is employed as reagent, facile bimolecular isotope exchange is revealed. This study represents the first observation of these processes at thermal energy.[15] For water and carbon dioxide, exchange occurs at or near the statistical limit, indicating that the oxygen atoms have become equivalent during the lifetime of the intermediate complex (70 and 2000 ps, respectively).[14a] In contrast, only 17% exchange is observed for O_2, where the complex lifetime is expected to be quite short (2 ps).[14b] Thus isotope-exchange reactions provide a valuable means for probing the time scales of these fundamental ion–molecule processes.

In conclusion, these results demonstrate that the injection of isotopically labeled ions from unenriched precursors can readily be accomplished in a FA–SIFT; such studies should be feasible for a wide variety of positive and negative ions and make possible a detailed investigation of ionic reaction mechanisms.

Acknowledgment. We are deeply grateful to David Fahey and Carl Lineberger for their generous contribution of time and ideas in the design of the flowing afterglow–selected ion flow tube. We also wish to thank Fred Fehsenfeld, David Smith, and Nigel Adams for many helpful discussions. We gratefully acknowledge support of this work by the National Science Foundation (Grants CHE-8503505 and CHE-8508629), the U.S. Army Research Office (Contract DAAG29-85-K-0046), and the donors of the Petroleum Research Fund (Grant 15990-AC4-C), administered by the American Chemical Society.

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Gas Phase Chemistry of $CH_2^{\bullet-}$

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Methylene, CH_2, as the prototypical carbene, is among the most studied of all reactive intermediates, but the *chemistry* of its anion, $CH_2^{\bullet-}$, is completely unknown.[1] We wish to report that in our tandem flowing afterglow–selected ion flow tube (FA–SIFT)[2] we can generate, separate, inject, and detect $CH_2^{\bullet-}$ ions with signals of up to 1000 counts/s and with noise ≤1 count/s. As a result we are able to determine products and, when desired, accurate rate constants for its reactions with a host of neutral reagents, both organic and inorganic.

Electron impact on either ethylene or methane produces a variety of negative ions among which $CH_2^{\bullet-}$ is a minor constituent, as shown in Figure 1a. Figure 1b shows the mass spectrum that results when the SIFT quadrupole mass filter is tuned to m/z 14. The HO^- signal at m/z 17 arises from the rapid reaction of $CH_2^{\bullet-}$ with traces of water in the downstream flow tube; the ratio of detected ion signals indicates that the water impurity is about 0.4 ppm.

As predicted from its physical properties,[1] $CH_2^{\bullet-}$ is an extremely strong base [$\Delta H^\circ_{acid}(CH_3^\bullet) = 407.4 \pm 0.9$ kcal/mol], the strongest whose chemistry has so far been studied in the FA.[3] It rapidly abstracts a proton from water ($\Delta H^\circ_{acid} = 390.8 \pm 0.3$ kcal/mol, $k = 3.1\ (\pm 0.2) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, reaction efficiency[4,5] = 1.2), ammonia ($\Delta H^\circ_{acid} = 403.6 \pm 0.8$ kcal/mol), and other compounds, including methyl vinyl ether, tetramethylsilane, propene, methanol, silane, acetone, and ketene. Proton abstraction from some carbon acids, including benzene and toluene, is slow. The reaction of $CH_2^{\bullet-}$ with methyl chloride proceeds by both proton abstraction and S_N2 displacement.

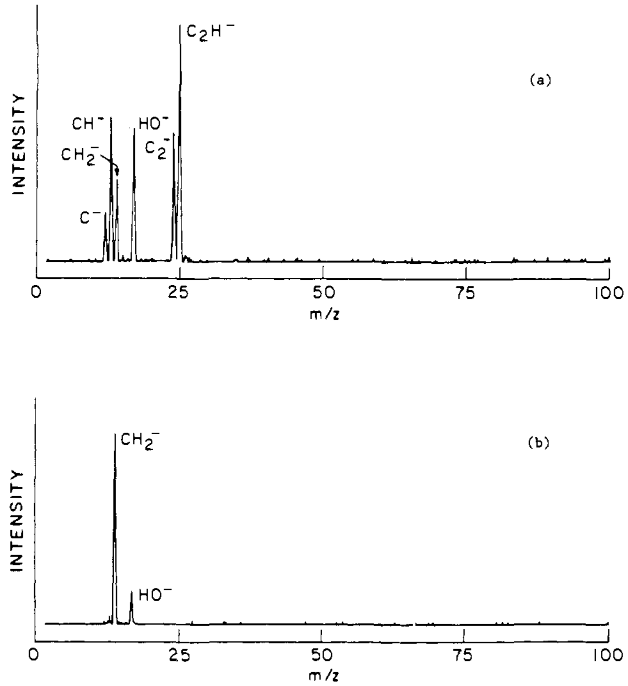

Figure 1. (a) Total ion spectrum resulting from electron impact on methane. (b) Spectrum of $CH_2^{\bullet-}$ after mass selection and injection.

Despite the great exothermicity of its reaction with water (17 kcal/mol), the reaction proceeds by way of a long-lived complex; this is demonstrated by the observation of multiple proton transfer in the reaction of $CH_2^{\bullet-}$ with $D_2{}^{18}O$ (eq 1) resulting in the production of some $H^{18}O^-$. In contrast, reaction of $CH_2^{\bullet-}$ with deuteriated ammonia, methanol, or acetone proceeds only by deuteron abstraction, and no H/D exchange is observed.

$$\begin{array}{l} CH_2^{\bullet-} + D_2{}^{18}O \rightarrow [CH_2D^\bullet\ D^{18}O^-] \rightarrow D^{18}O^- + {}^\bullet CH_2D \\ \qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\quad [CHD^{\bullet-}\ D^{18}OH] \rightarrow H^{18}O^- + {}^\bullet CHD_2 \end{array} \tag{1}$$

Because $CH_2^{\bullet-}$ is a radical anion, its reactions with neutral molecules will often lead to associative detachment unless one or more of the products has a positive electron affinity. Thus $CH_2^{\bullet-}$ reacts rapidly with CO ($k = 7.3\ (\pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, reaction efficiency = 0.68), but no ionic products are detected. Presumably ketene and an electron are formed (eq 2).[6] An

$$CH_2^{\bullet-} + CO \rightarrow CH_2{=}C{=}O + e \tag{2}$$

analogous reaction occurs between the isoelectronic ion $O^{\bullet-}$ and CO to form CO_2.[7] Electron detachment (associative or reactive) is also the only channel observed in the reaction of $CH_2^{\bullet-}$ with CO_2, and detachment occurs in competition with other reactions for many neutral reagents.

Of greater chemical interest, perhaps, are those reactions which lead to ionic products. Reaction with N_2O, which occurs rather slowly ($k = 2.8\ (\pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, reaction efficiency = 0.22),[8] gives rise to three ionic products, all of which

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(1) Leopold, D. G.; Murray, K. K.; Miller, A. E. S.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849.

(2) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M., preceding paper in this issue.

(3) The chemistry of the cyclopropyl anion [$\Delta H^\circ_{acid}(c\text{-}C_3H_6) \simeq 412$] was studied by FTMS. See: Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2853.

(4) Reaction efficiency = k_{expt}/k_{ADO}, where k_{ADO}, the collision rate constant, is calculated by the method of Su and Bowers (Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347).

(5) To ensure that $CH_2^{\bullet-}$ is not vibrationally excited, methane was added to the downstream flow tube for several rate constant determinations; no difference in the rate constant was observed with and without methane.

(6) Neutral products are, of course, not detected; in some cases, several product channels are exothermic.

(7) $k = 6.9 \times 10^{-10}$. Reference 2.

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can be accounted for by attack at the terminal nitrogen,[9] as shown in eq 3. These products have analogues in the reactions of other anions with N_2O.[10]

$$CH_2^{\bullet -} + N{=}N{=}O \rightarrow [{}^{\bullet}CH_2{-}N{=}N{-}O^-] \rightarrow CH_2{=}N^- + {}^{\bullet}NO \quad (3a)$$

$$\rightarrow CN^- + H_2 + {}^{\bullet}NO \quad (3b)$$

$$\rightarrow \dot{C}{=}N{=}N^- + H_2O \quad (3c)$$

Reaction with carbon disulfide also occurs by a number of channels (eq 4) reflecting the great reactivity of $CH_2^{\bullet -}$. Reaction

$$CH_2^{\bullet -} + S{=}C{=}S \rightarrow S^{\bullet -} + CH_2{=}C{=}S \quad (4a)$$

$$\rightarrow HS^- + \dot{C}H{=}C{=}S \quad (4b)$$

$$\rightarrow {}^-CH{=}C{=}S + HS^{\bullet} \quad (4c)$$

$$\rightarrow CH_2S^{\bullet -} + CS \quad (4d)$$

$$\rightarrow CS_2^{\bullet -} + CH_2 \quad (4e)$$

$$\rightarrow \text{neutral products} + e \quad (4f)$$

4a presumably occurs by addition with loss of $S^{\bullet -}$. Channels 4b and 4c result when reaction 4a is followed by hydrogen atom transfer or proton transfer, respectively, before the initial products separate. Direct carbanion attack on sulfur would lead to $CH_2S^{\bullet -}$ (eq 4d) while charge transfer would form $CS_2^{\bullet -}$ (eq 4e). Detachment (eq 4f) is, however, the major channel.

Reaction of $CH_2^{\bullet -}$ with O_2 forms $O^{\bullet -}$ exclusively (eq 5), while SO_2 produces both $SO^{\bullet -}$ (by attack on oxygen, eq 6a) and $SO_2^{\bullet -}$ (by electron transfer, eq 6b).

$$CH_2^{\bullet -} + O_2 \rightarrow O^{\bullet -} + CH_2{=}O \quad (5)$$

$$CH_2^{\bullet -} + SO_2 \rightarrow SO^{\bullet -} + CH_2{=}O \quad (6a)$$

$$\rightarrow SO_2^{\bullet -} + CH_2 \quad (6b)$$

The $CH_2^{\bullet -}$ and $O^{\bullet -}$ anions are isoelectronic species and, as such, show many parallels in reactivity. Nevertheless, there are important differences in their behavior, differences which shed light on the chemistry of both species.[11] For example, $O^{\bullet -}$ reacts with ethylene to form the vinylidene radical anion (eq 7),[12] while the analogous process with $CH_2^{\bullet -}$ does not occur despite its greater exothermicity[13-16] (eq 8). Similarly, we have no evidence for $H_2^{\bullet +}$ abstraction by $CH_2^{\bullet -}$ with other organic compounds, for example, benzene, in striking contrast to the chemistry of $O^{\bullet -}$.[9]

$$O^{\bullet -} + CH_2{=}CH_2 \rightarrow H_2O + {}^{-\bullet}C{=}CH_2 \qquad \Delta H \simeq -10 \text{ kcal/mol} \quad (7)$$

$$CH_2^{\bullet -} + CH_2{=}CH_2 \not\rightarrow CH_4 + {}^{-\bullet}C{=}CH_2 \qquad \Delta H \simeq -21 \text{ kcal/mol} \quad (8)$$

As our results show, even minor, highly reactive ions can be separated and studied in the FA-SIFT. We are currently extending our investigations to the chemistry of CH^- and $C^{\bullet -}$ and examining ion production from other neutrals (e.g., SiH_4 and PH_3) which should give rise to analogous anions. It seems likely that nearly any anion bound by 8–10 kcal/mol or more can be studied by this technique.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grants CHE-8503505 and CHE-8508629), the U.S. Army Research Office (Contract DAAG29-85-K-0046), and the donors of the Petroleum Research Fund (Grant 15990-AC4-C), administered by the American Chemical Society.

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[8] Nitrous oxide also reacts rather slowly with other anions. For example, for $NH_2^- + N_2O$, $k = 2.9 \times 10^{-10}$ (Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Phys. Chem.* **1984**, *88*, 1389).

[9] Evidence for carbanion attack at the terminal nitrogen in N_2O is provided by isotope labeling studies: Dawson, J. H. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1978**, *100*, 1928.

[10] Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 2849.

[11] For a summary of the reactions of $O^{\bullet -}$, see: Jennings, K. R. *Philos. Trans. R. Soc. London, Ser. A* **1979**, *293*, 125. Bruins, A. P.; Ferrer-Correia, A. J.; Harrison, A. G.; Jennings, K. R.; Mitchum, R. K. *Adv. Mass Spectrom.* **1978**, *7*, 355. Dawson, J. H. J.; Jennings, K. R. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 700.

[12] Lindinger, W.; Albritton, D. L.; Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1973**, *63*, 3238.

[13] Reaction enthalpies were calculated at 0 K by using heats of formation from the following sources: ref 14 for $O^{\bullet -}$, C_2H_4, H_2O, and CH_4; ref 15 and 16 for ${}^{-\bullet}C{=}CH_2$; ref 1 for $CH_2^{\bullet -}$.

[14] Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables*, NSRDS-NBS-37, 2nd ed.; National Bureau of Standards: Washington, DC, 1971.

[15] Burnett, S. M.; Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. *Chem. Phys. Lett.* **1983**, *100*, 124.

[16] Chandrasekhar, J.; Kahn, R. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *85*, 493.

Generation and Physical Properties of Enamines Related to the Key Intermediate in Thiamin Diphosphate Dependent Enzymatic Pathways

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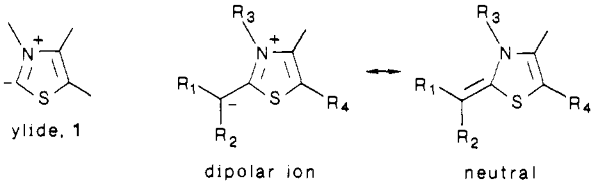
The catalytic power of the thiamin diphosphate coenzyme resides, in part, in the ability of its thiazolium ring to stabilize two intermediates: the ylide **1** and the putative enamine ($C2_\alpha$ carbanion) **2**.[1,2] We here report the first successful generation of structures analogous to the enamine **2** in model systems[3] and ^1H NMR spectroscopic characterization of such structures.



ylide, **1**

dipolar ion

neutral

enamine, **2**

The thiazolium models **3** synthesized[4] are listed in Table I. Protection of the hydroxy group was essential to avoid base-induced decomposition. The ^1H NMR spectra could be assigned unequivocally based on comparisons between the N–CH_3 and N–CD_3 compounds and the readily detectable long-range J coupling between C4–CH_3 and C5–H. Compounds **3a** and **3b** were useful in the spectral assignments and enabled assessment of the effect of the C2–C_α oxygen on enamine structure and stability.

Treatment of **3** with about 1.2 equiv of potassium *tert*-butoxide or $Na[(CH_3)_3Si]_2N$ ((trimethylsilyl)amide, pK_a in Me_2SO is 25[5]) in anhydrous pyridine-d_5 resulted in the shift to higher fields of the N–CH_3, C4–H, and C5–H (or C5–CH_3) resonances (Table II), consistent with reduction of the aromaticity and/or of the

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[1] Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719–3726.

[2] Krampitz, L. O. *Annu. Rev. Biochem.* **1969**, *38*, 213–240.

[3] Some model studies that implied the intermediacy of the enamine: (a) Rastetter, W. H.; Adams, J.; Frost, J. W.; Nummy, L. J.; Frowmer, J. E.; Roberts, D. B. *J. Am. Chem. Soc.* **1979**, *101*, 3785–3787. (b) Zoltewicz, J. A.; Helmick, L. S. *J. Org. Chem.* **1978**, *43*, 1718–1721, 3785–3787.

[4] Elemental analysis (C, H, N = ±0.3%) and ^1H NMR were consistent with the proposed structures.

[5] Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232–3234.