas other salts have a considerable effect in the less aqueous solvents, but no effect in the 33% aqueous solution. These results are in agreement with the bimolecular S_N2 mechanism of the hydrolysis, since non-common ion salts increase the rate by an ionic replacement reaction to give a benzoyl derivative which hydrolyses more rapidly than benzoyl chloride. The results obtained on the addition of common-ion salts show that the ionic strength of the medium has no effect on the rate of hydrolysis.

THE rates of substitution reactions are usually dependent on the solvent used, and to a lesser extent on the presence of added salts. The influence of the former on the hydrolysis of benzoyl chloride in aqueous acetone is very large (see Archer and Hudson, *J.*, 1950, 3259). Further useful information on the nature of the transition state may be obtained from a study of the much smaller salt effects.

A comprehensive study of the effects of salts on the kinetics of hydrolysis of halides which react by the unimolecular S_N1 process was made by Bateman, Hughes, Ingold, and Taher (*J.*, 1940, 979). Because of the preliminary rate-determining ionisation, $RCl \rightleftharpoons R^+ + Cl^-$, involving considerable separation of charge in the alkyl halide, neutral salts increase the velocity considerably. In addition, common-ion salts exert a retarding influence due to mass action, which in some cases predominates over the positive ionic-strength effect, particularly when the cation is relatively stable (*e.g.*, $CHPh_2Cl$). These general conclusions have been substantiated experimentally by use of the *tert.*-butyl and the diphenylmethyl halides. Similar observations were made in the hydrolysis of benzyl chloride by Beste and Hammett (*J. Amer. Chem. Soc.*, 1949, **71**, 2481), although in this case the increases in rate on the addition of neutral salts were attributed to specific attack by the anion on the halide in a replacement reaction. This treatment has recently been developed quantitatively by Hackett and Thomas (*ibid.*, 1950, **72**, 4962).

The benzoyl chlorides are known to react largely by the bimolecular S_N2 process, particularly in solvents of relatively low water content (Brown and Hudson, *Nature*, 1951, **167**, 819), although a tendency to react by the ionisation mechanism in highly aqueous media has been noted (Archer and Hudson, *loc. cit.*). It is highly probable, however, that in the solvent range employed in the present investigation (<33·3% of water by vol. in acetone), the unsubstituted chloride reacts mainly by the S_N2 process. The ionic-strength effect should be less in this reaction owing to the diffuse distribution of charge in the more complex transition state (see Hughes, *Trans. Faraday Soc.*, 1941, **37**, 632). In addition, as the proton and chloride ion are ejected simultaneously, common-ion salts cannot exert the mass-action effect as in S_N1 reactions, and should therefore only exert an ionic-strength effect. Non-common ions may react directly with the halide in an exchange reaction, so that if the product hydrolyses more rapidly than the original halide a further increase in the rate of hydrolysis may also be obtained.

The results obtained in the present work are in partial agreement with these predictions (see Table 1) and may be summarised as follows : (i) Common-ion salts have no effect on the rate in either of the two solvents used. (ii) The rate in 15% aqueous acetone is affected to different extents by equal concentrations of potassium nitrate and lithium bromide. (iii) The rate increase with neutral salts is very sensitive to changes in the solvent composition, so that potassium nitrate has no effect in 33·3% aqueous acetone solution.

It is proposed to treat these results on the basis of the two alternative mechanisms, and show that the S_N2 process is supported much more strongly than the S_N1 mechanism.

* Part III, preceding paper.

First, if the reaction is taken to be unimolecular, the absence of a common-ion salt effect may conceivably be due to the exact opposition of ionic strength and mass-law effects. The observations of Bateman *et al.* (*loc. cit.*) show that this condition obtains in the hydrolysis of diphenylmethyl chloride and bromide. This explanation is, however, improbable in the present case, for chlorides have no effect on the rate as the solvent is changed. Although the two effects could well be equal in a particular solvent, this balance would be disturbed as the solvent composition is varied.

The effect of inert salts may be examined by attributing the increases to the ionic-strength effect alone, and comparing theoretical and experimental values of the rate as the solvent is changed at constant salt concentration. This has been carried out by using the equation derived by Bateman *et al.* (*loc. cit.*), *viz.*, $(\ln k_1/k_0)/(\ln k_2/k_0) = (D_2T_2)^2/(D_1T_1)^2$, where k_1 and k_2 are the velocity constants in two solvents at a constant salt concentration, and k_0 is that in an infinitely dilute solution. That no correlation exists between the experimental and calculated values in the present case is evident from Table 1 (cols. 3 and 4). Hence it is probable that the ionic-strength effect is not the major cause of the increased velocities.

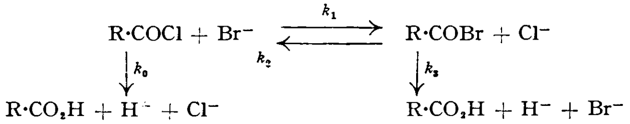
TABLE 1.

		Rate increases, %		
			Calculated : †	
Salt	Solvent	Obs.	Ionic strength	Exchange ‡
0·02N-KNO_3	15% H_2O	16·2	(16·2)	(16·2)
	33·3% H_2O	0	7·6	1·0
	15% H_2O	14·5	(14·5)	(14·5)
0·028N-LiBr	10% H_2O	43·0 *	19·2	38
	5% H_2O	200 *	25·4	220

* Calculated from initial rates. ‡ See p. 890.

† Values in parentheses were used as a basis for the calculated values.

As the reaction is probably proceeding by the alternative S_N2 process, the following series of reactions must be considered :



A formal solution of the appropriate rate equation cannot be obtained in this case, but an approximate treatment may be developed on account of the following experimental observations. (1) Benzoyl bromide is hydrolysed much more rapidly than the chloride, so that $k_3 \gg k_0$. (2) When the observed salt effects are relatively small, and no deviations from a first-order law can be detected, $k_3 \gg k_1$, so the steady state method may be employed. Hence

$$\text{Rate of reaction} = k_3[C_6H_5\cdot COBr] + k_0[C_6H_5\cdot COCl]$$

and

$$k_1[Br^-][C_6H_5\cdot COCl] = k_2[C_6H_5\cdot COBr][Cl^-] + k_3[C_6H_5\cdot COBr]$$

$$[C_6H_5\cdot COBr] = k_1[C_6H_5\cdot COCl][Br^-]/(k_3 + k_2[Cl^-])$$

$$\text{Whence, total rate of reaction} = k_0[C_6H_5\cdot COCl] + \frac{k_1k_3[C_6H_5\cdot COCl][Br^-]}{k_3 + k_2[Cl^-]}$$

The reaction follows a first-order rate law accurately only if $k_3 \gg k_2[Cl^-]$. This condition is realised by using either low concentrations of benzoyl chloride or high concentrations of water, because k_3 increases rapidly, whereas the velocity of ion–dipole reactions of this type usually decreases, with increasing water concentration (see Moelwyn-Hughes, " Kinetics of Reactions in Solution," 1947, Chapter V).

In the present case, direct determination of k_1 by studying the exchange reaction is impossible. For this reason the variation in k_1 over the same solvent range of an analogous process, the exchange of bromide ions with *n*-butyl bromide, has been utilised to assess the relative rate increases given in Table 3. The following figures determined by Sugden and Le Roux (*J.*, 1939, 1279) were used in these estimations :

Water (%) in acetone	95	90	(85)	80	(66·7)
k	11	5	3·8	3	1

It is seen from the estimated values given in Table 1 (col. 5), that the observed rate increases vary with solvent composition in a manner to be expected if the exchange reaction is the cause. Numerical agreement is not to be expected, although the effect of solvent is probably similar in the two exchange reactions.

Hence, from the above discussion it is apparent that the observed rate increases are due entirely to the ion-exchange process, and that the reaction is not influenced by a primary salt effect due to the ionic strength of the medium. This conclusion is supported by the form of the rate curves in the presence of a non-common ion salt over the solvent range 95—66·7% acetone. In all cases below 90% acetone, no significant deviations from a first-order rate constant could be detected as illustrated by the results in Table 2. This case was chosen because the highest concentrations of reactants were used, so that any deviations would have been observed most clearly here. As the water content of the medium decreases, however, considerable departures from the first-order law are observed. This is shown clearly in Fig. 1, where the salt effect is compared with the hydrolysis in the absence of salts. It is observed that in the presence of lithium bromide in 95% aqueous acetone, the rate is initially very high compared with that of the hydrolysis alone. The rate decreases rapidly, however, owing to the mass-action effect of the chloride ions

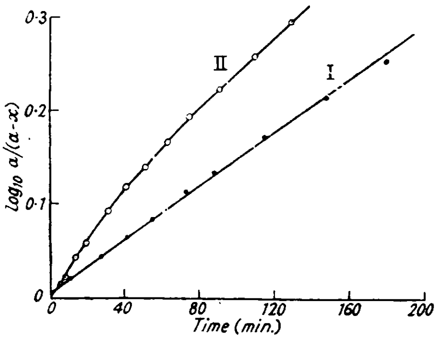


FIG. 1. *First-order plots for the hydrolysis of* 0·0150N-*benzoyl chloride in* 95% *aqueous acetone at* 25° *in the absence of salt* (I), *and in the presence of* 0·0285N-*lithium bromide* (II).

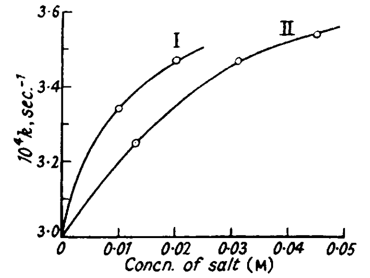


FIG. 2. *The effect of salt concentration on the rate of hydrolysis of benzoyl chloride in* 85% *aqueous acetone at* 25°: (I) KNO_3, (II) LiBr.

TABLE 2.

Composition of solvent = 18·32% w/w or 15% v/v of water. Temperature of reaction = 25·00° ± 0·002°. Concentration of salt = 0·01996M-KNO_3; resistance = 8567 ohms. Initial concentration of benzoyl chloride (a) = 0·01542M.

t_1, sec.	R_1, ohms	10^5x_1, N	t_2, sec.	R_2, ohms	10^5x_2, N	10^4k_1, sec.$^{-1}$
177	8420	79	2079	7220	782	1·498
197	8400	89	2186	7180	809	1·495
238	8360	109	2298	7140	839	1·500
281	8320	129	2419	7100	865	1·496
324	8280	150	2480	7080	879	1·496
368	8240	170	2545	7060	893	1·496
415	8200	191	2610	7040	910	1·502
461	8160	211	2678	7020	925	1·508
485	8140	222	2746	7000	942	1·508
534	8100	243	2817	6980	953	1·502
584	8060	267	2888	6960	968	1·502
635	8020	289	2965	6940	986	1·512
685	7980	308	3045	6920	1002	1·521
739	7940	330	3130	6900	1016	1·519
795	7900	353	3213	6880	1030	1·517
852	7860	376	3338	6860	1050	1·509
910	7820	399	3398	6840	1064	1·521
971	7780	422	3498	6820	1079	1·518
1033	7740	446	3598	6800	1096	1·521
1097	7700	470	3701	6780	1112	1·522
1164	7660	494	3809	6760	1130	1·525
1303	7580	543	4045	6720	1159	1·518
1451	7500	594	4377	6670	1199	1·510
1698	7380	673	4525	6650	1219	1·521
1787	7340	698	4602	6640	1227	1·521

Mean value of 10^4k = 1·510 ± 0·015 sec.$^{-1}$.

released, so that in time the rate approaches that of the hydrolysis in the absence of salt. In these cases, therefore, the increase in hydrolysis rate due to the addition of salt has to be determined from the initial rate. This gives an approximate value of the rate increase comparable with the values obtained for reaction in the more aqueous solvent, which is justified because the rate constant for the hydrolysis of the bromide is much greater than the increased rate estimated in this way. If the rate increases were due to an ionic-strength effect alone, the form of the rate curves would be expected to remain strictly of first order throughout the reaction in all solvents.

The exchange mechanism predicts a linear relation between k_1 and the concentration of salt. The appropriate values are plotted in Fig. 2; this shows considerable deviations, which may be due to the following causes: (1) Incomplete ionisation of the salt in acetone–water mixtures. (2) Removal of water by hydration of the salt. (3) The decrease in k_1 with increase in ionic strength of the medium when the collision is assisted by the ion–dipole field. (4) The increase in the rate of the reaction between benzoyl chloride and anions so that the rate of formation and rate of reaction of benzoyl bromide become of a similar order. This could not have a large effect on the rate, as deviation from first-order kinetics would be detected.

In the absence of direct information, it must be concluded that the deviations noted in Fig. 2 are due to a combination of several of the above effects, of which (1) and (4) are probably the most important.

EXPERIMENTAL

Rate Measurements.—The rate of reaction was measured by following the change in resistance of the hydrolysing solution by the procedure described previously (Archer and Hudson, *loc. cit.*). As the specific conductivities of the solutions containing added salts were considerably greater than those determined previously, a more suitable cell was employed. In order to keep its size within reasonable limits, a design similar to that of Gold (*Trans. Faraday Soc.*, 1948, **44**, 506) was adopted (Fig. 3). The cell *ABA* contained two etched electrodes *AA*, mounted in the same way as previously. The lower end had a side arm *C* sealed through the arm of a 100-ml. round, Pyrex flask *D* in which the reactants were mixed. In order to homogenise a solution in *D*, a saturated stream of nitrogen was passed through the cell from the saturating device. Cylinder nitrogen, after passing the combined manometer and release-valve *H*, travelled through the heater coil *J* into the saturator *K via* the sintered-glass disc *L*. The saturator was charged with the same solution as used in the actual hydrolysis. After saturation, the gas passed to the special tap *M*, a 2-way oblique tap with two extra holes drilled in the plug. It could be set in 3 different positions apart from the completely sealed position. This tap enabled *P* to be connected to *R* with *Q* connected to the atmosphere. In this position with tap *S* open, saturated gas passed through the reservoir *T* and then *via* the cell to bubble through the solution in *D*. The gas then escaped to the atmosphere *via Q*.

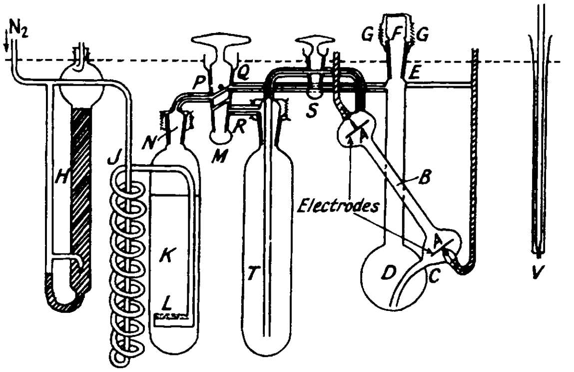


FIG. 3. *Conductivity cell used in salt-effect experiments.*

On turning of the tap through 90° a second hole came opposite *Q* but *R* was sealed off. This enabled the pressure in *T* to fall to nearly atmospheric. When the tap plug was turned through another 90° the connections shown in Fig. 3 were made with *P* connected to *Q* and *R* sealed off. Pressure was thus built up in *D* so that liquid rose into the cell *ABA*. Apart from acting as a reservoir, *T* was also packed with glass-wool and moistened with the aqueous acetone solvent, so as to ensure complete saturation of the gas used for stirring. The whole apparatus including the taps was immersed in the thermostat to prevent condensation. Reaction was started by dropping benzoyl chloride from a pipette into the solution in *D*, and turning *M* so that saturated nitrogen flowed through the solution in *D*, *via* taps *P* and *R* with tap *S* open. After the gas had bubbled through the solution for about 1 minute, the main cylinder valve was turned off, and *P* disconnected from *R*, with *Q* still connected to the atmosphere. When no more bubbles issued from the jet in *D*, the tap *M* was turned so as to connect *P* with *Q* to enable the liquid to rise in *B*. Finally, as the liquid reached the middle of the capillary, *S* and *M* were turned off, the oscillator was switched on, and times were noted at which the resistance of the cell passed suitable pre-determined values. Calibrations were made for each set of reaction conditions by determining the resistance of solutions of the reaction products of known concentration containing the inert salt.

TABLE 3. *Rate constants determined by titration experiments at 25°.*

Salt	Concn. of salt, N	a	10^4k, sec.$^{-1}$	$100(k - k_0)/k_0$	Salt	Concn. of salt, N	a	10^4k, sec.$^{-1}$	$100(k - k_0)/k_0$
Solvent : 5% of water (v/v) in acetone.					Solvent : 10% of water (v/v) in acetone.				
LiBr	0·0285	0·015	1·53	178	LiBr	0·030	0·031	2·20	43·8
	,,	0·035	1·65	200		,,	0·046	2·17	41·8
	,,	0·054	1·42	160	Nil	—	—	1·53	—
Nil	—	—	0·545	—					

TABLE 4. *Velocity constants determined by conductivity experiments at 25°.*

Salt	Concn. of salt	a	10^4k, sec.$^{-1}$		Mean	$100(k - k_0)/k_0$
Solvent : 15% of water (v/v) in acetone.						
KNO_3	0·0100	0·00832	0·34	0·05	3·34	11·3
,,	,,	0·00962	3·36	0·05		
,,	,,	0·01656	3·32	0·05		
,,	0·01996	0·01125	3·46	0·05	3·47	15·7
,,	,,	0·01542	3·48	0·05		
LiBr	0·01333	0·01347	3·25	0·02	3·25	8·3
,,	,,	0·01385	3·25	0·02		
,,	0·03125	0·01485	3·40	0·05	3·47	15·7
,,	,,	0·01258	3·47	0·05		
,,	,,	0·01124	3·48	0·05		
,,	0·04489	0·01701	3·62	0·05	3·54	18·0
,,	,,	0·02856	3·54	0·05		
,,	,,	0·03588	3·53	0·05		
KCl	0·02000	0·00805	3·04	0·05	3·03	1·0
,,	,,	0·01578	3·02	0·02		
,,	,,	0·01738	3·02	0·02		
LiCl	0·03712	0·00830	2·97	0·02	2·96	−1·3
,,	,,	0·00873	2·99	0·02		
,,	,,	0·01102	2·93	0·05		
Nil	—	—	3·00	0·02	3·00	—
Solvent : 33·33% of water (v/v) in acetone.						
HCl	0·00969	0·00541	14·3	0·30	14·3	1·3
KNO_3	0·02000	0·01125	14·08	0·14	14·10	0
,,	,,	0·01130	14·10	0·10		
,,	,,	0·01161	14·10	0·14		
KCl	0·02000	0·01243	14·20	0·30	14·2	0·7
Nil	—	—	14·10	0·20	14·10	—

The reactions in 95% and 90% aqueous acetone were sufficiently slow at 25° to be followed with accuracy by the titration method already described (preceding paper). The results of these experiments are given in Table 3.

Purification of Materials.—The acetone was purified and dried as in Part II (*J.*, 1950, 3259) by Timmermans and Gillor's method (*Rocz. Chem.*, 1938, **18**, 812) and the water was redistilled over alkaline permanganate; the specific resistances were *ca.* 2 × 10^7 and *ca.* 0·5 × 10^6 ohms/cm.^{3}, respectively. The aqueous acetone solvents used were made by direct weighing of the two components by use of the weight pipettes described before. The solvent composition is always referred to the volume percentage of one of the constituents.

Technical benzoyl chloride, redistilled twice in an all-glass apparatus, had b. p. 198° " AnalaR " potassium chloride and nitrate were recrystallised twice from conductivity water and dried at 150°. The purification of lithium chloride by recrystallisation is difficult owing to its very high solubility in water and its tendency to form supersaturated solutions. 50 G. of the crystallised salt were dissolved in the minimum volume of 75% aqueous acetone at the b. p. of the solvent. The solution was filtered, saturated with hydrogen chloride at 0°, and kept in ice overnight. The crystals were filtered off and placed in a vacuum desiccator. To remove the remaining combined water, the lithium chloride hydrate was mixed with twice its own volume of " AnalaR " ammonium chloride which had been further purified by recrystallisation from conductivity water, and heated to fusion in a silica dish. The dry salt was kept over phosphoric oxide until required. Lithium bromide cannot be purified as satisfactorily as the chloride by this method. The technical bromide was purified by crystallisation twice from water and twice from absolute alcohol which removes the water of crystallisation.

Results.—The complete data for a typical run in 15% water solution containing potassium chloride are given in Table 2, the value of k being calculated by the same method as before to eliminate the zero-time correction, and minimise possible errors in a, the initial concentration of benzoyl chloride. The deviations from the average value of $k = [1/(t_1 - t_2)] \log (a - x_1)/(a - x_2)$ are seen to be small and random, so the reaction appears to be strictly of first order throughout its course.

The rate values given in Table 3 were obtained from the initial rates of the hydrolyses followed by titration. In the case of the reactions in 90% aqueous acetone solution, these values were checked by determining the initial slope of the $\log a/(a - x)$–t graphs. The corresponding graphs for the experiments in 95% acetone, however, had considerable inflexions in the early stages of the reaction, so the values given in Table 3 are only approximate.

In all the conductivity runs the deviations from the first-order equation were extremely small. The rate constants given in Table 4 were therefore calculated from the first-order rate equation in all cases.

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