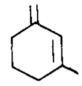
the steric bulk in **1** might give rise to the formation of the [4 + 3] cycloadduct **7** at the expense of the [3 + 2] cycloadducts without affecting the overall addition rate.

The rate constant for the 1,3-dipolar cycloaddition of **2** with 1-methyl-3-methylene-1-cyclohexene (**14**), a model compound



14

which reacts at the exocyclic double bond exclusively, is of the same order of magnitude ($k_2 = 4.4 \times 10^{-5}$ L mol^{-1} s^{-1}, toluene, 80 °C, determined by HPLC) as the corresponding value reported for the reaction of **2** with ethyl crotonate ($k_2 = 14 \times 10^{-5}$).[14] A slightly smaller value ($k_2 = 1.1 \times 10^{-5}$) is derived for the reaction of **1** with **2** from Figure 1. As a consequence of the discussion related to Figure 2, the close similarity of the reactivities of **1** and **14** implies that in reactions of **2** with normal 1,3-dienes, generally a stepwise mechanism should be accessible, the activation energy of which is at most 2–3 kcal/mol greater than that of the concerted process.

The intermediate diradical **4** profits from allylic resonance, which would not be the case for intermediates formed from nitrones and alkylethylenes. Therefore, the mechanistic considerations on those cycloadditions are not affected by this work.

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Supplementary Material Available: Analytical data (mp/bp, ^{1}H NMR, ^{13}C NMR, IR, mass spectrum) for **3a**, **3b**, and **7–13** (4 pages). Ordering information is given on any current masthead page.

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Gaseous Negative Ions from Neutral Molecules and Positive Ions: New Information for Neutralization–Reionization Mass Spectrometry

Rong Feng, Chrysostomos Wesdemiotis, and
Fred W. McLafferty*

Chemistry Department, Baker Laboratory
Cornell University, Ithaca, New York 14853-1301

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Collisional activation of fast gaseous ions can lead to dissociation and/or charge permutation processes.[1,2] Combinations of these are used in neutralization–reionization mass spectrometry (NRMS)[3] to prepare fast gaseous neutrals from mass-selected multikilovolt ions. A further collision can dissociate the neutrals into structurally indicative fragments which are collisionally reionized into positive ions for mass analysis.[4] In this way NRMS has been used recently to study unusual structures such as H$_2$C-FH,[4a] H$_2$Cl,[4b] and H$_3$C(HO)C:.[4c] We consider here the alternative reionization into negative ions, which previously has been applied only to D$_3$•, D•,[5] H$_3$•,[6a] H$_2$,[6b] H•,[6c] and C$_2$H$_2$[7] molecules. Collisional charge reversal of positive ion mixtures (not subjected to mass analysis) has been used to prepare negative ions such as Cl$^-$, HO$^-$, and S$^-$.[8] Gaseous anions have also been generated directly by electron impact, flowing afterglow, and chemical ionization techniques.[9] We report here that collisional electron transfer to mass-selected cations or neutrals provides an alternative route to negative ions; the resulting mass spectra contain novel information on the structures and chemistry of the precursor cations and neutrals, as well as the product anions.

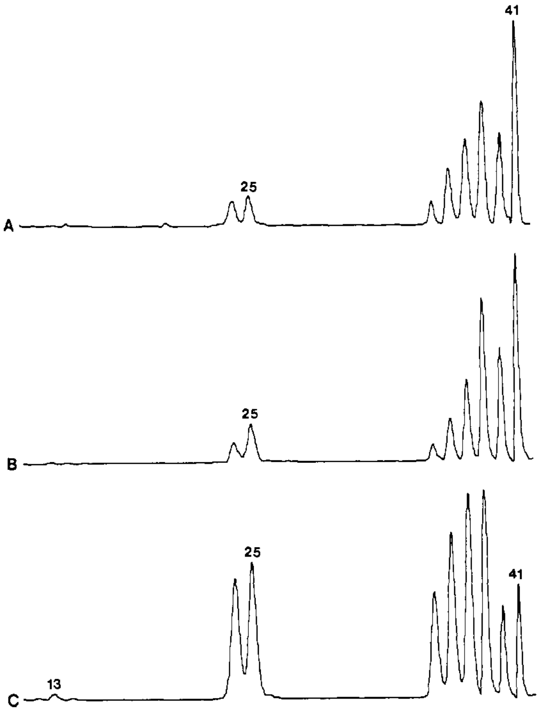

Figure 1. (A) Hg (70% *T*)/Xe (70% *T*), (B) Hg (15% *T*), and (C) Xe (15% *T*) NR$^-$ spectra of CH$_2$=CHCH$_2^+$ (from propene). Absolute abundance of CH$_2$=CHCH$_2^-$ (*m/z* 41) in percent of the unattenuated CH$_2$=CHCH$_2^+$ main-beam abundance: (A) 0.00012; (B) 0.00095; (C) 0.00038. Hg (70% *T*) neutralization of CH$_2$=CHCH$_2^+$ produces 1.8% CH$_2$=CHCH$_2$•.

Generation of Negative Ions. The appropriate multikilovolt precursor ions are generated and mass-selected in the first mass spectrometer (MS-I) of the tandem mass spectrometer described previously[2,3c] to yield neutral molecules by charge-exchange neutralization or dissociation.[3] These fast neutrals are reionized by collision to produce anions which, together with their anionic dissociation products, are measured by scanning MS-II. The spectrum obtained by Hg neutralization of allyl cations in the first collision region followed by deflection of the residual ions and subsequent Xe reionization in the second collision region ("Hg/Xe NR$^-$ spectrum") is shown in Figure 1A. Alternatively, a single target can effect the two-electron transfer;[5-8] Figure 1B shows the resulting charge-reversal spectrum with Hg ("Hg NR$^-$ spectrum") in the first collision region at 15% transmittance (*T*), at which the C$_3$H$_5^-$ yield is maximized. This is ~2.5 times greater than the yield from xenon (Figure 1C) under identical conditions. The 15% *T* value for maximum efficiency indicates[3c,10] that for

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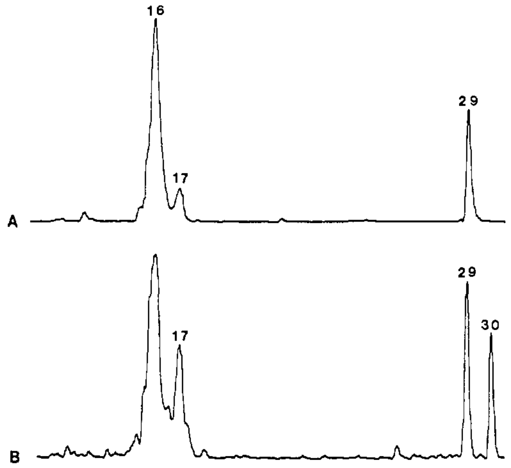

Figure 2. Hg (90% *T*)/Xe (30% *T*) NR$^-$ spectra of (A) $H_2CO^{\bullet +}$ and (B) $HCOH^{\bullet +}$ (from methanol). [29^-] in percent of the neutral-beam abundance: (A) 0.011; (B) 0.062. Hg neutralization (90% *T*) of $H_2CO^{\bullet +}$ and $HCOH^{\bullet +}$ yields 2.7% and 1.2% neutral molecules, respectively.

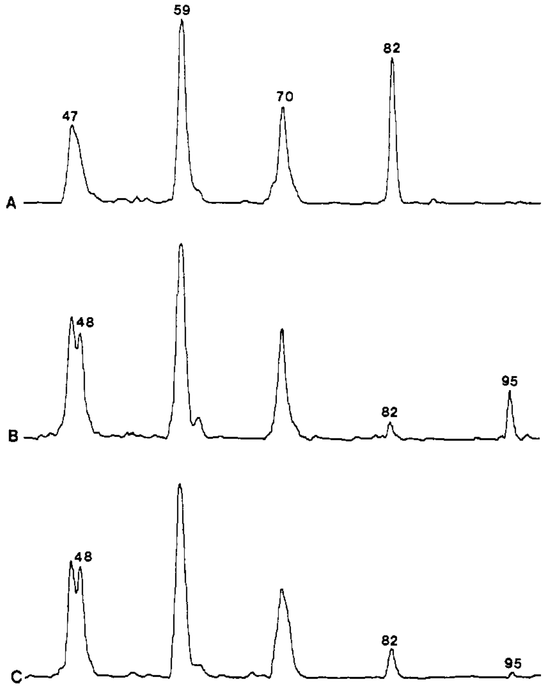

Figure 3. Partial Xe (10% *T*) NR$^-$ spectra of $C_2H_2{}^{35}Cl_2{}^{\bullet +}$ from (A) $H_2C{=}CCl_2$, (B) (*E*)-ClHC=CHCl, and (C) (*Z*)-ClHC=CHCl. [C_2Cl^-] (*m/z* 59) in percent of unattenuated [$C_2H_2Cl_2{}^{\bullet +}$]: (A) 0.00017; (B) 0.00012; (C) 0.00019. In all three spectra Cl^- is the base peak, with [Cl^-]:[C_2Cl^-] $\simeq$ 5.

a majority of anions the two electrons are transferred in separate collisions. The increased fragmentation in Figure 1C vs Figure 1B suggests a lower excitation in $C_3H_5{}^0 \rightarrow C_3H_5{}^-$ by Hg vs Xe, as Hg and Xe cause comparable excitation in neutralization.[3c] Thus, the mercury target appears to provide maximum sensitivity for producing nondissociating precursor anions.

The following polyatomic negative ions formed by these procedures can survive for the $>10^{-6}$ s needed to reach the collector (reported electron affinity of counterneutral in eV): $O_2{}^{\bullet -}$ (0.4),[11a] OH^- (1.8),[11a] HCO^- (0.3),[11b] $HCOH^{\bullet -}$, CH_3O^- (2.6),[11a] C_2HO^-, $CH_3{}^-$ (0.1),[11c] $CH_2{}^{\bullet -}$ (0.4),[11a] $C_3H_5{}^-$ (0.6),[11a,d] $C_3H_3{}^-$ (0.9),[11a] $C_3H_2{}^{\bullet -}$, C_3H^-, $C_3{}^{\bullet -}$ (2.5),[11a] $C_4H_3{}^-$, C_4H^-, $C_4{}^{\bullet -}$, $C_5H_5{}^-$ (1.8),[11a] $C_6H_7{}^-$ (1.7),[11a] and $C_7H_7{}^-$ (0.6)[11a].[12] In contrast, the following anions from double electron transfer give no appreciable parent signal under these conditions: $CO^{\bullet -}$ (−1.8),[11a] $H_2CO^{\bullet -}$ (−0.7),[11a] $HOCH_2{}^-$, CH_3CO^- (0.4),[11e] $CH_3COOCH_3{}^{\bullet -}$, $C_2H_2{}^{\bullet -}$ (−1.8),[11a] $C_2H_4{}^{\bullet -}$ (−1.8),[11a] $C_2H_5{}^-$ (−0.4),[11c,d] $C_3H_4{}^{\bullet -}$, $C_3H_6{}^{\bullet -}$ (−2.0),[11f] $C_4H_8{}^{\bullet -}$ (−2.2),[11f] $C_6H_5{}^-$ (1.1),[11c] $C_6H_6{}^{\bullet -}$ (−1.1),[11a] and $C_2H_2Cl_2{}^{\bullet -}$ (−0.9)[11g].[12]

Characterization of Isomeric Neutrals. Just as collisional reionization of hydroxymethyl radicals gives abundant $CH_2{=}O^+H$ cations,[13] that of the isomeric $CH_3O^\bullet$ yields intense parent anions, consistent with the expected stability of CH_3O^-.[11a] In contrast, $^\bullet CH_2OH$ produces no detectable $^-CH_2OH$, but predominantly $O^{\bullet -}$ and OH^- (from $CH_3O^\bullet$ [OH^-] is only 2% of [CH_3O^-]). Thus, cationization/anionization gives highly selective detection of either radical in the presence of its isomer.

Hydroxycarbene, HO(H)C:, has been suggested as a possible intermediate in various reactions;[14-17] its direct detection and characterization via spectroscopic means has not been reported. Gaseous HO(H)C:, prepared by neutralization from the stable $HCOH^{\bullet +}$ cation,[18,19] when reionized into positive ions yields a NR$^+$ spectrum similar to that from H_2CO.[12] However, the alternative reionization into negative ions (Figure 2B) gives rise to intense molecular anions at *m/z* 30 that must be $HCOH^{\bullet -}$, as, according to Figure 2A, H_2CO reionization does not generate any detectable $H_2CO^{\bullet -}$ signal. Thus, a substantial proportion of HCOH molecules must have survived $\sim 10^{-6}$ s, confirming theoretical predictions that hydroxycarbene is a stable equilibrium structure.[20]

Characterization of Positive Ions and Molecules. The charge-reversal NR$^-$ spectra of $H_2CO^{\bullet +}$ and $HCOH^{\bullet +}$ ions are structurally characteristic, but so are their spectra[18] from collisionally activated dissociation (CAD).[2] In contrast, the electron ionization, cation CAD, and NR$^+$ spectra of $H_2C{=}CCl_2$ and (*E*)- and (*Z*)-ClHC=CHCl poorly distinguish these isomers. However, the charge-reversal NR$^-$ spectra of their cations (Figure 3) allow an unequivocal differentiation: C=C cleavage (presumably from electron addition to an antibonding orbital) yields predominantly $CCl_2{}^-$ (*m/z* 82) from the 1,1-isomer but $CHCl^-$ (*m/z* 48) from the 1,2-isomers, and $H^\bullet$ loss (*m/z* 95) is $\sim$8 times more intense from (*E*)- than (*Z*)-ClHC=CHCl.

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