Hydrogen Isotope Effects for Nitramide, a Nitrogen Acid

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Summary Studies of the rates of decomposition of nitramide (NO_2NH_2) and deuteriated nitramide in H_2O and D_2O, containing a series of phenolate bases, show that the overall isotope effect for this nitrogen acid passes through a maximum in the region $\Delta pK = ca.\ 0$, behaviour which is similar to that observed for carbon acids; for catalysis by the nitramide anion the magnitude of the isotope effect is lower than expected.

In recent years both experimental and theoretical studies of the variation in primary kinetic hydrogen isotope effect have been developed[1] into a powerful method of assessing transition-state structure. The literature[2,3] now contains several examples of isotope effects passing through clearly defined maxima in the region ΔpK ($pK_{AH} - pK_{BH}$) close to zero. In all the experimental studies carbon acids, because of their readily measurable rates, have been employed as the substrates and usually k^H/k^D or k^H/k^T

has been determined. The present work reports the first example of an isotope effect maximum for a nitrogen acid.

Although studies of nitramide (NO_2NH_2) decomposition have contributed greatly to the development of modern theories of acid–base catalysis there have been only two reports of isotope effects being measured; one refers to work in a 91% D_2O medium containing three similar bases[4] and the other[5] to catalysis by dimethylaniline in anisole. Since that time the development of pressure transducers has much simplified the task of obtaining the rates of decomposition; these are summarised in the Table, k^H referring to non-deuteriated nitramide both in the absence and presence of phenolate bases and k^D to deuteriated nitramide in D_2O and also phenolate bases in D_2O.

TABLE. Isotope effects in the base-catalysed decomposition of nitramide at 298·2 K

Base	pK	k^H/(l mol^{-1} s^{-1})	k^H/k^D
Water	−1·74	8·5 × 10^{-7}	5·1
2,4-Dinitrophenol	4·09	0·0166	3·5
Nitramide ion	6·48	0·0368	5·4
Pentachlorophenol	5·25	0·0320	10·2
2,4,6-Trichlorophenol	6·00	0·449	9·0
2-Nitrophenol	7·17	1·84	6·3

The reported isotope effects are therefore the product of a solvent isotope effect and a primary isotope effect. The former can be estimated to be between 2·2, the value obtained for 2-ethoxycarbonylcyclopentanone[6] (Brönsted β value of 0·6) and 3·7, the value for t-butylmalononitrile[7] (β value of 0·98), if the solvent isotope effect and the β values are assumed to reflect the asymmetry of the transition state. The results for nitramide give a β value of 0·75.

The presence of a solvent isotope effect does not alter the fact that the results in the Table show a clearly defined k^H/k^D maximum for catalysis by 2,4,6-trichlorophenolate and pentachlorophenolate anions. As the pK of nitramide is 6·48[8] this behaviour is similar to that observed for carbon acids. This particular reaction also offers the unusual opportunity of studying catalysis by the anion of the substrate; in theory the isotope effect should be at its maximum value in this case. In practice the value is lower than expected. This could be due to the fact that the nitramide anion in aqueous solution is thought to possess the *aci*-form structure of nitramide. This would seem to be consistent with the observation that the catalytic coefficient for the nitramide anion is much lower than that predicted from the Brönsted relationship established by phenolate bases.

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