

**Figure 2.** Proton-decoupled 68-MHz  $^{13}\text{C}$  NMR spectra: (A)  $\alpha$ -chymotrypsin (2.0 mM) plus *p*-nitrophenyl (2.6 mM) prepared as in Figure 1, except the pH of solution was adjusted to 3.2 after 4 h; (B) this solution was adjusted to pH 8.0 at room temperature. After 30 min, the pH of solution was adjusted to 3.2 (the carbon signal marked with an asterisk is of unknown origin, but might be residual tetrahedral intermediate of the enzyme).

By measurement of the relative areas of the carbon signals reported here we anticipate obtaining detailed information on the quantity of intermediate present under different experimental conditions.

In order to study the mobility of the acetyl group in the active site environment of the enzyme, the spin-lattice relaxation time ( $T_1$ ) of the carbonyl carbon of the [ $1\text{-}^{13}\text{C}$ ]acetyl-chymotrypsin intermediate was determined. At the same time an average  $T_1$  value for the carbonyl signals of the enzyme backbone was measured by the progressive saturation method. The  $T_1$  value of the carbonyl carbon of the acetyl intermediate was 2.6 s, while the value for the enzyme backbone carbonyls was 2.9 s, under the same experimental conditions. From these results, it seems that the carbonyl of the acetyl group is restricted in motion in the intermediate. This may result from the hydrogen bond between the carbonyl oxygen of the acetyl group and either the NH of glycine-193 or serine-195, which has been suggested by the x-ray analysis of the complex of chymotrypsin with formyl-L-tryptophan by Steitz et al.<sup>14</sup> This explanation is also consistent with spectrophotometric studies of cinnamoyl-chymotrypsin<sup>9</sup> and cinnamoyl-elastase<sup>15</sup> in which a hydrogen bond between the carbonyl group of the acyl derivative and the enzyme backbone has also been proposed.

#### References and Notes

- (1) W. Egan, H. Shindo, and J. S. Cohen, *Annu. Rev. Biophys. Bioeng.*, in press.
- (2) V. Glushko, P. J. Lawson, and F. R. N. Gurd, *J. Biol. Chem.*, **247**, 3176 (1972).
- (3) R. T. Eakin, L. O. Morgan, and N. A. Matwiyoff, *Biochemistry*, **14**, 4538 (1975).
- (4) D. M. Blow, *Acc. Chem. Res.*, **9**, 145 (1976).
- (5) B. S. Hartley and B. A. Kilby, *Biochem. J.*, **50**, 672 (1952).

- (6) G. P. Hess in "The Enzyme", 3rd ed. Vol. 3, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1971, p 213, and earlier references cited therein.
- (7) M. L. Bender and J. V. Killheffer, *CRC Crit. Rev. Biochem.*, **1**, 149 (1973), and earlier references cited therein.
- (8) M. L. Bender, G. R. Schonbaum, and B. Zerner, *J. Am. Chem. Soc.*, **84** 2540 (1962).
- (9) P. R. Carey and H. Schneider, *J. Mol. Biol.*, **102**, 679 (1976).
- (10) R. A. Oosterbaan, M. van Adrichem, and J. A. Cohen, *Biochim. Biophys. Acta*, **63**, 204 (1962).
- (11) K. Okawa and S. Hase, *Bull. Chem. Soc. Jpn.*, **36**, 754 (1963).
- (12) M. L. Bender, F. J. Kezdy, and C. R. Gunter, *J. Am. Chem. Soc.*, **86**, 3714 (1964).
- (13) A. A. Kortt and T. Y. Liu, *Biochemistry*, **12**, 320 (1973).
- (14) T. A. Steitz, R. Henderson, and D. M. Blow, *J. Mol. Biol.*, **46**, 337 (1969).
- (15) E. J. Breaux and M. L. Bender, *Biochem. Biophys. Res. Commun.*, **70**, 235 (1976).

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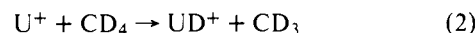
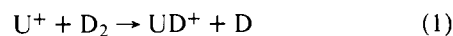
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#### Metal Atoms as Superbases: the Gas Phase Proton Affinity of Uranium

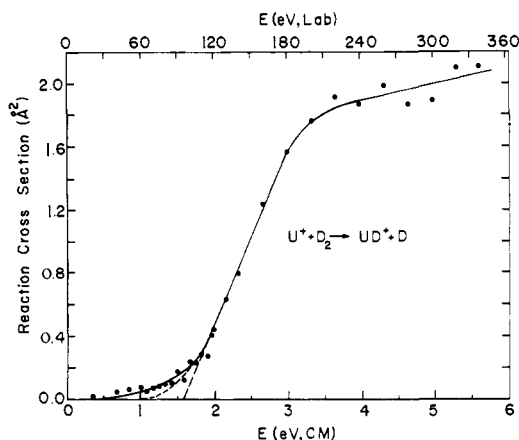
Sir:

The ability to determine the strengths of acids and bases in the gas phase makes possible the search for extremes in behavior for these properties. Discovery of a species having an unusually high acidity or basicity sheds light on the factors which determine these properties and suggests other studies and applications which derive advantage from the exceptional behavior. With this in mind, we would like to report that metal atoms can be very strong bases in the gas phase. This conclusion is based on the determination of the proton affinity of the technologically important uranium atom, for which we have measured  $\text{PA}(\text{U}) = 238 \pm 4$  kcal/mol.

The endothermic reactions of uranium ions with  $\text{D}_2$ , process 1, and  $\text{CD}_4$ , process 2, have been observed in an ion beam-collision chamber apparatus, previously described.<sup>1</sup> The uranium ion source comprises a tubular stainless steel tube, operated at approximately 700 K, which vaporizes solid  $\text{UF}_4$  onto a resistively heated rhenium ribbon at  $\sim 2300$  K, where dissociation and surface ionization occurs.<sup>2</sup> Uranium ions are accelerated to a selected energy and allowed to interact with the target gas in a collision chamber at 400 K. Product ions scattered in the forward direction are detected using a quadrupole mass spectrometer.<sup>3</sup>



Ion product abundance was measured as a function of target gas pressure to yield the cross section for reaction. The variation in cross section with relative kinetic energy for reaction 1 is shown in Figure 1. Significant Doppler broadening due to thermal motion of the target gas is evident in the threshold region. Using the analysis of Chantry<sup>4</sup> for a cross section which increases linearly with energy above threshold, an extrapolation of the straight line portion of the curve gives a threshold too low by  $3\gamma kT$  where  $T$  is the temperature of the target gas and  $\gamma = m_{\text{U}}/(m_{\text{U}} + m_{\text{AB}})$ ,  $m_{\text{U}}$  and  $m_{\text{AB}}$  being the incident particle



**Figure 1.** Variation of experimental cross section with relative kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale) for reaction 1. The solid curve is an approximate fit to the experimental points. The straight dashed line (—) is a linear extrapolation of the data in the threshold region. The curved dashed line (---) is the threshold behavior predicted by Chantry's analysis at a temperature of 400 K.

**Table I.** Proton Affinities of Selected Atomic and Molecular Species

Species	Ionization potential (eV)	Proton affinity (kcal/mol)	Ref for proton affinities
Li	5.39 <sup>e</sup>	193 ± 5	a, b
Mg	7.64 <sup>e</sup>	187 ± 5	b, d
Hg	10.44 <sup>e</sup>	128 ± 5	b, d
U	6.19 <sup>f</sup>	238 ± 4	This work
NMe <sub>3</sub>	7.87 <sup>g</sup>	222 ± 2	g
PMe <sub>3</sub>	8.01 <sup>g</sup>	224 ± 2	g
NEt <sub>3</sub>	7.42 <sup>h</sup>	229 ± 2	c
LiOH		241 ± 2	i
NaOH		248 ± 2	i
KOH		263 ± 2	i
CsOH		270 ± 2	i

<sup>a</sup> F. H. Field, NSRDS-NBS 26 (1969). <sup>b</sup> JANAF Thermochemical Tables, NSRDS-NBS 37 (1971). <sup>c</sup> J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, submitted. <sup>d</sup> G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand, New York, N.Y., 1965, Table 39. <sup>e</sup> B. Lakatos, J. Bohus, and G. Medgyesi, *Acta Chim. Acad. Sci. Hung.*, **20**, 1 (1959). <sup>f</sup> G. S. Jones, I. Itzan, C. T. Pike, R. H. Levy, and L. Levin, *J. Quantum Electronics*, **EQ-12**, 111 (1976). <sup>g</sup> R. V. Hodges and J. L. Beauchamp, *Inorg. Chem.*, **14**, 2887 (1975). <sup>h</sup> R. H. Staley, M. Taagepera, W. G. Henderson, J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, in press. <sup>i</sup> S. K. Searles, I. Dzidic, and P. Kebarle, *J. Am. Chem. Soc.*, **91**, 2810 (1969).

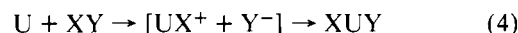
and target gas masses. The corrected threshold for reaction 1 is  $1.7 \pm 0.1$  eV giving a homolytic bond dissociation energy,  $D(\text{UD}^+)$ , of  $2.95 \pm 0.10$  eV for  $\text{UD}^+$  dissociating to  $\text{U}^+$  and D. A similar analysis of reaction 2 yields a value of  $3.0 \pm 0.3$  eV, in excellent agreement. An average value of  $D(\text{UD}^+) = 3.0 \pm 0.2$  eV is thus determined. In this analysis it is assumed that  $T\Delta S$  is approximately zero for reaction 1 and  $\Delta H_{400\text{ K}} = \Delta H_{298\text{ K}}$ .

To obtain the proton affinity of uranium, the substitution of protium (H) for deuterium (D) must be made. The difference in bond dissociation energies for the two isotopes,  $D(\text{UD}^+) - D(\text{UH}^+)$ , is estimated to be 1.7 kcal/mol, leading to the value,  $D(\text{UH}^+) = 2.9 \pm 0.2$  eV. Using eq 3,<sup>5</sup> where IP refers to the ionization potential of the indicated species, the proton affinity of uranium is calculated to be  $238 \pm 4$  kcal/mol.

$$\text{PA}(\text{U}) = D(\text{UH}^+) + \text{IP}(\text{H}) - \text{IP}(\text{U}) \quad (3)$$

The derived value for  $\text{PA}(\text{U})$  is compared to other available atomic and molecular proton affinities in Table I. Uranium clearly has the highest base strength of any atomic species for which reliable thermodynamic data are available. It is stronger than any organic monodentate base reported to date. Only the alkali hydroxides have a higher basicity. The high proton affinity of uranium is a result of a low ionization potential and a moderately high homolytic bond dissociation energy.

The base strength of uranium suggests that interactions between the metal and acidic species should be quite strong. Utilization of this fact could lead to the formation of new uranium complexes involving both cationic acids and neutral Lewis acids (e.g.,  $\text{UBF}_3$ ). The high basicity of uranium may also have implications for the mechanisms of oxidative addition reactions involving this species. Specifically, it is suggested that the heterolytic reaction scheme, process 4, may be the preferred mechanism for bond insertion reactions.<sup>6</sup>



The methodology developed here should be generally applicable to the determination of gas phase proton affinities for many atomic species. Related experiments are underway in our laboratory to determine a range of metal-hydrogen homolytic bond dissociation energies from which atomic base strengths can be directly evaluated.

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#### References and Notes

- (1) R. V. Hodges and J. L. Beauchamp, *Anal. Chem.*, **48**, 825 (1976).
- (2) G. R. Hertel, *J. Chem. Phys.*, **47**, 133 (1967).
- (3) The use of  $\text{D}_2$  and  $\text{CD}_4$  was dictated by the limited resolution of the quadrupole mass spectrometer.
- (4) P. J. Chantry, *J. Chem. Phys.*, **55**, 2746 (1971).
- (5) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
- (6) This type of scheme has been proposed by T. Marks, unpublished results, to explain the insertion reactions of thorium.

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#### Photochemical Addition of Aromatic Aldehydes to 1,3,5-Cycloheptatriene, a $6\pi_s + 2\pi_s$ Photocycloaddition

Sir:

According to the Woodward-Hoffmann rule of conservation of orbital symmetry, concerted  $6\pi_s + 2\pi_s$  cycloadditions are photochemically allowed processes but thermally "forbidden."<sup>1,2</sup> While there are several examples of  $6\pi_s + 2\pi_s$  thermal cycloadditions reported in the literature,<sup>3-7</sup> the only examples of  $6\pi_s + 2\pi_s$  photocycloadditions reported are additions of a benzenoid system to an olefin with the excited benzenoid system functioning as the  $6\pi$ -component.<sup>8-10</sup> The adducts formed from such photocycloadditions contain a four-membered ring derived from two adjacent positions of the benzenoid ring and the olefin (reaction 1).<sup>11</sup> In connection with our interest in the

