surface. A comparison of the charge reversal mass spectra of the adducts with those of the corresponding β-hydroxy carbonyl model compounds indicates that a small fraction of the positive species so produced is of tetrahedral geometry, and that the major fraction is a proton-bound enolate species. Little evidence for an ion–dipole species in the isotopically labeled acetone systems can be obtained from the charge reversal mass spectra. One explanation is that the cross section for charge stripping of the ion–dipole species is appreciably lower than that of either the tetrahedral or the proton-bound species, and that the favored process for ion–dipole complexes is to revert to starting materials. In other words, these loosely bound adducts never survive a charge-stripping collision. In general, loosely associated structures such as ion–dipole complexes are likely to be transparent to charge stripping.

In conclusion, species of tetrahedral geometry form to a small extent in base-initiated gas-phase aldol condensations of enolate negative ions with simple carbonyl compounds. The adducts of the aldol reactions and the corresponding deprotonated model compounds undergo fragmentation in a characteristic manner upon collisional activation. Nearly identical kinetic energy releases accompany the losses of $H^•$, H_2, H_2O, and CH_4 from both adducts and appropriate aldol model compounds. The charge reversal spectra, like the kinetic energy release data, of both adducts and β-hydroxy carbonyl model compounds are consistent with formation of a small amount of a species of tetrahedral geometry. Most of the adducts, however, are loosely bound ion–dipole and proton-bound complexes.

We are at present continuing our investigations of the gas-phase condensation reactions of carbanions with simple carbonyl systems.

Experimental Section

Mass Spectrometry. CA mass spectra were measured with a Kratos MS-50 triple analyzer mass spectrometer of EBE design, which was described previously.[30] Ion–molecule reactions were performed in a commercially available (Kratos Scientific Instrumentation Mark IV) chemical ionization source: ion source temperature, 100 °C, accelerating voltage, 8 kV. Liquids were introduced through a commercially available (Kratos Scientific Instruments) reagent gas inlet system or through a custom fabricated all-glass heated inlet system held at 100 °C. Carbanions were generated by H^+ (D^+) abstraction by MeO^-. MeO^- was generated from methyl nitrite by dissociative secondary electron (at 70 eV) resonance capture.[20] The indicated source pressure of methyl nitrite was typically 5×10^{-6} Torr, and the pressure of each substrate was typically 2×10^{-5} Torr, corresponding to an approximate total pressure of 0.1 Torr. The pressure of helium in the second collision cell was sufficient to produce a decrease in the main beam signal of 50%.

Compounds. All unlabeled compounds are known and were prepared by a standard procedure.[4] Acetaldehyde-d_4 (d_4 = 99.9%) and acetone-d_6 (d_6 = 99.9%) were obtained from Aldrich Chemical Co., Inc., of Milwaukee, WI. 4-Hydroxy-4-(methyl-d_3)-2-pentanone-*5,5,5*-d_3, 4-hydroxy-4-methyl-2-pentanone-*1,1,1,3,3*-d_5 were prepared from acetone-d_6 and acetone by a standard procedure.[4] [^{18}O]Acetone (^{18}O, 20%) was prepared by the method of Bennet, Sinnott, and Wijisundera.[31]

Acknowledgment. This research was supported by the Midwest Center for Mass Spectrometry, an NSF Regional Instrumentation Facility (Grant No. CHE-8620177).

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Characterization of Four C_4H_4 Molecules and Cations by Neutralization–Reionization Mass Spectrometry

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Abstract: The isomeric cations vinylacetylene ($\mathbf{a}^{•+}$), butatriene ($\mathbf{b}^{•+}$), methylenecyclopropene ($\mathbf{c}^{•+}$), and cyclobutadiene ($\mathbf{d}^{•+}$) can be distinguished by three methods: neutralization followed by collisionally activated dissociation (CAD) of the resulting ground-state neutrals ($^+NCR^+$ spectra); neutralization with an agent of ionization energy (6 eV) selected to produce excited C_4H_4 molecules that undergo characteristic dissociations ($^+NR^+$ spectra); and charge reversal to the unstable $C_4H_4^{•-}$ anions ($^+NR^-$ spectra). Concomitant isomerization is minimized, in sharp contrast to that accompanying CAD of the cations themselves or their neutralization by sodium. Separate CAD of the neutral C_4H_4 isomers provides information on their unimolecular isomerization and dissociation reactions; conditions dissociating 28% of **a** dissociate 66% of **d**, producing from **a** and **d** respectively 28% and 8% of $C_4H_3^•$, 38% and 19% of C_4H_2, and 14% and 59% of C_2H_2. Energy profiles are derived for both the neutral and the ionic isomers **a** and **d**. The $^+NCR^+$ and $^+NR^-$ spectra both show that 70-eV ionization of benzene yields $C_4H_4^{•+}$ ions that are 30% $\mathbf{a}^{•+}$, 0% $\mathbf{b}^{•+}$, 70% $\mathbf{c}^{•+}$, and 0% $\mathbf{d}^{•+}$.

Table I. Thermochemical Data of C_4H_4 and $C_4H_4^{•+}$ Isomers[a]

	IE, eV	$\Delta H_f°$(neutral), kJ mol^{-1}	$\Delta H_f°$(ion), kJ mol^{-1}
vinylacetylene (**a**)	9.58	305	1229
butatriene (**b**)	9.15	349	1232
methylenecyclopropene (**c**)	8.28[b,c]	410[d]	1209[e]
cyclobutadiene (**d**)	8.02[b,f]	464[g]	1238[d]

[a] Reference 8. [b] Reference 5c. [c] Also 8.15 eV (adiabatic): ref 11f. [d] $\Delta H_f°$(neutral) = $\Delta H_f°$(ion) − IE. [e] Also 1178 kJ mol^{-1}: ref 11f. [f] Also 8.10 eV: Kreile, J.; Münzel, N.; Schweig, A.; Specht, H. *Chem. Phys. Lett.* **1986**, *24*, 140–146. [g] Based on $\Delta H_f°$(**c**) and the theoretically calculated energy difference between **c** and **d** from ref 10c.

Isomeric characterization by dissociation of gaseous organic ions, especially hydrocarbon cations, can be seriously compromised because their isomerization often requires less energy than dissociation. Thus, mass spectra produced by electron ionization,[1] collisionally activated dissociation (CAD),[2] metastable ion (MI) dissociation,[3] and surface-induced dissociation,[4] are closely similar for isomeric ions such as $C_4H_4^{•+}$,[5] $C_6H_6^{•+}$,[1] $C_4H_8^{•+}$,[6] and $C_4H_9^+$.[6a] For the corresponding neutrals, isomerization barriers are often

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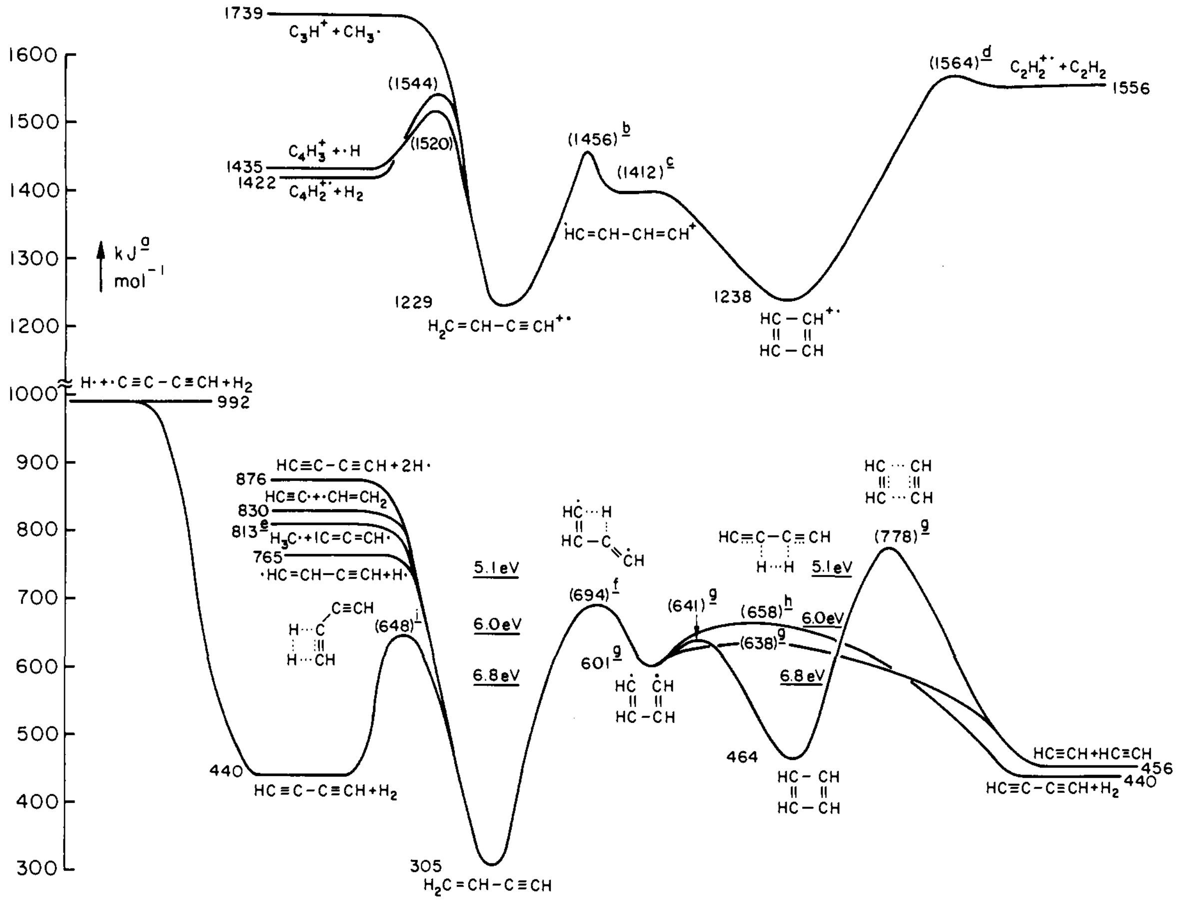
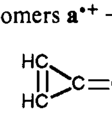


Figure 1. Isomerization and dissociation pathways of vinylacetylene and cyclobutadiene molecules and their radical ions. [a] Unless noted otherwise all thermochemical data are from Table I in ref 8. Also: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. No. 1. McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532. [b] From Table VII in: Bouchoux, A. *Mass Spectrom. Rev.* **1988**, *7*, 203–255. [c] $\Delta H_f°(^{\bullet}HC{=}CH{-}CH{=}CH^+) = \Delta H_f°(H_2C{=}CH{-}CH{=}CH^+) + D(C{-}H) - \Delta H_f°(H^{\bullet}) = 1412$ kJ mol^{-1} if $D(H{-}HC{=}CH{-}CH{=}CH^+) \approx D(H{-}CH{=}CH_2) = 460$ kJ mol^{-1} (ref *c* of footnote *a*). $\Delta H_f°(H_2C{=}CH{-}CH{=}CH^+)$ was estimated from $\Delta H_f°(H_2C{=}CH^+) = 1112$ kJ mol^{-1} assuming that the reactions $H_2C{=}CH_2 \rightarrow H_2{=}CH^+ + {}^{\bullet}H$ and $H_2C{=}CH{-}CH{=}CH_2 \rightarrow H_2C{=}CH{-}CH{=}CH^+ + {}^{\bullet}H$ require similar energies; then, $\Delta H_f°(H_2C{=}CH{-}CH{=}CH^+) = \Delta H_f°(H_2C{=}CH^+) + \Delta H_f°(H_2C{=}CH{-}CH{=}CH_2) - \Delta H_f°(H_2C{=}CH_2) = 1170$ kJ mol^{-1}: Bowen, R. D.; Williams, D. H.; Hvistendahl, G. *J. Am. Chem. Soc.* **1977**, *99*, 7509–7515. [d] This channel is of minor importance in the CAD spectra of $C_4H_4^{\bullet+}$ (<0.6% of H_2 loss). Its transition state is set, therefore, ~20 kJ mol^{-1} higher than that for H_2 loss. [e] $\Delta H_f°(C_3H^{\bullet}) = 667$ kJ mol^{-1} from: Kühnel, W.; Gey, E.; Spangenberg, H.-J. *Z. Phys. Chem.* **1982**, *263*, 641–645. [f] See text: activation energy for the similar 1,3-H rearrangement for $H_2C{=}CH{-}CH_3 \rightarrow H_3C{-}CH{=}CH_2$: Rodwell, W. R.; Bouma, W. J.; Radom, L. *Int. J. Quantum Chem.* **1980**, *18*, 107–116. [g] From $\Delta H_f°(c\text{-}C_4H_4)$ and activation energies or energy differences calculated in ref 10a. [h] The transition state of this second most favored dissociation channel (H_2 loss) was estimated to lie approximately 20 kJ mol^{-1} above that for the major fragmentation path to 2HC≡CH. [i] The two H atoms to be eliminated lie closer to each other than in $^{\bullet}HC{=}CH{-}CH{=}CH^{\bullet}$. This transition state is, therefore, set ~10 kJ mol^{-1} lower.

higher relative to those for dissociation; this has been exploited using neutralization–reionization (NR) mass spectrometry[7] to characterize the hydrocarbon ions $C_2H_5^+$ [7d] and five $C_4H_8^{\bullet+}$ isomers[6c] by dissociation of the corresponding neutrals. For the C_4H_8 isomers it was found possible to do this with minimum rearrangement by forming excited C_4H_8 through neutralization using a target of low ionization energy. In contrast, we describe here the characterization of four $C_4H_4^{\bullet+}$ isomers **a**$^{\bullet+}$ – **d**$^{\bullet+}$ (Table I)[8]

$H_2C{=}CHC{\equiv}CH$ **a**

$H_2C{=}C{=}C{=}CH_2$ **b**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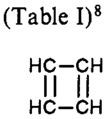
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by CAD of the corresponding ground-state neutrals and by charge reversal to the unstable $C_4H_4^{\bullet-}$ anions.[6c,7i,9] Further, the observed reactions provide additional evidence for the energy surfaces of the C_4H_4 neutrals and of the $C_4H_4^{\bullet+}$ ions (Figure 1).

For the neutral C_4H_4 species, theoretical calculations have predicted the existence of seven isomers,[10] and experimental evidence for the four most stable, **a**–**d**, has been reported.[11] The

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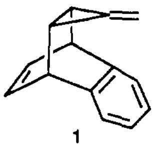
high reactivity of **c** and **d** has limited their chemical characterization to special techniques such as low-temperature matrices[10b,11,12] and fast trapping reactions;[13] further characterization, especially of **a** and **d**, from gas-phase unimolecular reactions is reported here.

Previous $C_4H_4^{\bullet+}$ cation studies are notable for the large number that have reached incomplete and often conflicting conclusions concerning isomeric identity. CAD and MI mass spectra of $C_4H_4^{\bullet+}$ ions from different precursors show[5] that both the product abundances (with one exception)[5b] and the kinetic energy release values for $H^\bullet$ and H_2 loss are, within experimental error, independent of the method of formation of $C_4H_4^{\bullet+}$. Presumably, these similarities arise from rearrangement to a mixture of ionic isomers, before or during dissociation. Bowers[5b] has reported that $C_4H_4^{\bullet+}$ ions formed under differing conditions show CAD m/z 26/27 ratios of 2.4–9.0, with the lowest value from the ionization of **a** and the highest from another isomer, postulated as $\mathbf{c}^{\bullet+}$. This is consistent with $C_4H_4^{\bullet+}$/molecule reaction studies of Ausloos and of Lifshitz,[5a,14] with kinetic energy release data and QET calculations of Baer,[15] and with charge neutralization cross-section measurements of Moran.[16] A third isomer, presumably $\mathbf{b}^{\bullet+}$, is indicated by ion photodissociation experiments.[17] Such studies were also hampered by the unavailability of suitable reference ions, especially $\mathbf{c}^{\bullet+}$ and $\mathbf{d}^{\bullet+}$; our preliminary communication[5c] describes their preparation from **1** and **2**,[13b,c] respectively, with CAD evidence from isotopically labeled $\mathbf{d}^{\bullet+}$ that these isomers do not freely interconvert.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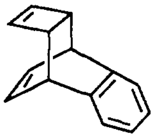
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Experimental Section

The measurements were performed on a tandem double focusing (EB–EB) mass spectrometer described in detail elsewhere.[18] Precursor ions were formed by 70-eV electron ionization (unless noted otherwise), accelerated through 10 kV, mass selected by MS-I, and charge-exchanged with a target gas (e.g., Hg or Na vapor) in a differentially pumped collision cell (Cls-I). Any remaining ions are removed by a deflector electrode (Dfl-I). The resulting fast neutrals undergo dissociating and/or reionizing collisions in a second collision cell (Cls-II, also differentially pumped). For the separate dissociation of neutrals in Cls-II, any newly formed ions are removed by Dfl-II, and the neutral products and remaining precursors are reionized in Cls-III. For charge-reversal experiments, a single target such as benzene was used for neutralization, dissociation, and reionization in the same cell (Cls-II).[9] The reionized products were mass analyzed in the second electrostatic analyzer. Neutral beam intensities for CAD cross-section values were measured using a retractable channeltron at Cls-III. Experimental conditions are described by abbreviations defined earlier:[6c,7i] e.g., a $^+$NR$^+$, Hg(90% T)/He(80% T), spectrum is one obtained by neutralization of cations at Cls-I with Hg at a pressure allowing 90% precursor transmittance, residual ion deflection (slash), and neutral reionization with He at pressure giving 80% transmittance of the original precursor ions at Cls-II; a $^+$NCR$^-$, benzene (25% T), spectrum combines neutralization, CAD, and anionization (and even CAD of the anions) by multiple collisions with benzene. Spectra shown represent 20–50 scans averaged by a computer system to be described separately.

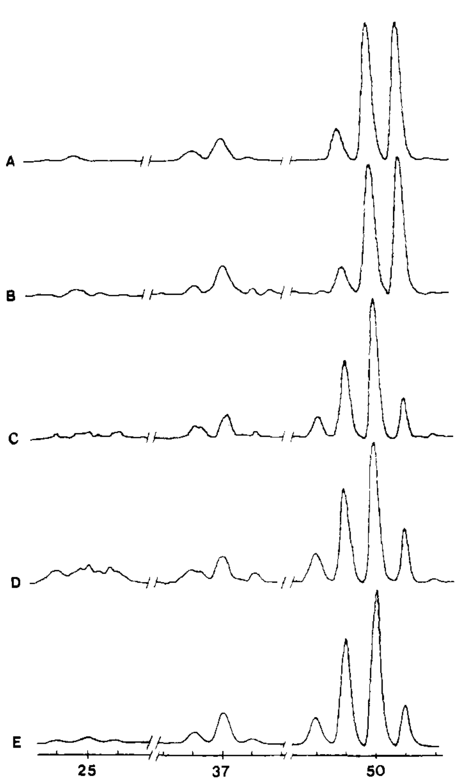

Figure 2. $^+$NR$^+$ spectra of m/z 52 from (A,C) $\mathbf{a}^{\bullet+}$ and (B,D) $\mathbf{d}^{\bullet+}$ using (A,B) Na(80% T)/He(80% T) {$[51^+]/I_0$ = (A) 2.4×10^{-2}, (B) 1.0×10^{-2}} and (C,D) Na(80% T)/He(30% T), and of (E) m/z 51 from **a**, Hg(90% T)/He(30% T).

6,7-Benzo-3-methylenetricyclo[3.2.2.0^{2,4}]nona-6,8-diene (**1**) was synthesized according to the procedure of Paquette, and 7,8-benzotricyclo-[4.2.2.0^{2,5}]deca-3,7,9-triene (**2**) was produced from benzobicyclo-[2.2.2]octatriene.[5c,13c,19] Butatriene was synthesized from 1,4-dibromo-2-butyne[11b] and tetra-*p*-anisylethylene by the method of Buckles.[20] All other reagents were commercially available and were used without further purification.

Results and Discussion

$C_4H_4^{\bullet+}$ formed by electron ionization of vinylacetylene, butatriene, *1*, and *2* were used as sources of the isomers $\mathbf{a}^{\bullet+}$ – $\mathbf{d}^{\bullet+}$, respectively. Three methods[6c,7e,i,9] for their isomeric characterization were tested: (a) neutralization with a low ionization energy target to form excited, unstable C_4H_4 neutrals; (b) formation of low-energy C_4H_4 neutrals followed by CAD to cause their dissociation; and (c) charge inversion to the unstable $C_4H_4^{\bullet-}$ anions. These methods minimize the isomerization of the $C_4H_4^{\bullet+}$ cations, for which the barriers are thought to be low (Figure 1) and require that the isomerization barrier for each C_4H_4 neutral is higher than the lowest energy dissociation. Any isomerization of the precursor $C_4H_4^{+\bullet}$ ions, of the resulting C_4H_4 neutrals, or of the reionized $C_4H_4^{+\bullet}$ ions will, of course, increase the similarity of the resulting NR spectra of the corresponding isomers.

Sodium Neutralization Forming Excited C_4H_4 Neutrals. Differentiation of five $C_4H_8^{\bullet+}$ isomers was achieved[6c] by neutralization with sodium, a target of much lower ionization energy (IE = 5.1 eV) than those of the C_4H_8 molecules. For vinylacetylene (**a**) and cyclobutadiene (**d**) this should lead to molecules of internal energies

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[20] Peak areas reproducible to ±<10%; the $^+$NR$^+$, Hg(90% T)/He(70% T) spectra (not shown) are less structurally characteristic.

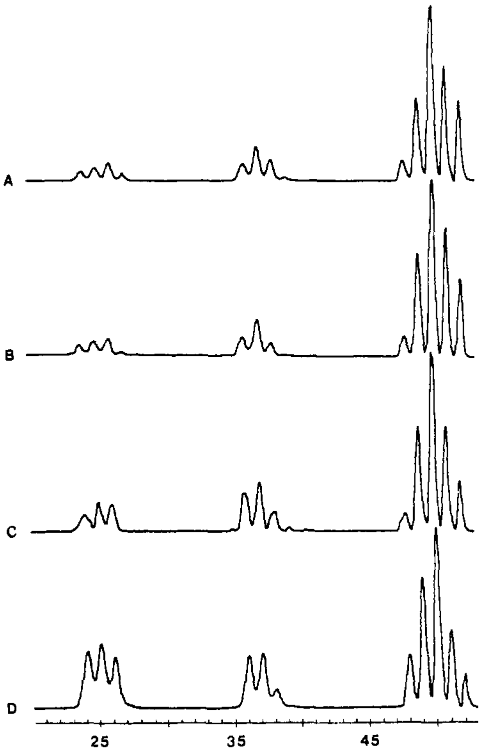


Figure 3. $^{+}$NCR^{+}, Hg(90% T)/He(30% T), spectra of (A) $\mathbf{a}^{\bullet+}$, (B) $\mathbf{b}^{\bullet+}$, (C) $\mathbf{c}^{\bullet+}$, and (D) $\mathbf{d}^{\bullet+}$. $[50^{+}]/I_0$ = (A) 1.0×10^{-4}, (B) 4.6×10^{-5}, (C) 4.8×10^{-5}, and (D) 4.9×10^{-5}.

of ~4.5 and 2.9 eV, respectively (Table I). These energies, at which mainly $C_4H_3^{\bullet}$ and C_4H_2 are formed (Figure 1), are greater than the dissociation thresholds, as negligible $C_4H_4^{\bullet+}$ peaks are found on helium reionization ($^{+}$NR^{+} spectra, Na(80% T)/He(80% T), Figure 2A,B). Unfortunately, these also appear to be above the rearrangement thresholds, as the spectra are nearly the same within experimental error. Reionization at a higher He pressure producing multiple collisions [Na(80% T)/He(30% T), Figure 2C,D] does not improve isomeric differentiation, appearing only to increase $C_4H_3^{\bullet}$ dissociation; these spectra are similar to the Hg(90% T)/He(30% T) spectrum of the m/z 51^{+} ion from **a** (Figure 2E). Neutralization with an agent of IE = 6 eV does give distinguishable $^{+}$NR^{+} spectra for **a** and **d** (vide infra).

CAD of C_4H_4 Neutrals. In a further attempt to minimize isomerization, separate dissociation of the C_4H_4 neutrals was studied. Electron transfer to the $C_4H_4^{\bullet+}$ ions with Hg yields neutralization efficiency values for the $\mathbf{a}^{\bullet+}$ – $\mathbf{d}^{\bullet+}$ ions of 2.0%, 0.9%, 0.6%, and 0.6%, respectively, consistent with the difference in ionization energy values of these isomers (Table I) versus that of Hg (10.4 eV)[16] and with the formation of low-energy C_4H_4 neutrals. Collisional activation of these neutrals at a sufficiently high pressure to induce both neutral dissociation and reionization results in the $^{+}$NCR^{+}, Hg(90% T)/He(30% T), spectra of Figure 3. Contrary to the close similarity of the CAD spectra, each of the four isomers $\mathbf{a}^{\bullet+}$ – $\mathbf{d}^{\bullet+}$ gives distinctly characteristic $^{+}$NCR^{+} spectra.[21] At least for $\mathbf{a}^{\bullet+}$ and $\mathbf{b}^{\bullet+}$, the spectra are relatively independent of ion internal energy, as ionization with 18-eV instead of 70-eV electrons did not change their $^{+}$NCR^{+} spectra beyond experimental error;[21] also there was little change in the $^{+}$NR^{+}, N(90% T)/He(70% T), spectra (not shown) of $\mathbf{a}^{\bullet+}$ and $\mathbf{d}^{\bullet+}$ when these ions were neutralized (N) with benzene (IE = 9.2 eV) instead of Hg.

The most apparent feature of the $^{+}$NCR^{+} spectra of Figure 3 is the strong dependency of the m/z 26/27 ratio on isomeric structure (for CAD spectra this ratio is dependent on the proportion of $\mathbf{a}^{\bullet+}$),[5b] with values of 2.4, 5.6, >25, and >25 for $\mathbf{a}^{\bullet+}$ – $\mathbf{d}^{\bullet+}$, respectively. Neutralized vinylacetylene ions should fragment without rearrangement to C_2H and C_2H_3 (ionized to m/z 25 and 27), while the cyclic isomers **c** and **d** should yield two C_2H_2 pieces (m/z 26). Although symmetrical cleavage of butatriene (**b**) would also yield C_2H_2, this requires double-bond cleavage. The relative abundance of the reionized molecule, $[C_4H_4^{\bullet+}]$, is a further useful characteristic of isomeric identity, with the values ordered by $\mathbf{a}^{\bullet+} > \mathbf{b}^{\bullet+} > \mathbf{c}^{\bullet+} > \mathbf{d}^{\bullet+}$. This order is also observed for $[C_4H_2^{\bullet+}]/[C_4H^{+}]$ and for $[C_3H_2^{\bullet+}]/[C_3^{\bullet+}]$.

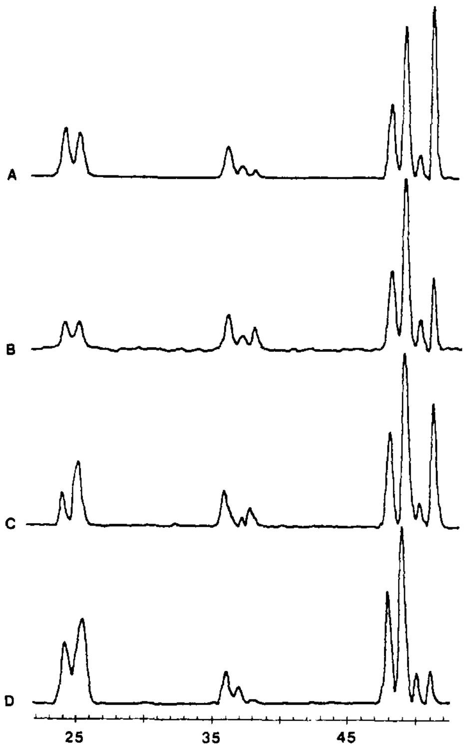
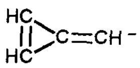


Figure 4. $^{+}$NR^{-}, benzene (25% T), spectra of (A) $\mathbf{a}^{\bullet+}$, (B) $\mathbf{b}^{\bullet+}$, (C) $\mathbf{c}^{\bullet+}$, (D) $\mathbf{d}^{\bullet+}$. $[51^{-}]/I_0$ = (A) 3.5×10^{-5}; $[49^{-}]/I_0$ = (B) 1.6×10^{-5}, (C) 1.5×10^{-5}, and (D) 1.7×10^{-5}.

Charge Reversal and Negative Ion Dissociation. The $C_4H_4^{\bullet+}$ isomers $\mathbf{a}^{\bullet+}$ – $\mathbf{d}^{\bullet+}$ can also be uniquely characterized by conversion to the corresponding negative ions[9] using multiple collisions with benzene, as shown by the $^{+}$NR^{-}, benzene (25% T), spectra of Figure 4. Cation fragmentation is not important, as closely similar spectra were obtained by neutralization with mercury (90% T), deflection of all ions (including those formed by fragmentation), and subsequent (10^{-6} s delay) anionization with benzene (50% T). No molecular ion (m/z 52) peaks are observed, consistent with the expected[9] instability of $C_4H_4^{\bullet-}$ anions. The $C_4H_3^{-}$ abundances are mainly consistent with their expected stabilities, with **a** – **d** showing $[C_4H_3^{-}]/[C_4H^{-}]$ values of 1.15, 0.42, 0.72, and 0.16, respectively. Isomer $\mathbf{a}^{-}$ should produce the resonance stabilized $\mathbf{e}^{-}$ ion; $\mathbf{b}^{-}$ should be less stable, and the two extra

$H_2C{=}CHC{\equiv}C^{-}$

$\mathbf{e}^{-}$



$\mathbf{f}^{-}$

$-CH_2-C{\equiv}C^{-}$

$\mathbf{g}^{-}$

electrons remaining after H loss from $\mathbf{d}^{-}$ should be much more difficult to delocalize with the 4π electrons of the cyclobutadiene ring. The surprisingly high abundance of $\mathbf{f}^{-}$ could indicate electron delocalization into the cyclopropene ring. Similarly, the higher abundance of m/z 38 ($C_3H_2^{\bullet-}$) from the isomers $\mathbf{b}^{-}$ and $\mathbf{c}^{-}$ containing the moiety $CH_2{=}C{-}C$ may be due to the higher stability of the isomer $\mathbf{g}^{-}$. The $[C_2^{\bullet-}]/[C_2H^{-}]$ ratio is also a useful characteristic of isomeric identity.

Characterization of $C_4H_4^{\bullet+}$ Isomeric Mixtures. Application of these complementary techniques to ion chemistry problems will be reported separately. As an example of preliminary data, the 70-eV ionization of benzene produces $C_4H_4^{\bullet+}$ ions that are 27% $\mathbf{a}^{\bullet+}$ and 73% $\mathbf{c}^{\bullet+}$ according to the $^{+}$NCR^{+} spectral data, while the $^{+}$NR^{-} spectra show values of 33% and 67%; in contrast to the

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[21] Danis, P. O.; Feng, R.; McLafferty, F. W. *Anal. Chem.* **1986**, *58*, 348–354.

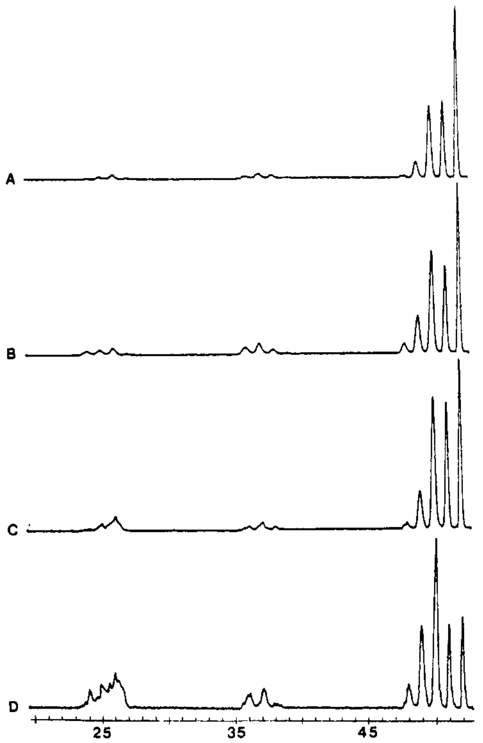

Figure 5. Spectra, without and with neutral dissociation, of (A,B) $\mathbf{a}^{\bullet+}$ and (C,D) $\mathbf{d}^{\bullet+}$: (A,C) $^+NR^+$, Hg(90% T)/O_2(70% T, Cls III); (B,D) $^+NCR^+$, Hg(90% T)/He(30% T)/O_2(70% T). $[50^+]/I_0$ = (A) 1.3×10^{-3}, (B) 3.0×10^{-4}, (C) 8.5×10^{-5}, and (D) 2.1×10^{-5}.

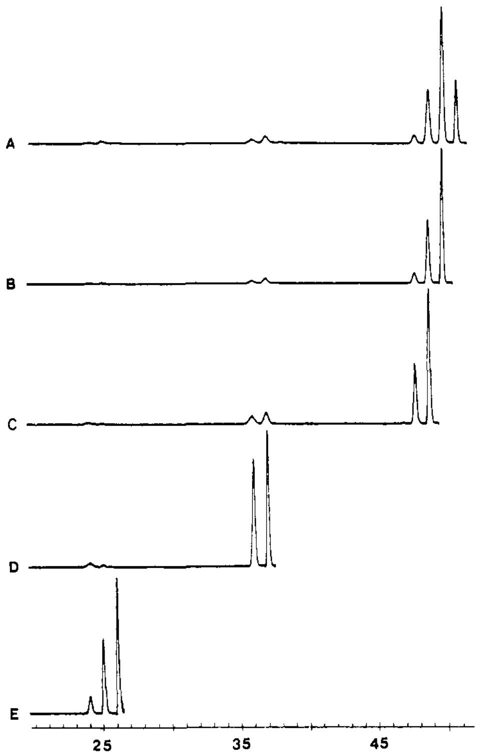

Figure 6. Reference $^+\overline{NR}^+$, Hg(90% T)/O_2(70% T, Cls III), spectra of (A) $C_4H_3^+$, $[51^+]/I_0 = 1.4 \times 10^{-4}$; (B) $C_4H_2^{\bullet+}$, $[50^+]/I_0 = 1.0 \times 10^{-3}$; (C) C_4H^+, $[49^+]/I_0 = 9.0 \times 10^{-4}$; (D) C_3H^+, $[37^+]/I_0 = 2.9 \times 10^{-4}$; (E) $C_2H_2^{\bullet+}$, $[26^+]/I_0 = 3.3 \times 10^{-4}$.

photodissociation results,[17b] no **b** (as well as **d**) is indicated by either spectrum.

Isomerization and Dissociation of $C_4H_4^{\bullet+}$ Cations. These experiments indicate (Figure 1) relatively high isomerization barriers for the $C_4H_4^{\bullet+}$ species, despite the nearly complete isomerization produced by CAD[5] and $^+NR^+$, Na/He (Figure 2). Consistent with the incomplete H/D scrambling observed in labeled $\mathbf{d}^{\bullet+}$,[5c] the $C_4H_4^{\bullet+}$ isomerization barriers must be nearly as high as those for dissociation, as $\mathbf{a}^{\bullet+}$ and $\mathbf{b}^{\bullet+}$ formed by 70-eV electron ionization yield $^+NCR^+$ spectra that are the same, within experimental error, as those from 18-eV ionization (Figure 1). Further, the large differences in the $^+NCR^+$ and the $^+NR^-$ spectra of Figures 3 and 4 show that the precursor $C_4H_4^{\bullet+}$ ions have maintained their isomeric identity for microseconds. Based on the $[m/z\ 27]$ and NR efficiency values of Figure 3, the cyclic precursor ions $\mathbf{c}^{\bullet+}$ and $\mathbf{d}^{\bullet+}$ contain <8% and <15% of $\mathbf{a}^{\bullet+}$, respectively. The CAD spectrum common to all four isomers indicates a lower activation energy barrier for $H^\bullet$ loss than for H_2 loss, despite the enthalpy advantage of the latter. The differences in the CAD m/z 26/27 ratio for **a** and **c**[5b] must result from the kinetic favorability of these dissociations at energies several hundred kJ mol^{-1} above those required for isomerization.

Isomerization and Dissociation of C_4H_4 Neutrals. A more detailed energy profile was also derived (Figure 1, bottom) for **a** and **d**, the C_4H_4 molecules of the lowest and highest values of heat of formation. Neutralization of $\mathbf{a}^{\bullet+}$ and $\mathbf{d}^{\bullet+}$ ions with sodium should produce **a** and **d** neutrals whose energies ($\Delta H_f°$ + internal energy) are[7d,e,h,16] approximately 739 and 744 kJ mol^{-1}, respectively (vide supra). This places an approximate upper limit on both the dissociation and isomerization energies of **a** and **d** (Figure 1), as the $^+NR^+$, Na/He spectra (Figure 2) are devoid of $C_4H_4^{\bullet+}$ and are closely similar. However, the spectra in Figures 3 and 4 clearly show that isomerization requires substantially more energy than dissociation.

To study the individual dissociation pathways of C_4H_4 neutrals with minimal interference from ionic dissociation, fast neutral beams of low energy **a** and **d** were (Figure 5) prepared by Hg (IE = 10.4 eV) neutralization, without and with helium collisional activation of the neutrals in Cls-II, deflection of any newly formed ions, and reionization by O_2 to minimize subsequent ion dissociation.[22] Thus, the differences in the spectra of Figure 5A,B and of Figure 5C,D should represent the CAD caused by the added helium for **a** and **d**, respectively. In other experiments (not shown), separate CAD of **a** and **d** neutrals was carried out similarly with He at 70% T and 30% T, but with He reionization. The yields of major products from these CAD experiments were estimated using reionization efficiencies of reference neutrals measured under the same conditions; 10 keV $C_4H_3^\bullet$, C_4H_2, $C_4H^\bullet$, $C_3H^\bullet$, and 5 keV C_2H_2, prepared from the corresponding cations, yield (upon O_2, 70% T, reionization) precursor ions with abundances relative to the neutral beam intensity of 0.24%, 0.83%, 0.64%, 0.24%, and 0.27%, respectively. Based on these efficiencies and reference $^+NR^+$ spectra (Figure 6), CAD of C_4H_4 neutrals at 30% T dissociates 28% of **a** but 66% of **d**, consistent with their different stabilities (Figure 1). This yields (±5%) from **a** 28% $C_4H_3^\bullet$, 38% C_4H_2, 3% $C_4H^\bullet$, 16% $C_3H^\bullet$, and 14% C_2H_2, and from **d** 8% $C_4H_3^\bullet$, 19% C_4H_2, 4% $C_4H^\bullet$, 10% $C_3H^\bullet$, and 59% C_2H_2. The major products from CAD of both **a** and **d** are stable closed-shell molecules; linear **a** forms mainly C_4H_2, presumably $HC{\equiv}CC{\equiv}CH$ ($\Delta H_f° = 440$ kJ mol^{-1}),[8] while cyclic **d** yields structurally indicative C_2H_2 ($\Delta H_f° = 456$ kJ mol^{-1} for two).[8] These products are considerably more abundant than that from hydrogen atom loss, consistent with the respective enthalpy changes (Figure 1). In a similar study of C_4H_8 neutrals,[6c] it was estimated that these collision conditions of 70% T and 30% T add ~1.7 eV (164 kJ mol^{-1}) and ~3.4 eV (328 kJ mol^{-1}), respectively, of energy, although with a broad distribution of values. These conditions cause relatively little fragmentation of **a**, suggesting a threshold for C_4H_4 dissociation well above the 135-kJ mol^{-1} enthalpy barrier (Figure 1). However, **d** shows extensive dissociation (note that at 30% T, 30% of C_4H_4 undergo no scattering collisions). The extent of dissociation of **d** with He at 70% is similar to that of **a** at 30% T, consistent with a barrier no higher than that of 177 kJ mol^{-1} indicated by the calculations of Dewar.[10a] The minor, even higher energy, product $C_4H^\bullet$ ($\Delta H_f° = 440 + 552 = 992$ kJ mol^{-1}) is presumably formed by multiple collisions. Both **a** and

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(22) Buckles, R. E.; Womer, D. E. *J. Am. Chem. Soc.* **1958**, *80*, 5055–5058. Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421–428.

d also show appreciable methyl loss, despite the H rearrangement required to form $^{\bullet}CH_3$ from either. As expected, the largest differences are the favored formation of $C_2H_3^{\bullet} + C_2H^{\bullet}$ from **a** (ΔH_f° = 830 kJ mol^{-1})[8] and $2C_2H_2$ from **d**.

Neutralization Agent of IE = 6 eV. These conclusions (Figure 1) are also supported by preliminary experiments with neutralization agents that should produce C_4H_4 neutrals somewhat less excited than those produced by Na. Neutralization of $\mathbf{a}^{\bullet+}$ and $\mathbf{d}^{\bullet+}$ by triphenylamine (IE = 6.8 eV)[8] and by Hg (10.4 eV), followed by He(70% T) cationization, gave essentially the same spectra, indicating that the **a** and **d** neutrals, formed with ~160 kJ mol^{-1} (6.8 − 5.1 eV) less internal energy than that of neutrals formed with Na, indeed have energies below their dissociation barriers. However, neutralization with tetra-*p*-anisylethylene (IE = 6 eV)[20] causes the dissociation of 26% of **a** and 49% of **d**. With internal energies ~90 kJ mol^{-1} less than those from Na neutralization, the indicated product abundances (±10%) from **a** and **d**, respectively, are $C_4H_3^{\bullet}$, 27% and 10%; C_4H_2, 33% and 19%; C_4H, 1% and 2%; C_3H, 20% and 11%; and C_2H_2, 19% and 58%. These values are surprisingly similar to those from CAD (30% T) above.

Conclusions

The substantial differences found for $^{+}$NR spectra of four $C_4H_4^{\bullet+}$ isomers show not only that the cyclic cations are surprisingly stable, but that all four isomers can be characterized successfully by two independent methods. Although sodium neutralization to form unstable C_4H_4 neutrals, a method of choice for the analogous $C_4H_8^{\bullet+}$ study,[6c] produces very extensive isomerization, use of a neutralization agent of optimal ionization energy (~6 eV) also yields characteristic NR spectra for **a** and **d**. The neutralization–reionization technique with dissociation of the neutrals can also provide unique information concerning the stabilities and unimolecular reactivities of such neutral, as well as ionic, isomers. This is of special value for highly reactive species such as **c** and **d**. For example, very recent photoelectron IP measurements point to $\mathbf{c}^{\bullet+}$ as the lowest energy *cyclic* $C_4H_4^{\bullet+}$ isomer;[11f] its dominant formation from benzene$^{\bullet+}$ shown here indicates it is the lowest energy form of all $C_4H_4^{\bullet+}$ isomers, consistent with the order of ΔH_f° values of Table I.

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Registry No. $\mathbf{a}^{\bullet+}$, 59699-48-8; $\mathbf{b}^{\bullet+}$, 65513-85-1; $\mathbf{c}^{\bullet+}$, 79105-72-9; $\mathbf{d}^{\bullet+}$, 34531-09-4.

Solid-State Chemistry of Molecular Metal Oxide Clusters. Multiple, Sequential C–H Activation Processes in the Hydrogenation of Coordinated Cyclooctene. Lattice Mobility of Small Organic Molecules

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Abstract: Reaction of solid $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ with D_2 gas produces cyclooctane containing up to 16 deuterium atoms. The c-$C_8D_nH_{16-n}$ isotopomer distribution is analyzed by Poisson statistics and interpreted in terms of C–H activation involving Ir-*D*–C-*H* exchange in an intermediate species containing coordinated cyclooctene. The results are compared with those from D_2 reduction of $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ in the solid state and in acetone solution, in which cases, an additional exchange process operates. Solid-state ^{2}H NMR shows that, even at low temperatures, small organic molecules such as cyclooctane and benzene undergo nearly isotropic motion.

While homogeneous organometallic chemistry is obviously a large, well-developed and well-appreciated area of science and technology, molecular level understanding of heterogeneous processes is less advanced.[1] We are interested in developing new solid-state organometallic chemistry based on highly reactive, cationic species held in matrices comprised of anionic molecular metal oxide clusters, here exemplified by the polyoxometalate $PW_{12}O_{40}^{3-}$.[2,3] This paper describes a quite unanticipated process resulting in multiple, sequential, Ir-*D*–C-*H* exchange reactions that occur as cyclooctadiene coordinated to iridium in $[(Ph_3P)_2Ir(C_8H_{12})]_3PW_{12}O_{40}$ is hydrogenated. Analogous C–H exchange occurs with $[(Ph_3P)_2Ir(C_8H_{12})][PF_6]$ both in the solid state and in solution, but analysis of the products shows that, in contrast, *two* different processes are involved. Finally, we use wide-line NMR spectroscopy to demonstrate mobility of small organic molecules in materials derived from metal oxide clusters.

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