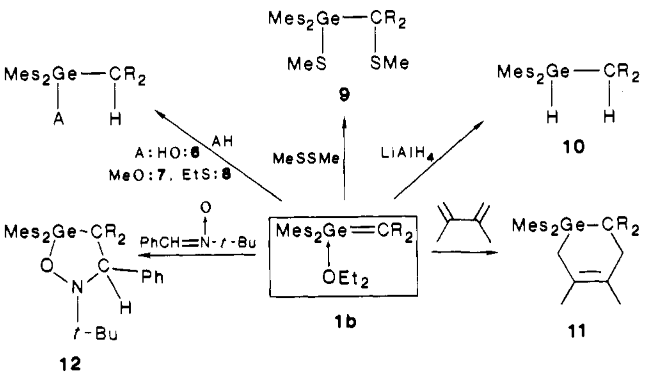
1a forms a very stable adduct **1b**[7] with a weak Lewis base such as diethyl ether. Addition of a stoichiometric amount of triethylamine to **1b** gives adduct **1c**[7] (eq 2). When addition of *t*-BuLi to **2** is carried out in THF, adduct **1d** (THF•$Mes_2Ge{=}CR_2$) was quantitatively obtained; **1d** was spectroscopically[7] and chemically (addition of methanol leading to **7**) characterized. All these adducts which are very thermally stable (no decomposition occurred after heating **1b** in a sealed tube at 85 °C for 15 h) are highly air-sensitive and present thermochromism: crystals of **1b**, **1c** and **1d** are yellow at −100 °C, orange at room temperature, and orange-red at 80 °C.

When the double bond is markedly polarized, the metal has a strong electrophilic character; therefore, it is easily complexed by Lewis bases such as ether oxides or amines, like in silenes[8] and silaimines.[9] Such complexation has not been observed in symmetric molecules $\rangle M{=}M\langle$ (M = Si,[1a,b] Ge,[2] Sn[10]) or in metallaphosphenes $\rangle M{=}P-$ (M = Si,[11] Ge,[3a] Sn[12]) where metal 14 is bound to phosphorus, a less negative atom than carbon or nitrogen.[13]

Germene **1** is stabilized owing to bulky groups on germanium and probably high mesomeric effects between the germanium–carbon double bond and the fluorenyl group. Such a group has already allowed the stabilization of phosphaalkenes $-P{=}C\langle$[14] and of a boraalkene $-B{=}C\langle$.[15]

The structure of **1b** was corroborated by its chemical behavior. A preliminary investigation reveals that **1b** is highly reactive; reactions proceed probably via the free germene **1a**, which is formed by previous dissociation of the adduct. Protic reagents (water, methanol, ethylthiol) and dimethyl disulfide add quantitatively on the Ge=C double bond of **1** to form respectively **6**, **7**, **8**, and **9**;[16] lithium aluminum hydride reduces **1b** to **10**.[16] 1,3-Cycloaddition has been observed with *N*-(*tert*-butyl)-α-phenylnitrone[16] and 1,4-cycloaddition with 2,3-dimethylbutadiene;[16] in the last case, the ene reaction has not been observed (Scheme I).

Scheme I



All these reactions are nearly quantitative and occur at room temperature. They demonstrate the existence of a true double bond between germanium and carbon. **1** is the first stable germene whereas some silenes have already been isolated.[1b,c,8] The stabilization of **1** seems to confirm recent calculations[17] that have predicted close π-bond energies for germenes and silenes.

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(16) **6**: white crystals, mp 72–73 °C; ^1H NMR (C_6D_6) δ 2.10 (s, 6 H, *p*-Me), 2.20 (s, 12 H, *o*-Me), 4.75 (s, 1 H, *H*CR_2), 6.65 (s, 4 H, aromatic Mes), 6.85–7.80 (m, 8 H, CR_2); IR (Nujol) ν(GeOH) 3420 cm^{-1}; mass spectrum (EI), *m/e* (relative intensity) 494 (M, 5), 429 (Mes_2GeOH, 100). Anal. Calcd for $C_{31}H_{32}GeO$: C, 75.49; H, 6.54. Found: C, 75.36; H, 6.30. **7**: white crystals, mp 55–57 °C; ^1H NMR (C_6D_6) δ 2.08 (s, 6 H, *p*-Me), 2.56 (s, 12 H, *o*-Me), 3.35 (s, 3 H, MeO), 4.90 (s, 1 H, *H*CR_2), 6.70 (s, 4 H, aromatic Mes), 7.03–7.93 (m, 8 H, CR_2). Anal. Calcd for $C_{32}H_{34}GeO$: C, 75.77; H, 6.76. Found: C, 75.66; H, 6.87. **8**: yellow-green crystals, mp 135–136 °C dec. ^1H NMR (C_6D_6) δ 1.00 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, CH_2CH_3), 1.60 (q, $^3J_{HH}$ = 7.0 Hz, 2 H, CH_2), 2.05 (s, 6 H, *p*-Me), 2.66 (s, 12 H, *o*-Me), 4.88 (s, 1 H, *H*CR_2), 6.62 (s, 4 H, aromatic Mes), 7.00–7.93 (m, 8 H, CR_2). Anal. Calcd for $C_{33}H_{36}GeS$: C, 73.77; H, 6.75. Found: C, 74.09; H, 7.02. **9**: white crystals, mp 184–186 °C; ^1H NMR (C_6D_6) δ 1.00 (s, 3 H, GeSMe), 1.55 (s, 3 H, CSMe), 2.00 (s, 6 H, *p*-Me), 2.10 (s, 12 H, *o*-Me), 6.53 (s, 1 H, aromatic Mes), 6.93–8.03 (m, 8 H, CR_2). Anal. Calcd for $C_{33}H_{36}GeS_2$: C, 69.61; H, 6.37. Found: C, 69.98; H, 6.66. **10**: white crystals, mp 110–111 °C; ^1H NMR (C_6D_6) δ 2.10 (s, 6 H, *p*-Me), 2.20 (s, 12 H, *o*-Me), 4.80 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, *H*CR_2), 5.20 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, GeH), 6.73 (s, 4 H, aromatic Mes), 6.93–7.93 (m, 8 H, CR_2); IR (Nujol) ν(Ge-H) 2070 and 2095 cm^{-1} (two bands, probably due to a Fermi resonance with band at 1040 cm^{-1}). Anal. Calcd for $C_{31}H_{32}Ge$: C, 78.03; H, 6.76. Found: C, 77.74; H, 7.04. **11**: white crystals, mp 123–124 °C; ^1H NMR (C_6D_6) δ 1.38 (s, 3 H, Me), 1.83 (s, 3 H, Me), 1.95 (s, 12 H, *o*-Me), 2.06 (s, 6 H, *p*-Me), 2.48 (s, 2 H, CH_2), 2.55 (s, 2 H, CH_2), 6.68 (s, 4 H, aromatic Mes), 7.05–7.91 (m, 8 H, CR_2). Anal. Calcd for $C_{37}H_{40}Ge$: C, 79.74; H, 7.23. Found: C, 79.50; H, 7.33. **12**: white crystals, mp 220–222 °C; ^1H NMR (C_6D_6) δ 1.80 (s, 3 H, *p*-Me), 1.86 (s, 3 H, *p*-Me), 1.93 (s, 6 H, *o*-Me), 2.01 (s, 6 H, *o*-Me), 4.73 (s, 1 H, CH), 6.38 (s, 4 H, aromatic Mes), 6.56–7.50 (m, 13 H, Ph and CR_2); mass spectrum (EI), *m/e* (relative intensity) 653 (M, 30), 638 (M-15, 5), 596 (M-*t*-Bu, 5), 566 (M-*t*-Bu-2Me, 5), 476 (**1a**, 100). Anal. Calcd for $C_{42}H_{45}GeNO$: C, 77.32; H, 6.95. Found: C, 77.50; H, 7.22.

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Tandem Flowing Afterglow-Selected Ion Flow Tube and Its Application to the Thermal Energy Reactions of $^{18}O^-$

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Since its development by Ferguson, Fehsenfeld, and Schmeltekopf[1] in 1963, the flowing afterglow (FA) has proven to be a valuable technique for studying the kinetics, thermochemistry, and detailed dynamics of gas-phase ion–molecule reactions. The capabilities of this method were greatly extended by Adams and Smith[2] in 1976 by their development of the selected ion flow tube (SIFT); in the last decade several research groups have applied this technique to a variety of important chemical problems. We wish to report the design and construction of a tandem FA–SIFT instrument with considerably enhanced sensitivity, resolution, and chemical versatility. With this instrument we have generated $^{18}O^-$ from isotopically unenriched precursors and studied its chemistry with a variety of reagents. These studies provide the first thermal energy rate constants for these processes and reveal several previously hidden reactions; in particular, it is found that isotope exchange competes with associative detachment in the reactions of O^- with CO and SO_2.

The new tandem FA–SIFT system is shown schematically in Figure 1. Ions are generated in the flowing afterglow source and extracted and focused into the SIFT quadrupole mass filter; the mass-selected ions are refocused and injected into the flow-drift tube where neutral reagents are added to carry out ion chemistry. The ionic reactants and products are detected with a quadrupole mass filter coupled with an electron multiplier. For this study the drift capability[3] was not employed.

With this instrument we have generated unexpectedly large

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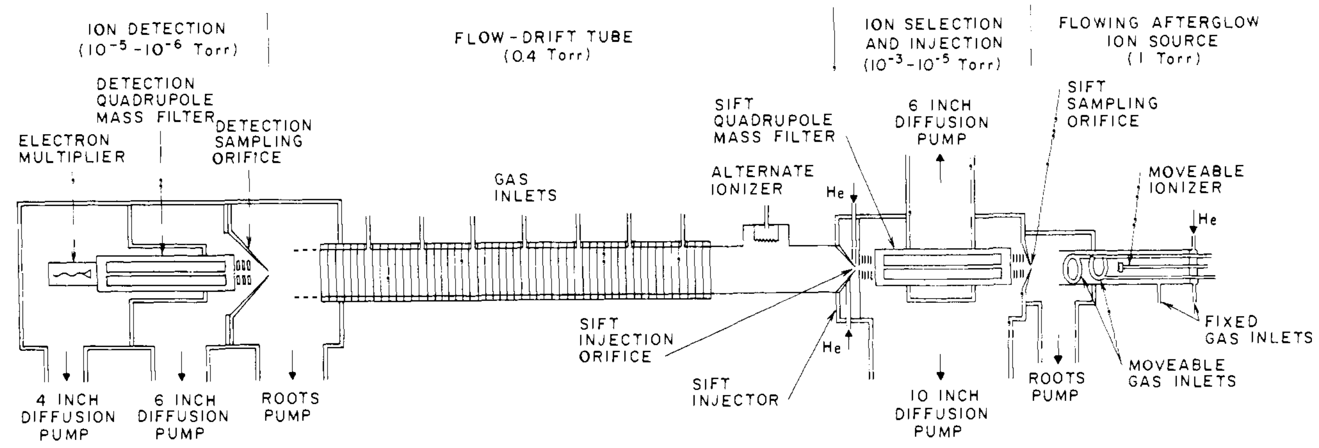

Figure 1. Tandem flowing afterglow-selected ion flow tube.

Table I. Kinetic Data for the Reactions of O^-

ion	neutral reactant	k ($cm^3\ s^{-1}$)[a]	efficiency[b]
$^{16}O^-$	CO	6.9 (±0.3) × 10^{-10}	0.68
$^{18}O^-$		7.8 (±0.3) × 10^{-10}	0.79
$^{16}O^-$	SO_2	2.1 (±0.1) × 10^{-9}	0.74
$^{18}O^-$		2.2 (±0.1) × 10^{-9}	0.81
$^{16}O^-$	NO	2.8 (±0.1) × 10^{-10}	0.30
$^{18}O^-$		4.7 (±0.2) × 10^{-10}	0.51
$^{16}O^-$	N_2O	2.3 (±0.1) × 10^{-10}	0.19
$^{18}O^-$		4.0 (±0.2) × 10^{-10}	0.35
$^{18}O^-$	H_2O	1.4 (±0.1) × 10^{-9}	0.41
$^{18}O^-$	CO_2	7.5 (±0.4) × 10^{-10}	0.67
$^{18}O^-$	O_2	1.5 (±0.1) × 10^{-10}	0.17

[a] Error bars represent one standard deviation from the mean; between three and seven determinations were made for each rate constant. The absolute errors are estimated to be ±20%. [b] Reaction efficiency = k_{expt}/k_c, where $k_c = k_{Langevin}$ (ref 16) for neutral reactants with no dipole moment, $k_c = k_{ADO}$ (ref 17) for neutral reactants with small dipole moments, and $k_c = k_{var}$ (ref 18) for neutral reactants with large dipole moments, i.e., H_2O and SO_2.

signal intensities for a wide variety of anions including highly reactive ions (CH_2^-),[4] solvated ions [$HO^-(H_2O)$], and ions which must be synthesized by a series of ion-molecule reactions ($C_3H_3N_2^-$).[5] Indeed, the efficiency and sensitivity of the system is sufficiently high that large signals of *naturally abundant* isotopically labeled ions (^{37}Cl, ^{34}S, ^{13}C, and ^{18}O) can be obtained with low background signals. For the study reported here, electron impact on N_2O (0.2% natural abundance oxygen-18) with mass selection and injection of $^{18}O^-$ produced signals of up to 5000 counts/s at the output of the ion detection system with ≤1 count/s noise; these signal intensities correspond to injected $^{18}O^-$ currents of ~1 nA just downstream of the SIFT injector.[6]

The gas-phase chemistry of O^- has been extensively investigated[7] and is both rich and varied. The associative detachment reaction which occurs when O^- reacts with carbon monoxide has been particularly well studied both experimentally[8] and theoretically,[9] not only in the forward direction but in the reverse direction as well, as has the presumed negative ion intermediate CO_2^-. Reaction of CO with $^{18}O^-$ reveals that a hitherto undetected reaction channel, oxygen exchange (eq 1a), competes with detachment (eq 1b). The efficiencies for reaction of $^{18}O^-$ and $^{16}O^-$ with $C^{16}O$

$$^{18}O^- + C^{16}O \rightarrow {}^{16}O^- + C^{18}O \tag{1a}$$

$$\rightarrow {}^{18}OC^{16}O + e \tag{1b}$$

are determined in separate experiments (Table I) with the difference representing the efficiency of isotope exchange. These data indicate that 11% of the collisions result in exchange of the oxygen atoms, presumably through formation of a CO_2^- intermediate. If the oxygen atoms have equal probability for leaving this molecular negative ion, then only half of these intermediates can be detected by the exchange reaction. Thus as many as 90% of the collisions of O^- with CO may be "reactive", rather than 67% as previously believed. Therefore, interpretations of this reaction as involving one nonreactive repulsive surface and two reactive attractive surfaces[8c,d] are clearly inadequate.

Similarly, reaction of $^{18}O^-$ with SO_2 forms $^{16}O^-$ in parallel with associative detachment even though detachment is efficient.[10] The associative detachment reaction of O^- with nitric oxide[11] and the atom-transfer reaction of O^- with nitrous oxide[12] to form NO^- occur at considerably slower rates. The reaction efficiencies are greatly enhanced when $^{18}O^-$ is the reactant and isotope exchange becomes observable. The exchange reactions of NO and N_2O have previously been studied at elevated kinetic energies.[13]

The reactions of O^- with H_2O, CO_2, and O_2 proceed only by moderately slow three-body association.[14] In contrast, when $^{18}O^-$

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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.

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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.

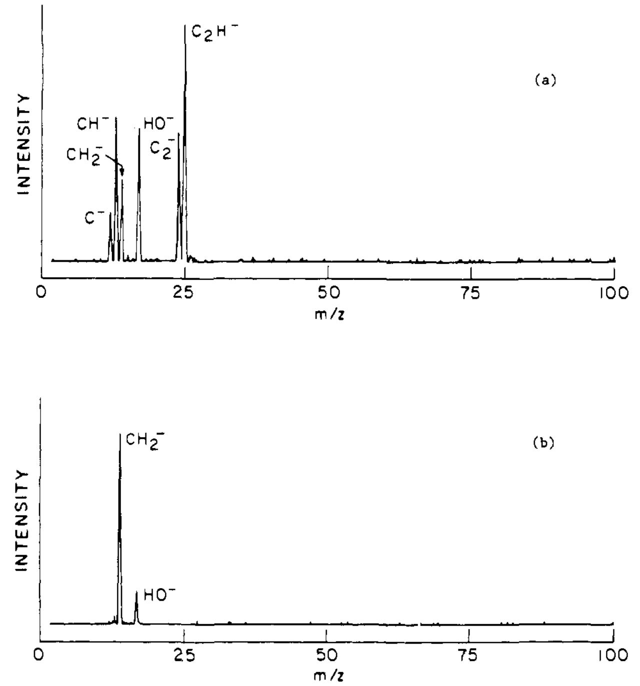

Figure 1. (a) Total ion spectrum resulting from electron impact on methane. (b) Spectrum of $CH_2^{\bullet-}$ after mass selection and injection.

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.

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.

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

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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(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.