



Evidence for the production of propene ion in the gas phase. Reaction of ionized dichlorocarbene with acetone

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Abstract—Experimental evidence for the production of propene ion in the gas phase reaction of ionized dichlorocarbene with acetone is provided owing to the use of an original hybrid tandem mass spectrometer of sector–quadrupole–sector configuration. Ionized dimethylcarbene is a transient intermediate that rapidly rearranges into its more stable isomer. Relative stabilities between both isomeric forms in different electronic states are evaluated using B3LYP/6-311++G(d,p) computations. © 2001 Elsevier Science Ltd. All rights reserved.

A multi-sector mass spectrometer incorporating a radiofrequency-only quadrupole collision cell (Qcell) fitted with deceleration and re-acceleration lenses, has been designed to perform ion–molecule reactions in addition to more conventional collisional activation (CA) experiments.¹ A major advantage of such a combination is that ion–molecule reaction products can be re-accelerated and collisionally fragmented in the high translational energy regime.² Under these energy conditions, doubly-charged ions are also usually formed and detected (charge stripping spectrum, CS). It has been shown in several occasions that such multiply charged ions can be used efficiently for isomer identification, especially when conventional CA techniques fail.³

A typical example of such a situation was shown by Aubry and Holmes⁴ who differentiated dimethylcarbene ions, $(\text{CH}_3)_2\text{C}^+$, from its propene and cyclopropane ion isomers on the basis of the CS spectra. While in the former case, the $\text{C}_3\text{H}_6^{2+}$ ions form the base peak of the CS spectrum, these ions are only marginally seen (if at all) for the other isomers. In these experiments, decarbonylation of metastable dimethylketene ions was the source of the dimethylcarbene ions.⁴

Keywords: dimethylcarbene; propene; 1,2-H shifts; tandem (hybrid) mass spectrometry; ab initio calculations.

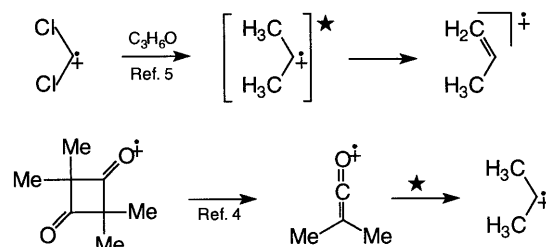
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Recently, the group of Kenttämaa⁵ described new ion–molecule reactions involving ionized dichlorocarbene and various neutral reagents making use of FT-ICR, Fourier-transform ion cyclotron resonance, experiments. Among the latter, some carbonylated compounds transfer $\text{O}^{\bullet-}$ to $\text{CCl}_2^{\bullet+}$ generating, in the case of acetone, $\text{C}_3\text{H}_6^{\bullet+}$ ions plus neutral phosgene (cf. Scheme 1). These authors⁵ proposed that a dimethylcarbene radical cation was initially formed in the reaction, but readily isomerized into the more stable propene radical cation. Nevertheless, no experimental evidence supporting this proposition has been obtained.

In this report, we set out to demonstrate that the sector–quadrupole–sector mass spectrometer can provide definitive experimental evidence for the production of propene ions in the reaction of ionized dichlorocarbene with neutral acetone.

First of all, we have repeated the experiments of Aubry and Holmes⁴ and found indeed that the m/z 21 peak in



Scheme 1.

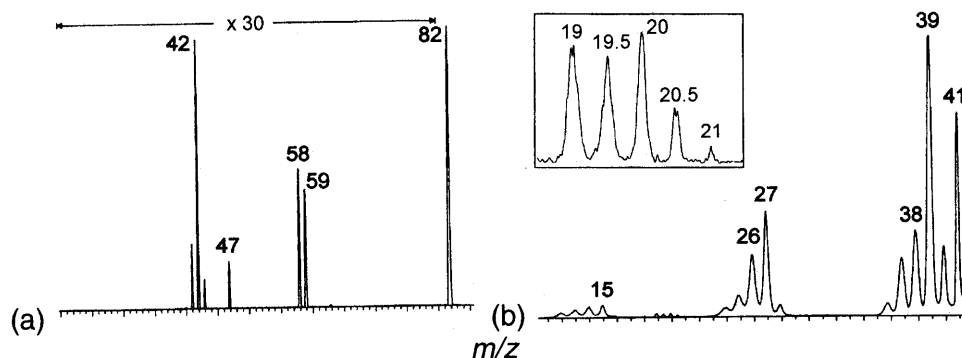


Figure 1. Ion–molecule reactions in the Qcell of dichlorocarbene ions (m/z 82) and neutral acetone. Mass spectrum (B scan) of the products (a) and CA (O_2) spectrum of the m/z 42 product ions (b).

the CS spectrum of metastably generated $C_3H_6^{*+}$ ions is significantly less intense in the case of the propene ions. This can be quantified by comparing the m/z 20: m/z 21 branching ratio of 9.4 for propene compared to 2.5 for the product of decarbonylation of dimethylketene.

The mass spectrum of the ion–molecule reaction products of mass-selected decelerated CCl_2^{*+} with acetone in the Qcell features a base peak at m/z 42 corresponding to the $O^{\bullet-}$ abstraction reaction with the production of $C_3H_6^{*+}$ ions (Fig. 1a). In contrast with the FT-ICR experimental results,⁵ other products are generated by charge exchange (m/z 58, ionized acetone) and protonation of acetone (m/z 59). The peak at m/z 47 (chlorocarbene ions) results from a collision induced dissociation process of the CCl_2^{*+} ions and the peak at m/z 43 corresponds to acetylium ions. The differences between both Qcell and FT-ICR experiments can be attributed to the absence of thermalization of the ions in the former case making observable slightly endothermic reactions.

Mass selection of the m/z 42 ions and collisional activation (O_2) in a collision cell situated in front of the last electric sector give rise to the CA spectrum depicted in Fig. 1b. The composition of the ions is clearly indicated by losses of hydrogens, and an analysis of the charge stripping region (inset of Fig. 1b) reveals that the $C_3H_6^{2+}$ ions are of reduced abundance (the m/z 20: m/z 21 branching ratio measured as ca. 8.0) thus confirming that the final product ions in the title reaction are effectively propene radical cations.

Although the energy barriers for 1,2-H shifts connecting both dimethylcarbene and propene isomers in the singlet neutral and ionized states were considered in

earlier studies,^{4,6} the reported results were not obtained at a comparable level of theory. Therefore, we have carried out ab initio quantum chemical calculations at a uniform level in order to obtain some quantitative relevant information. The relative energies derived at the B3LYP/6-311++G(d,p)+ZPE level⁷ are collected in Table 1.

A few points are worth noting: (i) in agreement with earlier studies,⁸ the neutral dimethylcarbene is found to have a singlet ground state, even though the corresponding triplet–singlet energy gap is very small, amounting to only 4 kJ/mol. Within the expected error of the computational method, both states can be regarded as quasi-degenerate; (ii) the adiabatic ionization energies of propene and dimethylcarbene are calculated to be 9.5 (experimental: 9.7 eV)⁹ and 7.5 eV, respectively. Assuming a simple systematic error of the method, a more realistic value for the carbene is about $IE_a(\text{dimethylcarbene}) = 7.7$ eV; (iii) due to a large difference of up to 2 eV between the IEs of both isomers, their energy difference becomes strongly reduced in the ionized state, thus in going from -264 kJ/mol in the singlet neutral to -73 kJ/mol in the ionized state, respectively, in favour of the propene form; (iv) as a consequence, the energy barrier for the 1,2-H shift is slightly increased upon ionization. Nevertheless, both barriers (31 kJ/mol in singlet neutral and 48 kJ/mol in ionized form; cf. Table 1) are relatively small; this is in line with the experimental fact mentioned above that the ionized carbene is likely not to survive within the time frame of an MS experiment (about 1 μ s). In addition, earlier theoretical calculations,⁵ also suggested that the collision complex between reactants apparently contains enough internal energy for incipient dimethylcarbene ion to overcome the small barrier seen above to

Table 1. Relative energies (kJ/mol) of dimethylcarbene, propene and transition state in the ionized state, the neutral singlet state and the neutral triplet state (B3LYP/G-311++G(d,p)+ZPE calculations)

State	Dimethylcarbene	Transition state (1,2-H shift)	Propene
Radical cation	0	48	-73
Singlet neutral	0	31	-264
Triplet neutral	0	175	-23

produce its more stable propene ion isomer; (v) in contrast, the carbene becomes much stabilized in the triplet neutral state, as indicated either by the relative stability (–23 kJ/mol) or the energy barrier (175 kJ/mol). These results suggest that if generated in this higher spin state (for example following a neutralization of the ion) the triplet neutral dimethylcarbene should be detectable.

In summary, the usefulness of a hybrid mass spectrometer of sector–quadrupole–sector configuration is highlighted in the present experiments, which demonstrates that propene radical cations are produced in the gas phase reaction of ionized dichlorocarbene with acetone.

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