cipitation of TMED·2BH_3 was complete within 0.5 h at 25 °C. The precipitate was then removed by centrifugation. The solution now contained ~10% Ipc_2BH.

Application of 8. Asymmetric Hydroboration of 1-Methylcyclopentene. The above reaction mixture was cooled to −25 °C, and 4.25 mL (40 mmol) of 1-methylcyclopentene added with stirring. The hydroboration was allowed to proceed for 4 h at −25 °C. The reaction mixture was then warmed to 0 °C, and 3.0 mL of water added to destroy excess hydride. This was followed by the addition of 16 mL of 3 M sodium hydroxide and 12.5 mL of 30% aqueous hydrogen peroxide. The reaction mixture was stirred at 50 °C for 1 h and cooled to 25 °C and the aqueous layer extracted with ether. The combined organic layer was washed twice with 2 × 20 mL of saturated brine solution. Following drying over anhydrous magnesium sulfate, the solvent was removed in a rotavapor under 15 mm of pressure. Distillation of the residue yielded 3.0 g (75%) of *trans*-2-methylcyclopentanol, bp 72–3 °C (16 mm). The alcohol was then purified by preparative GC through a 20% SE-30 column: n^{20}_D 1.4494. $[\alpha]^{23}_D$ +31.6°, 72% ee.

Methyl Nitrate, Hydrazoic Acid, and Their Conjugate Acids. A Configuration Interaction Study of the Gas-Phase Proton Transfer Equilibrium and of Acid-Catalyzed Fragmentation Reactions

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Methyl nitrate, hydrazoic acid, their conjugate acids, and selected reactions were studied with ab initio methods. Potential energy surfaces were explored at the RHF/6-31G* level, and electron correlation effects were estimated with third- or full fourth-order perturbation theory and with configuration interaction methods using the 6-31G*, 6-311G**, and 6-311G (df,p) basis sets. CH_3ONO_2 and its conjugate acids were also studied with semiempirical methods (MNDO, AM1, PM3). Relative isomer stabilities and conformational preferences of protonated CH_3ONO_2 are reported. Ester-O protonation is preferred over O_{term} protonation, and *inter*molecular proton transfer is more likely for their gas-phase isomerization. Aminodiazonium ion is greatly preferred over iminodiazenium ion, by 27.1 kcal/mol at CISD/6-311G**//MP2/6-31G*+ΔVZPE. In good agreement with experiment, the reaction energy of $\Delta E_3 = 2.9$ kcal/mol was found for the proton-transfer reaction $CH_3ONO_2 + H_2N_3^+ \Leftrightarrow (CH_3ONO_2)H^+ + HN_3$ at CISD/6-311G**//RHF/6-31G*+ΔVZPE. At this level, the gas-phase proton affinities of HN_3 and CH_3ONO_2 are $\Delta E_1 = 187.6$ and $\Delta E_2 = 184.7$ kcal/mol, respectively. The PA(HN_3) at this level is within 1 kcal/mol of our best value obtained at CISD/6-311G(df,p)//MP2/6-31G*. These theoretical results suggest that the reported experimental proton affinity of HN_3 (176.6 kcal/mol) might be too low as a consequence of evaluating the proton transfer equilibrium with an underestimated proton affinity of CH_3ONO_2. Ester-O protonated CH_3ONO_2 is best described as methanol-solvated NO_2^+, and its dissociation requires only 17.5 kcal/mol at CISD/6-311G**//RHF/6-31G*+ΔVZPE. In sharp contrast to prior semiempirical results, dediazotization of aminodiazonium ion is endothermic by 73.6 kcal/mol at CISD/6-311G(df,p)//RHF/6-31G*+ΔVZPE.

Introduction

Aliphatic diazonium ions are highly reactive intermediates in various deamination reactions[1] that are pertinent to synthetic organic chemistry as well as to the understanding of toxicological problems.[2] Since aliphatic diazonium ions have eluded a comprehensive characterization by physical organic techniques,[3] we have studied aliphatic diazonium ions with modern theoretical methods. Our studies of the bonding and the stability of prototypical diazonium ions[4–6] revealed that the *formal* charges in the commonly used Lewis structure do not appropriately reflect the *actual* charge distributions. A new bonding model was proposed that is consistent with their electron density distributions, and this model was shown to apply also to diazonium dication[7] and to aromatic diazonium ions,[8] and it was shown to be fully consistent with structural features associated with "incipient nucleophilic attack" in diazonium ions with proximate nucleophiles.[9] We were able to establish another crucial link between theory and experiment recently with the first single-crystal X-ray structure determination of an *aliphatic* diazonium ion.[10] Heterosubstituted diazonium ions[11,12] $(XNN)^+$, where X is F, HO, and NH_2,[13] were studied to further probe the nature of aliphatic diazonium ions and because they allow for another opportunity to compare theory with experiment. Cacace et al.[14] recently reported a joint ab initio and mass spectrometric study of aminodiazonium ion, and

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† Part of the projected Ph.D. dissertation of G.S.-C. Choy.

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(2) For reviews see chapters 12–14 in *Chemical Carcinogens*; Searle, Ch. E., Ed.; ACS Monograph 182; American Chemical Society: Washington, DC, 1984; Vol. 2.

(3) Alkyldiazonium ions have been observed in superacid media, and methyldiazonium ion has been studied in the gas phase. In the solid-state, alkyldiazonium ions can be stabilized in transition element complexes, but the alkyldiazonium ligands greatly differ from the free ions. See ref 4 and references cited therein.

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an experimental value of 176.6 ± 1.0 kcal/mol was given for the proton affinity of hydrazoic acid. While this value agrees excellently with their calculated MP2/6-31G*//RHF/6-31G* value, its agreement with our *higher* level calculations[13] is less satisfactory.

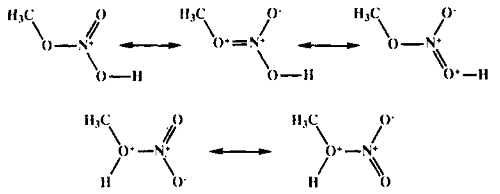
In this article, we first report the result of a study of the proton affinity of hydrazoic acid, reaction 1, at higher correlated levels of theory to confirm our earlier results. We then present results on methyl nitrate and its conjugate acids and report energies for the protonation, reaction 2.

$$HN_3 + H^+ \rightleftarrows H_2N_3^+ \tag{1}$$

$$CH_3ONO_2 + H^+ \rightleftarrows (CH_3ONO_2)H^+ \tag{2}$$

$$CH_3ONO_2 + H_2N_3^+ \rightleftarrows (CH_3ONO_2)H^+ + HN_3 \tag{3}$$

The proton affinity of methylnitrate is crucial for the determination of the proton affinity of HN_3 by Cacace et al. as the proton affinity of HN_3 was determined via the measurement of the equilibrium constant of reaction 3. Methyl nitrate and other esters of nitric acid are important nitrating agents in alkaline media as well as with proton and Lewis acid catalysts.[15] Several isomers of the conjugate acid of methyl nitrate are considered with regard to the regiochemistry of protonation and with regard to the methyl conformation. Preferential protonation at one of the terminal NO_2 oxygens might be expected because such protonation would allow for Y-conjugation in the protonated system while ester-O protonation does not. However, studies by Dewar et al.[16] suggested that ester-O protonation is greatly favored (>20 kcal/mol). Energies for the fragmentation reaction of protonated methyl nitrate leading to the nitrating reagent, reaction 4, are reported. With the higher level energies for hydrazoic acid and aminodiazonium ion, we also report reaction energies for the dediazotization reaction of aminodiazonium ion, reaction 5.



$$(CH_3ONO_2)H^+ \rightleftarrows CH_3OH + NO_2^+ \tag{4}$$

$$H_2N_3^+ \rightleftarrows NH_2^+ + N_2 \tag{5}$$

Table I. Hydrazoic Acid and Aminodiazonium Ion[a,b]

	energy		
method	HN_3	$H_2N_3^+$, **2a**	ΔE_1
RHF/6-31G* = A	−163.838696	−164.153431	197.50
MP2(full)/6-31G*//A	−164.34214[c]	−164.63402[c]	183.16
MP2(fc)/6-31G*//A	−164.331666	−164.623557	183.16
MP3(fc)/6-31G*//A	−164.321111	−164.624852	190.60
CISD(fc)/6-31G*//A	−164.278600	−164.584430	191.91
CISD(fc,ssc)/6-31G*//A	−164.335692	−164.638320	189.90
MP2(fu)/6-31G* = B	−164.351248	−164.643299	183.26
MP2(fc)/6-311G**/A	−164.406673	−164.706365	188.06
MP3(fc)/6-311G**//A	−164.391837	−164.704534	196.22
MP4(fc,sdtq)/6-311G**//A	−164.438404	−164.741353	190.10
MP2(fc)/6-311G**//B	−164.413012	−164.712710	188.06
MP3(fc)/6-311G**//B	−164.389973	−164.702741	196.27
MP4(fc,sdtq)/6-311G**//B	−164.446087	−164.747930	189.41
CISD(fc)/6-311G**//A	−164.346800	−164.660766	197.02
CISD(fc,ssc)/6-311G**//A	−164.407165	−164.718330	195.26
CISD(fu)/6-311G**//A	−164.397917	−164.712195	197.21
CISD(fu,ssc)/6-311G**//A	−164.465789	−164.777141	195.38
CISD(fc)/6-311G(df,p)//A	−164.393477	−164.706308	196.30
CISD(fc,ssc)/6-311G(df,p)//A	−164.459723	−164.769340	194.29
CISD(fc)/6-311G**//B	−164.343489	−164.657404	196.98
CISD(fc,ssc)/6-311G**//B	−164.408939	−164.719879	195.12
CISD(fu)/6-311G**//B	−164.394028	−164.708311	197.22
CISD(fu,ssc)/6-311G**//B	−164.467239	−164.778441	195.28
CISD(fc)/6-311G(df,p)//B	−164.388939	−164.701777	196.31
CISD(fc,ssc)/6-311G(df,p)//B	−164.460267	−164.769733	194.19

[a] Total energies in atomic units and reaction energies ΔE_1 in kilocalories per mole. [b] VZPEs (kcal/mol) at levels A and B are 14.56 and 13.51 for HN_3 and 23.10 and 21.32 for $H_2N_3^+$, respectively. At levels A and B, the VZPEs reduce the PA by 8.54 (7.69 scaled) and 7.81 kcal/mol, respectively. [c] Values reported by Cacace et al. (ref 14).

Computational Methods

Ab initio calculations were performed with GAUSSIAN88 and GAUSSIAN90.[17] Geometries were optimized, and the exact Hessian matrices were computed to assure the stationarity of the located extrema, to characterize these extrema as minima and transition-state structures, and to determine the harmonic vibrational frequencies and vibrational zero-point energies (VZPEs). VZPEs determined at the RHF level require scaling by the usual factor[18] of 0.9 while the MP2 values are used unscaled. In general, structural optimizations and the normal mode analyses were carried out at the restricted Hartree–Fock (RHF) level and, in some cases, subsequently at the second-order Møller–Plesset[19] level with the 6-31G* basis set,[20] MP2(full)/6-31G*. Higher order Møller–Plesset perturbation theory as well as configuration interaction theory with all single and double substitutions, CISD, were used to determine more reliable energies. For HN_3 and the aminodiazonium ion $H_2N_3^+$, **2a**, energy computations were carried out at the full fourth-order level of Møller–Plesset perturbation theory in the frozen core approximation with the fully polarized valence triple-ζ basis set[21] 6-311G** using both the RHF/6-31G* and the MP2(full)/6-31G* optimized structures. In addition, these molecules were studied at the CISD level without and with the frozen-core approximation and with the addition of second-order f-type polarization functions, 6-311G(df,p). Energies for methyl nitrate and its protonated ions were determined at the MP3/6-31G* and CISD/6-31G* levels with the

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Table II. Iminodiazenium Ion[a,b]

method	energy				E_{rel}, 2b vs 2a	E_A, 2c vs 2b	E_{rel}, 2d vs 2b	E_{rel}, 2e vs 2b
	2b, C_2	2c, C_s	2d, C_{2h}	2e, C_{2v}				
RHF/6-31G* = A	−164.090732	−164.066012	−164.063676	−164.063205	39.34	15.51	16.98	17.27
VZPE(A)	22.44 (0)	20.53 (1)	19.83 (2)	19.89 (2)				
MP2(fc)/6-31G*//A	−164.583719	−164.571106	−164.580543	−164.580612	25.00	7.91	1.99	1.95
MP3(fc)/6-31G*//A	−164.579006	−164.557104	−164.559109	−164.559070	28.77	13.74	12.49	12.51
CISD(fc)/6-31G*//A	−164.535259	−164.513566	−164.515333	−164.514986	30.86	13.61	12.50	12.72
CISD(fc,ssc)/6-31G*//A	−164.596350	−164.573044	−164.575813	−164.575556	26.34	14.62	12.89	13.05
MP2(fu)/6-31G* = B	−164.600467		−164.601398	−164.602504	26.88		−0.58	−1.28
VZPE(B)	19.97 (0)		21.25 (0)	22.02 (0)				
MP2(fc)/6-311G**//A	−164.665077	−164.653992		−164.662355	25.91	6.96		1.71
MP3(fc)/6-311G**//A	−164.656950	−164.635722		−164.636454	29.86	13.32		12.86
MP2(fc)/6-311G**//B	−164.668819		−164.669445	−164.670912	27.54		−0.39	−1.31
MP3(fc)/6-311G**//B	−164.654764		−164.633872	−164.634050	30.11		13.11	13.00
CISD(fc)/6-311G**//A	−164.609759	−164.589494		−164.589872	32.01	12.72		15.16
CISD(fc,ssc)/6-311G**//A	−164.674436	−164.652382		−164.653901	27.54	13.84		11.50
CISD(fc)/6-311G**//B	−164.606426		−164.586230	−164.585596	31.99		12.67	13.07
CISD(fc,ssc)/6-311G**//B	−164.674501		−164.655795	−164.656111	28.48		11.74	11.54

[a] Compare Figure 1. Total energies in atomic units, vibrational zero-point energies (VZPE) and relative energies are in kilocalories per mole. [b] Frozen-core approximation used as indicated (fc) and CISD(ssc) energies are size-consistency corrected.

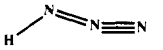
RHF/6-31G* structures and, where doubts existed, also with the larger 6-311G** basis set at those levels. Methyl nitrate and its conjugate acids were also studied with semiempirical methods with Dewar's original MNDO parameters,[22] with his more recent Austin Model 1 (AM1) parameter set,[23] as well as with Stewart's parametric model 3 (PM3)[24] using the program MOPAC.[25] An extensive review comparing these parameter sets is available.[26]

Results and Discussion

1. Hydrazoic Acid, Aminodiazonium Ion, and Iminodiazenium Ion. A. Aminodiazonium Ion.

The existence of aminodiazonium ion was originally suggested by Schmidt[27] and it was first characterized by Olah's group which succeeded in its preparation by protonation of hydrazoic acid in superacids.[28] Derivatives of aminodiazonium ions also have been invoked recently as intermediates in the intramolecular Schmidt reaction.[29]

Calculated total energies of hydrazoic acid, 1, and aminodiazonium ion, 2a, are compiled in Table I together with the calculated (negative) reaction energies ΔE_1 for the reaction $HN_3 + H^+ \rightarrow H_2N_3^+$ (eq 1). The CISD values were determined for the present study; some of the data in Table I and optimized structures were reported earlier.[13,30] While protonation at the central N of HN_3 leads to nitrene structures of high energy,[14] iminodiazenium ion formation might be competitive with aminodiazonium ion formation and the region on the potential energy surface representing $(HNNNH)^+$ was examined.



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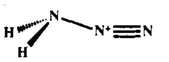

2a

B. Iminodiazenium Ion. Optimized structures are shown in Figure 1, and energy data are summarized in Table II. At the RHF/6-31G* level, C_2-**2b** is the most stable structure of iminodiazenium ion. Enantiomerization of **2b** proceeds via the transition-state structure C_s-**2c** with E_A = 15.5 kcal/mol at the RHF/6-31G* level. Both of the structures C_{2h}-**2d** and C_{2v}-**2e** are second-order saddle point structures at this level. The first imaginary frequency of each of these structures **2d** and **2e** is associated with an out-of-plane torsion that distorts **2d** and **2e** toward **2b**, and the second imaginary frequency is associated with in-plane motions of the hydrogens distorting the molecule toward the structure of **2c**. At the level of optimization, **2d** and **2e** are only slightly higher in energy than **2c**. With the RHF/6-31G* structures, we estimated electron correlation effects at the MP2, MP3, and CISD levels with the 6-31G* basis set. At these levels, **2d** and **2e** are always slightly more stable than **2c**. While **2c–e** all remain more than 13 kcal/mol less stable than **2b** at the MP3 and CISD levels, the MP2 energies would suggest much more significant stabilizations of these planar structures compared to **2b**.

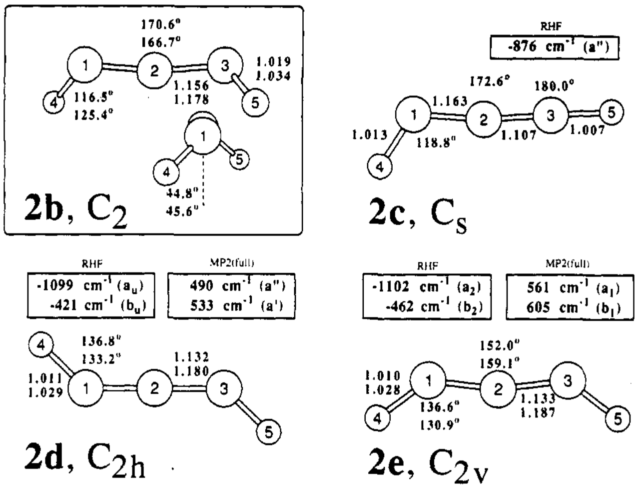

Figure 1. Optimized structures of iminodiazenium ion. Geometries are given in angstroms and degrees as determined at the RHF/6-31G* (top line) and MP2(full)/6-31G* levels. Frequencies given are those of the imaginary or lowest-energy vibrational modes. C_2-**2b** is the most stable structure for iminodiazenium ion.

Reoptimization of C_2-**2b** at the MP2(full)/6-31G* level changes the geometry only quantitatively, but the 2c-type structure vanishes as a transition state. Reoptimization of the RHF structure C_s-**2c** at the MP2/6-31G* level resulted in the de facto C_{2h} structure **2d**. Both **2d** and **2e**

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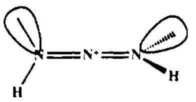
are *minima* at this correlated level. Our CISD energies suggest, however, that *the stabilities of 2d and 2e artificially are greatly overestimated at the MP2/6-31G* level.* The MP3 and the CISD energies calculated with the 6-311G** basis set and based on the RHF or MP2 optimized structures all indicate that **2d** and **2e** are less stable than **2b** by more than 10 kcal/mol (Table II).

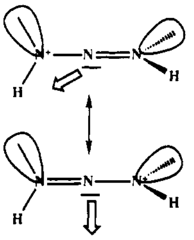
The structure **2b** is isoelectronic with allene, that is, it may be seen as containing two perpendicular 3-center-2-electron π-systems. In contrast to the linear C–C–C backbone in allene, however, the N–N–N skeleton is slightly bent (166.7°), indicating contributions of the (degenerate set of) resonance form **II**. The N–N–N bending occurs in such a way as to minimize the repulsion between the "σ lone pairs" at the central N and at the attached imine N, as schematically indicated for **IIa** and **IIb**. Note that **IIa** and **IIb** increase the electron density at the central N while maintaining C_2 symmetry and the allene-type electronic structure. This electronic structure contrasts with the allyl-cation-type electronic structure of the planar structure type, **III**. The electronic structure of **III** might involve either equivalent or nonequivalent N–N bonds but none of these possibilities is realized. Any optimization with the constraint to planarity results in structures of the types **2d** and **2e**, that is, 3-center-4-electron π-systems **IV**.

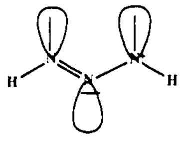
I



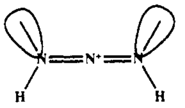
IIa

IIb





III



IV

The iminodiazenium ion **2b** is predicted to be less stable than the aminodiazonium ion **2a** at all levels of theory employed. At our highest level, CISD(fc,ssc)/6-311G**//MP2(full)/6-31G*, **2a** is 28.48 kcal/mol more stable than **2b** and with the inclusion of vibrational zero-point energies determined at the MP2(full)/6-31G* level a relative energy of 27.13 kcal/mol is obtained.

C. Proton Affinity of Hydrazoic Acid. Since spectroscopy and theory show that aminodiazonium ion **2a** is favored over the iminodiazenium ion **2b**, the ΔE_1 values in Table I are the reaction energies for the protonation of hydrazoic acid to give **2a** at 0 K in the motionless state. For the conversion of the ΔE_1 values to proton affinities, zero-point vibrational energies and corrections for the standard state need to be taken into account. Cacace et al. reported a proton affinity of 176.2 kcal/mol for HN_3 with these corrections. We will first discuss the ΔE_1 values and consider vibrational zero-point energy corrections later.

Cacace et al. reported the MP2(fc)/6-31G*//RHF/6-31G* ΔE_1 value of 183.16 kcal/mol which is in excellent agreement with their experimental proton affinity, and these workers estimated the uncertainty for this value to be around 4 kcal/mol. In our earlier work, we pointed up that calculated proton affinities may vary considerably depending on the theoretical level and that rather high levels of theory are required for their determination.[31] Our best ΔE_1 value of 189.41 kcal/mol reported there was determined at the MP4(fc,sdtq)/6-311G**//MP2(full)/6-31G* level. The quality of the calculated ΔE_1 value can be improved (a) by using better structures, (b) by using larger basis sets, and (c) by use of a better electron correlation treatment. We have carried out three sets of calculations for **1** and **2a** at the CISD level that were based on the RHF/6-31G* (A) and the MP2(full)/6-31G* (B) structures. CISD calculations with the 6-311G** basis set were carried out with and without the frozen core approximation, and the resulting ΔE_1 values differ by less than 0.3 kcal/mol. The CISD calculations with the largest basis set that included f-type functions on heavy atoms, 6-311G(df,p), were thus carried out using the frozen-core approximation. At our highest level, CISD(fc)/6-311G(df,p)//MP2(full)/6-31G*, a ΔE_1 value of 196.31 was found, and size-consistency corrections yield a value of 194.19 kcal/mol. Size-consistency corrections in general reduce the ΔE_1 value by about 2 kcal/mol. Second-order polarization functions are slightly more important for **1** than for **2** and cause ΔE_1 reductions of about 1 kcal/mol. Comparison between the ΔE_1 values derived with structures optimal at levels A and B, respectively, clearly shows that structural effects are marginal; they affect ΔE_1 by less than 0.2 kcal/mol. Our best ΔE_1 value (194.19 kcal/mol) is thus significantly higher than the value reported by Cacace et al. (by 11.03 kcal/mol) and it is also higher than our earlier MP4(fc,sdtq)/6-311G** value (by 4.78 kcal/mol). As can be seen from Table I, significant oscillations occur depending on the order of the Møller–Plesset perturbation treatment. Second- and fourth-order corrections reduce ΔE_1 while third-order corrections yield values in relatively close agreement with the RHF and the CISD results. In fact, it is noteworthy that the standard RHF/6-31G* level yields results in astonishingly close agreement with the CISD values.

The vibrational zero-point energies of **1** and **2a** calculated at the MP2(full)/6-31G* level are 13.51 and 21.32 kcal/mol, respectively. Consideration of the ΔVZPE value of 7.81 kcal/mol yields our *best estimate for the proton affinity of HN_3 at 0 K: 186.38 kcal/mol.* This value is about 10 kcal/mol higher than the experimental value of 176.6 ± 1.0 kcal/mol. The questions therefore are (a) whether the theoretical value is too high, (b) whether the experimental value is too low, or (c) whether both values are associated with significant errors. In the attempt to answer these questions, the proton affinity of methyl nitrate plays a central role because Cacace et al. determined the proton affinity of HN_3 via the measurement of the equilibrium constant of the proton transfer reaction between methyl nitrate and HN_3 (eq 3).

2. Thermochemical Properties of Methyl Nitrate and Its Conjugated Acids. Evaluation of eqs 1 and 3 requires the proton affinity of methyl nitrate, **3**, that is, the heats of formation of **3** and of its conjugate acid **4** in the gas phase under standard conditions. Gray and Smith reported a value of ΔH_f(**3**,liquid) = −37.2 kcal/mol.[32] Conversion of ΔH_f(**3**,liquid) to ΔH_f(**3**,gas) requires the heat of vaporization which was measured to be 7.73 kcal/mol by McKinley-McKee and Moelwyn-Hughes[33] and 7.80 kcal/mol by Thomson and Purkis.[34] Gray and Smith used the average of these values and arrived at ΔH_f(**3**,gas) = −29.43 kcal/mol with error bars of ±0.8 kcal/mol. Pedley, Naylor, and Kirby[35] reported a value of ΔH_f(**3**,gas) = −29.21

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[31] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley: New York, 1986, p 310ff.

[32] Gray, P.; Smith, P. L. *J. Chem. Soc.* **1953**, 2380.

[33] McKinley-McKee, J. S.; Moelwyn-Hughes, E. A. *Trans. Faraday Soc.* **1952**, *48*, 247.

[34] Thomson, H. W.; Purkis, C. H. *Trans. Faraday Soc.* **1936**, *32*, 674.

Table III. Energies of Methyl Nitrate and Its Conjugate Acids[a-f]

molecule	level	ΔH_f	VZPE	E_A	E_{rel}	ΔVZPE
ecl.-**3**	MNDO	−10.92	36.19 (1)	1.51		
	AM1	−30.28	35.24 (1)	1.04		
	PM3	−31.18	32.14 (1)	1.24		
ecl.-**4.1**	MNDO	172.93	42.72 (0)			6.02
	AM1	149.66	40.86 (0)			5.24
	PM3	145.88	40.33 (0)			7.74
ecl.-**4.2**	MNDO	186.84	43.36 (1)	1.49		
	AM1	170.74	41.29 (1)	1.29		
	PM3	175.74	39.33 (1)	1.35		
ecl.-**4.3**	MNDO	185.06	43.45 (1)	1.42		
	AM1	168.94	41.43 (1)	1.12		
	PM3	175.70	38.95 (1)	1.30		
ecl.-**4.4**	MNDO	186.70	43.39 (1)	1.79		
	AM1	170.53	41.32 (1)	1.78		
	PM3	177.51	39.16 (1)	1.88		
stag.-**3**[d]	MNDO	−12.43	36.70 (0)			
	AM1	−31.32	35.62 (0)			
	PM3	−32.42	32.59 (0)			
stag.-**4.1**	MNDO	173.26	42.64 (1)	0.33		
	AM1	150.30	40.60 (1)	0.64		
	PM3	146.28	39.90 (1)	0.40		
stag.-**4.2**	MNDO	185.35	43.84 (0)		12.42	7.14
	AM1	169.45	41.73 (0)		19.79	6.11
	PM3	174.39	39.77 (0)		28.51	7.18
stag.-**4.3**	MNDO	183.64	43.91 (0)		10.71	7.21
	AM1	167.82	41.84 (0)		18.16	6.22
	PM3	174.40	39.40 (0)		28.52	6.81
stag.-**4.4**	MNDO	184.91	43.92 (0)		11.98	7.22
	AM1	168.75	41.83 (0)		19.09	6.21
	PM3	175.63	39.71 (0)		29.75	6.52

[a] All values in kilocalories per mole. [b] Calculated heats of formation ΔH_f. [c] Vibrational zero-point energies (VZPE) and number of imaginary vibrations (in parentheses). [d] Activation barriers for methyl rotation, E_A. [e] Relative energies of isomeric acids with regard to *ecl.*-4.1. [f] Column ΔVZPE gives the corrections to proton affinities, $PA_{corr} = PA - \Delta VZPE$. [d] Cf. ref 26.

(±1.05) kcal/mol—which was determined based on the reaction of N_2O_5 with CH_3ONO to give N_2O_4/NO_2 and **3**—with reference to Ray and Orr[36] who first reported this value to be $\Delta H_f(\mathbf{3},\text{gas}) = -29.2$ (±0.3) kcal/mol. With $\Delta H_f(\mathbf{3},\text{gas}) = -29.21$ kcal/mol and the heat of vaporization of 8.15 kcal/mol determined by Gray and Pratt,[37] Pedley et al. reported the value of $\Delta H_f(\mathbf{3},\text{liquid}) = -37.36$ (±1.05) kcal/mol which is in very good agreement with the value by Gray and Smith. Thus, *the value of* $\Delta H_f(\mathbf{3},\text{gas}) = -29.21$ *(±1.05) kcal/mol is well established* by two independent methods, and all reported values fall into the range given by the error bars.

The *heat of formation of the conjugate acid of* **3**, $(CH_3ONO_2)H^+$ (**4**), *is less well established.* The proton affinity of **3** was given by Cacace et al. as PA(**3**,gas) = 176.0 kcal/mol with reference to a paper by Attina, Cacace, and Yanez.[38,39] Attina et al. estimated the PA(**3**) by measuring the equilibrium constant of the proton transfer between **4** and $CH_2(CN)_2$. With their PA(**3**,gas) and $\Delta H_f(\mathbf{3})$, they estimated the heat of formation of **4** as $\Delta H_f(\mathbf{4}) = 161$ kcal/mol. The only other report of a heat of formation of **4** we found was that by Dewar, Shanshal, and Worley.[40] Dewar et al. studied **3** and **4** based on assumed structures with the MINDO method and reported values of $\Delta H_f(\mathbf{3},\text{gas}) = -35.32$ kcal/mol, of $\Delta H_f(\mathbf{4},\text{gas}) = 150.5$ kcal/mol for the ester-O protonated isomer, of $\Delta H_f(\mathbf{4},\text{gas}) = 170.6$ kcal/mol for the terminal-O protonated isomer, and a heat of reaction of 41.3 kcal/mol for the dissociation of **4** into methanol and NO_2^+.[41]

3. Protonation of Methyl Nitrate. Methyl nitrate and four structure isomers of protonated methyl nitrate were considered with two methyl conformations in each case, as shown in Figure 2, both at semiempirical and at ab initio levels. All of these structures were calculated with C_s symmetry and vibrational frequencies were then computed to determine the characters of the stationary structures.

Potential Energy Surfaces at Semiempirical Levels. In Table III, the results of the semiempirical calculations with the MNDO, AM1, and PM3 parameters are summarized.[42] While structures **4.2**–**4.4** all are protonated nitrates, the geometries of **4.1** are best described as methanol solvated NO_2^+ ions. In Figure 2, conformers are circled, and the corresponding structures with different H_3C–O conformations are the transiton-state structures for methyl rotation. As can be seen, **3** and all of the O-(NO_2) protonated structures **4.2**–**4.4** prefer the staggered methyl conformation, whereas protonation of the ester-O leads to the eclipsed structure **4.1**. The activation barriers E_A for methyl rotation are given in Table III. Of the protonated molecules, **4.1** is greatly preferred over **4.2**–**4.4** at all levels (E_{rel} in Table I greater 10 kcal/mol but less than Dewar's value of 20.1 kcal/mol[16]), and the latter all are of comparable energy (within less than 2 kcal/mol). The proton affinities are the negative reaction energies of reaction 2 and with $\Delta H_f(H^+)$ of 326.67 kcal/mol (MNDO),

$$CH_3ONO_2\ (\mathbf{3}) + H^+ \rightleftarrows (CH_3ONO_2)H^+\ (\mathbf{4.1}) \qquad (2)$$

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(35) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986.

(36) Ray, J. D.; Orr, R. A., Jr. *J. Phys. Chem.* **1959**, *63*, 1522.

(37) Gray, P.; Pratt, M. W. T. *J. Chem. Soc.* **1957**, 2163.

(38) Attina, M.; Cacace, F.; Yanez, M. *J. Am. Chem. Soc.* **1987**, *109*, 5092.

(39) (a) No data on the PA(**3**) were found in this extensive compilation: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695. (b) The update to a also does not contain the PA(**3**): Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levi, R. D.; Mallard, W. S. *J. Phys. Chem. Ref. Data* **1988**, *17*.

(40) Dewar, M. J. S.; Shanshal, M.; Worley, S. D. *J. Am. Chem. Soc.* **1969**, *91*, 3590.

(41) Note that in Dewar's paper the experimental value of **3** is given as −29.05 kcal/mol because the heat of vaporization was taken from the paper by Gray and Williams (*Chem. Rev.* **1959**, *59*, 239) as 8.15 kcal/mol.

(42) Optimized structures determined at the semiempirical levels are given as supplementary material.

Table IV. Total, Relative, and Vibrational Zero-Point Energies of Methyl Nitrate and Isomers of Its Conjugate Acid and Protonation Energies ΔE_2[a-d]

molecule	level	energy	VZPE	E_A	E_{rel}	ΔE_2	ΔVZPE
ecl.-**3**	RHF	−318.469421	37.47 (1)	2.60			
	MP2	−319.308794		2.45			
	MP3	−319.301762		2.49			
	CISD(fc)	−319.182873		2.54			
	CISD(fc,ssc)	−319.319752		2.47			
ecl.-**4.1**	RHF	−318.749792	44.36 (0)			173.34	−5.89
	MP2	−319.604622				183.18	
	MP3	−319.581146				172.83	
	CISD(fc)	−319.465067				174.54	
	CISD(fc,ssc)	−319.604802				176.40	
	RHF/6-311G**	−318.849549				181.60	
	MP2	−319.801850				198.20	
	MP3	−319.772801				186.73	
	CISD(fc)	−319.641572				187.22	
	CISD(fc,ssc)	−319.796018				190.54	
ecl.-**4.2**	RHF	−318.759061	45.56 (1)	1.72			
	MP2	−319.589608		1.60			
	MP3	−319.587860		1.70			
	CISD(fc)	−319.469974		1.71			
	CISD(fc,ssc)	−319.606410		1.67			
ecl.-**4.3**	RHF	−318.757775	45.45 (1)	1.73			
ecl.-**4.4**	RHF	−318.753118	45.41 (1)	1.98			
stag.-**3**	RHF	−318.473562	37.81 (0)				
	MP2	−319.312705					
	MP3	−319.305730					
	CISD(fc)	−319.186923					
	CISD(fc,ssc)	−319.323686					
	RHF/6-311G**	−318.560156					
	MP2	−319.485996					
	MP3	−319.475236					
	CISD(fc)	−319.343215					
	CISD(fc,ssc)	−319.492372					
stag.-**4.1**	RHF	−318.748230	43.94 (1)	0.98			
	MP2	−319.602939		1.06			
	MP3	−319.579529		1.01			
	CISD(fc)	−319.463471		1.00			
	CISD(fc,ssc)	−319.603181		1.02			
stag.-**4.2**	RHF	−318.761795	45.81 (0)		−7.53	180.87	−7.20
	MP2	−319.592157			7.82	175.36	
	MP3	−319.590575			−5.92	178.74	
	CISD(fc)	−319.472697			−4.79	179.33	
	CISD(fc,ssc)	−319.609065			−2.68	179.08	
	RHF/6-311G**	−318.854908			−3.36	184.96	
	MP2	−319.775686			16.42	181.78	
	MP3	−319.771028			1.11	185.61	
	CISD(fc)	−319.638625			1.85	185.37	
	CISD(fc,ssc)	−319.788228			4.89	185.65	
stag.-**4.3**	RHF	−318.760509	45.69 (0)		−6.73	180.06	−7.09
stag.-**4.4**	RHF	−318.756266	45.72 (0)		−4.06	177.40	−7.12
5	RHF	−318.747126	44.72 (1)				
6	RHF	−318.693455	43.11 (2)				
ecl.-**7**	RHF	−318.668828	41.35 (2)				
stag.-**7**	RHF	−318.668278	41.34 (2)				

[a] Total energies in atomic units. All other values in kilocalories per mole. [b] All values are based on the RHF/6-31G* structures. MPx and CISD energies determined with the frozen-core approximation and with the 6-31G* basis set. The second sets of entries (after entry RHF/6-311G**) for *stag.*-**3**, *ecl.*-**4.1**, and *stag.*-**4.2** were determined with the 6-311G** basis set. [c] See legend to Table I. [d] Column ΔVZPE gives vibrational correction to ΔE_2, $\Delta E_{2,corr} = \Delta E_2 + \Delta VZPE$. The ΔVZPE values are scaled (factor 0.9).

314.92 (AM1), and 353.59 (PM3), proton affinities of 141.31 kcal/mol (MNDO), 133.94 (AM1), and 175.28 (PM3) result. As with the calculated heats of formation, the range spanned by these proton affinities is large and makes the prediction of PA(**3**) difficult. Note that the PA(**3**) computed with the PM3 parameters is rather close to the value used by Cacace et al. (176 kcal/mol), although the PM3 ΔH_f(**4**) value of 146 kcal/mol is about 15 kcal/mol lower than the value by Attian et al.[38]

Potential Energy Surfaces at the ab Initio Level. Geometries optimized at the ab initio level are depicted in Figure 2, and energies and structural parameters are summarized in Tables IV and V, respectively. In agreement with the semiempirical method, the ab initio results show that **3** and all of its conjugate acids **4.2**–**4.4** prefer the staggered methyl conformation, whereas protonation of the ester-O leads to the eclipsed structure **4.1**. The activation barrier for CH_3 rotation in CH_3ONO_2 is 2.60 kcal/mol at the RHF/6-31G* level, and the E_A is reduced slightly by 0.36 kcal/mol upon inclusion of the scaled vibrational zero-point energy corrections. Electron correlation effects on staggered and eclipsed **3** essentially cancel out; E_A is within the narrow range of 2.51 ± 0.1 kcal/mol (2.15 including ΔVZPE) at all levels. The activation barriers for CH_3 rotation in the ester-O and in the terminal-O protonated systems **4.1** and **4.2** are 1.02 and 1.67 kcal/mol, respectively, at the highest level. Again, the vibrational zero-point corrections reduced E_A slightly (0.38 and 0.23 kcal/mol), electron correlation effects essentially cancel ($\Delta < 0.08$ kcal/mol), and the E_A values of **4.3** and **4.4** are

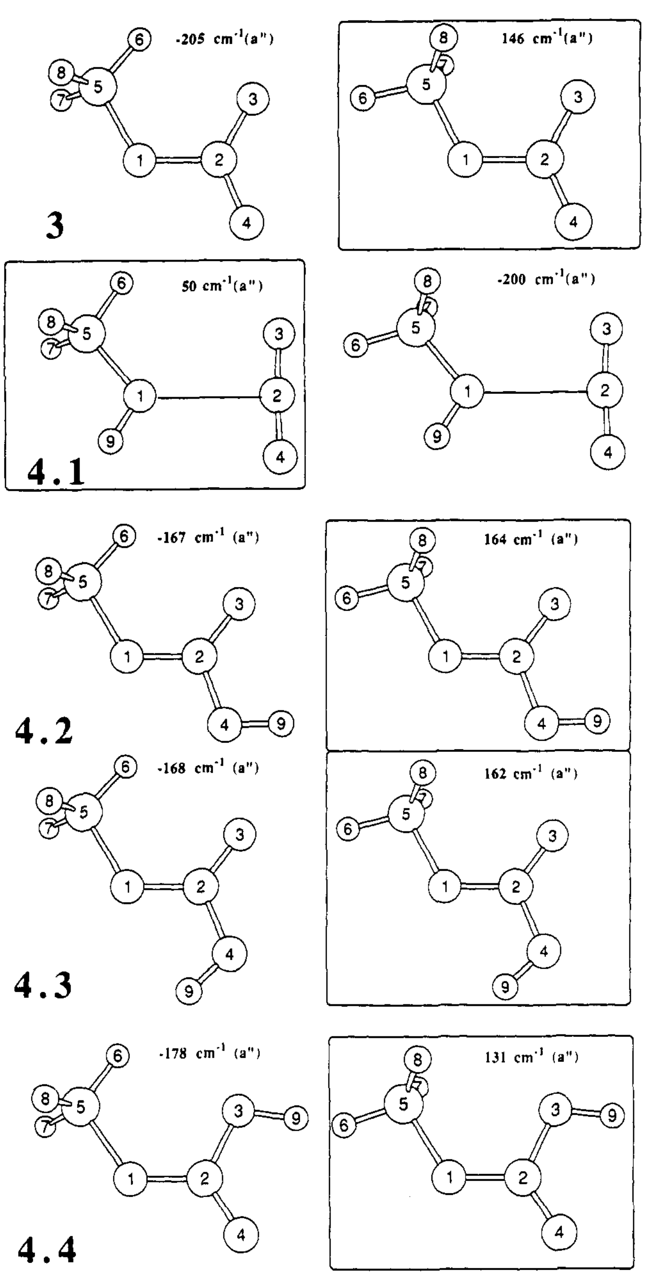
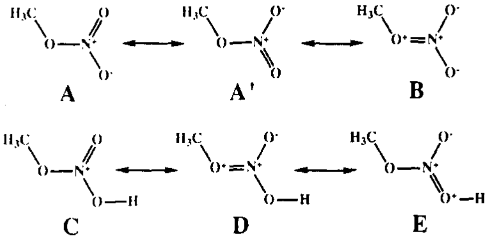


Figure 2. RHF/6-31G* optimized structures of methyl nitrate, 3, and of isomers of its conjugate acids, 4. Minima are circled, and the other conformations are the transition-state structures for methyl rotation. Frequencies are those of the lowest-energy vibrational modes.

close to E_A(4.2). O-Ester protonation thus results in E_A = 0.64 kcal/mol, a barrier[43] that is about one-third of E_A(3) and less than half of E_A(4.2). The higher E_A values in 3 and 4.2 indicate increased hyperconjugative interaction with the ester-O (resonance forms **B** and **D** below).

Structures and Lewis Representations. The N–O bond variations may serve as indicators of the electronic relaxation associated with protonation. The O1–N2 bond length of *stag.*-3 is 1.331 Å long and independent of the CH_3 conformation. The other N–O bonds in 3 both are significantly shorter (by 0.15 Å) and the cis N2–O3 bond (with regard to the CH_3 group) is slightly (0.01 Å) longer than the trans N2–O4 bond. *Ester-O protonation leads to structures that are best described as methanol solvated NO_2^+ cations, 4.1.* In the minimum *ecl.*-4.1, the N–O bond lengths are the same as in free NO_2^+ (1.091 Å), *d*(CO) is slightly elongated (by 0.033 Å) compared to CH_3OH, and the dative bond between the alcohol O and the nitronium N is 2.377 Å long. Protonation of a terminal oxygen results in a shortening of the remaining N–O_{term} bond (1.14 and 1.15 Å) by about 0.03 Å. The cis and trans N2–O3H bonds are 1.295 and 1.287 Å, respectively, and considering their relative lengths in 3 both are lengthened upon protonation by about 0.11 Å. Remarkably, the N1–O2 bonds *shorten significantly* upon protonation of a terminal oxygen, by about 0.08 Å (0.06) for the acids 4.2 and 4.4 (4.3), and H_3CO–N bonds are shorter than HO–N bonds. In 3, the O1–N2–O3 angle is somewhat larger than the O1–N2–O4 angle, and they both are less than 120°. These angular features result in an "opened" O3–N2–O4 angle of 128° and a tilt of the NO_2 group (relative to the O1–N2 axis) of 3° that could be rationalized by assuming a repulsive interactions between O3 and the methyl group. O4-Protonation increases this tilt to 6–8° and O3-protonation reduces it to 3° and reverses the direction of the tilt. These structural parameters indicate that 3 is well represented by resonance forms **A** and **A′**. In (all of) the conjugate acids resulting from O_{term} protonation, resonance forms **D** and **E** clearly contribute significantly—and **D** more so than **E**—which might be taken as evidence for Y-conjugation in these acids.



Relative Isomer Stabilities. Interestingly, at the RHF/6-31G* level, the order of stability of the ester-O protonated *ecl.*-4.1 over the terminal-O protonated isomers *stag.*-4.2–4.4 is reversed. Isomers 4.2, 4.3, and 4.4 are 7.53, 6.73, and 4.06 kcal/mol, respectively, more stable than 4.1 at the RHF level, and the E_{rel} values are reduced by 1.31, 1.20, and 1.22 kcal/mol, respectively, when scaled vibrational zero-point energies are included. Relative isomer stabilities E_{rel} are expected to be more sensitive to electron correlation effects than the E_A values because of the significantly different electronic structures of 4.1 compared to 4.2–4.4. For this reason, we also determined the relative stabilities of *ecl.*-4.1 and *stag.*-4.2 at correlated levels with the 6-31G* and with the more flexible valence triple-ζ 6-311G** basis sets. Perturbational theory results in significant E_{rel} fluctuations. Structure 4.2 is predicted 2.68 kcal/mol more stable than 4.1 at CISD(fc,ssc)/6-31G*, while isomer 4.1 is predicted 4.89 kcal/mol more stable than 4.2 at CISD(fc,ssc)/6-311G**. *At the highest level and including the RHF/6-31G*+ΔVZPE estimate, we obtain a preference of E_{rel} = 6.20 kcal/mol for the ester-O protonated acid.* The respective value of 20.1 kcal/mol for 4.1 reported by Dewar et al.[16] indicated a similar but larger preference. Correlation effects on structures (likely in favor of 4.1) as well as the use of better basis sets might still affect E_{rel} by a few kilocalories per mole, but our results indicate that ester-O and terminal-O protonation are competitive processes with a moderate preference for the former.

Proton Affinities. At our highest ab initio level, the determination of the proton affinity is based on the formation of *ecl.*-4.1. The negative reaction energies ΔE_2 of reaction 2 are the proton affinities for the motionless state at absolute zero. At the RHF/6-31G* level, ΔE_2 is 173.34

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[43] The experimental barrier in methanol is 1.1 kcal/mol.

Table V. Geometries of Methyl Nitrate and Its Conjugate Acids

parameter[a]	*ecl.*-3	*ecl.*-4.1	*ecl.*-4.2	*ecl.*-4.3	*ecl.*-4.4	*stag.*-3	*stag.*-4.1	*stag.*-4.2	*stag.*-4.3	*stag.*-4.4
O1–N2	1.3322	2.3765	1.2563	1.2718	1.2576	1.3305	2.3737	1.2589	1.2739	1.2617
N2–O3	1.1860	1.0906	1.1497	1.1407	1.2952	1.1866	1.0908	1.1493	1.1409	1.2942
N2–O4	1.1768	1.0911	1.2870	1.2878	1.1445	1.1771	1.0909	1.2859	1.2868	1.1437
C5–O	1.4324	1.4271	1.5012	1.5045	1.5085	1.4280	1.4306	1.4910	1.4941	1.4976
H6–C	1.0734	1.0806	1.0738	1.0739	1.0719	1.0774	1.0799	1.0740	1.0742	1.0741
H7–C	1.0788	1.0814	1.0750	1.0749	1.0747	1.0780	1.0812	1.0764	1.0762	1.0753
H8–O		0.9501	0.9661	0.9648	0.9670		0.9480	0.9662	0.8650	0.9673
O3–N2–O1	119.01	92.36	126.98	126.73	115.68	117.89	92.22	127.08	125.86	114.87
O4–N2–O1	113.21	92.65	109.79	113.06	121.89	113.91	92.77	110.21	113.51	122.17
C5–O1–N2	118.62	129.21	119.50	119.37	123.79	115.78	127.21	116.84	116.75	120.77
H6–C5–O1	111.22	107.36	109.48	109.12	110.11	103.26	110.48	101.49	101.60	100.78
H7–C5–O1	106.56	110.49	103.65	103.81	103.16	110.51	109.13	107.92	107.80	108.11
H9–O–N2		122.07	108.35	109.81	108.13		123.12	108.47	109.51	108.36
H6–C5–O1–N2	120.98	118.88	120.97	120.79	121.14	61.34	60.12	61.31	61.28	61.68

[a] In angstroms and degrees as determined at RHF/6-31G*.

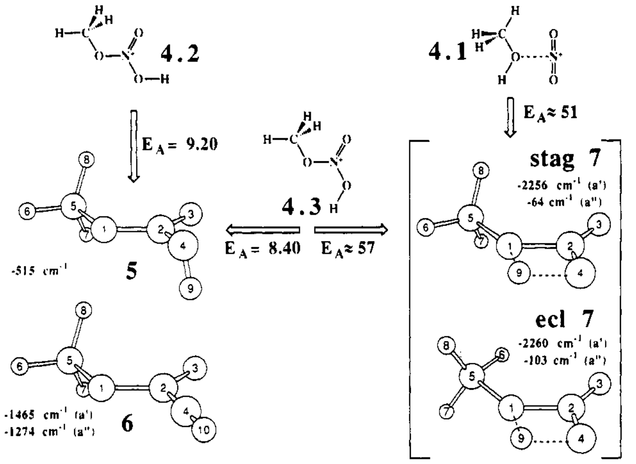

Figure 3. Isomerization of protonated methyl nitrates. Transition-state structures and second-order saddle point structures are identified via the frequencies of their imaginary modes. Activation energies are given in kilocalories per mole as determined at the RHF/6-31G* level.

kcal/mol. With the scaled ΔVZPE values given in Table IV, we obtain the value of 167.45 kcal/mol for the RHF/6-31G* estimate for the proton affinity of **3**. Inclusion of correlation effects on energies at the MP2, MP3, and CISD(scc) levels results in ΔE_2 values of 183.18, 172.83, and 176.40 kcal/mol, respectively. Note the relatively close agreement of the MP3 and CISD values. With the inclusion of the ΔVZPE values, we obtain estimates for the PA(**3**) of 166.94 (MP3) and 170.51 kcal/mol (CISD), respectively. Accurate determinations of proton affinities are difficult as the combination of a proton with a nucleophile is the worse case scenario for basis set superposition errors.[44] The best remedy against such errors is the enlargement of the basis set. Using the 6-311G** basis set, the ΔE_2 values are increased to 180.84 and 184.65 kcal/mol at the MP3 and CISD(fc,ssc) levels, respectively, and including vibrational zero-point energy corrections. These values are somewhat higher than the value of PA(**3**,gas) = 176.0 kcal/mol given by Attina, Cacace, and Yanez.[38]

Table VI. Intramolecular Proton Transfer in Protonated Methyl Nitrate

parameter[a]	5	6	*ecl.*-7	*stag.*-7
O1–N2	1.2630	1.2773	1.3662	1.3648
N2–O3	1.1422	1.1474	1.1374	1.1378
N2–O4	1.3151	1.2285	1.2208	1.2211
C5–O	1.4877	1.4820	1.5235	1.5195
H6–C	1.0741	1.0745	1.0763	1.0752
H7–C	1.0768	1.0765	1.0741	1.0748
H8–C	1.0770			
H9–O	0.9664	0.9674	1.2071	1.2051
O3–N2–O1	125.73	124.51	124.31	124.00
O4–N2–O1	112.20	112.21	100.48	100.60
C5–O1–N2	116.97	116.25	125.81	124.92
H6–C5–O1	101.80	101.64	104.91	101.95
H7–C5–O1	108.17	108.34	104.42	105.94
H8–C5–O1	107.81			
H9–O–N2	109.60	179.72	79.02	79.24
O4–N2–O1–O3	176.00			
C5–O1–N2–O3	−1.76			
H6–C5–O1–N2	180.12	61.38		
H7–C5–O1–N2	61.26		119.66	61.05
H8–C5–O1–N2	−61.20			
H9–O4–N2–C1	92.60			

[a] In angstroms and degrees as determined at THF/6-31G*.

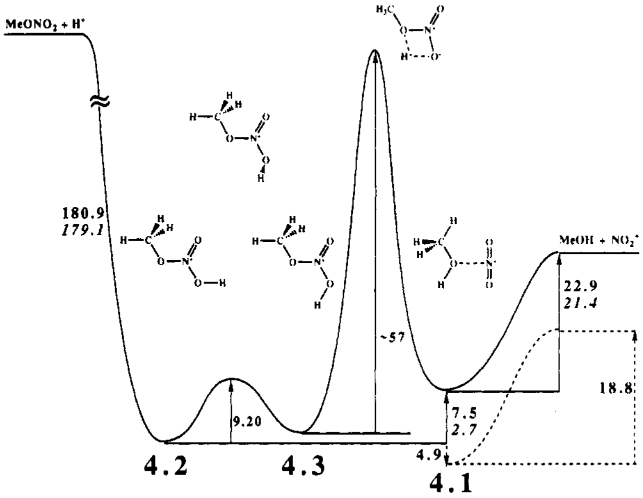

Figure 4. Schematic potential energy diagram for the NO_2^+ formation from protonated methyl nitrate as determined at the RHF/6-31G* level. Relative energies given in italics are CISD-(ssc)/6-31G* values. The dashed line indicates the relative stabilization of *ecl.*-**4.1** relative to *stag.*-**4.2** at the CISD(ssc)/6-311G** level.

Intramolecular Proton Transfer in Protonated Methyl Nitrate. The higher level ab initio results suggest that *ecl.*-**4.1**, the precursor for NO_2^+ formation, is the most stable isomer of **4**, but they also indicate that the kinetic formation of isomeric structures of **4** are competitive processes. Intramolecular proton transfer might be important and the pathways for isomerization of *stag.*-**4.2** and *ecl.*-**4.1** to *stag.*-**4.3** were thus examined. Several stationary structures were determined, they are shown in Figure 3, structural parameters are given in Table VI, and a schematic drawing of the potential energy surface is shown in

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(44) (a) Pullman, A.; Berthod, H.; Gresh, N. *Int. J. Quantum Chem.* **1976**, *10*, 59. (b) Hobza, P.; Zahradnik, R. *Chem. Rev.* **1988**, *88*, 871 and references therein.

Table VII. Proton Transfer Equilibrium between Methyl Nitrate and Hydrazoic Acid[a]

method	ΔE_1	$\Delta E_{1,\mathrm{corr}}$	ΔE_2	$\Delta E_{2,\mathrm{corr}}$	ΔE_3	$\Delta E_{3,\mathrm{corr}}$	log (K)
/6-31G*							
//RHF/6-31G*							
RHF	197.50	189.81	173.34	167.44	24.16	22.37	−16.27
MP2(fc)	183.16	175.48	183.18	177.29	−0.02	−1.81	1.31
MP3(fc)	190.60	182.91	172.83	166.93	17.77	15.98	−11.63
CISD(fc)	191.91	184.23	174.54	168.64	17.37	15.58	−11.33
CISD(fc,ssc)	189.90	182.22	176.40	170.51	13.50	11.71	−8.52
/6-311G**							
//RHF/6-31G*							
MP2(fc)	188.06	180.37	198.20	192.31	−10.14	−11.93	8.68
MP3(fc)	196.22	188.53	186.73	180.83	9.50	7.70	−5.60
CISD(fc)	197.02	189.33	187.22	181.33	9.79	8.00	−5.82
CISD(fc,ssc)	195.26	187.57	190.54	184.65	4.72	2.93	−2.13
Cacace et al.		176.6		176.0		0.60	0.54

[a] Values subscribed by "corr" include scaled vibrational zero-point energy corrections.

Figure 4. Isomerization of *stag.*-4.2 to *stag.*-4.3 via the transition-state structure 5 is a facile process that requires only 9.20 kcal/mol of activation energy at th RHF/6-31G* level, see Figure 3. This isomerization involves rotation around the N–O bond; the in-plane isomerization via structure 6 is disfavored by more than 30 kcal/mol, and 6 is a second-order saddle point. The location of stationary structures in the transition state region between *ecl.*-4.1 and *stag.*-4.3 is computationally demanding since the reaction coordinate involves changes in several internal coordinates and requires calculation of the forces at all steps. The transition state search was carried out with the constraint of C_s symmetry and the staggered and eclipsed structures 7 resulted. Both of these structures are found to be second-order saddle points; they exhibit two imaginary frequencies. Visual inspection of the imaginary modes with the program VIBRATE[45] shows that the imaginary low-frequency modes are associated in each case primarily with methyl rotation and not with an out-of-plane motion of the transferred proton. Hence, the actual transition-state structure should be rather close to 7 and the exact structure of the chiral transition state was not determined. With the energies of 7, the activation energy for the isomerization of *stag.*-4.3 to the ester-O protonated form can be estimated to be about 57 kcal/mol. This barrier suggests that *intra*molecular H transfer is slow and less important than *inter*molecular H transfer.

4. Proton Transfer between Methyl Nitrate and Hydrazoic Acid. With the proton affinities of CH_3ONO_2 and HN_3, we can evaluate the proton transfer equilibrium reaction between the conjugate acid of CH_3ONO_2 and HN_3 (eq 3). The equilibrium constant for reaction 3, K, can

$$CH_3ONO_2\ (stag.\text{-}3) + H_2N_3^+ \rightleftarrows (CH_3ONO_2)H^+\ (ecl.\text{-}4.1) + HN_3 \tag{3}$$

be well approximated via the equation $K = \exp[-(\Delta E_{3,\mathrm{corr}})/RT]$, where ΔE_3 is the reaction energy of reaction 3 and $\Delta E_{3,\mathrm{corr}} = \Delta E_{2,\mathrm{corr}} - \Delta E_{1,\mathrm{corr}}$, including vibrational zero-point energy corrections.

We evaluate reaction 3 first at the RHF/6-31G* level and at the MP2(fc), MP3(fc), and CISD(fc,ssc) levels with the 6-31G* basis set, with the RHF/6-31G* structures, and with the scaled VZPE values computed at RHF/6-31G* (Table VII). At the RHF level, the protonation of 3 is less exothermic than that of HN_3, and the equilibrium is predicted to lie on the left side of reaction 3 with $\Delta E_3 = +24.16$ kcal/mol. Electron correlation greatly affects this equilibrium. The large second-order Møller–Plesset corrections reverse the sign of ΔE_3 (ΔE_3 becomes −1.81 kcal/mol) and third-order corrections counteract to give a value of $\Delta E_3 = +15.98$ kcal/mol. Configuration interaction with single and double excitations yields $\Delta E_3 = +11.71$ kcal/mol. At the CISD level, ΔE_1 is *reduced* (by about 7.6 kcal/mol) compared to the RHF value while ΔE_2 is *increased* (by about 3 kcal/mol) and ΔE_3 is thus *reduced* by about 10.6 kcal/mol. The MP2 method greatly overestimates both of these effects.

Reaction 3 also was evaluated with the more flexible fully polarized valence triple-ζ basis sets 6-311G**. As can be seen from Tables I and VII, the ΔE_1 and ΔE_2 values computed with the larger basis set at the various levels all are higher by about 5 and 15 kcal/mol, repectively, than the respective values computed with the 6-31G* basis set. Consequently, ΔE_3 is reduced to 9.50 kcal/mol (MP3(fc)/6-311G**) and 4.72 kcal/mol (CISD(fc,ssc)/6-311G**), and with the vibrational zero-point energies considered we obtain $\Delta E_{3,\mathrm{corr}}$ values of 7.70 and 2.93 kcal/mol, respectively, at these levels.

The best established experimental value most likely is the equilibrium constants for reaction 3 and its reactin energy of 0.6 kcal/mol. This value together with the PA(3) = 176 kcal/mol results in the reported value of PA(1) = 176.6 kcal/mol.[14] The differences between the theoretical estimates for $\Delta E_{3,\mathrm{corr}}$ and the experimental value are 7.1 and 2.3 kcal/mol at the levels MP3(fc)/6-311G** and CISD(fc,ssc)/6-311G**, respectively. The agreement between the experimental value and the theoretical value determined at the CISD(fc,ssc)/6-311G**//RHF/6-31G*+ΔVZPE level is quite good. Of the values ΔE_1 and ΔE_2, we consider ΔE_1 to be more trustworthy because the ΔE_1 values determined at the MP3/- and CISD/6-311G**//RHF/6-31G* levels are within 1 kcal/mol of our best values determined with larger basis sets (Table I). With the calculated value of $\Delta E_1 = 187.6$ (±2.0) kcal/mol and the experimental value of $\Delta E_3 = 0.6$ kcal/mol, we obtain the value of $\Delta E_2 = 187.0$ (±2.0) kcal/mol. Our results suggest that the proton affinity of methyl nitrate used by Cacace et al. might be too low and that, as a consequence, the proton affinity of hydrazoic acid was assigned a value that also is too low.

5. Fragmentation Reactions. A. NO_2^+ Formation from Protonated Methyl Nitrate. Energies of the fragments formed in reaction 4, the generation of the linear nitronium ion NO_2^+ via methanol elimination from the conjugate acid of methyl nitrate, are summarized in Table VIII. At the RHF/6-31G* level and including the scaled vibrational zero-point energies, reaction 4 is endothermic

$$(CH_3ONO_2)H^+\ (ecl.\text{-}4.1) \rightleftarrows CH_3OH + NO_2^+ \tag{4}$$

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(45) VIBRATE by M. Kirk Hall and R. Glaser: Quantum Chemistry Program Exchange, QCPE no. 611. *QCPE Bull.* **1992**, *12*, 17.

Table VIII. Methanol Affinities of NO_2^+ and Nitrogen Affinity of NH_2^+ ($^1A_1$)[a]

		6-31G*			6-311G**	
molecule	level	energy	VZPE	E_{diss}	energy	E_{diss}
NO_2^+	RHF	−203.677805	8.34	22.95	−203.737299	22.90
1.0912	MP2	−204.220983		24.28	−204.329676	22.91
	MP3	−204.181562		24.35	−204.283809	23.05
	CISD(fc)	−204.145363		−14.17	−204.245773	−20.14
	CISD(fc,ssc)	−204.203144		21.36	−204.307232	18.77
MeOH	RHF	−115.035418	34.72		−115.075758	
	MP2	−115.344941			−115.435662	
	MP3	−115.360783			−115.452253	
	CISD(fc)	−115.342288			−115.427897	
	CISD(fc,ssc)	−115.367622			−115.458873	

		6-311G(df,p)		
molecule	level	energy	VZPE	E_{diss}
NH_2^+	RHF	−55.127292	12.36	51.58
1.0296	MP2	−55.291386		89.25
109.99	MP3	−55.311634		79.75
	CISD(fc)	−55.313017		57.62
	CISD(fc,ssc)	−55.320314		75.87
N_2	RHF	−108.943949	3.94	
1.0784	MP2	−109.323752		
	MP3	−109.318677		
	CISD(fc)	−109.301466		
	CISD(fc,ssc)	−109.328124		

[a] All values are based on the RHF/6-31G* structures.

by 21.68 kcal/mol. Basis set effects are modest; the reaction energy is 21.63 kcal/mol at RHF/6-311G**//RHF/6-31G*+ΔVZPE(6-31G*). Electron correlation effects on this reaction energy also are relatively small (Figure 4) since 4.1 already indicates essentially complete ionization of the ester O–N bond. At the MP2, MP3, and CISD(ssc) levels and including the RHF VZPE correction, the reaction energies for reaction 4 are 21.64, 21.78, and 17.50 kcal/mol, respectively, with the 6-311G** basis set. Note the deviations from Dewar's value of 41.3 kcal/mol for this reaction energy.[16]

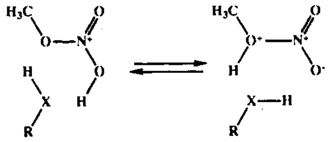
B. Dediazoniation of Aminodiazonium Ion. The endothermicity of the dediazoniation of heterosubstituted diazonium ions $(XNN)^+$ increases with the electronegativity of X.[13] For **2**, dediazoniation energies of 78.5 and 79.7 kcal/mol were determined at the MP4(fc,sdtq)/6-311G(df,p) level based on the RHF/6-31G* and MP2(fu)/6-31G* structures, respectively. For the evaluation

$$H_2N_3^+\ (\mathbf{2}) \rightleftharpoons NH_2^+\ (^1A_1) + N_2 \qquad (5)$$

of reaction 5, the singlet state $^1A_1$ of the amino cation[46] is relevant. The $^3B_1$ ground state of NH_2^+ is 30.2 kcal/mol more stable than the $^1A_1$ state, but its formation is spin-forbidden. With the size-consistency corrected CISD energies of **2a** (Table I) and the fragments (Table VIII), a dissociation energy of 75.87 kcal/mol results. Vibrational zero-point energy corrections (RHF/6-31G* level, scaled by the factor 0.9) reduce the reaction energy by 6.12 kcal/mol. The calculated dissociation energies thus fall within the range between 69.8 and 73.6 kcal/mol. In spite of the computational uncertainties, this estimate clearly points up that aminodiazonium ions are relatively stable toward dediazoniation—much more so than the alkyldiazonium ions—and this result supports the possibile intermediacy of aminodiazonium ion in the intramolecular Schmidt reaction[26] while it is in contrast with the dissociation energy of 1.7 kcal/mol reported by Cacace et al.[14]

Summary and Conclusion

Methyl nitrate **3** and its conjugate acids **4.2**–**4.4** prefer the staggered CH_3 conformation, whereas ester-O protonation leads to eclipsed methanol-solvated NO_2^+ ions **4.1**. The structures of **3** and **4** indicate that Y-conjugation is more important for the O_{term} protonated ions than for CH_3ONO_2. The activation barriers for CH_3 rotation can be determined adequately at the RHF level, but reliable relative isomer stabilities require good correlation methods in conjunction with well polarized valence triple-ζ basis sets. The model dependency reflects the dramatically different electronic reorganizations associated with ester-O vs O_{term} protonation. At our highest level, CISD(fc,ssc)/6-311G**//RHF/6-31G* and including the RHF/6-31G* ΔVZPE estimates, we obtain a preference of 6.2 kcal/mol for the ester-O protonated ion and a gas-phase proton affinity of 184.7 kcal/mol. Semiempirical methods give qualitatively similar results regarding conformational preferences and protonation site, but significant quantitative differences occur for relative isomer stabilities and proton affinities. We conclude that ester-O and terminal-O protonation of CH_3ONO_2 are competitive processes with a moderate preference for the former. These intrinsic preferences might qualitatively carry over to solution chemistry and ester-O protonation should be thermodynamically and kinetically favored as bimolecular pathways for proton transfer become easily accessible and the high barriers estimated for the *intra*molecular proton transfer (e.g. **4.3** to **4.1**) are avoided (as shown). At the CISD/6-311G**//RHF/6-31G*+ΔVZPE level, the gas-phase dissociation of the ester-O protonated CH_3ONO_2 is predicted to require only 17.5 kcal/mol of activation energy, and this



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low endothermicity explains why alkyl nitrates are such potent nitrating reagents in acid media.

In our recent study of heterosubstituted diazonium ions, we reported a protonation energy $\Delta E_{1,\mathrm{corr}}$ = 181.6 kcal/mol for the formation of aminodiazonium ion from HN_3 that was determined at the MP4(fc,sdtq)/6-311G**//MP2-(full)/6-31G*+ΔVZPE(MP2/6-31G*) level. The series of CI calculations presented here indicate that the agreement of the theoretical value reported by Cacace et al. with their experimental value is fortuitous. At our highest level, CISD(fc,ssc)/6-311G(df,p)//MP2/6-31G*+ΔVZPE-(MP2/6-31G*) we find a proton affinity of 186.4 kcal/mol for HN_3. Inclusion of core electrons in the active space of the CI calculation, addition of f-type functions, and structural effects were shown to affect this value only modestly. The theoretical estimate for the proton affinity is thus significantly higher (>10 kcal/mol) than the one reported by Cacace et al.

In good agreement with experiment, the reaction energy of ΔE_3 = 2.9 kcal/mol was calculated for the proton-transfer reaction $CH_3ONO_2 + H_2N_3^+ \rightleftharpoons CH_3ONO_2)H^+ + HN_3$ at CISD/6-311G**//RHF/6-31G*+ΔVZPE. These theoretical results suggest that the reported experimental proton affinity of HN_3 (176.6 kcal/mol) might be too low *as a consequence of evaluating the proton-transfer equilibrium with an underestimated proton affinity of* CH_3ONO_2.

With the CI energies of aminodiazonium ion **2a**, we have reconsidered the reaction energy for its dediazotization. Confirming the results obtained at full fourth-order Møller–Plesset levels and in sharp contrast to prior semiempirical results, the dediazotization of **2a** is predicted to be endothermic by 73.6 kcal/mol at the CISD/6-311G-(df,p)//RHF/6-31G*+ΔVZPE level.

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Registry No. 1, 7782-79-8; **2a**, 85990-23-4; 3, 598-58-3; 4.1, 99573-80-5; NO_2^+, 14522-82-8; NH_2^+, 15194-15-7.

Supplementary Material Available: Optimized structures determined at the semiempirical levels (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Carbon Acidity. 82. Equilibrium Cesium Ion Pair Acidities of Some Substituted 1,3-Dithianes

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The equilibrium cesium ion pair acidities in tetrahydrofuran have been determined at 25 °C for 2-*p*-biphenylyl-1,3-dithiane (29.1), 2-phenyl-1,3-dithiane (30.5), 4-methyl-2,6,7-trithiabicyclo[2.2.2]octane (30.2), 1,3-dithiane (36.5), and 2-methyl-1,3-dithiane (38.2). Studies of their acidities over a wide range of concentrations indicate that these dithianylcesium salts exist as monomeric ion pairs in solutions with concentrations ranging from 10^{-3} to 10^{-5} M. The corresponding ion pair acidities in cyclohexylamine have been reinvestigated, and the corrected pK_a values are 28.7, 30.0, 29.7, 37.5, and 37.8, respectively. Comparisons of these pK_a values with those in dimethyl sulfoxide show remarkable agreement despite the difference in the nature of the solvents.

Introduction

There is abundant evidence of the abilities of sulfur to markedly enhance both thermodynamic and kinetic acidities of protons on adjacent carbons.[2,3] Of the derived reagents useful in organic synthesis, 1,3-dithianes have been particularly valuable due to their abilities as masked nucleophilic acylating reagents.[4,5] Accordingly, a thorough understanding is desirable of the relative stabilities of dithianyl anions and the nature of their ion pairs in solutions such as that obtained by studying their equilibrium acidities. The pK_a values for several 1,3-dithianes have been previously reported for cesium salts in cyclohexylamine (CHA)[6,7] and lithium salts in tetrahydrofuran

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