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Rearrangement of phenylcarbene radical cation to dehydrotropylium cation

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Abstract

Dichlorocarbene radical cation reacts with benzaldehyde in the gas phase by oxygen radical anion abstraction, generating a new carbene radical cation population. The ion population consists of two isomeric carbene radical cations. Molecular orbital calculations, diagnostic ion-molecule reactions, and examination of ion-molecule reactions' kinetics and thermochemistry were utilized to elucidate the structures (phenylcarbene radical cation and dehydrotropylium cation), provide the relative abundances (20% and 80%, respectively) and propose a likely mechanism for the formation of the two isomeric carbene radical cations. A single potential energy surface was found to explain the formation of both carbene radical cations. Oxygen radical anion abstraction followed by prompt dissociation of the collision complex leads to the formation of the phenylcarbene radical cation. However, in a longer-lived collision complex, the phenylcarbene radical cation can rearrange to a more stable isomer, the dehydrotropylium cation.

Keywords: Phenyl carbene; Radical cation; Dehydrotropylium; Rearrangement

1. Introduction

The isomerization of arylcarbenes has fascinated chemists for many years. One of the most studied isomerization reactions is that of the prototypical arylcarbene, phenylcarbene [1–11]. Empirical evidence for the rapid isomerization of phenylcarbene to a ring-expanded form was first reported over three decades ago [6]. Much later, high-level ab initio molecular orbital calculations were used to help identify this intermediate as cycloheptatetraene and to provide insights into the mechanism of the rearrangement [7,9,10]. More recently, the negative ion analog of the neutral phenylcarbene, phenylcarbene radical anion, was experimentally and theoretically examined [12]. Experimental studies on the phenylcarbene radical anion have shown it to be stable toward rearrangement to cycloheptatetraene anion, and to be isolatable in isomerically pure form [12]. In contrast to the detailed reports involving the synthesis and structural characterization of the neutral and anionic phenylcarbenes, very little has been reported on the cationic form of this species, the phenylcarbene radical cation. In fact, in the few studies where C_7H_6 radical cations have been generated, the actual structure and isomeric purity of the ions have remained elusive [13,14].

A simple method has been previously introduced for the generation of carbene radical cations via $O^{\bullet -}$ abstraction from carbonyl compounds by the easily generated dichlorocarbene radical cation in a Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer [14]. In addition, it was shown that $O^{\bullet -}$ abstraction from benzaldehyde generates C_7H_6 radical cations which possess reactivity characteristic of carbene radical cations. However, the structure of these radical cations remained unclear [14,15]. Mechanistically, phenylcarbene radical cation is the most likely isomer to be generated upon $O^{\bullet -}$ abstraction by dichlorocarbene radical cation. Yet, the possibility of rearrangement into other $C_7H_6{}^{+\bullet}$ isomers cannot be ignored. The present study explores the structure of the radical cations formed upon $O^{\bullet -}$ abstraction from benzaldehyde by dichlorocarbene radical cation.

2. Experimental

All experiments were performed using a 3 T Extrel model FTMS 2001 dual cell FT-ICR mass spectrometer equipped with

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a Finnigan Odyssey data station and inlets for introduction of solid, liquid and gaseous reagents. One of the main features of this instrument is that it contains a differentially pumped dual cell [16]. The dual cell feature allows for one cell region to be used for ion generation while the other is used for ion–molecule reactions and detection. The two cells share a common central trap plate that can be temporarily held at 0 V, allowing ions to be transferred from one cell into the other through a 2 mm hole in the center of this plate. Prior to transfer, quadrupolar axialization (QA) was used for radial ion cloud compression to increase the efficiency of the ion transfer event [17].

The carbene radical cation was generated as described in the literature [14]. The ion population was isolated from unwanted ions via a series of stored-waveform inverse Fourier transform [18] (SWIFT) excitation pulses. The desired ions were transferred into the other cell where they were cooled by multiple collisions with argon pulsed into the cell ($\sim 5 \times 10^{-7}$ Torr nominal peak pressure) and IR photon emission (1 s) [19]. The structure and the reactivity of the ions was probed by subsequent ion-molecule reactions with selected neutral reagents present at a static pressure of about 6×10^{-8} Torr (nominal pressure measured by an ion gauge). All spectra were subjected to background subtraction. The background spectra were generated by SWIFT ejection of the ion population of interest prior to the reaction.

Ion–molecule reaction efficiencies (the fraction of collisions leading to reaction; a reaction with an efficiency of 0.5 occurs at every second collision) are obtained by dividing the second-order rate constant of a reaction ($k_{reaction}$) by the theoretical collision rate constant ($k_{collision}$), and are given as $k_{reaction}/k_{collision}$. The second-order reaction rate constants ($k_{reaction}$) were extracted from the plot of the relative abundance of the reactant ion over time. The theoretical collision rate constants ($k_{collision}$) were calculated using a parameterized trajectory theory [20]. Ion gauges were used to measure the reagent pressures needed for the derivation of the second-order reaction rate constants ($k_{reaction}$). The pressure readings were corrected for the sensitivity of the ion gauge toward each neutral reagent [21] and its distance from the center of the ICR cell [22].

All computational results reported in this work were calculated with the Gaussian 98 suite of programs [23]. Geometry optimizations and vibrational frequency calculations involving diiodocarbene radical cation were performed at the B3LYP/LANL2DZdp level of theory. Calculations of all other systems were performed at the B3LYP/AUG-cc-pVDZ level of theory. All stationary points were verified by vibrational frequency analysis to possess the correct number of imaginary frequencies: 0 for minima, 1 for transition states. All theoretical energies correspond to 0 K and include zero-point vibrational energy corrections.

3. Results and discussion

3.1. Determination of the presence of multiple isomers

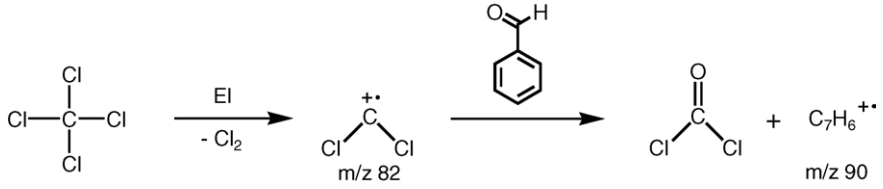
The C_7H_6 radical cation population was formed by $O^{\bullet -}$ abstraction from benzaldehyde by dichlorocarbene radical cation (Scheme 1) in a FT-ICR mass spectrometer. Under the conditions employed (a small number of analyte ions relative to that of the neutral reagent molecules), the reactions of an isomerically pure ion population should follow pseudo-first-order reaction kinetics. However, the kinetics data obtained for the reaction of $C_7H_6^{+\bullet}$ with some reagents (cyclohexane: 100% hydrogen atom abstraction; toluene: 100% addition accompanied by loss of the methyl radical; benzylchloride: 100% addition accompanied by loss of a chlorine atom) do not fit a simple pseudo-first-order kinetics model. For example, although the carbene ion population reacts completely away with cyclohexane by hydrogen atom abstraction, one portion of the ion population reacts faster than the other. This finding provides evidence for the presence of at least two distinct ionic species that react to form $C_7H_7^+$. When the kinetics data were fit to a model consisting of multiple concurrent parallel reactions, the carbene ion population was found to consist of two carbene radical cation isomers. Therefore, the kinetics data for these reactions takes the form of two concurrent pseudo-first order reactions (Eq. (1)).

$$\frac{[A_1]_t + [A_2]_t}{[A_1]_0 + [A_2]_0} = \frac{[A_1]_0}{[A_1]_0 + [A_2]_0} \exp(-k_1 t) + \frac{[A_2]_0}{[A_1]_0 + [A_2]_0} \exp(-k_2 t) \quad (1)$$

The relative abundances of the ionic isomers, represented by $[A_1]$ and $[A_2]$, and the corresponding second-order reaction rate constants, k_1 and k_2, were extracted by fitting the data with Eq. (1). This analysis revealed that the more reactive ion (efficiency = 5.2%) makes up 80% of the ion population while the less reactive ion (efficiency = 0.3%) makes up 20% of the ion population (Fig. 1).

3.2. Computational evaluation of possible ion structures

Although kinetics analysis shows the presence of two distinct ionic species and provides the relative abundance of each,



Scheme 1.

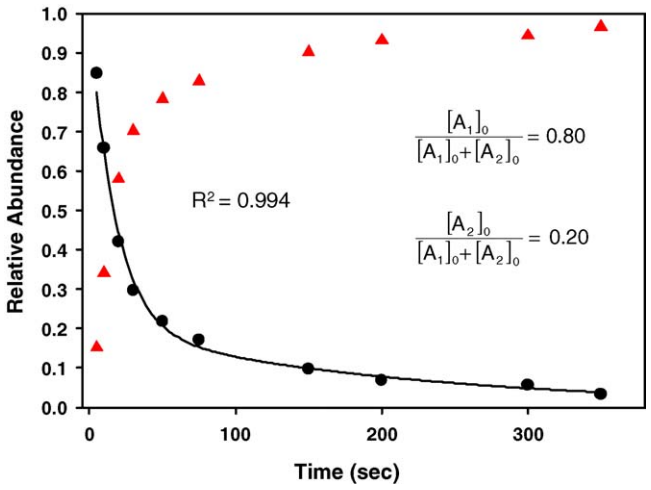


Fig. 1. Kinetics data for reaction of $C_7H_6^{+\bullet}$ with cyclohexane fit with Eq. (1). Circles represent the carbene radical cation mixture, and the triangles represent the hydrogen atom abstraction product (tropylium and benzyl cation).

the structures of the two isomeric ions remain unknown. Molecular orbital calculations were performed at the B3LYP/AUG-cc-pVDZ level of theory to evaluate the relative energies of nine C_7H_6 radical cation structures (Fig. 2). Three structures were found to be significantly lower in energy than the other six; 2-dehydrobenzyl cation, phenylcarbene radical cation and dehydrotropylium cation. Phenylcarbene radical cation and 2-dehydrobenzyl cation were found to be nearly isoenergetic (the phenylcarbene radical cation is 0.5 kcal/mol more stable) and about 12 kcal/mol above the dehydrotropylium cation.

The simplest mechanism that can be proposed for the $O^{\bullet -}$ abstraction from benzaldehyde by dichlorocarbene radical cation leads to the generation of the phenylcarbene radical cation and phosgene (Scheme 2). Therefore, it is likely that the mechanism for the formation of the other ionic isomer involves a phenylcarbene radical cation intermediate. The formation of 2-dehydrobenzyl cation from phenylcarbene radical cation requires a 1,3-hydrogen atom shift which is associated with a very high barrier of 41.9 kcal/mol (calculated at the B3LYP/AUG-cc-pVDZ level of theory; Fig. 3). The maximum amount of energy available to drive unimolecular rearrangement of the phenylcarbene radical cation to 2-dehydrobenzyl cation is equal to the exothermicity of the phenylcarbene radical cation synthesis. Since the exothermicity of this synthesis was calculated to be 36.5 kcal/mol (B3LYP/AUG-cc-pVDZ level of theory; Scheme 3), formation of the 2-dehydrobenzyl cation from isolated phenylcarbene radical cation is unlikely. The observation that an even lower-energy synthesis method

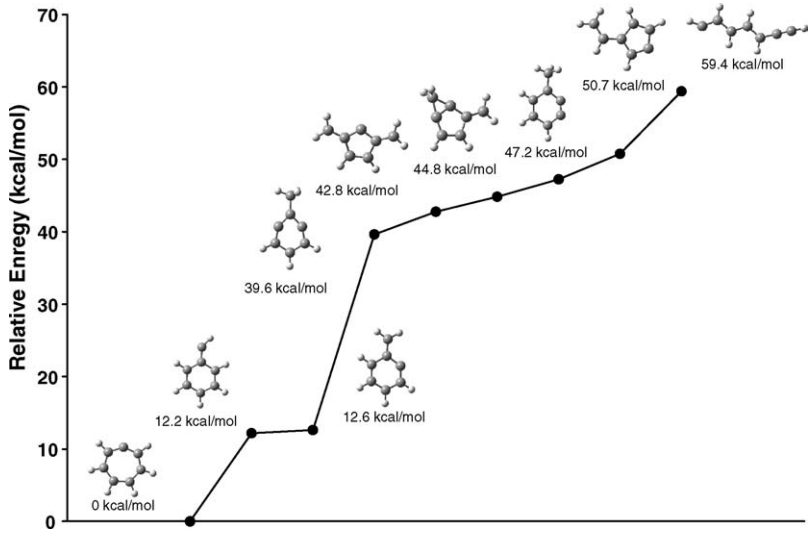
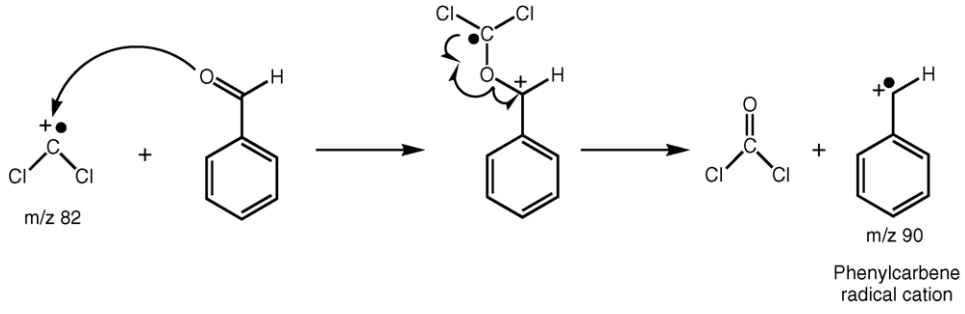


Fig. 2. Relative energies of possible C_7H_6 radical cation isomers calculated at the B3LYP/AUG-cc-pVDZ level of theory.



Scheme 2.

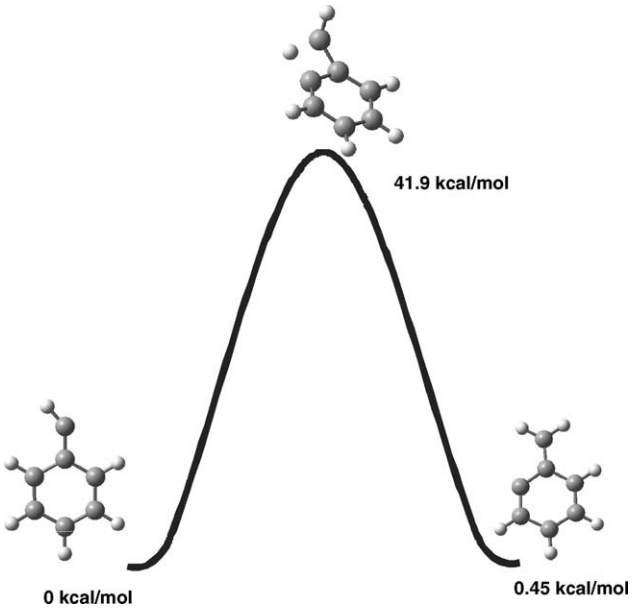


Fig. 3. Potential energy surface calculated at the B3LYP/AUG-cc-pVDZ level of theory for the rearrangement of phenylcarbene radical cation to 2-dehydrobenzyl cation.

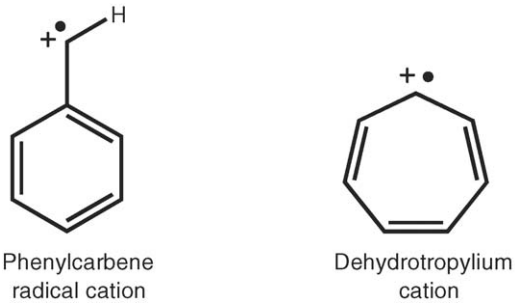
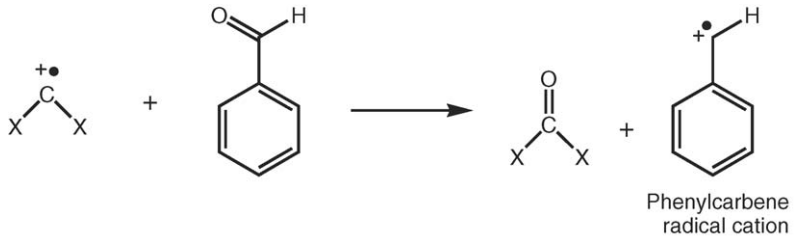


Fig. 4. The two likely structures of the C_7H_6 carbene radical cation.

(exothermicity 12.6 kcal/mol; these results are discussed in the next section) results in isomerization rules out this structure. The two remaining structures, phenylcarbene radical cation and dehydrotropylium cation (Fig. 4), were considered further.

3.3. Elucidation of the likely mechanism of carbene radical cation formation

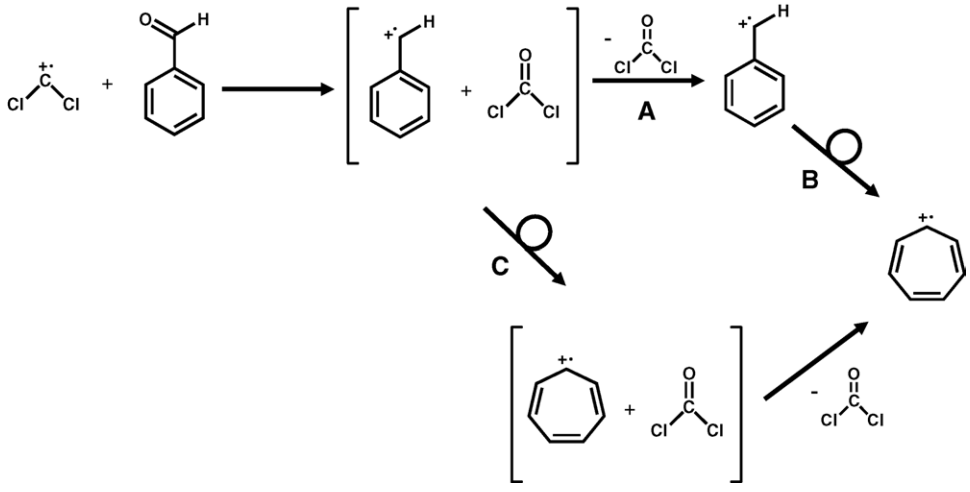
The simplest pathways for the formation of the dehydrotropylium cation involve unimolecular rearrangement of the



If X = Cl, reaction exothermicity = 36.5 kcal/mol

If X = I, reaction exothermicity = 12.6 kcal/mol

Scheme 3.



Scheme 4.

phenylcarbene radical cation after its formation and release from the collision complex (path B in Scheme 4), and rearrangement within the collision complex (path C in Scheme 4). The viability of the unimolecular rearrangement mechanism (path B in Scheme 4) was probed computationally by calculating the potential energy surface (PES) for this rearrangement process (Fig. 5). Based on these calculations, the phenylcarbene radical cation requires at least 19.2 kcal/mol to rearrange to dehydrotropylium cation. The calculated exothermicity of $O^{\bullet -}$ abstraction from benzaldehyde by dichlorocarbene radical cation (Scheme 3) is 36.5 kcal/mol, as mentioned above. Therefore, the newly generated phenylcarbene radical cation is expected to have more than enough energy to undergo rearrangement into dehydrotropylium cation (pathway B in Scheme 4). The existence of this pathway can be probed experimentally by adjusting the thermochemistry of the $O^{\bullet -}$ abstraction reaction such that the phenylcarbene radical cation does not have enough energy to undergo unimolecular rearrangement outside the collision complex. Computations at the B3LYP/LANL2DZdp level of theory predict that $O^{\bullet -}$ abstraction from benzaldehyde by diiodocarbene radical cation (accessible by EI of carbon tetraiodide) is only 12.6 kcal/mol exothermic (Scheme 3). Therefore, this method of $C_7H_6^{+\bullet}$ synthesis does not provide enough energy to phenylcarbene radical cation to surmount the barrier to rearrangement, as depicted in Fig. 5 (this eliminates pathway B in Scheme 4). Nevertheless, $C_7H_6^{+\bullet}$ generated via this synthetic procedure was found to display similar reaction kinetics as $C_7H_6^{+\bullet}$ generated from dichlorocarbene radical cation (deviation from the simple pseudo-first-order kinetics model), thus providing evidence for the presence of two carbene ion isomers. Hence, pathway B (and the 2-dehydrobenzyl cation structure) can be ruled out.

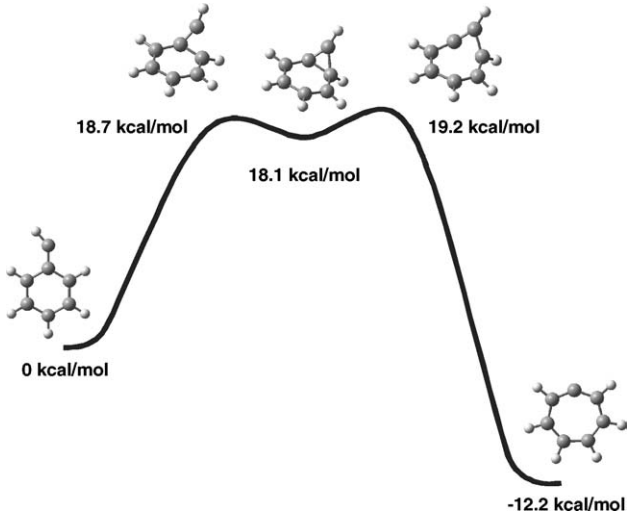


Fig. 5. Potential energy surface calculated at the B3LYP/AUG-cc-pVDZ level of theory for the rearrangement of phenylcarbene radical cation to dehydrotropylium cation (via pathway B shown in Scheme 3).

The mechanism for the formation of the dehydrotropylium cation by rearrangement of the phenylcarbene radical cation in the collision complex with phosgene after the $O^{\bullet -}$ abstraction from benzaldehyde by dichlorocarbene radical cation (pathway C, Scheme 4) was examined computationally by constructing a PES for the reaction (B3LYP/AUG-cc-pVDZ level of theory; Fig. 6). This computational investigation revealed that the mechanism for the rearrangement of the phenylcarbene radical cation in the collision complex is identical to the unimolecular rearrangement mechanism (Fig. 5). However, if the isomerization takes place in the complex of the carbene radical cation and

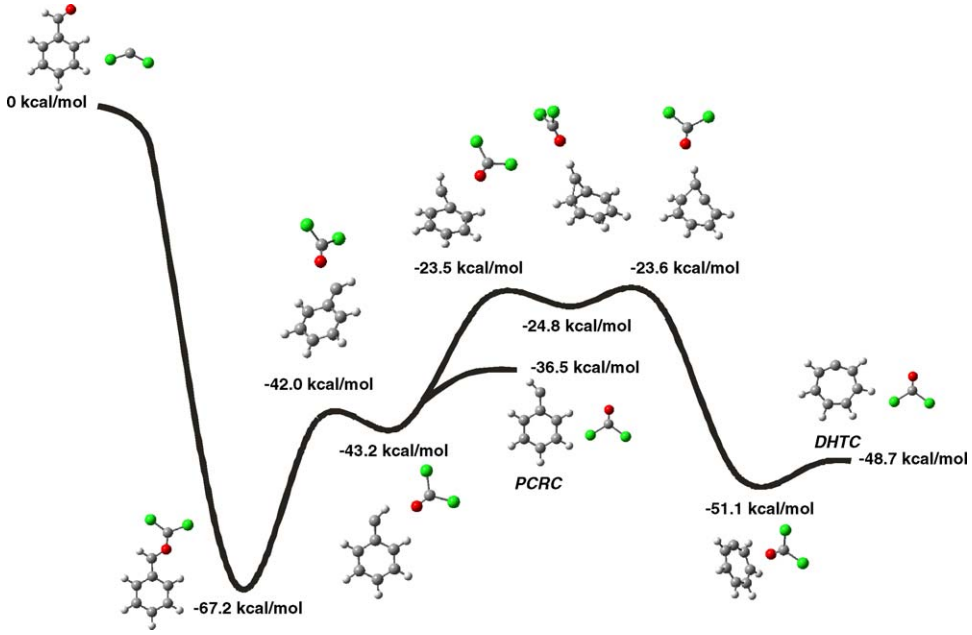
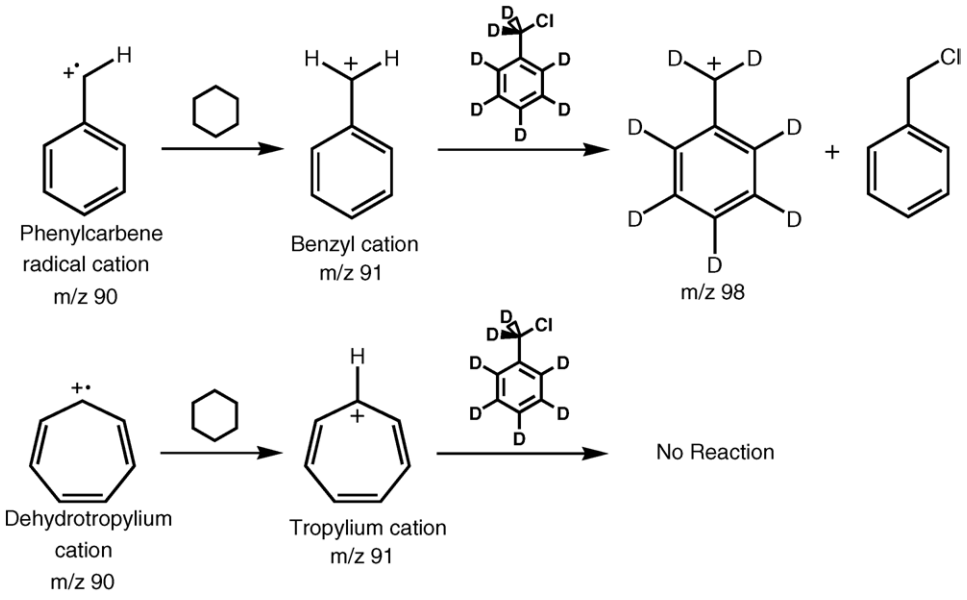


Fig. 6. Potential energy surface calculated at the B3LYP/AUG-cc-pVDZ level of theory for the isomerization of the phenylcarbene radical cation (formed via pathway A; Scheme 4) to the dehydrotropylium cation within the complex with phosgene (via pathway C; Scheme 4). For comparison, the left side of the surface shows the isolated carbene radical cation and phosgene whose formation is exothermic by 36.5 kcal/mol (in reality, the molecules don't exit the complex before rearrangement).



Scheme 5.

phosgene, then solvation energy is available to overcome barriers to rearrangement, in addition to the exothermicity of the reaction that formed the carbene radical cation, Hence, this reaction pathway is thermochemically feasible (Fig. 6). This pathway provides an explanation for the presence of two distinct $C_7H_6^{+\bullet}$ isomers (phenyl carbene radical cations that exited the collision complex before rearrangement, and those that rearranged to the dehydrotropylium cation) even when generated via a low-energy synthetic method ($O^{\bullet -}$ abstraction from benzaldehyde by diiodocarbene radical cation).

3.4. Structure elucidation of the carbene radical cations

The above evidence suggest that diiodocarbene and dichlorocarbene radical cations react with benzaldehyde to form the phenylcarbene radical cation which sometimes undergoes isomerization to dehydrotropylium cation. Interestingly, the two C_7H_6 radical cations (referred to as A_1 and A_2 below) generated from diiodocarbene radical cation are formed in different relative abundances than when the dichlorocarbene radical cation is used. For example, analysis of the kinetics of the reaction of benzylchloride with $C_7H_6^{+\bullet}$ (100% addition accompanied by the loss of a chlorine atom; this reaction pathway was verified by the use of polydeuterated benzylchloride) generated from diiodocarbene radical cation reveals that $[A_1] = 52\%$ and $[A_2] = 48\%$, as apposed to 19% and 81%, respectively, for $C_7H_6^{+\bullet}$ generated from dichlorocarbene radical cation. Since the exothermicity of $C_7H_6^{+\bullet}$ synthesis using the diiodocarbene radical cation is lower than when using the dichlorocarbene radical cation, less rearrangement may be expected for the initially formed phenylcarbene radical cation. This should result in an increase in the relative abundance of the phenylcarbene radical cation relative to that of the dehydrotropylium cation. These considerations suggest that ion A_1 represents the phenylcarbene radical cation and ion A_2 represents the dehydrotropylium cation.

Further support for this assignment was obtained by converting the carbene radical cations into more stable even-electron cations. This can be accomplished by allowing the aromatic carbene radical cations (generated from dichlorocarbene radical cation) to abstract a hydrogen atom from cyclohexane, thus converting the phenylcarbene radical cation and dehydrotropylium cation into benzyl and tropylium cations, respectively (Scheme 4). Two methods have been demonstrated to be successful in the differentiation between benzyl cation and tropylium cation [24,25]. One of these methods involves the reaction with benzylchloride. Benzylchloride transfers chloride anion only to the benzyl cation (Scheme 5; perdeuterated benzylchloride was used to verify that the reaction indeed is hydride transfer from benzyl chloride to the carbene radical cation rather than chloride anion transfer from benzyl chloride to the carbene radical cation). No chloride transfer was observed here, indicating the presence of only tropylium cation (suggesting that dehydrotropylium cation was present prior to the hydrogen atom abstraction from cyclohexane). Yet, this result conflicts with the observation of two distinct carbene ion populations upon kinetics analysis. However, the undertaking of this experiment proved difficult due to the extensive ion processing involved in the many reaction and isolation events leading up to the halide transfer reaction. This resulted in a low signal-to-noise ratio, thus making interpretation of the experimental results difficult. However, this experiment does indicate that the most abundant carbene radical cation isomer (ion A_2; dichlorocarbene radical cation precursor) is the dehydrotropylium cation while the lower abundance isomer (ion A_1), the phenylcarbene radical cation, is believed to have been lost during the extensive ion processing. Therefore, the lack of halide transfer for the C_7H_7 ion population, along with the increase in the abundance of ion A_1 when diiodocarbene instead of dichlorocarbene radical cation was used to generate $C_7H_6^{+\bullet}$, strongly suggest that the more reactive ion, A_1, is phenylcarbene radical

cation and that the less reactive ion, A_2, is dehydrotropylium cation.

4. Conclusions

$O^{\bullet -}$ abstraction from benzaldehyde by dichlorocarbene radical cation generates a mixture of carbene radical cation isomers and phosgene. Examination of the kinetics of reactions of this mixture revealed the presence of two carbene radical cation isomers, one representing 80% and the other 20% of the ion population. Molecular orbital calculations predict the likely structures of the isomeric species to be phenylcarbene radical cation and dehydrotropylium cation. Evidence obtained from the examination of ion–molecule reaction thermochemistry and the potential energy surfaces calculated for the ion synthesis suggest that the phenylcarbene radical cation is generated initially. Some of the phenyl carbene radical cations exit the product complex to release phosgene and the phenyl carbene radical cation, but others undergo isomerization to the dehydrotropylium cation while still being solvated by phosgene. The observed increase in the relative abundance of the less abundant carbene radical cation when a less exothermic method was used to form the phenylcarbene radical cation mixture provides support for the identity of that ion being the phenylcarbene radical cation. The lack of halide transfer for the C_7H_7 radical cations (generated by hydrogen atom abstraction from cyclohexane by the isomeric $C_7H_6{}^{+\bullet}$ cations) from perdeuterated benzylchloride strongly suggests that the more abundant and slower reacting ion is the dehydrotropylium cation.

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References

[1] W.D. Crow, M.N. Paddon-Row, J. Am. Chem. Soc. 94 (1972) 4746.
[2] W.D. Crow, M.N. Paddon-Row, Aust. J. Chem. 26 (1973) 1705.
[3] M.J.S. Dewar, D. Landman, J. Am. Chem. Soc. 99 (1977) 6179.
[4] P.P. Gaspar, J.P. Hsu, S. Chari, M. Jones Jr., Tetrahedron 41 (1985) 1479.
[5] C.M. Geise, C.M. Hadad, J. Org. Chem. 67 (2002) 2532.
[6] R.C. Joines, A.B. Turner, W.M. Jones, J. Am. Chem. Soc. 91 (1969) 7754.
[7] S. Matzinger, T. Bally, E.V. Patterson, R.J. McMahon, J. Am. Chem. Soc. 118 (1996) 1535.
[8] S. Matzinger, T. Bally, J. Phys. Chem. A 104 (2000) 3544.
[9] E.V. Patterson, R.J. McMahon, J. Org. Chem. 62 (1997) 4398.
[10] P.R. Schreiner, W.L. Karney, P.V.R. Schleyer, W.T. Borden, T.P. Hamilton, H.F. Schaefer III, J. Org. Chem. 61 (1996) 7030.
[11] M.W. Wong, C. Wentrup, J. Org. Chem. 61 (1996) 7022.
[12] R.A. Seburg, B.T. Hill, R.R. Squires, J. Chem. Soc.: Perkin Trans. 2 (1999) 2249.
[13] H.E. Audier, J.F. Dupin, M. Fétison, Y. Hoppilliard, Tetrahedron Lett. 19 (1966) 2077.
[14] E.D. Nelson, S.E. Tichy, H.I. Kenttämaa, J. Chem. Soc.: Perkin Trans. 2 (1999) 2267.
[15] R. Flammang, M.T. Nguyen, G. Bouchoux, P. Gerbaux, Int. J. Mass Spectrom. 202 (2000) A8.
[16] D.P. Littlejohn, S. Ghaderi, U.S. Patent 4,581,533, 1986.
[17] L. Schweikhard, S. Guan, A.G. Marshall, Int. J. Mass Spectrom. Ion Process. 120 (1992) 71.
[18] A.G. Marshall, T.C.L. Wang, L. Chen, T.L. Ricca, ACS Symp. Ser. 359 (1987) 21.
[19] R.C. Dunbar, Mass Spectrom. Rev. 11 (1992) 309.
[20] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.
[21] J.E. Bartmess, R.M. Georgiadis, Vacuum 33 (1983) 149.
[22] M.A. Watkins, J.M. Price, B.E. Winger, H.I. Kenttämaa, Anal. Chem. 76 (2004) 964.
[23] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Buran, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Revision A.9, Gaussian 98, Pittsburgh, PA, 1998.
[24] J.L.M. Abbound, W.J. Hehre, R.W. Taft, J. Am. Chem. Soc. 98 (1976) 6072.
[25] J. Shen, R.C. Dunbar, G.A. Olah, J. Am. Chem. Soc. 96 (1974) 6227.