A Retentive S_N1 Hydrolysis in Aqueous Acrylonitrile and the Polymerization of Acrylonitrile Initiated by the S_N1 Hydrolysis Intermediate

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(Received July 13, 1966)

As a result of continuation of our search[1] for the solvent systems in which the S_N1 solvolysis of simple alkyl derivatives involves retention of configuration, we found the water-acrylonitrile system being added to the examples of such retentive solvents. We also found that the acrylonitrile, used as the solvolytic solvent, concomitantly polymerizes, most probably being initiated by the S_N1 ion-pair intermediate.

The hydrolysis of α-phenylethyl chloride (2.61 g., α_D[2] $+31.00°$) was conducted in 97 wt.% aqueous acrylonitrile (90 cc.) in the presence of added triethylamine (0.201 M) at 90—91°C for 50 hr. Polyacrylonitrile[3] (16.1 wt.% of the starting nitrile), resulted in during the course of the reaction, was separated after treatment of the reaction mixture with ether and water; the ethereal solution was worked up in the usual way and then distilled in vacuo. The fraction A (0.842 g., b. p. 42—58°C/2.5 mmHg; the mixture of styrene, α-phenylethyl alcohol and unchanged α-phenylethyl chloride) and the succeeding fraction B (0.157 g., bath temp. 30—40°C/0.15 mmHg; almost pure α-phenylethyl alcohol) were respectively acetylated with acetic anhydride in pyridine to give α-phenylethyl acetates[4] with α_D $+2.01°$ and α_D $+2.02°$. The content of the unchanged chloride (0.440 g.) in the fraction A was estimated from the chloride ion analysis of the water washings of the acetylation products; styrene (0.113 g.) was recovered from the acetylation products as a component eluted by *n*-hexane in the elution chromatography over basic alumina; α-phenylethyl acetate was eluted by benzene. The rotation of the unchanged chloride (α_D $+0.264°$) was calculated on the basis of the rotations of the fraction A and the α-phenylethyl alcohol,[5] contained in the fraction A. From the titrimetric chloride ion analysis of the washings of the reaction mixture the completion of the hydrolysis was estimated to be 58.1%.

These results indicate that 6.31%[6] of the optical activity of the starting chloride was retained in the acetate derived from α-phenylethyl alcohol, and that the acetate possesses the same configuration as that of the chloride. In other words, the hydrolysis to 58.1% completion gave α-phenylethyl alcohol with 6.31% of retention of the configuration, since the acetylation process gives no change to the optical purity and the configuration of the alcohol.[7] Although the titrimetric first-order rate constant for this hydrolysis showed appreciable decreasing tendency, the S_N1-character of this hybrolysis seems to be undoubtful on the basis of the predominant racemization of the product (93.7%) and of the unchanged chloride (99.1%). The specific solvation of the acrylonitrile molecule to the S_N1 ion-pair intermediate would be responsible for this unusual steric course of the hydrolysis.

The rate of the concomitant polymerization of acrylonitrile, estimated from wt.% yield of polyacrylonitrile at intervals, was as high as about eight fold of the rate in the absence of α-phenylethyl chloride; this rate increased with the increasing initial concentration of α-phenylethyl chloride and decreased with the decreasing water content in aqueous acrylonitriles. The added triethylammonium chloride and styrene, in the absence of the chloride, were found to have no appreciable accelerating action on this polymerization. From these findings, we conclude that this polymerization is most probably initiated by the S_N1 ion-pair intermediate produced from α-phenylethyl chloride and that the specific solvation above mentioned may also be responsible for this initiation.

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[1] a) K. Okamoto, K. Takeuchi and H. Shingu, This Bulletin, **35**, 521 (1962); b) K. Okamoto, H. Yamada, I. Nitta and H. Shingu, ibid., **39**, 299 (1966); c) K. Okamoto, M. Hayashi and H. Shingu, ibid., **39**, 408 (1966).

[2] α_D signifies the rotation, neat, 1 dm., at 20—22°C.

[3] The almost identical infrared spectrum with the authentic polyacrylonitrile. The inherent viscosity, 0.525 (DMF, 0.5%).

[4] n_D^{25} 1.4931 and 1.4915, respectively. The acetate, the alcohol and styrene were identified by their infrared spectra.

[5] The rotation of this alcohol, α_D $+0.690°$, estimated from that observed for the corresponding acetate. The maximum rotation of R-(+)-α-phenylethyl acetate, α_D 129° (lit. α_D^{28} 117°, H. R. Snyder and J. H. Brewster, *J. Am. Chem. Soc.*, **71**, 291, 4165 (1949)), determined from the results of the preliminary acetylation of the optically active α-phenyl ethyl alcohol. The maximum rotation of R-(+)-α-phenylethyl alcohol, α_D 44.2° (cf. Ref. 1b or 1c).

[6] Calculated from the mean value of the rotations of the acetates obtained from the fraction A and B. The maximum rotation of R-(+)-α-phenylethyl chloride was taken as 125° (cf. Ref. 1b or 1c).

[7] The second run (71% completion) afforded α-phenylethyl alcohol with 4.7% of retention of the configuration.