635. *The Mechanism of the Hydrolysis of Acid Chlorides. Part II. The Effect of Temperature and Solvent Composition.*

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The rates of hydrolysis of benzoyl chloride in aqueous acetone, containing 5—75% (v/v) of water, have been measured at 0°, 15°, 25°, and 35° by potentiometric and conductometric methods. A kinetic equation has been developed, expressing the rate of reaction in terms of the concentrations of water and acetone. Increasing the water content increases the activation energy, which indicates a change in mechanism. This is supported by the positive temperature coefficient of activation energy and by the increased effect of water on the reaction rate in highly aqueous solvents.

According to the electronic theory of organic reactions, the presence of an oxygen atom at the reactive centre ($C_{(\alpha)}$) of an alkyl halide should favour a bimolecular solvolysis (see Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603; Baker, *ibid.*, p. 632). The electron affinity of the oxygen atom increases the positive charge on the α-carbon atom and thus increases the attraction for a water dipole. Steric considerations also favour a bimolecular process for the hydrolysis of benzoyl chloride, as the geometrical structure of the molecule is considerably more open in this case. The increased positive charge also explains the rate of reaction of benzoyl chloride being greater than that of benzyl chloride.

In a previous communication (Hudson and Wardill, *J.*, 1950, 1729) dealing with the effect of substituents and hydroxyl ions on the rate of hydrolysis, it was shown that the above deduction is not supported by experimental results. This suggests that the comparison drawn between the two types of compound, differing in electronic and geometrical structure at the reactive carbon atom, may not be significant in relation to the mechanism of the reaction. A comparison between the rates of alcoholysis (Branch and Nixon, *J. Amer. Chem. Soc.*, 1936, **58**, 2499) and hydrolysis of substituted benzoyl chlorides, however, indicates that the hydrolysis may proceed according to alternative mechanisms, *i.e.*, a bimolecular substitution or a unimolecular ionisation, depending on the nature of the substituents.

The alcoholysis of benzoyl chloride in a solution of relatively low dielectric constant is known to be bimolecular (Branch and Nixon, *loc. cit.*) and it seems to be highly probable that in a similar solvent the hydrolysis of unsubstituted benzoyl chloride should proceed by an analogous mechanism.

In highly aqueous solvents, however, the possibility of a change to an ionisation mechanism must be considered. The results recorded below show that the effect of solvent composition on the rate of hydrolysis at various temperatures is consistent with the operation of a dual mechanism, a unimolecular ionisation preponderating at high water concentrations.

In most of the following experiments the rate of reaction was measured by the change in resistance of a conductivity cell containing the reacting solution, the cell having been calibrated previously by filling with solutions of the products of reaction of known concentration. The resistance was measured by the usual non-inductive bridge incorporating a Wagner earth to eliminate asymmetrical potentials and to balance the capacity to earth on opposite sides of the bridge. In the following section, the design of the apparatus, and the procedure of taking a rate measurement, are described fully since it is essential that the velocity constants shall be of sufficient accuracy to lead to significant activation energies.

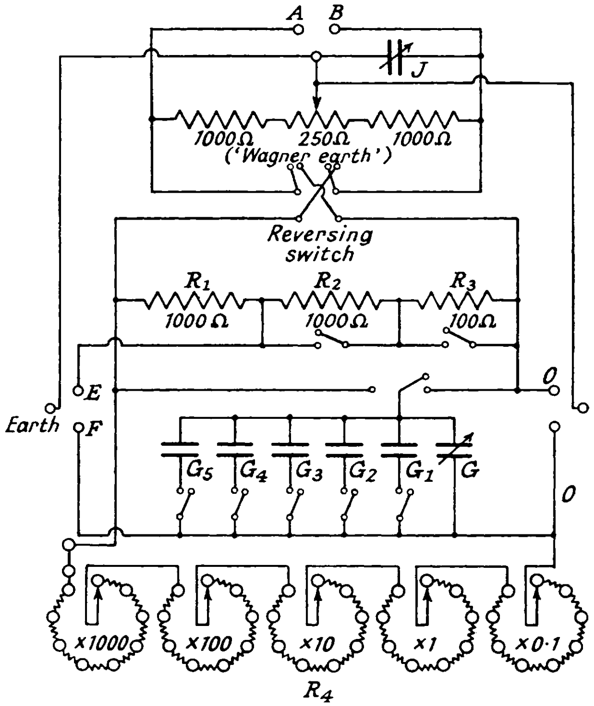
The conductivity method was not employed to study the rate of hydrolysis in the highly aqueous solvents owing to the rapid rate of reaction. For these measurements the change in E.M.F. of a cell containing a silver–silver chloride electrode and a glass electrode immersed in the reaction mixture was followed continuously with a pH meter. Limited results only could be obtained, because of the lack of reproducibility when the rate of reaction became extremely rapid.

EXPERIMENTAL.

Construction of Apparatus.—The bridge (Fig. 1), constructed from standard components, consisted of the conventional resistance network with Wagner ground as recommended by Jones and Josephs (*J. Amer. Chem. Soc.*, 1928, **50**, 1047). Standard bifilar-wound manganin resistors R_1, R_2, R_3, of low inductance and accurate within 0·01% were used as the ratio arms (1 : 1 and 1 : 10). The cell, oscillator, and amplifier were connected across the bridge at *OO*, *AB*, and *EF* respectively. To compensate for the capacity inherent in the conductivity cell and 10,000-ohm resistance box R_4, a bank of condensers G_1—G_5 and a variable air condenser, *G*, fitted with slow motion drive and linear capacity scale, were incorporated. The similar variable air-condenser *J* was used to compensate for any difference in capacity between the two sides of the oscillator output and earth. Copper wire (16 S.W.G.) was used for all

FIG. 1.

Conductivity bridge.



$G_5 = 0·002\,\mu$F.
$G_4 = 0·002\,\mu$F.
$G_3 = 0·001\,\mu$F.
$G_2 = 0·0005\,\mu$F.
$G_1 = 0·0003\,\mu$F.
$G = 0·0005\,\mu$F.

internal wiring, and connections to the oscillator, conductivity cell, and amplifier were made through two-way flexible screened cable.

A variable frequency sine wave, valve oscillator (Ex. W.D. Type 66A) was used, which had a maximum output of 10 v. R.M.S. As sufficient sensitivity in the setting of the bridge could be obtained in all cases by using 2 v. output, this was used to minimise heating of the conductivity cell. For the sake of consistency all measurements were made at a frequency of 1000 c/s. The wave form was found by means of a cathode-ray oscillograph to be perfectly sinusoidal. A simple, two-stage, untuned, transformer-coupled amplifier was constructed so as to increase the signal received in the telephones from the bridge. The first amplifying valve, a screened pentode (Mullard S.P.2) giving a high gain, was coupled to a triode (Marconi P.2) *via* the volume-control potential divider. By use of a pair of diaphragm-type earphones, the measuring bridge could be set within 0·002% with respect to the resistance.

FIG. 2.

Kinetic conductivity cell.

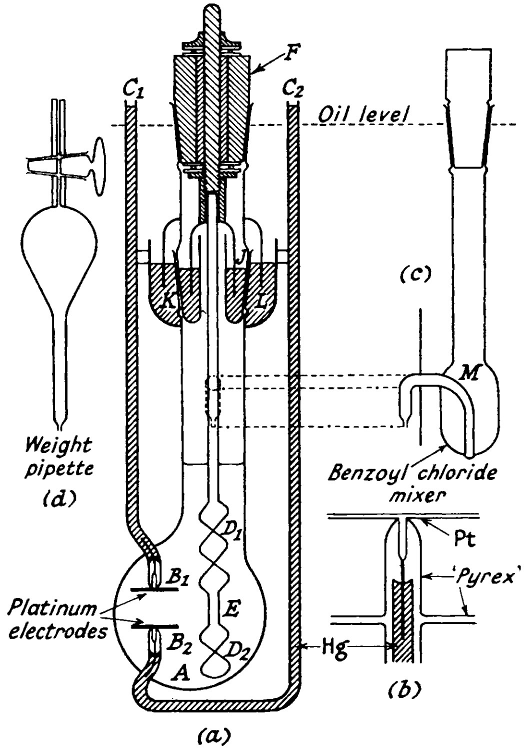
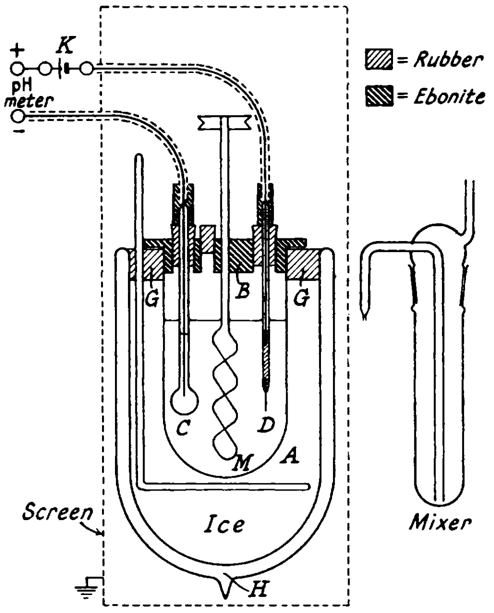


FIG. 3.

Potentiometric cell.



Owing to the high temperature coefficient of resistance, accurate temperature control was essential. A conventional type of thermostat was used, filled with Shell P.31 oil to eliminate errors due to the Parker effect at high cell resistances. The low specific heat of the oil necessitated a very careful control of the heat input which was provided by a series of auxiliary background heaters in addition to the small regulated lamp. The power of the background heaters used was determined by the atmospheric temperature. The Post Office-type relays, control resistances, switches, etc., were all enclosed in an earthed tin plate box, and all wiring was carried out in single-way screened flex to reduce electrical radiation to the conductivity cell. The heater bulbs were silvered on the outside, and the metallic layer was earthed.

Conductivity Cell.—The bulb *A* (Fig. 2*a*) was a 100-ml. Pyrex flask, into which the platinum electrodes B_1 and B_2 were sealed, with mercury-filled tubes C_1 and C_2 for electrical contact. The 1-cm. square electrodes were specially made from 90% Pt–10% Ir alloy, 0·2 mm. thick, according to the specification of Washburn (*J. Amer. Chem. Soc.*, 1916, **38**, 2431). The plates were welded in the centre to 1-mm.-thick platinum–iridium rods which were in turn welded to pieces of 0·015″ platinum wire (Fig. 2*b*). Before being sealed in, the electrodes were etched with warm 50% aqua regia.

The coustruction and mounting of the stirrer presented considerable difficulties, as the apparent resistance varied with its position. The final design consisted of two short twisted Pyrex blades D_1 and D_2 connected by a rod *E* which was kept opposite the electrodes. In order to mount the stirrer, a steel bearing containing ball races *F* was made, which fitted into the B24 standard socket. The mercury seal *J* was of the conventional type, except that it was built into the ground part of the B24 cone *K*, so that there was no contact between the moving and stationary glass surfaces, which could result in wear and contamination of the electrolyte with powdered glass. A second mercury seal *L* was joined to the neck of the flask to prevent oil seeping through the ground joint *K* when the cell was immersed in oil. Lastly, the device shown in Fig. 2*c* was sealed through the side of the neck of the flask. This enabled the reaction to be initiated by adding benzoyl chloride dissolved in acetone from *M* to the acetone–water mixture in *A*, after the whole apparatus had been in the thermostat for at least one hour, by increasing the pressure in *M*. The small directly-coupled electric motor which drove the stirrer was connected to the 110-v. D.C. mains by single-way screened flex, and the casing of the motor was also earthed.

The cell constant was determined by measuring the resistance when filled with 0·001molal-potassium chloride solution at 25° (see Jones and Bradshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780). The potassium chloride was twice recrystallised from conductivity water, dried at 150° for 2 hours, and cooled in a desiccator over phosphoric oxide. All weights were corrected for air buoyancy. The cell resistance of 177·93 ± 0·01 ohms led to the cell constant of 0·25064.

Calibration of Cell.—About 1 l. of aqueous acetone, purified and dried by the method of Timmermann and Gillor (*Rocznicki Chem.*, 1938, **18**, 812) was made up by weight for each water percentage. 50 Drops of pure, redistilled benzoyl chloride were added to 250 ml. of the stock solvent and left overnight. 150 Ml. of the resulting hydrochloric acid–benzoic acid–acetone–water solution were placed in the cell and brought to the required temperature in the thermostat. The equilibrium value of the cell resistance was measured on the A.C. bridge and the mean of 6 such readings was recorded, the divergence from the mean never being greater than 0·05%. The remaining solution was analysed gravimetrically for chloride.

After the conductivity cell had been removed from the thermostat and left for at least 1 hour to attain room temperature, a known volume was removed and diluted to 150 ml. The cell was then emptied, washed, dried, and refilled with the second solution, the conductivity of which was then measured. This was repeated six or seven times for each solvent and temperature, and graphs were constructed of the logarithm of the chloride ion concentration plotted against the logarithm of the cell resistance. These calibration graphs were used to derive the concentration of chloride ion released during a kinetic run.

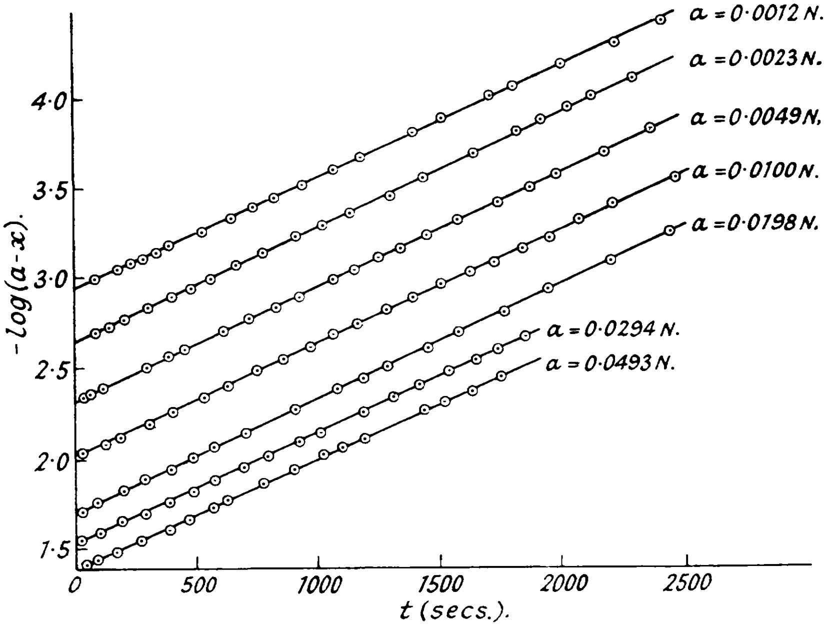
Procedure for Rate Determination.—Slightly less than the required amount of conductivity water was weighed into the cell from a weight-pipette, and 10 ml. of pure acetone were pipetted into the side-vessel *M* (Fig. 2*c*) of the cell. The volume of acetone delivered by *M* had been previously determined. Then the remainder of the acetone required for the experiment was weighed from a weight-pipette into the body of the cell. It was impossible to obtain the exact ratio of water to acetone in the cell without repeated weighings, with a chance of an appreciable error by evaporation. Hence the small volume of water still needed to attain the right ratio was calculated and added from a 1-ml. graduated pipette. The stirrer was then placed in the cell, and the top sealed with mercury before the cell was placed in the thermostat. After an hour the short-circuit which had been kept across the electrodes was removed, and the necessary volume of benzoyl chloride placed in *M*. The dials of the bridge were set to the highest resistance expected, and the acetone and benzoyl chloride forced over from *M* into the cell. The oscillator and stop watch were started, and the times noted at which the resistance of the cell passed pre-set values on the bridge. Readings were taken every 20 seconds for the fastest runs but only every 2—3 minutes for the slowest, some fifty or sixty readings being taken during each run. As the resistance of the cell changed, the capacity across the coils needed to secure perfect silence altered rapidly, but it was possible to keep it sufficiently well adjusted to enable the times of minimum sound to be read to the nearest second. The resistance when all the benzoyl chloride had hydrolysed was taken as the average of several readings obtained over a protracted period, starting when at least twenty half-life periods had elapsed.

The Potentiometric Method.—The following method was employed for the reactions in the more highly aqueous solutions, owing to the rapid rates. The change in E.M.F. of a cell, composed of a silver–silver chloride electrode, *D* (Fig. 3), and a glass electrode, *C*, immersed in the reacting solution, was determined. As the former electrode is sensitive to the negative chloride ion and the latter to the positive hydrogen ion, the changes in E.M.F. observed were twice those which would be obtained by using a single electrode and a calomel half-cell. The electrodes were held by rubber stoppers through a piece of ebonite *B* which served as a cover for the glass cell, *A*, containing the reaction solution. A stirrer (*M*), driven by an electric motor situated at a considerable distance from the cell, was also inserted through the ebonite. The cell, *A*, was supported by a cork ring *GG* in the neck of a Dewar vessel *H* filled with ice. Finally, a hole was made in the ebonite, through which the second reactant could be admitted. The whole apparatus was enclosed in a tinplate screening box to prevent hand-capacity effects on the pH meter. A standard Weston cell *K* was connected between the silver–silver chloride electrode and the positive terminal of the meter, so that the highly insulated glass electrode could always be connected to the grid of the pH meter. This was necessary because the silver–silver chloride electrode was more negative than the glass electrode under the conditions of the experiment, and if the glass electrode were connected to the positive terminal considerable errors would result owing to current leakage. The silver–silver chloride electrodes were prepared by the method of Brown (*J. Amer. Chem. Soc.*, 1934, **56**, 646).

The system was calibrated for each experiment by a method analogous to that used in the conductivity experiments. The potential of the cell was measured with the aid of a Cambridge pH-meter used as a millivoltmeter, and a graph plotted of E.M.F. against the logarithm of the chloride ion concentration.

In a typical experiment, the calculated quantity of water was run into the cell from a burette, and the required quantity of acetone run into the tube of the calibrated mixing device. After the water had cooled to 0° by immersion of the cell in powdered ice, and the acetone had reached a pre-determined low temperature by cooling in acetone–carbon dioxide, the benzoyl chloride was added to the acetone and the mixture forced over into the water. With the stirrer running, the stop-watch was started when the

FIG. 4.



25° ; 33·33% H_2O (*v*/*v*).

TABLE I.

t_1 (secs.).	R_1 (ohms).	x_1 (N.).	$k_1' \times 10^4$ (sec.$^{-1}$).	$k_1 \times 10^4$ (sec.$^{-1}$).	t_2 (secs.).	R_2 (ohms).	x_2 (N.).	$k_1' \times 10^4$ (sec.$^{-1}$).	$k_1 \times 10^4$ (sec.$^{-1}$).	$k_2 \times 10^4$ (sec.$^{-1}$).
30	9000	0·00027	3·110	1·280	2171	460	0·00640	1·303	1·280	1·279
41	8000	0·00031	2·658	1·280	2249	450	0·00655	1·300	1·279	1·276
50	7000	0·00035	2·300	1·295	2333	440	0·00671	1·298	1·279	1·273
90	5000	0·00050	1·822	1·281	2522	420	0·00708	1·296	1·279	1·279
126	4000	0·00062	1·628	1·250	2628	410	0·00726	1·293	1·275	1·275
151	3500	0·00072	1·532	1·264	2742	400	0·00746	1·291	1·275	1·278
186	3000	0·00084	1·505	1·250	2868	390	0·00767	1·290	1·274	1·278
236	2500	0·00102	1·452	1·251	3007	380	0·00793	1·299	1·281	1·285
313	2000	0·00129	1·407	1·253	3162	370	0·00815	1·291	1·275	1·278
413	1600	0·00164	1·374	1·257	3243	365	0·00828	1·291	1·276	1·282
487	1400	0·00190	1·361	1·271	3330	360	0·00840	1·290	1·278	1·278
590	1200	0·00225	1·354	1·271	3425	355	0·00853	1·289	1·273	1·275
658	1100	0·00247	1·349	1·277	3524	350	0·00869	1·293	1·280	1·280
742	1000	0·00274	1·341	1·279	3628	345	0·00881	1·289	1·273	1·272
988	800	0·00348	1·321	1·279	4275	320	0·00962	1·283	1·280	1·280
1076	750	0·00374	1·326	1·279	4402	316	0·00975	1·291	1·279	1·278
1137	720	0·00391	1·321	1·279	4539	312	0·00991	1·289	1·281	1·282
1180	700	0·00403	1·319	1·280	4688	308	0·01002	1·293	1·272	1·269
1228	680	0·00416	1·319	1·279	4843	304	0·01019	1·289	1·278	1·279
1278	660	0·00431	1·320	1·281	5097	298	0·01042	1·288	1·278	1·277
1333	640	0·00446	1·320	1·283	5192	296	0·01050	1·288	1·279	1·277
1395	620	0·00461	1·315	1·289	5289	294	0·01059	1·290	1·281	1·270
1460	600	0·00479	1·319	1·285	5393	292	0·01069	1·298	1·286	1·283
1532	580	0·00497	1·313	1·281	5500	290	0·01074	1·285	1·278	1·270
1611	560	0·00515	1·310	1·280	5613	288	0·01084	1·289	1·279	1·279
1699	540	0·00536	1·310	1·281	5731	286	0·01091	1·282	1·273	1·272
1797	520	0·00557	1·300	1·273	5856	284	0·01099	1·275	1·271	1·271
1907	500	0·00583	1·308	1·280	5989	282	0·01102	1·281	1·275	1·273

Composition of solvent : water, 29·76% (w/w) or 25·00% (v/v) at 25°.
Temp., 15·00° ± 0·002°.
Initial concn. of benzoyl chloride (*a*), 0·01337N.
Time correction, 38 secs.
Mean value of $k_1 = 0{\cdot}0001278 \pm 0{\cdot}0000028$ sec.$^{-1}$.
Mean value of $k_2 = 0{\cdot}0001277 \pm 0{\cdot}0000010$ sec.$^{-1}$.
$k_1' = [\log a/(a-x)]/t_{\text{obs.}}$. $k_1 = [\log a/(a-x)]/t_{\text{corr.}}$. $k_2' = [\log (a-x_1)/(a-x_2)]/(t_1-t_2)$.

last of the acetone had passed into the water, and readings taken at short time intervals. After approx. 20 half-lives had elapsed, the equilibrium E.M.F. of the cell was measured, and then the solution was transferred quantitatively to a beaker and the chloride determined gravimetrically as silver chloride. The density of acetone at room temperature and also that of aqueous acetone at 0° being known (Int. Crit. Tables, Vol. III, p. 112), the volume of mixed solvent used in the reaction was calculated, and hence the concentration of chloride in the final reaction solution. To eliminate errors caused by changes in the asymmetry potential of the glass electrode, the potential which the cell should have had at the end of the reaction was found from the calibration graph, and the necessary correction made to the observed potentials obtained during the reaction. The corresponding concentrations of chloride ion were then read off from the calibration graph, and the velocity constants evaluated as for the conductivity runs.

TABLE II.

Run no.	Water, % (v/v).	[H_2O], g.-mol./l.	*a*.	$10^4k_2 = 2{\cdot}303k_2' \times 10^4$.	Mean.
15°.					
66	15	8·66	0·01291	1·36 ± 0·02	
67	15	,,	0·01966	1·35 ± 0·02	1·36
65	25	14·51	0·01337	2·95 ± 0·02	
64	25	,,	0·01361	2·90 ± 0·02	2·93
62	33·3	19·40	0·00646	5·50 ± 0·05	
56	33·3	,,	0·01057	5·49 ± 0·05	
57	33·3	,,	0·01202	5·46 ± 0·05	
63	33·3	,,	0·02254	5·46 ± 0·05	5·48
60	40	23·30	0·00640	9·33 ± 0·11	
59	40	,,	0·01271	9·45 ± 0·09	
58	40	,,	0·01364	9·47 ± 0·09	
61	40	,,	0·02377	9·33 ± 0·09	9·40
25°.					
92	5	2·77	0·00944	0·548 ± 0·04	
93	5	,,	0·00948	0·553 ± 0·04	0·551
32	15	8·52	0·00522	3·02 ± 0·03	
33	15	,,	0·01069	2·98 ± 0·03	
31	15	,,	0·01112	3·00 ± 0·03	
30	15	,,	0·01870	2·98 ± 0·03	3·00
27	25	14·34	0·00413	6·95 ± 0·07	
25	25	,,	0·00733	6·91 ± 0·07	
26	25	,,	0·00799	6·98 ± 0·07	
24	25	,,	0·00832	6·93 ± 0·07	
23	25	,,	0·01722	6·91 ± 0·07	6·94
12	33·33	19·20	0·00122	14·15 ± 0·11	
13	33·33	,,	0·00241	14·03 ± 0·14	
9	33·33	,,	0·00490	14·28 ± 0·21	
4	33·33	,,	0·00980	14·20 ± 0·14	
5	33·33	,,	0·00999	14·17 ± 0·14	
3	33·33	,,	0·01963	14·08 ± 0·14	
6	33·33	,,	0·01982	14·09 ± 0·11	
17	33·33	,,	0·02944	13·88 ± 0·14	
14	33·33	,,	0·03990	13·91 ± 0·14	14·11
37	40	23·07	0·00566	25·40 ± 0·92	
35	40	,,	0·01091	25·20 ± 0·32	
38	40	,,	0·01982	25·20 ± 0·32	
39	40	,,	0·01986	25·20 ± 0·10	25·25
35°.					
91	5	2·73	0·00986	1·05 ± 0·2	
88	5	,,	0·01052	1·05 ± 0·02	
49	15	8·41	0·00538	6·49 ± 0·07	
48	15	,,	0·00552	6·47 ± 0·07	
46	15	,,	0·01230	6·43 ± 0·07	
50	15	,,	0·02301	6·45 ± 0·05	
51	15	,,	0·02317	6·43 ± 0·07	
42	25	14·18	0·00533	16·21 ± 0·16	
43	25	,,	0·00504	16·00 ± 0·16	
40	25	,,	0·01094	16·12 ± 0·09	
45	25	,,	0·02393	16·12 ± 0·13	
44	25	,,	0·02612	16·06 ± 0·13	16·12
54	33·33	18·99	0·00601	33·80 ± 0·30	
55	33·33	,,	0·01047	34·25 ± 0·28	
53	33·33	,,	0·01189	33·95 ± 0·32	34·00

Results.—(a) *Calculation of velocity constants.* Owing to the indeterminacy in the starting time of the reaction, the values of the velocity constant, k_1', calculated from the simple expression for a first-order reaction from the experimental zero time show very large deviations from constancy, for various values of the time t (see columns 4 and 9, Table I). By constructing graphs of log $(a - x)$ against t (Fig. 4) and extrapolating back to $x = 0$, values of the starting time correction were obtained, and used to correct the observed values of t.

The results in Table I for a typical run show that the deviations of k_1 from the mean are small and random, so that it was concluded that the reaction was of the first order throughout its course. This method leads to inaccurate results because of the impossibility of estimating the time correction to better than 2 secs., and so a modification of Guggenheim's method was employed (*Phil. Mag.*, 1926, **2**, 538). Any constant error in t_1 and t_2 is eliminated, and as the values of $t_2 - t_1$ are larger than the individual values of t in the early stages of the reaction, the errors are considerably reduced. Furthermore, any errors in the value of the initial concentration a are minimised.

(b) *Effect of solvent on* k. Table II summarises the most important experiments made to study the effect of solvent composition on the rate of hydrolysis. The initial concentration of benzoyl chloride, a, is expressed in g.-mol./l. and the velocity constants calculated by the Guggenheim method in sec.$^{-1}$. Maximum deviations from the mean value of each velocity constant are given, so that the significance of these values may be appreciated.

It is observed from several sets of data (Fig. 4) that the velocity constant remains almost constant over a wide concentration range (*e.g.*, 0·001—0·05N. at 25° for 33% water content), showing the reaction to be truly unimolecular with respect to the chloride.

Limited results obtained by the potentiometric method for solutions containing 50%, 66·7%, and 75% of water are given in Table III. Owing to the lower accuracy of this method and the rapid rates of reaction, activation energies could not be obtained with any certainty in this range of solvent composition.

TABLE III.

Potentiometric results (0° c.).

Run no.	H_2O, % (v/v).	$[H_2O]$, g.-mol./l.	a.	$10^4k_2 = 2{\cdot}303k_2' \times 10^4$.	Mean.
p28	50	29·49	0·00491	6·9	
p27	50	,,	0·00523	7·4	
p26	50	,,	0·00830	7·4	
p25	50	,,	0·01012	7·6	7·3
p22	66·67	38·64	0·00326	38·0	
p17	66·67	,,	0·00670	38·2	
p15	66·67	,,	0·00961	39·6	
p16	66·67	,,	0·01002	39·2	38·8
p13	75	43·06	0·00340	98·4	
p11	75	,,	0·00573	97·9	
p10	75	,,	0·00626	97·8	98·0

DISCUSSION.

(a) *Reaction in the* 0—30% *Water Concentration Range.*—The results given in Tables II and III show that no simple relation exists between the first-order rate constant and the concentration of water, although the former is independent of the initial concentration of benzoyl chloride. This is due to the fact that the true order of the reaction is masked by the solvating influence of the reaction medium and is probably modified further by a change in mechanism which is discussed below. It is found that the rate of reaction is approximately a linear function of the square of the water concentration over a considerable range of solvent composition (5—30% of water). In highly aqueous solution, however (50—75% of water), the rate is dependent on the water concentration to a much higher power (*ca.* 7·5).

Although the graphs of k_2 against $[H_2O]^2$ are nearly linear, they do not pass through the origin but cut the ordinate at definite values. In other solvolyses, a similar effect obtains at low water concentrations, with solvents capable of extensive solvation. In most of the cases studied, the rate of solvolysis, represented by k_2, increases linearly with water concentration over a very limited range of solvent composition, *e.g.*, the hydrolysis of *n*-butyl bromide in formic acid (Bateman and Hughes, *J*,. 1937, 1187) and the hydrolysis of α-phenylethyl chloride in acetic acid (Steigman and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2636). This general similarity has been discussed fully by Hughes, Ingold, *et al.* (*J.*, 1940, 935).

It is generally recognised that nucleophilic reactions cannot proceed without extensive solvation of the transition complex. Thus Ogg and Polanyi (*Trans. Faraday Soc.*, 1935, **31**, 604) recognised the importance of the solvation of the chloride ion, in the energetics of hydrolysis, in reducing the activation energy. These workers proposed the following mechanism :

$$H_2O \cdots\cdots RCl \cdots\cdots H_2O \longrightarrow [R \leftarrow H_2O]^+ + Cl^-{\cdot}H_2O \longrightarrow H_3O^+ + ROH + Cl^-{\cdot}H_2O$$

This termolecular process requires third-order kinetics which are seldom realised in solvolytic reactions owing to the complex process of solvation in such media. When the solvent is of very low solvating power compared with water, however, third-order kinetics are observed, for example in the alcoholysis of *p*-nitrobenzoyl chloride in ether (Ashdown, *J. Amer. Chem. Soc.*, 1930, **52**, 268), the reaction between alcohol and triphenylmethyl chloride in benzene (Swain and Eddy, *ibid.*, 1948, **70**, 1119), and the hydrolysis of acetyl chloride in dioxan (Hudson and Macleod, to be published).

In ionising solvents, this simple process is modified by the solvating influence of the solvent. When the solvent participates in the transition-state formation of the reaction between RCl and A to a marked extent, a general expression of the following type would be expected to hold:

$$dx/dt = k'[\mathrm{RCl}][\mathrm{A}][\mathrm{S}]^m + k''[\mathrm{RCl}][\mathrm{A}]^n \quad . \; . \; . \; . \; . \; . \quad (1)$$

where [RCl] = concn. of halide in g.-mol./l, [A] = concn. of substituting agent, *e.g.*, water, and [S] = concn. of " inert " solvent, *e.g.*, acetone;

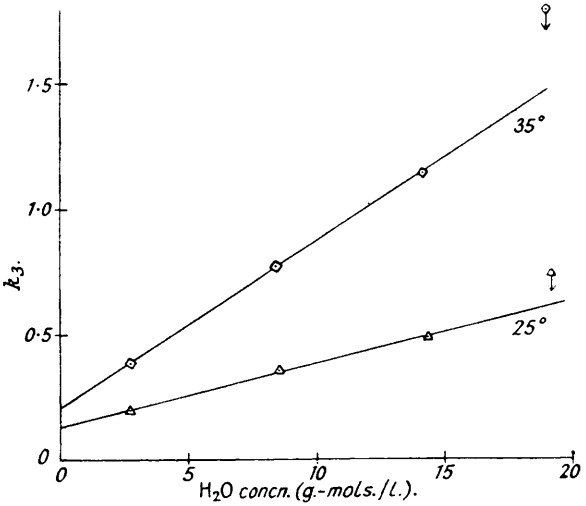
or

$$k_2 = k'[\mathrm{A}][\mathrm{S}]^m + k''[\mathrm{A}]^n \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

or

$$k_3 = k_2/[\mathrm{A}] = k'[\mathrm{S}]^m + k''[\mathrm{A}]^{n-1} \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

FIG. 5.



where *m* and *n* may be assumed to be constant over a specific range of solvent composition. In the present case *n* has been found equal to 2. It is impossible to derive with certainty a value for *m*, although by analogy with the termolecular transition state (see above) a value of unity may be assumed. As the first term in equation 3 is only significant in regions of very low water content, $k'[\mathrm{S}]^m$ may be assumed to be approximately constant, so that under these conditions k_3 varies linearly with water concentration. Fig. 5 shows that this relation is obeyed accurately at 25° and 35° in the 0—30% water range. In a completely inert solvent the first term disappears altogether so that equation (1) reduces to the relation proposed by Swain and Eddy (*loc. cit.*), *viz.*, Rate = $k''[\mathrm{RCl}][\mathrm{A}]^2$.

An alternative approach to the problem of the solvation of the transition state may be made by considering the variation in the rate of reaction with dielectric constant of the medium. Although the above mechanism is kinetically termolecular, only one water molecule is directly concerned with the breaking of covalent bonds. Thus from this point of view (see Ingold *et al.*, *loc. cit.*) the reaction is bimolecular as the association of the chloride ion with a water molecule is probably not an activated process. The reaction being assumed to be bimolecular, velocity constants (k_3) may be calculated, from which it may be seen that the parameter *A* of the Arrhenius equation increases rapidly with increase in dielectric constant of the medium. This is typical of a process in which the activated complex is more polar than the initial reactants. The difference may be investigated as follows. Kirkwood (*J. Chem. Physics*, 1934, **2**, 351) has calculated the free energy of transfer of a strong dipole μ, from a vacuum to a medium of dielectric constant D to be

$$F = kT \log_e a = -\frac{\mu^2}{r^3} \cdot \frac{D-1}{2D+1}$$

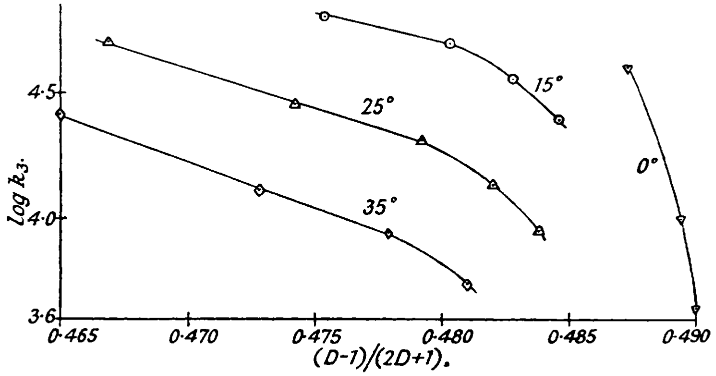
where r is the molecular radius. Thus for the reaction $H_2O + RCl \longrightarrow H_2O^{\delta+} \cdots\cdot R \cdots\cdot Cl^{\delta-} \longrightarrow$ Products, substitution in the Brønsted–Bjerrum activity relation gives

$$\log_e k_3 = \log_e k_3^0 - \frac{1}{kT} \cdot \frac{D-1}{2D+1}\left(\frac{\mu^2_{RCl}}{r^3_{RCl}} + \frac{\mu^2_{H_2O}}{r^3_{H_2O}} - \frac{\mu^2_{Tr}}{r^3_{Tr}}\right)$$

This assumes that dipole forces are much greater than van der Waals forces, which is probably true when considerable separation of charge occurs in the transition complex. It is observed from Fig. 6 that the graphs of log k_3 against $(D - 1)/(2D + 1)$ are linear at 25° and 35° in the 0—30% water range (cf. Fig. 5). The values of D were interpolated from the results of Akerlöf (*J. Amer. Chem. Soc.*, 1932, **54**, 4125). From the slope it is inferred that a considerable increase in the polarity of the transition state occurs, so that it seems that the activated complex closely resembles the reaction products as in the case of similar reactions.

FIG. 6.

Dielectric constant and reaction rate.



(b) *Evidence for a Change in Reaction Mechanism.*—In Part I (*J.*, 1950, 1729) it was concluded that benzoyl chloride may be hydrolysed by a dual mechanism such that substituents which release electrons to the seat of reaction promote a unimolecular S_N1 mechanism, and substituents which withdraw electrons promote a reaction involving nucleophilic attack (S_N2). The nature of the second process has been discussed above. It must be emphasised here that the authors do not consider this termolecular process to be an ionisation (S_N1) reaction, as has been suggested by some authors (Swain and Eddy, *loc. cit.*)

The measurements in acetone containing high proportions of water suggest strongly that a change in mechanism occurs when the ionising power of the solvent is increased. It has been observed that in the 0—30% water region, the plots of log k against $(D - 1)/(2D + 1)$ are linear and almost parallel for the three temperatures employed (Fig. 6). Above the 30% water concentration, however, a very marked increase in slope is observed, which shows that the transition state has changed. The rate becomes much more dependent on water concentration, so that in the 50—75% range the rate is approximately proportional to the concentration of water to the power 7·5. This in itself indicates that an ionisation mechanism is operative (see Hughes, *Trans Faraday Soc.*, 1941, **37**, 621). A change in mechanism is also supported by the observed *increase* in activation energy with water content (Table V).

TABLE V.

% Water in solvent.		Activation energies (cals.).	
v/v.	w/w.	15—25°.	25—35°.
40·00	45·87	16,900	—
33·3	38·95	16,320	16,110
25·00	29·76	14,850	15,380
15·00	18·32	13,580	14,190
5·00	6·22	—	11,730

It is to be expected that for a reaction leading to a transition state which is stabilised by solvation the reverse would be the case (Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw Hill, New York, 1941, p. 402). Hughes (*J.*, 1937, 1187) has observed that in the solvolysis of *tert.*-butyl chloride the activation energy changes little with the solvent composition (using acetone) which shows that the observed change in E here is not caused by a change in the structure of the solvent. Several similar observations showing an increase in E with ionising power of the solvent have been recorded. Thus Leimu and Salomaa (*Acta Chem. Scand.*, 1947, **1**, 353) have shown that in the alcoholysis of 1-chloro-ethers the energy of activation is approximately 8000 cals./g.-mol. in dioxan solution 2N. in ethyl alcohol, but 14,000 cals./g.-mol. in pure alcohol. The introduction of a methoxy-group into a methyl chloride molecule would promote a unimolecular mechanism $(\overset{\curvearrowright}{CH_3O}{\cdot}\overset{\curvearrowright}{CH_2{\cdot}}Cl^-)$ and increase the rate of hydrolysis. When the value of the activation energy for the alcoholysis in pure alcohol of benzoyl chloride given by Norris and Young (*J. Amer. Chem. Soc.*, 1935, **57**, 1420) (15,530 cals.) is compared with that obtained by Branch and Nixon (*loc. cit.*) for alcoholysis in 60% ether (14,400 cals.), a similar though less marked change is observed.

Recently Linetskaya and Sapozhnikova (*J. Appl. Chem. U.S.S.R.*, 1948, **21**, 876) have found that the activation energy for the hydrolysis of benzenesulphonyl chloride is less in 65—80% acetone than in 50% acetone. That this characteristic change in activation energy occurs in solvolytic reactions in three very different solvents, with reactions where an S_N1 mechanism is possible, indicates that it is not due to a change in solvent structure, but to a mechanistic change to an ionisation process.

Finally it is observed that over the 5—33% water range the value of dE/dT is positive. By the method of Svirbely and Warner (*J. Amer. Chem. Soc.*, 1935, **57**, 1883), who made allowance for the effect of temperature on the dielectric constant of the medium, the velocity constant of a reaction is given by

$$d \log_e k = \left(\frac{\partial \log_e k}{\partial\left(\frac{1}{T}\right)}\right) . d\left(\frac{1}{T}\right) . \left(\frac{\partial \log_e k}{\partial D}\right)_T . dD$$

and

$$E_d = \mathbf{R}\left(\frac{\partial \log_e k}{\partial D}\right)_T \cdot \frac{\partial D}{\partial\left(\frac{1}{T}\right)}$$

where

$$E_d = -\mathbf{R}\frac{\partial \log_e k}{\partial\left(\frac{1}{T}\right)} = \text{isodielectric activation energy,}$$

and

$$E = \mathbf{R}\frac{\partial \log_e k}{\partial\left(\frac{1}{T}\right)} = \text{apparent activation energy.}$$

As Table VI shows, there is little difference between E and E_d, the general trend in the values is the same in each case, and the divergence from the Arrhenius law is greater in the case of the isodielectric activation energies than in that of the apparent values.

Thus the positive value of dE/dT is not due to changes in the dielectric constant and must be due therefore to the change in mechanism. The unimolecular mechanism, which has the higher activation energy, becomes more important at higher temperatures.

TABLE VI.

Concn. of water, %.	33·33.		25·0.		15·0.	
	E.	E_d.	E.	E_d.	E.	E_d.
15—25°	16,320	16,770	14,850	15,240	13,580	13,890
25—35°	16,110	16,550	15,380	15,780	14,190	14,600
Difference	—210	—220	530	540	610	710

From these considerations therefore we may conclude that in highly aqueous solvents benzoyl chloride is hydrolysed by a unimolecular ionisation mechanism (S_N1). This process is differentiated from the termolecular (S_N2) process, operative in the 0—30% water range, by the way in which the transition complex is formed. Whereas the latter process requires activated collision with the activated water molecule substituting in the halide, the former is an internal ionisation process. The chloride is virtually surrounded and polarised by a shell of water molecules and consequently the rate-determining ionisation proceeds without attack by any one specific water molecule. In the subsequent step, which probably requires little activation energy, all the water molecules have an equal probability of combining with the cation to complete the hydrolysis.

The authors thank Professor H. V. A. Briscoe for his interest in this work, and the Central Research Fund for the financial assistance which enabled it to be completed.

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[*Received, May 24th,* 1950.]