395. *The Mechanism of Saponification of Phenyl Benzoate in Aqueous Ethyl Alcohol.*

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THE rate of saponification of phenyl benzoate by potassium hydroxide in ethyl-alcoholic solution (composition not specified, but, from the method of preparation, about 99·5% alcohol) was examined by McCombie and Scarborough (J., 1914, **105**, 1304). Titration of the excess alkali with acid at intervals indicated that complete saponification at 30° required several days. Further, the reaction gave a definite velocity constant for the bimolecular equation $Ph{\cdot}CO_2Ph + KOH = Ph{\cdot}CO_2K + PhOH$, the rapidly attained equilibrium $PhOH + KOH \rightleftharpoons PhOK + H_2O$ not producing any apparent disturbance.

Subsequent work by these authors (J., 1915, **107**, 156; 1921, **119**, 970) showed that, for a wide range of ethyl esters of both aliphatic and aromatic acids, alkaline saponification could always be represented as a bimolecular reaction, but that the actual value of the velocity constant varied in a very definite manner with the composition of the aqueous ethyl alcohol used as solvent.

In view of the great applicability of saponification measurements of alkyl esters in the quantitative development of theories of polarity, the present authors, after discussion with Drs. McCombie and Scarborough, have reinvestigated the alkaline hydrolysis of aryl esters in alcohol–water mixtures of definite composition. The problem, however, appears to be so complex that the following qualitative account, indicating the mechanism of the reaction, is communicated pending a more complete quantitative investigation.

The saponification of phenyl benzoate in ethyl alcohol is by no means so simple a reaction as that of ethyl benzoate in the same solvent, since in the quaternary system, phenyl benzoate–sodium hydroxide–ethyl alcohol–water, alternative saponification processes (A) and (B) are possible :

$$\begin{array}{llllll}
\text{A.} & \text{(i)} & Ph{\cdot}CO_2Ph & + NaOH \longrightarrow & Ph{\cdot}CO_2Na & + PhOH \\
 & \text{(ii)} & PhOH & + NaOH \rightleftharpoons & PhONa & + H_2O \\
\text{B.} & \text{(i)} & EtOH & + NaOH \rightleftharpoons & EtONa & + H_2O \\
 & \text{(ii)} & Ph{\cdot}CO_2Ph & + NaOEt \longrightarrow & Ph{\cdot}CO_2Et & + NaOPh \\
 & \text{(iii)} & Ph{\cdot}CO_2Et & + NaOH \longrightarrow & Ph{\cdot}CO_2Na & + EtOH
\end{array}$$

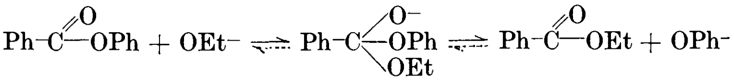
of which A (i), B (ii), and B (iii) may all be slow and possibly of comparable rates. It follows that the rate of formation of sodium benzoate, which is that measured by titration of excess alkali after definite times, is not necessarily the same as the rate of liberation of phenol (or sodium phenoxide). Consequently, a reaction mixture containing initially 0·03*N*-phenyl benzoate and 0·09*N*-sodium hydroxide was titrated at about hourly intervals (*a*) for excess alkali, using hydrochloric acid with phenolphthalein as indicator, and (*b*) for free phenol, using the bromine-titration method (Francis and Hill, *J. Amer. Chem. Soc.*, 1924, **46**, 2498). The first titrations, taken after 2 hours' reaction, indicated that whereas only 20% of the ultimate amount of sodium benzoate had been liberated, already over 97% of the ultimate amount of phenol had been liberated, the residual phenol being, in fact, of the same order as the experimental error in the titration of the 10 c.c. portions of reaction mixture used. Continuation of the hydrolysis indicated a practically constant value for free phenol (97—100%), and a very gradual liberation of free benzoate, 50% only being formed in 12 hours and 75% in 24 hours. During the whole period the electrical conductivity of the solution gradually decreased.

It is thus evident that the saponification of phenyl benzoate in ethyl-alcoholic solution must proceed by process (B), in which reaction (ii) must be very much faster than (iii), the ratio of the rates of these two reactions being apparently of the order 1000 : 1.

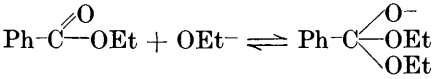
This conclusion has been confirmed qualitatively (i) by showing the presence of free phenol (by reaction with bromine water and by coupling with a diazo-solution) in an alcoholic mixture of phenyl benzoate and sodium hydroxide after less than one minute; (ii) by separating, purifying, and identifying ethyl benzoate, formed in practically quantitative yield, after 5 minutes' reaction only, after which time no unchanged phenyl benzoate could be found. Similar qualitative reactions were given by ethyl-alcoholic and by methyl-alcoholic solutions. Further, *p*-iodophenyl benzoate reacted similarly to phenyl benzoate.

Jones and Lapworth (P., 1914, **30**, 142) have observed the same sequence of reactions in the decomposition of phenyl acetate by both acid and alkaline alcoholic solutions.

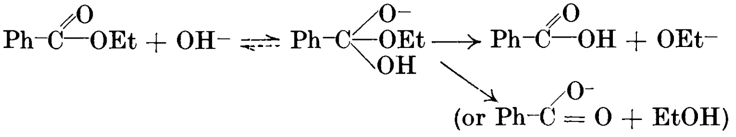
In view of the well-recognised catalysis of ester hydrolysis by hydroxyl ions, it seems probable that the saponification process in the mixed solvent proceeds by an ionic addition mechanism in which the anions OH′, OEt′, and OPh′ are the reactive entities :

(*a*).


$$\mathrm{Ph{-}C(=O){-}OPh + OEt^- \rightleftharpoons Ph{-}C(O^-)(OPh)(OEt) \rightleftharpoons Ph{-}C(=O){-}OEt + OPh^-}$$

(*b*)


$$\mathrm{Ph{-}C(=O){-}OEt + OEt^- \rightleftharpoons Ph{-}C(O^-)(OEt)(OEt)}$$

(*c*)


$$\mathrm{Ph{-}C(=O){-}OEt + OH^- \rightleftharpoons Ph{-}C(O^-)(OEt)(OH) \longrightarrow Ph{-}C(=O){-}OH + OEt^-}$$
$$\mathrm{(or\ Ph{-}C(O^-){=}O + EtOH)}$$

Following generally accepted theories of polarity, the relative orders of the rates of reaction, *viz.*, B (ii) >A (or *a* and *b* >*c* on the ionic interpretation), would be in accord with the relative reactivities of the anions : OEt′ (Alkyloxy) >OPh′ (Aryloxy) >OH′, the inverse of their stabilities in the free state.

From a number of reaction-velocity measurements, covering a range of concentrations of both ester and alkali, it appears that no one bimolecular reaction-velocity constant can be obtained for the saponification of phenyl benzoate in the aqueous alcohol. Since the investigated reaction mixtures have been shown to consist, after a very short time, of ethyl benzoate in an alkaline solution partly neutralised by phenol, it follows that a complete quantitative examination must involve a detailed study of the buffering of alcohol–water mixtures for which no reference standards are yet available.

The rate of saponification of ethyl benzoate by sodium hydroxide is greatly decreased by the presence of phenol. Also, by the use of very weak alkalis, it is possible to obtain a slow liberation of phenol from phenyl benzoate.

EXPERIMENTAL.

Pure $\mathrm{Ph{\cdot}CO_2Ph}$ was saponified with NaOH in 95% EtOH at 30°, and was titrated at intervals for PhOH (Francis and Hill, *loc. cit.*) and for excess alkali, 0·05*N*-acid and phenolphthalein being used. The following results were indicated :

After 2 hours, phenol liberated = 97%; benzoate = 25%
„ 12 „ „ „ = 98% „ = 53%
„ 24 „ „ „ = 99% „ = 75%

but the bimolecular velocity const., calc. from the acid titres, fell steadily from 0·023 to 0·011 (in l./g.-mol./min.).

The method of phenol estimation did not affect the course of the saponification, since when pure Ph·CO_2Ph dissolved in 95% EtOH was treated in a stoppered test-tube with 1 drop of Br aq., Br remained after 4 hrs. Addition of dil. H_2SO_4, as in the PhOH estimations, had no perceptible effect.

The following tests verified the rapid liberation of free PhOH and production of Ph·CO_2Et :

A. Ph·CO_2H in 95% EtOH was treated with alc. NaOH at room temp., acidified after 1 min., and then treated with Br aq. A thick ppt. of tribromophenol formed immediately, with decoloration of the Br. MeOH solutions of Ph·CO_2Ph acted similarly. *p*-Iodophenyl benzoate also yielded the free phenol under these conditions. Water added in bulk to the acidified solution produced only an emulsion of suspended Ph·CO_2Et.

B. To an alc. solution of Ph·CO_2Ph was added a cold diazotised solution of *p*-toluidine in dil. acid, and the mixture was then made alk. The cold solution darkened rapidly, the colour reaching its max. intensity in about 10 secs., and then matching the tint of the azo-dye produced by coupling, in similar concn., diazotised *p*-toluidine and an alk. solution of PhOH.

C. Ph·CO_2Ph (10 g.) in abs. EtOH (100 c.c.) was treated, at about 30°, with a solution of NaOEt, prep. by dissolving Na (2 g.) in abs. EtOH (50 c.c.). A faint yellow colour formed at once, and the mixture had a distinct smell of Ph·CO_2Et. After 5 mins., the mixture was poured into 750 c.c. of H_2O, which produced a white emulsion but no trace of solid. The emulsion was rapidly extracted with Et_2O, and the residual aq. layer was found to contain free PhOH. The ethereal extract yielded on distillation 7 g. of a colourless liquid, b. p. 195—200°, consisting of Ph·CO_2Et contaminated with PhOH, and no residue of higher b. p. remained. The distillate, after being washed with NaOH, yielded 4 g. of pure Ph·CO_2Et, b. p. 209—210°, which was hydrolysed by aq. alkali to EtOH (identified by the CHI_3 reaction) and Ph·CO_2H, m. p. 121°.

Ph·CO_2Ph in 95% EtOH was not hydrolysed either by C_5H_5N or by $Mg(OH)_2$. With $Ca(OH)_2$ and $Ba(OH)_2$ in suspension, PhOH was slowly liberated, but concordant reaction-velocity measurements were not obtained.

Ph·CO_2Et in 95% EtOH was hydrolysed much more rapidly than Ph·CO_2Ph : K (bimolecular) = 0·0775 l./g.-mol./min. Addition of free PhOH decreased the velocity of hydrolysis, but even a considerable excess did not inhibit it entirely.

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