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Energy Barriers for Isomerization of Gaseous $C_3H_5^+$ Ions

Richard D. Bowen,[1a] Dudley H. Williams,*[1a] Helmut Schwarz,[1b] and Chysostomos Wesdemiotis[1b]

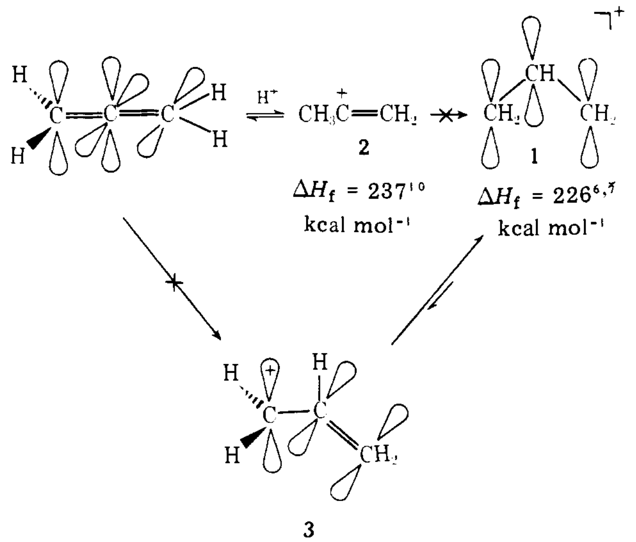
Contribution from the University Chemical Laboratories, Cambridge CB2 1EW, England, and the Department of Organic Chemistry, Technical University, D1000 Berlin 12, West Germany. *Received August 17, 1978*

Abstract: It is shown from collisional activation studies on the $C_3H_5^+$ ion in the mass spectra of allyl and 2-propenyl bromides that low-energy, nondecomposing allyl and 2-propenyl cations do not interconvert. In contrast, similar studies on cyclopropyl and 1-propenyl bromides reveal that the $C_3H_5^+$ ions in the mass spectra of these compounds have the allyl structure. These results are consistent with a small or negligible energy barrier to rearrangement of gaseous 1-propenyl or cyclopropyl cations to allyl cation. Complementary conclusions may be deduced from a consideration of the kinetic energy release which accompanies Br· loss from the molecular ions of the C_3H_5Br isomers. Loss of Br· from ionized allyl or 2-propenyl bromides is accompanied by only a small release of kinetic energy; this is consistent with these reactions being simple bond cleavages occurring without rearrangement of the incipient $C_3H_5^+$ ion. Considerably more kinetic energy release is associated with elimination of Br· from ionized cyclopropyl or 1-propenyl bromides, thus suggesting that rate-determining rearrangement of the potential $C_3H_5^+$ cations to a more stable structure(s) occurs prior to dissociation.

Introduction

In examining the reactions of ions, and the energy barriers to rearrangement of isomeric structures, there are distinct advantages associated with conducting the experiments in the absence of solvent, i.e., in the gas phase.[2] Thus, for example, collisional activation (CA) mass spectrometry may be applied to discover which isomeric structures of an ion of given chemical formula exist in significant potential energy wells.[3] Complementary information may also be obtained from the kinetic energy release which is observed to accompany dissociation of the ion in question.[2b,4] These data are not accessible from solution experiments because collisions between reactant, product, and solvent molecules lead to rapid absorption of any kinetic energy released upon fragmentation into the various vibrational, rotational, and translational modes of the system. In constrast, these data are readily available for decompositions occurring in the gas phase from measurement of the metastable peak for the process concerned. Conceptually, these metastable peaks constitute a "direct picture" of what happens when dissociation takes place. In particular, the rate-determining isomerization of an ion may be detected from a broadening of the metastable peak for the relevant decomposition channel.[5]

Scheme I



Results and Discussion

The $C_3H_5^+$ system has been the subject of several investigations, both experimental[6,7] and theoretical.[8,9] Recently, the heat of formation of 2-propenyl cation, **2**, was measured by protonation of propyne and allene.[10] The value (237 kcal mol^{-1}) obtained[10] was significantly higher than that (226 kcal mol^{-1}) previously[6,7] measured for allyl cation, **1**. The reason given[10] for the formation of 2-propenyl, rather than the thermodynamically more stable allyl cation, via protonation of allene, was that center protonation of allene gives rise to a conformation of allyl cation, **3**, in which the π bond and unoccupied p orbital are orthogonal, Scheme I. In this conformation, stabilization by overlap of the π electrons and the unoccupied p orbital is minimized, thus resulting in a relatively unstable $C_3H_5^+$ cation. End protonation of allene, to form 2-propenyl cation, is therefore energetically more favorable. Two important conclusions in addition to the heat of formation of 2-propenyl cation, **2**, may be deduced from these results. First, there must be a significant energy barrier toward rearrangement of 2-propenyl to allyl cation. Were this not so, exothermic collapse of 2-propenyl to allyl cation would occur and reversible protonation of allene would result in the formation of allyl cation, **1**. This is excluded since the heat of formation of the $C_3H_5^+$ isomer formed[10] differs by 11 kcal mol^{-1} from that known for allyl cation.[6,7] Second, the heat of formation of "perpendicular" allyl cation, **3**, must be higher than 237 kcal mol^{-1}. If this were not the case, protonation of

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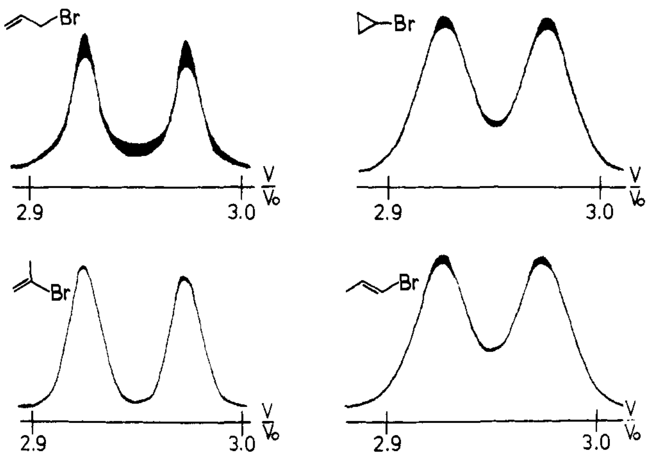


Figure 1. Metastable peaks for loss of Br· from the molecular ions of four isomers of C_3H_5Br. These peaks were recorded using an MS 902 instrument for ions decomposing in the first field-free region. The abscissas are in units of V/V_0 where V_0 is the accelerating voltage used to transmit the main beam (nominally 2 kV) and V is the corresponding voltage required to transmit $C_3H_5^+$ ions formed in the first field-free region.

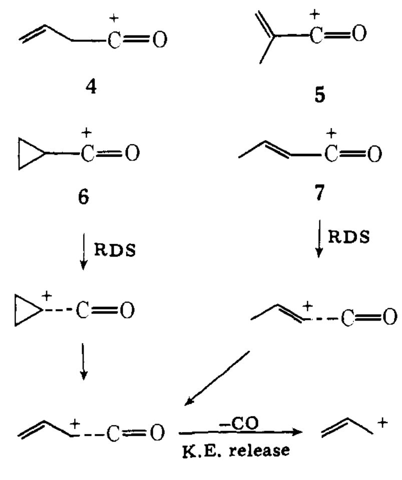
allene would again be expected to produce allyl cation rather than 2-propenyl cation.

The first of these conclusions may be tested by examining the collisional activation (CA) spectra of the $C_3H_5^+$ ions (m/e 41) in suitable compounds. Allyl cation might exhibit a greater preference for CH_2 loss in CA spectroscopy than 2-propenyl because it contains two CH_2 groups whereas 2-propenyl possesses only one. A similar diagnostic loss of CH_2 in collisional activation has previously been observed in some $C_7H_7^+$ ions,[11] thus indicating that these ions have a benzylic structure. Conversely, 2-propenyl cation might show more CH_3 elimination than allyl because it contains a CH_3 group whereas allyl does not. This is found to be the case; under CA conditions the m/e 41 ions in the mass spectra of allyl bromide and 2-propenyl bromide eliminate CH_2 and CH_3 in the ratios 1.0 and 0.4, respectively. Similar results are obtained for the m/e 41 ions in the mass spectra of methyl but-3-enoate ($CH_2{=}CHCH_2CO_2CH_3$) and methyl 2-methylpropenoate ($CH_2{=}C(CH_3)CO_2CH_3$). This diagnostic difference is considerably greater than the experimental error involved in the measurements and constitutes strong evidence that allyl and 2-propenyl cations exist in significant potential energy wells in the gas phase. Further evidence in favor of this view may be found from a consideration of the kinetic energy release which accompanies Br· loss from ionized allyl bromide and 2-propenyl bromide. In each case, a narrow Gaussian metastable peak is observed (Figure 1; note that two metastable peaks are observed owing to the two possible Br isotopes which occur in approximately equal abundance). The very small average[12] kinetic energy releases, 0.1 (7) and 0.1 (4) kcal mol^{-1}, respectively, associated with Br· loss from ionized allyl and 2-propenyl bromides are consistent with simple bond cleavage of the C–Br bonds occurring without rearrangement of the incipient $C_3H_5^+$ ion. Were Br· elimination from ionized 2-propenyl bromide to be accompanied by rearrangement of the potential 2-propenyl cation to the more stable allyl structure, some of the potential energy released would be partitioned as translation and a broader metastable peak, indicating more kinetic energy release, would be expected.[5]

In contrast, however, loss of Br· from the molecular ions of cyclopropyl and 1-propenyl bromides is accompanied by considerably more average[12] kinetic energy release, 0.9 and 0.6 kcal mol^{-1}, respectively. The increase in kinetic energy release, relative to that found for Br· loss from ionized allyl and 2-propenyl bromides, is clearly visible from the metastable peaks for the processes which are depicted in Figure 1. These results indicate that, as Br· is lost from ionized cyclopropyl and 1-propenyl bromides, rearrangement of the incipient $C_3H_5^+$ cation occurs. Some of the potential energy released by the isomerization is partitioned as kinetic energy release accompanying the dissociation.[5] Although the kinetic energy release data reveal that isomerization of the potential $C_3H_5^+$ cations in cyclopropyl bromide and 1-propenyl bromide molecular ions occurs, they do not give information as to which isomer of $C_3H_5^+$ is formed after rearrangement. This question may be resolved by CA studies, which reveal that the m/e 41 ions in the mass spectra of cyclopropyl and 1-propenyl bromides eliminate CH_2 and CH_3 in the ratio 1.0 and 0.9, respectively. These values are very close to that measured for allyl cation (1.0) and are clear evidence that the m/e 41 ions formed from ionized cyclopropyl and 1-propenyl bromides have the allyl structure, **1**.

Similar results are obtained for the m/e 41 ions in the mass spectra of methyl cyclopropanecarboxylate ($\overline{CH_2CH_2}CHCO_2CH_3$) and methyl crotonate ($CH_3CH{=}CHCO_2CH_3$). These experiments were performed in order to minimize the possibility that bond weakening within the hydrocarbon portions of cyclopropyl and 1-propenyl bromide molecular ions (which contain odd electrons) might allow rate-determining isomerization of the C_3H_5 portion before the bromine radical is in the process of departing. Thus, the acylium ions **6** and **7** both lose CO with considerably larger average releases of kinetic energy (ca. 6.8 and 2.3 kcal mol^{-1}, respectively) than do **4** and **5** (0.5 and 0.7 kcal mol^{-1}, respectively). Moreover, the CA data establish that dissociation of **5** produces the 2-propenyl cation, whereas dissociation of **4**, **6**, and **7** leads to allyl cation.

These results provide evidence that, as CO leaves **6** and **7**, the required bond stretching constitutes the rate-determining step (RDS); the potential energy of the systems then decreases as the incipient unstable cations isomerize to the more stable allyl ion, with a resultant increase in vibrational energy. Finally, some of the excess of vibrational energy (over that required to cause dissociation to an allyl ion and CO) may fluctuate into the dissociation coordinate (e.g., on a statistical basis) resulting in a larger average kinetic energy release than for dissociation of **4**.



We conclude that cyclopropyl and 1-propenyl cations either do not exist in potential energy wells, or that such wells are quite shallow. According to our analysis, the maximum well depth would correspond to the residual binding energy between CO and the incipient cations at the extended bond lengths which allow rearrangement of the incipient cyclopropyl and 1-propenyl ions to occur. Calculations on $C_3H_5^+$ isomers have previously suggested that cyclopropyl cations collapse to allyl ions essentially without activation energy.[8,9]

Experimental Section

The collisional activation (CA)[3,11,13] spectra were obtained using a Varian MAT 311A double-focusing mass spectrometer, in which ions pass through the magnetic field before entering the electric field. The collision cell was differentially pumped and situated in front of the energy resolving slit. Samples were introduced via the gas inlet system and run at an accelerating voltage of 3 kV, with a nominal electron beam energy of 70 eV and a source temperature of 170 °C. The magnetic and electric fields were adjusted to transmit $C_3H_5^+$ ions (m/e 41); air was then introduced into the collision cell via a variable leak until the precursor ion abundance decreased to $1/3$ of its original value. CA spectra were then obtained by scanning the electric field, recorded on an XY recorder and normalized to the total ion current due to all fragment ions. Only peak heights were measured and the abundances were not corrected for reduced multiplier response. The reported CA spectra are the means of at least four independent measurements.

The kinetic energy release measurements were obtained using an AEI MS 902 double-focusing mass spectrometer. Ions decomposing in the second field-free region were detected in normal mode operation, with an accelerating voltage of 8 kV and a nominal electron beam energy of 70 eV. Ions dissociating in the first field-free region were observed by increasing the accelerating voltage, from an initial value of 2 kV, at constant electric and magnetic field strengths.[14] Samples were introduced via the all glass heated inlet system (AGHIS) and run consecutively under identical operating conditions. The reported kinetic energy releases are the means of the results from at least four scans; no correction was applied for the width of the main beam.

All compounds were commercially available or synthesized by unexceptional procedures; samples were purified by preparative GLC.

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Excited-State Energy Distribution between Dissimilar Carbonyl Molecules Produced from 1,2-Dioxetanes

William H. Richardson,* Merylin B. Lovett, Mary E. Price, and James H. Anderegg

Contribution from the Department of Chemistry, San Diego State University, San Diego, California 92182. *Received May 2, 1978*

Abstract: The distribution of excitation energy between dissimilar carbonyl products, obtained from the thermolysis of unsymmetrically substituted 1,2-dioxetanes, is reported. The excited-state carbonyl products were trapped with olefins to give oxetanes. From the yield of oxetane and the quantum yield for the oxetane-olefin reaction, specific efficiencies (α_{T_1}) of the excited-state carbonyl products were calculated. With 3-phenyl-3-methyl-1,2-dioxetane (PMD), triplet acetophenone was produced with 2.3% efficiency. By difference from the total triplet efficiency (15%), formaldehyde was produced with 12.7% efficiency. Within our detectability limits, no excited-state acetone was produced from 3,3-dimethyl-1,2-dioxetane (DMD) and thus all of the excitation energy (α_{T_1} = 13%) was associated with formaldehyde. To confirm the olefin trapping procedure with DMD, a similar experiment was performed with tetramethyl-1,2-dioxetane. Here, acetone was produced with 40% efficiency, which is in excellent agreement with the efficiency obtained by the emission method with 9,10-dibromoanthracene (DBA) (α_{T_1} = 36%). The ratio of specific efficiencies of benzophenone/benzaldehyde, produced from triphenyl-1,2-dioxetane (TPD), was found to be 92 by the olefin trapping procedure. For the three simply substituted dioxetanes (PMD, DMD, and TPD), the distribution of excited-state triplet energy can be rationalized in terms of a Boltzmann distribution of carbonyl triplet energies. Precise adherence to a Boltzmann distribution is uncertain due to error limits in the triplet carbonyl energies and the efficiency values. The approach to a Boltzmann distribution pertains to simply substituted dioxetanes, where a stepwise biradical mechanism appears to be operative. With certain substituted dioxetanes, where this mechanism does not appear to be applicable, there is a clear deviation from the Boltzmann distribution. From a consideration of other data, it appears that the Boltzmann distribution with simply substituted dioxetanes pertains to the birth of the carbonyl species from the dioxetane rather than to energy transfer in the solvent cage. An alternative vibrational model for excited-state energy distribution appears unlikely, based on the results with PMD and DMD.

A considerable body of data now suggests that simply substituted 1,2-dioxetanes undergo thermolysis to give electronically excited state carbonyl products, where typically high triplet to singlet (S_1) ratios are observed.[1] Recently, it has been reported that 1,2-dioxetanes with amino substituents produce predominantly singlets (S_1) rather than high triplet yields.[2] This change in the T_1/S_1 carbonyl product ratio appears to be associated in a change in the mechanism of thermolysis of simply substituted dioxetanes vs. dioxetanes bearing an amino substituent.

Unsymmetrically substituted dioxetanes will undergo thermolysis, where the excitation energy is distributed between

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