[CONTRIBUTION FROM UNIVERSITY COLLEGE, LONDON, ENGLAND]

Hydrolysis of Secondary and Tertiary Alkyl Halides

BY EDWARD D. HUGHES

Comment has recently been passed[1,2] on the relative proportions in which alcohols and olefins are formed by the hydrolysis of secondary and tertiary alkyl halides. We wish to direct attention to some considerations relating to the same topic.

One of the reactions to be considered involves substitution by a nucleophilic reagent. Hughes, Ingold and Patel[3] recognized two mechanisms of this type of substitution, namely, a bimolecular mechanism (S_N2) involving attack by hydroxide ions, and a unimolecular mechanism (S_N1) kinetically dependent on the ionization of the alkyl halide.

$$\mathrm{Alk.\,Hal + OH^- \longrightarrow Alk.\,OH + Hal^-}\ (S_N2)$$

$$\left.\begin{array}{l}\mathrm{Alk.\,Hal \longrightarrow Alk^+ + Hal^-}\text{, followed by}\\ \mathrm{Alk^+ + OH^- \longrightarrow Alk.\,OH}\ \text{(instantaneously)}\end{array}\right\}(S_N1)$$

It was anticipated that there would be a change-over from the bimolecular to the unimolecular mechanism toward the right-hand end of the series: CH_3, CH_2Me, $CHMe_2$, CMe_3. This was later realized.[4] The writer has now located the change-over (in dilute aqueous alcoholic solution)[5] between the ethyl and isopropyl groups.

The other reaction to be discussed involves the elimination of a β-hydrogen atom. Hughes, Ingold and Patel showed that this reaction would normally possess a bimolecular mechanism which for alkyl halides may be formulated as follows

$$\mathrm{OH^- + H \vdots\!-\!\!-CR_2CR_2 \vdots\!-\!\!-Hal \longrightarrow H_2O + CR_2{=}CR_2 + Hal^-}\quad (E2)$$

The dotted lines indicate the direction of the electron transfers. If the halogen atom is first ionized, however, another mechanism intervenes. No detailed study of this elimination mechanism has yet been published from these Laboratories, but it may be stated that it leads to a unimolecular reaction of the type

$$\left.\begin{array}{l}\mathrm{H{-}CR_2CR_2 \vdots\!-\!\!-Hal \longrightarrow H{-}CR_2C^+R_2 + Hal^-}\text{, followed by}\\ \mathrm{H \vdots\!-\!\!-CR_2C^+R_2 \longrightarrow H^+ + CR_2{=}CR_2}\ \text{(instantaneously)}\end{array}\right\}(E1)$$

The intermediate cation may, of course, effect a substitution in accordance with mechanism S_N1. In the simplest examples of hydrolysis this is the fate of most of the cations, but increasing alkylation will favor the rearrangement with proton ejection.

French, McShan and Johler[1] examined the hydrolysis of *s*-butyl bromide in a variety of aqueous alkaline solutions, and found a regular variation of the percentage of olefin with the concentration of the reagent.[6] Quantitative interpretation of the data is rendered impossible by the presence of two liquid phases, but the figures are consistent with the operation of the combination of mechanisms S_N1 and E2.

The writer has examined the hydrolysis of isopropyl and *s*-butyl bromides in homogeneous solution in 60% alcohol. In dilute alkaline solutions, when the reaction is almost exclusively hydrolytic, decomposition follows a unimolecular law, and the velocity is identical with that obtained in acid solution. In more strongly alkaline solutions, when the olefin formation becomes important, the velocity is partly dependent on the hydroxide-ion concentration, and a comparison with the data relating to acid media supports the assumption that the elimination process is bimolecular.

French, McShan and Johler have also shown that the hydrolysis of *t*-butyl bromide proceeds much more rapidly than that of the secondary compound, and that the production of olefin, under the conditions employed, is very small. The writer has confirmed these statements, and has shown that the hydrolysis of *t*-butyl chloride in homogeneous solution is unimolecular.[7] In *t*-butyl halides ionization has been so far increased that reaction S_N1, which involves ionization, predominates over all reactions such as E2, which do not.

With further alkylation, as in *t*-amyl chloride, reaction E1 attains importance. Woodburn and Whitmore[2] have shown that the hydrolysis of *t*-amyl chloride proceeds with almost

---

[1] French, McShan and Johler, THIS JOURNAL, **56**, 1346 (1934).

[2] Woodburn and Whitmore, *ibid.*, **56**, 1394 (1934).

[3] Hughes, Ingold and Patel, *J. Chem. Soc.*, 526 (1933).

[4] *Cf.* Hughes and Ingold, *Nature*, **132**, 933 (1933).

[5] The position of the point of mechanistic change must depend, *inter alia*, on the medium and the concentration, for non-ionizing media and high concentrations will favor mechanism S_N2.

[6] Silver oxide was exceptional, but this may be omitted from consideration as it is well known that the reactions between alkyl halides and silver compounds are heterogeneously catalyzed by precipitating silver halide (*cf.* Baker, *J. Chem. Soc.*, 987 (1934)).

[7] Hughes, *J. Chem. Soc.*, 255 (1935).

the same velocity whether the reagent is dilute sodium carbonate, water or dilute sulfuric acid, although both alcohol and olefin are formed in large amount. This surely indicates that the total decomposition is unimolecular, and that the speed is independent of reagent anions. The mechanisms at work here are S_N1 and E1. The unimolecular character of the reaction in homogeneous solution has been confirmed by the writer.

Experimental

The bimolecular character of the alkaline hydrolysis of methyl and ethyl halides has been previously established.[8] The point of mechanistic change in the alkyl series is illustrated by the figures in the subjoined table, selected from dynamical experiments which will be published in detail later. They refer to experiments in which the concentration of the alkyl halide does not appreciably change during the reaction. The velocity in dilute alkaline solution is then constant and is identical with that in acid solution. The first five lines are self-explanatory. The figures in lines 6 and 7 show the average changes in titer per hour; they relate to 10 cc. of the reaction mixtures and are expressed in cc. of 0.005 *N* acid and alkali, respectively.

Halide	*i*-PrBr	*s*-BuBr	*t*-AmCl
Moles halide per mole KOH	70	63	38
Medium, % EtOH	60	60	90
Temperature, °C.	45	45	25
Range of readings alkaline *N* ⟶ acid *N*	0.0030–.0040	0.0029–.0035	0.0043–.0030
Velocity in alk. soln.	2.60	2.52	3.00
Velocity in acid soln.	2.58	2.44	3.12

The author wishes to express his indebtedness to Professor C. K. Ingold, F.R.S., for his invaluable help.

Summary

The dynamics of the hydrolysis of certain secondary and tertiary alkyl halides have been investigated and the mechanism of the reaction is discussed.

LONDON, ENGLAND RECEIVED NOVEMBER 30, 1934

---

[8] Bruyn and Steger, *Rec. trav. chim.*, **18**, 311 (1899); Grant and Hinshelwood, *J. Chem. Soc.*, 258 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride. IX. The Alkylation of Phenol with Alcohols[1]

BY F. J. SOWA, G. F. HENNION AND J. A. NIEUWLAND

In a recent publication[2] it was shown by conductivity measurements that the system phenol-boron fluoride possessed acid properties considerably stronger than phenol. Evidence was also presented for compound formation from one mole of boron fluoride and two moles of phenol. Boron fluoride has been used as an agent in the formation of alkyl phenyl ethers from olefins and phenols,[2] from ethers and phenols[3] and as an esterifying agent.[4] These properties should make this agent particularly adaptable in the reaction between alcohols and phenols.

Altogether neither methyl nor ethyl alcohol reacted with phenol in the presence of boron fluoride by heating at atmospheric pressure, they did react quite readily when heated in a sealed tube. The products were mainly anisole and phenetole, respectively. Small quantities of substituted phenols and alkyl phenyl ethers were also formed.

Isolated cases of reactions between alcohols and phenols using various catalysts have been reported.[5,6,7,8] Some of these experimenters claim to have obtained *p*-isobutylphenol from the condensation of isobutyl alcohol with phenol. It has since been demonstrated[9] that isobutyl phenyl ether rearranges to tertiary butylphenol. In none of these investigations was there any attempt made to prove the mechanism of condensation between the alcohol and phenol.

Attempts are reported in this paper to determine, first, if the reaction between alcohols and phenols involves the removal of the elements of water, as in most esterification reactions, equation I

$$C_6H_5OH + C_nH_{2n+1}OH \longrightarrow C_6H_5OC_nH_{2n+1} + H_2O \quad (I)$$

---

[1] Paper VIII, Dorris, Sowa and Nieuwland, THIS JOURNAL, **56**, 2689 (1934).

[2] Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3402 (1933).

[3] Hennion, Hinton and Nieuwland, *ibid.*, **55**, 2857 (1933).

[4] Hinton and Nieuwland, *ibid.*, **54**, 2017 (1932).

[5] Liebmann, *Ber.*, **15**, 150 (1882).

[6] Senkowski, *ibid.*, **24**, 2974 (1891).

[7] Mazzara, *J. Chem. Soc.*, **62**, 838 (1882).

[8] Mazzara, *Gazz. chim. ital.*, **12**, 505 (1882).

[9] Smith, THIS JOURNAL, **55**, 3718 (1933).