Dimethylcarbene, Its Radical Cation and Dication

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Received April 15, 1997[⊗]

Abstract: The dimethylcarbene radical cation, $(CH_3)_2C^{\bullet+}$, has been generated in the gas phase. Experimental identification was achieved by charge stripping mass spectrometry whereby the stable dimethylcarbene dication, $(CH_3)_2C^{2+}$, is observed. Electron impact appearance energy measurements and G2 ab initio molecular orbital calculations have been used to investigate the thermochemistry of the dimethylcarbene radical cation. The carbene radical cation is calculated to lie 84 kJ mol^{-1} above the propene radical cation and to be separated from it by a barrier of 35 kJ mol^{-1}.

Introduction

Dimethylcarbene has received considerable attention from experimentalists[1] and theoreticians.[2] The neutral carbene has been indirectly identified from trapping experiments,[1b,c] but experiments have failed to produce and identify its radical cation and dication, both of which are predicted by ab initio molecular orbital calculations to be stable gas-phase species.[3]

Four isomeric $C_3H_6^{\bullet+}$ ions (*m/z* 42) have been postulated to exist in the gas phase, namely the propene radical cation, the cyclopropane radical cation, the trimethylene distonic ion, and the dimethylcarbene radical cation.[4] While it is unclear from experiment whether the cyclopropane radical cation and the trimethylene distonic ion are distinct entities, recent theoretical calculations[5] predict a single isomer corresponding to a partially ring-opened structure. Charge stripping (CS) mass spectrometry (the tandem mass spectrometric study of doubly-charged ions produced by collisional excitation of the mass selected ion of interest)[6] has been used to distinguish between ionized propene and ionized cyclopropane. Neither ion was found to produce a significant yield of stable, doubly-charged $C_3H_6^{2+}$ (*m/z* 21) species, and identification rested upon the ratio of the *m/z* 20.5 to *m/z* 20 or *m/z* 19 fragment peak intensities.[4,7] The ions can also be distinguished by measuring their reactivity in ion–molecule reactions.[8]

The possible formation of ionized dimethylcarbene by the loss of C_2H_4 from ionized 1,1-dimethylcyclopropane was in-vestigated by McLafferty et al.[4] They concluded from CS experiments that the $C_3H_6^{\bullet+}$ ion produced was primarily ionized propene, and they therefore suggested that the carbene ion was of relatively low stability.

We report here the first experimental observation of both singly- and doubly-charged dimethylcarbene ions, a search for the neutral carbene generated from its radical cation, and the results of new theoretical calculations.

Experimental Methods

All mass spectra were recorded on a modified VG ZAB-2F mass spectrometer of BEE geometry which has been described in detail elsewhere.[9] Kinetic energy release values, $T_{0.5}$, were obtained from the peak widths at half-height and evaluated by established methods.[10] Energy resolution was such that the width at half-height of the main ion beam was 4 V. For CS experiments, O_2 was used as the collision gas at a pressure sufficient to reduce the $C_3H_6^{\bullet+}$ beam by 15% (i.e., approximately single collision conditions). Corrections for the contribution of the ^{13}C overlap from the adjacent ions of lower mass were carried out by measuring the CS mass spectrum of both the ion of interest (*m/z* 42) and the preceding peak (*m/z* 41) on a chart recorder. The required correction was made by using the difference in amplifier gain, the intensities of the respective signals, and the natural abundance of the ^{13}C isotope multiplied by the number of carbon atoms in the ion. In the neutralization–reionization (NR) experiments Xe and O_2 were used for neutralization and reionization, respectively; their pressures were adjusted to give a main beam transmission of 85% for each stage. The appearance energy (AE) of the dimethylcarbene radical cation (*m/z* 42) was measured by using a AEI MS-902S mass spectrometer and determined by measuring the ion abundance vs electron energy over a small energy range (2–3 V) above the threshold. The data were treated as described in detail elsewhere.[11] 2,2,4,4-Tetramethyl-1,3-cyclobutanedione was purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification; research grade propene and cyclopropane were obtained from Phillips Petroleum Co. (Bartlesville, OK) and Matheson of Canada (Whitby, ONT), respectively.

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

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(2) See, for example: (a) Evanseck, J. D.; Houk, K. N. *J. Am. Chem. Soc.* **1990,** *112,* 9148–9156. (b) Matzinger, S.; Fülscher, M. P. *J. Phys. Chem.* **1995,** *99,* 10747–10751. (c) Richards, C. A., Jr.; Kim, S.-J.; Yamaguchi, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1995,** *117,* 10104–10107.

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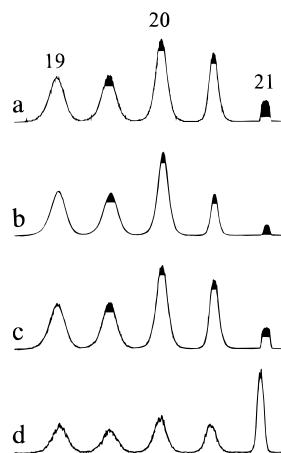(11) Burgers, P. C.; Holmes, J. K. *Org. Mass Spectrom.* **1982,** *17,* 123–126.

Figure 1. CS mass spectra of (a) ionized propene, (b) ionized cyclopropane, (c) source generated carbene radical cation, and (d) metastably generated carbene radical cation. Ion translational energies 5 kV for spectra a−c and 4.8 kV for spectrum d. Shaded areas correspond to contributions from the $^{13}CC_2H_5^+$ ions.
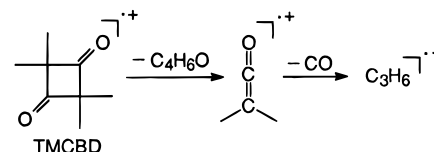
Computational Methods

Standard ab initio molecular orbital calculations[12] were carried out with the GAUSSIAN 94[13] suite of programs. Geometries were optimized and harmonic vibrational frequencies (scaled by 0.9646) were obtained at the MP2(FULL)/6-31G(d) level of theory according to the G2(ZPE=MP2) scheme.[14] G2 theory effectively corresponds to a QCISD(T)/6-311+G(3df,2p)//MP2(FULL)/6-31G(d) energy adjusted by an empirical higher level correction (HLC) and zero-point vibrational energy (ZPE). The HLC in G2(ZPE=MP2) theory is slightly different from that in standard G2 theory (5.32 mh rather than 5.00 mh per electron pair).[14] Heats of formation at 0 K ($\Delta_f H°_0$) were evaluated by the atomization method as outlined by Nicolaides et al.,[15] using experimental $\Delta_f H°_0$ values for the atoms,[16] and corrected to 298 K with the use of scaled theoretical harmonic frequencies for the species of interest and enthalpy corrections ($H°_{298} - H°_0$) for the constituent elements in their standard states evaluated by using experimental data.[17]

Results and Discussion

Experimental Findings. The electron impact mass spectrum of 2,2,4,4-tetramethyl-1,3-cyclobutanedione (TMCBD) contains a significant peak at m/z 42 (37% of the m/z 70 base peak). We find through high resolution mass spectrometry that the ion is *solely* of formula $C_3H_6^{•+}$. Unlike ionized propene and ionized cyclopropane, this ion source generated $C_3H_6^{•+}$ species displays a significant m/z 21 peak in its CS mass spectrum (Figure 1). The $C_3H_6^{•+}$ ion (m/z 42) in the mass spectrum of TMCBD

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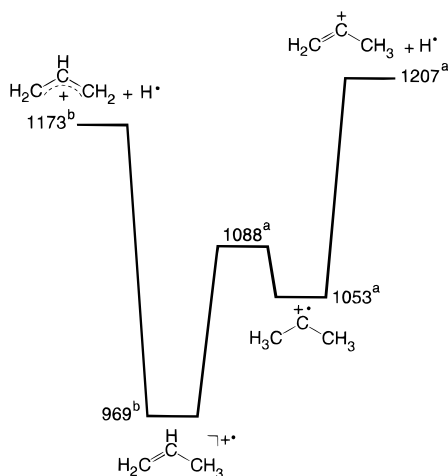
originates by loss of CO from m/z 70, which has the dimethylketene structure.[18]

The m/z 42 peak resulting from dissociation of metastable dimethylketene ions is composite, a narrow Gaussian peak atop a broad second component, showing that for metastable m/z 70 ions there are two reaction channels that lead to m/z 42. The kinetic energy releases, $T_{0.5}$, calculated from the half-height widths of the narrow and broad components of the above metastable peak are 18 and 200 meV, respectively. By selecting ions from the centroid of the narrow component and from one edge of the broad component, it was shown by a collision experiment[19] that the latter are propene ions, while the former (which we propose below to be dimethylcarbene ions) produced m/z 21 as a major signal in the charge stripping region (Figure 1d). Although ionized ketene (also m/z 42) displays a sizable m/z 21 peak in its O_2 collision induced dissociation (CID) mass spectrum,[20] the absence of m/z 29 in all our CID mass spectra rules out the generation of any $C_2H_2O^{•+}$ ions from metastable ionized dimethylketene.

The theoretical study of Lammertsma et al.[3b] concluded that the dimethylcarbene and trimethylene dications are the two most stable $C_3H_6^{2+}$ isomers. They are predicted to have comparable energies, with the propene dication lying about 50 kJ mol^{-1} higher in energy. Both the dimethylcarbene and the trimethylene dications were predicted to be observable in the gas phase. However, the likelihood of the present experiment producing the trimethylene dication is small, since an intricate rearrangement would be required.[21] We therefore propose that metastable ionized dimethylketene produces both propene and dimethylcarbene ions on the microsecond time scale. It is noteworthy that the possible production of the carbene radical cation was dismissed in favor of ionized propene in a previous mass spectrometry study of TMCBD by Olivares et al.[22] Their CID mass spectrum of the m/z 42 ion resembled that of ionized propene, but the CS region of the spectrum was not reported. This latter point is significant because, apart from the charge stripping region of the CID mass spectrum, the observations on this new ion are indeed similar to those for ionized propene and cyclopropane, so that only the doubly-charged ions provide the significant structure indicative features.

CS experiments (see Figure 1) in which the various isomeric $C_3H_6^{•+}$ ions had closely similar translational kinetic energies showed that ionized propene, even after correction for contributions from $^{13}CC_2H_5^+$ ions, produced a small, non-zero yield of $C_3H_6^{2+}$ ions.[4,7] It is possible that these are dimethylcarbene dications produced from the small fraction of propene radical cations which can isomerize to $(CH_3)_2C^{•+}$ below the dissociation limit of $CH_3CH=CH_2^{•+}$ and prior to undergoing CS. This is

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(22) Olivares, J. A.; Flesch, G. D.; Svec, H. J. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *56*, 293−305.

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Figure 2. G2 potential energy diagram for the dissociation and interconversion of propene and dimethylcarbene radical cations. All values correspond to 298 K and are in units of kJ mol^{-1}. Superscript a indicates data from this work. Superscript b indicates data from ref 23. For experimental values see text and ref 16. No attempt was made to calculate transition structures (and hence reverse barriers) for the H[•] loss reactions.

supported by the results of theoretical calculations (see below) and is illustrated in the potential energy diagram (Figure 2).

The appearance energy (AE) of m/z 42 generated at threshold from metastable m/z 70 ions was found to be 12.1 ± 0.1 eV. The AE will be an upper limit because this secondary fragmentation of ionized TMCBD is subject to a competitive shift. Using $\Delta_fH°_{298}[CO] = -110.5$ kJ mol^{-1},[16] $\Delta_fH°_{298}[TMCBD] = -308$ kJ mol^{-1},[16] and $\Delta_fH°_{298}[(CH_3)_2CCO] = -92$ kJ mol^{-1} [24] gives $\Delta_fH°[(CH_3)_2C^{•+}] \leq 1062$ kJ mol^{-1}. It should also be noted that this value could alternatively represent the energy of the transition structure for the formation of the propene radical cation component of the composite metastable peak.

We have attempted to observe the neutral carbene by neutralization−reionization (NR) mass spectrometry.[6] The ion source and metastably generated m/z 42 ions both give a significant recovery signal (>40% of base peak), showing that $C_3H_6^{•+}$ ions have been reduced to a stable neutral counterpart. However, the CS regions of the NR mass spectra failed to contain any peak at m/z 21. Moreover, a separate CS experiment on the mass selected recovery ions also failed to show m/z 21. The absence of the dication signal (42^{2+}) suggests that any neutral carbene formed (which may be generated in an excited state) was not stable on the time scale (μs) of the NR experiment and that the detected $C_3H_6^{•+}$ recovery signal is ionized propene.

Computational Findings. Calculations at the G2(ZPE=MP2) level[14] give $\Delta_fH°_{298}[(CH_3)_2C^{•+}] = 1053$ kJ mol^{-1}, consistent with the experimental upper limit of 1062 kJ mol^{-1} reported above. The $(CH_3)_2C^{•+}$ ion is predicted, at the MP2(FULL)/6-31G(d) level, to have C_2 symmetry with C−C bond lengths of 1.418 Å and a ∠CCC angle of 141.3° (Figure 3). The geometry was also optimized at the MP2/6-311+G(2df,p) and QCISD/6-31G(d) levels, and was found not to change to any significant extent (Figure 3). Scaled vibrational frequencies[25] were obtained at both the MP2(FULL)/6-31G(d) and QCISD/6-31G(d) levels and gave almost identical zero-point vibrational energy.

(24) Scott, A. P.; Radom, L. *Int. J. Mass Spectrom. Ion Proc.* **1997**, *160*, 73−81. This value, calculated at the G2 level of theory, is appreciably higher than the value in ref 16 of −134 kJ mol^{-1} which is based on an additivity estimation. Using −134 kJ mol^{-1} leads to a $\Delta_fH°_{298}$ for the carbene ion of 1104 kJ mol^{-1}.

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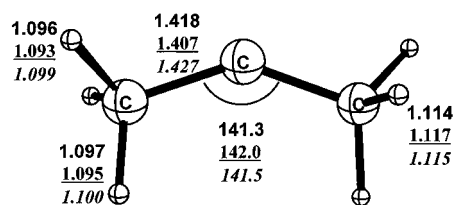
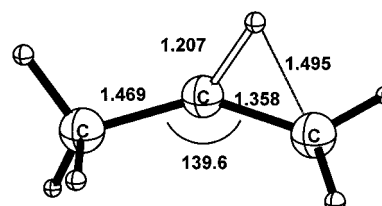**Transition Structure for 1, 2 - Hydrogen Shift**

Figure 3. Optimized geometries of dimethylcarbene radical cation and the transition structure for the 1,2-hydrogen shift connecting dimethylcarbene and propene radical cations. MP2(FULL)/6-31G(d) geometries are given in bold text. For dimethylcarbene radical cation, MP2/6-311+G(2df,p) geometries are shown in underlined text and QCISD/6-31G(d) geometries in italics. Bond lengths in Å, angles in deg.

Thus, the G2 heat of formation of $(CH_3)_2C^{•+}$ is not particularly sensitive to the level of theory used to optimize the structure or to calculate the frequencies. Previous ab initio calculations at the HF/6-31G level predicted a similar structure and energy for the dimethylcarbene radical cation.[3a]

We also calculated the $\Delta_fH°_{298}$ of the product ion resulting from H[•] loss (the 2-propenyl cation, $[CH_3C=CH_2]^+$), 989 kJ mol^{-1}, and the energy of the transition structure for the 1,2-hydrogen shift to give ionized propene, 1088 kJ mol^{-1} (Figure 2). The geometry for the transition structure is given in Figure 3. The dimethylcarbene radical cation is predicted to reside in a fairly shallow well, requiring only 35 kJ mol^{-1} for isomerization to the propene radical cation. This prediction suggests that the density of states of the propene radical cation will be much larger than that of the carbene radical cation and is consistent with the experimental observation that very little $(CH_3)_2C^{•+}$ is formed in the ion source.

Conclusion

Combined experimental and theoretical results show that ionized dimethylcarbene, $(CH_3)_2C^{•+}$, and the corresponding dication, $(CH_3)_2C^{2+}$, have been generated by using 2,2,4,4-tetramethyl-1,3-cyclobutanedione as the precursor. Experimental identification of the dimethylcarbene radical cation is based on its charge stripping mass spectrum, which contains a large m/z 21 signal, unlike the other $C_3H_6^{•+}$ isomers. G2 ab initio molecular orbital calculations show that the dimethylcarbene radical cation resides 84 kJ mol^{-1} above $CH_3CH=CH_2^{•+}$ and is separated from it by an isomerization barrier of 35 kJ mol^{-1}.