is a linear combination of $d_{x^2-y^2}$ and d_{z^2} orbitals on each cobalt. These orbitals are arranged in phase with respect to each other, and no bridge-ligand character is present in this level. The level labeled 2bu consists of the linear combination of these same orbitals; however, in this case they are combined in an antibonding manner. Bridge-ligand character is present in this level. From the molecular orbital diagram of Figure 5, the orbital containing the metal–metal antibonding combination of orbitals lies lower in energy than the one containing the bonding combination. The counterintuitive reversal of these two levels occurs via the participation of the bridge ligands, but in particular the nitrosyl bridge. The nitrosyl 2π character accounts for almost 25% of the orbital character in this molecular orbital. The carbonyl 2π level contributes slightly more than 5%. Overall, both bridge ligands are present in this orbital, but the nitrosyl bridge character is present in a much larger amount and contributes a strong stabilizing influence to this level, stabilizing the orbital containing the metal–metal antibond relative to the level containing the metal–metal bond. The flip-flop of the expected ordering of molecular orbitals in $Cp_2Co_2(CO)(NO)$ compared to $[CpCo(CO)]_2$ is reflected in $[CpFe(NO)]_2$ shown in Figure 3. The energetic proximity of the nitrosyl 2π level to the cobalt orbitals, relative to that of the carbonyl 2π, clearly accounts for the reversal in levels found in $Cp_2Co_2(CO)(NO)$ relative to $[CpCo(CO)]_2$.

The electrochemistry of $Cp_2Co_2(CO)(NO)$ described by Bernal and co-workers[9] indicates that this complex is easily and reversibly reduced to $[Cp_2CO_2(CO)(NO)]^-$, a compound isoelectronic to $[CpCo(NO)]_2$. The oxidation of $Cp_2Co_2(CO)(NO)$ is not reversible. Formation of the cation $[CpCo(CO)(NO)]^+$ would yield a complex isoelectronic to $[CpCo(CO)]_2$ which is itself unstable with respect to decomposition in solution. The values shown in Table I reflect the energy of the metal and ligand orbitals and the changes in those levels that occur upon oxidation of $Cp_2Co_2(CO)(NO)$ to the hypothetical cation $[Cp_2Co_2(CO)(NO)]^+$. Since the electron is removed from an orbital primarily metal in character, but more importantly containing no bridge-ligand character, there is a substantial change in the relationship between the metal and ligand levels, resulting overall in a much poorer match between these two types of orbitals. Most noticeable from the data presented in Table I is the loss of strong metal–2π interactions. The change in metal orbital levels relative to ligand 2π levels is most striking. In the hypothetical cation the difference in energy between these levels is 6.21 eV for the metal–nitrosyl interaction and 10.77 eV for the metal–carbonyl one. These values are both greater than the difference between the metal and bridge-ligand orbitals in the neutral $Cp_2Co_2(CO)(NO)$. The acceptor capacity of the 2π levels is not diminished upon oxidation, but the ability of the metal to transfer electron density into these levels has been substantially reduced.

Lowering the metal levels with respect to the bridge-ligand 2π levels in an oxidation increases the ability of the metal levels to interact with the 5σ levels of the bridge ligand. Table I reveals the energy differences between the metal d orbitals and the carbonyl and nitrosyl 5σ levels. Clearly the cobalt 5σ interaction becomes enhanced. From Table I, it is clear that the difference between the metal d levels and carbonyl 5σ levels in the neutral complex $Cp_2Co_2(CO)(NO)$ and the hypothetical cation becomes smaller upon oxidation. The effect of oxidation on the metal–nitrosyl 5σ interaction is the same, i.e., the metal levels are in closer proximity to the nitrosyl 5σ levels. However, the difference between metal and 5σ levels in both the neutral and cationic species is still much greater than the metal–carbonyl difference. In the neutral compound, $Cp_2Co_2(CO)(NO)$, the cobalt d orbitals are separated from the nitrosyl 5σ levels by 7.00 eV. In the hypothetical cationic species, this value is 6.21 eV, and indicative overall of virtually no increase in the amount of cobalt d orbital interaction with the nitrosyl 5σ levels. Overall, the amount of metal d level–carbonyl 2π interaction decreases substantially upon oxidation of $Cp_2Co_2(CO)(NO)$, and the metal d–carbonyl 5σ interactions increase. However, the increase in proximity of the metal d and nitrosyl 5σ orbitals does not result in any significant change in the bonding since these levels still remain quite far apart energetically. Consequently, the loss in cobalt–2π interaction coupled with the lack of a significant and compensatory cobalt–nitrosyl 5σ interaction upon oxidation can be construed as the trigger to the decomposition of $Cp_2Co_2(CO)(NO)$.

Conclusion

The instability of $[CpCo(CO)]_2$ with respect to decomposition in solution can be best understood in light of the perturbations on this system that are manifested in $[CpCo(CO)]_2^-$ and $Cp_2CO_2(CO)(NO)$. The neutral paramagnetic $Cp_2Co_2(CO)(NO)$ undergoes decomposition in solution when it is oxidized to $[Cp_2Co_2(CO)(NO)]^+$, isoelectronic to neutral $[CpCo(CO)]_2$. Similarly, the paramagnetic monoanion $[CpCo(CO)]_2^-$ remains stable in solution as well. Placing an electron into a molecular orbital containing no bridge-ligand character brings the metal d orbitals into closer proximity with the ligand 2π levels than they were in the neutral complex. The overall stability of $[CpCo(CO)]_2^-$ relative to its neutral parent appears to be mediated through the occupation of a molecular orbital primarily metal–metal antibonding in character.

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Unimolecular Dissociation of Primary Alkanediazonium Ions. Ab Initio and Semiempirical Molecular Orbital Calculations

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Abstract: Molecular orbital calculations for the loss of nitrogen from the methane, ethane, and propanediazonium ions are reported with use of semiempirical (MNDO, AM1) and ab initio procedures. At the MP3/6-31G**//HF/6-31G* level, corrected to 298 K, the enthalpies of dissociation to the classical ions are predicted to be 38, 11, and 10 kcal mol^{-1}, respectively. The semiempirical methods led to similar, although slightly higher dissociation enthalpies. MNDO calculations are reported for the dissociation of related diazonium ions.

Although the existence of alkane diazonium ions is well established, their precise role in reactions involving them is still not fully resolved.[1] Neither is there as yet any experimental structural information for any simple alkanediazonium ion.[2] One uncer-

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Table I. Total Energies of Fully Optimized Structures

molecule	symmetry	HF/STO 3G	HF/3-21G	HF/6-31G*	MP2/6-31G*[a]
$CH_3N_2^+$ (**1**)	C_{3v}	−146.362 38	−147.367 32	−148.216 06	−148.666 12
$C_2H_5N_2^+$ (**2**)	C_s	−184.958 70	−186.200 01	−187.264 41	
$C_3H_7N_2^+$ (**3**)	C_s	−223.542 54	−225.023 16	−226.302 67	
CH_3^+ (**4**)	D_{3h}	−38.779 48[b]	−39.009 13[b]	−39.230 64[c]	−39.329 44
$C_2H_5^+$ (**5**)	C_s	−77.408 06[b]	−77.872 60[b]	−78.311 23[c]	
$C_3H_7^+$ (**6**)	C_s	−115.996 32[b]	−116.705 26[b]	−117.351 11[c]	
N_2 (**7**)	$D_{\infty h}$	−107.500 65[b]	−108.300 95[b]	−108.943 95[b]	−109.261 57

[a] Core electrons included in MP2 calculation. Corresponding frozen core energies at these geometries: $CH_3N_2^+$, −148.65471; CH_3^+, −39.32538; N_2, −109.25528. [b] Reference 23. [c] Reference 22.

Table II. Total Energies at the HF/6-31G* Geometries

molecule	HF/6-31G**	HF/6-311G**	MP2/6-31G*	MP2/6-31G**	MP3/6-31G*	MP3/6-31G**	MP4(SDQ)/ 6-31G**
$CH_3N_2^+$ (**1**)	−148.221 28	−148.256 07	−148.645 85	−148.668 06	−148.653 68	−148.677 25	−148.688 21
$C_2H_5N_2^+$ (**2**)	−187.272 75	−187.313 46	−187.822 72	−187.861 09	−187.840 08	−187.880 83	−187.893 47
$C_3H_7N_2^+$ (**3**)	−226.313 99	−226.360 86	−226.991 59	−227.046 34	−227.018 25		
CH_3^+ (**4**)	−39.236 29[a]	−39.243 64[b]	−39.325 14[a]	−39.346 53[a]	−39.341 58[a]	−39.364 50[a]	−39.367 37[a]
$C_2H_5^+$ (**5**)	−787.320 51[a]	−78.333 86	−78.542 89[a]	−78.580 25[b]	−78.568 52[a]	−78.608 08[a]	−78.612 44[a]
$C_3H_7^+$ (**6**)	−117.363 32[a]	−117.382 60	−117.712 90[a]	−117.766 46	−117.748 28[a]		
N_2 (**7**)	−108.943 95[b]	−108.971 72[b]	−109.248 19[b]	−109.248 19[b]	−109.245 34[b]	−109.245 34[b]	−109.253 24

[a] Reference 22. [b] Reference 23.

Table III. Basis Set Effects on Diazonium Ion Dissociation (kcal mol^{-1})

	optimized geometries			HF/6-31G* geometries	
$RN_2^+ \rightarrow R^+ + N_2$	HF/STO-3G	HF/3-21G	HF/6-31G*	HF/6-31G**	HF/6-311G**
CH_3	51.6	35.9	26.0	25.8	25.5
C_2H_5	31.4	16.6	5.8	5.2	4.9
C_3H_7	28.6	10.6	4.8	4.2	4.1

tainty concerns the thermodynamics of nitrogen loss (eq 1). This has generally been assumed to be extremely exothermic,[1c] with one estimate[3] as high as 80 kcal mol^{-1}. Expectations of such large

$$R\text{-}N_2^+ \rightarrow R^+ + N_2 \qquad (1)$$

energy release prompted the suggestion[4] that diazonium ion decomposition should lead to unusually energetic or "hot carbonium ions" with properties different from those formed in other ways.

The dissociation enthalpy of the first member of the series, $CH_3N_2^+$ (**1**), admittedly a special case, has recently been measured in the gas phase. While the available data differ somewhat (38[5] and 49 + 2[6] kcal mol^{-1}), this process is clearly not exothermic at all but is surprisingly endothermic. Ab initio molecular orbital calculations also suggest that the gas-phase dissociation of **1** is endothermic, although the values predicted with different basis sets varied widely.[7,8] In neither case were the effects of electron correlation included.

In the present paper the unimolecular dissociation of the methane- (**1**), ethane- (**2**), and 1-propane- (**3**) diazonium ions have been examined at uniformly high levels of ab initio molecular orbital theory. These are discussed in terms of their chemistry and compared with the results of parallel semiempirical MNDO and AM1 calculations.

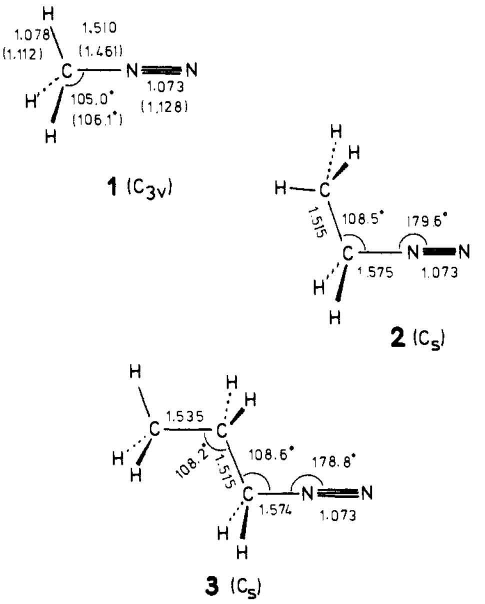

Figure 1. Calculated diazonium ion geometries with use of the HF/6-31G* and, in parentheses, MP2/6-31G* procedures.

Theoretical Methods

Ab initio STO 3G, 3-21G, and 6-31G* calculations[9] were carried out with complete geometry optimization within the specified point groups on Harris Corp. H100 or H800 minicomputers with GAUSSIAN 77.[10] Single-point calculations (6-31G* geometries) with larger basis sets (6-

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Table IV. Correlation Effects on Diazonium Ion Dissociation with use of the 6-31G** Basis Set and HF/6-31G* Geometries

$RN_2^+ \rightarrow R^+ + N_2$	HF	MP2	MP3	MP4(SDQ)
CH_3	25.8	46.0	42.3	42.4
C_2H_5	5.2	20.5	17.2	17.4
C_3H_7	4.2	19.9	(16.2)[a]	

[a] "Projected" from MP2 data, see text.

31G** and 6-311G**) and Møller-Plesset second[11] (MP2), third[12] (MP3), and partial[13] fourth (MP4(SDQ)) order valence electron correlation corrections were carried out on an IBM 3081D with standard options in the GAUSSIAN 82[14] program system.

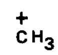
Semiempirical MNDO[15] calculations were performed with Harris versions of programs originating in the laboratory of M. J. S. Dewar and AM1[16] calculations with an IBM[17] version of the MOPAC package.[18]

Zero-point energies, thermal enthalpies, and absolute entropies at 298 K were obtained from the calculated harmonic frequencies and moments of intertia within the rigid-rotor harmonic-oscillator approximation.[19]

Results

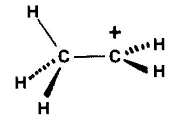
Geometries. Key features of the 6-31G* geometries of the diazonium ions (**1**–**3**) are shown in Figure 1. The rather short NN bond lengths discussed by Vincent and Radom[7] in their earlier calculations on **1** were evident in the present work at all levels. Thus with the 6-31G* basis set, both with and without inclusion of electron correlation (MP2), the NN bond distances were calculated (Figure 1) to be 0.005 Å shorter than in N_2 itself.[20] The unexpectedly long CN bond lengths in the HF/6-31G* geometries appear to be artifacts associated with the neglect of electron correlation. In the optimized MP2/6-31G* geometry of **1** this is comparable to the value[20] for methylamine (although still longer than the 1.39–1.43 Å determined experimentally for the benzenediazonium ion[21]).

Dissociation Energies. Total energies of the fully optimized species **1**–**7** are collected in Table I, with the higher level single point calculations (HF/6-31G* geometries) in Table II. Many of the data for **4**–**7** were available from the work of Pople and co-workers[22,23] and are included here for convenience. The dissociation energies (eq 1) calculated with progressively larger basis sets, but with no allowance for electron correlation, are summarized in Table III. While it is now generally accepted that little useful energy data can be obtained at the STO-3G level[24], these data are included both for comparison with the semiempirical calculations and to clarify the nature and magnitudes of the basis set effects in these reactions. Although initially large, these appear to be rather systematic and essentially saturated at the 6-31G* level. Thus, the addition of polarization functions on hydrogen (6-31G**) and the additional flexibility of the triple-ζ valence shell (6-311G**) modified the 6-31G* values by less than 1.0 kcal mol^{-1}. For the methanediazonium ion (**1**) the predicted dissociation energies appear to converge to a value close to 26 kcal mol^{-1} and, for the ethane (**2**) and propane (**3**) analogues, to 4–5 kcal mol^{-1}.



$\overset{+}{C}H_3$

4



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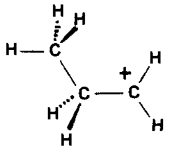

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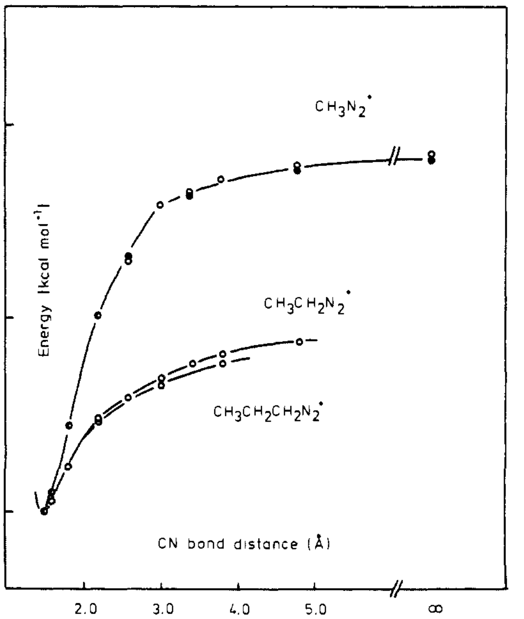

Figure 2. Calculated energy profiles for nitrogen loss from RN_2^+ as a function of the CN bond distance. Single-point MP3/6-31G* calculations with use of HF/6-31G* geometries (•); MP3/6-31G* calculations with use of MNDO geometries (○); alternative techniques differ by ≤0.5 kcal mol^{-1} (◐).

The STO 3G result for **1** is identical with that of Vincent and Radom[7] while their 4-31G value (28.5 kcal mol^{-1}) fell between the present 3-21G and 6-31G* data. However, both the 25.2 kcal mol^{-1} reported by Simmonetta and co-workers[8] using Dunning's [4s2p] contraction of Huzinaga's 9s/5p basis set[25] and the 18.4 kcal mol^{-1} obtained when augmented with polarization functions seem too small.[26]

The very significant effects of electron correlation (neglected in the previous[7,8] studies) are summarized for the 6-31G** basis set in Table IV. As expected, the largest corrections occur at the MP2 level, while it appears that MP4(SDQ) but not MP3 corrections may be safely neglected. For **3**, where only MP2 calculations were feasible with this basis set, the third-order corrections were "projected"[22] from the smaller 6-31G* basis.[27] Although the inclusion of electron correlation is vital for a proper description of the dissociation energies, the use of geometries calculated without correlation seems to introduce little error. The 6-31G* dissociation energies of **1** optimized with and without electron correlation (MP2) differed by only 1 kcal mol^{-1}. Thus, it seems unlikely that more sophisticated treatments would result in dissociation energies for these ions that differed from the

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Table V. Thermal Energies, Absolute Entropies, and Heats of Formation[a]

	HF/6-31G*// HF/6-31G*		MNDO (lit)	
	E'[b]	$S°$	$S°$	ΔH_f
$CH_3N_2^+$ (**1**)	33.0	58.3	58.1	223.5 (223,[c] 209.4[d])
$C_2H_5N_2^+$ (**2**)	53.9	67.3	68.5	213.8
$C_3H_7N_2^+$ (**3**)			76.5	208.0
CH_3^+ (**4**)	22.9	44.5	44.6	243.9 (261.3[e])
$C_2H_5^+$ (**5**)	42.6	57.3	60.2	219.7 (221.8[f])
$C_3H_7^+$ (**6**)			69.4	212.4 (210.5[f])
N_2 (**7**)	5.4	45.7	45.8	8.0 (0.0)

[a] Energy units, kcal mol^{-1}, entropy units, cal mol^{-1} deg^{-1}. [b] Sum of zero-point and vibrational, rotational, and translation energies at 298 K. [c] Reference 5. [d] Reference 6. [e] Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647–3652. [f] Reference 34.

MP3/6-31G**//HF/6-31G* data by more than 1–2 kcal mol^{-1}.

The variation in the calculated energy as a function of the CN distance is shown in Figure 2 for single-point MP2/6-31G* calculations at both the optimized HF/6-31G* and MNDO geometries for **1** (C_{3v} symmetry) and the MNDO geometries only for **2** and **3** (C_s symmetry). The close agreement between the two approaches for **1** (the largest difference between the two curves was 0.5 kcal mol^{-1}) suggests that the simpler procedure should usefully approximate the full MP2/6-31G*//HF/6-31G* calculations in the latter cases. For all three ions the energy is predicted to rise monotonically from reactants to products with no intevening maxima.

Dissociation Enthalpies and Free Energies. The quantities in Table IV, obtained directly from the calculated total energies, refer to the vibrationless species at 0 K. Those at the highest level for which actual or projected data were available (MP3/6-31G**//HF/6-31G*) were recast as thermodynamic quantities ΔH and ΔG with use of eq 2 and 3. Here, E' refers to the sum

$$\Delta H = \Delta E_{SCF} + \Delta E' + RT \qquad (2)$$

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

of the zero-point, vibrational, rotational, and translational energies at 298 K (Table V). While no problems arise for the dissociation of **1**, there is some uncertainty in the calculated entropies of **2**, **3**, and the corresponding carbocations, where low-frequency torsional motions were treated as harmonic vibrations. However, careful tests on closely related molecules show that absolute entropies calculated in this way are underestimated by only 1–2 cal mol^{-1} deg^{-1} relative to the experimental values.[28] Moreover, in the present case, where only ΔS is of concern, such errors should partially cancel.

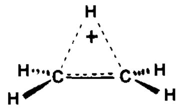
Table VI also includes ΔH and ΔG calculated by the semiempirical MNDO and AM1 procedures. For **1**, the MNDO calculations are complicated by the large but nonsystematic error in $\Delta H_f(CH_3^+)$ (Table V). In this particular case the experimental, rather than the calculated, heat of formation was used. With this "adjustment" all methods predict dissociation enthalpies of **1** to fall at, or between, the reported experimental values.[5,6]

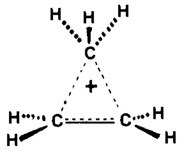
The MNDO geometries and energies of **1** and **2** have been discussed in detail elsewhere.[29] It is noteworthy that both semiempirical methods lead to results close to those obtained at rather high levels of ab initio theory with of course a minute fraction of the computational effort.

The 10–12 kcal mol^{-1} difference between the calculated dissociation free energies and enthalpies (Table VI) is a manifestation of the large positive entropy associated with the additional rotational and translational degrees of freedom in the fully dissociated products. While the exact form of the free energy profile cannot be determined without direct calculations,[30] it must nevertheless lie below the enthalpy surface throughout the reaction. Thus, if the forms of the potential energy surfaces represented in Figure 2 are correct, the overall free energy barriers will not be greater than the corresponding ΔH values.

Discussion

Relation to Alkanediazonium Ion Chemistry. Of the simple alkanediazonium ions, the methyl analogue (**1**) is predicted to be the most stable with respect to nitrogen loss. Indeed, this species has been observed spectroscopically in nonnucleophilic solvents at low temperatures.[31] From the calculated data it seems most unlikely that similar observations could be made for the higher homologues (unless substituted with electron-withdrawing groups, see below). In practice, nitrogen loss from **2** and **3** will be somewhat more exothermic than implied by the results in Table VI since the resulting ions will almost certainly have the lower energy[22] nonclassical structures **8** and **9**. With use of the 3 kcal mol^{-1} estimated by Houle and Beauchamp[32] for the energy difference between **5** and **8**, ΔH for the overall process **2** → **5** → **8** is predicted to be 8 kcal mol^{-1} at the MP3/6-31G** level. In the case of **3**, the intermediate nonclassical carbenium ion, **9**, will rapidly[33] isomerize to **10**. Taking the energy difference between **6** and **10** to be 20.8 kcal mol mol^{-1}[34] leads to ΔH = −11 kcal mol^{-1} for **3** → **9** → **10**.


8


9

McGarrity[35] has pointed out that solvation effects in these reactions are unlikely to be large. While no direct information on this point is available, the solvation enthalpy of 1-$C_3H_7C{\equiv}O^+$ in polar nonnucleophilic solvents is estimated[36] to be only ca. 3 kcal mol^{-1} more negative than that of **10**. If a similar situation holds for the isoelectronic diazonium ion (**3**), the predicted exothermicity of nitrogen loss seems unremarkable. It is, for example, comparable to the analogous ionization of 2°-chlorides in similar solvents.[41] However, here the activation free energies ($\Delta G^{\ddagger}$) fall[41] in the neighborhood of 30 kcal mol^{-1}, whereas an upper limit for

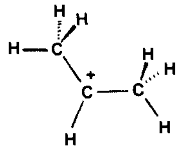

10

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Table VI. Diazonium Ion Dissociation Enthalpies and Free Energies at 298 K

	ΔH				ΔG		
reaction	exptl	MP3/6-31G**	MNDO	AM1	MP3/6-31G**	MNDO	AM1
$CH_3N_2^+ \rightarrow CH_3^+ + N_2$	38,[b] 49[c]	38	46[d]	42	28	36[d]	32
$C_2H_5N_2^+ \rightarrow C_2H_5^+ + N_2$		11	14	17	1	3	4
$C_3H_7N_2^+ \rightarrow C_3H_5^+ + N_2$		10[e]	12	15	0[e]	1	4

[a] Units, kcal mol^{-1}. [b] Reference 6. [c] Reference 5. [d] Calculated by using the experimental heat of formation of CH_3^+, see text. [e] $\Delta E'$ and ΔS for **2** → **5** + **7** used.

Table VII. Relative Dissociation Enthalpies (ΔH_4) and RN_2^+ (ΔH_5) and R^+ (ΔH_6) Stabilization Enthalpies[a,b]

	MNDO			HF/6-31G**[c]			MP3/6-31G**[c]		
R	ΔH_4	ΔH_5	ΔH_6	ΔH_4	ΔH_5	ΔH_6	ΔH_4	ΔH_5	ΔH_6
$(CH_3)_2CH$	-44.8	2.7	47.5						
C_3H_7	-33.4	2.5	35.9	-21.5	11.5	33.0	-26.1[d]	10.6[d]	36.8[d]
C_2H_5	-31.9	1.9	33.8	-20.6	9.4	29.9	-25.1	8.6	33.7
$CH_3C(=O)CH_2$	-19.5	-1.9	17.6						
CF_3CH_2	-9.4	-21.8	-12.4						
$(CF_3)_2CH$	-4.0	-38.1	-34.1						
CH_3	0	0	0	0	0	0	0	0	0

[a] Units, kcal mol^{-1}. Positive values of ΔH_5 and ΔH_6 indicate that RN_2^+ and R^+ are more stable than $CH_3N_2^+$ and CH_3^+, respectively. [b] Based on the experimental heat of formation of CH_3^+, see text. Other data from this work and ref 15. [c] Single-point calculations at HF/6-31G* geometries. Data from this work, ref 23, and propane (C_{2v}): HF = -118.27616; MP2 = -118.72526. [d] Data "projected" from MP2 and correlation correction with 6-31G* basis set, see text.

nitrogen loss from **3** is predicted to be 10 kcal cal mol^{-1}.

Relative Stabilities of Alkanediazonium Ions. The dissociation energies of the diazonium ions can be compared with that of $CH_3N_2^+$ (**1**) by using eq 4. The energy of this process is then conveniently expressed as the difference between the stabilization energies[22] of RN_2^+ (eq 5) and R^+ (eq 6) relative to the methyl analogues ($\Delta H_4 = \Delta H_5 - \Delta H_6$). These data (Table VII) confirm

$$RN_2^+ + CH_3^+ \rightarrow R_+ + CH_3N_2^+ \quad (4)$$

$$RN_2^+ + CH_4 \rightarrow RH + CH_3N_2^+ \quad (5)$$

$$R^+ + CH_4 \rightarrow RH + CH_3^+ \quad (6)$$

the intuition that the lower dissociation energies of diazonium ions containing electron releasing groups are due to preferential stabilization of the carbenium ions. When substituted with electron-withdrawing groups diazonium ions are far more stable with respect to nitrogen loss. This is reflected in the calculated dissociation energies of $CF_3CH_2N_2^+$ and $(CF_3)_2CHN_2^+$, both of which have been observed at low temperatures in nonnucleophilic solvents.[42] Similarly, the ease of nitrogen loss from the 2-oxopropanediazonium ion is predicted to be intermediate between **1** and **3**.

Alkylation of Nucleic Acids by Diazonium Ion Prrcursors. These relationships are of special interest in connection with the alkylation of nucleic acids by carcinogenic precursors of alkanediazonium ions.[43-45] The tendencies of certain alkylating agents to lead to higher proportions of O-alkylated adducts has been widely discussed, but only partially understood.[46,47] In previous work we have shown[29] that the higher proportion of O-alkylation observed[46-48] for **2** (compared to **1**) is associated with the greater ease of nitrogen loss in the corresponding unimolecular dissociation. While the carbenium ions themselves are not involved,[44] the energetics of nitrogen loss appear to control the shapes of the potential surfaces for the corresponding *bimolecular* processes (see ref 29 for complete discussion). The 2-oxopropanediazonium ion provides a further example of this kind. The ratio of O- to N-alkylation of guanine by presumed precursors of this ion[49] is intermediate between those observed[43] for **1** and **3**. Similar relationships are evident in alkylation by agents that can be formulated as precursors of the 2-hydroxypropyl,[49] 2-chloroethyl,[50] and especially the 2-fluoroethyl[50] diazonium ions.

Conclusions

Primary, unfunctionalized alkanediazonium ions, other than **1**, are predicted to undergo unimolecular loss of N_2 in a reaction which is very facile ($\Delta G^{\ddagger} \leq 10$ kcal mol^{-1}) but not remarkably exothermic. The thermodynamics of nitrogen loss relative to $CH_3N_2^+$ are principally determined by substituent stabilization or destabilization of the resulting carbenium ions. Further examples of the relationship[29] between the latter and the relative extents of O- vs. N-alkylation of nucleic acids and their constituents by diazonium ion precursors are cited.

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