A Novel Reaction Pathway in Alkaline Hydrolysis of α-Nitroisobutyramide

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WE report preliminary results on the kinetics of alkaline hydrolysis of α-nitroisobutyramide.

Kinetic data for the alkaline hydrolysis of α-nitroisobutyramide at 25°

$[OH^-]$	$[k(NH_3) + k(CNO)]$	NH_3/CNO^-	$k(NH_3)$	$k(CNO)$
0·05N	0·020 min.$^{-1}$	0·34	0·005 min.$^{-1}$	0·015 min.$^{-1}$
0·10	0·038	0·36	0·010	0·028
0·20	0·069	0·34	0·018	0·051

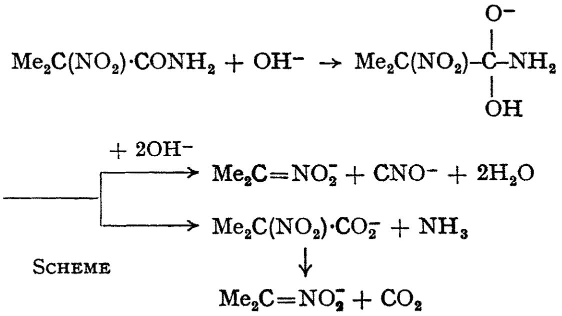
$k(NH_3)$ and $k(CNO)$ are the pseudo-first-order rate constants for the formation of ammonia and cyanate, respectively.

Alkaline hydrolysis of amides generally goes through C–N bond fission and gives a carboxylate ion and an amine. The only exception to this route is the alkaline hydrolysis of trichloroacetanilide,[1] in which a distinct odour of phenyl isocyanate was detected from the reaction mixture.

The rate of decrease in the concentration of α-nitroisobutyramide followed first-order kinetics at constant hydroxyl ion concentration, but the pH–rate profile was different from that of ethyl α-nitroisobutyrate, which undergoes the usual ester hydrolysis followed by decarboxylation.[2] Analysis of the reaction mixture showed that the products were 2-nitropropane aci-ion, cyanate ion, and ammonia, indicating that the process comprises not only C–N but also C–C bond fission. The ratio of cyanate to ammonia in the reaction mixture, determined by Shaw and Bordeaux's method,[3] was almost independent of the reaction time and alkali concentration, but was strongly dependent on temperature. The mean values of $[NH_3]/[CNO^-]$ were 0·62, 0·45, and 0·36 at 15, 20, and 25°, respectively. The rate of increase in the total concentration of cyanate and ammonia followed first-order kinetics at constant hydroxyl ion concentration. The reaction, therefore, is considered to be a parallel first-order reaction.

Activation energies and entropies calculated from $[k(NH_3) + k(CNO)]$, $k(NH_3)$, and $k(CNO)$ were 19·5 kcal./mole and $-9·1$ e.u., 14·3 kcal./mole and $-29·2$ e.u., and 21·5 kcal./mole and $-3·0$ e.u.

The reaction process is assumed to be as in the Scheme, but the detailed mechanism is not yet clear.



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