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The Base-Catalyzed Decomposition of Nitramide: A New Look at an Old Reaction

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Abstract: A new spectroscopic method of monitoring the base-catalyzed decomposition of nitramide, NH_2NO_2, has permitted detailed study of this reaction in basic solutions where accurate data could not be obtained previously, and that has led to the discovery of a second reaction pathway in addition to the traditional route. Newly determined catalytic coefficients for the traditional pathway plus some literature values describe an accurately linear Bronsted relation with $\beta = 0.79 \pm 0.01$ which extends from $-\log(qK_a/p) = 1$ to 8 and to which oxygen and nitrogen bases of different charge type (−2, −1, 0, +1) adhere well. Above $-\log(qK_a/p) = 8$, this Bronsted relation begins to curve downward and disperse into different correlations for nitrogen and oxygen bases. Corresponding behavior is shown by kinetic isotope effects on the decomposition reaction: these are constant at $k_H/k_D = 2$–3 and independent of base type up to $-\log(qK_a/p) = 8$, but beyond this point, they rise and begin to define maxima which again are different for oxygen and nitrogen bases. This behavior is interpreted in terms of a reaction mechanism in which the proton transfer and heavy atom bonding changes required to convert nitramide into its decomposition products, N_2O and H_2O, are not concerted but rather occur in separate reaction steps.

Nitramide was first prepared and found to undergo base-catalyzed decomposition, eq 1, nearly a century ago,[1] and since then

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

this reaction has figured prominently in the development of our ideas on acid-base catalysis. It was, for example, the system used by Bronsted and Pedersen in their pioneering work which led to the discovery of general-base catalysis and the Bronsted relation,[2] and it has been employed to investigate a variety of other phenomena, including specific ion effects, catalysis in nonaqueous solvents, solvent isotope effects, activation energies, and catalysis by fluoride ion.[3]

In all of this work, rates of reaction were measured by monitoring the evolution of N_2O gas. This is a cumbersome method, requiring the use of fair substrate concentrations, comparable to those of the catalysts. Since nitramide is acidic ($pK_a = 6.55$, vide infra) whereas the reaction products are not, reaction between the substrate and the basic catalyst produces changes in catalyst concentration which vary during a kinetic run, and that complicates the data analysis. Self-catalysis by the nitramide ion, a moderately strong base, also becomes significant at pH's near and above the nitramide pK_a. These difficulties have, with only a few exceptions,[4] limited previous investigations of nitramide decomposition to pH's safely below its pK_a and thus to the use of only fairly weak bases.

We have found that nitramide decomposition can also be monitored spectroscopically: nitramide has a strong UV absorption band with $\lambda_{max} = 206$ nm,[5] whereas the reaction products, N_2O and H_2O, have no significant absorption in this region. With this method, low substrate concentrations can be used, and problems associated with catalyst consumption and self-catalysis may consequently be avoided.

By using this new technique, we have been able to examine nitramide decomposition in strongly basic solutions. That in turn has led to the discovery of a second base-catalyzed reaction pathway in which the nitramide anion is the immediate reactant, eq 2, and it has also provided new mechanistic details for the

$$NHNO_2^- \xrightarrow{B} N_2O + HO^- \qquad (2)$$

traditional pathway, eq 1. We describe our work on the traditional route here,[6] and in the following paper in this issue[7] we discuss the mechanism of the second reaction pathway.

Experimental Section

Materials. Nitramide was prepared from ethyl carbamate via nitrourethane and potassium nitrocarbamate[8] and was stored in methanol or butanol solution at 0 °C; such solutions were found to be stable for several months. Phosphonic acids were samples that had been synthesized before,[9] and the bromide salt of 3-(trimethylammonio)propylamine was prepared by a Gabriel synthesis.[10] All other materials were best available commercial grades.

Solutions were made with dionized H_2O, purified further by distillation, or D_2O (99.7 atom % D; Merck, Sharpe and Dohme) as received.

Kinetics. Rates of decomposition of nitramide were measured spectroscopically at λ = 225 nm by using Cary Model 118 or 2200 spectrometers whose cell compartments were thermostatted at 25.0 ± 0.1 °C. Three-milliliter aliquots of aqueous catalyst solutions contained in cuvettes were first allowed to come to temperature equilibrium with the cell compartment; reactions were then initiated by adding a few microliters of stock nitramide solution (methanol or butanol solvent), and continuous recording of absorbance was begun. Initial nitramide concentrations in the reaction mixtures were ca. 1×10^{-4} M. Reactions were followed to completion. The data obeyed the first-order rate law well, and observed rate constants were obtained as slopes of plots of $\ln(A - A_\infty)$ vs time.

In order to verify that this spectroscopic determination was measuring the same process as the previously employed N_2O gas evolution method, some rates of reaction were also determined by the latter technique. Gas evolution was monitored by using a pressure transducer (Schaevitz Engineering, Camden, NJ) to follow changes in pressure produced by reactions conducted in a closed system. The reaction vessel consisted of a flask fitted with a horizontal side arm leading to a ground glass joint through which a platform positioned above the reaction solution could be rotated. An appropriate amount of substrate contained in a glass cup was placed on that platform before the beginning of a kinetic run, and the run was initiated by rotating the platform and dropping the substrate into the magnetically stirred reaction solution. Reaction solutions were

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saturated with N_2O gas before runs by several evacuating and filling cycles, and temperature control was provided by immersing the apparatus in a constant temperature bath operating at 25.0 ± 0.02 °C. The kinetic data adhered to the first-order rate law well, and observed first-order rate constants were evaluated as slopes of appropriate linear functions.

pK_a Determination. The pK_a of nitramide was determined spectroscopically using a wavelength (λ = 225 nm) at which the nitramide anion absorbs more strongly than does nitramide itself. Measurements were made in aqueous biphosphate buffer solutions of various pH (6.0–7.5, measured with a Beckman Model 1019 pH meter) containing a constant stoichiometric concentration of nitramide (10^{-4} M). Indicator ratios, I ($[NH_2NO_2]/[NHNO_2^-]$), of these solutions were determined by using eq 3, in which A_{N^-} and A_{NH} are the absorbances of solutions in which

$$I = (A_{N^-} - A)/(A - A_{NH}) \qquad (3)$$

nitramide is completely in its acidic and basic forms, respectively, and A is the absorbance of a solution containing nitramide in both forms; A_{NH} was measured in 0.1 M hydrochloric acid and A_{N^-} was measured in 10^{-4} M sodium hydroxide. Measurements were made with a Cary Model 118 spectrophotometer at 25.0 ± 0.1 °C, and, when necessary, the data were extrapolated back to the time nitramide was added to the solution in order to compensate for its decomposition.

Results

pK_a Determination. Measurements of pH and indicator ratio (I) of partially ionized aqueous (H_2O) nitramide solutions were made in biphosphate buffers at four different ionic strengths, μ = 0.10, 0.080, 0.050, and 0.010 M, and apparent acidity constants, $(K_a)_{app}$, were calculated according to eq 4; these results were then

$$p(K_a)_{app} = pH + \log I \qquad (4)$$

extrapolated to zero ionic strength to give a thermodynamic acidity constant, K_a. Values of I were weighted in this calculation in order to allow for variation in their precision,[11] and an extrapolation function, eq 5, based upon the expressions of eqs 6[12] and 7[13] for

$$p(K_a)_{app} + 0.5115\sqrt{\mu}/(1 + \sqrt{\mu}) = pK_a + (B - b)\mu \qquad (5)$$

the activity coefficients of nitramide, f, and the nitramide ion, f_-, was used. The data conformed to this expression well, and linear

$$\log f = b\mu \qquad (6)$$

$$\log f_- = -0.5115\sqrt{\mu}/(1 + \sqrt{\mu}) + B\mu \qquad (7)$$

least-squares analysis gave pK_a = 6.547 ± 0.013 and $(B - b)$ = −1.322 ± 0.184. This pK_a is in excellent agreement with pK_a = 6.54 determined by a colorimetric method which employed 2-nitrophenol as an indicator,[4] when that work is adjusted by using a modern value for the pK_a of the indicator,[14] and it is also consistent with pK_a = 6.59 reported for nitramide at 15 °C.[15]

Measurements of the extent of ionization of nitramide were also made in D_2O solution, at one ionic strength, μ = 0.10 M. The results gave an apparent acidity constant which, when extrapolated to zero ionic strength using the slope parameter determined in H_2O solution, provided $(pK_a)_{D_2O}$ = 7.120. Combination of this with the value for H_2O gives the solvent isotope effect K_H/K_D = 3.74, which is a reasonable value for an acid of this strength.[16]

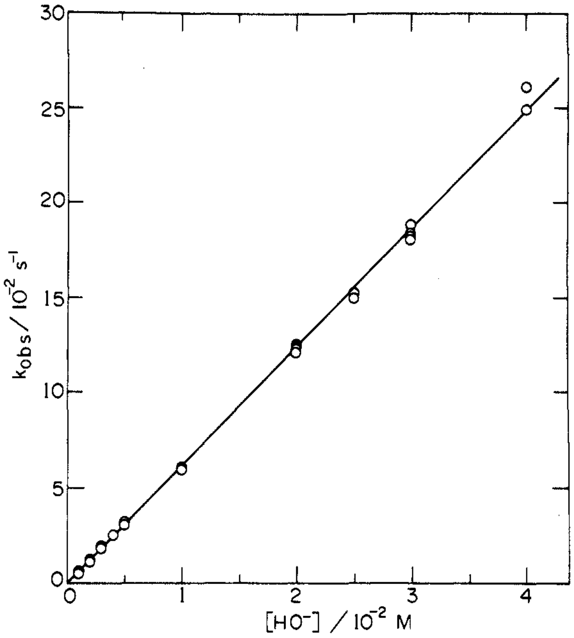
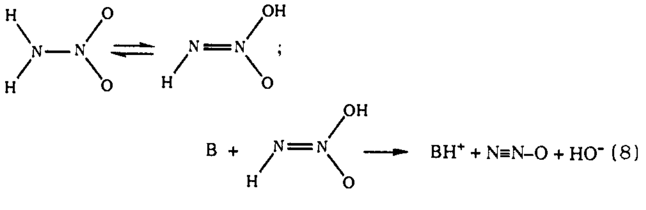


Figure 1. Relationship between rates of nitramide decomposition and hydroxide ion concentration in aqueous solution at 25 °C, ionic strength = 0.1 M.

Comparison of Spectroscopic and Gas Evolution Methods. Rates of reaction were measured by these two methods in $CCl_3PO_3H^-/CCl_3PO_3^{2-}$ buffer solutions at a pH (4.5) well below the pK_a of nitramide (pK_a = 6.6). Series of solutions of constant buffer ratio (1.00) and constant ionic strength (0.10 M) but changing buffer concentration (0.005–0.025 M) were used. Three sets of experiments were performed, two by the spectroscopic method, carried out by two different operators, and one by the gas evolution method, carried out by a third operator. In all three cases, observed first-order rate constants were linear functions of buffer base concentrations, and least-squares analysis gave the following slope parameters, $(\Delta k_{obs}/\Delta[B])/10^{-2}\ M^{-1}\ s^{-1}$ = 6.91 ± 0.24 (spectroscopic method), 7.27 ± 0.20 (spectroscopic method), and 7.51 ± 0.26 (gas evolution method). These results agree within their combined statistical uncertainties, and that serves to establish the validity of the spectroscopic method of measuring rates of nitramide decomposition.

Kinetics. The generally accepted reaction mechanism for the base-catalyzed decomposition of nitramide by the traditional pathway consists of isomerization of the substrate to its *aci*-nitro form, followed by rate-determining removal of the remaining proton bound to nitrogen and expulsion of a hydroxide ion, eq 8.[3,17]



This mechanism is supported by several lines of evidence, chief among which are the facts that acid ionization of nitramide, as measured by the rate of hydrogen exchange, is faster than base-catalyzed decomposition and that homologs of nitramide such as methylnitramine, CH_3NHNO_2, do not undergo the same reaction.[3] The first of these pieces of evidence shows that removal of the first hydrogen cannot be rate-determining in the decomposition reaction, and the second piece of evidence shows that removal of both hydrogens is necessary. This scheme is, of course, also consistent with the fact that the reaction shows simple general-base catalysis, eq 9, at pH's below the pK_a of nitramide.

$$k_{obs} = \sum k_{B_i}[B_i] \qquad (9)$$

At pH's above the pK_a of nitramide, this rate law must be modified to take into account conversion of part of the substrate into the presumably nonreactive nitronate ion. This can be done

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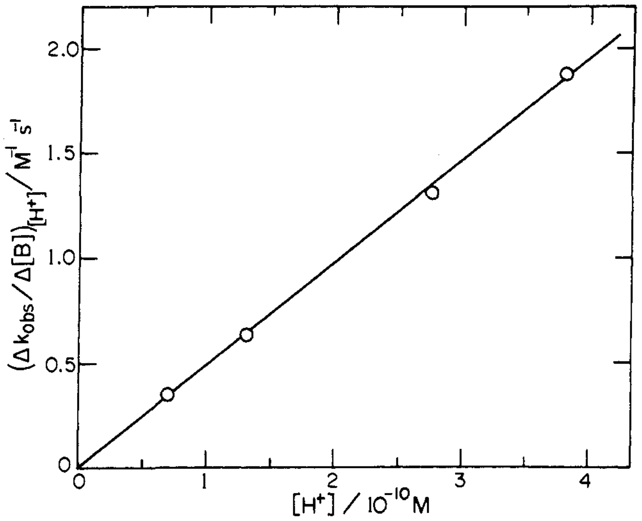


Figure 2. Relationship between $(\Delta k_{obs}/\Delta[B])_{[H^+]}$ and $[H^+]$ for the decomposition of nitramide in HCO_3^-/CO_3^{2-} buffer solutions at 25 °C, ionic strength = 0.1 M.

by adding to the rate law a factor, $[H^+]/([H^+] + Q_a)$, which represents the fraction of nitramide present in un-ionized form, as shown in eq 10. The quantity Q_a in this expression is the

$$k_{obs} = (\Sigma k_{B_i}[B_i])[H^+]/([H^+] + Q_a) \qquad (10)$$

concentration quotient for acid dissociation of nitramide appropriate to the ionic strength used.

This rate law predicts that in sodium hydroxide solutions, where $[H^+] \ll Q_a$ and HO^- is the only kinetically effective base, observed first-order specific rates of nitramide decomposition should be constant and independent of hydroxide ion concentration, eq 11.

$$k_{obs} = k_{HO^-}[HO^-][H^+]/Q_a = k_{HO^-}K_w/Q_a \qquad (11)$$

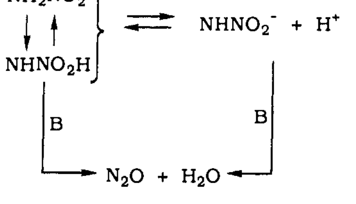
We have found, however, that in such solutions rates of decomposition of nitramide are directly proportional to hydroxide ion concentration. This is illustrated in Figure 1. Least-squares analysis of the data represented there gives $k'_{HO^-} = 6.23 \pm 0.06$ M^{-1} s^{-1}.

Deviations from the behavior expected on the basis of the rate law of eq 10 also appear when nitramide decomposition is catalyzed by bases other than hydroxide ion. This rate law requires changes in observed rate constant brought about by changes in general-base concentration at constant $[H^+]$, $(\Delta k_{obs}/\Delta[B])_{[H^+]}$, measured in solutions where $[H^+] \ll Q_a$, to be a linear function of $[H^+]$ with zero intercept, eq 12. Such behavior is sometimes

$$(\Delta k_{obs}/\Delta[B])_{[H^+]} = k_B[H^+]/Q_a \qquad (12)$$

observed experimentally, as is shown, for example, in Figure 2 for data obtained in carbonate buffer solutions. Some other buffers, however, give linear relationships with nonzero intercepts, as shown in Figure 3, and still others provide values of $\Delta k_{obs}/\Delta[B])_{[H^+]}$ which do not depend upon $[H^+]$ at all, as is illustrated in Figure 4.

This behavior is consistent with incursion of a second general-base-catalyzed pathway for nitramide decomposition in which the nitramide anion is the substrate. That requires addition of a second route to the traditional mechanism, as is shown in eq 13, and new terms must consequently be added to the previous rate law.



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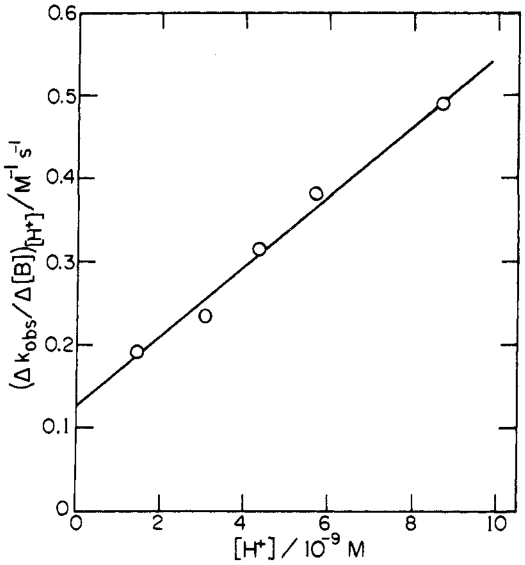

Figure 3. Relationship between $(\Delta k_{obs}/\Delta[B])_{[H^+]}$ and $[H^+]$ for the decomposition of nitramide in $(CH_3O)_2CHCH_2NH_3^+/(CH_3O)_2CHCH_2NH_2$ buffer solutions at 25 °C, ionic strength = 0.1 M.

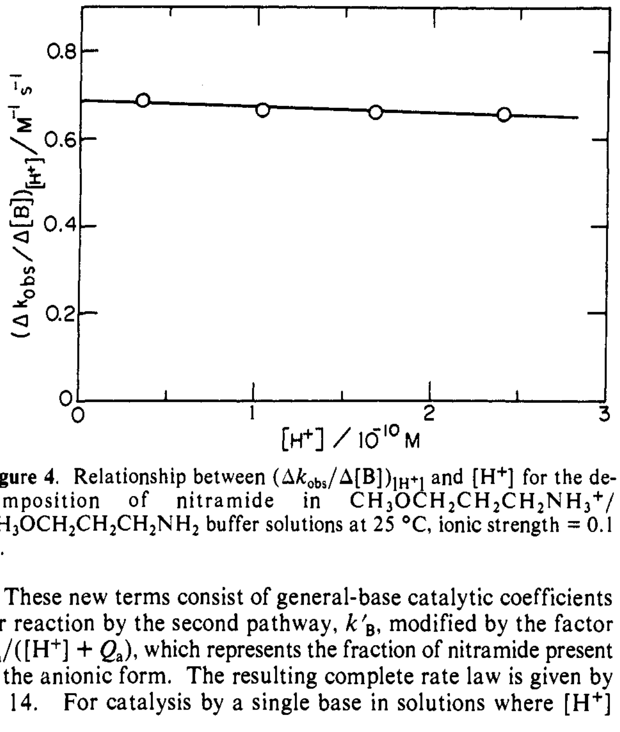

Figure 4. Relationship between $(\Delta k_{obs}/\Delta[B])_{[H^+]}$ and $[H^+]$ for the decomposition of nitramide in $CH_3OCH_2CH_2CH_2NH_3^+/CH_3OCH_2CH_2CH_2NH_2$ buffer solutions at 25 °C, ionic strength = 0.1 M.

These new terms consist of general-base catalytic coefficients for reaction by the second pathway, k'_B, modified by the factor $Q_a/([H^+] + Q_a)$, which represents the fraction of nitramide present in the anionic form. The resulting complete rate law is given by eq 14. For catalysis by a single base in solutions where $[H^+]$

$$k_{obs} = (\Sigma k_{B_i}[B_i])[H^+]/([H^+] + Q_a) + (\Sigma k'_{B_i}[B_i])Q_a/([H^+] + Q_a) \qquad (14)$$

$\ll Q_a$, it gives the relationship shown in eq 15. The various kinds of behavior illustrated in Figures 2–4 may then be understood as

$$(\Delta k_{obs}/\Delta[B])_{[H^+]} = k_B[H^+]/Q_a + k'_B \qquad (15)$$

examples of systems in which reaction via the traditional pathway is dominant (Figure 2), in which reaction occurs simultaneously by both pathways (Figure 3), and in which reaction by the new pathway is dominant (Figure 4).

This rate law was used in the present study to analyze results obtained in a number of different buffer systems. For each system, rates of reaction were measured in series of solutions of constant buffer ratio and constant ionic strength (0.1 M) but varying buffer concentrations. Observed first-order rate constants proved to be linear functions of buffer concentration in all cases; buffer dilution plots of k_{obs} vs [B] were therefore constructed, and linear least-squares analysis gave values of the slope parameters, $(\Delta k_{obs}/$

Table I. Summary of Catalytic Coefficients for the Base-Catalyzed Decomposition of Nitramide in Aqueous Solution at 25 °C[a]

base	pK_{BH}	k_B, $M^{-1}\ s^{-1}$ [b]	$(k_B)_H/(k_B)_D$	k'_B, $M^{-1}\ s^{-1}$ [c]	$(k'_B)_H/(k'_B)_D$
$CCl_3PO_3^{2-}$	4.93[d]	0.0869	2.36		
$CHCl_2PO_3^{2-}$	5.60[d]	0.259	1.78		
$CH_2ClPO_3^{2-}$	6.59[d]	1.84	2.59		
$HOPO_3^{2-}$	7.20[e]	9.50	2.85		
$HOCH_2PO_3^{2-}$	7.36[d]	7.11	2.56		
$CH_3PO_3^{2-}$	8.00[d]	24.1	2.48		
$(CH_3)_3CPO_3^{2-}$	8.71[d]	155.	2.20		
CO_3^{2-}	10.33[f]	3120.	3.45		
$CH_3CO_2^-$	4.76[g]	0.0643	2.54		
$C_6H_2Cl_3O^-$	6.23[h]	0.721	2.91		
CH_3ONH_2	4.60[i]	0.0461	2.99		
$CF_3CH_2NH_2$	5.59[j]	0.375	3.06		
$CN(CH_2)_2NH_2$	7.80[k]	13.5	4.08		
$(CH_2OH)_3CNH_2$	8.07[l]	9.09	5.78	0.0826	3.05
$(CH_3O)_2CHCH_2NH_2$	8.54[k]	26.6	5.35	0.124	3.16
NH_3	9.25[m]	30.0	5.62	0.208	2.88
$HOCH_2CH_2NH_2$	9.50[n]			0.528	
$CH_3O(CH_2)_3NH_2$	9.92[j]			0.667	
$CH_3(CH_2)_2NH_2$	10.57[o]			1.44	
$^-O_2CCH_2NH_2$	9.78[p]	89.5	3.06	0.203	2.76
$^-O_2CCH(CH_3)NH_2$	9.87[q]	64.3	3.39	0.190	2.77
$(CH_3)_3N^+(CH_2)_3NH_2$	8.35[r]	50.8		0.335	
CN^-	9.21[s]			0.00747	
$(CF_3)_2CHO^-$ [t]	9.39	112.0		0.0592	

[a] Ionic strength = 0.1 M. [b] Rate constant for reaction via the traditional pathway. [c] Rate constant for reaction via the second pathway. [d] Reference 9. [e] Grybowski, A. K. *J. Phys. Chem.* **1958**, *62*, 555–559. [f] Harned, H. S.; Scholes, S. R., Jr. *J. Am. Chem. Soc.* **1941**, 63, 1706–1709. [g] Harned, H. S.; Ehlers, R. W. *J. Am. Chem. Soc.* **1933**, *55*, 652–656. [h] Fischer, A.; Leary, G. J.; Topsom, R. D.; Vaughn, J. *J. Chem. Soc. B* **1967**, 686–687. [i] Bissot, T. C.; Parry, R. W.; Campbell, D. H. *J. Am. Chem. Soc.* **1957**, *79*, 798–800. [j] Love, P.; Cohen, R. B.; Taft, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 2455–2462. [k] Lin, A. C.; Chiang, Y.; Dahlberg, D. B.; Kresge, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 5380–5386. [l] Datta, S. P.; Grzybowski, A. K.; Weston, B. A. *J. Chem. Soc.* **1963**, 792–796. [m] Bates, R. G.; Pinching, G. D. *J. Res. Natl. Bur. Stand.* **1949**, *42*, 419–430. [n] Bates, R. G.; Pinching, G. D. *J. Res. Natl. Bur. Stand.* **1951**, *46*, 349–352. [o] Cox, M. C.; Everett, D. H.; Landsman, D. A.; Hunn, R. J. *J. Chem. Soc. B* **1968**, 1373–1379. [p] King, E. J. *J. Am. Chem. Soc.* **1951**, *73*, 155–159. [q] Nims, L. F.; Smith, P. K. *J. Biol. Chem.* **1933**, *101*, 401–412. [r] Reference 23d. [s] Izatt, R. M.; Christensen, J. J.; Pack, R. T.; Bench, R. *Inorg. Chem.* **1962**, *1*, 828–831. [t] Reference 7.

$\Delta[B])_{[H^+]}$. The latter were then separated into k_B and k'_B by using a version of eq 15, shown in eq 16 which does not contain the

$$(\Delta k_{obs}/\Delta[B])_{[H^+]}([H^+] + Q_a) = k_B[H^+] + k'_BQ_a \quad (16)$$

simplification $[H^+] \ll Q_a$; this was necessary because in some cases $[H^+]$ was comparable to or even exceeded Q_a. Linear least-squares analysis gave k_B as the gradient of $(\Delta k_{obs}/\Delta[B])_{[H^+]}([H^+] + Q_a)$ upon $[H^+]$ and k'_BQ_a as the intercept, and, from the latter and knowledge of Q_a, k'_B was obtained.

A value of Q_a appropriate to ionic strength = 0.10 M, $Q_a = 6.15 \times 10^{-7}$ M, was used in this analysis. This was obtained from the value of $(pK_a)_{app}$ for ionic strength = 0.10 M calculated by using eq 5 and an activity coefficient for H^+, $f = 0.83$, recommended by Bates.[18] Values of $[H^+]$ were obtained for the most part from pH meter readings in the buffer solutions used, and $f = 0.83$ was again used for the activity coefficient of H^+ needed to convert activity into concentration. In some cases $[H^+]$ values were also obtained by calculation by using literature K_a values for the buffer acids and recommended activity coefficients for ionic species;[18] good agreement between the two methods was found.

Rate measurements for some buffers were also made in D_2O solution, and the data were treated in the same manner as for H_2O solutions, by using $Q_a = 1.65 \times 10^{-7}$ for the concentration quotient of nitramide at 0.10 M ionic strength in D_2O. The results obtained plus those for H_2O solution are summarized in Table I.

Only one of the catalytic coefficients determined here has been measured before at the presently used temperature; that result, $k_B = 5.68 \times 10^{-2}\ M^{-1}\ s^{-1}$ for acetate ion,[19] is in reasonable agreement with our value, $k_B = 6.43 \times 10^{-2}\ M^{-1}\ s^{-1}$.

The data of Table I show that, for neutral amine catalysts, nitramide decomposition via the traditional pathway dominates for weak bases with pK_{BH} up to ca. 8 and that reaction via the second pathway dominates for strong bases with pK_{BH} greater than ca. 10; in the range between these two limits, reaction by both routes can be detected. For the doubly negative charged phosphonate ions and CO_3^{2-}, however, reaction via the second pathway cannot be detected even wtih pK_{BH} as high as 10. This difference is consistent with the scheme of eq 13, which shows the second pathway as a reaction of the nitronate ion with the catalyzing base, inasmuch as reaction via this route should be retarded by electrostatic repulsion between the substrate anion and the dinegative catalyst, and that provides support for use of a kinetic analysis based upon this scheme.

Determination of the hydroxide ion catalytic coefficient for reaction by the traditional pathway posed a special problem. This constant could not be measured in sodium hydroxide solutions because reaction there occurs entirely by the second pathway: the intercept of the plot shown in Figure 1, which would contain a contribution from reaction by the traditional pathway catalyzed by hydroxide ion, is zero within the experimental uncertainty. The intercepts of most buffer dilution plots were also zero, i.e., general-base catalysis is very strong, and essentially no catalysis by hydroxide ion, through either pathway, could be detected. This was not the case, however, in HCN/CN^- buffers: CN^- is a poor catalyst,[20] and buffer dilution plots for this system consequently had significant intercepts.

These intercepts represent catalysis by water as well as by hydroxide ion, with reaction occurring by either pathway. The complete rate law, eq 17, therefore consists of four terms containing the rate constants k_0 and k_{HO^-} for the water and hydroxide

$$\text{intercept} = (k_0 + k_{HO^-}[HO^-])[H^+]/([H^+] + Q_a) + (k'_0 + k'_{HO^-}[HO^-])Q_a/([H^+] + Q_a) \quad (17)$$

ion catalyzed reactions via the traditional pathway and k'_0 and k'_{HO^-} for the corresponding reactions via the second pathway. In the HCN/CN^-, buffers used $[H^+] \ll Q_a$, and introduction of this simplification plus some rearrangement leads to eq 18.

$$\text{intercept} = k_0[H^+]/Q_a + k_{HO^-}K_w/Q_a + k'_0 + k'_{HO^-}[HO^-] \quad (18)$$

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(18) Bates, R. G. *Determination of pH. Theory and Practice*; Wiley: New York, 1973; p 49.

(19) Baughan, E. C.; Bell, R. P. *Proc. Roy. Soc.* **1937**, *A158*, 464–478.

(20) Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7117–7126.

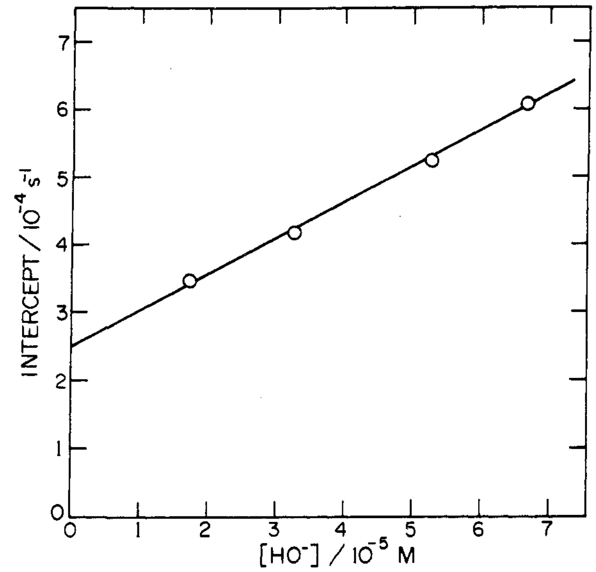

Figure 5. Relationship between hydroxide ion concentration and intercepts of buffer dilution plots for the decomposition of nitramide in HCN/CN⁻ buffer solutions at 25 °C, ionic strength = 0.1 M.

The first term of this rate law, $k_0[H^+]Q_a$, can be shown to make a negligible contribution under the present conditions in the following way. The rate constant k_0 has been reported as 4.7×10^{-5} s^{-1},[19,21] which is consistent with $k_0 = 4.6 \times 10^{-5}$ s^{-1} measured here, and the highest value of $[H^+]$ reached in the present HCN/CN⁻ buffers was 9.4×10^{-10} M. It follows, then, that $k_0[H^+]Q_a \leq 0.00072 \times 10^{-4}$ s^{-1}, which is much less than the range of intercepts obtained in the present work, $3\text{–}6 \times 10^{-4}$ s^{-1}.

Neglect of the first term of eq 18 then leads to eq 19, which requires the intercepts to be a linear function of [HO⁻]. Figure

$$\text{intercept} = k_{HO^-}K_w/Q_a + k'_0 + k'_{HO^-}[HO^-] \qquad (19)$$

5 shows that this is indeed the case. Linear least-squares analysis produces the relationship, intercept = $(2.50 \pm 0.10) \times 10^{-4} + (5.23 \pm 0.21)[HO^-]$, which provides a hydroxide ion catalytic coefficient for reaction by the second pathway, $k'_{HO^-} = 5.23 \pm 0.21$ M^{-1} s^{-1}, in reasonable agreement with the value determined directly from the measurements in sodium hyroxide solutions shown in Figure 1, $k'_{HO^-} = 6.23 \pm 0.06$ M^{-1} s^{-1}.

The remaining term of this least-squares relationship represents reaction by the second pathway catalyzedby water, k'_0, as well as reaction by the traditional pathway catalyzed by hyroxide ion, $k_{HO^-}/K_w/Q_a$. These two quantities have exactly the same dependence upon acidity and therefore cannot be separated experimentally, but a value of k'_0, 4.4×10^{-5} s^{-1}, can be estimated from a Bronsted relation for reaction via the second pathway catalyzed by uncharged bases.[7] This leads to the result $k_{HO^-} = 8.0 \times 10^3$ M^{-1} s^{-1}, which is consistent with $k_{HO^-} = 12 \times 10^3$ M^{-1} s^{-1} produced by a complicated analysis of measurements made by the gas evolution method.[4]

Discussion

Bronsted Relation. The presently determined rate constants for the base-catalyzed decomposition of nitramide via the traditional pathway, together with some additional values from the literature measured under the same conditions, are presented in terms of a Bronsted relation in Figure 6. It can be seen that over much of the large range represented, from $-\log (qK_{BH}/p) = 1$ to 8, all of the catalysts adhere to a single linear correlation quite well, despite the fact that several different charge types are included. Separate least-squares analysis on the individual groups, using only catalysts for which $-\log (qK_{BH}/p)$ is less than 8.00, gives $\log (k_B/q) = -(5.12 \pm 0.06) - (0.800 \pm 0.009) \log (qK_{BH}/p)$ for six doubly negative anions from Table I, $\log (k_B/q) = -(5.09 \pm 0.05) - (0.798 \pm 0.013) \log (qK_{BH}/p)$ for two single negative anions from Table I plus seven carboxylate ions from the literature,[19] and $\log (k_B/q) = -(4.86 \pm 0.07) - (0.771 \pm 0.015) \log (qK_{BH}/p)$ for three neutral amines from Table I plus five primary anilines from the literature.[21b] These correlations are not significantly different from one another, nor are they different from one based upon all three data sets combined: $\log (k_B/q) = -(5.02 \pm 0.04) - (0.791 \pm 0.010) \log (qK_{BH}/p)$.[22]

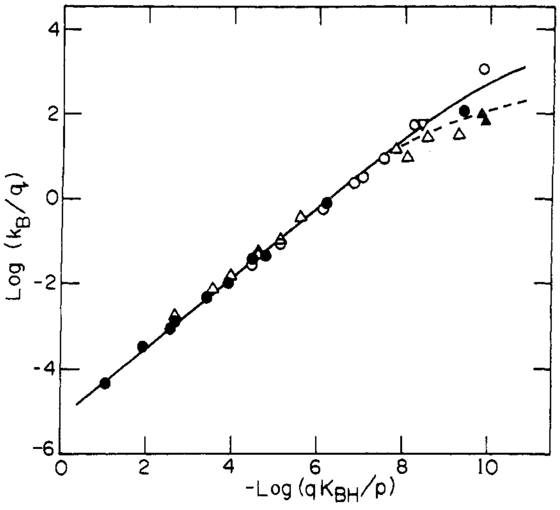

Figure 6. Bronsted relation for the base-catalyzed decomposition of nitramide by the traditional pathway in aqueous solution at 25 °C: (○) doubly negative charged oxygen bases, (●) singly negative charged oxygen bases, (△) neutral primary amines, (▲) negatively charged primary amines, and (▽) positively charged primary amines.

This good adherence to a single Bronsted relation for bases of different charge type is unusual, inasmuch as electrostatic interactions generally cause catalysts of different charge to disperse into separate correlations.[23] A classic example of this is in fact claimed for the nitramide decomposition reaction catalyzed by bases with two negative charges, one negative charge, no charge, and two positive charges.[17,24] The dispersion provided by the first three of these catalyst types, however, is small and not much greater than the experimental scatter. The doubly positive bases, on the other hand, are clearly different from the others: they react about two orders of magnitude more rapidly than do the neutral and negatively charged catalysts. The reason for this is not clear, but it is also not clear that the doubly positive bases react by the same mechanism as the other catalysts: these doubly positive bases are all hydrated metal ions, whereas the other catalysts are carboxylate ions and amines.

Figure 6 shows that the present good linear Bronsted relation deteriorates above $-\log (qK_{BH}/p) = 8$: the correlation begins to curve downward, and there is a suggestion of dispersion with nitrogen bases showing earlier curvature than oxygen bases. Similar dispersion into separate groups for oxygen and nitrogen bases is shown by isotope effects on the reaction rates in this region. This is described in the following section, and its mechanistic significance is discussed in the section after that.

Isotope Effects. Kinetic isotope effects on the base-catalyzed decomposition of nitramide by the traditional pathway determined here are displayed in Figure 7. It may be seen that the more

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(21) (a) Marlies, C. A.; La Mer, V. K. *J. Am. Chem. Soc.* **1935**, *57*, 1812–1820. (b) Bell, R. P.; Wilson, G. L. *Trans. Faraday Soc.* **1950**, *46*, 407–411.

(22) The following statistical factors were used in these correlations: $p = 1, q = 3$ for RPO_3^{2-}; $p = 2, q = 3$ for HPO_4^{2-}; $p = 1, q = 2$ for RCO_2^-; and $p = q = 1$ for ArO⁻ and RNH_2.

(23) (a) Kresge, A. J.; Chiang, Y. *J. Am. Chem. Soc.* **1973**, *95*, 803–806. (b) Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475–503. (c) Chwang, W. K.; Eliason, R.; Kresge, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 805–808. (d) Dahlberg, D. B.; Kuzemko, M. A.; Chiang, Y.; Kresge, A. J.; Powell, M. F. *J. Am. Chem. Soc.* **1983**, *105*, 5387–5390. A rationalization for the lack of dispersion in the present case is offered in the following paper in this issue.[7]

(24) Bell, R. P. *Acid-Base Catalysis*; Oxford University Press: London, 1941; pp 86–87.

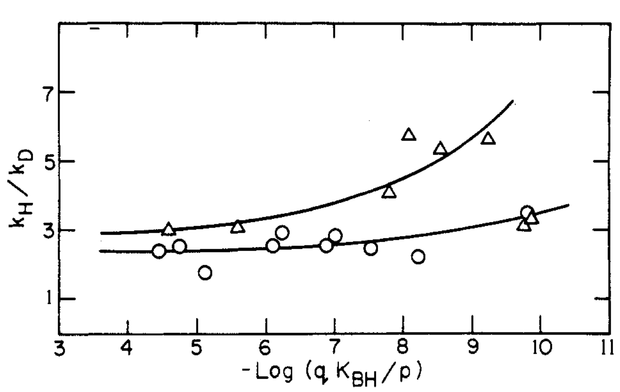

Figure 7. Kinetic isotope effects on the base-catalyzed decomposition of nitramide in aqueous solution at 25 °C: (○) oxygen bases and (△) nitrogen bases.

weakly basic catalysts give small isotope effects, in the range $k_H/k_D = 2-3$, and that there is little dependence of isotope effect upon catalyst base strength and little difference in the values obtained with oxygen and nitrogen bases. This similarity ceases, however, near log $(qK_{BH}/p) = -8$, and dispersion sets in, with isotope effects for nitrogen bases rising with increasing catalyst strength while those for oxygen bases still remain relatively constant. Finally, with the strongest oxygen base, there is the beginning of an increase in isotope effect with increasing catalyst strength for oxygen bases as well. The two strongest nitrogen bases, glycine and alanine carboxylate ions, do not fit this pattern; the reason for this is not clear.

This dispersion of the isotope effects into two categories, one for oxygen bases and one for nitrogen bases, parallels the dispersion of these two kinds of base into separate Bronsted relations noted above. The two phenomena have the same origin; its mechanistic significance will be discussed below.

The isotope effects determined here are quite different from values reported for the decomposition and nitramide catalyzed by a series of aryl oxide ions.[25] The latter isotope effects are for the most part larger than those found here, and they vary systematically with catalyst base strength, passing through a maximum value of $k_H/k_D = 9-10$ when $-\log(qK_{BH}/p) = 5-6$. This maximum falls near the pK_a of nitramide, 6.55, and this pattern was consequently taken to be an example of the Melander–Westheimer effect,[26] which requires hydrogen isotope effects to pass through a maximum when the transition state is symmetrical; for proton-transfer reactions, this occurs when the pK_a's of the proton donor and the proton acceptor are similar: $\Delta pK \cong 0$.[27]

In the case of nitramide, however, $pK_a = 6.55$ refers to ionization of the first proton from the nitro form, eq 20, whereas the

$$H_2NNO_2 \rightleftarrows H^+ + HNNO_2^- \qquad (20)$$

proton removed by the catalyzing base in the decomposition reaction via the traditional pathway is that left on nitrogen in the *aci*-nitro form of the substrate, eq 8. The pK_a of this proton is certaintly greater than 6.55, and the estimate $pK_a \cong 11-12$ can in fact be made (vide infra). The maximum in the isotope effect curve for nitramide decomposition should therefore occur with catalysts much stronger than those that have $pK_{BH} = 5-6$.

Another difficulty with these isotope effects for aryl oxide ions stems from a lack of correspondence of the reported maximum with the shape of the Bronsted plot. Reactions involving proton transfer between electronegative atoms, such as the present system, which show isotope effect maxima also give biphasic "Eigen-type"[28] Bronsted plots with relatively sharp transitions from slopes near unity to slopes near zero in the region of the isotope effect maximum.[29] The Bronsted plot for nitramide decomposition shown in Figure 6 gives no indication of such a break in slope at $pK_{BH} = 5-6$, nor do the rate constants upon which the aryl oxide ion isotope effects were based[25] show a break. The Bronsted plot of Figure 6, on the other hand, does reveal the beginning of such a break at its high end, which corresponds with the rise toward an isotope effect maximum visible in Figure 7.

The isotope effects reported for nitramide decomposition catalyzed by aryl oxide ions[25] were based upon rates of reaction measured by the gas evolution method under conditions requiring a complex kinetic analysis,[4,30] and it is possible that work ran afoul of the difficulties inherent in this technique. In order to investigate this matter, we used our spectroscopic method, which is free of these difficulties, to determine the isotope effect for one of the bases used in the previous study, 2,4,6-trichlorophenoxide ion.[25] This was a difficult experiment, because the trichlorophenoxide buffer system absorbs strongly at $\lambda = 225$ nm, the wavelength required to monitor nitramide disappearance. However, by using a Cary double beam spectrometer with buffer solution in the reference beam and buffer plus substrate in the sample beam, and taking advantage of the great sensitivity of Cary spectrometers, we were able to perform the required measurements. These gave $k_H/k_D = 2.9$, which is much less than the value claimed in the previous study, $k_H/k_D = 9.0$, but is consistent with the isotope effects measured here for other catalysts of comparable basic strength. It would seem, therefore, that the previously measured isotope effects for nitramide decomposition using aryl oxide catalysts[25] are artifacts.

Reaction Mechanism. Isotope effects on proton transfer between electronegative atoms such as oxygen and nitrogen are never very large when the proton transfer is concerted with heavy atom bond making or bond breaking.[31] Such concerted reactions, moreover, generally give Bronsted relations that are linear over extended ranges with no sharp breaks.[32] Proton transfers between electronegative atoms not concerted with heavy atom bonding charges, on the other hand, give larger isotope effects which pass through maximum values near $\Delta pK = 0$, and such reactions also show Eigen-type Bronsted plots whose breaks coincide with the isotope effect maxima.[29] The relatively large isotope effects on the decomposition of nitramide provided by the stronger nitrogen bases shown in Figure 7, as well as the manner in which they increase with increasing catalyst strength defining the beginning of an isotope effect maximum, indicate that the proton transfer which occurs in this reaction is not concerted with the changes in bonding between heavy atoms that must also take place to convert the reactants into products. This is supported by the Bronsted plot of Figure 6, which shows the beginning of a break in the region of rising isotope effects.[33]

Bronsted plots with Eigen-type curvature are produced by proton transfers between electronegative atoms not concerted with

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[25] Jones, J. R.; Rumney, T. G. *J. Chem. Soc., Chem. Commun.* **1975**, 995–996.

[26] Melander, L. *Isotope Effects on Reaction Rates*; Ronald Press: New York, 1960; pp. 24–31. Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265–273.

[27] More O'Ferrall, R. A. In *Proton Transfer Reactions*; Caldin, E., Gold, V., Eds.; Chapman and Hall: London, 1975; Chapter 8. Kresge, A. J. In *Isotope Effects on Enzyme-Catalyzed Reactions*; Cleland, W. W., O'-Leary, M. H., Northrup, D. B., Eds.; University Park Press: Baltimore, 1976; Chapter 2. Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 130–139.

[28] Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1–19.

[29] (a) Bergman, N.-A.; Chiang, Y.; Kresge, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 5954–5956. (b) Cox, M. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1978**, *100*, 5956–5957; **1981**, *103*, 572–580. (c) Fischer, H.; DeCandis, F. X.; Ogden, S. D.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 1340–1347. Yang, C. C.; Jencks, W. P. *J. Am. Chem. Soc.* **1988**, *110*, 2972–2973.

[30] Rumney, T. G. Ph.D. Thesis, University of Surrey, England, 1975.

[31] Swain, C. G.; Kuhn, D. A.; Schowen, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 1553–1561. Showen, R. L. *Prog. Phys. Org. Chem.* **1972**, *9*, 275–332. Eliason, R.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1978**, *100*, 7037–7041.

[32] Bell, R. P.; Higginson, W. C. E. *Proc. Roy. Soc.* **1949**, *197A*, 141–159. Bell, R. P. *Adv. Phys. Org. Chem.* **1966**, *4*, 1–29. Gravitz, N.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 507–515. Funderburk, L. H.; Aldwin, L.; Jencks, W. P. *J. Am. Chem. Soc.* **1978**, *100*, 5444–5459. Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J. *J. Org. Chem.* **1979**, *44*, 1639–1642. Sorensen, P. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4675–4690. Cox, B. G.; Kresge, A. J.; Sorensen, P. E. *Acta Chem. Scand.* **1988**, *A42*, 202–213.

[33] Unfortunately these trends in isotope effect and Bronsted relation cannot be extended to more strongly basic catalysts because reaction by the second pathway becomes overwhelming in the presence of stronger bases, and catalytic coefficients for the traditional pathway cannot be determined.

heavy atom bonding changes because these reactions are essentially diffusion-controlled processes, with either encounter of the proton donor and proton acceptor, eq 21, or separation of the proton-transfer products, eq 23, thus being rate determining. The

$$\mathrm{B + HA \rightarrow B{\cdot}HA} \tag{21}$$

$$\mathrm{B{\cdot}HA \rightarrow BH^{+}{\cdot}A^{-}} \tag{22}$$

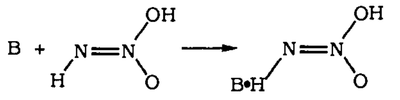
$$\mathrm{BH^{+}{\cdot}A^{-} \rightarrow BH^{+} + A^{-}} \tag{23}$$

horizontal portions of Eigen plots with slopes ≅ 0 represent encounter of the reactants, and the rising portions with slopes ≅ 1 represent separation of the products. In the transition region between these two portions, the proton-transfer step, eq 22, usually becomes partly rate determining. Since this step can have an appreciable isotope effect whereas the other steps cannot, the changes in the rate-determining step from encounter, to proton transfer, and then to separation also produce an isotope effect maximum.

Proton transfers between two nitrogen atoms are intrinsically slower than those between oxygen and nitrogen, and they are consequently partly rate determining over a broader range of ΔpK and more fully rate determining when $\Delta pK = 0$.[28,34] Proton transfers between two nitrogen atoms therefore have broader isotope effect maxima with larger maximum values and have Bronsted plots with wider Eigen-type breaks than do proton transfers between oxygen and nitrogen. Such differences appear in Figures 6 and 7, and this provides further evidence that proton transfer is not concerted with changes in bonding between heavy atoms in the decomposition of nitramide by the traditional pathway.

Downward curvature in Bronsted plots of the kind seen in Figure 6 has also been attributed to desolvation of the catalysts that becomes increasingly difficult as the bases become stronger,[35] rather than to Eigen-type curvature. This is unlikely to be the case here, however, for desolvation is less apt to exert such an influence in reactions with Bronsted exponents as large as that for nitramide decomposition ($\beta = 0.79$),[35c] and desolvation would also produce a decrease in isotope effect[35a] rather than the increase seen in Figure 1.

The long linear portion of the Bronsted plot for nitramide decomposition seen in Figure 6 may then be taken to be the rising part of an Eigen plot. This region refers to a process in which encounter of the reactants, eq 24, and proton transfer, eq 25, are complete, and some subsequent step is rate determining. It is unlikely that this rate-determining step is separation of the proton-transfer products, for such a process would lead to a Bronsted exponent of unity. The observed exponent, $\beta = 0.79$, is rather more consistent with a process in which the heavy atom bonding changes required to convert reactants into products are rate determining and take place directly from the hydrogen-bonded complex or ion pair formed by proton transfer, eq 26. This step is then followed by separation of the reaction products, eq 27.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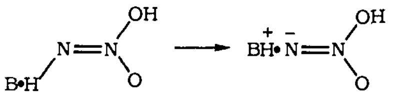
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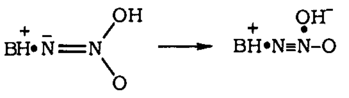
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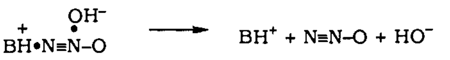
(27)

$$\mathrm{\overset{+}{B}H{\bullet}N{\equiv}N\text{-}O{\overset{OH^{-}}{\bullet}} \longrightarrow BH^{+} + N{\equiv}N\text{-}O + HO^{-}} \tag{27}$$

This assignment of the rate-determining step is based upon the fact that the difference between the observed Bronsted exponent and unity, 1.00 − 0.79 = 0.21, is similar to the magnitude of Bronsted slopes observed for hydrogen bond formation.[36] The relevance of this may be seen by considering the mechanism of eqs 24–27 in reverse. The reverse reaction is a preassociation process[37] in which the reactants, N_2O and HO^-, and an acid catalyst, BH^+, are assembled and then rate-determining heavy atom bonding changes occur before proton-transfer takes place. The acidic catalyst therefore does not function kinetically as a proton-transfer agent: it simply stabilizes the rate-determining transition state by hydrogen bonding. The Bronsted exponent for the reverse reaction will consequently be that for hydrogen bond formation, $\alpha \cong 0.2$,[36] and the exponent for the forward process will be unity minus the reverse value, $\beta = 1.0 - 0.2 \cong 0.8$. Bronsted exponents of the order of $\alpha = 0.2$ have in fact been observed for a number of preassociation reactants.[29b,37b]

Further support for the mechanism of eqs 24–27 comes from the magnitude of the isotope effects observed for nitramide decomposition in the region which corresponds to the linear portion of the Bronsted plot. These have the relatively constant value $k_H/k_D = 2$–3. They refer to a process in which proton transfer is complete and the transferred proton is held in a hydrogen bond, and they are thus equilibrium isotope effects on hydrogen bond formation. Hydrogen bonding is known to reduce the zero-point energy of the hydrogens involved and thus produce isotope effects in the normal direction, $K_H/K_D > 1$, and values of the order of $K_H/K_D = 2$–3 are not uncommon.[38]

The larger isotope effects observed in the region above these relatively constant values refer, of course, to a process in which proton transfer, eq 25, has become partly rate determining. This shift in the rate-determining step takes place because, as the catalyst becomes stronger, proton transfer in the forward direction of eq 25 becomes faster and that in the reverse direction becomes slower; these changes will eventually make the rate of the reverse proton-transfer reaction comparable to that of the heavy atom bond-breaking step, eq 26, and proton transfer will then be partly rate determining.

Equilibrium Constant Estimates. The curvature seen in the Bronsted plot of Figure 6 suggests that rate constants for nitramide decomposition will level off at a limiting value whose magnitude will be of the order of $k_B = 10^4$ M^{-1} s^{-1}. The rate-determining step in this region will be the encounter of the reactants, eq 24, and this limiting rate constant will therefore be equal to the rate constant for this step, k_d times the equilibrium constant for isomerization of nitramide to its reactive *aci*-nitro form, eq 28,


(28)

K_T: $k_B = k_d K_T$. On the assumption that k_d has the diffusion-controlled value 10^{10} M^{-1} s^{-1}, $pK_T = 6$ may be calculated. This result is consistent with $pK_T = 7$ for the similar nitro to *aci*-nitro tautomerization of nitromethane.[39]

This tautomerization constant is also equal to the ratio of acidity constants of nitramide ionizing from its nitro form, eq 29, and *aci*-nitro form, eq 30: $K_T = K_a^{nitro}/K_a^{aci}$. Use of the value of K_a^{nitro}

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(34) Kresge, A. J.; Powell, M. F. *J. Am. Chem. Soc.* **1981**, *103*, 972–973. Kresge, A. J. *Pure Appl. Chem.* **1981**, *53*, 189–200.

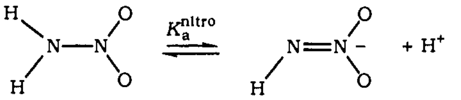
(35) (a) Hupe, D. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 451–464. (b) Hupe, D. J.; Wu, D. *J. Am. Chem. Soc.* **1977**, *99*, 7653–7659. Jencks, W. P.; Brant, S. R.; Gandler, J. R.; Fendrich, G.; Nakamura, C. *J. Am. Chem. Soc.* **1982**, *104*, 7045–7051. (c) Jencks, W. P.; Haber, M. T.; Herschlag, D.; Nazaretian, K. L. *J. Am. Chem. Soc.* **1986**, *108*, 479–483.

(36) Taft, R. W.; Gurka, D.; Joris, L.; Schleyer, P. v. R.; Rakshys, J. W. *J. Am. Chem. Soc.* **1969**, *91*, 4801–4808. Stahl, N.; Jencks, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 4196–4205.

(37) (a) Jencks, W. P. *Acc. Chem. Soc.* **1976**, *9*, 425–432. (b) Jencks, W. P. *Ibid.* **1980**, *13*, 161–169.

(38) Kreevoy, M. M.; Liang, T. M. *J. Am. Chem. Soc.* **1980**, *102*, 3315–3322.

(39) Streitwieser, A.; Hammons, J. H. *Prog. Phys. Org. Chem.* **1965**, *3*, 44.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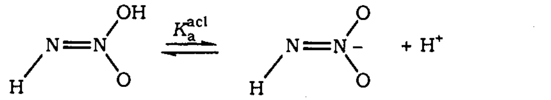
(30)

measured here, $pK_a^{nitro} = 6.55$, with the estimate of K_T made above then leads to $pK_a^{aci} = 0.55$. This result makes *aci*-nitramide somewhat less acidic than its isoelectronic relative, nitric acid, $O{=}NO_2H$, $pK_a = -1.38$,[40] in which an oxygen atom has replaced the HN group of *aci*-nitramide, $HN{=}NO_2H$; such a difference is consistent with the lesser electronegativity of nitrogen and its consequent lower acidifying effect.

An estimate of the pK_a of the hydrogen remaining on nitrogen in *aci*-nitramide can also be made. This is the hydrogen that is removed in the decomposition reaction, and its acidity constant will therefore be similar to that of the conjugate acid of the catalyzing base at the center of the isotope effect maximum where $\Delta pK = 0$. It is difficult to make an accurate estimate of this point, but Figure 7 suggests that this might be at $-\log (qK_{BH}/p) = 11-12$, which leads to $pK_a = 11-12$ for this hydrogen.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[40] Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973, p 28.

The Base-Catalyzed Decomposition of Nitramide: Mechanism of the Second Reaction Pathway

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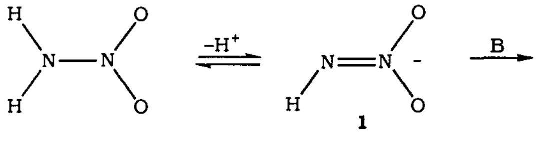
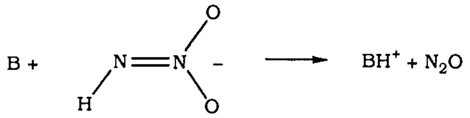
Abstract: Rates of decomposition of nitramide via a new base-catalyzed reaction pathway, in which the nitronate anion is the reactive species, were measured in aqueous buffer solutions of six monofunctional alcohol anions, RO^-, and two bifunctional *gem*-diol monoanions, $R_2C(OH)O^-$. The monofunctional anions give a good Bronsted relation with the slope $\beta = 0.44 \pm 0.02$, from which the bifunctional anions deviate in a direction that makes them more reactive than predicted. This suggests that the latter are acting as bifunctional acid-base catalysts which donate and remove protons through a cyclic transition state; this hypothesis is supported by differences in entropies of activation for the two kinds of catalyst. Other bases of different charge type show systematic deviations from the Bronsted relation based on the monofunctional anions; these deviations are consistent with electrostatic interactions in the transition state, and a rationalization is offered explaining why these effects are present here but absent in nitramide decomposition by the traditional pathway.

In the preceding paper in this issue[1] we reported discovery of a second pathway for the base-catalyzed decomposition of nitramide. This new process occurs only in more basic solutions, and both its rate law and the effect of catalyst charge type on reactivity indicate that it involves reaction of a base with nitramide in its ionized anionic form **1**, eq 1. Such a pathway was postulated some time ago,[2] and an estimate of its rate constant for catalysis by the hydroxide ion was made: $k'_{HO} = 1.0 \times 10^2\ M^{-1}\ s^{-1}$. That estimate, however, is more than an order of magnitude greater than our directly measured value, $k'_{HO} = 6.23\ M^{-1}\ s^{-1}$. The previous estimate, moreover, was based on a very small difference between an observed rate of reaction and the rate calculated assuming its absence,[2] and, since this did not constitute a very convincing demonstration of the occurrence of such a reaction, its existence has been largely ignored.


(1)

We have found that reaction by this second pathway shows general-base catalysis,[1] which suggests that its mechanism involves removal of the remaining proton of the nitramide ion accompanied by expulsion of an oxide ion, eq 2. This mechanism, however, suffers from the fact that the oxide ion is a very unstable species.[3] This difficulty could be overcome by simultaneous proton transfer to the departing oxygen, thus replacing the oxide ion by a much more reasonable hydroxide ion. Such a process might be expected to show simultaneous general-acid and general-base catalysis, but we found no evidence of this in the aqueous buffer solutions we used in our investigation.[1] The proton donor, however, could be a solvent water molecule instead of a buffer acid species, and water should in fact compete quite favorably with the rather weak acid constituents of the basic buffers we had to use in order to observe nitramide decomposition by this second pathway.


(2)

Bifunctional catalysts with acidic groups situated in appropriate relation to basic functions might be expected to compete with water more effectively than separate acid species. In order to learn whether or not this is so in the present case, and thereby gain information about the mechanism of nitramide decomposition via the second pathway, we have examined the reaction catalyzed by

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[1] Arrowsmith, C. H.; Awwal, A.; Euser, B. A.; Kresge, A. J.; Lau, P. P. T.; Onwood, D. P.; Tang, Y. C.; Young, E. C. *J. Am. Chem. Soc.*, preceding paper in this issue.

[2] Tong, L. K. J.; Olson, A. R. *J. Am. Chem. Soc.* **1941**, *63*, 3406-3411.

[3] Guthrie, J. P.; Cossar, J.; Klyn, A. *J. Am. Chem. Soc.* **1984**, *106*, 1351-1360.