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 O2, where the complex lifetime is expected to be quite short (2 ps).^{14b} Thus isotopeexchange 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.

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Gas Phase Chemistry of CH2*-

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Methylene, CH₂, 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 $CH_2^{\bullet\bullet}$ 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 CH2⁻⁻ 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 CH₂⁻⁻ 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 CH2. is an extremely strong base $[\Delta H^{\circ}_{acid}(CH_3) = 407.4 \pm 0.9 \text{ kcal/mol}]$, the strongest whose chemistry has so far been studied in the FA.³ It rapidly abstracts a proton from water ($\Delta H^{\circ}_{acid} = 390.8 \pm 0.3 \text{ kcal/mol}$, k = 3.1 (±0.2) × 10⁻⁹ cm³ molecule⁻¹ s⁻¹, reaction efficiency^{4,5}



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

= 1.2), ammonia (ΔH°_{acid} = 403.6 ± 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 CH₂^{•-} with methyl chloride proceeds by both proton abstraction and $S_N 2$ displacement.

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.

Because CH2^{•-} 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 CH2* reacts rapidly with CO ($k = 7.3 (\pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} , reaction efficiency = 0.68), but no ionic products are detected. Presumably ketene and an electron are formed (eq 2).⁶ An

$$CH_2 - + CO \rightarrow CH_2 = C = O + e$$
 (2)

analogous reaction occurs between the isoelectronic ion O⁻⁻ and CO to form CO₂.⁷ Electron detachment (associative or reactive) is also the only channel observed in the reaction of CH2.- 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 N2O, which occurs rather slowly $(k = 2.8 (\pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, reaction efficiency = 0.22),⁸ gives rise to three ionic products, all of which

⁽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 $[\Delta H^{o}_{acid}(c-C_{3}H_{6}) \approx 412]$ 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 CH2^{•-} 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.

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

$$\rightarrow CN^- + H_2 + \cdot NO \tag{3b}$$

$$\rightarrow \dot{C} = N = N^{-} + H_2 O \qquad (3c)$$

Reaction with carbon disulfide also occurs by a number of channels (eq 4) reflecting the great reactivity of CH2. Reaction

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

$$\rightarrow$$
 HS⁻ + CH=C=S (4b)

-CH==C==S + HS• (4c)

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

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

 \rightarrow neutral products + e (4f)

4a presumably occurs by addition with loss of S⁻⁻. 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 CH2S*-(eq 4d) while charge transfer would form $CS_2^{\bullet-}$ (eq 4e). De-

tachment (eq 4f) is, however, the major channel. Reaction of $CH_2^{\bullet-}$ with O_2 forms $O^{\bullet-}$ exclusively (eq 5), while SO₂ produces both SO⁻⁻ (by attack on oxygen, eq 6a) and SO₂⁻⁻ (by electron transfer, eq 6b).

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

$$CH_2^{\bullet-} + SO_2 \rightarrow SO^{\bullet-} + CH_2 = 0$$
 (6a)

$$\rightarrow$$
 SO₂⁻ + CH₂ (6b)

The CH₂^{•-} and O^{•-} 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

$$O^{-} + CH_2 = CH_2 \rightarrow$$

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

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

analogous process with CH2 *- does not occur despite its greater exothermicity¹³⁻¹⁶ (eq 8). Similarly, we have no evidence for H_2^{+} abstraction by CH₂^{•-} with other organic compounds, for example, benzene, in striking contrast to the chemistry of O^{•-,9}

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⁻⁻ and examining ion production from other neutrals (e.g., SiH₄ and PH₃) 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.

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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_{α} carbanion) $2^{1,2}$ We here report the first successful generation of structures analogous to the enamine 2 in model systems³ and ¹H NMR spectroscopic characterization of such structures.



The thiazolium models 3 synthesized⁴ 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-CH₃ and N-CD₃ compounds and the readily detectable long-range Jcoupling between C4-CH₃ 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[(CH₃)₃Si]₂N ((trimethylsilyl)amide, pK_a in Me₂SO is 25⁵) in anhydrous pyridine- d_5 resulted in the shift to higher fields of the N-CH₃, C4-H, and C5-H (or C5-CH₃) resonances (Table II), consistent with reduction of the aromaticity and/or of the

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