

**Figure 3.** Modification of the fluorescence intensity ( $\lambda_{\text{exc}}$  421 nm,  $\lambda_{\text{em}}$  648 nm) of  $\text{In}_2\text{O}_3\text{-CG}$  (a) and  $\sim 8 \times 10^{-10}$  mol/cm<sup>2</sup> ZnTPP on  $\text{In}_2\text{O}_3\text{-CG}$  (b) as the applied potential is scanned from 0.0 to 1.0 V and back. Trace (a) illustrates only the absence of any change in intensity due to the substrate. The dip in (b) represents a loss in intensity of about 20%. The zero of the background trace has been moved for clarity.

evaporating to dryness under a stream of  $\text{N}_2$  or by soaking the end of the strip in the solution for several minutes and rinsing off the excess with distilled water.

Fluorescence spectra indicate that the ZnTPP applied to the electrode in this manner does not merely crystallize and adhere to the surface. Excitation and emission spectra of various forms of ZnTPP are shown in Figure 1. Experimental spectra of the solution phase are very comparable to previously reported ones for both absorption<sup>21-24</sup> and fluorescence.<sup>25,26</sup>

Work with crystalline material is hampered by artifacts caused by full absorption of the excitation beam and reabsorption of emission, but we find that purified crystalline powder dusted onto glass and either immersed in 1 M HCl or left in air shows a long-wavelength emission peak at 658 nm, which is red shifted by about 10 nm from the value observed in toluene or with the electrodes.<sup>27</sup>

No evidence of demetalation of the ZnTPP is observed, even though demetalation in solution by HCl is a known reaction.<sup>28</sup> Our spectra have none of the features distinctive to metal-free porphyrin ( $\text{H}_2\text{TPP}$ ), i.e., excitation peaks near 515, 550, 595, and 650 nm and emission peaks at ca. 660 and 720 nm.<sup>27,28</sup> An authentic sample of  $\text{H}_2\text{TPP}$  applied to the electrodes does show these features.

The ability to observe a fluorescence signal from ZnTPP applied to BPPG as indicated by preliminary experiments is particularly noteworthy. Similar systems are of great interest from a technological standpoint, and a simple monitoring method for adsorbates in operating cells would be valuable to kinetic studies.

Cyclic voltammograms of the adsorbed ZnTPP shown in Figure 2 exhibit two closely spaced oxidation peaks at ca. 820 and 900-1000 mV vs. Ag/AgCl. The two corresponding reduction peaks occur near 700 mV and between 150 and 300 mV. The magnitudes of the peak currents of the two oxidations do not exhibit the same dependences on scan rate,  $v$ . The 820-mV peak, which does not shift more than 10 mV as  $v$  increases from 100 to 250 mV/s, grows linearly with  $v$ . This indicates that the electroactive species is bound to the surface.<sup>29</sup> The peak potential of the second oxidation shifts to a more positive value by ca. 60 mV as  $v$  changes from 100 to 300 mV/s and exhibits a more complex dependence on  $v$ . Previous studies of ZnTPP in aprotic solutions<sup>23,24</sup> show that successive reversible, one-electron ring oxidations occur at 0.8 and 1.1 V vs. SCE. The difference between

the peak potentials, 0.3 V, is much larger than that observed in the present experiments. Our results could suggest that the electroactive material is undergoing essentially the same electrode process, but in at least two different environments. At present, the precise nature of the electrode process is not clear, and it is not essential to our purpose here to define it. It is chemically reversible since one can run cyclic voltammograms repeatedly with only minor changes in response; however, the splittings between anodic and cathodic peaks show that slow kinetics exist, either in charge transfer or in chemical changes to the molecular structure. Data presented below show that oxidation is fast, but re-reduction is quite slow. The simplest explanation is that a cation radical is formed by oxidation and that it is stabilized by its interaction with the electrode against chemical attack. Other more complicated possibilities involving reversible alteration of the molecular structure may be more likely.

If  $8 \times 10^{-10}$  mol of ZnTPP (2  $\mu\text{L}$ ) are applied to a 1-cm<sup>2</sup> portion of the electrode and dried, the amount oxidized during the potential scan is close to  $2 \times 10^{-10}$  equiv (as determined by estimating the area under the anodic peak). If about 1 cm<sup>2</sup> of the electrode is soaked for ca. 10 min in the solution and the excess is rinsed off with water, then only ca.  $6 \times 10^{-11}$  equiv are oxidized; if the excess is allowed to dry, again  $2 \times 10^{-10}$  equiv are electroactive. The deposition, though, is not irreversible. If the electrode is rinsed well with toluene, the cyclic voltammogram obtained is identical with that of a fresh electrode.

Simultaneous electrochemical and fluorometric experiments provide evidence that at least a portion of the fluorescent material on the surface is also electroactive. The peak fluorescence intensity is diminished as the potential is scanned past the oxidations as shown in Figure 3(b). This attenuation is equal to approximately one-fifth of the original peak intensity, a fraction that correlates well with the ratio of electroactive equivalents estimated from the voltammetric response to the number of moles applied by syringe.<sup>30,31</sup> After completion of the potential scan, the fluorescence intensity does not revert completely to its initial value in this figure because of slow re-reduction; however, there is some irreversible loss of material with time.

Excitation and emission spectra of the ZnTPP on an electrode being held at 1000 mV show qualitative differences, as well as an overall attenuation of peaks by about one-quarter, from those obtained with the electrode at open circuit.<sup>30</sup>

On BPPG, the fluorescence intensity of the ZnTPP is also attenuated by oxidation. Further investigation of this system is currently being conducted.

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(30) In recent work, we have observed attenuation exceeding 50%. The residual fluorescence may have a contribution from the oxidized form.

(31) Whether the fluorescence observed from the ZnTPP on a substrate is emitted from a layer directly adjacent to the surface is not entirely clear at present. Using a syringe to apply the solution to the electrode does not result in uniform surface coverage, and multilayer regions must exist. However, fluorescence is observed even if the electrode is soaked for several minutes in the ZnTPP solution and rinsed with distilled water, a method which seems to result in greater uniformity and closer to monolayer coverage.

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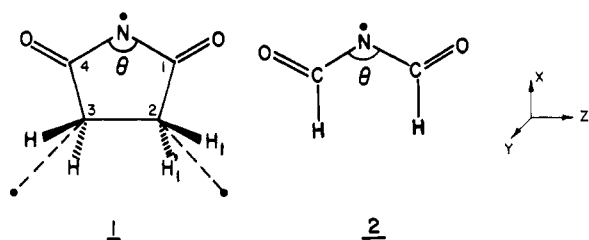
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### The $\Pi$ and $\Sigma_N$ Electronic States of the Succinimidyl Radical. Can Nitrogen-Centered Radicals Have $\Sigma_N$ Ground States? An ab Initio Study

Sir:

The succinimidyl radical **1** was first proposed as an intermediate almost 40 years ago,<sup>1</sup> but its chemical properties remained a

mystery. An important breakthrough, the generation of two



succinimidyl radicals, a ground state and an excited state, with distinct chemical properties, was achieved recently by Skell et al.<sup>2</sup> This is the first reported generation of an excited-state radical in a thermal chain reaction.<sup>2</sup> All attempts to observe the two succinimidyl radicals by spectroscopic methods<sup>2,3</sup> were unsuccessful, leaving their intimate properties poorly characterized.<sup>2</sup> We report the first ab initio calculations<sup>4,5</sup> for the ground state and for the first excited state of **1**. We find that the ground state of **1** [ ${}^2B_1$  ( $1\pi$ )] is  $\sim 20$  kcal·mol<sup>-1</sup> ( $\Delta E$ ) more stable than the first excited state [ ${}^2A_1$  ( $1\sigma$ )]. In other imidyl or amidyl radicals, either cyclic or acyclic,  $\Delta E$  is predicted to be  $\geq 20$  kcal·mol<sup>-1</sup>. Smaller  $\Delta E$  or even  $\Sigma_N$  ground states are predicted for sterically crowded aminyl radicals.

Calculations were carried out with the GAUSSIAN-70<sup>6a</sup> and GAUSSIAN-76<sup>6b</sup> series of programs by using the unrestricted Hartree-Fock (UHF) procedure.<sup>7</sup> Complete geometry optimizations within  $C_{2v}$  symmetry were carried out for the  ${}^2A_1$  ( $1\sigma$ ) and the  ${}^2B_1$  ( $1\pi$ ) states of **1** and of the acyclic analogue **2** (i.e.,  $2\sigma$  and  $2\pi$ ), using the STO-3G basis set.<sup>8a</sup> Single-point calculations with the 4-31G basis set<sup>8b</sup> followed.<sup>8c</sup> In  $1\pi$  and  $2\pi$ , the unpaired electron is formally delocalized over the entire  $\pi$  framework ( $\Pi$  radical) while in  $1\sigma$  and  $2\sigma$  it is formally localized in the  $sp_x^2$  orbital of nitrogen ( $\Sigma_N$  radical).

The optimized structures of  $1\pi$  and  $1\sigma$  (or of  $2\pi$  and  $2\sigma$ ) are similar except for the C=O bond lengths and the CNC angles (Figure 1).<sup>9</sup> The carbonyl bond lengths are longer in the  $\Pi$  radicals (1.314 and 1.320 Å in  $1\pi$  and  $2\pi$ , respectively) than in the  $\Sigma_N$  radicals (1.242 Å in  $1\sigma$ , 1.253 Å in  $2\sigma$ ), or in succinimide (1.215 Å at STO-3G).<sup>10</sup> The presence of five  $\pi$  electrons in the  $\Pi$  radicals compared with six in the other compounds is probably responsible for this bond lengthening. The C-N bond lengths are similar in  $1\sigma$ ,  $1\pi$ ,  $2\sigma$ , and  $2\pi$  (1.431, 1.429, 1.423, and 1.410 Å, respectively), and in succinimide (1.424 Å, STO-3G).<sup>11</sup> The CNC bond angle ( $\theta$ ) is smaller in  $1\pi$  (106.4°) than in  $1\sigma$  (117.7°) or in succinimide (115.35°, STO-3G).<sup>10</sup> The transformation of the

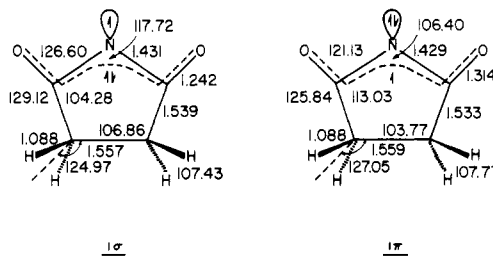


Figure 1. Optimized structures (STO-3G,  $C_{2v}$ ) of  $1\pi$  and  $1\sigma$ .

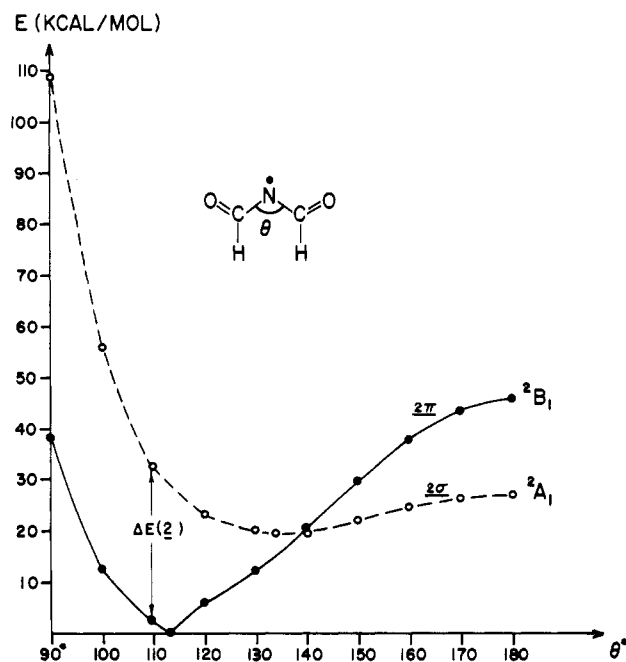


Figure 2. Angular potentials ( $\theta \angle \text{CNC}$ ) for  $2\sigma$  and  $2\pi$ .<sup>23b</sup>

$\Sigma_N$  state to the  $\Pi$  state involves the transfer of an electron from a  $\pi$  orbital [mainly N( $2p_y$ )], whose energy is insensitive to changes in  $\theta$ , to a  $\sigma$  orbital [mainly N( $sp_x^2$ )], which favors strongly small  $\theta$  angles.<sup>12</sup> In  $1\sigma$ , ring constraints prevent further broadening of  $\theta$  ( $\theta = 133.6^\circ$  in  $2\sigma$  and  $144^\circ$  in the  ${}^2A_1$  state of  $\text{H}_2\text{N}\cdot$ ).<sup>13</sup>

$1\pi$  is the ground state of the succinimidyl radical, and  $1\sigma$  is the lowest excited state. The ordering of the states is the same in **2**, in  $\text{H}_2\text{N}\cdot$ ,<sup>13</sup> and in substituted amidyl radicals.<sup>14</sup> The energy difference between the two states [ $\Delta E(1)$ ] is 55.0 kcal·mol<sup>-1</sup> at STO-3G. However, calculations of  $\text{H}_2\text{N}\cdot$  [ $\Delta E(\text{experimental}) = 29\text{--}32$  kcal·mol<sup>-1</sup>]<sup>13a</sup> reveal that at STO-3G  $\Delta E$  (49.2 kcal·mol<sup>-1</sup>)<sup>13b</sup> is overestimated. At 4-31G, however,  $\Delta E = 26.4$  kcal·mol<sup>-1</sup>, only 3–5 kcal·mol<sup>-1</sup> smaller than either the experimental or the best theoretical<sup>13c</sup> estimates. In **2**,  $\Delta E = 52.1$  kcal·mol<sup>-1</sup> at STO-3G and 19.9 kcal·mol<sup>-1</sup> at 4-31G. Assuming that the same correction for the STO-3G deficiencies applies to  $\Delta E(2)$  and  $\Delta E(1)$ ,<sup>8c</sup> we estimate that the  $1\pi\text{--}1\sigma$  splitting is 20–25 kcal·mol<sup>-1</sup>.<sup>15</sup> Analysis of the charge densities reveals that the carbonyl groups are more polarized in  $1\sigma$  than in  $1\pi$ , suggesting that  $\Delta E(1)$  may be reduced in polar solvents. Both  $1\sigma$  and  $1\pi$  are less stable than the corresponding states of  $\text{H}_2\text{N}\cdot$  (eq 1);<sup>16</sup> conjugation is apparently less

$$\text{H}_2\text{N}\cdot (\Pi \text{ or } \Sigma_N) + \text{succinimide} \rightarrow 1\pi \text{ (or } 1\sigma) + \text{NH}_3 \quad (1)$$

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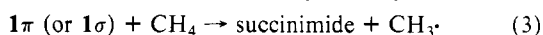
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important in the radicals than in succinimide. As eq 2 is nearly thermoneutral,<sup>17a</sup> the reactions of  $1\pi$  and  $1\sigma$  with methane (eq 3) are calculated to be exothermic by  $\sim 15$  and  $35 \text{ kcal}\cdot\text{mol}^{-1}$ , respectively. The high exothermicity of hydrogen abstraction by  $1\sigma$  is consistent with the observed low selectivity.<sup>2</sup> As the dissociation energies of N-Cl bonds are by  $\sim 30 \text{ kcal}\cdot\text{mol}^{-1}$  smaller than those of C-Cl bonds,<sup>17b,c</sup> we conclude that the generation of  $1\sigma$  [from  $\text{CH}_3 + N\text{-chlorosuccinimide (NCS)}]$ <sup>2</sup> is endothermic by  $\sim 5 \text{ kcal}\cdot\text{mol}^{-1}$ .<sup>18a</sup> The generation of  $1\pi$  from  $\text{Cl}\cdot + \text{NCS}$  is endothermic by  $\sim 12 \text{ kcal}\cdot\text{mol}^{-1}$ .<sup>18b,c</sup> These conclusions are different from the qualitative energetic scheme suggested by Skell.<sup>2,18</sup>

PMO theory<sup>19</sup> provides a basis for explaining the different chemistries of the two states. For example,  $1\pi$  is more selective than  $1\sigma$  in hydrogen abstraction reactions<sup>2</sup> because its SOMO ( $-12.10 \text{ eV}$  in  $1\pi$ ;  $-13.22 \text{ eV}$  in  $1\sigma$ )<sup>20,21</sup> and the HOMO of the alkane ( $-12.52 \text{ eV}$  in ethane)<sup>20</sup> are closer in energy and therefore interact more strongly.<sup>19</sup> Aromatic compounds, on the other hand, react preferably with  $1\sigma^{2c}$  which possess a lower LUMO than  $1\pi$ .<sup>22</sup> The lower  $k(\text{neopentane})/k(\text{CH}_2\text{Cl}_2)$  ratios observed for  $1\pi$ <sup>2b</sup> can be rationalized similarly.

The experimental study of  $\Sigma_N$  radicals could be greatly facilitated if additional systems with small  $\Pi-\Sigma_N$  splittings or preferably with  $\Sigma_N$  ground states were available.<sup>23a</sup> A search for such radicals can be carried out computationally. Figure 2<sup>23b</sup> shows that the  $2\pi-2\sigma$  energy difference,  $\Delta E(2)$ , is dependent on the CNC bond angle ( $\theta$ ). Thus,  $\Delta E(2)$  increases sharply at  $\theta < 110^\circ$ ; e.g., at  $\theta = 90^\circ$ ,  $\Delta E(2) \sim 70 \text{ kcal}\cdot\text{mol}^{-1}$  (Figure 2). Widening of  $\theta$ , on the other hand, reduces  $\Delta E(2)$ . At  $\theta > 140^\circ$ ,  $2$  is predicted to be a  $\Sigma_N$  ground state. Experimentally, it is simpler, however, to design systems with small CNC angles than to constrain  $\theta$  to angles  $> 140^\circ$ . Examples include glutarimidyl, phthalimidyl, maleimidyl, and the malonimidyl radicals where  $\theta$  is smaller (or similar) than in  $1$ , and  $\Delta E$  is therefore  $\geq 20 \text{ kcal}\cdot\text{mol}^{-1}$ . Cyclic imines with  $\theta > 130^\circ$ , where the corresponding  $\Pi$  and  $\Sigma_N$  imidyl radicals are expected to be nearly degenerate (Figure 2), are unknown. Steric repulsions between bulky substituents (B strain) can produce considerable widening of bond angles. However, the application of this idea to acyclic iminyl radicals (e.g.,  $2$ , H substituted by *t*-Bu) will probably fail because the steric interactions can be relieved in a *E,Z* or *Z,Z*, or in intermediate twisted conformations.<sup>24</sup> The same considerations apply to  $\text{RCONR}'$ .<sup>25</sup>

(16) At STO-3G, the energies of reaction 1 are similar with either  $1$  or  $2$  and we assume that this holds at 4-31G.<sup>8c</sup> At 4-31G, reaction 1 is estimated to be endothermic by 11 and 16  $\text{kcal}\cdot\text{mol}^{-1}$  for  $1\sigma$  and  $1\pi$ , respectively.

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(18) (a) Exothermic by  $0.8 \text{ kcal}\cdot\text{mol}^{-1}$ , according to MNDO.<sup>5</sup> (b) Exothermic by  $14.6 \text{ kcal}\cdot\text{mol}^{-1}$ , according to MNDO.<sup>5</sup> (c) The MNDO energetic scheme<sup>5</sup> is inconsistent with available thermodynamic data.  $\Delta H_f^\circ$  of  $\text{CH}_3$  is  $5 \text{ kcal}\cdot\text{mol}^{-1}$  higher than  $\Delta H_f^\circ$  of  $\text{Cl}\cdot$  and  $\Delta H_f^\circ$  of  $\text{CH}_3\text{Cl}$  is  $20.6 \text{ kcal}\cdot\text{mol}^{-1}$  lower than  $\Delta H_f^\circ$  of  $\text{Cl}_2$ .<sup>17b</sup> If  $1\pi$  is more stable than  $1\sigma$  by only  $13.8 \text{ kcal}\cdot\text{mol}^{-1}$ , then the energy of  $1\pi + \text{Cl}_2$  must be higher (by  $\sim 7 \text{ kcal}\cdot\text{mol}^{-1}$ ) than that of  $1\sigma + \text{CH}_3\text{Cl}$ , contrary to the MNDO predictions.<sup>5,18a,b</sup>

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(22) The HOMO(radical)-HOMO(arene) separations are large ( $\sim 5 \text{ eV}$ ), so that these three-electron interactions are destabilizing (more strongly for  $1\pi$ ), supporting the same conclusion. See: Bernardi, F.; Cherry, W.; Shaik, S.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 1352.

(23) (a)  $\text{O}_2\text{N}\cdot$  is a ground-state  $\Sigma_N$  radical; see: Atkins, P. W.; Symons, M. C. R. "The Structure of Inorganic Radicals", Elsevier: New York, 1967; p 131. (b) The potential curves are based on STO-3G calculations (bond lengths and bond angles except  $\theta$  are held constant). The curve for  $2\sigma$  is corrected for the overestimation of the  $\Pi-\Sigma_N$  splitting by STO-3G (see text). A complete 4-31G potential curve is too expensive but several representative points at 4-31G fit Figure 2.

(24) See, for example: Noe, E. A.; Raban, M. *J. Am. Chem. Soc.* **1975**, *97*, 5811.

In amino radicals  $\text{RR}'\text{N}\cdot$ , however, steric repulsions can be minimized only by the widening of the CNC angle. Widening of  $\theta$  (in the region  $120-170^\circ$ ) results in a small change in the energy of the  $\Sigma_N$  radical (Figure 2).<sup>25</sup> We suggest, therefore, the use of crowded haloamines (several are known) as convenient precursors to ground state  $\Sigma_N$  radicals. Our predictions call for experimental verification.

**Note Added in Proof:** Two recent ESR studies have provided definitive proof for  $\pi$  ground state configurations in *N*-alkyl-carboxamidyl and sulfonamidyl radicals. See: Lessard, J.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 3262; Dannen, W. C.; Gellert, R. W. *Ibid.* **1980**, *102*, 3264, respectively.

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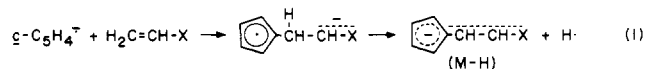
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## Identification of Nucleophilic 1,2- and 1,4-Addition Processes with $\alpha,\beta$ -Unsaturated Molecules in the Gas Phase<sup>1</sup>

Sir:

The ability to observe and largely control 1,2- vs. 1,4-addition processes of various nucleophiles to  $\alpha,\beta$ -unsaturated compounds allows these reactions to be useful in synthetic organic chemistry. Gas-phase studies of such nucleophilic addition reactions have met with limited success with "naked" nucleophiles<sup>2</sup> but appear to be more promising with the nucleophile solvated.<sup>3</sup> We report certain related gas-phase results with hypovalent anion radicals which allow both 1,2- and 1,4-addition reactions to be observed.

Our studies were carried out in a flowing afterglow apparatus ( $298 \text{ K}$ ,  $v = 80 \text{ m s}^{-1}$ ,  $P_{\text{He}} = 0.5 \text{ torr}$ ). Cyclopentadienylidene anion radical ( $c\text{-C}_5\text{H}_4\cdot^-$ )<sup>4</sup> was produced from diazocyclopentadiene by dissociative electron attachment. From the reactions of  $c\text{-C}_5\text{H}_4\cdot^-$  with acrylonitrile and methyl acrylate, the delocalized M-H adducts were produced.<sup>5</sup> The magnitude of substituent effects in  $\text{H}_2\text{C}=\text{CHX}$ , where  $\text{X} = \text{CN}$ ,  $\text{CO}_2\text{CH}_3$ , and  $\text{H}$ , on the rate constants for addition by  $c\text{-C}_5\text{H}_4\cdot^-$  (Table I) requires a nucleophilic (not radical) addition mechanism.<sup>6</sup> That this simple addition/fragmentation process (eq 1) is a special function of the



(1) Paper 8 in the series "Hypovalent Radicals"; for paper 7, see: McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 5118.

(2) Bowie, J. H. *Acc. Chem. Res.* **1980**, *13*, 76, and references therein.

(3) Bartmess, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 2483.

(4) Cyclic structure and electronic configuration ( $\sigma^1\pi^2$ ) of  $c\text{-C}_5\text{H}_4\cdot^-$ ; Pa-  
( $c\text{-C}_5\text{H}_4\cdot^-$ ) =  $377 \pm 2 \text{ kcal}\cdot\text{mol}^{-1}$ ,  $D^0(c\text{-C}_5\text{H}_4\text{-H}^-) = 104 \pm 5 \text{ kcal}\cdot\text{mol}^{-1}$ ; McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.*, in press.

(5) Addition of  $\text{O}\cdot$  to acrylonitrile followed by loss of  $\text{H}\cdot$  gave the M-H adduct as a minor reaction channel: Dawson, J. H. J.; Nibbering, N. M. M. *Int. J. Mass Spectrum. Ion Phys.* **1980**, *33*, 3.

(6) Kerr, J. A.; Parsonage, M. J. "Evaluated Kinetic Data on Gas Phase Addition Reactions", Butterworths: London, 1972.