Base-catalysed Decomposition of Nitramide: Kinetic Isotope Effects

By A. J. KRESGE,* Y. C. TANG, and A. AWWAL

(Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario, M1C 1A4 Canada)

and D. P. ONWOOD

(Department of Chemistry, Indiana University–Purdue University at Fort Wayne, Fort Wayne, Indiana 46805)

Summary Kinetic hydrogen isotope effects on the decomposition of nitramide catalysed by a series of phosphonate anions and the 2,4,6-trichlorophenoxide ion were found to be small (k_H/k_D ca. 2—3) with no sign of a maximum value of pK_a (catalyst conjugate acid) ca. 6, in disagreement with a previously reported claim but consistent with the expected pK_a of the reactive form of the substrate.

KINETIC isotope effects on proton transfer between normal, *i.e.* oxygen and nitrogen, acids and bases are rare and,

until recently, were believed to be non-existent.[1] The report[2] of effects as great as $k_H/k_D = 10$ on the decomposition of nitramide catalysed by a series of aryloxide ions, a process which involves proton transfer from nitrogen to oxygen,[3] was therefore quite remarkable.

These isotope effects were determined by comparing rates of reaction in H_2O and D_2O, and they consequently contained solvent and secondary isotope effect contributions. However, the latter are unlikely to be greater than $k_H/k_D = 2$—3, and rate ratios as large as $k_H/k_D = 10$ must have appreciable primary isotope effect components. These

isotope effects on nitramide decomposition, moreover, passed through a maximum value as the base strength of the catalyst increased, as required of primary effects by isotope effect theory,[4] and the maximum was quite narrow, as expected for an intrinsically fast reaction.[4a,5] Such maxima appear when the pK_a difference between proton donor and protonated proton acceptor (ΔpK_a) is zero, and it was therefore considered significant that this maximum occurred with basic catalysts whose conjugate acids had pK_a ca. 6, inasmuch as nitramide is a weak acid with $pK_a = 6.55$.

This pK_a, however, refers to the ionization of nitramide in its nitro form, equation (1), whereas the proton removed in the slow stage of the decomposition reaction is that

$$H_2NNO_2 \rightleftharpoons H^+ + HNNO_2^- \qquad (1)$$

remaining on nitrogen after nitramide has tautomerized to its aci-nitro isomer, equation (2). It is likely that this

$$H_2NNO_2 \rightleftharpoons HNNO_2H \xrightarrow{B} N_2O + H_2O \qquad (2)$$
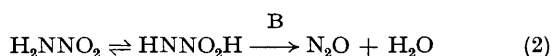
proton is considerably less acidic than is implied by $pK_a = 6$. Moreover, proton transfers between normal acids and bases which give isotope effect maxima also show biphasic Brønsted plots with breaks occurring at the positions of the isotope effect maxima, [5b] but the Brønsted plot for nitramide decomposition is perfectly linear in the region about pK_a (catalyst conjugate acid) $= 6$. These inconsistencies prompted us to re-examine this system; we have been unable to corroborate the original findings.

We measured rates of nitramide decomposition spectrally by monitoring the absorbance decrease at 225 nm. This technique allows substrate concentrations to be much lower than those required by the gas (N_2O) evolution method used in previous work on this reaction, and that eliminates certain complications[6] and greatly simplifies the kinetic analysis. Our new method, however, is not readily applicable to reactions catalysed by aryloxide ions, such as those for which the large isotope effects were claimed, for these substances themselves absorb strongly at $\lambda = 225$ nm, and we therefore did the bulk of our work with a series of phosphonate ions, RPO_3^{2-}, as catalysts. These span the same pK_a range as the aryloxide ions, but, as the Figure shows, they produce isotope effects which are much smaller than $k_H/k_D = 10$ and give no evidence of a maximum at pK_a (catalyst conjugate acid) $= 6$. Using a differential spectroscopic method, we were also able to obtain less accurate data for catalysis by 2,4,6-trichlorophenoxide ion which give $k_H/k_D = 2.5 \pm 1.0$, in agreement with the phosphonate ion data but in disagreement with the claim of $k_H/k_D = 9.0$.[2]
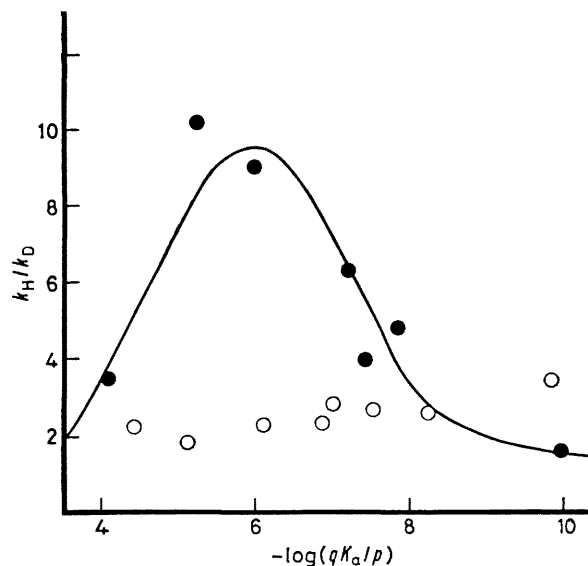

FIGURE. Kinetic isotope effects on nitramide decomposition [equation (2)] via the first reaction pathway catalysed by oxygen bases obtained in this study ($\bigcirc$) (B $= RPO_3^{2-}$) compared with those reported in ref. 2 ($\bullet$) (B $= ArO^-$).

Although these new isotope effects show no sign of a maximum at pK_a (catalyst conjugate acid) $= 6$, they do tend to increase with increasing catalyst strength. This suggests that a maximum may exist at high catalyst strength, which is where it would be expected to come on the basis of the weak acidity of the proton being transferred. This region, unfortunately, is experimentally inaccessible since decomposition by a new reaction pathway takes over above pK_a (catalyst conjugate acid) ca. 10.[3a]

It is significant that the isotope effects on nitramide decomposition measured here for weakly basic catalysts level off to a lower limit of $k_H/k_D = ca.$ 2 (Figure), inasmuch as the mechanism suggested for this reaction in this region has a transition state in which proton transfer has already occurred but the protonated catalyst is still held to an anionic form of the substrate by a strong hydrogen bond.[3a] Hydrogen-bonded hydrogens are known to have reduced zero-point energy, and the reduction is in some cases quite dramatically large;[7] they can therefore give rise to sizeable secondary isotope effects, and a limiting value of k_H/k_D considerably in excess of unity should in fact be expected in the present case.

[1] See e.g. G. C. Swain, D. A. Kuhn, and R. L. Schowen, J. Am. Chem. Soc., 1965, 87, 1553.
[2] J. R. Jones and T. G. Rumney, J. Chem. Soc., Chem. Commun., 1975, 995.
[3] (a) A. J. Kresge and Y. C. Tang, preceding paper; (b) for a review of previous mechanistic evidence, see R. P. Bell, 'The Proton in Chemistry,' 2nd edn., Cornell Univ. Press, Ithaca, New York, 1973, p. 160.
[4] (a) A. J. Kresge in 'Isotope Effects on Enzyme-Catalyzed Reactions,' eds. W. W. Cleland, M. H. O'Leary, and D. B. Northrup, University Park Press, Baltimore, Md., 1977, ch. 2; (b) R. A. More O'Ferrall in 'Proton Transfer Reactions,' eds. E. F. Caldin and V. Gold, Chapman and Hall, London, 1975, ch. 8; R. P. Bell, Chem. Soc. Rev., 1974, 3, 513.
[5] (a) A. J. Kresge, D. S. Sagatys, and H. L. Chen, J. Am. Chem. Soc., 1977, 99, 7228; (b) N. A. Bergman, Y. Chiang, and A. J. Kresge, ibid., 1978, 100, 5954; M. M. Cox and W. P. Jencks, ibid., 1978, 100, 5956.
[6] L. K. J. Tong and A. R. Olson, J. Am. Chem. Soc., 1941, 63, 3406.
[7] M. M. Kreevoy, T-m. Liang, and K-c. Chang, J. Am. Chem. Soc., 1977, 99, 5207.