## 102. *The Mechanism of Hydrolysis of Acid Chlorides. Part VI.* * *Formolysis of* para-*Substituted Benzoyl Chlorides.*

### By E. W. Crunden and R. F. Hudson.

The rates of solvolysis of several *para*-substituted benzoyl chlorides in formic acid–water mixtures have been determined conductimetrically and have been shown to increase regularly with electron release to the carbonyl-carbon atom. The rates of reaction of *p*-toluoyl and benzoyl chloride are almost independent of the water concentration, and addition of formate ions does not increase the rate of reaction of the unsubstituted chloride. On the other hand, the rate of substitution of the *p*-nitro-compound is increased considerably by the addition of formate ions, and is also approximately proportional to the water content.

These results show that the various chlorides react by different mechanisms, *p*-nitro- and 2 : 4 : 6-trinitro-benzoyl chloride participating in an $S_N2$ type of process whereas compounds containing electron-releasing groups react by an $S_N1$ type of process. Comparison of the rates of reaction in formic acid and in an aqueous medium of equal solvating power enables the extent of the $S_N1$ process in 65% aqueous acetone † to be determined approximately to give the following values; *p*-Me, 70%; *p*-H, 40%; *p*-Br, 10%; *p*-NO$_2$ and 2 : 4 : 6-(NO$_2$)$_3$, nil. The nature of the $S_N1$ type of process is briefly discussed.

CONSIDERABLE evidence has been presented in previous papers of this series * to show that acid chlorides may be hydrolysed by one of two alternative mechanisms depending on the structure of the chloride and the reaction conditions. The mechanistic point has been roughly defined for benzoyl chloride in acetone–water mixtures,[1] and has recently been fixed more accurately.[2] There is no doubt that if we were dealing with a saturated system these two mechanisms could be identified with $S_N1$ and $S_N2$ substitutions, but the position is more complex for acyl halides. Thus the influence of a third reactive centre (the carbonyl-oxygen atom) must be taken into account, particularly in view of the observations that electrophilic reagents interact preferentially with this atom.[3]

In addition, the unsaturated nature and the strong polarisability of the carbonyl group raise the possibility that this group may open during the reaction as in the analogous reactions of esters.[4] Recent exchange data [5] show this to be the case, and hence it now appears likely that reaction proceeds through one or more addition intermediates. Owing to the instability of these intermediates the reaction cannot be differentiated kinetically from an $S_N2$ process at a saturated carbon atom.

The mechanism which resembles an $S_N1$ process is difficult to follow in aqueous solvents owing to the competing reaction which involves a rate-determining nucleophilic attack. For this reason the present experiments are confined to measurements of solvolysis rates in formic acid and formic acid–water mixtures. Formic acid is a useful solvent for suppressing the bimolecular reaction and promoting a rate-determining ionisation owing to its low nucleophilic power and high solvating power.[6] Thus the reactivity of *p*-nitrobenzoyl chloride, determined mainly by the bond-forming process,[7] is extremely low in formic acid

* Part V, *J.*, 1953, 3352.
† The solvent composition is represented in this way throughout the paper : 65% aqueous acetone refers to a solvent containing 65 ml. of water in a total volume of 100 ml.

[1] Archer and Hudson, *J.*, 1950, 3259.
[2] Gold, Hilton, and Jefferson, *J.*, 1954, 2756.
[3] Dilke, Eley, and Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 261; Surz and Cooke, *Helv. Chim. Acta*, 1954, **37**, 1280.
[4] Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626.
[5] Bunton, Lewis, and Llewellyn, *Chem. and Ind.*, 1954, 1154.
[6] Bateman, Hughes, Ingold, and Taher, *J.*, 1940, 979.
[7] Brown and Hudson, *J.*, 1953, 3352.

alone, and increases rapidly with water concentration (Table 4) and on the addition of formate ions (Table 1).

TABLE 1. *The effect of formate ions on the rate of reaction of benzoyl chloride and* p-*nitrobenzoyl chloride.*

| Acid chloride | Concn. (N) | Formate concn. (N) | $10^4 k_1$ (sec.$^{-1}$) | $10^2 k_2$ (1. mole$^{-1}$ sec.$^{-1}$) | $10^{-3} k_2 [H_2O]/k_1$ |
|---|---|---|---|---|---|
| $C_6H_5 \cdot COCl$ * ................. | 0·0282 | 0·180 | 38·6 | — | — |
| | | Nil | 39·2 | | |
| $p$-$NO_2 \cdot C_6H_4 \cdot COCl$ † ......... | 0·00602 | 0·0233 | — | 8·33 | 3·4 |
| | 0·0149 | ,, | — | 8·44 | 3·44 |
| | | Nil | 0·185 | | |

  * Solvent 4·6% aqueous formic acid at 9°.          † Solvent 1·4% aqueous formic acid at 20·1°.

On the other hand, the rates of reaction of benzoyl and *p*-toluoyl chloride are almost independent of the water concentration, and formate ions have no effect. With *p*-bromobenzoyl chloride the rate of the second-order reaction with water becomes appreciable.

These results show therefore that the effect of water on the rate of reaction increases with the tendency for covalent-bond formation at the reactive carbon atom (Table 3).

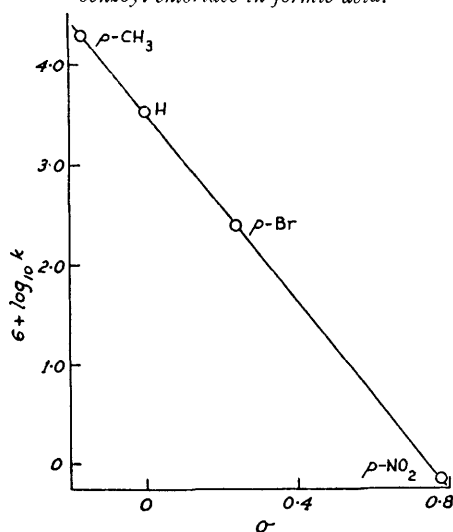FIG. 1. *The Hammett relation for* p-*substituted benzoyl chlorides in formic acid.*



TABLE 2. *Order of reactivities of* p-*substituted benzoyl chlorides. The effect of changing the nucleophilic and solvating conditions of the medium.**

| Reactant | $NO_2$ | Br | $CH_3$ | $CH_3O$ |
|---|---|---|---|---|
| Aniline [a] ......... | 8·5 | 1·5 (Cl) | 0·56 | — |
| Ethanol [b] ......... | 32 | 2·5 | 0·47 | 0·25 |
| Water [c] ............ | 35 | 3·2 | 0·55 | 0·60 |
| | | | (0·47) [d] | (0·36) [d] |
| Water [e] ............ | ~0 | 0·086 | 6·6 | V. fast |

[a] In benzene.          [b] In 40% alcoholic ether.
[c] In 5% aqueous acetone.          [d] In 5% aqueous dioxan.
[e] In formic acid.

  * The rates are relative to that of the unsubstituted compound.

The rate of reaction in formic acid alone increases with electron release to the carbon atom, and the rate order is the complete reverse of that observed in more nucleophilic media (Table 2).

The results are not sufficiently accurate to afford a value of the rate of reaction of the *p*-nitro-compound in formic acid alone, but extrapolation shows the rate to be very small compared with the values for the other chlorides. The Hammett relation is obeyed for the other three chlorides (Fig. 1), and extrapolation of the log $k$–σ graph leads to a value of *ca.* $10^{-6}$ sec.$^{-1}$ at 9° for the nitro-compound. There is some doubt, however, as to whether Hammett's relation holds for $S_N1$ processes, particularly on substitution of electron-releasing groups.[8] This extrapolated value may therefore be too high.

The very small rate constant for the *p*-nitro-compound in formic acid alone shows that the nucleophilic power of a formic acid molecule is negligible compared with that of a

  [8] Kochi and Hammond, *J. Amer. Chem. Soc.*, 1953, **75**, 3442.

water molecule, since bond formation is most important in this reaction. It follows that the considerably greater reactivities of the other chlorides in formic acid refer to processes controlled by solvation forces alone,[9] and hence such rates may be taken to be those of the $S_N1$ reactions in this medium.

It is of interest to compare these rates with the corresponding rates in a more nucleophilic solvent of equal solvating power. Although solvation in non-aqueous and mixed aqueous systems is too complex to be treated theoretically, empirical values of solvating power may be obtained from the rate constants of a reference reaction known to proceed by the $S_N1$ mechanism.[10] If change of solvent has no effect on the transition-state structure, it follows that the rates of an ionisation reaction should be equal in solvents of the same solvating power (denoted by $Y$ by Grunwald and Winstein [10]).

With reference to the present results, it is found that formic acid and 65% aqueous acetone have approximately equal $Y$ values. The exact composition of the aqueous solvent giving a medium of solvating power equal to that of formic acid cannot be determined with certainty, since Grunwald and Winstein's law is only approximate and two sets of $Y$ values have been used. These two sets, however, converge rapidly in highly aqueous media and the corresponding values are almost equal in the solvent range considered here. The rate constants change very rapidly with water content, which also adds to the difficulty of estimating the exact $Y$ value.

The appropriate rate constants for the four chlorides in formic acid and 65% aqueous acetone are compared in Table 3.

TABLE 3. *Comparison of the rates of reaction of* p-*substituted benzoyl chlorides in solvents of equal solvating power at* 9°.

| | $k_1$ (sec.$^{-1}$) in | | % $S_N1$ | Effect of water |
|---|---|---|---|---|
| Substituent | 65% aqueous acetone | formic acid | reaction | on rate * |
| CH$_3$ ..................... | $28 \times 10^{-3}$ | $19 \times 10^{-3}$ | 70 | ~0 |
| H ..................... | $8.9 \times 10^{-3}$ | $3.5 \times 10^{-3}$ | 40 | 10% |
| Br ..................... | $2.2 \times 10^{-3}$ | $2.4 \times 10^{-4}$ | 10 | 50% |
| NO$_2$ ..................... | $3.0 \times 10^{-2}$‡ | $1.0 \times 10^{-6}$ † | ~0 | 625% |

* Increase (%) in rate on changing the water concentration from 0.8 to 5.0 vol. %.
† Obtained from the Hammett relation. ‡ Extrapolated from Brown and Hudson's data.[7]

In all cases the rate is greater in the aqueous acetone solutions, but the greater the ease of electron release to the reaction centre the closer are the two corresponding rate constants. Thus the rate of reaction of *p*-toluoyl chloride is almost the same in these two media of considerably different nucleophilic power. This suggests that most of the molecules react by the $S_N1$ type of mechanism in 65% aqueous acetone. On the other hand, the rate of hydrolysis of *p*-nitrobenzoyl chloride is at least $10^4$ times greater in the more nucleophilic solvent, showing that the reaction proceeds entirely by the $S_N2$ type of process in 65% aqueous acetone, in agreement with previous considerations.

If it is assumed that the rate of the $S_N1$ type of process is equal in the two solvents, it follows that the excess rate in the aqueous acetone solution is that of the alternative $S_N2$ process. This comparison thus leads to estimates of the proportion of the reaction proceeding by each mechanism. In this estimation it is assumed that, in each reaction, some molecules are hydrolysed by preliminary ionisation ($S_N1$), and some by an activated reaction between a nucleophilic water molecule and an acid chloride molecule ($S_N2$). There is considerable controversy as to whether borderline mechanisms proceed in this way, or whether all the molecules pass through a transition state of intermediate structure.[7, 11]

The available evidence is difficult to explain without assuming that the transition state of an $S_N2$ process may change as the medium changes to one of greater polarity and solvating

[9] See, however, Strietwieser, *J. Amer. Chem. Soc.*, 1955, **77**, 1117.
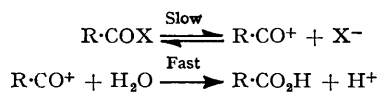[10] Grunwald and Winstein, *ibid.*, 1948, **70**, 846.
[11] Winstein, Grunwald, and Jones, *ibid.*, 1951, **73**, 2700; Swain and Langsdorf, *ibid.*, p. 2813; Bird, Hughes, and Ingold, *J.*, 1954, 634.

power, resulting in increased bond stretching and decreased interaction with the nucleophilic reagent. This leads to an apparent increase in $S_N1$ character of the reaction, as judged by solvent and substitution effects, although the rate-determining step remains bimolecular. In the present reaction, for example, the rate constant of the *bimolecular* reaction with water and *p*-bromo- is *ca.* 3 times that of *p*-nitro-benzoyl chloride (Table 4), *i.e.*, the reverse of the rate order usually observed for the $S_N2$ reaction (Table 2).

As the polarity of the medium increases and/or electron-releasing groups accumulate in the alkyl radical, the transition state may change to such an extent that some of the molecules ionise without receiving an energy contribution from the nucleophilic (water) molecule, the remainder of the molecules decomposing by the bimolecular mechanism, with bond-breaking the dominant process. The simultaneous occurrence of both mechanisms in a limited range of reaction conditions follows from the statistical nature of reactions, so that the reacting systems have different energies and configurations, only the mean of which can be determined experimentally.
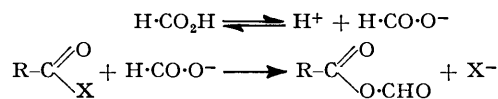
In the reaction discussed here, independent evidence has been advanced to show that in highly aqueous media, reaction proceeds by both unimolecular and bimolecular processes in a narrow solvent range.[2] The data of Table 3 show the effect of substitution on the extent of participation of the two alternative processes. The reaction of *p*-bromobenzoyl chloride is observed to proceed mainly by the $S_N2$ process, whereas the unsubstituted chloride reacts to approximately equal extents by both mechanisms, in agreement with previous conclusions.[1]

These results suggest strongly that the rate-determining step of the $S_N1$ type of mechanism involves electrostatic interaction only between solvent and acid chloride molecule, to give an intermediate with an increased reactivity towards nucleophilic reagents. Analogy with the alkyl halide series suggests that the intermediate is an acyl ion formed in a typical $S_N1$ process :

$$\text{R·COX} \underset{\text{Fast}}{\overset{\text{Slow}}{\rightleftharpoons}} \text{R·CO}^+ + \text{X}^-$$

$$\text{R·CO}^+ + \text{H}_2\text{O} \longrightarrow \text{R·CO}_2\text{H} + \text{H}^+$$

This mechanism is supported by cryoscopic measurements in sulphuric acid indicating the presence of the mesitoyl ion [12] and the formation of acyl derivatives which are reputed to behave as weak electrolytes in sulphur dioxide.[13]

*The Reaction of* p-*Nitrobenzoyl Chloride.*—As already mentioned, the rate of reaction of this chloride is proportional to the water concentration up to *ca.* 5—10% (v/v) of water. The high reactivity towards formate ions (Table 1) raises the possibility that the reaction proceeds with formate ions due to the ionisation of formic acid promoted by water :

$$\text{H·CO}_2\text{H} \rightleftharpoons \text{H}^+ + \text{H·CO·O}^-$$

$$\text{R–C}\!\!\begin{array}{c}\nearrow\text{O}\\\searrow\text{X}\end{array} + \text{H·CO·O}^- \longrightarrow \text{R–C}\!\!\begin{array}{c}\nearrow\text{O}\\\searrow\text{O·CHO}\end{array} + \text{X}^-$$

This explanation is in agreement with the direct proportionality between conductivity of the solvent and rate constant (Fig. 2).

This possibility is, however, discounted by the observation that the rate of hydrolysis is strictly of first order over the whole course of the reaction (Fig. 3). If the reaction involved formate ions, the rate constant would decrease continuously owing to the common-ion effect provided that the hydrogen-ion concentration produced in the hydrolysis is greater than that produced by ionisation of the formic acid. The conductivity values show that this requirement is fulfilled; *e.g.*, in 1% aqueous formic acid the conductivity increases from $10^{-5}$ to $6\cdot2 \times 10^{-5}$ mho on hydrolysis of 0·02M-chloride at 9°. Conductivity measurements also show that the mobility of the formate ion is slightly greater than that of the chloride, so the differences in conductivity observed during the reaction may be attributed mainly to changes in hydrogen-ion concentration.

[12] Treffers and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1708.
[13] Seel and Bauer, *Z. Naturforsch.*, 1947, **26**, 374.

It may therefore be concluded that reaction occurs between water and halide with a rate considerably less than that in acetone or dioxan containing the same concentration of water. Whereas the rate of reaction of the unsubstituted chloride is 220 times greater in 5% aqueous formic acid than in 5% aqueous acetone, the rate of the *p*-nitro-compound is 30 times less and that of the 2 : 4 : 6-trinitro-compound is 150 times less. It is noteworthy that the rate for these last two compounds decreases with increasing dielectric constant and solvating power, although the transition state is more polar than the reactants. It is necessary therefore to resort to a molecular model of the reacting system in order to explain solvent effects in this kind of medium satisfactorily.

Extrapolation of the rate data [7] in acetone–water mixtures leads to a rate constant for the *p*-nitro-compound of *ca.* $10^{-2}$ sec.$^{-1}$ at 0° in 65% aqueous acetone compared with a value of $1\cdot4 \times 10^{-6}$ sec.$^{-1}$ in $1\cdot3$% aqueous formic acid. The corresponding activation

FIG. 2. *Relation between the pseudo-unimolecular rate constants for the hydrolysis of* p-*nitrobenzoyl chloride and specific conductivity of formic acid–water mixtures at 20°.*
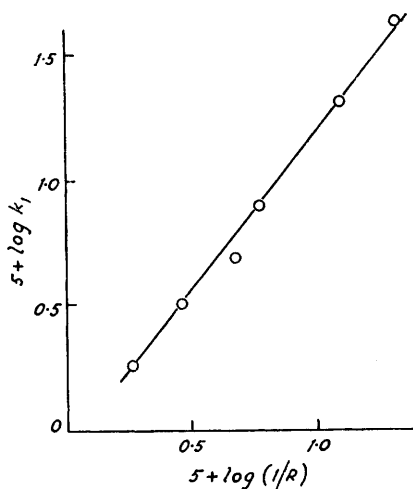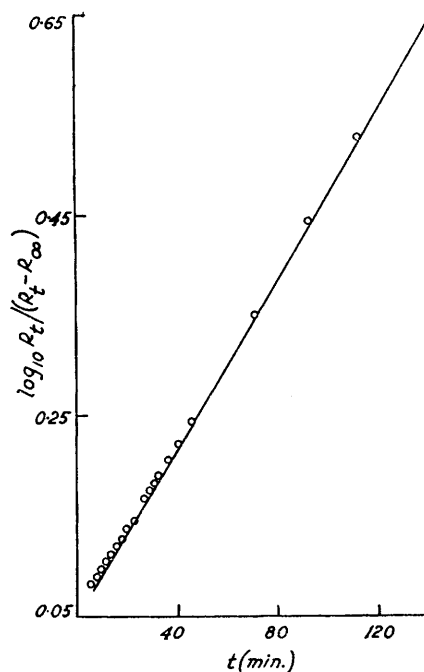
FIG. 3. *First-order plot for the solvolysis of* p-*nitrobenzoyl chloride* (0·0307M) *in* 1·3% *aqueous formic acid at 40°.*



energies are $17\cdot5$ and 20 kcal./mole, respectively. Second-order rate constants of $3 \times 10^{-3}$ and $1\cdot9 \times 10^{-5}$ l. mole$^{-1}$ sec.$^{-1}$ are obtained if the rate of the bimolecular reaction is assumed to be proportional to water content. From these values, the entropies of activation in the two media are found to be similar ($-6\cdot4$ and $-5\cdot9$ e.u. respectively). The difference in rate of hydrolysis of *p*-nitrobenzoyl chloride in these two solvents is therefore due mainly to the activation energy difference of *ca.* $2\cdot5$ kcal. mole$^{-1}$.

The bimolecular rate constants are compared in media of equal solvating power as it has been suggested that a change in the $S_N2$ transition state is produced by changing the medium.[7] Thus the reaction of *p*-nitrobenzoyl chloride remains bimolecular in the 5—65% water concentration range, but the contribution of the bond-breaking process increases considerably owing to increased solvation.

The increased energy required for the reaction in formic acid may be attributed to the formation of a stable adduct between formic acid and water molecules, with a bond energy greater than that between individual water molecules :

$$H_2O + H\cdot CO_2H \rightleftharpoons H_2O \ldots H\cdot CO_2H$$

S
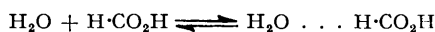
In 65% aqueous acetone, on the other hand, the reactive water molecule is obtained from a group of water molecules. It is well known that the hydrogen bond in carboxylic acids is appreciably stronger than in alcohols and water. It is difficult to obtain comparable data but the spectroscopic value for the gaseous dimer $(H \cdot CO_2H)_2$ of 7·06 kcal./mole may be compared with the value of 5 kcal./mole usually taken for water.[14] The difference of *ca.* 2 kcal. mole$^{-1}$ is of the same order as the difference in activation energy observed. Reduced rates of $S_N2$ reactions in solvents of high ionising power may therefore be explained semi-quantitatively by the increased bonding energy between solvent molecules and the nucleophilic reagent. When this effect is observed, it may be concluded that covalent-bond formation between the two reacting molecules makes a greater contribution to the activation energy than the bond-breaking process.

The effect is more pronounced in the case of 2 : 4 : 6-trinitrobenzoyl chloride owing to the presence of the three strongly electron-attracting groups. The rate in 15% aqueous formic acid is 150 times less than in 15% aqueous acetone, thus suggesting that the contribution of the bond-breaking process is less than in the case of the *p*-nitro-compound. Consequently, little change in transition-state structure is expected even in highly aqueous solvents, and observations in aqueous acetone appear to support this prediction.[7]

<center>EXPERIMENTAL</center>

The solvolysis rates were measured conductimetrically in the apparatus described previously.[1] The bridge was modified to allow 1 : 10, 1 : 1, and 10 : 1 ratios to be used so that cell resistances up to 100,000 ohms could be measured conveniently. Oil-thermostats were used except for measurements below 10°, for which the cell was immersed in a large Dewar vessel containing ice–water. In order to obtain a sharp balance point, the water was connected to the earth terminal of the bridge.

The experimental procedure was that previously described,[15] the high-resistance cell being used. For the fast reactions the chloride was forced into the solvent kept at the desired temperature, from a micropipette fitted with a plunger. The tip of this pipette was held just below the solvent. Some of the liquid was then sucked back into the pipette, and the plunger pressed sharply. This procedure, twice repeated, caused quite a vigorous stirring action. The liquid was then raised into the cell without passing any air through it, and the first reading immediately taken. This method eliminated the possibility of droplets of acid chloride collecting in and running down the neck of the cell, and also eliminated the necessity of passing air through the solution.

The water–formic acid solutions were not prepared in the same way as the acetone–water and dioxan–water mixtures by weighing water into the pure solvent, as it is impossible to dry formic acid completely. In most cases, drying with phthalic anhydride [16] and distillation gave a product not much drier than the original " AnalaR " sample. For this reason, solutions of suitable water contents were prepared and the water concentrations determined accurately by the Karl Fischer reagent (B.D.H.). The water concentration of solutions up to 5% (v/v) could be determined to within $\pm 0.05\%$.

In the case of the more concentrated solutions, the samples had to be diluted with methanol before the water estimation, and less consistent results were obtained. The compositions of the more concentrated solutions were determined from a calibration graph of water content, obtained by direct weighing into a sample of formic acid of known (low) water content, against conductivity.

The rate constant was calculated by assuming that the concentration of hydrogen chloride produced is proportional to the conductivity. This was confirmed by making up a solution of *p*-nitrobenzoyl chloride in aqueous formic acid. The chloride was allowed to hydrolyse completely, and then the resistance measured. The solution was successively diluted with formic acid of the same water content, and the resistance measured each time. The reciprocal of the resistance was found to be directly proportional to the concentration of chloride.

If $a$ is the initial concentration of chloride and $x$ the concentration change in time $t$, it follows that $a = K(1/R_\infty - 1/R_0)$ and $x = K(1/R_t - 1/R_0)$, where $R_0$, $R_t$, and $R_\infty$ are the resistances at

[14] Bernal and Fowler, *J. Chem. Phys.*, 1935, **1**, 515; Rowlinson, *Trans. Faraday Soc.*, 1951, **47**, 1200.
[15] Archer, Hudson, and Wardill, *J.*, 1953, 888.
[16] Rodd, " The Chemistry of Carbon Compounds," Elsevier, Amsterdam, 1951, 1, A, p. 542.

zero time, at time $t$, and at the completion of the reaction respectively, and $K$ is a proportionality constant.

Substitution in the first-order equation shows that

$$k_1 t = 2 \cdot 303 \times \log_{10} R_t(R_0 - R_\infty)/R_0(R_t - R_\infty)$$

so that $\log R_t/(R_t - R_\infty) = k_1 t/2 \cdot 303 + \log R_0/(R_0 - R_\infty)$. The rate constant $k_1$ is obtained from the graph of $\log R_t/(R_t - R_\infty)$ against $t$ (Fig. 3). $R_\infty$ was measured after a period of 10—20 half-lives. For the slowest reactions, the cell was placed in a thermostat at *ca.* 50° until the reaction was complete, and then returned to the original thermostat for the final reading to be taken. The results of these measurements are given in Tables 4 and 5.

TABLE 4. *The effect of water concentration on the rate of solvolysis of substituted benzoyl chlorides.*

| Substituent | Temp. | $H_2O$ (vol. %) | $10^4 k_1$ (sec.$^{-1}$) | Substituent | Temp. | $H_2O$ (vol. %) | $10^4 k_1$ (sec.$^{-1}$) |
|---|---|---|---|---|---|---|---|
| *p*-Me | 9·0° | 1·1 | 186 | *p*-NO$_2$ | 10·0° | 18·3 | 3·96 |
| ,, | ,, | 5·8 | 198 | ,, | 20·0 | 1·6 | 0·18 |
| (H) | 9·0 | 1·0 | 34·4 | ,, | ,, | 2·7 | 0·32 |
| ,, | ,, | 1·6 | 36·8 | ,, | ,, | 4·6 | 0·48 |
| ,, | ,, | 2·7 | 38·0 | ,, | ,, | 5·8 | 0·78 |
| ,, | ,, | 4·6 | 39·2 | ,, | ,, | 11·2 | 2·05 |
| *p*-Br | 9·0 | 1·1 | 2·43 | ,, | ,, | 16·9 | 9·24 |
| ,, | 20·0 | 1·1 | 9·59 | ,, | 30·0 | 16·7 | 12·4 |
| ,, | ,, | 1·9 | 10·64 | ,, | 40·0 | 1·6 | 1·63 |
| ,, | ,, | 5·8 | 11·98 | ,, | 61·0 | 1·6 | 11·6 |
| ,, | ,, | 11·2 | 15·4 | 2 : 4 : 6-(NO$_2$)$_3$ | 61·0 | 16·9 | 0·767 |

(The rates of reaction of *p*-methoxy- and 2 : 4 : 6-trimethyl-benzoyl chlorides are too great to be measured in 1% aqueous formic acid at 9°.)

TABLE 5. *Solvolysis in 65% aqueous acetone.*

| Temp. | $H_2O$ (%) | $10^4 k_1$ (sec.$^{-1}$) | Temp. | $H_2O$ (%) | $10^4 k_1$ (sec.$^{-1}$) |
|---|---|---|---|---|---|
| | *p*-Toluoyl chloride | | | *p*-Bromobenzoyl chloride | |
| −13·0° | 65·0 | 15·8 | 9·0° | 63·8 | 20·6 |
| − 4·0 | ,, | 57·9 | ,, | 65·0 | 22·0 |
| + 2·0 | ,, | 114 | ,, | ,, | 22·0 |
| + 9·0 | ,, | 278 * | ,, | ,, | 22·5 |

* Value obtained by extrapolation of the Arrhenius plot.

To determine the effect of added formate ions on the rate, a stock solution of formic acid of known water content containing a known concentration of calcium formate was prepared. The normality of this solution refers to the number of equivalents of formate ion per litre. The resistance of the reaction mixture was found to increase in contrast to the reaction with water alone, showing that chloride ions are less conducting in this medium than formate ions.

In cases where the rate of reaction was found to increase, the rate constant was calculated by assuming that the concentrations of formate and chloride ions are proportional to the corresponding conductivities. If $b$ is the initial concentration of formate ions, it follows that $1/R_0 = Bb$, $1/R_t = Ax + B(b - x)$, and $1/R_\infty = Aa + B(b - a)$, where $A$ and $B$ are proportionality constants connecting concentration and conductivity for chloride and formate ions respectively.

Substitution for $(a - x)$ and $(b - x)$ in $k_2 t = [1/(b - x)] \ln a(b - x)/b(a - x)$, the second-order rate equation, leads to the expression

$$\log_{10} \frac{(1/a - 1/b)/R_0 - (1/aR_\infty - 1/bR_t)}{(1/R_t - 1/R_\infty)} = \frac{k_2(b - a)t}{2 \cdot 303} - \log a$$

The second-order rate constants can then be obtained by plotting the log function against $t$.