$$H_2N\cdot\ (\Pi) + CH_4 \rightarrow CH_3\cdot + NH_3 \qquad (2)$$

$$\mathbf{1}\pi\ (\text{or } \mathbf{1}\sigma) + CH_4 \rightarrow \text{succinimide} + CH_3\cdot \qquad (3)$$

important in the radicals than in succinimide. As eq 2 is nearly thermoneutral,[17a] the reactions of **1**π and **1**σ with methane (eq 3) are calculated to be exothermic by ~15 and 35 kcal·mol^{-1}, respectively. The high exothermicity of hydrogen abstraction by **1**σ is consistent with the observed low selectivity.[2] As the dissociation energies of N–Cl bonds are by ~30 kcal·mol^{-1} smaller than those of C–Cl bonds,[17b,c] we conclude that the generation of **1**σ [from $CH_3\cdot$ + *N*-chlorosuccinimide (NCS)][2] is endothermic by ~5 kcal·mol^{-1}.[18a] The generation of **1**π from Cl· + NCS is endothermic by ~12 kcal·mol^{-1}.[18b,c] These conclusions are different from the qualitative energetic scheme suggested by Skell.[2,18]

PMO theory[19] provides a basis for explaining the different chemistries of the two states. For example, **1**π is more selective than **1**σ in hydrogen abstraction reactions[2] because its SOMO (–12.10 eV in **1**π; –13.22 eV in **1**σ)[20,21] and the HOMO of the alkane (–12.52 eV in ethane)[20] are closer in energy and therefore interact more strongly.[19] Aromatic compounds, on the other hand, react preferably with **1**σ[2c] which possess a lower LUMO than **1**π.[22] The lower k(neopentane)/k(CH_2Cl_2) ratios observed for **1**π[2b] can be rationalized similarly.

The experimental study of Σ_N radicals could be greatly facilitated if additional systems with small Π–Σ_N splittings or preferably with Σ_N ground states were available.[23a] A search for such radicals can be carried out computationally. Figure 2[23b] shows that the **2**π–**2**σ energy difference, ΔE(**2**), is dependent on the CNC bond angle (θ). Thus, ΔE(**2**) increases sharply at $\theta < 110°$; e.g., at $\theta = 90°$, ΔE(**2**) ~70 kcal· mol^{-1} (Figure 2). Widening of θ, on the other hand, reduces ΔE(**2**). At $\theta > 140°$, **2** is predicted to be a Σ_N *ground state*. Experimentally, it is simpler, however, to design systems with small CNC angles than to constrain θ to angles >140°. Examples include glutarimidyl, phtalimidyl, maleimidyl, and the malonimidyl radicals where θ is smaller (or similar) than in **1**, and ΔE is therefore ≥20 kcal·mol^{-1}. Cyclic imines with $\theta > 130°$, where the corresponding Π and Σ_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* a *Z*,*Z*, or in intermediate twisted conformations.[24] The same considerations apply to $RCO\dot{N}R'$.[25] In amino radicals RR′N·, however, steric repulsions can be minimized only by the widening of the CNC angle. Widening of θ (in the region 120–170°) results in a small change in the energy of the Σ_N radical (Figure 2).[25] We suggest, therefore, the use of crowded haloamines (several are known) as convenient precursors to *ground state* Σ_N radicals. Our predictions call for experimental verification.

Note Added in Proof: Two recent ESR studies have provided definitive proof for π ground state configurations in *N*-alkylcarboxamidyl 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.

Acknowledgment. We thank Dr. E. Hedaya for bringing this problem to our attention and for numerous discussions, Dr. T. Clark for communicating his results prior to publication, Dr. P. Bishof for calculating **1** by his MINDO/3-UHF method, Dr. J. Chandrasekhar for help with the GAUSSIAN-76 program, and Professor P. v. R. Schleyer for his hospitality during Y.A.'s visit to Erlangen, where this work was completed.

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Received February 25, 1980

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(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.[8c] At 4-31G, reaction 1 is estimated to be endothermic by 11 and 16 kcal·mol^{-1} for **1**σ and **1**π, respectively.

(17) (a) Franklin, J. L.; Dillard, J. D.; Rosenstock, H. M.; Herron, Y. T.; Draxl, K.; Field, F. M. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1969**, No. 26. (b) Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502. (c) Howard, P. B.; Skinner, H. A. *J. Chem. Soc. A.* **1966**, 1536.

(18) (a) Exothermic by 0.8 kcal·mol^{-1}, according to MNDO.[5] (b) Exothermic by 14.6 kcal·mol^{-1}, according to MNDO.[5] (c) The MNDO energetic scheme[5] is inconsistent with available thermodynamic data. $\Delta H_f°$ of $CH_3\cdot$ is 5 kcal·mol^{-1} higher than $\Delta H_f°$ of Cl· and $\Delta H_f°$ of CH_3Cl is 20.6 kcal·mol^{-1} lower than $\Delta H_f°$ of Cl_2.[17b] If **1**π is more stable than **1**σ by only 13.8 kcal·mol^{-1}, than the energy of **1**π + Cl_2 must be *higher* (by ~7 kcal·mol^{-1}) than that of **1**σ + CH_3Cl, contrary to the MNDO predictions.[5,18a,b]

(19) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions", Wiley: New York, 1976; Chapter 5.

(20) STO-3G orbital energies correlate well with experimental ionization potentials; see, for example: Domelsmith, L. N.; Houk, K. N.; Regenhardt, C. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 100.

(21) In $H_2N\cdot$, the SOMO of the Π and Σ_N states are very close in energy (–12.27 eV, STO-3G).

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

(23) (a) $O_2N\cdot$ is a ground-state Σ_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 θ are held constant). The curve for **2**σ is corrected for the overestimation of the Π–Σ_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.

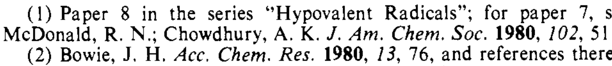
(25) Plots which are similar to Figure 2 are obtained also for $HCO\dot{N}H$ and $\cdot NH_2$. For similar INDO calculations, see: Koenig, T.; Hoobler, J. A.; Klopfenstein, C. E.; Hedden, G.; Sunderman, F.; Russell, B. R. *J. Am. Chem. Soc.* **1974**, *96*, 4573.

Identification of Nucleophilic 1,2- and 1,4-Addition Processes with α,β-Unsaturated Molecules in the Gas Phase[1]

Sir:

The ability to observe and largely control 1,2- vs. 1,4-addition processes of various nucelophiles to α,β-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[2] but appear to be more promising with the nucleophile solvated.[3] 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 K, v = 80 m s^{-1}, P_{He} = 0.5 torr). Cyclopentadienylidene anion radical (c-$C_5H_4^-\cdot$)[4] was produced from diazocyclopentadiene by dissociative electron attachment. From the reactions of c-$C_5H_4^-\cdot$ with acrylonitrile and methyl acrylate, the delocalized M–H adducts were produced.[5] The magnitude of substituent effects in $H_2C{=}CHX$, where X = CN, CO_2CH_3, and H, on the rate constants for addition by c-$C_5H_4^-\cdot$ (Table I) requires a nucleophilic (*not* radical) addition mechanism.[6] That this simple addition/fragmentation process (eq 1) is a special function of the



(1)

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(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-$C_5H_4^-\cdot$; Pa-(c-$C_5H_4^-\cdot$) = 377 ± 2 kcal mol^{-1}, $D°$(c-C_5H_4–H^-) = 104 ± 5 kcal mol^{-1}: McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.*, in press.

(5) Addition of $O^-\cdot$ to acrylonitrile followed by loss of H· 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.

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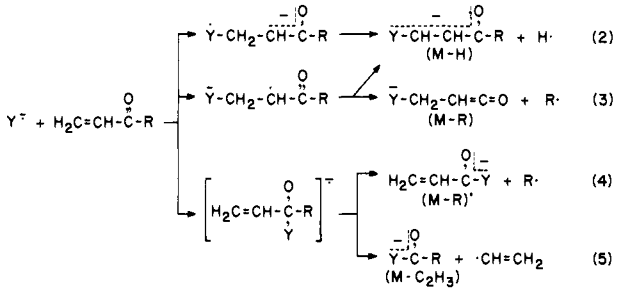
Table I. Summary of Kinetic and Product Data for the Ion-Molecule Reactions of c-$C_5H_4^{-}\cdot$, c-$C_5H_5^{-}$, and $PhN^{-}\cdot$

reaction	ion + neutral reactants	products (assumed neutral)	fraction of product ion signal	k_{total},[a] cm^3 $molecule^{-1}$ s^{-1}
1a	c-$C_5H_5^{-}\cdot + CH_2{=}CHCN$	c-$C_5H_4CH{=}CHCN^{-}$ [+ $H\cdot$]	0.31	$(8.2 \pm 0.1) \times 10^{-10}$ [b,c]
1b		CN^{-}	0.57	
1c		$CH_2{=}CCN^{-}$ [+ c-$C_5H_5\cdot$]	0.10	
1d		c-$C_5H_5^{-}$ [+ $C_3H_2N\cdot$]	0.02	
2a	c-$C_5H_5^{-}\cdot + CH_2{=}CHCO_2CH_3$	c-$C_5H_4CH{=}CHCO_2CH_3^{-}$ [+ $H\cdot$]	0.74	$(1.1 \pm 0.1) \times 10^{-10}$ [b,d]
2b		c-$C_5H_5^{-}$ [+ $C_4H_5O_2\cdot$]	0.26	
3	c-$C_5H_4^{-}\cdot + CH_2{=}CH_2$	none observed		$\leqslant 10^{-13}$
4	c-$C_5H_5^{-} + CH_2{=}CHCN$	c-$C_5H_5CH_2CHCN^{-}$	1.00	$(2.3 \pm 0.1) \times 10^{-11}$
5	c-$C_5H_5^{-} + CH_2{=}CHCO_2CH_3$	c-$C_5H_4CHCHCO_2CH_3^{-}$ [+ H_2]	1.00	$(1.6 \pm 0.4) \times 10^{-12}$ [b,d]
6	$PhN^{-}\cdot + CH_2{=}CHCN$	$PhN{=}CHCHCN^{-}$ [+ $H\cdot$]	1.00	$(1.4 \pm 0.2) \times 10^{-10}$ [b,d]
7a	$PhN^{-}\cdot + CH_2{=}CHCO_2CH_3$	$PhN{=}CHCHCO_2CH_3^{-}$ [+ $H\cdot$]	0.10	$(5.9 \pm 0.2) \times 10^{-12}$ [b,d]
7b		$H_2C{=}CHCONPh^{-}$ [+ $\cdot OCH_3$]	0.90[e]	
8a	$PhN^{-}\cdot + CH_2{=}CHCOCH_3$	$PhN{=}CHCHCOCH_3^{-}$ [+ $H\cdot$]	0.02	$(5.8 \pm 0.4) \times 10^{-11}$ [b,d]
8b		$H_2C{=}CHCONPh^{-}$ [+ $\cdot CH_3$]	0.82[e]	
8c		$PhNCOCH_3^{-}$ [+ $\cdot CH{=}CH_2$]	0.05	
8d		$H_2C{=}CHCOCH_2^{-}$ [+ $PhNH\cdot$]	0.11	

[a] k values are estimated to be accurate to ±30%. Errors given are standard deviations from multiple determinations. [b] Increasing P_{He} from 0.5 to 1.1 torr gave no change in k. [c] Increasing P_{He} diminished channels 1b and 1c with an increase in channel 1a. [d] Increasing P_{He} had no effect on the product channels. [e] The anion product of this reaction channel may have the anilide ketene structure of eq 3 or may be a mixture of these isomeric anions.

adduct anion radical was demonstrated by the reactions of cyclopentadienyl anion (c-$C_5H_5^-$)[7a] with acrylonitrile and methyl acrylate where the adduct M and M – 2 anions, respectively, were observed (Table I).

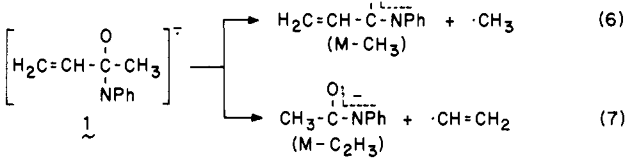
It appeared that this addition/fragmentation process by a nucleophilic hypovalent anion radical with α,β-unsaturated compounds could be a useful probe to observe competitive 1,2- and 1,4-addition reactions (eq 2–5). Since both 1,4- and 1,2-addition processes (eq 3 and 4) could conceivably yield isomeric M – R and M – R′ product ions, the test for 1,2-addition would be observation of the M – C_2H_3 ion. The large H^+ and H· affinities of c-$C_5H_4^{-}\cdot$ precluded such studies with a large number of α,β-unsaturated substrates.[4]



The H^+ (PA = 373 ± 2 kcal mol^{-1}) and H· [$D°(PhNH{-}H^-) \leq 96$ kcal mol^{-1}] affinities of phenylnitrene anion radical ($PhN^{-}\cdot$) were determined from the results of bracketing reactions.[7b,1] Thus, $PhN^{-}\cdot$ should serve as a useful reagent to probe for competitive 1,2- and 1,4-addition reactions. As expected, the fast reaction between $PhN^{-}\cdot$ and acrylonitrile produced only the M – H adduct formed by conjugate 1,4-addition/fragmentation (eq 2 and/or 3).

The reaction of $PhN^{-}\cdot$ with methyl acrylate produced both M – OCH_3 and M – H adducts, the former being the dominant anion product (9:1). Even if 1,2-addition were to occur in this reaction, loss of $\cdot OCH_3$ would be strongly preferred to loss of the $\cdot CH{=}CH_2$ group, assuming that normal bond dissociation energies ($C{-}OCH_3$ vs. C–vinyl) contribute to these fragmentation processes.

The reaction between PhN^{-}. and methyl vinyl ketone gave three product ions from addition/fragmentation processes, m/z 146 (M – CH_3), m/z 134 (M – C_2H_3), and m/z 160 (M – H), and the ion m/z 69, the product of proton transfer. *Formation of the ion m/z 134 (M – C_2H_3) requires the 1,2-addition/fragmentation mechanism via intermediate* **1** *in this reaction.* Since $D°(R_3C{-}C_2H_3) > D°(R_3C{-}CH_3)$, observation of even a small amount of the M – C_2H_3 product anion suggests that the acrylanilide anion structure (eq 6) must be the prinicpal or exclusive ion of m/z 146.



This further suggests that the major reaction channel of $PhN^{-}\cdot$ with methyl vinyl ketone in the gas phase is addition to the carbonyl group to yield **1**. Experiments are in progress to establish the structures of the M – R ions (eq 3 and 4) which will allow the percent of the competitive 1,2- vs. 1,4-addition pathways to be calculated for various α,β-unsaturated substrates.

One additional comment is necessary on reaction channel lc, Table I, in the reaction of c-$C_5H_4^{-}\cdot$ with acrylonitrile. The product ion m/z 52 is assumed to be the vinyl anion $H_2C{=}CCN^-$. This is formally the deprotonation product from acrylonitrile. However, the direct proton-transfer pathway giving m/z 52 was ruled out when this reaction channel was essentially eliminated when the buffer gas-flow pressure was increased from 0.5 to 1.1 torr; the overall rate constant was independent of pressure. This suggests that the original adduct formed with excess energy has three fragmentation exit channels, loss of H· (la), loss of CN^- (lb) with probable rearrangement of the neutral, and loss of c-$C_5H_5\cdot$, yielding $H_2C{=}CCN^-$ (lc), with the latter two channels shut off by collisional stablization by the buffer gas. It therefore appears possible that the m/z 52 anion formed in the reaction of CH_3O^- + $H_2C{=}CHCN$ in an ICR spectrometer would also have been produced by a similar addition/elimination pathway from an energetically "hot" conjugate addition adduct.[3]

Acknowledgment. We gratefully acknowledge support of this research from the Army Research Office (DAAG29-77-G-0142) and the National Science Foundation (equipment Grant CHE76-80382) and encouragement from Professor D. W. Setser.

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Received June 21, 1980

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(7) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W., unpublished results. (a) c-$C_5H_5^-$ was produced from the reaction of CH_3O^- (from $CH_3ONO + e^-$) + c-C_5H_6. (b) $PhN^{-}\cdot$ was prepared from phenyl azide by dissociative electron attachment.