

## Does Nitroalkane Anomaly Exist in the Gas Phase?

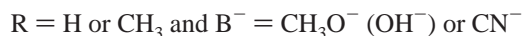
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Anomalous relation between rates and equilibria for the proton-transfer reactions of nitroalkanes is known as nitroalkane anomaly.<sup>1,2</sup> In a typical example, the  $pK_a$  value of  $RCH_2NO_2$  decreases in the order  $CH_3NO_2 > CH_3CH_2NO_2 > (CH_3)_2CHNO_2$  in water, whereas the rate of proton abstraction by hydroxide ion decreases in the same order.<sup>1</sup> Here the reaction is slower for a more acidic substrate. The anomaly can be characterized by an abnormal Brønsted coefficient (a slope  $\alpha$  outside the range of 0 to 1). The above example gives a negative  $\alpha$  value. An analogous system with an electron-withdrawing CN substituent, i.e.,  $RCH_2CN$ , has recently been shown to exhibit normal rate–equilibrium relationship in water.<sup>3</sup> The reactions of  $XC_6H_4CHRNO_2$  with a base are another well-known abnormal case ( $\alpha > 1.0$ ).<sup>2</sup> The nitroalkane anomaly has been analyzed in terms of four interactions: electrostatic and conjugative effects of the substituent which operate both at the product and transition state (TS), and interactions between the substituent and the base and between the substituent and a partial negative charge localized at  $C_\alpha$  which are effective only at the TS.<sup>1,4</sup>

Questions arise in two ways. First, does the nitroalkane anomaly arise from the inherent nature of the substrates, or in other words does the anomaly exist in the gas phase? Second, do the interactions raised in the literature indeed operate in the reaction? Here, we report a combined experimental/theoretical study on the proton-transfer reactions of nitroalkanes in the gas phase, which answers the questions: no for the first question and yes for the second.

Ab initio MO and DFT calculations were carried out for the reactions of  $CH_3NO_2$  and  $CH_3CH_2NO_2$  with  $OH^-$  or  $CN^-$  (eq 1)



at the HF/6-31+G\*, B3LYP/6-31+G\*, MP2/6-31+G\*, and MP2/6-311+G\*\* levels of theory, and the calculated energies are listed in Table 1.<sup>5</sup> At HF/6-31+G\*, both reactions with  $OH^-$  and  $CN^-$  gave well-characterized TSs with one imaginary frequency corresponding to the proton-transfer reaction coordinate, as well as reactant and product complexes. Thus, the reactions follow a double-well potential, as is often assumed for proton-transfer reactions. At a higher level of calculations, however, no TS was detected in the reaction with  $OH^-$ , and the energy of the system

monotonically decreases from the separated reactants to the product complex. Thus, the deprotonations of  $CH_3NO_2$  and  $CH_3CH_2NO_2$  with  $OH^-$  give the product complex without an appreciable barrier. This is due to extremely large exothermicity of the reactions (ca.  $-30 \text{ kcal mol}^{-1}$ , at MP2/6-311+G\*\*). In contrast, the reactions with a weaker base,  $CN^-$ , showed a double-well potential at all levels of calculations. The nitroalkane anomaly can be analyzed computationally for reactions with this base assuming that the anomaly is due to the nature of the acid but not to the base. This assumption is supported by the fact that deprotonations of nitroalkanes with an amine base also show anomaly.<sup>2</sup>

The gas-phase proton-transfer reactions of nitroalkanes with  $CH_3O^-$  base were followed by using a FT-ICR mass spectrometer at 25 °C.<sup>6</sup> The direct measurement of proton-transfer equilibrium between  $CH_3NO_2$  and  $CH_3CH_2NO_2$  showed that  $CH_3NO_2$  is only  $0.2 \text{ kcal mol}^{-1}$  less acidic than  $CH_3CH_2NO_2$ . This number agrees with that calculated from the data compiled in the literature,<sup>7</sup> and is qualitatively consistent with the present calculations. Absolute rate constants could not be determined with precision due to large exothermicity of the reactions and relative values were obtained by a competition experiment, which revealed that the proton-transfer rate is slightly faster for  $CH_3NO_2$  than for  $CH_3CH_2NO_2$  ( $0.76 \pm 0.03$ ). The collision rate constants for these reactions estimated by averaged dipole orientation theory<sup>8</sup> are essentially the same ( $2.8 \times 10^{-9}$  and  $3.0 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for  $CH_3NO_2$  and  $CH_3CH_2NO_2$ , respectively) and these values suggest that the observed reactivity difference reflects the number of hydrogens that come into the reaction for these barrier-less processes. It should be noted that the product complex could not be detected although the product complex is more stable than the separated reactants by about  $8 \text{ kcal mol}^{-1}$  according to the calculations (MP2/6-311+G\*\*). This is probably due to excess kinetic energy buildup that makes the lifetime of the complex extremely short. The reactions with  $CN^-$  could not be followed due to unfavorable thermochemistry of the reactions with this weak base.

Table 1 shows that the relative activation and reaction energies ( $CH_3NO_2$  vs  $CH_3CH_2NO_2$ ) are similar for the B3LYP and MP2 methods, and the results at MP2/6-311+G\*\* are used in the

(5) All calculations were carried out with the Gaussian 94 package of programs, and full frequency analyses were done to confirm that the calculated structures are on a minimum or saddle point on the potential energy surface. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian Inc.: Pittsburgh, PA, 1995.

(6) Relative rate constants were measured using an Extrel FTMS2001 equipped with a 3.0 T superconducting magnet. Partial pressures of nitroalkanes were  $1 \times 10^{-7}$  to  $3 \times 10^{-7}$  Torr, measured with an ionization gauge calibrated in the range  $10^{-3}$  to  $10^{-5}$  Torr against an MKS Baratron capacitance manometer. Ionization gauge-Baratron readings were linear in this range. Methoxide ion was generated by electron impact (0.3–0.5 eV) on methyl nitrite at the pressure of  $(1-2) \times 10^{-7}$  Torr. All anions except the methoxide anion were ejected from the ICR cell using the SWIFT technique. The pseudo-first-order formation of the nitronate anions in a reaction between methoxide and nitroalkanes was recorded over a period of 200–300 ms. The ratio of two product anions was constant in this period. The relative rate constants were determined from the ratios of product anions and the reactant gas pressures. Several runs were carried out at different ratios of reactant gas pressure. Equilibrium constant of proton-transfer reaction was determined in a period of 10–15 s. Relative pressures ( $[C_2H_5NO_2]/[CH_3NO_2]$ ) and relative rates ( $k_{CH_3NO_2}/k_{CH_3CH_2NO_2}$ ) are as follows: 1.310, 0.756; 1.380, 0.755; 1.948, 0.827; 2.441, 0.752; 2.466, 0.753; 4.142, 0.726. Mean value =  $0.76 \pm 0.03$ . Marshall, A. G.; Wang, T.-C. L.; Ricca, T. L. *J. Am. Chem. Soc.*, **1985**, *107*, 7983; Cody, R. B. *Analysis* **1988**, *16*, 30. Guan, S.; Marshall, A. G. *Int. J. Mass Spectrom. Ion Process* **1997**, *157/158*, 5.

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**Table 1.** Reaction and Activation Free Energies for Proton Transfer of RCH<sub>2</sub>NO<sub>2</sub> with CN<sup>-a</sup>

RNO <sub>2</sub>	reactant complex	TS	product complex	products <sup>b</sup>
CH <sub>3</sub> NO <sub>2</sub>	-6.8, (-6.5), {-6.4}, [-7.9]	16.1, (0.4), {5.4}, [3.5]	0.3, (-7.0), {-5.5}, [-3.2]	16.2, (9.3), {12.7}, [13.2]
CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>	-6.6, (-6.8), {-8.2}, [-8.7]	18.1, (-0.6), {4.6}, [2.7]	0.6, (-9.2), {-7.5}, [-4.0]	16.8, (7.2), {11.4}, [11.9]
ΔΔG <sup>c</sup>	0.2, (-0.3), {-1.8}, [-0.9]	2.0, (-1.0), {-0.8}, [-0.8]	0.3, (-2.2), {-2.0}, [-0.8]	0.6, (-2.1), {-1.3}, [-1.3]

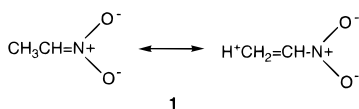
<sup>a</sup> Relative energies vs separated reactants in kcal mol<sup>-1</sup> at 25 °C at HF/6-31+G\*, (B3LYP/6-31+G\*), {MP2/6-31+G\*}, and [MP2/6-311+G\*\*].  
<sup>b</sup> Energy of products is for nitronate anion + HCN. <sup>c</sup> Energy difference, ΔG(CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub>) - ΔG(CH<sub>3</sub>NO<sub>2</sub>).

**Table 2.** Reaction and Activation Free Energies for Proton Transfer of X-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NO<sub>2</sub> with CN<sup>-a</sup>

X	reactant complex	TS	product complex	products <sup>b</sup>
CH <sub>3</sub> O	-6.9	-2.0	-18.1	-5.0
H	-7.2	-3.7	-20.5	-7.6
NO <sub>2</sub>	-14.9	-13.7	-36.6	-27.5

<sup>a</sup> Relative energies vs separated reactants in kcal mol<sup>-1</sup> at 25 °C calculated at B3LYP/6-31+G\*. <sup>b</sup> Energy of products is for nitronate anion + HCN.

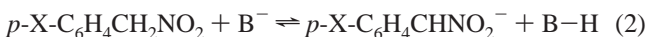
following discussion. The trend that CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub> is slightly more acidic than CH<sub>3</sub>NO<sub>2</sub> is the same as that in water, where the pK<sub>a</sub> values of CH<sub>3</sub>NO<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub> are 10.22 and 8.60.<sup>1</sup> Two factors were considered to account for the observed stronger acidity of CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub> than CH<sub>3</sub>NO<sub>2</sub>: the acid-weakening polar effect of the CH<sub>3</sub> group in CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub>, and hyperconjugative stabilization of nitronate ion (**1**), the latter being dominant.<sup>1</sup> The



present calculations show the contribution of the hyperconjugative resonance structure in **1** in a shorter C-C bond length (1.491 vs 1.520 Å) and a longer C-H bond length (1.100 vs 1.093 Å) in ethyl nitronate ion than in nitroethane. Thus, the same acidity order as in water is observed in the experimental and theoretical determination in the gas phase, and the rationalization given in the literature for the acidity difference is supported by the calculation.

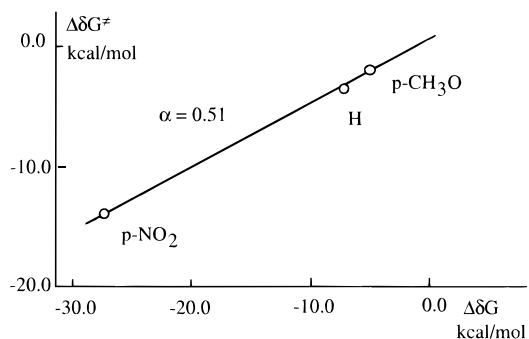
In contrast to the acidity, a larger reactivity of CH<sub>3</sub>NO<sub>2</sub> than CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub> in water (*k*<sub>OH<sup>-</sup></sub> = 27.6 vs 5.19 L mol<sup>-1</sup> s<sup>-1</sup>; ΔG<sup>‡</sup> = 16.14 vs 16.89 kcal mol<sup>-1</sup> at 25 °C)<sup>1</sup> was not observed in the gas-phase determination. The TS was calculated to be more stable for CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub> than for CH<sub>3</sub>NO<sub>2</sub>. The energy difference at the TS is about 60% of that in the anion, corresponding to the Brønsted coefficient of 0.6. Thus, there is no anomaly in the gas-phase reaction.

In Table 2 are listed the activation and reaction free energies for reaction 2



calculated at the B3LYP/6-31+G\* level. Here again the reactions obey a double-well potential, and we will discuss substituent effects on the TS and the product anion because nitroalkane anomaly should relate to these states. Substituent effects are large for reaction 2, and it is clear that the electron-withdrawing substituent stabilized more the anion than the TS. The Brønsted-type plot in Figure 1 shows that the substituent effect is normal giving α of 0.51.

The most important factor proposed in the literature to account for the anomaly in water is the Coulomb interaction between the substituent and negative charge buildup on the α-carbon at the TS.<sup>1</sup> It was assumed that the negative charge generated in the TS partly localized on the α-carbon due to favorable Coulomb interaction with positively charged hydrogen in flight, whereas the negative charge is perfectly localized on the NO<sub>2</sub> group in

**Figure 1.** Brønsted-type plot for reaction 2 based on energies calculated at B3LYP/6-31+G\*.**Table 3.** Group Charges for Stationary Structures of Proton Transfer of RCH<sub>2</sub>NO<sub>2</sub> with CN<sup>-a</sup>

	CH <sub>3</sub> NO <sub>2</sub>	TS	CH <sub>2</sub> NO <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>	TS	CH <sub>3</sub> CHNO <sub>2</sub>
CH <sub>2</sub>		-0.21	-0.12	CH <sub>3</sub> CH	-0.20	-0.07
NO <sub>2</sub>		-0.54	-0.88	NO <sub>2</sub>	-0.56	-0.93
CH <sub>2</sub> NO <sub>2</sub>		-0.75	-1.00	CH <sub>3</sub> CHNO <sub>2</sub>	-0.76	-1.00
CH <sub>2</sub> /CH <sub>2</sub> NO <sub>2</sub>		0.28	0.12	CH <sub>3</sub> CH/CH <sub>3</sub> CHNO <sub>2</sub>	0.26	0.07

<sup>a</sup> Natural population at MP2/6-311+G\*\*.

the product. Such partial charge delocalization at a TS has been noticed for the identity proton transfers by Bernasconi,<sup>9</sup> who succeeded in showing computationally that in the CH<sub>3</sub>NO<sub>2</sub>/CH<sub>2</sub>=NO<sub>2</sub><sup>-</sup> and the CH<sub>3</sub>CH=O/CH<sub>2</sub>=CHO<sup>-</sup> systems the TS is imbalanced in the sense that charge delocalization into the π-electron acceptor group lags behind the proton transfer.<sup>10</sup>

The calculated charge distribution for reaction 1 (B<sup>-</sup> = CN<sup>-</sup>) listed in Table 3 clearly shows that the charge delocalization lags behind proton transfer in nitroalkane deprotonation as originally suggested by Kresge. For CH<sub>3</sub>NO<sub>2</sub> (or CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub>) the amount of charge localized on CH<sub>2</sub> is 12% (7%) of the total charge in the anion, whereas it is 28% (26%) at the TS. Similar but less clear imbalance takes place for PhCH<sub>2</sub>NO<sub>2</sub>.

In conclusion, nitroalkane anomaly does not exist in the gas phase. Proton transfer and charge delocalization occur asynchronously, which, however, does not cause anomaly. The nitroalkane anomaly is not totally due to an intrinsic character of nitroalkane as has been assumed, but occurs in the presence of solvent. Elucidation of effects of solvent is crucial in understanding the phenomenon.<sup>11</sup>

**Acknowledgment.** Numerical calculations were in part carried out on the SP2 at the computer center of the Institute for Molecular Science.

**Supporting Information Available:** Geometries of stationary points (in Cartesian coordinate) for reactions 1 and 2 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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