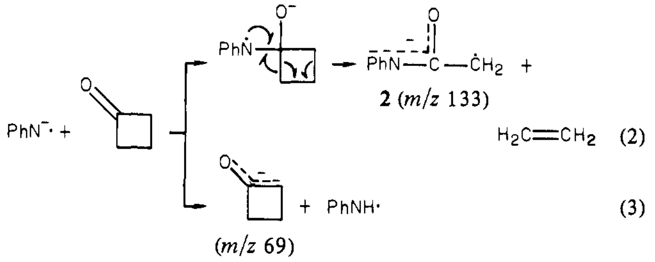

but discernible, ion signals for addition adducts **1** were observed for a slow ($\mathrm{CH_3COCH_3}$) and a fast ($\mathrm{CF_3COCF_3}$) reactant, it is reasonable to assume that these adducts are tetrahedral anion radicals rather than loss complexes[2] and that these addition/fragmentation reactions proceed via such an intermediate.[2,3,11,12]

The fragmentation products from the acyclic carbonyl compounds studied establish the following group fragmentation order for adduct **1**: $\mathrm{CH_3O \sim CH_3CO > H > CH_3 > CF_3}$. From our previous report of the reactions of $\mathrm{PhN^{-}\cdot}$ with methyl vinyl ketone, we found $\mathrm{CH_3 > CH_2{=}CH}$ fragmentation from the 1,2-addition adduct.[1] This fragmentation order appears to largely reflect the expected stabilities of the acylanilide anionic products.[13]

Part of our present studies involves developing the related chemistry of other molecular and atomic hypovalent anion radicals. It is hoped that these results, especially of the atomic species, will better lend themselves to theoretical calculations of the potential surfaces for these reactions.

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[11] Brauman et al.[2a] favor a double-minimum well model for the reactions of acid halides with nucleophiles.

[12] (a) A theoretical study (ab initio) for addition of $\mathrm{HO^-}$ to the carbonyl group of formamide indicated no barrier to addition: Alagona, G.; Scrocco, E.; Tomasi, J. *J. Am. Chem. Soc.* **1975**, *97*, 6976. (b) A triple-minimum potential surface appears to be required to explain our data for these addition/fragmentation reactions.

[13] R. N. McDonald and A. K. Chowdhury (unpublished results) have found $\mathrm{PA(PhNCOCH{=}CH_2^-)} \leq 345$ kcal mol^{-1} compared to $\mathrm{PA(PhNCOCH_3^-)} = 358 \pm 2$ kcal mol^{-1} (Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1) (PA = proton affinity).

Gas-Phase Ion-Molecule Reactions of Phenylnitrene Anion

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The recent report[1] of the production of phenylnitrene anion, $\mathrm{PhN^{-}\cdot}$, in a flowing afterglow and its subsequent reactions with $\mathrm{PhN_3}$ prompts us to communicate some preliminary results of our independent investigations into the chemistry of this interesting species. We have found it possible to generate and trap $\mathrm{PhN^{-}\cdot}$ from electron impact on $\mathrm{PhN_3}$ at low pressure ($<10^{-7}$ torr) in a pulsed ion cyclotron resonance (ICR) spectrometer. Nitrene anion formation from azides under our conditions appears to be a general phenomenon, as trimethylsilyl azide[2] and ethyl azide[3] also produce the corresponding nitrene anions upon electron impact. We report here some unusual bimolecular reactions involving $\mathrm{PhN^{-}\cdot}$ which have no precedent in ion-molecule chemistry.

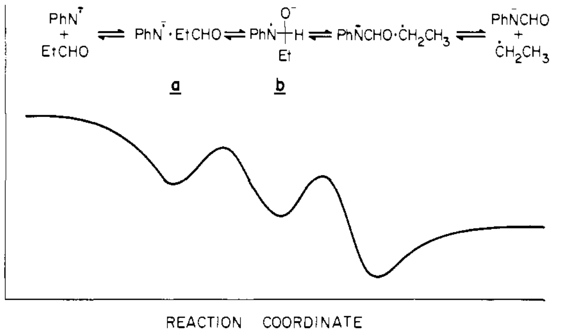

Figure 1. Proposed potential-energy-reaction coordinate diagram for the major pathway in reaction 1. The relative heights of the minima are based on rough thermochemical estimates.

Using the acidity bracketing technique,[4] we place the proton affinity (PA) of $\mathrm{PhN^{-}\cdot}$ between those of t-$\mathrm{BuO^-}$ and $\mathrm{PhCH_2O^-}$; thus we obtain $\mathrm{PA(PhN^{-}\cdot)} = 371 \pm 3$ kcal/mol, in good agreement with the previous value.[1a] However, in the presence of $\mathrm{CH_3CH_2CHO}$, which is 3.7 kcal/mol more acidic[4] than $\mathrm{PhCH_2OH}$, no ($<5\%$) proton abstraction by $\mathrm{PhN^{-}\cdot}$ is seen. Instead, two fairly slow reactions ($k_{1a} + k_{1b} = 7.0 \pm 0.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) produce anions with m/e 120 (1a, $\sim$75%) and 148 (1b, $\sim$25%). We believe these reactions to proceed as shown in reaction 1.

$$\mathrm{PhN^{-}\cdot + CH_3CH_2CHO \not\rightarrow Ph\dot{N}H + CH_3\bar{C}HCHO} \qquad \Delta H° = -6\ \mathrm{kcal/mol}$$

$$\xrightarrow{k_{1a}} \mathrm{Ph\bar{N}CHO + CH_3CH_2\cdot} \qquad \Delta H° = -17\ \mathrm{kcal/mol}$$

$$\xrightarrow{k_{1b}} \mathrm{Ph\bar{N}COCH_2CH_3 + H\cdot} \qquad \Delta H° = -9\ \mathrm{kcal/mol} \quad (1)$$

Reaction of $\mathrm{PhN^{-}\cdot}$ with $\mathrm{CH_3CHO}$ produces $\mathrm{Ph\bar{N}CHO}$ and $\mathrm{Ph\bar{N}COCH_3}$ and again gives no enolate. (Proton transfer here is 5 kcal/mol exothermic.) In this case, however, the H-atom displacement is the major pathway, in contrast to the reaction with propionaldehyde. With the substantially more acidic $\mathrm{CH_3COCF_3}$, the major reaction channel ($\sim$80%) is rapid proton transfer; a minor product ($\sim$20%) is m/e 188, which we believe is $\mathrm{Ph\bar{N}COCF_3}$ (reaction 2).

$$\mathrm{PhN^{-}\cdot + CH_3COCF_3 \xrightarrow{a} Ph\dot{N}H + \bar{C}H_2COCF_3} \qquad \Delta H° = -22\ \mathrm{kcal/mol}$$

$$\xrightarrow{b} \mathrm{Ph\bar{N}COCF_3 + CH_3\cdot} \qquad \Delta H° = -30\ \mathrm{kcal/mol} \quad (2)$$

Although N-alkylation of $\mathrm{PhN^{-}\cdot}$ is strongly exothermic, reactions with $\mathrm{CH_3Br}$ and $\mathrm{CF_3CO_2\ CH_3}$ do not proceed with appreciable velocity through the commonly observed[5] $\mathrm{S_N2}$ reaction channels. We observe only slow reaction (reaction 3) with $\mathrm{CH_3Br}$ ($k_3 = 1.9 \pm 0.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}), while with $\mathrm{CF_3CO_2CH_3}$ a rapid reaction ($k_4 = 6.2 \pm 0.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) produces $\mathrm{Ph\bar{N}COCF_3}$ as the only detectable product (reaction 4).

$$\mathrm{PhN^{-}\cdot + CH_3Br \rightarrow Ph\bar{N}CH_3 + Br^-} \qquad \Delta H° = -48\ \mathrm{kcal/mol} \quad (3)$$

Occurrence of proton transfer (reaction 2) and radical displacement (reaction 1) pathways show that $\mathrm{PhN^{-}\cdot}$ can exhibit both free-radical and anionic behavior; to the extent that a single Lewis structure suffices, it may be described by a structure in which the negative charge is delocalized into the phenyl ring and the odd

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† National Science Foundation Fellow, 1977-1980.

[1] (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1980**, *102* 5118. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. "Abstracts", Fifth IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, Aug 17-22, 1980, p 51.

[2] Jackson, R. L.; Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.*, in press. However, the chemistry of (trimethylsilyl)nitrene anion is not conveniently studied due to a rapid reaction with the parent azide to produce $\mathrm{N_3^-}$.

[3] Rynard, C. M., unpublished results.

[4] Bartmess, J. E.; McIver, R. T. *Gas Phase Ion Chem.* **1979**, *2*, Chapter 11.

[5] Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

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$$\mathrm{PhN^{-}\cdot + CF_3CO_2CH_3 \not\rightarrow Ph\dot{N}CH_3 + CF_3CO_2^{-}} \qquad \Delta H^\circ = -54\ \mathrm{kcal/mol}$$
$$\rightarrow \mathrm{Ph\bar{N}COCF_3 + CH_3O\cdot} \qquad \Delta H^\circ = -14\ \mathrm{kcal/mol} \tag{4}$$

electron occupies an in-plane orbital on nitrogen.[1a] The acylation reactions are most easily rationalized with a mechanism in which the product-determining step is fragmentation of an intermediate formed by addition of $\mathrm{PhN^{-}\cdot}$ to the carbonyl group (b, Figure 1, illustrated for reaction 1). This species is the radical anion of a 1,3-biradical and must be delocalized; however, as the negative charge is more stable on oxygen, we represent it in Figure 1 as an alkoxide. This process is thus the ionic analogue of an alkoxy radical fragmentation to an alkyl radical and a carbonyl compound. Formation of the chemically activated addition product in Figure 1 is estimated[6] to be 15 kcal/mol exothermic; this should be sufficient to overcome the barrier to decomposition to products. Alkoxy radical fragmentation barriers are typically[9] ~13 kcal/mol; we expect a lower barrier in this case due to the net exothermicity of the decomposition and the formation of the delocalized $\mathrm{Ph\bar{N}CHO}$.

The mechanism in Figure 1 accounts for the observed products in reactions 1 and 4 but not in 2. Proton transfer in reaction 1 and $\mathrm{S_N2}$ displacement in reaction 4 would each require 1,2-eliminations from the corresponding carbonyl addition products. The *A* factors for these processes are expected to be considerably lower than those for simple cleavage leading to the observed products; hence (assuming comparable activation energies) the reactions should proceed exclusively along the latter path. However, reaction 2 shows that proton transfer can dominate provided it is sufficiently exothermic. We now show that this observation is incompatible with a mechanism in which proton transfer in reaction 2 occurs via elimination from the carbonyl adduct.

Reaction with $\mathrm{CH_3CH_2CHO}$ produces only acylation while reaction with $\mathrm{CH_3COCF_3}$ produces mainly proton transfer, although in the latter case acylation is still the most exothermic channel. While both product channels in reaction 2 are more exothermic than those in reaction 1, formation of the $\mathrm{PhN^{-}\cdot + CH_3COCF_3}$ addition product is also more exothermic than the corresponding addition to $\mathrm{CH_3CH_2CHO}$. This is due to the biradical's electron affinity increase of[10] ~11 kcal/mol (estimated) arising from substitution of trifluoromethyl for ethyl. Thus, starting from the respective intermediates and assuming for the moment that proton transfer and acylation both proceed via these intermediates, ΔH°'s for the proton transfers in reactions 1 and 2 are approximately equal; the same holds for the acylations. The main difference between reactions 1 and 2 is therefore that the $\mathrm{CH_3COCF_3}$ addition product is formed with more internal energy than is that with $\mathrm{CH_3CH_2CHO}$. Quantum RRK calculations[11] show, however, that this extra activation will not cause the elimination (proton transfer) to dominate in the $\mathrm{CH_3COCF_3}$ case, even with the assumption that elimination has a lower activation energy than cleavage. This is due to the *A* factor favoring the cleavage (acylation) pathway. Thus, this model, with branching occurring from the carbonyl adduct, cannot account for the different product distributions in reactions 1 and 2. We conclude that in these reactions proton transfer and acylation proceed via different pathways, with proton transfer becoming accessible only when it is strongly exothermic. The branching must thus occur before the carbonyl addition product is reached, presumably at *a*, the loose reactants complex. The product distribution is then governed by the relative energies of the transition states leading to proton transfer and carbonyl addition rather than by relative stabilities of the final products.

To our knowledge, these reactions have no counterpart in previous studies of gas-phase negative ion-molecule chemistry. We know of no other cases in which an anion displaces a free radical from a carbonyl center, although reactions involving nucleophilic attack on a carbonyl group are well-known.[12] However, there is a strong analogy with neutral free-radical chemistry. Alkyl radical displacements from carbonyl groups are common,[13] although reactions involving alkoxy radical displacement (analogous to reaction 4) seem to be unknown. It is currently accepted that these alkyl displacements involve alkoxy radical intermediates rather than direct displacements.[13]

We are currently continuing our investigations into the chemistry of $\mathrm{PhN^{-}\cdot}$ as well as efforts to measure its photodetachment spectrum.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and Dr. J. M. Jasinski for helpful discussions. We thank Professor R. N. McDonald for sharing his data with us prior to publication.

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(6) ΔH°'s computed based on the following data: $\Delta H_f^\circ(\mathrm{PhN^{-}\cdot}) = 60$ kcal/mol;[1a] $\Delta H_f^\circ(\mathrm{Ph\bar{N}COCF_3}) = -196.5$ kcal/mol, based on group additivity[7] and estimated $\Delta H^\circ_{\mathrm{acid}}(\mathrm{PhNHCOCF_3}) = 338$ kcal/mol; $\Delta H_f^\circ(\mathrm{Ph\bar{N}CHO}) = -29.4$ kcal/mol, based on estimated $\Delta H^\circ_{\mathrm{acid}}(\mathrm{PhNHCHO}) = 351$ kcal/mol; $\Delta H_f^\circ(\mathrm{Ph\bar{N}COCH_2CH_3}) = -47$ kcal/mol, based on estimated $\Delta H^\circ_{\mathrm{acid}}(\mathrm{PhNHCOCH_2CH_3}) = 352$ kcal/mol; ΔH_f°(b, Figure 1) = 0 kcal/mol, assuming $\mathrm{EA(Ph\dot{N}\text{-}\dot{C}H(O\cdot)CH_2CH_3)} = 50$ kcal/mol (EA = electron affinity). All other ΔH_f°'s are taken from ref 4, 7, and 8.

(7) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976.

(8) O'Neal, H. E.; Benson, S. W. *Free Radicals* **1973**, *2*, Chapter 17.

(9) Kochi, J. K. *Free Radicals*, **1973**, *2*, Chapter 23.

(10) Based on calculated electron affinities of $\mathrm{\dot{O}CH_2CH_2CH_3}$ and $\mathrm{\dot{O}CH_2CF_3}$ using bond strength and gas-phase acidity data from ref 4.

(11) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972; Chapter 3.

(12) (a) Asubiojo, O. I.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3715. (b) Bowie, J. H. *Acc. Chem. Res.* **1980**, *13*, 76.

(13) See, for instance: Ingold, K. U; Roberts, B. P. "Free-Radical Substitution Reactions"; Wiley-Interscience: New York, 1971; p 86 ff and references cited therein.

Internal Rotation in Liquid 1,2-Dichloroethane and *n*-Butane[1]

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Solvent effects on the conformational preferences of 1,2-dihaloethanes have been extensively analyzed with diffraction and spectroscopic techniques.[2] The increased gauche/trans ratios observed in polar solvents have been explained traditionally by simple electrostatics; the gauche rotamers have large dipole moments which lead to dipole-dipole stabilization in condensed phases.[2] The ability to perform meaningful theoretical studies of such conformational problems in liquids appears to be possible by using molecular dynamics[3] and Monte Carlo statistical mechanics calculations.[4] However, to date, the theoretical work has not modeled a system for which experimental conformational data are available. Consequently, a Monte Carlo simulation of liquid 1,2-dichloroethane (DCE) has been carried out. The results presented here confirm that this method can reproduce the observed solvent shifts. In addition, pure liquid *n*-butane has been modeled for comparison and to reinvestigate the predicted condensed phase effect on the conformational equilibrium for this important prototype system.[3,5]

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† Camille and Henry Dreyfus Foundation Teacher-Scholar, 1978-1983; Alfred P. Sloan Foundation Fellow, 1979-1981.

(1) Quantum and Statistical Mechanical Studies of Liquids. 15. Work supported by the National Science Foundation (CHE78-19446).

(2) For a review, see: Abraham, R. J.; Bretschneider, E. In "Internal Rotation in Molecules"; Orville-Thomas, W. J., Ed.; Wiley: London, 1974; Chapter 13.

(3) (a) Ryckaert, J.-P.; Bellemans, A. *Discuss. Faraday Soc.* **1978**, *66*, 95. (b) Weber, T. A. *J. Chem. Phys.* **1978**, *69*, 2347. (c) Rebertus, D. W.; Berne, B. J.; Chandler, D. *Ibid.* **1979**, *70*, 3395.

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