# The Decomposition of Nitrourea in Aqueous Solution

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The pH profile of the rate of decomposition of nitrourea in the pH range 1—11 is consistent with unimolecular decomposition of the conjugate base of nitrourea.

RECENTLY the decomposition of nitrourea in acidic solutions (pH 3 to $H_0 - 4\cdot5$) has been discussed.[1] The results confirm our own findings. We now report on the decomposition in the pH range 1—11. The products of the overall reaction are cyanic acid and nitrous oxide [1,2] [equation (1)]. Nitramide is a probable intermediate.

$$H_2N\cdot CONH\cdot NO_2 \longrightarrow HNCO + N_2O + H_2O \qquad (1)$$

A polarographic study [3] has shown that nitrourea is stable at ambient temperature in the pH range 1—3 but that decomposition is promoted by increasing temperature and increasing pH. No simple correlation of rate with increasing pH was established and it was concluded that the order of reaction changed with increasing pH. Our data (Table) show that the rate of

Decomposition of nitrourea in aqueous solution at 50 °C

Effect of pH

| pH | 0·96 | 1·67 | 1·88 | 2·39 | 2·80 | 3·50 |
|---|---|---|---|---|---|---|
| $10^5 k_{obs}/s^{-1}$ | 0·12 | 0·60 | 0·97 | 2·80 | 4·91 | 13·5 |
| $10^5 k_{corr}/s^{-1}$ | 39·3 | 38·5 | 38·7 | 36·5 | 27·8 | 26·0 |
| pH | 4·05 | 4·42 | 5·69 | 8·20 | 10·30 | |
| $10^5 k_{obs}/s^{-1}$ | 20·1 | 22·5 | 24·1 | 24·7 | 23·9 | |
| $10^5 k_{corr}/s^{-1}$ | 25·4 | 25·0 | 24·2 | 24·7 | 23·9 | |

Isotope effect

$[Na_2CO_3] = 0\cdot1M$

| $10^4 k_{obs}/s^{-1}$ ($H_2O$) | 2·32 |
|---|---|
| $10^4 k_{obs}/s^{-1}$ ($D_2O$) | 1·97 |

Effect of temperature

pH = 10

| $t/°C$ | 40·2 | 49·9 | 60·1 |
|---|---|---|---|
| $10^4 k_{obs}/s^{-1}$ | 0·616 | 2·39 | 8·63 |

decomposition reaches a maximum value at ca. pH 5·5 and that further increase in pH does not affect the rate. Nitrourea is a weak acid; $pK_a = 3\cdot87 \pm 0\cdot04$ in water, and $3\cdot47 \pm 0\cdot04$ in 1M-sodium chloride solution. Decomposition would appear to be predominantly via the conjugate base of nitrourea. The observed first-order rate constant ($k_{obs}$) when divided by the fraction of nitrourea present as the conjugate base gives a value ($k_{corr}$) which shows little variation with pH when compared with the variation in $k_{obs}$. The small increase in $k_{corr}$ with decreasing pH could reflect a small contribution to the overall rate from decomposition of un-ionised nitrourea. The onset of the acid-catalysed

reaction could also make a contribution. No general base catalysis was detected in acetic acid–sodium acetate buffer (pH 3·8) nor in sodium hydrogen carbonate–sodium hydroxide buffer (pH 8·0). The small solvent isotope effect ($k_{H_2O}/k_{D_2O} = 1\cdot18$) is consistent with the absence of either general base or specific base catalysis.[4] These observations may be rationalised by the reaction scheme shown in equations (2) and (3) ($k_{-1} \gg k_1 \gg k_2$).

$$NH_2\cdot CONH\cdot NO_2 \xrightarrow{K_a} NH_2\cdot CO\bar{N}\cdot NO_2 + H^+ \qquad (2)$$



$$(3)$$
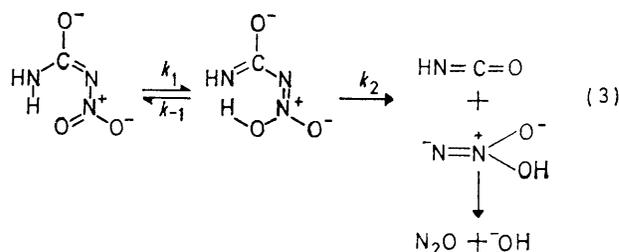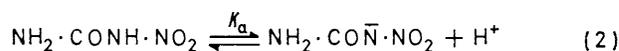
A thermally allowed 1,5-sigmatropic shift in the conjugate base of nitrourea is followed by a rate-determining unimolecular elimination to yield cyanic acid and a tautomeric form of the conjugate base of nitramide. The nitramide would then decompose to nitrous oxide in the buffer solutions used in our experiments.[5] Nitrourea will undergo complete hydrogen exchange in deuterium oxide so that the absence of any significant change in rate in the deuteriated solvent, at a pH where all the nitrourea is ionised, is evidence for the hydrogen shift occurring before the elimination step. For a rate-determining sigmatropic shift, or synchronous shift and elimination, a sizeable isotope effect would be expected.[6] Unimolecular elimination of the conjugate base of an acyl derivative has previously been observed for acylation reactions of carbamates [7] and esters.[8] However, for these reactions the anionic centre of the conjugate base lies in the acyl portion of the molecule.

The Arrhenius energy of activation ($E_a = 27\cdot5$ kcal mol$^{-1}$) and entropy of activation ($\Delta S^\ddagger = 7\cdot7$ cal mol$^{-1}$ K$^{-1}$) for the decomposition of nitrourea at pH 10 are similar to the values calculated for decomposition in 7·05M-sulphuric acid [1] ($E_a = 27\cdot5$ kcal mol$^{-1}$, $\Delta S^\ddagger = 0\cdot8$

[1] F. Dewhurst and A. H. Lamberton, *J. Chem. Soc. (B)*, 1971, 788.

[2] T. L. Davis and K. C. Blanchard, *J. Amer. Chem. Soc.*, 1929, **51**, 1790.

[3] K. Namba and K. Suzuki, *J. Indus. Explosives Soc. Japan*, 1954, **15**, 171; K. Namba and K. Suzuki, *Bull. Chem. Soc. Japan*, 1955, **28**, 620.

[4] T. C. Bruice and S. Benkovic, ' Bioorganic Mechanisms,' vol. 2, Benjamin, New York, 1966, p. 35.

[5] J. N. Brønsted and K. Pedersen, *Z. phys. Chem.*, 1924, **108**, 185.

[6] H. Kloosterziel and A. P. Ter Borg, *Rec. Trav. chim.*, 1965, **84**, 1305; W. R. Roth and J. Konig, *Annalen*, 1966, **699**, 24.

[7] K. D. Kopple, *J. Amer. Chem. Soc.*, 1957, **79**, 6442; M. L. Bender and R. B. Homer, *J. Org. Chem.*, 1965, **30**, 3975; J. F. Bunnett and M. B. Naff, *J. Amer. Chem. Soc.*, 1966, **88**, 4001.

[8] B. Holmquist and T. C. Bruice, *J. Amer. Chem. Soc.*, 1969, **91**. 2993, 3003.

cal mol$^{-1}$ K$^{-1}$). This suggests that the rate-determining step is also unimolecular for the acid-catalysed reaction.

EXPERIMENTAL

Nitrourea was prepared by the method of Davis and Blanchard,[2] and was twice recrystallised from methanol. The acid dissociation constant was obtained from the pH at half-neutralisation with a Beckman Research pH meter. The recorded values are the mean for the nitrourea concentration range 0·01—0·1M at 23 °C. Un-ionised nitrourea has u.v. absorption $\lambda_{max.}$ 226 nm ($\varepsilon$ 9060) (in 0·1M-hydrochloric acid). The conjugate base has absorption at 259 nm ($\varepsilon$ 9910) (in 0·1M-sodium hydroxide). There is an isosbestic point at 239 nm. The reported uncertainty [1] in the spectra for nitrourea in pure water is due entirely to variability of the pH of such solutions and not to significant decomposition of the nitrourea. Spectra were recorded on a Unicam SP 800 spectrometer.

*Kinetic Arrangements.*—The decomposition of nitrourea shows an appreciable salt effect (largely reflected in the effect on the p$K_a$) and all reactions were performed in 1M-sodium chloride solution. Buffer solutions in 1M-sodium chloride were prepared with sodium hydrogen carbonate–sodium hydroxide, sodium carbonate, sodium hydroxide–sodium dihydrogen phosphate, acetic acid–sodium acetate, chloroacetic acid–sodium chloroacetate, and hydrochloric acid. Reaction solutions were prepared in volumetric flasks and equilibrated in a thermostatted bath. Solid nitrourea, to give *ca.* 5 × 10$^{-3}$M solution, was added to initiate the reaction. Samples were diluted 50-fold with acetate buffer (pH 4·5) and the reaction was followed by observing the decrease in absorption at 260 nm by use of a Zeiss PHQII spectrophotometer. No deviation from first-order kinetics was observed. Rate constants were reproducible to ±3%.