Base-catalysed Decomposition of Nitramide: Brønsted Relations and a Second Reaction Pathway

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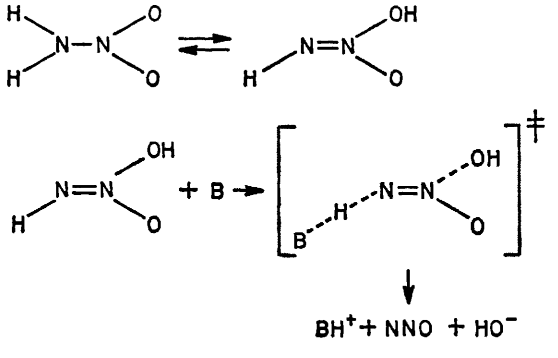
Summary A new spectroscopic technique for measuring the rate of nitramide decomposition revealed a second pathway for this reaction and allowed extension of the Brønsted relation for the first (traditional) pathway into more basic regions where the onset of relatively sharp curvature was detected; these results suggest a mechanism for the first reaction pathway in which proton transfer is not concerted with heavy atom reorganization.

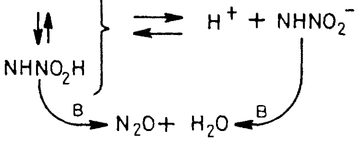
THE base-catalysed decomposition of nitramide, equation (1), is a much studied reaction which has figured prominently in investigations of acid–base catalysis over the past half

$$NH_2NO_2 \xrightarrow{B} N_2O + H_2O \qquad (1)$$

century.[1] In all this previous work, the reaction was followed by monitoring N_2O gas evolution, but we have found that reaction rates can be measured conveniently by standard spectroscopic techniques which avoid certain complications inherent in the previously used method.[2] Using this new technique, we have found a second base-catalysed reaction pathway. We have also constructed Brønsted relations whose behaviour in the more strongly basic regions, taken together with isotope effects,[3] suggests new mechanistic detail for the original reaction pathway.


(2)

The generally accepted mechanism for nitramide decomposition involves isomerization of the substrate into its *aci*-nitro form followed by elimination of H^+ and HO^- from this species, equation (2). This mechanism requires the rate of this reaction to be independent of hydroxide ion concentration in solutions where nitramide, which is an acid of $pK_a = 6{\cdot}55$, is essentially completely ionized. We have found, however, that observed first-order rate constants based on nitramide disappearance increase in direct proportion to $[HO^-]$ in dilute NaOH solutions. In strongly basic buffers, moreover, the system shows simple general base catalysis instead of the specific hydrogen ion–general base catalysis predicted by equation (2). In buffer solutions of less strong bases, both kinds of catalysis may be found, and in weakly basic buffers only the form of catalysis required by equation (2), and traditionally observed, may be seen.


(3)

These results suggest two parallel decomposition pathways equation (3): (i) the traditional general-base catalysed reaction of *aci*-nitramide and (ii) general-base catalysed decomposition of the nitramide anion. Additional support for this formulation of the second pathway comes from the effect of charged catalysts upon its rate: positively charged bases are more effective than their basic strengths would suggest, as expected for an anionic substrate, and negatively charged bases show the opposite behaviour. The existence of a second reaction pathway similar to this, though not proceeding by general base catalysis, was postulated before and an estimate of its hydroxide ion catalytic coefficient was made;[3] that estimate, however, is more than an order of magnitude greater than the present directly measured value.

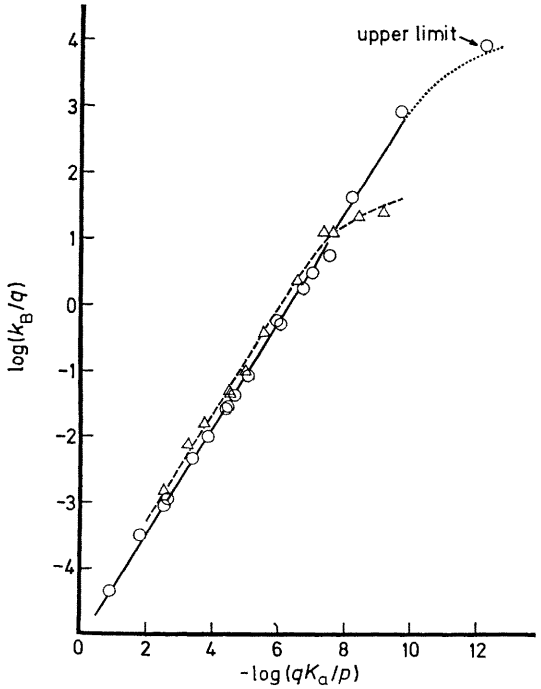


FIGURE 1. Brønsted plot for the decomposition of nitramide [equation (1)] *via* the first reaction pathway catalysed by primary amine (– △ –) and negatively charged oxygen (– ○ –) bases.

Similar, albeit somewhat smaller, systematic differences attributable to catalyst charge type appear also in reaction by the first (traditional) decomposition pathway. Figure 1 shows that neutral primary amine catalysts (mostly derivatives of aniline and of ethylamine) define a Brønsted relation parallel to and above one based upon negatively charged oxygen bases (mostly carboxylate and phosphonate ions; the highest point refers to 2,2,2-trifluoroethoxide ion†). Both these Brønsted relations have long linear portions which give way, at higher catalyst strength, to curved regions. This curvature occurs earlier, *i.e.* with weaker catalysts, in the case of nitrogen bases than in the case of oxygen bases.

This behaviour may be understood in terms of a mechanism in which encounter of the catalyst and substrate [equation (4)] is followed by proton transfer [equation (5)], which is then followed by heavy atom reorganization [equation (6)], with the rate of proton transfer varying

$$\mathrm{B + HNNO_2H \rightleftharpoons B{\cdot}HNNO_2H} \qquad (4)$$

$$\mathrm{B{\cdot}HNNO_2H \rightleftharpoons \overset{+}{B}H{\cdot}\overset{-}{N}NO_2H} \qquad (5)$$

$$\mathrm{\overset{+}{B}H{\cdot}\overset{-}{N}NO_2H \rightarrow BH^+ + N_2O + OH^-} \qquad (6)$$

with free energy of reaction in a Hammond postulate[4] or Marcus theory[5] manner. When the catalyst is a weak base (Figure 2, left side), proton transfer is a strongly uphill process; its reverse [equation (5), back reaction] is therefore very fast and heavy atom reorganization, which takes place before the proton transfer products can separate (Figure 2, broken lines), is rate-determining. This produces a linear Brønsted plot whose slope is large but not unity (β 0·8) inasmuch as the products of proton transfer are held together by a good hydrogen bond: hydrogen bond formation is known to give a correlation of the Brønsted type with slope *ca.* 0·2.[6] As the catalyst becomes stronger (Figure 2, right side) and the barrier for proton transfer in the forward direction decreases, that for its reverse rises (Hammond postulate) and proton transfer begins to be at least partly rate-determining. This introduces curvature into the Brønsted plot.

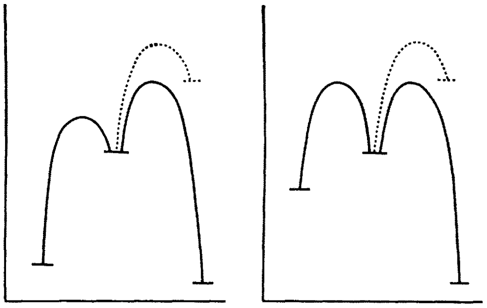


FIGURE 2. Schematic representation of nitramide decomposition *via* the first reaction pathway catalysed by weak (left side) and strong (right side) bases. The solid line denotes proton transfer [equation (5)] and heavy atom reorganization [equation (6)], and the broken line shows separation of the proton transfer products.

We are grateful to Professor J. P. Guthrie for valuable discussion and to the Natural Sciences and Engineering Research Council of Canada for financial support.

(*Received*, 15*th October* 1979; *Com.* 1097.)

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† Reaction in the presence of this catalyst occurred only by the second pathway, but, from the observed rates, an upper limit for decomposition by the first pathway could be estimated.

[1] For a review, see R. P. Bell, 'The Proton in Chemistry,' 2nd edn., Cornell Univ. Press, Ithaca, New York, 1973, p. 160.
[2] See, *e.g.* L. K. J. Tong and A. R. Olsen, *J. Am. Chem. Soc.*, 1941, **63**, 3406.
[3] A. J. Kresge and Y. C. Tang, following paper.
[4] G. S. Hammond, *J. Am. Chem. Soc.*, 1955, **77**, 334.
[5] R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891; A. J. Kresge, *Chem. Soc. Rev.*, 1973, **4**, 475.
[6] R. W. Taft, D. Gurka, L. Joris, P. Von Schleyer, and J. W. Rakshys, *J. Am. Chem. Soc.*, 1961, **91**, 4801.