# *Tracer Studies on Ester Hydrolysis. Part I. Triphenylmethyl Acetate.*

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The kinetics of hydrolysis and methanolysis of triphenylmethyl acetate have been examined in aqueous dioxan and absolute methyl alcohol respectively. The position of bond fission has been determined by the use of $^{18}O$ as a tracer in hydrolysis, and by product-isolation in methanolysis. The results show that in initially neutral and weakly alkaline solutions the reactions follow the mechanism $B_{\mathrm{Al}}1$. Both reactions are subject to powerful acid-catalysis, with predominant fission of the alkyl–oxygen bond, by mechanism $A_{\mathrm{Al}}1$. With an increase in alkali concentration the mechanism $B_{\mathrm{Ac}}2$ intervenes. The effects of added ions have been studied, and can be interpreted in terms of a rate-determining formation of a carbonium ion in the reactions which involve fission of the alkyl–oxygen bond.

THE hydrolysis of carboxylic esters, in the presence of acids and bases, and the analogous transesterification reactions with alcohols, normally proceed with fission of the acyl–oxygen bond. Day and Ingold (*Trans. Faraday Soc.*, 1941, **37**, 686), however, pointed out that fission of the alkyl–oxygen bond would be facilitated by electron accession to the α-alkyl-carbon atom. Such systems are those in which the lability of the alkyl–oxygen bond in esters, alcohols, and ethers has been demonstrated by racemisation (Kenyon and his co-workers, papers beginning in *J.*, 1937), and other examples include the ethanolysis of triphenylmethyl benzoate (Hammond and Rudesill, *J. Amer. Chem. Soc.*, 1950, **72**, 2769), and the methanolysis and hydrolysis of *tert.*-alkyl esters (Cohen and Schneider, *J. Amer. Chem. Soc.*, 1941, **63**, 3382; Bunton, Comyns, and Wood, *Research*, 1951, **4**, 383; Bunton, Hughes, Ingold, and Meigh, *Nature*, 1950, **166**, 679).

The position of bond fission in alcoholysis is proved directly by the nature of the products :

$$(a)\quad CH_3{\cdot}CO\vdots{-}O{\cdot}CPh_3 + ROH \rightleftharpoons CH_3{\cdot}CO_2R + CPh_3{\cdot}OH$$

$$(b)\quad CH_3{\cdot}CO{\cdot}O{-}\vdots CPh_3 + ROH \longrightarrow CH_3{\cdot}CO_2H + CPh_3{\cdot}OR$$

In hydrolysis the position of bond fission can often be determined by means of some property dependent on the type of alkyl group (Kenyon and his co-workers, *locc. cit.*), but a more general method is that using $^{18}O$ as isotopic tracer (Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508).

Product formation in alcoholysis as a criterion of bond fission lacks the sensitivity of the isotopic tracer method, and moreover may give misleading results unless kinetic control is applied. Transesterification [reaction (*a*)] is reversible, whereas ether formation [reaction (*b*)], is irreversible, and thermodynamic control may therefore force the products into those of reaction (*b*) independently of mechanism (cf. Bunnett, Robison, and Pennington, *J. Amer. Chem. Soc.*, 1950, **72**, 2328, who with methyl benzoate with sodium methoxide in methanol, where transesterification regenerated the reactants, were able to observe the very slow attack of the methoxide ion on the alkyl-carbon atom).

*Hydrolysis in Aqueous Dioxan.*—Fission of the alkyl–oxygen bond, which is of major importance in alcoholysis of triphenylmethyl acetate, is also observed in hydrolyses carried out in various conditions in aqueous dioxan. The reactions were carried out with water enriched in $^{18}O$, and the position of bond fission given directly by isotopic analysis of the products, since alkyl–oxygen fission (*b*) gives $^{18}O$ only in the alcohol, and acyl–oxygen fission gives it only in the acid. Isotopic oxygen exchange between water and the ester, shown by Bender (*J. Amer. Chem. Soc.*, 1951, **73**, 1626) to occur with acyl–oxygen fission, does not interfere since all our reactions involve predominantly alkyl–oxygen fission.

In general, the position of bond fission was determined by isolation of the acetic acid as its silver salt, and isotopic assay of the carbon dioxide produced by decarboxylation of this salt. As a supplement, triphenylmethyl alcohol was on occasions isolated and pyrolysed to carbon monoxide whose isotopic abundance ($\alpha$) was determined by mass spectrometry. Blank tests excluded extraneous isotopic exchange by the products. The results (Tables 1 and 2) show that in all conditions alkyl–oxygen fission predominates, although in alkaline solution there is a small amount of acyl–oxygen fission. It is probable that the mechanism could be forced into that of acyl–oxygen ($B_{Ac}2$), by a large increase in alkali concentration if this were not precluded by the low solubilities of the ester and the alkali in aqueous dioxan (although the analogous product can be isolated in methanolysis); even in some of the hydrolyses with our low concentrations of alkali, slight cloudiness indicated separation into two phases. Such experiments are marked ‡ in Table 1.

TABLE 1. *Position of bond fission in hydrolysis in* 80% *dioxan, determined by isolation of acetic acid.*

| Conditions | $\alpha$ for $H_2O$ (atoms % excess) | $\alpha$ for $CH_3{\cdot}CO_2H$ (atoms % excess) | Alkyl–oxygen fission (%) * |
|---|---|---|---|
| Initially neutral | 1·134 | 0·03, 0·04 | 96, 94 |
| Alkaline, 0·015M-NaOH † | ,, | 0·127,‡ 0·127 ‡ | 78, 78 |
| 0·028M-LiOH | 0·846, 1·07 | 0·063, 0·098 | 85, 82 |
| Acid, 0·0446M-$HClO_4$ | 1·134 | 0·058 | 94 |
| 0·037M-$HClO_4$ | 1·93 | 0·116 | 92 |

In control tests ($\alpha_{H_2O}$ 1·134), $\alpha_{CH_3{\cdot}CO_2H}$ was 0·003—0·007, 0·00—0·002, and 0·024 (twice) for initially neutral, alkaline, and acid (0·0446M-$HClO_4$) respectively.

* Corrected for controls. † In aqueous 71·5% dioxan. ‡ See text.

TABLE 2. *Position of bond fission in hydrolysis, determined by isolation of triphenylmethyl alcohol.*

| Conditions | $\alpha$ for $H_2O$ (atoms % excess) | $\alpha$ for $Ph_3C{\cdot}OH$ * (atoms % excess) |
|---|---|---|
| Acid, 0·03701M-$HClO_4$ | 1·93 | 1·84 |
| 0·036M-$HClO_4$ | 0·442 | 0·410, 0·420 |
| Initially neutral | 0·442 | 0·398, 0·407 |
| *Controls.* | | |
| Acid, 0·036M-$HClO_4$ | 0·442 | 0·094 |
| Initially neutral | 0·442 | 0·060 |

* Corrected for contamination of ester by alcohol (2—3%).

The kinetics of hydrolysis were followed titrimetrically, for initially neutral conditions, in the presence of acids and bases and with added salts (see Table 3). The effects of alkali and neutral salts are not large, but there is very marked acid-catalysis, the rate with M-sulphuric acid being *ca.* 3000 times that under initially neutral conditions. This general kinetic form is very similar to that observed in methanolysis. The isotopic results on bond fission show that both these reactions involve alkyl–oxygen fission, and the neutral reaction, proceeding at similar rates in neutral and alkaline solutions, can be only the rate-determining ionisation of the ester molecule; it is followed by rapid reaction between the triphenylmethyl cation and the aqueous solvent (the mechanism $B_{Al}1$ of Day and Ingold, *loc. cit.*) :

$$\left.\begin{array}{l} CH_3{\cdot}CO{\cdot}O{-}\!\!\vdots CPh_3 \overset{\text{Slow}}{\rightleftharpoons} CH_3{\cdot}CO{\cdot}O^- + CPh_3^+ \\ Ph_3C^+ + H_2O \xrightarrow{\text{Fast}} CPh_3{\cdot}OH + H^+ \end{array}\right\} \quad \ldots\ldots \quad (A)$$

Analogously the acid-catalysed mechanism must involve the ionisation of the conjugate acid of the ester (mechanism $A_{Al}1$) :

$$CH_3{\cdot}CO_2CPh_3 + H^+ \overset{\text{Fast}}{\rightleftharpoons} [CH_3{\cdot}CO_2H{\cdot}CPh_3]^+$$

$$[CH_3{\cdot}CO_2H{\cdot}CPh_3]^+ \overset{\text{Slow}}{\rightleftharpoons} CH_3{\cdot}CO_2H + CPh_3^+$$

$$Ph_3C^+ + H_2O \xrightarrow{\text{Fast}} CPh_3{\cdot}OH + H^+$$

The isotopic results in alkaline solution indicate the presence of a small amount of acyl–oxygen fission. This mechanism ($B_{Ac}2$) is dependent on hydroxide-ion concentration :

$$CH_3{\cdot}CO\!\vdots\!{-}O{\cdot}CPh_3 + OH^- \longrightarrow CH_3{\cdot}CO_2^- + CPh_3{\cdot}OH$$

It should lead to a corresponding increase of rate by hydroxide ion, which however is not observed (although the results in alkaline solution are much more scattered than in initially neutral solution). Various reasons are possible for this : (i) Benfey, Hughes, and Ingold, (*J.*, 1952, 2494) have shown that hydroxide ions can have a weak retarding effect on $S_N1$ reactions in aqueous solvents. (ii) As would be predicted, the rate of hydrolysis is highly dependent on the water content of the solvent, a decrease of the water content by 5 vol. % giving *ca.* sixfold decrease in rate (Table 3), and co-ordination of water with the lithium cation could reduce the rate by reducing the effective water content of the solvent (Lucas and Hammett, *J. Amer. Chem. Soc.*, 1942, **64**, 1928).

TABLE 3.

| Solvent (% of dioxan) | Temp. | Reagent or catalyst | Concn. of reagent (moles l.$^{-1}$) | $10^4k_1$ (sec.$^{-1}$) | Solvent (% of dioxan) | Temp. | Reagent or catalyst | Concn. of reagent (moles l.$^{-1}$) | $10^4k_1$ (sec.$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 80 | 65·0° | — | — | 8·31 [a] | 82·5 | 65·0° | — | — | 4·00 |
| ,, | ,, | AcOH | 0·03 | 8·50 | 85·0 | ,, | — | — | 1·46 |
| ,, | ,, | $Et_4N{\cdot}OH$ | 0·0263 | 6·64 | 80 | 35·1 | — | — | 0·253 |
| ,, | ,, | ,, | ,, | 7·22 | ,, | 44·6 | — | — | 0·86 [b] |
| ,, | ,, | $Et_3N$ | 0·00031 | 7·20 | ,, | 55·2 | — | — | 2·72 [b] |
| ,, | ,, | $C_5H_5N$ | 0·00025 | 7·52 | ,, | 25·0 | $H_2SO_4$ | 0·0116 | 2·14 |
| ,, | ,, | ,, | 0·0025 | 7·67 | ,, | ,, | ,, | 0·0229 | 5·25 |
| ,, | ,, | LiOH | 0·0297 | 7·67 | ,, | ,, | ,, | 0·0233 | 5·75 |
| ,, | ,, | ,, | 0·0266 | 7·50 [b] | ,, | ,, | ,, | 0·0349 | 7·45 |
| ,, | ,, | LiCl | 0·294 | 6·14 | ,, | ,, | ,, | 0·0418 | 9·59 |
| ,, | ,, | LiOAc | 0·272 | 1·92 | 85 | ,, | ,, | 0·0229 | 4·05 |
| 81 | ,, | — | — | 5·75 | 90 | ,, | ,, | 0·0229 | 3·40 |

[a] Mean of 5 values. [b] Mean of 2 values.

It is possible that this " salting-out " effect of a metal cation is also responsible for the decrease of hydrolysis rate in the presence of the non-common-ion salt lithium chloride (Table 3), whereas such salts usually accelerate $S_N1$ reactions (Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979). It is noteworthy that lithium acetate, which should give a " mass-law " retardation of the $S_N1$ reaction of this ester, in fact shows a considerably greater retardation than does lithium chloride (Table 3). It seems therefore that salt-effects on the ionisation of the neutral ester molecule are complicated by solvation of the lithium cation. This complication is absent from reactions in methyl alcohol which provides a more convenient solvent for kinetic study of the effects of alkali ions and of neutral salts.

Tetraethylammonium hydroxide slightly retarded hydrolysis: it seemed possible that this was due to small amounts of triethylamine initially present or formed during the reaction. Indeed, small amounts of tertiary bases also retarded the hydrolysis, presumably by co-ordination with the carbonium ion, thereby delaying its capture by the water molecules (cf. Gelles, Hughes, and Ingold, *J.*, 1954, 2918).

The corresponding solvent effect on the acid-catalysed hydrolysis rate is somewhat more complicated. Experimentally we observe a small rate increase (*ca.* 40%) in going from aqueous 90% dioxan to the more aqueous solvent, aqueous 80% dioxan. Theoretically one expects a two-fold effect, on the protonation of the neutral molecule and on the breakdown of the protonated molecule. Indicator measurements with hydrochloric acid in aqueous dioxan (Braude and Stern, *J.*, 1948, 1976) show that in the solvent range used in our hydrolyses the tendency to donate a proton to a neutral base decreases with an increase in the water content of the solvent. If this is also true of sulphuric acid the breakdown of the protonated ester molecule must be facilitated by an increase in the water content of the solvent. By analogy with the $S_N1$ reactions of sulphonium salts we would expect a retardation of breakdown of the protonated ester molecule, but it is probable that the presence of the polar carbonyl group complicates this simple analogy.

The temperature coefficient of the neutral hydrolysis was measured in aqueous 80% dioxan to allow a comparison to be made between the neutral and the acid rate. The "activation energy," in the exponential term in the Arrhenius equation, was 23·6 kcal./mole, and that for the non-exponential term was $2{\cdot}6 \times 10^{12}$ sec.$^{-1}$.

*Reactions in Absolute Methyl Alcohol.—Neutral and alkaline solution.* Gomberg and Davies (*Ber.*, 1903, **36**, 3926) observed that triphenylmethyl acetate and benzoate in ethyl alcohol gave ethyl triphenylmethyl ether, and similarly we observe the formation of methyl triphenylmethyl ether in methyl alcohol both initially neutral and in the presence of 0·1M-sodium methoxide. Control tests showed that this product could not have been formed by a side reaction between triphenylmethyl alcohol and methyl alcohol.

The rates of methanolysis were measured by acid–alkali titration, in initially neutral solution and with sodium methoxide. The kinetic form was generally similar to that observed in the reaction of triphenylmethyl benzoate in an ethyl alcohol–ethyl methyl ketone solvent (Hammond and Rudesill, *loc. cit.*). The reaction observed is a neutral solvolysis, whose rate is independent of acid and base (Table 4), and the kinetic form and product isolation prove that it must be following the mechanism $B_{Al}1$ (cf. reactions *A*, p. 1356). The effects of added lithium acetate and chloride are in accord with this mechanism, the former showing a mass-law retardation typical of an $S_N1$ reaction, and the latter a typical ionic-strength acceleration.

TABLE 4.

| Temp. | Reagent or catalyst | Concn. of reagent (mole/l.$^{-1}$) | $10^4k_1$ (sec.$^{-1}$) | Temp. | Reagent or catalyst | Concn. of reagent (mole/l.$^{-1}$) | $10^4k_1$ (sec.$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 35·1° | — | — | 9·94[a] | 20·0° | — | — | 1·77 |
| ,, | NaOMe | 0·066 | 9·73 | ,, | NaOMe | 0·324, 0·869 | 3·11,[c] 5·20[c] |
| ,, | ,, | 0·112 | 9·87 | 35·1 | LiCl | 0·076 | 11·08 |
| | Mean in presence of NaOMe | | 9·80[b] | ,, | LiOAc | 0·076 | 8·98 |

[a] Mean of 4 values. [b] Mean of 5 values. [c] Detd. by dilatometry.

With higher concentrations of sodium methoxide (*ca.* 1·6M) triphenylmethyl alcohol was isolated from the reaction mixture, suggesting the intervention of the base-accelerated mechanism ($B_{Ac}2$) :

$$\mathrm{CH_3{\cdot}CO}\,\vdots\!\!-\!\mathrm{OCPh_3} + \mathrm{OMe^-} \rightleftharpoons \mathrm{CH_3{\cdot}CO_2Me} + \mathrm{CPh_3{\cdot}O^-}$$

$$\mathrm{CPh_3{\cdot}O^-} + \mathrm{MeOH} \rightleftharpoons \mathrm{CPh_3{\cdot}OH} + \mathrm{MeO^-}$$

This formally reversible reaction is driven to the right-hand side because the second equilibrium is heavily in favour of the methoxide ion and the triphenylmethyl alcohol in our experimental conditions. The total concentration of alkoxide ion does not change during the reaction, and it is therefore impossible to follow this reaction by direct acid–alkali titration, but it can be followed dilatometrically. This method is not entirely satisfactory, the volume changes being small, and, if the fission is not purely of the acyl–oxygen bond, a change in alkoxide-ion concentration occurs during the run and the order should deviate from unity. The limited results obtained (Table 4), show a definite acceleration of transesterification by a high concentration of methoxide ion and, with the product isolation, demonstrates the existence of the $B_{Ac}2$ mechanism in this system.

With intermediate concentration of methoxide ion (*ca.* 0·3M) the two mechanisms should co-exist, with a mixture of acyl–oxygen and alkyl–oxygen fission. Both are of the first order with respect to ester, but in the acyl–oxygen fission of first order with respect to the approximately constant concentration of methoxide ion. It should therefore be possible to predict approximately the product compositions from the measured rates. The proportions of the two mechanisms were estimated by measurement of the triphenylmethyl ether (giving the proportion of alkyl–oxygen fission) and of methyl acetate (giving that of acyl–oxygen fission). The results obtained with 0·324M-sodium methoxide at 20° are given in the Experimental section; they are probably as good as can be expected from a method which is sensitive to the fractionation errors of product isolation. Comparison of the observed and the calculated product proportions suggests that the assumptions involved in the use of dilatometry for the measurement of reaction rates at these high alkali concentrations are justified.

*Acid solution.* In the presence of even small concentrations of dry hydrogen chloride (*ca.* M/30) the methanolysis becomes too fast for convenient measurement. Under these conditions methyl triphenylmethyl ether was again isolated, but under comparable conditions a control test showed that the alcohol in methanol gave 27% of this ether and it is therefore impossible to exclude completely the existence of the acid-catalysed acyl–oxygen fission ($A_{Ac}2$); but, if this mechanism obtains, it is of minor importance compared with the mechanism $A_{Al}1$.

The Arrenhius parameters for neutral methanolysis (deduced from two temperatures only) are, for the "activation energy" 20·5 kcal./mole, and for the non-exponential term $4{\cdot}0 \times 10^{11}$ sec.$^{-1}$.

## EXPERIMENTAL

*Preparation of Materials.*—Methyl alcohol was dried over magnesium by Lund and Bjerrum's method (*Ber.*, **1931**, **64**, 210) and further purified by fractional distillation.

Dioxan was purified by refluxing it with dilute hydrochloric acid in a stream of nitrogen, drying it first over potassium hydroxide, then over metallic sodium, and finally distilling it from sodium.

Solutions of aqueous dioxan were made up by volume, *e.g.*, aqueous 80% dioxan by mixing 20 vols. of water with 80 vols. of dioxan at room temperature.

Sodium methoxide solutions were prepared by dissolving sodium, freshly washed in dry methyl alcohol, in dry methyl alcohol.

Triphenylmethyl acetate was prepared by the general methods of Gomberg and Davies (*loc. cit.*). Excess of dried silver acetate was refluxed with triphenylmethyl chloride in dry benzene for 3 hr., or, better, shaken with triphenylmethyl chloride in dry ether until reaction was complete (*ca.* 48 hr.). After filtration and evaporation of the solvent the crude ester was purified by recrystallisation from light petroleum, light petroleum–ethyl acetate, or preferably di*iso*propyl ether. The ester decomposed when kept in a desiccator, and freshly prepared samples were used. A typical specimen had m. p. 83° (Found: C, 83·6; H, 5·9. Calc. for $C_{21}H_{18}O_2$: C, 83·4; H, 6·0%).

Tetraethylammonium hydroxide solutions were prepared by refluxing tetraethylammonium iodide with ethyl iodide, washing the mixture with ether to remove unchanged ethyl iodide and any triethylamine, and shaking the tetraethylammonium iodide solution with excess of silver oxide in carbonate-free water.

Lithium hydroxide was prepared similarly by treating lithium chloride with silver oxide in carbonate-free water.

*Reactions in Aqueous Dioxan.*—*Position of bond fission.* Hydrolysis of the ester was carried out in aqueous dioxan under kinetic conditions, with water enriched in $^{18}O$. After reaction the solvent was removed under reduced pressure, the residue neutralised, and the acetic acid isolated as silver acetate. After drying, first over $P_2O_5$, and then in a high vacuum, the silver acetate was decarboxylated by heating *in vacuo*. The carbon dioxide was analysed for $^{18}O$ in a 180° mass spectrometer of conventional design.

When the triphenylmethyl alcohol was isolated it was purified by crystallisation from light petroleum, and its isotopic abundance determined by pyrolysis *in vacuo* in a carbon tube heated by a 1-kw R.F. induction heater. The carbon monoxide was collected over liquid air and analysed mass-spectrometrically. This general method has been checked by catalytic conversion of the carbon monoxide into carbon dioxide, and the absence of air-contamination was shown by the absence of argon. The isotopic abundances ($\alpha$) quoted are in atoms % of $^{18}O$ above normal, determined for the acid and alcohol by the above methods, and for the water by equilibriation with carbon dioxide.

If $R$ is the ratio of the peaks, for $^{12}C^{16}O^{16}O$ and $^{12}C^{16}O^{18}O$, and for $^{12}C^{16}O$ and $^{12}C^{18}O$, then the abundances of $^{18}O$ are given in atoms % by :

for $CO_2$, $\alpha' = 100/(2R + 1)$ ;

for $H_2O$, $\alpha' = 100/(2KR + 1)$, where $K = 1{\cdot}038$ at 25° ;

for $CO$, $\alpha' = 100/(R + 1)$

and the excess abundance, $\alpha = \alpha'(\text{sample}) - \alpha'(\text{normal})$.

Control experiments were carried out by the same methods and under the same conditions.

*Kinetics.* The reactions were followed by acid–alkali titration with thymol-blue as indicator. Those catalysed by sulphuric acid at 25° were carried out in stoppered flasks, but sealed tubes were used at higher temperatures.

*Reactions in Absolute Methyl Alcohol.*—The products of methanolysis were isolated in good yield from kinetically controlled reactions; *e.g.*, in initially neutral methyl alcohol at 35° the ester (6 g.) after 5 hr. gave the methyl triphenylmethyl ether, m. p. 83·5°, in 82% yield.

Similarly the ester (0·85 g.) with 1·7M-sodium methoxide gave after 4 hr. at 35° triphenylmethyl alcohol, m. p. 162°, in 55% yield.

In an experiment with 0·324M-sodium methoxide 0·293 g. of ester gave after 4 hr. at 20° 63·6% of methyl triphenyl ether (estimated by methoxyl determination on the solid residue), and 34% of methyl acetate (estimated by alkaline hydrolysis of the distillate). This gives a proportion of alkyl–oxygen fission of *ca.* 64% (the value estimated from the kinetics is 57%).

The products obtained are listed in Table 5. Control tests showed that the alcohol was not converted into the ether under neutral or alkaline conditions.

TABLE 5. *Products of methanolysis.*

| Reagent | Product | Yield (%) | Fission | Reagent | Product | Yield (%) | Fission |
|---|---|---|---|---|---|---|---|
| Neutral .............. | Ether | 82 | Alkyl | 0·1N-NaOMe ...... | Ether | 83 | Alkyl |
| M/30-HCl ........... | Ether | 75 | Alkyl | 1·7M-NaOMe ...... | Alcohol | 55 | Acyl |
| M/30-HCl (control) | Ether (27%) * | — | — | 0·33M-NaOMe ... | Alcohol<br>Ether | 34 †<br>64 | Mixed |

* Estimated from OMe determination of solid product. † Estimated indirectly.

*Kinetics.* The reaction was followed by acid–alkali titration, where possible, with thymol-blue–cresol-red as indicator. In concentrated alkali the reaction proceeded without change of alkalinity, and the reactions were therefore followed by dilatometry. Dilatometers of the tap-less two-arm type were used (Benford and Ingold, *J.*, 1938, 931), the movement of the meniscus being followed by a cathetometer, and the thermostat temperature controlled to *ca.* 0·001° First-order rate coefficients were obtained graphically by Guggenheim's method (*Phil. Mag.*, 1926, 2, 538). A typical result is tabulated.

Temp. 20·0°. $[\text{Ester}]_0 = 0{\cdot}0406$M. Portions of 5·00 c.c. titrated against 0·0413M-NaOH; $(a - x)$ expressed in c.c. of this NaOH. A mixed indicator of thymol-blue and cresol-red was used.

| $t$ (min.) ......... | 0 | 13·0 | 16·0 | 19·0 | 25·5 | 33·0 | 44·0 | 52·5 | 60·0 | 70·33 | 80·33 | 120 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(a - x)$ ......... | 4·92 | 4·28 | 4·18 | 4·00 | 3·80 | 3·47 | 3·05 | 2·83 | 2·59 | 2·34 | 2·03 | 1·31 |
| $10^4 k_1$ (sec.$^{-1}$) ... | — | 1·80 | 1·72 | 1·81 | 1·66 | 1·77 | 1·75 | 1·75 | 1·78 | 1·77 | 1·78 | 1·72 |

Mean value of $10^4 k_1 = 1{\cdot}77$ sec.$^{-1}$.

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