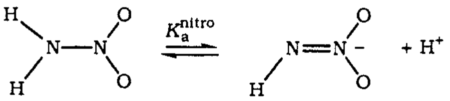

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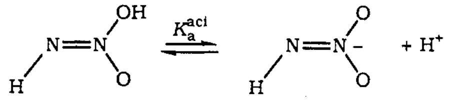

(30)

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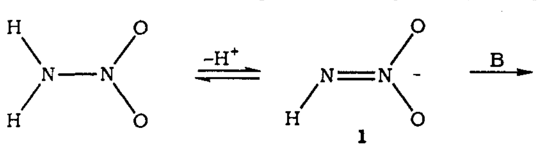
The Base-Catalyzed Decomposition of Nitramide: Mechanism of the Second Reaction Pathway

C. H. Arrowsmith, A. J. Kresge,* and Y. C. Tang

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada. Received May 16, 1990

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.

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Table I. Acidity Constants of Fluoroalcohols at 25 °C

ROH	pK_a	ROH	pK_a
$(CHF_2)_2C(OH)_2$	9.11	$CF_3CF_2CH_2OH$	12.39
$(CF_3)_2CHOH$	9.39	CF_3CH_2OH	12.40
$(CF_3)_2(CH_3)COH$	9.93	$(CF_3)(CH_3)CHOH$	12.70
$(CF_3)(CH_3)C(OH)_2$	10.57	$(CF_3)(CH_3)_2COH$	13.13

Table II. Acidity Constants of Fluoroalcohols at Other Temperatures

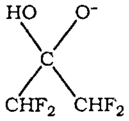
ROH	T, °C	pK_a
CF_3CH_2OH	15.1	12.64
CF_3CH_2OH	20.4	12.53
CF_3CH_2OH	30.4	12.26
$(CF_3)(CH_3)C(OH)_2$	13.4	10.88
$(CF_3)(CH_3)C(OH)_2$	16.4	10.83
$(CF_3)(CH_3)C(OH)_2$	20.4	10.64
$(CF_3)(CH_3)C(OH)_2$	30.4	10.49

Table III. General Base Catalytic Coefficients for the Decomposition of Nitramide by the Second Pathway in Aqueous Solution at 25 °C[a]

base	k'_B, M^{-1} s^{-}	base	k'_B, M^{-1} s^{-}
$(CF_3)_2CHO^-$	0.0592[b]	$(CF_3)(CH_3)CHO^-$	1.52
$(CF_3)_2(CH_3)CO^-$	0.125	$(CF_3)(CH_3)_2CO^-$	3.34
$CF_3CF_2CHO^-$	1.28	$(CHF_2)_2C(OH)O^-$	1.16
$CF_3CH_2O^-$	1.27	$(CF_3)(CH_3)C(OH)O^-$	1.64

[a] Ionic strength = 0.10 M. [b] k_B = 112 M^{-1} s^{-1} for reaction by the traditional pathway.

two bifunctional molecules, the monoanions of the *gem*-diols, tetrafluoroacetone hydrate, **2**, and trifluoroacetone hydrate, **3**. To



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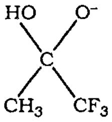

3

RO^-

4

be able to assess the efficacy of these bifunctional catalysts, we have also measured rate constants for a series of monofunctional alcohol anions, **4**. We have, in addition, made a further comparison of monofunctional and bifunctional catalysts by determining activation parameters for **3** and $CF_3CH_2O^-$.

Experimental Section

Materials. Nitramide was prepared as before[1] from potassium nitrocarbamate[4] and was stored in methanol or butanol solution at 0 °C. All other materials were best available commercial grades. Solutions were prepared by using deionized water, purified further by distillation.

Kinetics. Rates of reaction were measured spectrophotometrically by monitoring the decrease in nitramide absorbance at λ = 225 nm; Cary Model 118 and 2200 spectrometers were used for the slower runs and a Durrum-Gibson stopped-flow apparatus was used for the faster ones. Initial nitramide concentrations in the reaction mixtures were ca. 1×10^{-4} M.

Reactions were followed to completion. The data conformed to the first-order rate law accurately, and observed first-order rate constants were calculated by least-squares fitting to linear and/or exponential functions.

pK_a Determinations. Acid dissociation constants of the fluoroalcohols were determined by making pH measurements on buffer solutions of these alcohols with a Beckman Model 1019 pH meter. Measurements were made at a constant ionic strength, μ = 0.10 M, and pH readings were converted into hydroxide ion concentrations by using f = 0.76 as the activity coefficient of the hydroxide ion.[5] These hydroxide ion concentrations were used to correct stoichiometric buffer concentrations for hydrolysis, and the results were then converted into basicity constant concentration quotients, $Q_B = [ROH][HO^-]/[RO^-]$. These were taken to be the same as thermodynamic basicity constants, K_B, on the assumption that the activity coefficients of the alkoxide and hydroxide ions were equal, and pK_a's were calculated from the relationship pK_a = 14 − pK_B.

Results

Acidity Constants. The literature contains conflicting reports of the pK_a's of some of the alcohols used as catalysts in the present study, and acidity constants of the entire set were therefore determined here. This was done by making pH measurements of buffer solutions of the alcohols at a number of different buffer concentrations and also generally a number of different buffer ratios. The 10–20 individual values so obtained were averaged; the results are listed in Table I. The statistical uncertainties in these results were consistently of the order of 0.01 pK unit (standard deviation of the mean), but systematic errors probably raise this error limit to 0.02–0.03 pK unit.

The result obtained here for CF_3CH_2OH, pK_a = 12.40, agrees well with values reported for this alcohol by Ballinger and Long, pK_a = 12.37,[6] and McBee, pK_a = 12.3.[7] Other literature values for CF_3CH_2OH are pK_a = 12.8 reported by Dyatkin[8] and pK_a = 11.4 reported by Henne.[9] The Henne result, however, is of dubious validity inasmuch as he also gives a pK_a for phenol which is 1.0 pK unit below the known value for this substance, and his results for $(CF_3)(CH_3)CHOH$ and $(CF_3)(CH_3)_2COH$ differ from ours for these alcohols in the same direction by comparable amounts. There is good agreement between our value for $(CF_3)_2CHOH$, pK_a = 9.39, and the literature values pK_a = 9.42[10] and 9.3,[8] and our value for $(CHF_2)_2C(OH)_2$, pK_a = 9.11, is broadly consistent with the literature result, pK_a = 8.79.[11] There are also literature values for $(CF_3)_2CHOH$, $(CHF_2)_2C(OH)_2$, and $(CF_3)(CH_3)C(OH)_2$ measured at ionic strength = 1.0 M which are lower than our results by 0.1–0.2 pK unit.[12]

Acidity constants were also determined for two fluoroalcohols, CF_3CH_2OH and $(CF_3)(CH_3)C(OH)_2$, at temperatures other than 25 °C. The data were treated as for 25 °C, by using activity coefficients and ion products of water appropriate to the temperatures of the measurements. The results are listed in Table II.

Arrhenius plots constructed by using these pK_a's at other temperatures plus the 25 °C values give $\Delta H°$ = 9.9 ± 0.6 kcal mol^{-1} and $\Delta S°$ = −23.7 ± 2.1 cal K^{-1} mol^{-1} for the ionization of CF_3CH_2OH and $\Delta H°$ = 9.6 ± 1.3 kcal mol^{-1} and $\Delta S°$ = −15.9 ± 4.3 cal K^{-1} mol^{-1} for $(CF_3)(CH_3)C(OH_2)$. These results are consistent with values obtained for other fluoroalcohols of similar structure; in particular the differences in $\Delta S°$ between the present monohydroxy alcohol and the *gem*-diol is consistent with that reported for $(CF_3)_2CHOH$, $\Delta S°$ = −21.7 cal K^{-1} mol^{-1} and $(CF_3)_2C(OH)_2$, $\Delta S°$ = −10.3 cal K^{-1} mol^{-1}.[10]

Kinetics. Rates of nitramide decomposition catalyzed by six monohydroxy alcohol anions and two *gem*-diol monoanions were measured in buffer solutions of these substances. Measurements were made in series of buffers of constant stoichiometric buffer ratio and constant ionic strength (0.10 M) but systematically changing buffer concentration. This served to keep hydroxide ion concentrations along such buffer series constant for the weaker bases, but buffer failure[13] occurred with the stronger bases causing hydroxide ion concentrations to drop significantly as the buffer was diluted. These changes were compensated for by adjusting observed rate constants to a common (highest) hydroxide ion concentration, by using the known hydroxide ion catalytic coefficient for nitramide decomposition by the second pathway, k'_{HO^-} = 6.23 M^{-1} s^{-1},[1] and hydroxide ion concentrations calculated from values of Q_B for the buffer bases determined here (vide supra).

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Table IV. General Base Catalytic Coefficients for the Decomposition of Nitramide by the Second Pathway in Aqueous Solution at Other Temperatures[a]

catalyst	*T*, °C	k'_B, M^{-1} s^{-1}
$CF_3CH_2O^-$	15.1	0.619
$CF_3CH_2O^-$	20.4	0.951
$CF_3CH_2O^-$	30.4	1.87
$(CH_3)(CF_3)C(OH)O^-$	13.4	0.808
$(CH_3)(CF_3)C(OH)O^-$	16.4	0.954
$(CH_3)(CF_3)C(OH)O^-$	20.4	1.26
$(CH_3)(CF_3)C(OH)O^-$	30.4	2.15
HO^-	13.9	2.48
HO^-	19.1	3.51
HO^-	35.2	10.1

[a] Ionic strength = 0.10 M.

Table V. Activation Parameters for the Decomposition of Nitramide by the Second Pathway in Aqueous Solution[a]

catalyst	ΔH^*, kcal mol^{-1}	ΔS^*, cal K^{-1} mol^{-1}
$CF_3CH_2O^-$	11.9 ± 0.3	−18.2 ± 1.1
$(CH_3)(CF_3)C(OH)O^-$	9.5 ± 0.2	−25.8 ± 0.7
HO^-	11.3 ± 1.1	−17.3 ± 3.8

[a] Ionic strength = 0.10 M.

Observed or adjusted first-order rate constants were found to be linear functions of buffer base concentration in all cases, and slopes of buffer dilution plots were evaluated by linear least-squares analysis. These slopes proved to be constant and independent of buffer ratio in all cases but one, showing that reaction was occurring only by the second pathway; general base catalytic coefficients, k'_B, were therefore evaluated as simple averages of buffer dilution plot slopes. The single exception was the reaction catalyzed by the weakest base used, $(CF_3)_2CHO^-$. Here slopes of buffer dilution plots rose as the buffers became more acidic, signifying that decomposition by the traditional pathway was also occurring in this case. The data were therefore treated as before,[1] and catalytic coefficients for both the traditional pathway, k_B, and the second pathway, k'_B, were evaluated. The results obtained are summarized in Table III.

Rates of nitramide decomposition catalyzed by $CF_3CH_2O^-$ and $(CH_3)(CF_3)C(OH)O^-$ were also measured at temperatures other than 25 °C in order to determine the activation parameters for these reactions. The temperature variation of the hydroxide ion catalytic coefficient, k'_{HO^-}, was determined as well, inasmuch as values of this rate constant were needed to make buffer failure adjustments to observed rate constants. The catalytic coefficients so obtained are summarized in Table IV, and the activation parameters derived from them plus the 25 °C values (Table III) are listed in Table V.

Discussion

Reaction Mechanism. The rate constants for nitramide decomposition via the second pathway catalyzed by the six monofunctional alcohol anions examined here provide the Bronsted relation shown in Figure 1. The slope of this relation, $\beta = 0.44 \pm 0.02$, is quite different from the Bronsted exponent for nitramide decomposition by the traditional pathway, $\beta = 0.79 \pm 0.01$. It was argued in the previous paper[1] that the large value of the latter exponent indicates that reaction by the traditional pathway is not a concerted process in which proton transfer and heavy atom bonding changes occur in the same reaction step. The central value, near 0.5, of the present exponent, on the other hand, is typical of concerted reactions[14] and suggests that proton transfer and heavy atom bonding changes do occur in the same reaction step in nitramide decomposition by the second pathway.

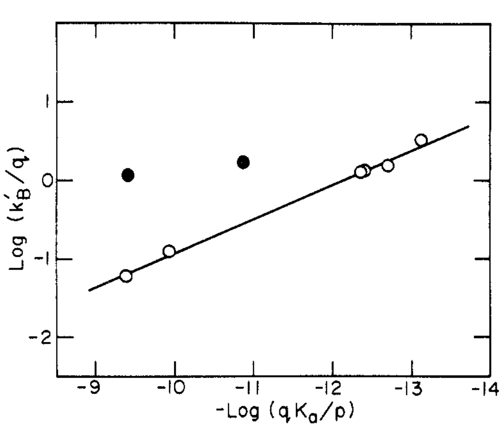
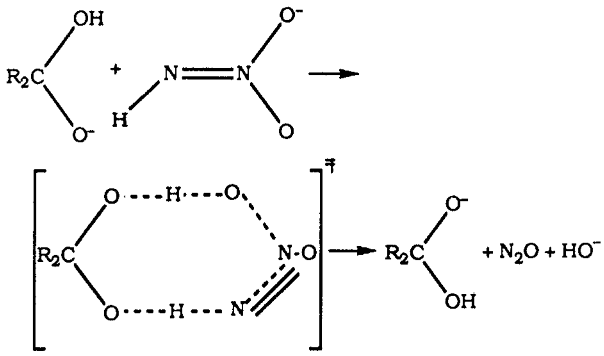


Figure 1. Bronsted relation for nitramide decomposition via the second pathway catalyzed by monofunctional alcohol anions in aqueous solution at 25 °C (○): the filled circles represent catalytic coefficients for the bifunctional catalysts $(CHF_2)_2C(OH)O^-$ and $(CH_3)(CF_3)C(OH)O^-$.

This is supported by the behavior of the bifunctional catalysts studied here. As Figure 1 shows, both of these lie above the Bronsted line by significant amounts: by a factor of 18 for $(CHF_2)_2C(OH)O^-$ and by a factor of 6 for $(CH_3)(CF_3)C(OH)O^-$.[15] These catalysts are clearly doing something in addition to fulfilling the proton removal function of the monofunctional catalysts, and an obvious candidate for this additional role is replacing water as the proton donor needed to avoid oxide ion formation as heavy atom bonding changes accompany proton removal from nitrogen. Bifunctional catalysts will be more effective proton donors because they can react through the cyclic transition state shown in eq 3, which utilizes the greater efficiency of intramolecular over intermolecular reactions.[16]



(3)

This mechanism is supported by a difference in entropies of activation for monofunctional and bifunctional catalysts. Table V shows that the entropies of activation for nitramide decomposition catalyzed by CF_3CHO^- and HO^-, both monofunctional catalysts, are closely similar and appreciably negative, as expected for a bimolecular process. Both of these values, however, are considerably more positive than that for the reaction of the bifunctional catalyst $(CH_3)(CF_3)C(OH)O^-$. This is consistent with the fact that a cyclic transition state, such as that shown for the bifunctional process in eq 3, is more ordered than the open transition state in the reactions of a monofunctional catalyst, and formation of the cyclic transition state will therefore be accompanied by a greater reduction in entropy.

Electrostatic Effects. Some additional catalytic coefficients for nitramide decomposition via the second pathway are available from the previous paper.[1] Of these, a group of five uncharged primary amines gives the Bronsted relation shown in Figure 2,[17] where the correlation based upon the negatively charged catalysts

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(16) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183–278.

(17) Statistical factors of $p = q = 1$ were used for the primary amines.

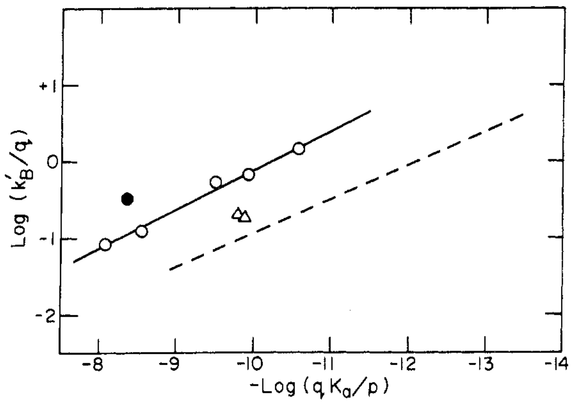


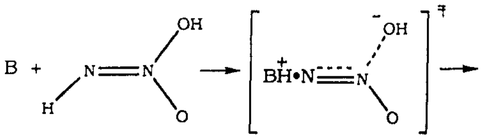
Figure 2. Bronsted relation for nitramide decomposition via the second pathway catalyzed by uncharged primary amines in aqueous solution at 25 °C (○): the other symbols represent a positively charged primary amine (●) and two negatively charged primary amines (△). The broken line represents the Bronsted relation of Figure 1.

of Figure 1 is represented by a broken line. It may be seen that, although the two Bronsted relations have similar slopes, $\beta = 0.51 \pm 0.03$ for the amines and $\beta = 0.44 \pm 0.02$ for the anions, they are clearly different: the amine correlation lies above the anion relation by 0.7–0.9 log units, which corresponds to factors of 6–8 in rate constant.

The differences between these two Bronsted relations is consistent with expectation on the basis of electrostatic effects. The neutral amine catalysts are receiving a proton in this reaction and are therefore becoming positively charged. This positive charge will interact with the negative charge of the anionic substrate in an energy-lowering fashion, stabilizing the transition state and reducing the free energy of activation. The negatively charged catalysts, on the other hand, will still have retained some of their charge in the transition state, and they will therefore interact with the anionic substrate in an energy-raising, destabilizing fashion, which will increase the free energy of activation. The neutral amine catalysts should therefore react more rapidly than the anionic catalysts, as observed.

Further electrostatic effects of this kind are provided by the positively charged amine $(CH_3)_3N^+CH_2CH_2CH_2NH_2$ (Figure 2, filled circle), which reacts three times faster than predicted from the neutral amine correlation, and by two negatively charged primary amines, the glycine and alanine carboxylate anions (Figure 2, triangles), which react three and four times more slowly than predicted from the correlation. These deviations are similar in direction and magnitude to electrostatic effects found on the rates of hydrolysis of vinyl ethers,[18] hydrogen exchange of chloroform,[19] and ionization of 2-nitropropane.[19b]

These electrostatic effects on the decomposition of nitramide via the second pathway stand in striking contrast to the effect of catalyst charge type on the rate of nitramide decomposition by the traditional pathway; in the latter reaction, neutral, singly positive, singly negative, and doubly negative catalysts give a single, good linear correlation.[1] An explanation for this difference can be advanced on the basis of the different mechanisms proposed for the two reaction pathways. Reaction by the traditional pathway is believed[1] to take place by a mechanism in which proton transfer has already occurred by the time the rate-determining step is reached, with the rate-determining step being a process in which hydroxide ion is expelled from an ion pair or complex consisting of the nitrogen-deprotonated *aci*-nitramide anion and the conjugate acid of the catalyzing base, eq 4. In the transition



$$BH^+ + N_2O + HO^- \qquad (4)$$

state of such a rate-determining step, the charge on the catalyst will be some distance away from that on the departing hydroxide ion, and electrostatic interaction between the two charges will consequently be minimized.

The mechanism proposed here for reaction by the second pathway, on the other hand, involves rate-determining proton transfer from the substrate to the basic catalyst. It is likely that in the transition state of this process, negative charge will build up on the nitrogen atom from which the proton is being transferred, and that will place this charge in close proximity to the charge on the catalyst. The situation is similar to that responsible for the nitroalkane anomaly, where negative charge builds up on the atom from which a proton is being transferred in the ionization of aliphatic nitro compounds.[20] It has been suggested[20b] that this charge accumulation occurs because the π-system, through which charge is delocalized onto the nitro group in the reaction product, is not yet fully formed in the transition state, inasmuch as the orbital residing on the atom from which the proton is being transferred, which must contribute to this π-system, is still engaged in (partial) bonding to the leaving proton. A similar situation occurs in proton transfer from the nitramide anion: although there is a π-bond between the two nitrogens of this ion, the N–H bond being broken lies in a node of this π-system, and effective charge delocalization must await formation of another π-bond orthogonal to the first. In contrast to this, in reaction by the traditional pathway, proton removal is complete by the time the rate-determining transition state is reached; rehybridization and formation of the new π-system has consequently already occurred, and charge relocation has been facilitated.

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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