

Intrinsic Barriers and Transition State Structures in the Gas Phase Carbon-to-Carbon Identity Proton Transfers from Nitromethane to Nitromethide Anion and from Protonated Nitromethane to *aci*-Nitromethane. An *ab Initio* Study

Claude F. Bernasconi,^{*,†} Philip J. Wenzel,[†] James R. Keeffe,[‡] and Scott Gronert[‡]

Contribution from the Department of Chemistry and Biochemistry of the University of California, Santa Cruz, California 95064, and Department of Chemistry and Biochemistry of San Francisco State University, San Francisco, California 94132

Received October 7, 1996. Revised Manuscript Received January 24, 1997[⊗]

Abstract: The identity carbon-to-carbon proton transfers between nitromethane and nitromethide anion and between oxygen protonated nitromethane and *aci*-nitromethane have been studied by *ab initio* methods. Group charges calculated by Mulliken and NPA methods as well as geometrical parameters such as pyramidal angles and C–N bond lengths indicate that the transition states of these reactions are strongly imbalanced. Further evidence for the imbalance comes from a consideration of the relative energies of the various corners representing hypothetical intermediates on More O'Ferrall–Jencks diagrams. Our results for the CH₃NO₂/CH₂=NO₂[−] system, in conjunction with previous findings on other CH₃Y/CH₂=Y[−] systems, indicate an increase in the imbalance in the order CN ≪ CH=O ≤ CH=CH₂ ≤ NO₂ consistent with the notion that imbalances increase with π-acceptor strength of Y. However, when comparing the CH₃N⁺O₂H/CH₂=NO₂H system with the CH₃NO₂/CH₂=NO₂[−] system, the results are somewhat ambiguous as to whether the stronger π-acceptor (N⁺O₂H) leads to a stronger imbalance. In contrast to numerous observations in solution reactions, there is no simple relationship between reaction barrier and imbalances in the gas phase, as becomes apparent when comparing our results with those for the systems CH₃CH=O/CH₂=CHO[−], CH₃CH=O⁺H/CH₂=CHOH, CH₃CN/CH₂CN[−], and CH₃CH=CH₂/CH₂=CHCH₂[−] reported in the literature. It is shown that the dependence of the barriers on the π-acceptor is the result of a complex interplay among resonance/imbalance effects, inductive/field effects, and electrostatic/hydrogen bonding effects.

Introduction

We are interested in the factors that determine transition state structure and intrinsic barriers¹ in proton transfers from carbon acids activated by π-acceptors. For solution reactions there is a substantial body of evidence which indicates that π-acceptors play a dominant role and lead to high intrinsic barriers. These high barriers are a consequence of a transition state imbalance² in the sense that charge delocalization into the π-acceptor of the incipient carbanion lags behind proton (or charge) transfer.³ The barrier enhancing effect of delayed charge delocalization at the transition G_{res}[‡] state can be understood in terms of eq 1^{3–5} where δΔG₀[‡](res) is the change in

$$\delta\Delta G_0^{\ddagger}(\text{res}) = (\lambda_{\text{res}} - \beta)\delta\Delta G_{\text{res}}^{\circ} \quad (1)$$

ΔG₀[‡] (intrinsic barrier)¹ due to the introduction of a π-acceptor,

[†] University of California.

[‡] San Francisco State University.

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

(1) For a reaction with a forward rate constant *k*₁ and a reverse rate constant *k*_{−1} the intrinsic barrier is defined as ΔG₀[‡] = ΔG₁[‡] = ΔG_{−1}[‡] when ΔG[°] = 0.

(2) (a) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948.

(b) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511.

(3) For a recent review, see: Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 116.

(4) (a) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301. (b) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9.

(5) In previous papers^{3,4} eq 1 was usually expressed in terms of rate and equilibrium constants instead of free energies, i.e., δlog *k*₀ = (λ_{res} − β)δlog *K*₁^{res} where δlog *k*₀ is the change in the intrinsic rate constant (*k*₀ = *k*₁ = *k*_{−1}, when ΔG[°] = 0) and δlog *K*₁^{res} is the change in equilibrium constant caused by the resonance induced stabilization of the carbanion. Both forms of the equation are of course equivalent.

δΔG_{res}[°] is the decrease in the free energy of the reaction caused by the π-acceptor induced resonance stabilization of the carbanion, β is a measure of proton transfer at the transition state and is usually equated with the Brønsted coefficient, β_B, determined by varying the p*K*_a of the proton acceptor,⁶ and λ_{res} is a measure of resonance development at the transition state. If charge delocalization/resonance development lags behind proton transfer, we have λ_{res} < β and λ_{res} − β may be regarded as a measure of the imbalance. With both δΔG_{res}[°] and λ_{res} − β having negative values, eq 1 predicts δΔG₀[‡](res) to be >0, i.e., the introduction of a π-acceptor leads to a higher intrinsic barrier.

An interesting question is how to understand the effect of changing π-acceptor strength on ΔG₀[‡]. The experimental evidence shows that ΔG₀[‡] increases with increasing π-acceptor strength. One possible interpretation of this increase is that it arises solely from a more negative δΔG_{res}[°] value in eq 1, while the imbalance, λ_{res} − β, remains constant. Alternatively, the increase in ΔG₀[‡] might be a consequence of more negative values of both δΔG_{res}[°] and λ_{res} − β.

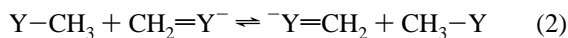
Recent *ab initio* studies^{9,10} have begun to address this question as well as additional issues such as the possible influence of factors other than the imbalance on intrinsic barriers. These

(6) The traditional view⁷ that the Brønsted coefficient β_B is at least an approximate measure of proton transfer as long as the base B is devoid of any resonance effects is not universally accepted.⁸

(7) Lefler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963; p 156. (b) Kresge, A. J. *Acc. Chem. Res.* **1975**, *8*, 354. (c) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511.

(8) Pross, A. *J. Org. Chem.* **1984**, *49*, 1811. (b) Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 4737. (c) Pross, A.; Shaik, S. S. *New J. Chem.* **1989**, *13*, 427.

studies refer to gas phase carbon-to-carbon identity proton transfers of the type of eq 2 with a

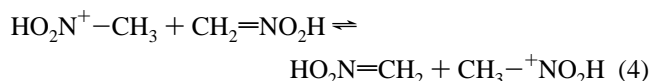
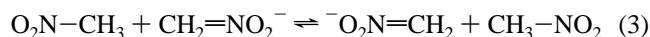


number of Y groups such as CH=O,^{9,10} CH=O⁺H,^{10b} CN,^{9b} and CH=CH₂.^{9b} In these reactions both the proton donor and proton acceptor contain a π -acceptor. This means that the transition state may be characterized by a 2-fold imbalance in the sense that localization of the charge onto the *reactant* anion is ahead of proton transfer, while delocalization of the charge into the Y group of the *product* anion lags behind proton transfer.

Based on Mulliken and NPA group charges the transition state of these reactions was indeed found to be imbalanced in the sense described above. The degree of imbalance was shown to increase in the order CN \ll CH=CH₂ \leq CH=O < CH=O⁺H which corresponds roughly to the order of π -acceptor strength of the Y groups. This implies that in eq 1 $|\lambda_{res} - \beta|$ is not constant but increases with π -acceptor strength.

With regard to the relationship between intrinsic barriers and π -acceptor strength, no simple correlation was found. The absence of such a correlation was attributed to a competition between the barrier *lowering* effect of increased acidity of the carbon acid which follows the order CH=CH₂ < CN < CH=O \ll CH=O⁺H, and the combined barrier enhancing effects of the greater π -acceptor strength ($\delta\Delta G_{res}^{\ddagger}$ in eq 1) and increased imbalance (larger $|\lambda_{res} - \beta|$ in eq 1) which follows the order CN \ll CH=CH₂ < CH=O < CH=O⁺H. Electrostatic or hydrogen bonding interactions between the positively charged transferred proton and the negatively charged α -carbons at the transition state were also shown to affect the barrier,¹⁰ and in the CH₃CN/CH₂CN⁻ system polarizability effects were assumed to play a role in stabilizing the transition state.^{9b}

In the present paper we report an *ab initio* study of the carbon-to-carbon identity proton transfers from nitromethane to nitromethide anion, eq 3, and from protonated nitromethane to aci-nitromethane, eq 4. Because of the unusually strong π -acceptor ability of the nitro group in the solution phase, the



transition state of the deprotonation of nitroalkanes has long epitomized the concept of imbalanced transition states.^{3,11,12} This is reflected in the large number of studies of solution proton transfer reactions involving nitroalkanes which, more than any other reactions, have contributed to our understanding of the relationship between intrinsic barriers and transition state imbalances.^{3,4} Hence eq 3 is an obvious candidate for a theoretical study, while eq 4 should allow interesting comparisons to be made with eq 2 when Y is CH=O⁺H.

Results and Discussion

General Features. For consistency with our previous calculations of the CH₃CH=O/CH₂=CHO⁻ and CH₃CH=O⁺H/

(9) (a) Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 5400. (b) Saunders, W. H., Jr.; Van Verth, J. E. *J. Org. Chem.* **1995**, *60*, 3452. (c) Saunders, W. H., Jr. Personal communication.

(10) (a) Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 5405. (b) Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 10494.

(11) Bordwell, F. G.; Boyle, W. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3907.

(12) Kresge, A. J. *Can. J. Chem.* **1974**, *52*, 1897.

CH₂=CHOH systems,¹⁰ it was desirable to perform the present calculations at the same computational levels, i.e., HF/6-311+G**//HF/6-311+G**, MP2/6-311+G**//HF/6-311+G**, and MP2/6-311+G**//MP2/6-311+G**. With respect to the latter two levels, given our resources this turned out to be practical only for the CH₃NO₂/CH₂=NO₂⁻ (eq 3) but not for the CH₃N⁺O₂H/CH₂=NO₂H (eq 4) system; for this latter reaction the calculations were performed at the HF/6-311+G**//HF/6-311+G**, MP2/6-311+G**//HF/6-311+G**, MP2/6-311+G**//MP2/6-311+G**, and MP2/6-311+G**//MP2/6-311+G** levels. A limited set of calculations of the CH₃NO₂/CH₂=NO₂⁻ system at the levels used for the CH₃N⁺O₂H/CH₂=NO₂H system indicates that comparable gas phase acidities are obtained at all levels except for MP2/6-311+G**//MP2/6-311+G**. This suggests that meaningful comparisons should be feasible between the results obtained for eqs 2 (Y: CH=O and CH=O⁺H), 3, and 4 despite the different computational levels used for eq 4.

Absolute energies and zero point energies of various species relevant to eqs 3 and 4 are summarized in Tables S1 and S2 of the Supporting Information,¹³ respectively. Applying the counterpoise method,¹⁴ we have also calculated basis set superposition errors (BSSE) for the various transition states at some selected computational levels. In view of the lack of agreement about the validity of such corrections,¹⁵ the absolute transition state energies (Tables S1 and S2) and the reaction barriers (Tables 1 and 2; Tables S3 and S4)¹³ are reported with and without such corrections. 3-D representations are shown in Figures 1 and 2, respectively, while geometric parameters at the MP2/6-311+G** for the CH₃NO₂/CH₂=NO₂⁻ and at the MP2/6-311+G** level for the CH₃N⁺O₂H/CH₂=NO₂H system are reported in Figures 3 and 4, respectively. Note that Table S1¹³ and Figure 3 include entries for the hypothetical structures H⁺CH₂=NO₂⁻ and ⁻CH₂NO₂; the meaning of these structures will be discussed later. Note also that for the transition state of eq 3 two different structures have been calculated. TS(optim) is a fully optimized structure and can be regarded as the "true" transition state of the reaction. TS(constr) is not a true transition state, because it is not a stationary point on the energy surface. It is a structure whose carbons have been constrained to be planar and is taken to be a model for a transition state in which charge delocalization is more advanced than in TS(optim), i.e., a transition state with a smaller imbalance, as discussed in detail below.

One point of particular interest is that, even though completely planar at the HF/6-311+G** level, the nitromethide anion has a slightly pyramidalized CH₂ group at the MP2/6-311+G** level. The same result was reported by Lammertsma et al.¹⁶ at the MP2/6-311+G* level.

Energies and Gas Phase Acidities. The staggered and eclipsed conformations of CH₃NO₂ have virtually identical electronic energies and differ by less than 0.1 kcal/mol with respect to the zero point energies (Table S1).¹³ This is similar to the results obtained by Lammertsma et al.¹⁶ at still higher computational levels, including G1.

The protonated nitromethane can exist in a cis and a trans configuration which differ in the orientation of the OH hydrogen relative to the other oxygen, and each may again adopt either a staggered or an eclipsed conformation. In this work we have restricted our calculations to the eclipsed conformers; the energies of the staggered conformers are expected to be very

(13) See paragraph concerning Supporting Information at the end of this paper.

(14) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(15) Davidson, E. R.; Chakravorty, S. *J. Chem. Phys. Lett.* **1994**, *217*, 48.

(16) Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1993**, *115*, 2348.

Table 1. Ionization Enthalpies, Reorganization Enthalpies, and Reaction Barriers for the $\text{CH}_3\text{NO}_2/\text{CH}_2=\text{NO}_2^-$ System

process	ΔH (kcal/mol)		
	HF/6-311+G**// HF/6-311+G**	MP2/6-311+G**// HF/6-311+G**	MP2/6-311+G**// MP2/6-311+G**
CH_3NO_2 (stag) \rightarrow $\text{CH}_2=\text{CH}_2\text{NO}_2^- + \text{H}^+$	360.7	358.6	359.8 ^a
CH_3NO_2 (ecl) \rightarrow $\text{CH}_2=\text{NO}_2^- + \text{H}^+$	360.8	358.6	359.8 ^a
CH_3NO_2 (stag) \rightarrow $\text{H}^+ \text{CH}_2=\text{NO}_2^-$	45.3	34.2	34.3
CH_3NO_2 (ecl) \rightarrow $\text{H}^+ \text{CH}_2=\text{NO}_2^-$	45.3	34.3	34.3
CH_2NO_2^- (stag) \rightarrow $\bar{\text{C}}\text{H}_2\text{NO}_2$	15.3	14.2	9.4
reactants (stag) \rightarrow TS (optim)	8.2	-5.7	-7.0
reactants (stag) \rightarrow TS (optim) _{corr} ^b	9.0	-2.5	-3.6
reactants (ecl) \rightarrow TS (optim)	8.2	-5.7	-7.0
reactants (ecl) \rightarrow TS (optim) _{corr} ^b	9.0	-2.5	-3.6
reactants (stag) \rightarrow TS (constr)	29.6	10.3	9.8
reactants (ecl) \rightarrow TS (constr)	29.7	10.3	9.9

^a Experimental gas phase acidity is 356.4 ± 2.9 kcal/mol, ref 18. ^b Corrected for BSSE.

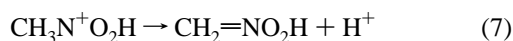
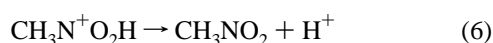
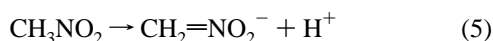
Table 2. Ionization Enthalpies, Tautomerization Enthalpies, and Reaction Barriers for the $\text{CH}_3\text{NO}_2\text{H}^+/\text{CH}_2=\text{NO}_2\text{H}$ System

process	ΔH (kcal/mol)			
	HF/6-311+G**// HF/6-311+G**	MP2/6-311+G**// HF/6-311+G**	MP2/6-31G**// MP2/6-31G**	MP2/6-311+G**// MP2/6-31G**
CH_3NO_2 (ecl) \rightarrow $\text{CH}_2=\text{NO}_2^- + \text{H}^+$	360.8 ^{a,b}	358.7 ^{a,b}	377.0 ^{a,b}	360.0 ^{a,b}
CH_3NO_2 (ecl) \rightarrow $\text{CH}_2=\text{NO}_2\text{H}$ (cis)	15.8 ^c	18.7 ^c	20.0 ^c	18.7 ^c
CH_3NO_2 (ecl) \rightarrow $\text{CH}_2=\text{NO}_2\text{H}$ (trans)	25.4	25.3	27.3	24.7
$\text{CH}_3\text{N}^+\text{O}_2\text{H}$ (cis, ecl) \rightarrow CH_3NO_2 (ecl) + H^+	182.6 ^d	173.9 ^d	178.6 ^d	174.0 ^d
$\text{CH}_3\text{N}^+\text{O}_2\text{H}$ (trans, ecl) \rightarrow CH_3NO_2 (ecl) + H^+	176.4	167.6	171.0	167.4
$\text{CH}_3\text{N}^+\text{O}_2\text{H}$ (cis, ecl) \rightarrow $\text{CH}_2=\text{NO}_2\text{H}$ (cis) + H^+	198.4	192.4	198.4	192.6
$\text{CH}_3\text{N}^+\text{O}_2\text{H}$ (trans, ecl) \rightarrow $\text{CH}_2=\text{NO}_2\text{H}$ (trans) + H^+	201.7	192.9	198.3	192.1
$\text{CH}_3\text{N}^+\text{O}_2\text{H}$ (cis, ecl) + $\text{CH}_2=\text{NO}_2\text{H}$ (cis) \rightarrow TS (cis, syn)	28.2	1.4	-1.2	-1.0
$\text{CH}_3\text{N}^+\text{O}_2\text{H}$ (cis, ecl) + $\text{CH}_2=\text{NO}_2\text{H}$ (cis) \rightarrow TS (cis, syn) _{corr} ^e			2.0	2.1
$\text{CH}_3\text{N}^+\text{O}_2\text{H}$ (cis, ecl) + $\text{CH}_2=\text{NO}_2\text{H}$ (trans) \rightarrow TS (cis, anti)	28.3	1.5	-1.3	-0.9
$\text{CH}_3\text{N}^+\text{O}_2\text{H}$ (cis, ecl) + $\text{CH}_2=\text{NO}_2\text{H}$ (trans) \rightarrow TS (cis, anti) _{corr} ^e			1.9	2.3

^a Experimental gas phase acidity is 356 ± 2.9 kcal/mol, ref 18. ^b At G1 level: $\Delta H = 355.2$ kcal/mol, ref 16; at G2 level: 355.9 kcal/mol, ref 19. ^c At G1 level: 14.2 kcal/mol, ref 16; at G2 level: 14.1 kcal/mol, ref 19. ^d Experimental gas phase acidity is 179.2 kcal/mol, ref 20a; more recent work suggests ca. 177 kcal/mol (refs 20b and 21). ^e Corrected for BSSE.

close to those of the eclipsed conformers which is the optimized structure. Our calculations indicate that the cis isomer is, depending on the computational level, about 6.2–7.6 kcal/mol more stable than the trans isomer, as seen from the ionization enthalpies reported in Table 2. For the *aci* form of nitromethane, $\text{CH}_2=\text{NO}_2\text{H}$, there is also a cis and trans configuration and again the cis isomer is 6–7.3 kcal/mol more stable than the trans isomer¹⁷ (see ΔH for conversion of CH_3NO_2 into $\text{CH}_2=\text{NOH}$, Table 2), in agreement with results obtained at the G1 level.¹⁶ As noted by Lammertsma and Prasad,¹⁶ the trans isomer should actually be considered a transition state for the N–OH bond rotation. In calculating reaction barriers, only the reaction of the cis isomers of $\text{CH}_3\text{N}^+\text{O}_2\text{H}$ with $\text{CH}_2=\text{NO}_2\text{H}$ have been considered.

Ionization enthalpies according to eqs 5–7 are reported in Tables 1 and 2, while ionization energies are summarized in Tables S3 and S4.¹⁷ ΔH for eq 5 with CH_3NO_2 (ecl) is around 360 kcal/mol (Tables 1 and 2) and quite insensitive to the



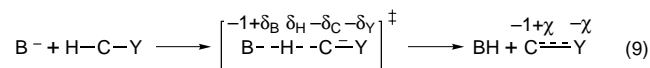
computational level except for a high value of 377 kcal/mol at MP2/6-31G**//MP2/6-31G** (Table 2). This compares with the experimental gas phase enthalpy of ionization of $356.4 \pm$

(17) Except for the HF/6-311+G**//HF/6-311+G** level where the difference is 9.6 kcal/mol.

2.9 kcal/mol¹⁸ and $\Delta H = 355.2$ kcal/mol at the G1¹⁶ level or 355.9 kcal/mol at the G2 level.¹⁹ ΔH for eq 6 (Table 2) shows a stronger dependence on the computational level with values ranging from 173.9 to 182.6 kcal/mol for $\text{CH}_3\text{N}^+\text{O}_2\text{H}$ (cis,ecl). Interestingly, the MP2/6-31G**//MP2/6-31G** value of 178.6 kcal/mol agrees better than any other with the experimental values for the gas phase acidities of $\text{CH}_3\text{N}^+\text{O}_2\text{H}$ (cis,ecl);²⁰ this is probably fortuitous since at this level ΔH for eq 5 deviates the most from the experimental value. ΔH for eq 7 (Table 2) was obtained as the sum of ΔH for eq 6 and ΔH for eq 8 (Table 2). These ΔH values for eq 7 are relatively insensitive to the computational level and range between 192 and 202 kcal/mol for both the cis and trans isomers.



Transition State Structure. A. Charge Imbalance. Equation 3 may schematically be represented by eq 9 where Y = NO_2 and B⁻ is the nitromethide anion. Equation 9 shows how



charges develop and move in going from reactants to the transition state and on to products. In a similar way, eq 10

(18) (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. E.; Levin, R. D.; Holmes, J. L.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry: *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(19) Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1994**, *116*, 642.

(20) (a) 179.2 kcal/mol reported by Lias, S.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695. (b) 177 kcal/mol is estimated based on revised data²¹ for isobutylene and propane used for bracketing the proton affinity of CH_3NO_2 .

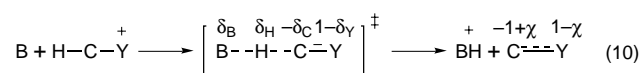
Table 3. Group Charges on CH₃NO₂, CH₂=NO₂⁻ and the Transition States of eq 3

group	HF/6-311+G**// HF/6-311+G**		MP2/6-311+G**// HF/6-311+G**		MP2/6-311+G**// MP2/6-311+G**		MP2/6-311+G**// MP2/6-31G**	
	Mulliken	NPA	Mulliken	NPA	Mulliken	NPA	Mulliken	NPA
CH ₃ NO ₂ (stag)								
NO ₂	-0.278	-0.280	-0.226	-0.227	-0.234	-0.244	-0.240	-0.249
CH ₃	0.278	0.280	0.226	0.227	0.234	0.244	0.240	0.249
CH ₃ NO ₂ (ecl)								
NO ₂	-0.276	-0.280	-0.225	-0.227	-0.233	-0.244	-0.240	-0.249
CH ₃	0.276	0.280	0.225	0.227	0.233	0.244	0.240	0.249
CH ₂ =NO ₂ ⁻								
NO ₂	-0.725	-0.878	-0.706	-0.853	-0.703	-0.854	-0.726	-0.878
CH ₂	-0.275	-0.122	-0.294	-0.147	-0.297	-0.146	-0.274	-0.122
TS (optim)								
NO ₂	-0.417	-0.484	-0.419	-0.478	-0.451	-0.535	-0.466	-0.551
CH ₂	-0.287	-0.169	-0.253	-0.153	-0.202	-0.093	-0.185	-0.075
H (transferred)	0.408	0.307	0.345	0.260	0.306	0.253	0.302	0.250
TS (constr)								
NO ₂	-0.426	-0.561	-0.438	-0.549	-0.461	-0.582		
CH ₂	-0.199	-0.110	-0.151	-0.094	-0.122	-0.060		
H (transferred)	0.250	0.343	0.177	0.286	0.164	0.286		

Table 4. Group Charges on CH₃N⁺O₂H, CH₂=NO₂H and the Transition States of eq 4

group	HF/6-311+G**//HF/6-311+G**		MP2/6-31G**//MP2/6-31G**		MP2/6-311+G**//MP2/6-31G**	
	Mulliken	NPA	NPA		Mulliken	NPA
CH ₃ N ⁺ O ₂ H (cis, ecl)						
NO ₂ H	0.513	0.575	0.601		0.507	0.597
CH ₃	0.487	0.425	0.399		0.493	0.403
CH ₂ =NO ₂ H (cis)						
NO ₂ H	-0.158	-0.262	-0.161		-0.158	-0.171
CH ₂	0.158	0.262	0.161		0.158	0.171
TS (cis, syn)						
NO ₂ H (1)	0.351	0.321	0.224		0.301	0.208
NO ₂ H (2)	0.327	0.305	0.223		0.277	0.207
CH ₂ (1)	-0.039	0.036	0.145		0.019	0.172
CH ₂ (2)	-0.037	0.038	0.146		0.038	0.172
H (transferred)	0.398	0.299	0.259		0.365	0.240
TS (cis, anti)						
NO ₂ H (1)	0.348	0.317	0.224		0.296	0.207
NO ₂ H (2)	0.348	0.317	0.224		0.296	0.207
CH ₂ (1)	-0.045	0.034	0.146		0.025	0.172
CH ₂ (2)	-0.045	0.034	0.146		0.025	0.173
H (transferred)	0.394	0.300	0.259		0.358	0.240

represents eq 4 with Y⁺ = N⁺O₂H and B being CH₂=NO₂H. For both



reactions, a lag in charge delocalization into the Y group behind proton transfer is indicated if the ratio of the negative charge generated on Y (or the positive charge lost on Y in eq 10) to the negative charge developed on C is smaller at the transition state than in the product ion, i.e., $\delta_Y/\delta_C < \chi/(1-\chi)$.

As shown previously,¹⁰ an alternative and convenient quantitative measure of the imbalance is the n value in eq 11, an equation based on a model originally proposed by Kresge¹²

$$\delta_Y = \chi(\delta_C + \delta_Y)^n \quad (11)$$

and later refined by us.^{3,4b,10a} For a perfectly balanced transition state $n = 1$, whereas for an imbalanced transition state in the sense described in the Introduction $n > 1$, with n increasing with increasing size of the imbalance; n is easily calculated from

eq 12. As shown previously,^{10b} the

$$n = \frac{\log(\delta_Y/\chi)}{\log(\delta_C + \delta_Y)} \quad (12)$$

relationship between n and λ_{res} in eq 1 is given by eq 13 which indicates a decrease in λ_{res} with

$$\lambda_{\text{res}} = (\delta_C + \delta_Y)^n \quad (13)$$

increasing n^{22} and hence an increase in $|\lambda_{\text{res}} - \beta|$

Group charges on CH₃NO₂, CH₂=NO₂⁻ and the transition state of eq 3 are reported in Table 3; group charges on CH₃N⁺O₂H, CH₂=NO₂H, and the transition state of eq 4 are in Table 4. All group charges are based on atomic charges calculated by the Mulliken²³ and the NPA²⁴ method and are summarized in Tables S5 and S6.¹³

(21) Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839.

(22) This is because $(\delta_C + \delta_Y) < 1$.

(23) See, e.g.: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; p 25.

δ_Y ,²⁵ χ ,²⁵ δ_C ,²⁵ and quantities calculated therefrom are reported in Table S7¹³ for the $\text{CH}_3\text{NO}_2/\text{CH}_2=\text{NO}_2^-$ and Table S8¹³ for the $\text{CH}_3\text{N}^+\text{O}_2\text{H}/\text{CH}_2=\text{NO}_2\text{H}$ system, while the n values which are our main focus are summarized in Table 5, along with n values for other systems.

The n values are considerably larger than unity for both eqs 3 and 4, irrespective of computational level or method (Mulliken or NPA) used, indicating the presence of a substantial imbalance. This is similar to our findings in the $\text{CH}_3\text{CH}=\text{O}/\text{CH}_2=\text{CHO}^-$ and $\text{CH}_3\text{CH}=\text{O}^+\text{H}/\text{CH}_2=\text{CHOH}$ systems¹⁰ as well as for the $\text{CH}_3\text{CN}/\text{CH}_2\text{CN}^-$ and $\text{CH}_3\text{CH}=\text{CH}_2/\text{CH}_2=\text{CHCH}_2^-$ systems; the n values for the last two systems were calculated based on group charges reported by Saunders et al.^{9b} and by Saunders.^{9c}

There is a rather strong trend toward decreasing n values with increasing computational level and also a tendency for n based on NPA charges to be smaller than n based on Mulliken charges. These trends and the fact that for some systems n is only available at one or two levels that are below the highest levels used in this study makes comparisons between the various systems somewhat difficult. Nevertheless, with respect to the systems with neutral Y groups there is sufficient consistency to allow the following interpretation. Based on Mulliken charges at the highest computational level (MP2/6-311+G***/MP2/6-311+G**), n for NO_2 is significantly larger than for $\text{CH}=\text{O}$; the NPA n value for NO_2 is also larger than for $\text{CH}=\text{O}$ although here the difference between the two is smaller. NPA n values are also available for $\text{CH}=\text{CH}_2$, $\text{CH}=\text{O}$, and CN albeit at a lower level (MP2/6-31+G***/MP2/6-31+G*): they increase in the order $\text{CN} \ll \text{CH}=\text{O} < \text{CH}=\text{CH}_2$.²⁶ Since n for $\text{CH}=\text{O}$ is significantly smaller at the higher computational level, it is reasonable to expect that n for CN and $\text{CH}=\text{CH}_2$ would also be significantly lower at the MP2/6-311+G***/MP2/6-311+G** level. This suggests that the overall rank order is $\text{CN} \ll \text{CH}=\text{O} \leq \text{CH}=\text{CH}_2 \leq \text{NO}_2$.

In the light of solution phase results and assuming there exists a correlation between n and π -acceptor strength,²⁷ the smaller n value for CN compared to $\text{CH}=\text{O}$ and NO_2 is not unexpected. On the other hand, the finding that n for NO_2 may be only marginally larger than for $\text{CH}=\text{O}$ or $\text{CH}=\text{CH}_2$ is perhaps surprising in view of the exceptionally large imbalances observed for solution phase proton transfers from nitroalkanes, especially in protic solvents.^{3,4,11} However, the above rank order is consistent with the gas phase substituent resonance effect

parameters σ_R ²⁸ which are quite similar for $\text{CH}=\text{CH}_2$ (0.16), NO_2 (0.18), and $\text{CH}=\text{O}$ (0.19) but significantly lower for CN (0.10).²⁹

Regarding the large imbalances in the deprotonation of nitroalkanes in solution, they are the result of the strong solvation of the nitronate ion which in effect enhances the π -acceptor strength of the NO_2 group,^{30,31} and of the fact that at the transition state this solvation lags behind proton transfer, thus adding to the imbalance caused by the lag in charge delocalization.^{3,4,30} It is likely, though, that in the deprotonation of simple aldehydes or ketones in solution late solvation of the incipient enolate ion also leads to a strong enhancement of the imbalance. Support for this contention comes from the fact that the solvation of $\text{CH}_2=\text{CHO}^-$ is not dramatically weaker than that of $\text{CH}_2=\text{NO}_2^-$, as suggested by ΔG_0 (gas \rightarrow aq) = -22 kcal/mol for $\text{CH}_2=\text{NO}_2^-$ and -19 kcal/mol for $\text{CH}_3\text{COCH}_2^-$.³² Hence the exceptional status of nitroalkanes in solution proton transfers may have more to do with the absence of relevant data on simple aldehydes or ketones³³ than with special properties of nitronate ions.

Turning to TS(constr), the transition state whose carbon is constrained to be planar, the n value is substantially smaller than for TS(optim); at the MP2/6-311+G***/MP2/6-311+G** level $n = 1.34$ (Mulliken) and 1.33 (NPA) compared to $n = 1.80$ (Mulliken) and 1.59 (NPA) for TS(optim). A similar lowering of n was observed for the constrained transition state in the $\text{CH}_3\text{CH}=\text{O}/\text{CH}_2=\text{CHO}^-$ ^{10a} reaction. This decrease in n is not surprising since the constrained planarity of the carbon is presumed to enhance π -overlap with the nitro group at the transition state, thereby facilitating charge delocalization into the nitro group and decreasing the lag in the delocalization behind proton transfer.

The n values for the systems with a positively charged Y group ($\text{CH}_3\text{N}^+\text{O}_2\text{H}/\text{CH}_2=\text{NO}_2\text{H}$ and $\text{CH}_3\text{CH}=\text{O}^+\text{H}/\text{CH}_2=\text{CHOH}$) present a less consistent picture. Assuming that a $\text{N}^+\text{O}_2\text{H}$ is a stronger π -acceptor than NO_2 and $\text{CH}=\text{O}^+\text{H}$ a stronger π -acceptor than $\text{CH}=\text{O}$, one would expect that n follows the orders $\text{N}^+\text{O}_2\text{H} > \text{NO}_2$ and $\text{CH}=\text{O}^+\text{H} > \text{CH}=\text{O}$.²⁷ For n based on Mulliken charges we indeed have $\text{N}^+\text{O}_2\text{H} > \text{NO}_2$ as well as $\text{CH}=\text{O}^+\text{H} > \text{CH}=\text{O}$; for n based on NPA charges the order $\text{CH}=\text{O}^+\text{H} > \text{CH}=\text{O}$ is maintained but for the nitro compounds we have $\text{N}^+\text{O}_2\text{H} < \text{NO}_2$. As described in the next section, the

(24) (a) Glendenning, E. D.; Reed, A. E.; Carpenter, E.; Weinhold, F. NBO Version 3.1 in Gaussian 92 (ref 59). (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(25) For the $\text{CH}_3\text{NO}_2/\text{CH}_2=\text{NO}_2^-$ system, δ_Y and χ should correspond to the charges on the NO_2 group at the transition state and on $\text{CH}_2=\text{NO}_2^-$, respectively, while δ_C should be equal to the charge on the CH_2 group of the transition state. Similarly, for the $\text{CH}_3\text{N}^+\text{O}_2\text{H}/\text{CH}_2=\text{NO}_2\text{H}$ system, δ_Y and χ should be equal to $1 - (\text{charge on } \text{NO}_2\text{H})_{\text{TS}}$ and $1 - (\text{charge on } \text{NO}_2\text{H})_{\text{CH}_2=\text{NO}_2\text{H}}$, respectively, while δ_C should correspond to $-(\text{charge on } \text{CH}_2)_{\text{TS}}$. However, since in CH_3NO_2 the group charges are not exactly zero, and in $\text{CH}_3\text{N}^+\text{O}_2\text{H}$ the charge on the $\text{N}^+\text{O}_2\text{H}$ moiety is somewhat less than +1 and the charge on the CH_3 group somewhat larger than zero, we define δ_Y , χ , and δ_C as follows: for the $\text{CH}_3\text{NO}_2/\text{CH}_2=\text{NO}_2^-$ system, $\chi = (\text{charge on } \text{NO}_2)_{\text{CH}_2=\text{NO}_2^-} - (\text{charge on } \text{NO}_2)_{\text{CH}_3\text{NO}_2}$; $\delta_Y = |(\text{charge on } \text{NO}_2)_{\text{TS}} - (\text{charge on } \text{NO}_2)_{\text{CH}_3\text{NO}_2}|$; $\delta_C = |(\text{charge on } \text{CH}_2)_{\text{TS}} - (\text{charge on } \text{CH}_3)_{\text{CH}_3\text{NO}_2}|$; for the $\text{CH}_3\text{N}^+\text{O}_2\text{H}/\text{CH}_2=\text{NO}_2\text{H}$ system, $\chi = |(\text{charge on } \text{NO}_2\text{H})_{\text{CH}_2=\text{NO}_2\text{H}} - (\text{charge on } \text{NO}_2\text{H})_{\text{CH}_3\text{N}^+\text{O}_2\text{H}}|$; $\delta_Y = (\text{charge on } \text{NO}_2\text{H})_{\text{TS}} - (\text{charge on } \text{NO}_2\text{H})_{\text{CH}_3\text{N}^+\text{O}_2\text{H}}|$; $\delta_C = |(\text{charge on } \text{CH}_2)_{\text{TS}} - (\text{charge on } \text{CH}_3)_{\text{CH}_3\text{N}^+\text{O}_2\text{H}}|$.

(26) According to Saunders et al.^{9b} the rank order between $\text{CH}=\text{O}$ and $\text{CH}=\text{CH}_2$ is reversed, i.e., $\text{CH}=\text{CH}_2 < \text{CH}=\text{O}$. The reason for this reversal is that Saunders et al. define χ and δ_Y as the negative charge on the $\text{CH}=\text{O}$ moiety and δ_C as the negative charge on the CH_2 group, whereas our definition is in terms of differences of charges on the respective groups between anion (χ) and CH_3Y and between the transition state (δ_Y , δ_C) and CH_3Y (see ref 25).

(27) Note, however, that there is no requirement that n correlates with π -acceptor strength.^{10b}

(28) (a) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1. (b) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(29) In view of the fact that the σ_R parameters have been obtained from systems where the substituent is in a remote position from the reaction center rather than directly attached to it as in the cases of CH_3Y , the σ_R scale is probably at best an approximate measure of the resonance effect in $\text{CH}_2=\text{Y}^-$. Hence not much importance should be attached to the finding that n for $\text{CH}=\text{O}$ is slightly smaller than for NO_2 and $\text{CH}=\text{CH}_2$ even though σ_R is slightly larger for $\text{CH}=\text{O}$ than for NO_2 and $\text{CH}=\text{CH}_2$.

(30) Keeffe, J. R.; Morey, J.; Palmer, C. A.; Lee, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1295.

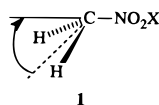
(31) (a) Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017. (b) Mishima, M.; McIver, R. T.; Bordwell, F. G.; Olmstead, W. N. *J. Am. Chem. Soc.* **1984**, *106*, 2717.

(32) Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 332.

(33) There are experimental data in aqueous solution that clearly demonstrate transition state imbalances in the deprotonation of simple aldehydes or ketones,³⁴ but a quantitative assessment of the magnitude of the imbalance, which is typically based on comparing the Brønsted α_{CH} value (variation of carbon acid) with the Brønsted β_{B} value (variation of the buffer base),^{3,4} is more difficult. This is because in these systems the variation in the carbon acid $\text{p}K_{\text{a}}$ leads to $\alpha_{\text{CH}} < \beta_{\text{B}}$ instead of $\alpha_{\text{CH}} > \beta_{\text{B}}$, and because α_{CH} is based on the reaction with OH^- , while β_{B} is based on reactions with buffers. Furthermore the solvent effects on the imbalance have not been assessed. In the case of 1,3-diketones such as acetylacetone,^{35a} 1,3-indandione,^{35b} or ketoesters such as $\text{ArCH}_2\text{CH}(\text{COCH}_3)\text{COOEt}$ ³⁶ the imbalances in solution proton transfer are relatively modest, which is consistent with the smaller solvation energies of the respective enolate ions, e.g., -9.4 kcal/mol for $\text{CH}(\text{COCH}_3)_2^-$.³²

geometric parameters also indicate a slightly smaller imbalance for N^+O_2H than for NO_2 , consistent with the NPA charge imbalance. This suggests that n based on NPA charges may be more reliable. Furthermore, solution phase data on the breakdown of $Tr(CRR')N^+O_2H$ type ions ($Tr =$ tropylium) into $RR'C=NO_2H$ and Tr^+ suggest a smaller imbalance than that observed in the deprotonation of nitroalkanes.³⁷

B. Geometries. Changes in geometrical parameters in moving from reactants to the transition state and to products are consistent with the imbalanced nature of the transition states. One such parameter is the pyramidal angle which may be regarded as an approximate measure of pyramidalization of the carbon atom. This angle is defined as shown in **1** ($X = H$ or lone pair)



where the solid line is the projection of the $C-NO_2X$ bond and the dashed line is the bisector of the HCH group. Note that for a planar molecule or ion this angle is zero. Values for these angles in reactants, products, and respective transition states of eqs 3 and 4 are reported in Table 6. For both reactions pyramidalization at the transition state is still extensive. This is best seen from the *fractional* progress (last column in Table 6) of the pyramidal distortion at the transition state which is far below 0.5 in all cases. These findings suggest retention of a considerable degree of sp^3 character, consistent with the large fraction of negative charge on the CH_2 groups at the transition state. The slightly larger fractional change with N^+O_2H compared with NO_2 suggests a slightly smaller imbalance for N^+O_2H , consistent with n based on NPA charges.³⁸ Similar results were reported for the CH_2 groups in $CH_3CH=O/CH_2=CHO^-$ ^{10b} system and also in the $CH_3CH=O^+H/CH_2=CHOH$ system with the $CH_3CH=O^+H$ (anti,stag) or $CH_3CH=O^+H$ (syn,stag) as the acids.^{10b} On the other hand, with the eclipsed conformers of $CH_3CH=O^+H$ the fractional change in the pyramidal angle was around 0.5;^{10b} part of this abnormal result was attributed to an artifact arising from an unusually large pyramidal angle ($>60^\circ$) in $CH_3CH=O^+H$ (anti,ecl) and $CH_3CH=O^+H$ (syn,ecl).³⁹

Other parameters of interest are the $C-N$ and $N-O$ bond lengths. They are summarized in Table 7 for the $CH_3NO_2/CH_2=NO_2^-$ system and in Table 8 for the $CH_3N^+O_2H/CH_2=NO_2H$ system; also reported in these tables are the changes in bond length in moving from reactants to the transition state (Δr^\ddagger) and to product (Δr^p) and the *fractional* changes in bond lengths at the transition state ($\Delta r^\ddagger/\Delta r^o$). It is these latter values that are of greatest relevance. In the $CH_3NO_2/CH_2=NO_2^-$ system they are $\Delta r_{CN}^\ddagger/\Delta r_{CN}^o = 0.577$ and $\Delta r_{NO}^\ddagger/\Delta r_{NO}^o = 0.479$ for TS(optim), while for TS(constr) they are $\Delta r_{CN}^\ddagger/\Delta r_{CN}^o = 0.715$ and $\Delta r_{NO}^\ddagger/\Delta r_{NO}^o = 0.521$. The fractional bond changes

(34) (a) Chiang, Y.; Hojatti, M.; Keeffe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 4000. (b) Keeffe, J. R.; Kresge, A. J. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley & Sons: New York, 1990; p 399.

(35) (a) Bernasconi, C. F.; Bunnell, R. D. *Isr. J. Chem.* **1985**, *26*, 420. (b) Bernasconi, C. F.; Paschalis, P. *J. Am. Chem. Soc.* **1986**, *108*, 2969.

(36) Bell, R. P.; Grainger, S. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1367.

(37) Erden, I.; Keeffe, J. R.; Xu, F.-P.; Zheng, J.-B. *J. Am. Chem. Soc.* **1993**, *115*, 9834.

(38) This agreement between fractional change in the pyramidal angle and n may be fortuitous, because the relationship between the charge on the carbon and pyramidalization is undoubtedly a complex one since sp^3 hybridization is not a prerequisite for the carbon to be able to carry a partial negative charge. More on this in ref 10b.

(39) This is probably not the whole explanation.³⁸

are significantly larger for TS(constr) than for TS(optim), especially $\Delta r_{CN}^\ddagger/\Delta r_{CN}^o$. This is consistent with the greater progress in charge delocalization into the nitro group for TS(constr) which implies greater progress in $C-N$ double bond formation and greater loss in $N-O$ double bond character. Very similar findings were reported for the $C-C$ and $C-O$ bonds in the $CH_3CH=O/CH_2=CHO^-$ ^{10a} system, again showing larger $\Delta r_{CC}^\ddagger/\Delta r_{CC}^o$ and $\Delta r_{CO}^\ddagger/\Delta r_{CO}^o$ ratios for the constrained compared to the optimized transition state. We also note that the $\Delta r_{CN}^\ddagger/\Delta r_{CN}^o$ and $\Delta r_{NO}^\ddagger/\Delta r_{NO}^o$ ratios for the $CH_3N^+O_2H/CH_2=NO_2H$ system are slightly larger than for the $CH_3NO_2/CH_2=NO_2^-$ system, suggesting a slightly smaller imbalance for the $CH_3N^+O_2H/CH_2=NO_2H$ system, consistent with the pyramidal angles and NPA charges.

A final point is that the $\Delta r_{CN}^\ddagger/\Delta r_{CN}^o$ ratio of 0.577 for TS(optim) of the $CH_3NO_2/CH_2=NO_2^-$ system is close to the total negative charge generated on the entire CH_2NO_2 -moiety at the transition state, i.e., from Table S5,¹³ $\delta_C + \delta_Y = 0.651$ (Mulliken) or 0.626 (NPA), and much larger than the charge generated on the NO_2 group, i.e., $\delta_Y = 0.226$ (Mulliken) or 0.302 (NPA). The same is true in the $CH_3N^+O_2H/CH_2=NO_2H$ system where $\Delta r_{CN}^\ddagger/\Delta r_{CN}^o = 0.649$ (from Table S8,¹³ $\delta_C + \delta_Y = 0.583$ (Mulliken) or 0.642 (NPA), and $\delta_Y = 0.228$ (Mulliken) or 0.338 (NPA)). This is similar to the results obtained for the $CH_3CH=O/CH_2=CHO^-$ system¹⁰ where $\Delta r_{CC}^\ddagger/\Delta r_{CC}^o$ is close to $\delta_C + \delta_Y$ and much larger than δ_Y ; it is consistent with the model underlying eq 11 as elaborated upon previously.^{10a}

Reaction Barriers. In keeping with previously introduced terminology we shall use the term "barrier" for the enthalpy difference between the transition state and reactants.⁴⁰ These barriers are summarized in Tables 1 (for eq 3) and 2 (for eq 4), respectively; values with and without counterpoise corrections for the BSSE¹⁴ are reported. At a given computational level the BSSE corrections depend little on the specific reaction and are quite similar to the ones for the $CH_3CH=O/CH_2=CHO^-$ and $CH_3OH=O^+H/CH_2=CHOH$ systems.^{10b} We shall focus our discussion primarily on the ΔH values obtained at the highest computational levels, i.e., MP2/6-311+G**//MP2/6-311+G** for the $CH_3NO_2/CH_2=NO_2^-$ system and MP2/6-311+G**//MP2/6-31G** for the $CH_3N^+O_2H/CH_2=NO_2H$ system. They, along with the barrier pertaining to the $CH_3CH=O/CH_2=CHO^-$ and $CH_3OH=O^+H/CH_2=CHOH$ systems as well as Saunderson's^{9b} barriers for several other identity carbon to carbon proton transfers, are collected in Table 9; in view of the controversial nature of the BSSE corrections¹⁵ and the fact that Saunders et al.^{9b} did not apply them, our discussion will be based on the uncorrected values. The entries in Table 9 are arranged in the order of decreasing gas phase acidities.

A. Barriers in $CH_3Y/CH_2=Y^-$ Systems. Figure 5 shows a plot of barriers vs. acidity for the $CH_3Y/CH_2=Y^-$ (i.e., neutral acid/anionic base) systems. The plot is similar to one reported by Saunders et al.^{9b} except that it now includes the $CH_3NO_2/CH_2=NO_2^-$ system. The points for $Y = CHO, NO_2$, and $CH=CH_2$ are seen to deviate positively, the one for CN negatively from the correlation line defined by the CH_4/CH_3^- , $CH_2=CH_2/CH_2=CH^-$, and $HC\equiv CH/HC\equiv C^-$ systems.⁴²

In discussing how special properties of Y (e.g., resonance) may affect the reaction barriers beyond their influence on the acidities of CH_3Y , Saunders et al.^{9b} regarded the deviations from the correlation line in Figure 5 as a measure of these special effects. According to this analysis, the positive deviations for NO_2 (3.0 kcal/mol), $CH=O$ (7.5 kcal/mol),⁴⁴ and $CH=CH_2$ (6.7 kcal/mol) may be regarded as a reflection of the barrier enhancing effect of π -acceptors. It is surprising, though, that the nitro group which presumably is the strongest π -acceptor

Table 5. Imbalance Parameter, *n*, for Various CH₃Y/CH₂=Y⁻ and CH₃Y⁺/CH₂=Y Systems

	HF/6-311+G**//MP2/6-31+G**//		MP2/6-311+G**//MP2/6-31G**//		MP2/6-311+G**//MP2/6-31G**//		MP2/6-311+G**//MP2/6-311+G**//		MP2/6-311+G**//MP2/6-311+G**//	
	HF/6-311+G**		MP2/6-31+G*		HF/6-311+G**		MP2/6-31G**		MP2/6-31G**	
	Mulliken	NPA	NPA	Mulliken	NPA	NPA	Mulliken	NPA	Mulliken	NPA
CH ₃ CN/CH ₂ CN ⁻			1.77 ^b							
CH ₃ CH=O(ecl)/CH ₂ =CHO ⁻	1.84	2.04	1.94 ^b	1.70	1.63				1.56	1.52
CH ₃ CH=CH ₂ /CH ₂ =CHCH ₂ ⁻			2.02 ^b							
CH ₃ NO ₂ (ecl)/CH ₂ =NO ₂ ⁻ : TS (optim)	3.30	2.52		2.28	1.98		1.78	1.57	1.80	1.59
CH ₃ NO ₂ (ecl)/CH ₂ =NO ₂ ⁻ : TS (constr)									1.34	1.33
CH ₃ CH=O ⁺ H(anti,ecl)/CH ₂ =CHOH(anti)	2.22	2.12		1.78	1.68				1.68	1.69
CH ₃ CH=O ⁺ H(syn,ecl)/CH ₂ =CHOH(syn)	2.34	2.18		1.93	1.72				1.89	1.73
CH ₃ N ⁺ O ₂ H(cis,ecl)/CH ₂ =NO ₂ H(cis) ^a	3.89	2.72				1.52	2.96	1.42		

^a Reaction via TS(cis,anti). ^b Calculated based on group charges in CH₂=Y⁻ and TS reported in ref 9b and group charges in CH₃Y reported in ref 9c.

Table 6. Pyramidal Angles in Reactants, Products, and Transition States of eqs 3 and 4^a

Y	acid	base	transition state	fractional ^b change
NO ₂	56.4° (stag)	13.4°	46.8° (optim)	0.223
NO ₂	59.0° (ecl)	13.4°	46.8° (optim)	0.268
N ⁺ O ₂ H	59.2° (cis, ecl)	0.0°	43.1° (cis, syn) ^c	0.272
N ⁺ O ₂ H	59.2° (cis, ecl)	0.0°	43.1° (cis, anti) ^c	0.272

^a For Y = NO₂ angles calculated at the MP2/6-311+G** level, for Y = N⁺O₂H at the MP2/6-31G** level. ^b Defined as {angle(TS) - angle(acid)}/{angle(base) - angle(acid)}. ^c Average from the two sides of the transition state.

Table 7. C-N and N-O Bond Lengths in CH₃NO₂, CH₂=NO₂⁻ and the Transition State of eq 3^a

bond	CH ₃ NO ₂ (stag)	CH ₃ NO ₂ (ecl)	CH ₂ =NO ₂ ⁻	TS (optim)	TS (constr)
<i>r</i> _{CN}	1.493	1.493	1.356	1.414	1.395
<i>r</i> _{NO}	1.230	1.230	1.278	1.253	1.255
Δ <i>r</i> _{CN} (stag)			-0.137	-0.079	-0.098
Δ <i>r</i> _{CN} (ecl)			-0.137	-0.079	-0.098
Δ <i>r</i> _{NO} (stag)			0.048	0.023	0.025
Δ <i>r</i> _{NO} (ecl)			0.048	0.023	0.025
Δ <i>r</i> _{CN} [‡] /Δ <i>r</i> _{CN} [°] (ecl) ^b				0.577	0.715
Δ <i>r</i> _{CN} [‡] /Δ <i>r</i> _{CN} [°] (stag) ^b				0.577	0.715
Δ <i>r</i> _{NO} [‡] /Δ <i>r</i> _{NO} [°] (ecl) ^b				0.479	0.521
Δ <i>r</i> _{NO} [‡] /Δ <i>r</i> _{NO} [°] (stag) ^b				0.479	0.521

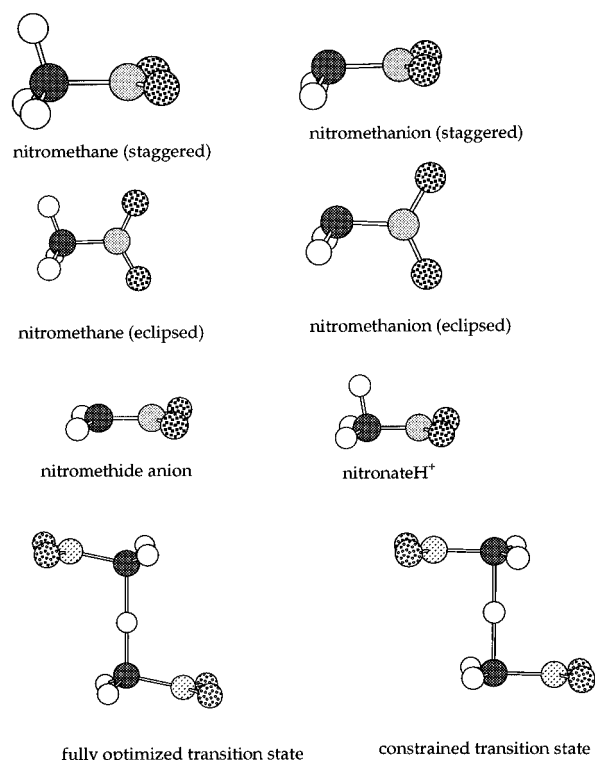
^a Bond lengths in Å at the MP2/6-311+G** level. ^b Δ*r*[‡] = *r*(TS) - *r*(CH₃NO₂), Δ*r*[°] = *r*(CH₂=NO₂⁻) - *r*(CH₃NO₂), hence Δ*r*[‡]/Δ*r*[°] is the fractional change in the bond length.

Table 8. C-N and N-O Bond Lengths in CH₃N⁺O₂H, CH₂=NO₂H and the Transition State of eq 4^a

bond	CH ₃ N ⁺ O ₂ H (cis, ecl)	CH ₂ =NO ₂ H	TS (cis,syn) ^b	TS (cis,anti)
<i>r</i> _{CN}	1.483	1.315	1.373; 1.374	1.374
<i>r</i> _{NO}	1.205	1.237	1.226; 1.228	1.228
<i>r</i> _{NOH}	1.317	1.424	1.374; 1.369	1.369
Δ <i>r</i> _{CN}		-0.168 ^c	-0.110; -0.109 ^d	-0.109 ^d
Δ <i>r</i> _{NO}		0.032 ^c	0.021; 0.023 ^d	0.023 ^d
Δ <i>r</i> _{NOH}		0.107 ^c	0.057; 0.052 ^d	0.052 ^d
Δ <i>r</i> _{CN} [‡] /Δ <i>r</i> _{CN} [°] ^e			0.655; 0.649	0.649
Δ <i>r</i> _{NO} [‡] /Δ <i>r</i> _{NO} [°] ^e			0.656; 0.719	0.719
Δ <i>r</i> _{NOH} [‡] /Δ <i>r</i> _{NOH} [°] ^e			0.533; 0.486	0.486

^a Bond lengths in Å at the MP2/6-31G** level. ^b This transition state is unsymmetrical, i.e., the geometric parameters on the two sides are slightly different. ^c Δ*r*[°] = *r*(CH₂=NO₂H) - *r*(CH₃N⁺O₂H). ^d Δ*r*[‡] = *r*(TS) - *r*(CH₃N⁺O₂H). ^e Δ*r*[‡]/Δ*r*[°] is the fractional change in the bond length.

and is associated with the largest *n* value (Table 5) of all the neutral acid/anionic base systems leads to the smallest positive deviation. Another unusual feature is that the point for the CH₃CN/CH₂CN⁻ system deviates *negatively* from the correlation line by about 1.9 kcal/mol. As pointed out by Saunders et al.,^{9b}

**Figure 1.** 3-D representations of the various structures relevant to the CH₃NO₂/CH₂=NO₂⁻ system.

even though the CN group is only a weak π-acceptor and the imbalance in the CH₃CN/CH₂CN⁻ reaction is relatively small, CN is a π-acceptor nevertheless, and one should have expected a small positive deviation from the correlation line in Figure 5. Saunders et al.^{9b} suggest that the negative deviation may reflect a transition state stabilization by the polarizability of the cyano group which overcompensates the small barrier enhancing π-resonance effect.

(40) In gas phase ion-molecule reactions the transition state is typically preceded by an ion-dipole complex⁴¹ formed between the reactants and the term "barrier" is sometimes used for the enthalpy difference between the transition state and this ion-dipole complex. These ion-dipole complexes have little relevance to the main focus of this paper (see, e.g., ref 9b), and we have not included them in our calculations.

(41) (a) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891. (b) Moylan, C. R.; Brauman, J. I. *Ann. Rev. Phys. Chem.* **1983**, *34*, 187. (c) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993.

(42) The HCN/CN⁻ system also falls on the correlation line: Gronert, S., unpublished results. The lowering of the barrier with increasing acidity was first pointed out by Cybulski and Scheiner;⁴³ it was mainly attributed to shortening of the C-H-C distance at the transition state.⁴³

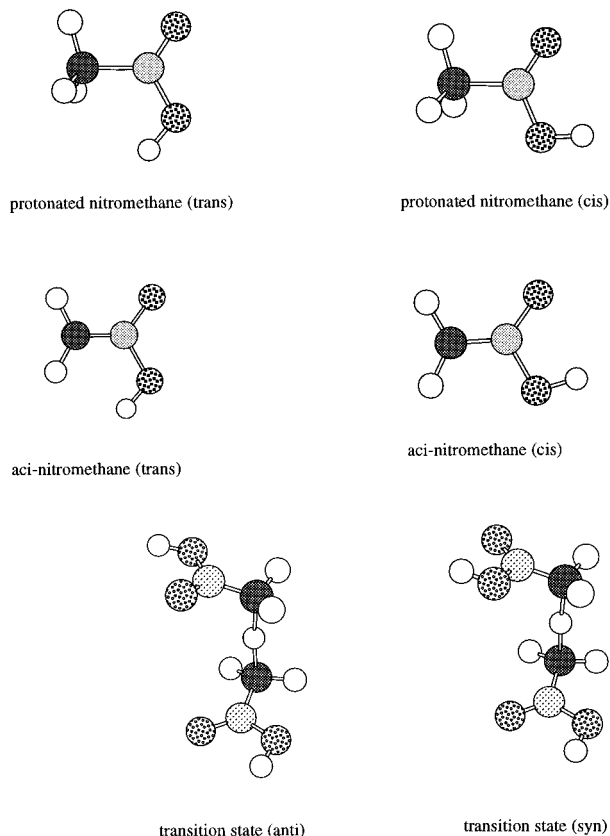
(43) Cybulski, S. M.; Scheiner, S. *J. Am. Chem. Soc.* **1987**, *109*, 4199. See, also: Scheiner, S.; Wang, L. *J. Am. Chem. Soc.* **1992**, *114*, 3650. Scheiner, S. *J. Mol. Struct. (Theochem)* **1994**, *307*, 65.

(44) At MP2/6-311+G**//MP2/6-311+G**.

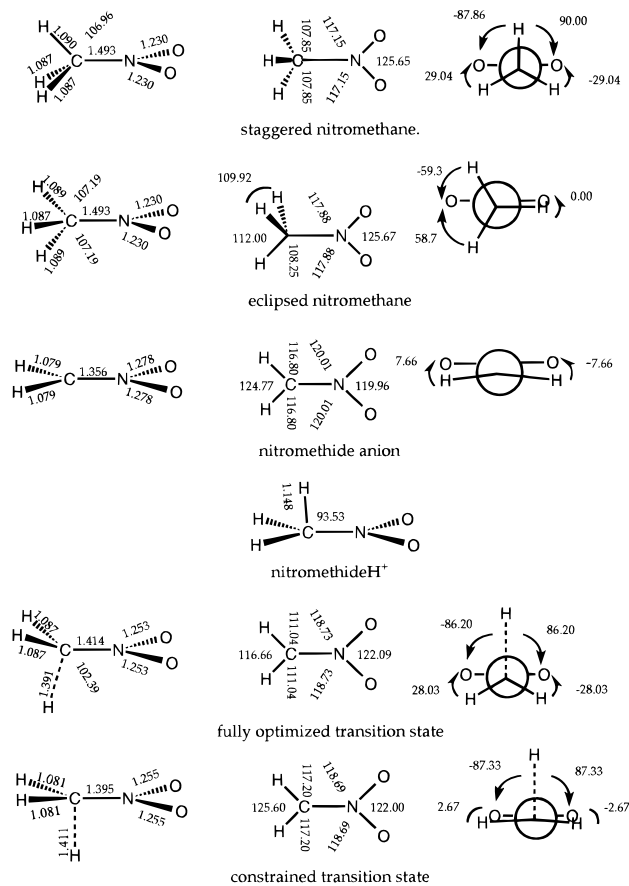
Table 9. Summary of Gas Phase Acidities and Proton Transfer Barriers

system	level	$\Delta H_{\text{barrier}}$, kcal/mol	ΔH_{acid} , kcal/mol	ref
$\text{CH}_3\text{N}^+\text{O}_2\text{H}$ (cis,ecl)/ $\text{CH}_2=\text{NO}_2\text{H}$ (cis)	MP2/6-311+G**//MP2/6-31G**	-1.0	192.6	this work
$\text{CH}_3\text{CH}=\text{O}^+\text{H}$ (syn,ecl)/ $\text{CH}_2=\text{CHOH}$ (syn)	MP2/6-311+G**//MP2/6-311+G**	-1.9	193.0	10b
$\text{CH}_3\text{CH}=\text{O}^+\text{H}$ (anti,ecl)/ $\text{CH}_2=\text{CHOH}$ (anti)	MP2/6-311+G**//MP2/6-311+G**	-5.1	195.0	10b
CH_3NO_2 (ecl)/ $\text{CH}_2=\text{NO}_2^-$	MP2/6-311+G**//MP2/6-311+G**	-7.0 ^a	359.8	this work
$\text{CH}_3\text{CH}=\text{O}$ (ecl)/ $\text{CH}_2=\text{CHO}^-$	MP4/6-31+G**//MP2/6-31+G*	2.9	367.1	9b
$\text{CH}_3\text{CH}=\text{O}$ (ecl)/ $\text{CH}_2=\text{CHO}^-$	MP2/6-311+G**//MP2/6-311+G**	0.3	368.2	10a
$\text{HC}\equiv\text{CH}/\text{HC}\equiv\text{C}^-$	MP4/6-31+G**//MP2/6-31+G*	-4.8	375.1	9b
$\text{CH}_3\text{CN}/\text{CH}_2\text{CN}^-$	MP4/6-31+G**//MP2/6-31+G*	-6.5 ^b	375.9	9b
$\text{CH}_3\text{CH}=\text{CH}_2/\text{CH}_2=\text{CHCH}_2^-$	MP4/6-31+G**//MP2/6-31+G*	7.8 ^b	392.5	9b
$\text{H}_2\text{C}=\text{CH}_2/\text{H}_2\text{C}=\text{CH}^-$	MP4/6-31+G**//MP2/6-31+G*	6.2	408.7	9b
$\text{CH}_4/\text{CH}_3^-$	MP4/6-31+G**//MP2/6-31+G*	10.4 ^b	419.4	9b

^a $\Delta H_{\text{barrier}}$ for reaction through TS(constr) is 9.9 kcal/mol. ^b At MP2/6-31+G**//MP2/6-31+G* $\Delta H_{\text{barrier}}$ is -7.8 kcal/mol for $\text{CH}_3\text{CN}/\text{CH}_2\text{CN}^-$, 6.5 kcal/mol for $\text{CH}_3\text{CH}=\text{CH}_2/\text{CH}_2=\text{CHCH}_2^-$ and 9.8 kcal/mol for $\text{CH}_4/\text{CH}_3^-$.

**Figure 2.** 3-D representations of the various structures relevant to the $\text{CH}_3\text{N}^+\text{O}_2\text{H}/\text{CH}_2=\text{NO}_2\text{H}$ system.

It needs to be stressed that the above analysis relies on the implicit assumption that in the absence of special effects such as resonance or polarizability the barriers for the $\text{CH}_3\text{Y}/\text{CH}_2\text{Y}^-$ systems would follow the correlation line defined by the $\text{CH}_4/\text{CH}_3^-$, $\text{CH}_2=\text{CH}_2/\text{CH}_2=\text{CH}^-$, and $\text{HC}\equiv\text{CH}/\text{HC}\equiv\text{C}^-$ systems. In trying to assess whether or not this assumption is valid one needs to address the possible reasons why the increased acidity in the series $\text{CH}_4 < \text{CH}_2=\text{CH}_2 < \text{HC}\equiv\text{CH}$ leads to lower barriers. The changes in acidity result from changes in hybridization. The more s-character, the more electronegative the orbital is and the more compact the lone pair of the carbanion is. This not only increases the acidity but in the transition state it also enhances the hydrogen bonding between the transferring proton and the two bases (see also ref 43). This hydrogen bonding must be substantial, because the transferring proton carries a positive charge of approximately +0.3^{9c} units which implies that each of the two base fragments carry more than half a negative charge (≈ -0.65). In this way the change in hybridization can have a greater effect on the transition state

**Figure 3.** Geometric parameters at the MP2/6-311+G** level of the various structures relevant to the $\text{CH}_2\text{NO}_2/\text{CH}_2=\text{NO}_2^-$ system.

than on the reactant/product states and a barrier reduction is seen.⁴⁵ In fact from the slope of 0.34⁴⁷ in the Saunders plot we deduce that the transition state receives 134% of the stabilization found in the reactant/product states.

Turning to the $\text{CH}_3\text{Y}/\text{CH}_2=\text{Y}^-$ systems we note that all of them have a lower barrier than the $\text{CH}_4/\text{CH}_3^-$ system. Since by definition reaction progress is 50% at the transition state, this finding implies that all Y-substituents provide more stabilization to the transition state than to the reactant/product states. If there were a perfect balance between the stabilizing

(45) This is reminiscent of a similar situation in the identity proton transfers from first- and second-row nonmetal hydrides to their conjugate bases.⁴⁶

(46) Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258.

(47) (a) According to Kreevoy⁴⁸ this slope should be a measure of the positive charge on the transferring proton at the transition state. The NPA charges on the proton of approximately 0.3 determined by Saunders et al.^{9b} are indeed close to the slope (0.34).

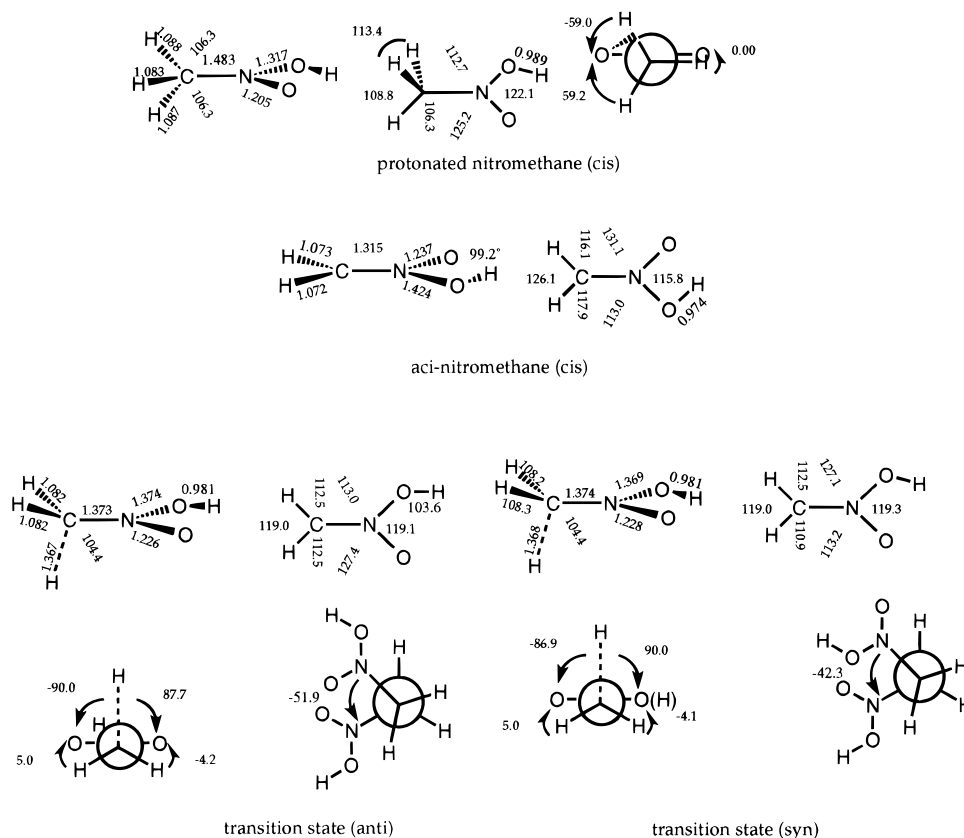


Figure 4. Geometric parameters at the MP2/6-31G** level of the various structures relevant to the $\text{CH}_3\text{N}^+\text{O}_2\text{H}/\text{CH}_2=\text{NO}_2\text{H}$ system.

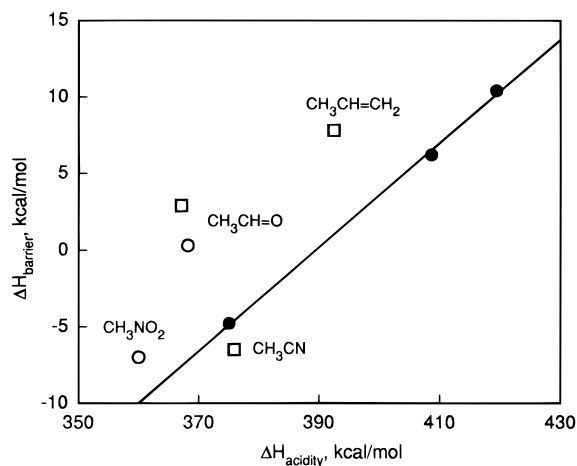


Figure 5. Plot of $\Delta H_{\text{barrier}}$ of identity proton transfers vs ΔH_{acid} of carbon acid. Data from Table 9. ●: $\text{CH}_4/\text{CH}_3^-$, $\text{CH}_2=\text{CH}_2/\text{CH}_2=\text{CH}^-$, $\text{HC}\equiv\text{CH}/\text{HC}\equiv\text{C}^-$ at MP4/6-31+G**//MP2/6-31+G*; ○: $\text{CH}_3\text{CH}=\text{O}/\text{CH}=\text{CHO}^-$, $\text{CH}_3\text{NO}_2/\text{CH}_2=\text{NO}_2^-$ at MP2/6-311+G**//MP2/6-311+G***, □: $\text{CH}_3\text{CH}=\text{CH}_2/\text{CH}_2=\text{CHCH}_2^-$, $\text{CH}_3\text{CN}/\text{CH}_2\text{CN}^-$, $\text{CH}_3\text{-CH}=\text{O}/\text{CH}_2=\text{CHO}^-$ at MP4/6-31+G**//MP2/6-31+G*.

effect of Y in the transition state and the reactant/product state, each fragment (CH_2Y) of the transition state would attain 50% of the stabilization that Y provides to the reactant/product states. I.e., the sum of the stabilization for the two transition state fragments would equal the stabilization found in the reactant/product states and the Y-group would have the same effect on reactants/products as on the transition state in every case. In other words, in a reaction series with perfectly balanced transition states the increased acidity of CH_3Y is exactly canceled by the decreased basicity of $\text{CH}_2=\text{Y}^-$ and the plot of barrier vs. acidity would have a zero slope.

What conclusions can be drawn from the fact that the barriers for the $\text{CH}_3\text{Y}/\text{CH}_2=\text{Y}^-$ systems deviate from the line in Figure

5? The only *certain* conclusion is that for the points that fall above the line the Y-group provides less than 134%, for the point that falls below the line the Y-group provides more than 134% of the transition state stabilization that results from changes in hybridization. However even for the points that fall above the line, the Y-groups provide more than 100% because these systems have lower barriers than the $\text{CH}_4/\text{CH}_3^-$ system.

The difficulty with interpreting the deviations from the Saunders line is that on this line changes in acidity and barrier result from changes in hybridization, while for the $\text{CH}_3\text{Y}/\text{CH}_2=\text{Y}^-$ systems the changes are the combined result of inductive/field, resonance, and possibly polarizability effects of the Y group. Hence, whether or not a point is on or off the line cannot provide definitive evidence for a particular effect.

We therefore propose a different analysis. We start with the premise that inductive/field and resonance effects are the most important factors that determine both the acidities and the barriers. This suggests that eqs 14 and 15 should hold, with $\Delta\Delta H_{\text{acid}} = \Delta H_{\text{acid}}(\text{CH}_4) - \Delta H_{\text{acid}}(\text{CH}_3\text{Y})$ and $\Delta\Delta H_{\text{barrier}} =$

$$\Delta\Delta H_{\text{acid}} = \rho_{\text{F}}^{\circ}\sigma_{\text{F}} + \rho_{\text{R}}^{\circ}\sigma_{\text{R}} \quad (14)$$

$$\Delta\Delta H_{\text{barrier}} = \rho_{\text{F}}^{\ddagger}\sigma_{\text{F}} + \rho_{\text{R}}^{\ddagger}\sigma_{\text{R}} \quad (15)$$

$\Delta H_{\text{barrier}}(\text{CH}_4/\text{CH}_3^-) - \Delta H_{\text{barrier}}(\text{CH}_3\text{Y}/\text{CH}_2=\text{Y}^-)$; σ_{F} and σ_{R} are the gas phase field effect and resonance substituent parameters,²⁸ respectively. The two-parameter fits of ΔH_{acid} and $\Delta H_{\text{barrier}}$,⁴⁹ shown in Figures 6 and 7, respectively, are indeed quite good, with r^2 values of 0.986 for the acidity and $r^2 = 0.995$ for the barrier. This supports the validity of eqs 14 and 15. They yield $\rho_{\text{F}}^{\circ} = 45.5$ and $\rho_{\text{R}}^{\circ} = 177.8$ for the acidities, and $\rho_{\text{F}}^{\ddagger} = 25.8$ and

(48) Kreevoy, M. M.; Lee, I. H. *J. Am. Chem. Soc.* **1984**, *106*, 2550.

(49) For the $\text{CH}_4/\text{CH}_3^-$, $\text{CH}_3\text{CN}/\text{CH}_2\text{CN}^-$, and $\text{CH}_3\text{CH}=\text{CH}_2/\text{CH}_2=\text{CH-CH}_2$ systems $\Delta H_{\text{barrier}}$ calculated at the MP2/6-31+G**//MP2/6-31+G* level^{9b} (see footnote in Table 9) were used.

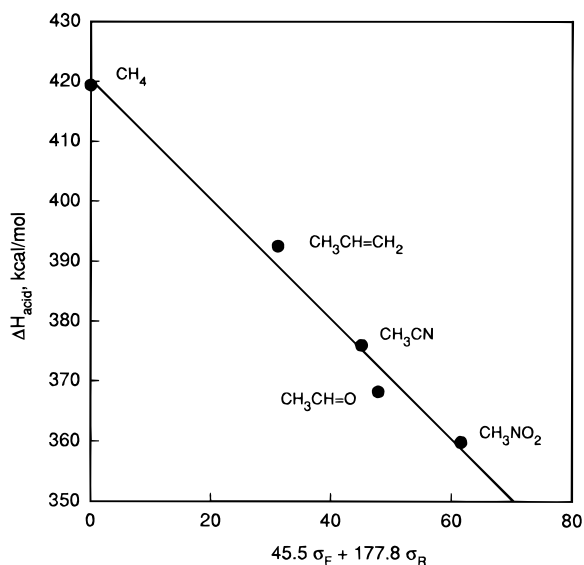


Figure 6. Plot of ΔH_{acid} vs. $\rho_{\text{F}}^{\ddagger} \sigma_{\text{F}} + \rho_{\text{R}}^{\ddagger} \sigma_{\text{R}}$; ρ -values obtained by least squares fitting.

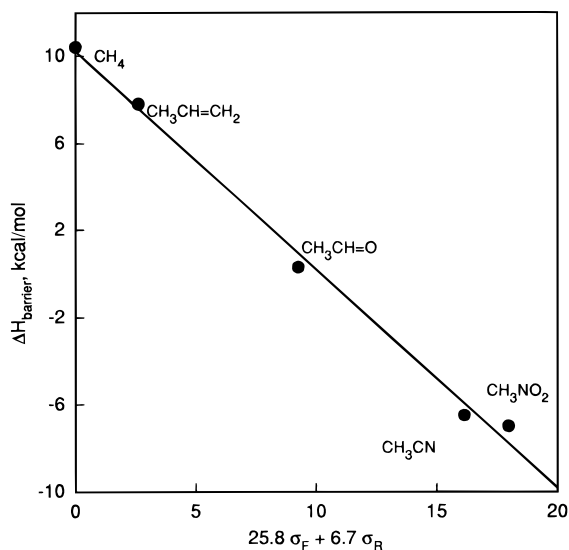


Figure 7. Plot of $\Delta H_{\text{barrier}}$ vs. $\rho_{\text{F}}^{\ddagger} \sigma_{\text{F}} + \rho_{\text{R}}^{\ddagger} \sigma_{\text{R}}$; ρ -values obtained by least squares fitting.

$\rho_{\text{R}}^{\ddagger} = 6.7$ for the barriers. The contributions of the inductive/field and resonance effects to $\Delta\Delta H_{\text{acid}}$ ($\rho_{\text{F}}^{\ddagger} \sigma_{\text{F}}$ and $\rho_{\text{R}}^{\ddagger} \sigma_{\text{R}}$) and $\Delta\Delta H_{\text{barrier}}$ ($\rho_{\text{F}}^{\ddagger} \sigma_{\text{F}}$ and $\rho_{\text{R}}^{\ddagger} \sigma_{\text{R}}$) are summarized in Table 10.

The interpretation of the ρ values for the acidities is straightforward; they indicate that resonance is the dominant factor in the stabilization of all the anions except for CH_2CN^- (Table 10). With respect to $\rho_{\text{F}}^{\ddagger}$ and $\rho_{\text{R}}^{\ddagger}$, in keeping with the reasoning used in explaining the effect of changing hybridization, their positive values imply that both the inductive/field effect and the resonance effect on the transition state are greater than on the reactant/product states. Specifically, the transition state enjoys 157% ($100 \times (\rho_{\text{F}}^{\ddagger} + \rho_{\text{F}}^{\ddagger})/\rho_{\text{F}}^{\ddagger}$) of the inductive/field effect stabilization and about 104% ($100 \times (\rho_{\text{R}}^{\ddagger} + \rho_{\text{R}}^{\ddagger})/\rho_{\text{R}}^{\ddagger}$) of the resonance stabilization found in the reactant/product states. The following conclusions emerge from this analysis.

(1) The exalted stabilizing effects on the transition state may be attributed to the fact that both CH_2Y fragments carry more than half a negative charge (Table 3). This not only magnifies the substituent effect resulting from the interaction of the Y group with the negative charge but also leads to additional transition state stabilization by electrostatic/hydrogen bonding

effects between the positive transferring proton and the negative fragments.

(2) The particularly strong barrier lowering influence of the inductive/field effect results from the fact that each CH_2 group at the transition state carries more than half of the negative charge that resides on the CH_2 group in the anion $\text{CH}_2=\text{Y}^-$. This is a consequence of the imbalance as well as of the CH_2Y fragments at the transition state each carrying more than half a negative charge.

(3) The much smaller resonance compared to the inductive/field effect on the barriers is, of course, a direct result of the transition state imbalance. If there were no imbalance, the ratio of inductive/field effect to resonance effect on the barrier should be the same as on the acidities, i.e., $\rho_{\text{F}}^{\ddagger}/\rho_{\text{R}}^{\ddagger} = \rho_{\text{F}}^{\ddagger}/\rho_{\text{R}}^{\ddagger}$. The imbalance increases the $\rho_{\text{F}}^{\ddagger}/\rho_{\text{R}}^{\ddagger}$ ratio not only by reducing the resonance effect but also by enhancing the inductive/field effect. This is because in the imbalanced transition state there is more negative charge on the CH_2 moiety for Y to interact with than in a more balanced transition state.

(4) It is noteworthy that despite the imbalance, resonance has actually a small barrier *lowering* effect rather than the usual barrier enhancing effect found in solution. This is another consequence of the large negative charge on the CH_2Y fragments of the transition state.

(5) The importance of electrostatic/hydrogen bonding effects on the barriers can be further observed by comparing TS(constr) with TS(optim). In the $\text{CH}_3\text{NO}_2/\text{CH}_2=\text{NO}_2^-$ system the barrier through TS(constr) is 16.8 kcal/mol higher than that through TS(optim) (Table 1), while in the $\text{CH}_3\text{CH}=\text{O}/\text{CH}_2=\text{CHO}^-$ system the energy of TS(constr) exceeds that of TS(optim) by 10.5 kcal/mol.^{10a} The higher energy of TS(constr), despite the larger resonance effect, probably results mainly from the fact that the product of the positive charge on the proton and the negative charge on the CH_2 groups (Table 3)⁵⁰ is smaller for TS(constr) than for TS(optim) which reduces the electrostatic/hydrogen bonding stabilization. Further, to the extent that resonance delocalization of the negative charge into the NO_2 groups occurs, the inductive/field effect of these groups is diminished. The greater tightness of TS(optim) seen in the shorter C—H—C distances ($2 \times 1.391 \text{ \AA}$ vs. $2 \times 1.411 \text{ \AA}$ for CH_3NO_2 ,⁴⁴ $2 \times 1.447 \text{ \AA}$ vs. $2 \times 1.484 \text{ \AA}$ for $\text{CH}_3\text{CH}=\text{O}$ ⁵¹) is likely to play a stabilizing role as well although this effect may be a consequence of the electrostatic effect rather than an independent factor.

(6) Our conclusion with respect to resonance effects is similar to that presented by Saunders et al.^{9b} except that our reference point is the $\text{CH}_4/\text{CH}_3^-$ system while theirs is the correlation line of Figure 5. Saunders et al. do not specifically mention inductive/field effects on barriers, but one may presume that the correlation line in Figure 5 is a reasonable approximation of the relationship between inductive/field effects on barriers and acidities. Our analysis does not allow conclusions regarding the potential role played by polarizability. However, if the gas phase polarizability substituent parameters, σ_{α} ,²⁸ are used as a guide, the polarizability effect should increase in the order NO_2 ($\sigma_{\alpha} = -0.26$) < $\text{CH}=\text{O}$ ($\sigma_{\alpha} = -0.46$) = CN ($\sigma_{\alpha} = -0.46$) < $\text{CH}=\text{CH}_2$ ($\sigma_{\alpha} = -0.50$). This means that the cyano group should not stand out with respect to a potential barrier lowering polarizability effect.

B. Barriers in $\text{CH}_3\text{Y}^+/\text{CH}_2=\text{Y}$ Systems. $\text{CH}_3\text{N}^+\text{O}_2\text{H}$ is about 168 kcal/mol more acidic than CH_3NO_2 and CH_3-

(50) For the $\text{CH}_3\text{CH}=\text{O}/\text{CH}_3=\text{CHO}^-$ system the Mulliken group charges at the MP2/6-311+G**//HF/6-311+G** level are for TS(optim): CH_2 , -0.362; H, 0.285; TS(constr): CH_2 , -0.270; H, 0.187.^{10a}

(51) At MP2/6-311+G**//HF/6-311+G**.^{10a}

Table 10. Dissection of the Contribution of Inductive/Field and Resonance Effects to $\Delta\Delta H_{\text{acid}}$ and $\Delta\Delta H_{\text{barrier}}$

	σ_{F}^b	σ_{R}^b	$\Delta\Delta H_{\text{acid}}^a$		$\Delta\Delta H_{\text{barrier}}^a$	
			$\rho_{\text{F}}^{\circ}\sigma_{\text{F}}$	$\rho_{\text{R}}^{\circ}\sigma_{\text{R}}$	$\rho_{\text{F}}^{\ddagger}\sigma_{\text{F}}$	$\rho_{\text{R}}^{\ddagger}\sigma_{\text{R}}$
$\text{CH}_4/\text{CH}_3^-$	0	0	0	0	0	0
$\text{CH}_3\text{CH}=\text{CH}_2/\text{CH}_2=\text{CHCH}_2^-$	0.06	0.16	2.7	28.4	1.5	1.1
$\text{CH}_3\text{CH}=\text{O}/\text{CH}_2=\text{CHO}^-$	0.31	0.19	14.1	33.8	8.0	1.3
$\text{CH}_3\text{NO}_2/\text{CH}_2=\text{NO}_2^-$	0.65	0.18	29.6	32.0	16.8	1.2
$\text{CH}_3\text{CN}/\text{CH}_2\text{CN}^-$	0.60	0.10	27.3	17.8	15.5	0.7

^a In kcal/mol. ^b Reference 28.

$\text{CH}=\text{O}^+\text{H}$ is about 175 kcal/mol more acidic than $\text{CH}_3\text{CH}=\text{O}$ (Table 9), yet the barriers for their deprotonation fall within the same range as the barriers for the deprotonation of $\text{CH}_3\text{-NO}_2$ and $\text{CH}_3\text{CH}=\text{O}$. This shows that the $\text{CH}_3\text{Y}^+/\text{CH}_2=\text{Y}$ systems constitute a different family with much higher barriers relative to their acidities than the $\text{CH}_3\text{Y}/\text{CH}_2=\text{Y}^-$ systems.

The most important reason for the higher barrier is likely to be the electrostatic or hydrogen bonding effect that arises from the interaction of the positively charged transferred proton with the CH_2 group and/or the entire CH_2Y fragments at the transition state. In the $\text{CH}_3\text{Y}/\text{CH}_2=\text{Y}^-$ systems the CH_2Y fragments are negatively charged which leads to a strong stabilizing interaction with the transferred proton and a concomitant reduction of the barrier. In the $\text{CH}_3\text{Y}^+/\text{CH}_2=\text{Y}$ systems the electrostatic stabilization is lost altogether and even replaced by a destabilization since the CH_2Y moieties in the transition state are positively charged and this is expected to lead to a substantial increase in the barrier. The notion that these electrostatic effects are likely to be important is supported by observations in the study of the barriers of identity proton transfers between nonmetal hydrides and their conjugate anions.⁴⁶ Within the group of first-row hydrides there is a good correlation between barriers and acidities, and the same is true within the group of second-row hydrides. However, for a given acidity, the barriers for the second-row hydrides are much higher than for the first-row hydrides. This difference was attributed to the fact that in the transition states of the first-row systems the transferred proton is strongly positive which leads to electrostatic and hydrogen bonding stabilization, while in the second-row systems the proton is negative which leads to electrostatic destabilization.

C. Comparison with Solution Reactions. With regard to the relative importance of the various barrier affecting factors, there are some significant differences between gas and solution phase reactions. In the gas phase inductive/field and electrostatic/hydrogen bonding effects are dominant and lead to a decrease in the barrier. Resonance effects also lower the barrier, but the effect is very small because of the imbalance. In solution the imbalance factor which leads to a substantial increase in the barrier is dominant. This reversal is not unreasonable. In solution, solvation of the negative charge on the Y group enhances the resonance stabilization of $\text{CH}_2=\text{Y}^-$ which makes $\delta\Delta G_{\text{res}}^{\circ}$ more negative (eq 1) and thus increases the barrier enhancing effect of the imbalance. There may also be an increase in the imbalance, n , as discussed in ref 10a, which would lead to a smaller λ_{res} (see eq 13) and a larger $|\lambda_{\text{res}} - \beta|$ in eq 1, i.e., a further enhancement of the barrier. On the other hand, the high dielectric constant of the medium strongly attenuates any effect which has to do with charges such as the electrostatic/hydrogen bonding effect⁵² and the inductive/field

(52) Electrostatic/hydrogen bonding effects do play a significant role in proton transfers from normal acids to normal bases⁵³ but can sometimes affect barriers in proton transfers from carbon acids as well.⁵⁴ Field effects exerted by remote substituents have also been shown to affect the intrinsic barriers of proton transfers from carbon acids activated by π -acceptors;^{3,4a} this effect is again not the result of some special characteristics of the substituent but a consequence of the imbalance.

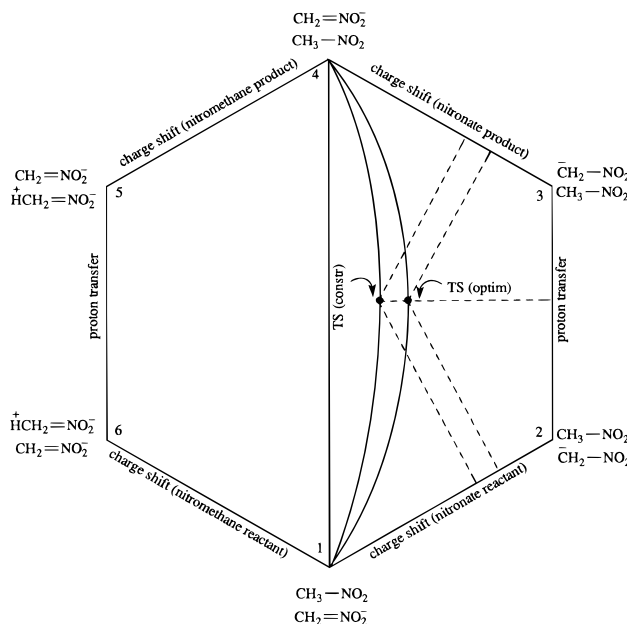
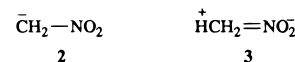


Figure 8. More O'Ferrall-Jencks diagram with separate axes for proton transfer and charge shifts, illustrating the imbalance in eq 3.

effect. In the gas phase, these latter effects are large, while the absence of solvation decreases the resonance stabilization of $\text{CH}_2=\text{Y}^-$ and thus reduces the barrier enhancing effect of the imbalance. As the comparison between $\text{TS}(\text{optim})$ and $\text{TS}(\text{constr})$ indicates, the barrier enhancing effect of the resonance/imbalance can be more than offset by a stronger electrostatic/hydrogen bonding effect.

More O'Ferrall-Jencks Diagrams. Reactions with imbalanced transition states are conveniently described by More O'Ferrall⁵⁵-Jencks⁵⁶ diagrams. In reactions where both proton donor and proton acceptor contain a π -acceptor, there may be a 2-fold imbalance which requires a representation by a six-corner diagram.⁵⁷ Such a diagram is shown in Figure 8 for the $\text{CH}_3\text{NO}_2/\text{CH}_2=\text{NO}_2^-$ system. Corners 1 and 4 are the reactants and products, respectively. Corners 2 and 3 are hypothetical states in which the nitromethane anion has undergone localization of the charge on the carbon (2), while corners 5 and 6 are hypothetical states in which the



nitromethane has been polarized in a manner shown in 3.

(53) (a) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, 3, 1. (b) *Proton Transfer Reactions*; Caldin, E. F., Gold, V., Eds.; Wiley & Sons: New York, 1975. (c) Hibbert, F. *Compr. Chem. Kin.* **1977**, 8, 97.

(54) (a) Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, 107, 7117. (b) Bernasconi, C. F.; Wiersema, D.; Stronach, M. W. *J. Org. Chem.* **1993**, 58, 217.

(55) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274.

(56) Jencks, W. P. *Chem. Rev.* **1972**, 72, 705.

(57) For a more detailed description of various features of such six-corner diagrams, see ref 10a.

Approximate energies have been calculated for **2** and **3** (Table S1),¹³ while ΔH for the conversion of $\text{CH}_2=\text{NO}_2^-$ into **2** and of CH_3NO_2 into **3** is reported in Table 1. At the MP2/6-311+G**//MP2/6-311+G** level, corners 5 and 6 are seen to be 34.3 kcal/mol above the level of reactants and products, while corners 2 and 3 are 9.4 kcal/mol higher in enthalpy than corners 1 and 4. This indicates that the energy surface defined by the diagram exhibits a strong downward tilt from left to right, suggesting that the reaction coordinate should be located in the right half of the diagram. This is consistent with the observed imbalance according to which charge shift from the nitro group toward the carbon of the reactant nitromethide anion is ahead of proton transfer and the charge shift from the carbon to the nitro group in the incipient product nitromethide anion lags behind proton transfer. We also note that the smaller imbalance observed for TS(constr) requires placement of this transition state to the left of TS(optim) but still in the right half of the diagram; this move to the left is also the direction of increased energy, consistent with the higher energy calculated for TS-(constr).

The features and conclusions from Figure 8 are very similar to those obtained from the corresponding diagram for the $\text{CH}_3\text{CH}=\text{O}/\text{CH}_2=\text{CHO}^-$ system,^{10a} including the left-to-right downward tilt of the surface and the relative placement of TS(optim) and TS(constr) within the right half of the diagram. What is particularly noteworthy is that in the $\text{CH}_3\text{CH}=\text{O}/\text{CH}_2=\text{CHO}^-$ system there is a smaller energy difference (15 kcal/mol) between corners 5 and 6 ($\text{H}^+\text{CH}_2=\text{CH}-\text{O}^- + \text{CH}_2=\text{CHO}^-$), on the one hand and corners 2 and 3 ($\text{CH}_3\text{CH}=\text{O} + \bar{\text{C}}\text{H}_2-\text{CH}=\text{O}$), on the other hand than in the $\text{CH}_3\text{NO}_2/\text{CH}_2\text{NO}_2^-$ system (24.9 kcal/mol). This should place the transition state of the $\text{CH}_3\text{CH}=\text{O}/\text{CH}_2=\text{CHO}^-$ system to the left of that of the $\text{CH}_3\text{NO}_2/\text{CH}_2\text{NO}_2^-$ system, in agreement with the smaller n value.

Conclusions. It is well established that in solution proton transfer from carbon acids activated by π -acceptors the intrinsic barrier is dominated by the influence of the π -acceptor; in a nutshell stronger π -acceptors lead to higher intrinsic barriers, because charge delocalization and concomitant solvation at the transition state lags behind proton transfer (transition state imbalance). Our calculations on the reactions shown in eqs 3 and 4 as well as similar calculations for the $\text{CH}_3\text{CH}=\text{O}/\text{CH}_2=\text{CHO}^-$ and $\text{CH}_3\text{CH}=\text{O}^+\text{H}/\text{CH}_2=\text{CHOH}$ systems reported previously indicate that transition state imbalances are not just a solvation induced phenomenon but also prevail in the gas phase.

The most important general conclusion from the present study is that, in contrast to solution reactions, the transition state imbalances do not lead to a significant increase in the intrinsic gas phase barriers (in fact there is a slight decrease). The reason for this unexpected finding is that the weak resonance development at the transition state is offset by the fact that the total amount of charge on the two CH_2Y fragments available for delocalization is significantly greater than in $\text{CH}_2=\text{Y}^-$. On the other hand, inductive/field and electrostatic/hydrogen bonding effects have a very strong influence on the gas phase intrinsic barrier. This is again a consequence of the greater total amount of negative charge on the two CH_2Y fragments in the transition state compared to the charge on $\text{CH}_2=\text{Y}^-$, combined with the absence of a dielectric medium. The result is a lowering of the barrier. In solution the inductive/field and electrostatic/hydrogen bonding effects are greatly attenuated, while at the same time the resonance effect is enhanced by solvation, making resonance/imbalance effects the dominant influence.

Some more specific conclusions from this work relate to the

degree of imbalance as a function of the Y substituent. For example, the imbalance calculated for the $\text{CH}_3\text{NO}_2/\text{CH}_2=\text{NO}_2^-$ system is somewhat larger than for other $\text{CH}_3\text{Y}/\text{CH}_2=\text{Y}^-$ systems, with n following the order $\text{NO}_2 \geq \text{CH}=\text{CH}_2 \geq \text{CH}=\text{O} > \text{CN}$. This corresponds roughly to the order of the gas phase resonance substituent effect parameters σ_R , consistent with the notion that the imbalance increases with π -acceptor strength of Y. These results indicate that, in contrast to findings in solution proton transfers, the nitro group does not stand out among π -acceptors in terms of producing extraordinarily large imbalances in gas phase proton transfers. This supports the notion that the strong solvation of nitronate ions, especially in protic solvents, contributes greatly to the imbalance in solution reactions.

Regarding the $\text{CH}_3\text{N}^+\text{O}_2\text{H}/\text{CH}_2=\text{NO}_2\text{H}$ system, in contrast to previous findings that n is larger for the cationic $\text{CH}=\text{O}^+\text{H}$ compared to the neutral $\text{CH}=\text{O}$ group, n for $\text{N}^+\text{O}_2\text{H}$ appears to be somewhat smaller than for NO_2 , at least based on NPA charges. A slightly smaller imbalance for $\text{N}^+\text{O}_2\text{H}$ compared to NO_2 is also suggested by the geometric parameters, a conclusion which is further supported by solution phase data.³⁷

Methods

Optimizations, force field calculations, and Møller–Plesset⁵⁸ calculations were carried out using the GAUSSIAN 92 suites of programs.⁵⁹ The standard basis sets were used with diffuse (+) and polarization functions (d on second row, p on hydrogen atoms) described by Pople.^{59,60} Optimizations were performed using MP2 gradients at 6-311+G** or 6-31G** with SCF=DIRECT. Since force fields could not be practically computed for the transition states at the MP2 level, the force fields at RHF/6-311+G** and RHF/6-31G** optimized geometry was used, scaled by 0.91.⁶¹

Fully Optimized Transition State. A Z-matrix⁶⁰ was constructed exploiting the symmetry of the transition state. Variables were assigned such that the transferred proton represented a point of inversion for each assigned parameter in the structure. During optimization rotation about the CHC axis was relaxed, and the symmetry operators were turned off to allow for a change in point group. No such change was observed; the optimized structure belonged to the C_{2h} point group.

Constrained Transition State. Optimization was as above with the dihedral angle for the nontransferred hydrogens fixed at 90.0° . The dihedral angle in this instance is defined between the planes (1) determined by the transferred hydrogen, methylene carbon, and the nitrogen atom and (2) non-transferred hydrogen, methylene carbon, and nitrogen atom. No other constraints were imposed. The structure belongs to the C_{2h} point group.

$^-\text{CH}_2\text{NO}_2$, $^-\text{CH}_2\text{NO}_2(\text{e})$ and $^-\text{CH}_2\text{NO}_2(\text{s})$ refers to structures derived from the optimized nitromethane structures. Nitromethane(s) is the nitromethane molecule with one of the methyl hydrogens fixed at a 90.0° dihedral relative to one of the oxygens of the nitro group. Nitromethane(e) is the nitromethane molecule with one of the methyl hydrogens fixed at a 0.0° dihedral relative to one of the oxygens of the nitro group. The corresponding $^-\text{CH}_2\text{NO}_2$ structures are generated by removing a hydrogen, as its ion, and running a frequency calculation on the remaining anionic fragment. $^-\text{CH}_2\text{NO}_2(\text{s})$ has the hydrogen ion removed from a point above the plane of the nitro group, $^-\text{CH}_2\text{NO}_2(\text{e})$ from within the plane of the nitro group.

(58) (a) Moeller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91. (c) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244. (d) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 281.

(59) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gompers, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92, Revision B*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(60) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(61) Pople, J. A.; Scott, A. P.; Long, M. W.; Radom, L. *Isr. J. Chem.* **1995**, *33*, 345.

$\text{H}^+\text{CH}_2=\text{NO}_2^-$. This structure was fully optimized yielding a C_{2v} point group symmetric structure at the RHF levels. The structure is slightly pyramidalized when optimized using the MP2 method at either basis set for which MP2 was employed. To generate the $\text{H}^+\text{CH}_2=\text{NO}_2^-$ a hydrogen ion was added to the nitronate ion structure. The HCN angle and the C—H bond distance was allowed to vary, but the proton was fixed above the plane of the nitro group by fixing the dihedral angle to one of the oxygen atoms to 90.0° . In the case of the pyramidalized structure care was taken to fix the hydrogen above the nitro group, opposite the face to which the non transferred hydrogens pointed.

Acknowledgment. This work has been supported by Grants No. CHE-9307659 (CFB) and CHE-9208895 (SG) from the

National Science Foundation. Additional support was provided by NSF Grants through the San Diego Supercomputing Center on the CRAY 90, account numbers CSC202 and CSC651, and through the Pittsburgh Computing Center on the CRAY YMP/832, Grant No. CH#920015P. We are also indebted to Professor William H. Saunders, Jr. for providing us with unpublished results.

Supporting Information Available: Tables S1–S8, energies, and group charge differences (15 pages). See any current masthead page for ordering and Internet access instructions.

JA963492H