given in Table I. In these anions, as in allylic anions[11,12] and enolates,[13] one finds some correlation between the favored reaction site and the carbon of greatest electron density, for *in the cyclic anions* IV–VI, *more reaction occurs at the central atom than in the acyclic anions* I and III. Electron density is certainly not the sole factor governing reaction site in these anions,[14] but the above correlation suggests its involvement.

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Homogeneous Catalysis of a Gas-Phase, Ion–Molecule Reaction

Sir:

In contrast to the general observation that many exothermic ion–molecule reactions exhibit similar rate constants and have no activation energy,[1a] we have observed that gas-phase proton-transfer reactions involving highly delocalized anions (*viz.* benzyl, allyl, enolates, etc.) appear to be unusually slow.[1b] This phenomenon is accentuated when both reactant and product are resonance stabilized. Indeed, we have not been able to observe certain proton transfers, which are known to be exothermic, by the usual ion cyclotron resonance (icr) double resonance technique.[2] For example, while reactions 1 and 2 are observable, 3 does not appear to occur on the normal double resonance time scale.[3a]

$$CH_3OH + CH_2{=}CHCH_2^- \xrightarrow{k_1} CH_3O^- + CH_3CH{=}CH_2 \quad (1)$$

$$C_6H_5CH_3 + CH_3O^- \xrightarrow{k_2} C_6H_5CH_2^- + CH_3OH \quad (2)$$

$$C_6H_5CH_3 + CH_2{=}CHCH_2^- \xrightarrow{k_3} C_6H_5CH_2^- + CH_2{=}CHCH_3 \quad (3)$$

These observations suggest the possibility of catalysis of an ion–molecule reaction.[4] In this communication we report the rate constants for reactions 1, 2, and 3 and the direct observation of a homogeneously catalyzed, gas-phase, ion–molecule reaction: the transfer of a proton from toluene to the allyl anion catalyzed by methanol.

The technique utilized in this study was the trapped ion, pulsed icr method[5] which allows us to observe conveniently reactions as slow as 3. Ion intensities followed as a function of time allowed calculation of rate constants.[6] Exclusive detection of a particular reaction channel was facilitated by application of one-, two-, or three-ion ejection irradiating frequencies. Primary negative ions (OH^-, H^-) from water were used to form the ions during the grid pulse.[5] Hydroxide ion was then ejected from the cell and the process of interest followed.

Because each of the reactions 1–3 is exothermic, the disappearance of allyl anion would be accelerated at high methanol concentration regardless of the size of k_1. However, true catalysis implies an increased rate of formation of benzyl anion and thus requires $k_2 > k_3$. Furthermore, for the effect to be observed at modest methanol concentrations, we require $k_1 > k_3$. In the present case these criteria for catalysis are met, the rate constants[7] being $k_1 = 2.5 \pm 0.3 \times 10^{-10}$, $k_2 = 2.0 \pm 0.2 \times 10^{-10}$, and $k_3 = 7.5 \pm 0.7 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}. In accord with these individually determined rate constants, allyl anion and toluene are converted to benzyl anion and propylene more rapidly in the presence of methanol (see Figure 1). This is true even when the total concentration of reactive neutral gases remains constant. Consistent with our previous observation that toluene lies between ethanol and methanol in acidity,[3] ethanol was found not to catalyze reaction 3. We have also determined the rate constant for the reaction of methoxide ion with ethanol and find $k = 1.2 \pm 0.3 \times 10^{-9}$ cm^3 molecule^{-1} sec^{-1}. This rate constant is significantly larger than any of the others observed above and is typical for ion–molecule reactions which have no apparent activation barrier.

Utilizing our rate constants, we can predict the behavior of the toluene–propylene system with and without methanol and compare experimental and calculated results. In Figure 1, with allyl anion as the sole initial reactant (multiple radiofrequency ejection of all other anions), we see the calculated and observed catalytic effect. Similar agreement between experimental results and calculations was observed for mixtures in which the methanol concentration ranged from 10 to 75% of the toluene concentration. In every case, intermediate buildup of methoxide, followed by its decay and the ultimate appearance of benzyl anion, was observed. Both rates of decay of allyl anion and appearance of benzyl anion were increased when methanol was present.

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(3) (a) L. K. Blair, Ph.D. Dissertation, Stanford University, 1970, and manuscript in preparation; also ref 13a. (b) However, see D. K. Bohme, E. Lee-Ruff, and L. B. Young, *J. Amer. Chem. Soc.*, **94**, 5153 (1972).

(4) For definitions of catalysis see G.-M. Schwab, H. S. Taylor, and R. Spence, "Catalysis," Van Nostrand, New York, N. Y., 1937, p 20; A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, Chapter 9; K. F. Herzfeld, *Z. Phys. Chem.*, **98**, 169 (1921).

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(6) An MKS Baratron was used to measure the pressure of gaseous mixtures.

(7) Rate constants can be transformed to M^{-1} sec^{-1} by multiplication by 6.02×10^{20} M^{-1} molecule cm^{-3}.

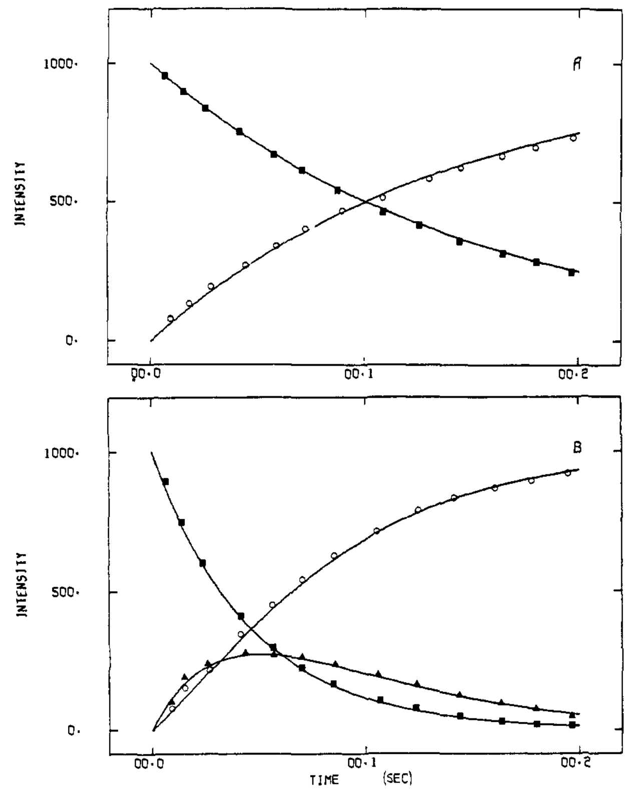

Figure 1. Proton transfer from toluene to the allyl anion. Ion intensities *vs.* time: $C_6H_5CH_2^-$ (○), $C_3H_5^-$ (■), CH_3O^- (▲). (A) Uncatalyzed reaction, pressure in 10^{-6} Torr: propene 7.0, toluene 3.0. (B) Catalyzed reaction, pressure in 10^{-6} Torr: propene 5.1, toluene 3.0, methanol 1.9. Curves were calculated from rate constants given in the text.

The observation of small rate constants and a catalytic pathway for proton transfer for these compounds in the gas phase is significant in terms of their solution chemistry. Alcohols have previously been shown to catalyze similar proton-transfer reactions in solution.[8,9] Ritchie's studies[10] have indicated that isolated molecule properties, as well as solvent reorganization, may be responsible for the well-known low "kinetic acidity" of certain carbon acids.[11] Our work constitutes a direct demonstration that intrinsic, isolated molecule and ion properties are definitely involved.

The apparent barriers in these reactions may be associated with some unique features of delocalized carbanion systems. To the extent that two of the electrons in π system become localized in the developing C-H bond as the protonation transition state is reached, delocalization must be reduced; the loss of this delocalization may be responsible for the observed barriers. This effect is not observed when protonation occurs at oxygen or nitrogen. We suggest that this is because the lone-pair electrons on these atoms allow protonation to occur orthogonal to the π system, obviating loss of delocalization. This is also in accord with the inability to observe hydrogen bonding to delocalized carbanions, the putative hydrogen bonded species having great similarities to the transition state for proton transfer. Consistent with this picture, we find that the barriers are not associated with carbanions, *per se*, since acetylide ions appear to behave normally in the gas phase.[8a,12,13c]

Recent studies have indicated that gas-phase ion chemistry can be used to help in understanding solution thermodynamic properties.[13-16] It is now apparent that in some cases insight can be gained into transition state properties as well. Work is currently underway to elucidate the nature of the activation barrier.

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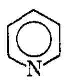
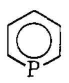
Photoelectron Spectra of Phosphabenzene, Arsabenzene, and Stibabenzene[1]

Sir:

In Figure 1 are shown the photoelectron (pe) spectra of pyridine (I), phosphabenzene[2] (II), arsabenzene[2] (III), and stibabenzene[3] (IV). The (vertical) ionization potentials $I_{\mathrm{v},J}$, *i.e.* the values corresponding to the positions of the band maxima, and a tentative assignment are given in Table I and in the correlation diagram of Figure 2.



I



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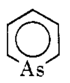

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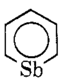

IV

The orbital sequence for I has been deduced previously from its photoelectron spectrum[4] and con-

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