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Reaction of the Butadiene Cation with Ethylene in the Gas Phase

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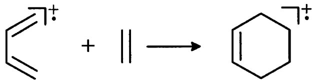
The structure of the addition product formed in the reaction of the *trans*-1,3-butadiene radical cation with ethylene is examined by using a flowing afterglow−triple quadrupole instrument. Energy-resolved collision-induced dissociation studies show the product not to be the cyclohexene radical cation but likely the 2,4-hexadiene radical cation. It is shown that thermodynamics accounts for the preference of the 2,4-hexadiene ion over the cyclohexene ion but does not account for the preference of the 2,4-hexadiene ion over the 1-methylcyclopentene ion. Reaction of the 1-bromobutadiene radical cation with ethylene suggests but does not require that the cyclohexene cation be accessed as an intermediate in the reaction. It is suggested that the mechanism involves the concerted addition of ethylene to a C−H bond in the butadiene cation, as has been described previously for the cis ion.

Introduction

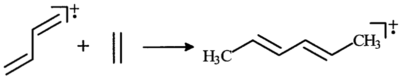
Changes in electronic and thermodynamic properties caused by ionization can often lead to reactivity in radical cations that is dramatically different from that of the corresponding neutral molecules. A well-examined example that illustrates this phenomenon is the Cope rearrangement of 1,5-hexadiene. Whereas the reaction of the neutral reagent has an activation energy of 34 kcal/mol,[1,2] the barrier is completely eliminated for the radical cation.[3] In fact, the cyclohexane-1,4-diyl structure that corresponds to the transition state on the neutral potential energy surface is found to be a stable minimum for the radical cation[3] and has been observed in chlorofluorocarbon matrixes.[4,5]

The effect of ionization on the Diels−Alder reaction has also been examined experimentally and theoretically. Bauld and co-workers have carried out extensive studies that have shown the cation Diels−Alder reaction (eq 1) to be a useful tool in organic synthesis[6,7] and have carried out pioneering theoretical studies on the mechanism of the reaction.[8,9] Although mass spectrometry has long been used to investigate the mechanisms of radical cation pericyclic reactions,[10] the only gas-phase study of the parent reaction of the unsubstituted 1,3-butadiene radical cation with ethylene has been reported by Bouchoux and Salpin,[11] who examined the reaction using an ion cyclotron resonance (ICR) mass spectrometer. Two reaction pathways were identified in the study. The first involves a degenerate methylene exchange process leading to the formation of the butadiene radical cation, **1**$^+$, and ethylene, which is only observed when using deuterium-labeled reagents. The second pathway involves the addition and loss of a methyl radical. Methyl radical loss is a commonly observed reaction for all activated $C_6H_{10}^{\bullet+}$ cations,[12] and so the fact that it occurs in the reaction of the butadiene cation with ethylene is not surprising. The adduct of the butadiene radical cation and ethylene is not observed in the low-pressure conditions of the ICR. Therefore, the structures of the intermediates in the reactions could not be determined.



1$^+$ **2**$^+$ (1)

Theoretical studies have also been employed to provide insight into the mechanism of the radical cation Diels−Alder reaction. Early work by Bauld and co-workers[8] showed that by using orbital symmetry considerations the pericyclic reaction of **1**$^+$ with ethylene is formally a forbidden process. Therefore, the formation of the cyclohexene radical cation (**2**$^+$) cannot occur by concerted reaction. Subsequent high-level molecular orbital calculations by Haberl et al.[13] and by Hofmann and Schaefer[14,15] have provided insight into the potential energy surfaces for the stepwise radical cation Diels−Alder reaction and into the formation of the methylcyclopentene cation, the lowest energy $C_6H_{10}^{\bullet+}$ isomer presumed to be an intermediate in the gas-phase reaction. As part of our studies of pericyclic reactions of organic ions,[16] we have now carried out the cationic Diels−Alder reaction under high-pressure conditions in a flowing afterglow, where adduct formation is possible. We show that the reaction of the *trans*-butadiene radical cation with ethylene in the gas phase is *not* a Diels−Alder-like reaction but that the trans isomer of **1**$^+$ reacts with ethylene to form the 2,4-hexadiene radical cation, **3**$^+$ (eq 2).



3$^+$ (2)

Experimental Section

The experiments were carried out using a flowing afterglow−triple quadrupole instrument that has been described previously.[17] Butadiene radical cations are generated in the 1-m × 7.3-cm helium flow reactor (P(He) = 0.400 Torr, flow(He) = 200 std cc/s) by charge transfer with the C_6H_6 radical cation, prepared by the electron ionization of benzene (IE(C_6H_6) = 9.24 eV, IE(C_4H_6) = 9.07 eV).[18] The ions in the flow tube, thermalized to ambient temperature by ca. 10^5 collisions with the helium buffer gas, are extracted from the flow tube through

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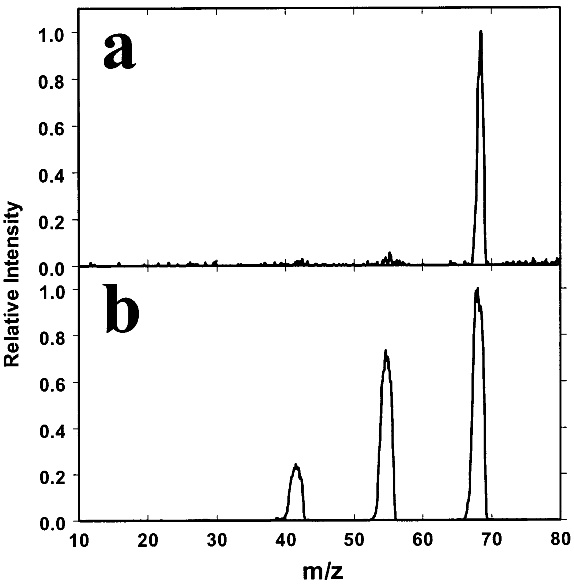


Figure 1. Collision-induced dissociation mass spectra of (a) the adduct of the butadiene radical cation and ethylene and (b) the cyclohexene radical cation.

a 1-mm orifice and then focused into an EXTREL triple quadrupole analyzer.

Ions with the desired mass-to-charge ratio are selected by using the first quadrupole (Q1) and are then injected into the second quadrupole (Q2, radio frequency only), where they undergo collisions with the argon target. Appearance curves are obtained by monitoring the product formation while the Q2 rod offset is scanned. The reactant and product ions are analyzed with the third quadrupole (Q3) and are detected with an electron multiplier operating in pulse-counting mode.

Results

Because of the experimental conditions, the butadiene ions examined in this work are likely to be predominately in trans geometry.[19,20] The butadiene radical cation reacts very slowly with ethylene added downstream in the flow tube, at an apparent bimolecular rate of 3.9×10^{-11} s^{-1} (efficiency = 3.5%) at a He pressure of 0.400 Torr. The observed products of the reaction at this pressure include an adduct ion, *m*/*z* 82, and an *m*/*z* 67 product corresponding to the addition and loss of methyl radical. The methylene exchange pathway observed by Bouchoux and Salpin[11] is not observed without isotopically labeled reagents.

The structure of the thermalized *m*/*z* 82 adduct ion formed as the product in the reaction was examined by using collision-induced dissociation (CID) in the triple quadrupole analyzer. The CID mass spectrum for the adduct ion, measured at a collision energy of 15 eV (laboratory frame) with an argon target, $P(\text{Ar}) = 0.080$ mTorr, is shown in Figure 1a. The only product observed is the ion at *m*/*z* 67, which corresponds to the loss of methyl radical. For comparison, the CID mass spectrum of the cyclohexene radical cation, prepared by ionization of either cyclohexene or 1,2-dichlorocyclohexane, contains three observable products with *m*/*z* 67, 54, and 41 in characteristic yields of 1:0.8:0.2 (Figure 1b).[16,21] The absence of the *m*/*z* 54 and 41 products in the CID mass spectrum of the adduct ion indicates that the *m*/*z* 82 product in the reaction of butadiene cation with ethylene is *not* the cyclohexene radical cation.[21]

Although the CID mass spectrum of the adduct rules out cyclohexene as the product of the reaction, it cannot be used to positively identify the structure of the ion because the fragmentation pattern found for the adduct (Figure 1a) is commonly observed upon CID of other $C_6H_{10}^{\bullet+}$ cations.[12,16] However, isomeric ions that give similar CID mass spectra can be distinguished by using energy-resolved CID.[16] Because the different ion isomers have different energetic and dynamic requirements for decomposition by loss of methyl radical, the shapes of the appearance curves for the formation of the *m*/*z* 67 ion are different. Therefore, unknown ion structures can be determined by comparing the shape of the CID appearance curve with those for authentically prepared ions.

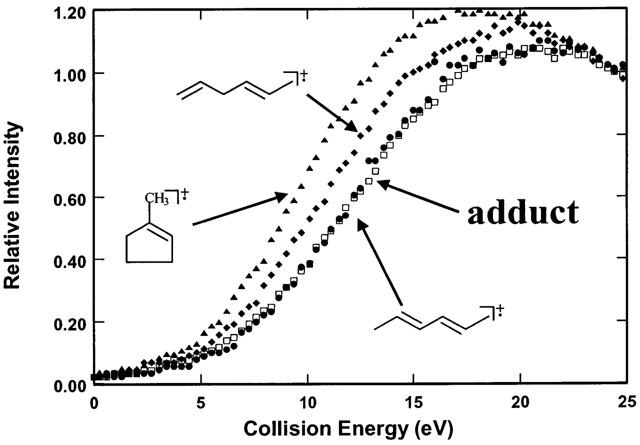


Figure 2. Collision-induced dissociation appearance curves for the formation of $C_5H_7^+$ cations from $C_6H_{10}^{\bullet+}$ cation precursors. The curves are normalized to the signal at a collision energy of 25 eV (laboratory frame).

The appearance curve for the formation of the *m*/*z* 67 ion fragment upon CID of the **1**$^+$/ethylene adduct ion is shown in Figure 2. Also shown in the Figure are the appearance curves for the *m*/*z* 67 fragment obtained upon CID of methylcyclopentene, 1,3-hexadiene, and 2,4-hexadiene radical cations, measured on the same day and under the same instrumental conditions[22] as that for the adduct. The appearance curve obtained for the adduct is similar to that obtained for 2,4-hexadiene but does not agree with those for the other ions or for any of the ions we have examined.[16]

A quantitative comparison of the *m*/*z* 67 appearance curves is provided in Table 1, where we list the "onset energy", E_{onset}, which is the lowest energy where the relative signal is at least 0.2 times that observed at 25 eV,[23] the energy where the signal maximum occurs, E_{max}, and the relative intensity at the maximum, I_{max}. The onset energy, the energy at which the ion is observed, should not be confused with the "threshold energy" for the dissociation, which is the energy required to dissociate the ion.[24] Whereas the threshold energy depends only on the energy required for dissociation, the measured onset energy depends on the rate of dissociation of the ion, which is a function of the energetics and dynamics. The data in Table 1 show that onset energies for *m*/*z* 67 formation from linear ions are generally higher than those for cyclic ions, likely because of higher energy barriers and tighter transition states for rearrangement. However, within a given class, the lower-energy ions have higher energy onsets.

From Table 1, the $C_6H_{10}^{\bullet+}$ ion whose parameters agree best with those for the adduct is the 2,4-hexadiene radical cation, where the appearance curve has the same onset and maximum energy as that for the adduct, whereas the intensity of the maximum agrees to within 2%. The next best agreement is for the 1,4-hexadiene radical cation, which has a significantly lower energy onset (by 20%) and a slightly different energy and intensity at the maximum. However, as shown in Figure 2, these

TABLE 1: Quantitative Comparison of *m*/*z* 67 Appearance Curves from CID of $C_6H_{10}^{\bullet+}$ Isomers

$C_6H_{10}^{\bullet+}$ isomer	$\Delta H_{f,298}$ (kcal/mol)[a]	E_{onset} (% dev)[b,c]	E_{max} (% dev)[c,d]	I_{max} (% dev)[c,e]
adduct[f]		8.4 ± 0.7	21.1 ± 0.5	1.09 ± 0.01
2,4-hexadiene[g]	199	8.4 ± 0.7 (0.0)	21.1 ± 0.5 (0.0)	1.07 ± 0.01 (1.8)
1,4-hexadiene[g]	225	6.7 ± 0.5 (20)	20.4 ± 1.1 (3.3)	1.16 ± 0.07 (6.6)
1-methylcyclopentene[g]	197	6.6 ± 0.6 (21)	19.0 ± 0.4 (10)	1.21 ± 0.09 (12)
cyclohexene[h]	205	4.0 ± 0.7 (52)	13.9 ± 0.6 (29)	1.62 ± 0.09 (49)
1,3-hexadiene[h]	210	6.6 ± 0.5 (21)	20.4 ± 0.3 (3.3)	1.14 ± 0.04 (4.6)
methylenecyclopentane[h]	203−209	4.1 ± 0.6 (51)	15.6 ± 0.7 (26)	1.42 ± 0.11 (30)
2,3-dimethylbutadiene[h]	210	6.3 ± 0.7 (25)	17.4 ± 0.4 (18)	1.49 ± 0.12 (37)
3-methyl-1,3-pentadiene[h]	204	6.4 ± 0.7 (24)	18.2 ± 0.2 (14)	1.35 ± 0.07 (24)

[a] Ion heats of formation taken from ref 18. [b] The lowest energy where the yield of the *m*/*z* 67 product is greater than 0.2, relative to the signal at 25 eV. Values correspond to eV in the laboratory frame. [c] Uncertainties are standard deviations in absolute values from replicate measurements. Relative uncertainties are smaller. Values in parentheses are the percent deviation from the value measured for the adduct ion. [d] The energy where the maximum yield of the *m*/*z* 67 product is observed. Values are in eV, laboratory frame. [e] The intensity of the *m*/*z* 67 signal at the maximum, relative to the yield at 25 eV. [f] Values obtained from the *m*/*z* 67 appearance curve for CID of the butadiene radical cation/ethylene adduct shown in Figure 2. [g] Figure 2. [h] Reference 16.

parameters correspond to a visually large difference between the appearance curves for the 1,4-hexadiene radical cation and the adduct. Although the ions listed in Table 1 do not constitute an exhaustive list of $C_6H_{10}^{\bullet+}$ isomers, other possibilities such as strained bicyclic systems or distonic radical cations are expected to be significantly higher in energy[13,14,18] and are expected to have lower energy onsets for the formation of *m*/*z* 67.[16] Moreover, a distonic structure for the ion is ruled out by the reaction of the ion with dimethyldisulide, which proceeds by only electron transfer. If the product were a distonic ion, methylthio abstraction would be expected.[25]

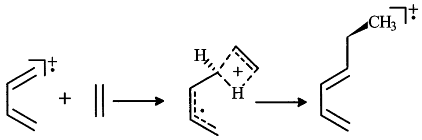
Given that the *m*/*z* 67 appearance curve obtained for the adduct best agrees with that for the 2,4-hexadiene radical cation, we conclude that the addition product formed in the reaction of the 1,3-butadiene radical cation with ethylene under the conditions of our experiment is most likely the 2,4-hexadiene radical cation. Although the 1,3- and 1,4-hexadiene structures cannot be unambiguously ruled out, those ions are >10 kcal/mol higher in energy than the 2,4-isomer,[16,18] and their *m*/*z* 67 appearance curves do not agree as well with that for the adduct. Similarly, because the 2,4-hexadiene cation has the highest onset energy among the $C_6H_{10}^{\bullet+}$ cations, any impurity in the ion beam would shift the appearance curve to lower energy such that a mixture of ion isomers is considered unlikely. Ion mixtures have been detected previously using this approach.[16]

Discussion

The formation of a linear hexadiene radical cation in the reaction of the butadiene radical cation with ethylene has not been observed or predicted previously. The origin of the preference for the formation of the 2,4-hexadiene radical cation over $\mathbf{2}^+$ in the reaction is likely thermochemical. Formation of the (*E*,*E*)-2,4-hexadiene radical cation is energetically favored over the formation of $\mathbf{2}^+$ by 6 kcal/mol, and the (*E*,*Z*)- and (*Z*,*Z*)-ion isomers are lower in energy than the cyclohexene radical cation by 4.1 and 3.9 kcal/mol, respectively.[18] Moreover, the formation of a ring-opened diene cation is entropically favored as well. The entropies for the (*E*,*E*)-2,4-hexadiene and cyclohexene radical cations, calculated from (unscaled) B3LYP/6-31+G* frequencies, are 86.2 and 75.6 cal/mol K, respectively.[26] However, thermodynamics is not the only consideration, as the methylcyclopentene radical cation, the global minimum on the potential energy surface, is *not* the final product of the reaction, despite the fact that the energy of this isomer is ca. 2 kcal/mol lower than that for the (*E*,*E*)-2,4-hexadiene cation.

The formation of $\mathbf{3}^+$ as the final product does not rule out other structures as potential intermediates in the reaction.[27] For example, as predicted by theoretical studies,[13,14] the cyclohexene radical cation may be formed but then react faster than it can be cooled by collisions with helium (the ion/helium collision rate is ~$10^7 s^{-1}$ at 0.400 Torr). Attempts to trap the cyclohexene radical cation by solvating the butadiene radical cation with water, acetonitrile, and dichloromethane were unsuccessful, as no noticeable differences in the *m*/*z* 54 intensity in the CID mass spectrum were observed. The reaction of the 1-bromobutadiene radical cation with ethylene results in the formation of an ion with *m*/*z* 81 ($C_6H_9^+$), which corresponds to addition with loss of the bromine atom. Energy-resolved CID studies show that the *m*/*z* 81 product formed in the reaction is the cyclohexenyl cation, which is consistent with formation of the cyclohexene radical cation followed by loss of bromine. However, the results do not require that the cyclohexene cation be formed before the bromine is lost, and it is possible that the bromine is lost before cyclization occurs. Last, neither cyclopentadiene nor cyclohexadiene radical cations are found to undergo any reaction with ethylene under thermal conditions, suggesting that the trans geometry of the reactant may play a role in dictating the final product.

Additional insight into the reaction comes from considering the geometry of the 2,4-hexadiene cation product. The appearance curve for an authentic 2,4-hexadiene radical cation is for ions derived from a mixture of (E,E), (E,Z), and (Z,Z) geometries of the neutral dienes. Therefore, the excellent agreement between the CID appearance curve for the adduct indicates that the structural distribution for the adduct is similar to that for the authentic ions or that there are only minor differences among the appearance curves for the three isomers.



(3)

The mechanism by which the 2,4-hexadiene ion is formed is not known. The formation of $\mathbf{3}^+$ as a product has not been considered in any of the experimental or theoretical studies that have been reported. Bouchoux and Salpin have described potential pathways to account for the formation of the cyclopentenyl cation in the reaction,[11] but they did not consider the formation of the 2,4-hexadiene radical cation. Hofmann and Schaefer[15] have identified a barrierless pathway for the formation of the 1,3-hexadiene radical cation in the reaction of the cis ion with ethylene that involves a concerted 1,2 addition of ethylene to the C−H bond of the butadiene cation (eq 3). Given that the formation of the 1,3-hexadiene cation in the reaction is exothermic by more than 35 kcal/mol,[18] the product will have enough energy to rearrange to the 2,4 or 1,4 isomers.[15] If a

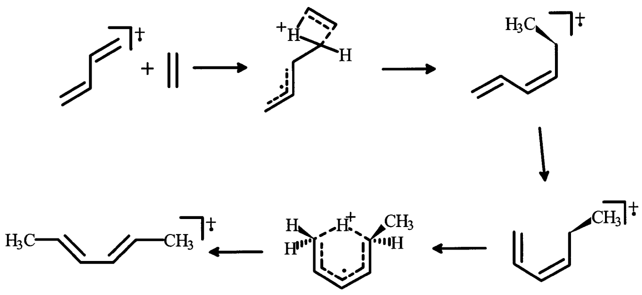


Figure 3. Possible mechanism for the formation of the 2,4-hexadiene radical cation upon reaction of the butadiene cation with ethylene.

similar pathway could be found for the trans ion (Figure 3), it could account for the formation of $\mathbf{3}^+$. However, attempts to locate the first step of this pathway at the B3LYP/6-31+G* level of theory have thus far been unsuccessful.

Conclusions

Energy-resolved collision-induced dissociation experiments show that the adduct formed in the reaction of the *trans*-butadiene radical cation with ethylene in a flowing afterglow apparatus is not the cyclohexene or methylcyclopentene radical cation but most likely has a 2,4-hexadiene structure. The formation of the cyclohexenyl cation in the reaction of the bromobutadiene radical cation with ethylene suggests that cyclohexene may be formed as an intermediate in the reaction but it rearranges before it can be collisionally cooled. Attempts to trap the cyclohexene cation by solvating the reactants were unsuccessful. A suggested mechanism for the reaction involves the addition of ethylene to a C−H bond of the butadiene cation, as has been described previously for the *cis*-butadiene cation.

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(19) At the CCSD(T)) level of theory,[20] the *cis*-butadiene radical cation is calculated to be ca. 4 kcal/mol higher in energy than the trans isomer and therefore can be only barely accessed in the reaction between the benzene radical cation and *trans*-butadiene. Therefore, the amount of *cis*-butadiene radical cation is not likely greater than the thermal population of neutral *cis*-butadiene, $<1\%$ at room temperature. The barrier for cis−trans isomerization in the butadiene radical cation is calculated to be about 25 kcal/mol,[20] and the reaction will not occur appreciably under thermal conditions.

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(23) Normalization at 25 eV is arbitrary and is chosen to match the appearance curves shown in Figure 2. The conclusions of this study do not depend on the energy chosen as the normalization point.

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