Gas-phase reactions of the dichlorocarbene radical cation

Eric D. Nelson, Shane E. Tichy and Hilkka I. Kenttämaa

Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393, USA

Received (in Cambridge, UK) 17th May 1999, Accepted 3rd September 1999

The gaseous dichlorocarbene radical cation is reported to behave as a highly reactive electrophile rather than a radical toward various organic substrates in a Fourier-transform ion cyclotron resonance mass spectrometer. For example, the carbene ion reacts with alkyl halides (R–X) *via* fast electrophilic addition to form a covalently bonded, internally excited intermediate $Cl_2C–X–R^{+\bullet}$. The intermediate fragments either homolytically or heterolytically to produce net halogen atom or halide ion transfer products, respectively. The observed ionic reaction product is determined by the ionization energies of the two possible neutral fragments ($CCl_2X^\bullet$ and $R^\bullet$). The fragment with the lower ionization energy preferentially retains the charge. Most reactions observed for heteroatom-containing organic compounds also appear to follow this electrophilic addition–elimination mechanism. In some cases, addition of carbonyl compounds to the carbene ion is followed by homolytic cleavage of the C–O bond to yield a new carbene radical cation.

Introduction

In sharp contrast to the extensive chemical studies carried out on neutral carbenes,[1] the chemical properties of carbene radical cations are largely unexplored.[2] High level *ab initio* molecular orbital calculations suggest the $^2A_1$ ground state for $H_2C^{+\bullet}$, *i.e.*, this radical cation is predicted to be a $\sigma^\bullet/\pi^+$ species (the $^2B_1$ or $\sigma^+/\pi^\bullet$ state was estimated to lie ~20 kcal mol^{-1}[3] higher in energy).[4] Similarly, the diphenylcarbene radical cation has been demonstrated spectroscopically to have the $\sigma^\bullet/\pi^+$ ground state.[5] The spatial separation of spin and charge in these carbene radical cations is expected to result in radical as well as electrophilic reactivity.[2,5] Indeed, a recent examination of the reactions of the bis(*p*-methylphenyl)carbene radical cation revealed both types of reactivity, though electrophilic reactivity was more prevalent.[6]

While carbene radical cations are a fairly new field of study in condensed phases, they have an established history in mass spectrometry. Several species have been generated in the gas phase and identified based on dissociation reactions, including $HCOH^{+\bullet}$,[7] $HOCOH^{+\bullet}$,[8–10] $H_2NCNH_2^{+\bullet}$,[11] $CH_3COH^{+\bullet}$,[12,13] $CH_3OCOH^{+\bullet}$,[12] $FCOH^{+\bullet}$,[14] and $CH_3CCH_3^{+\bullet}$.[15] However, the reactivity of these carbene radical cations was not examined.[16]

We report here a survey of the reactions of the gaseous dichlorocarbene radical cation studied using Fourier-transform ion cyclotron resonance mass spectrometry. The observations are readily explained by a single electrophilic addition–elimination mechanism.

Experimental

Two different Fourier-transform ion cyclotron resonance mass spectrometers (FT/ICR) were used in this study. Both instruments have been described previously.[17,18] Preliminary experiments were performed in a custom-built, single-cell FT/ICR donated by Finnigan FT/MS. More detailed examination of the reactions was carried out in an Extrel FT/MS 2001. This instrument[17] contains a differentially pumped dual cell. Hence, two independent regions can be used for chemical reactions, which provides considerable flexibility in the experimental sequence. Carbon tetrachloride was introduced at a nominal pressure of approximately 6.0×10^{-8} Torr into one side of the dual cell using an Andonian leak valve. Electron ionization yielded the dichlorocarbene radical cation. This ion was transferred into the other side of the dual cell and kinetically and vibrationally cooled for 300 ms by multiple collisions with neutral argon that was introduced into the cell *via* a pulsed valve inlet (peak pressure in the cell $\sim 1.0 \times 10^{-5}$ Torr). The dichlorocarbene radical cation was isolated by ejecting all unwanted ions from the cell through the application of a series of SWIFT (stored-waveform inverse Fourier transform[19]) excitation pulses to the excitation plates of the cell (Extrel SWIFT module). The ions were allowed to undergo reactions for a variable period of time (typically eight data points were collected between 0.1 to 5 s) with a neutral reagent present at a constant nominal pressure of about 6.0×10^{-8} Torr. All reaction spectra are the average of at least 30 transients and were background corrected using a previously reported procedure.[20c]

Experiments in the custom-built instrument[18] were constrained by the presence of only one cell. To compensate for the lack of separate ion generation and reaction regions, carbon tetrachloride was introduced *via* pulsed valves at a nominal peak pressure of 2×10^{-6} Torr in the presence of a much lower constant pressure of the neutral reagent to be studied. The dichlorocarbene radical cation was produced by electron ionization during the carbon tetrachloride pulse. After a short delay of approximately one second to allow the neutral carbon tetrachloride to pump out of the cell, the radical cation was isolated by applying a series of radio frequency sweeps to the excitation plates of the cell.

Reactions studied under the conditions described above follow pseudo-first-order kinetics. The second-order rate constants (k_{reaction}) of some of the reactions were derived from the semilogarithmic plot of the relative abundance of the reactant ion *versus* time. The collision rate constants (k_{coll}) were calculated by using a parameterized trajectory theory.[21] The reaction efficiencies (the fraction of collisions leading to reaction) are given as $k_{\text{reaction}}/k_{\text{coll}}$. The pressure readings were corrected for the sensitivity of the ion gauge toward each neutral reagent.[22] Primary products were identified based on their fixed relative abundances (branching ratios) at short reaction times.

The energies of various stationary points on the potential energy surfaces of two reactions were calculated with the use of GAUSSIAN94.[23] Optimized geometries, vibrational frequencies, and zero-point vibrational energies were calculated at the HF/6-31G(d,p) level of theory. Since Hartree–Fock calculations are known to overestimate vibrational frequencies, the zero point energies were scaled by a factor of 0.9181.[24] A better

Table 1 Reactions of the dichlorocarbene radical cation with various halogenated compounds

Neutral reagent (mol. wt.)	Ionization energy of the neutral reagent/ eV[a]	Observed product ions[b] m/z (%)	Reaction
tert-Butyl iodide (184)	9.0	57 (34)	I^- abstraction
		184 (66)	Electron abstraction
2-Iodopropane (170)	9.2	43 (69)	I^- abstraction
		170 (31)	Electron abstraction
Allyl iodide (168)	9.3	168 (47)	Electron abstraction
		209 (53)	$I^\bullet$ abstraction
Carbon tetrabromide (328)	10.3	249 (100)	Br^- abstraction
Dibromodichloromethane (240)	10.4	117 (8)	$Cl^\bullet$ abstraction
		205 (19)	Cl^- abstraction
		161 (73)	$Br^-/Br^\bullet$ abstraction[c]
Bromine (158)	10.5	161 (100)	$Br^\bullet$ abstraction
Bromoform (250)	10.5	161 (100)	$Br^\bullet$ abstraction
Methylene chloride (84)	11.3	117 (100)	$Cl^\bullet$ abstraction
Carbon tetrachloride (152)	11.5	117 (100)	$Cl^\bullet/Cl^-$ abstraction[c]
Hexachloroacetone (262)	12.0	117 (100)	$Cl^\bullet$ abstraction

[a] Ref. 25. [b] Only primary reaction products and most abundant isotopes are listed. [c] Both product fragments have the same chemical formula.

estimate for the relative energies was obtained by single point calculations at the MP2/6-31G(d,p) level of theory corrected by the scaled Hartree–Fock zero-point energy. All structures were determined to be local energy minima at the HF/6-31G(d,p) level of theory based on the absence of imaginary frequencies.

The above theoretical procedure was anchored to experiment to estimate the ionization energy (IE) of reaction intermediates for which no experimental values exist. In this method, a thermochemical cycle is constructed in which an electron is transferred between each target molecule and a similar molecule (CCl_3 or HCO) for which an experimental IE value[25] exists. The derived difference in IE between reference and target is added to the experimentally determined IE of the reference compound to provide an improved estimate for the IE of the target compound. This procedure is analogous in philosophy to the use of an isodesmic reaction,[26] and has the net effect of correcting for systematic errors in the calculations (in this case, an underestimation of the IE's by ~0.3 eV).

Results and discussion

The dichlorocarbene radical cation may be expected to react either like a σ-radical (*e.g.*, by abstracting monovalent atoms) or like a carbocation (*e.g.*, by electrophilic addition). Products corresponding to both reactions were observed. However, various pieces of evidence suggest that both products arise *via* the same mechanism, *i.e.*, electrophilic addition followed by heterolytic or homolytic bond cleavage in the covalently bonded adduct.

$X^\bullet$ and X^- abstraction

$CCl_2^{+\bullet}$ reacts with alkyl halides by net-halide and net-halogen atom abstraction (also electron transfer occurs for neutral reagents with ionization energies of 9.5 eV and below[27]). For example, $CCl_2^{+\bullet}$ abstracts a halide anion from *tert*-butyl iodide, 2-iodopropane, and carbon tetrabromide, and a halogen atom from methylene chloride, allyl iodide, and bromoform (Table 1). All reactions occur rapidly (*i.e.*, a significant fraction of collisions result in product formation), but generally only one of the two reactions is observed for a given alkyl halide. When only one reaction is observed, it is the more exothermic of the two.

Halide-abstraction is a familiar gas-phase reaction between carbocations and alkyl halides.[28,29] The reaction proceeds by the facile formation of a dialkylhalonium ion intermediate (Fig. 1). This intermediate is internally excited and fragments at one of the R–X bonds to either regenerate the reactants or form a new carbocation and alkyl halide. The branching ratio between the two fragmentation pathways is controlled by the relative stability of the two possible carbocation/alkyl halide pairs. Like hydride affinities, halide affinities provide a convenient index of carbocation stability.[29] We calculate the chloride affinity of $CCl_2^{+\bullet}$ to be 25 kcal mol^{-1} greater than that of CCl_3^+. This places $CCl_2^{+\bullet}$ in the high end of the chloride affinity scale, slightly above CF_3^+.[29b] Halide abstraction by $CCl_2^{+\bullet}$ from most alkyl halides is thus significantly exothermic, and fragmentation of the dialkylhalonium ion strongly favors product formation over regeneration of the reactants. Since the addition and fragmentation steps occur with a negligible barrier,[30] the net reaction is also rapid.[29a]

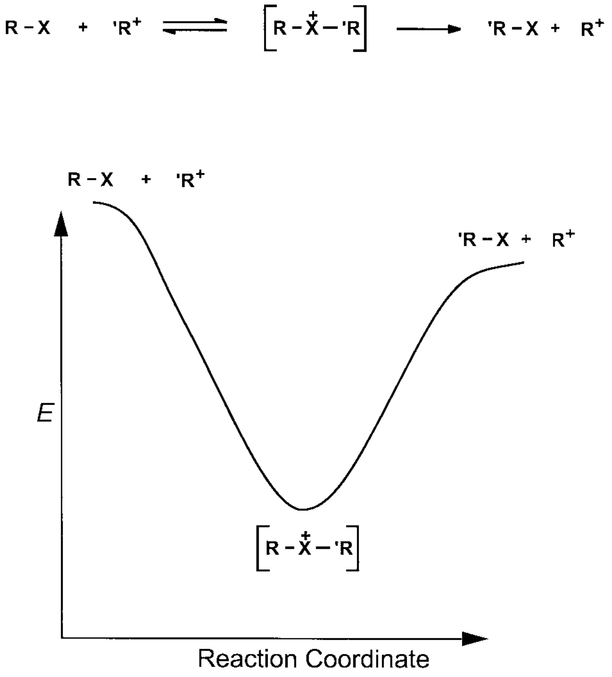

Fig. 1 A schematic potential energy surface for halide abstraction from an alkyl halide by a carbocation.

Unlike the halide abstractions, which can be explained in the context of familiar reactivity, the halogen-atom abstractions exhibited by $CCl_2^{+\bullet}$ depart significantly from expectations of free radical reactivity. Free radical reactions are typically accompanied by non-negligible energy barriers and tight transition states,[31] in sharp contrast to the barrierless, loose addition–elimination profile of halide abstraction. Such radical processes

Table 2 Ionization energies of selected free radical reaction products

Radical	IE/eV[a]	Source	Radical	IE/eV[a]	Source
tert-butyl	6.7	ref. 25	$CClBr_2$	8.0	this work[b,c]
iso-propyl	7.4	ref. 25	CCl_2Br	8.2	this work[b,c]
allyl	8.1	ref. 25	CCl_2I	7.8	this work[c,f]
methyl	9.8	ref. 25	CBr_3	7.5	ref. 25
ethyl	8.3	ref. 25	$CHBr_2$	8.3	ref. 25
formyl	8.1	ref. 25	CCl_2OH	7.4	this work[b,c]
acetyl	6.4	this work[b,d,g]	$CCl_2O\ CH_3$	6.9	this work[b,c]
$CH_3OC{=}O$	7.3	this work[b,d]	$CCl_2O\ CH_2CH_3$	6.8	this work[b,c]
CH_2Cl	8.8	ref. 25	$O{=}P\ (OCH_3)_2$	11.0	ref. 25[e]
CCl_3	8.1	ref. 25	Br	11.8	ref. 25

[a] All values are rounded to the nearest 0.1 eV. [b] Calculated at the MP2/6-31G(d,p)//HF/6-31G(d,p)+ZPVE level of theory. [c] Calculated using an isodesmic cycle with CCl_3. [d] Calculated using an isodesmic cycle with HCO. [e] Vertical value; this provides an upper limit to the adiabatic value. [f] Calculated at the MP2/3-21G(d,p)//HF/3-21G(d,p)+ZPVE level of theory to allow for iodine. [g] This differs significantly from the value of 7.0 eV reported in ref. 25, but both values correctly predict the experimental observations.

would be expected to compete only poorly with exothermic halide abstraction. However, in many cases we observe exclusive halogen-atom abstraction although halide abstraction is also exothermic. Perhaps the most striking case is the allyl iodide reaction. For this reagent, both iodide and iodine atom abstractions are significantly exothermic. The resonance-stabilized allyl cation is estimated[32] to have an iodide affinity of $\sim$40 kcal mol^{-1} less than $CCl_2^{+\bullet}$, a situation that would be predicted to result in fast iodide abstraction. Yet only iodine-atom abstraction and charge transfer are observed. Clearly, these halogen-atom abstractions have a competitive aptitude that cannot be explained in the context of normal free radical reactions.

Insight into the origin of the observed exclusive halogen-atom abstractions can be found by reexamining the addition–elimination mechanism described above for halide abstraction. The dialkylhalonium ion intermediate fragments predominantly to give the most stable products. In the case of $CCl_2^{+\bullet}$, the formation of two tricoordinated species (a cation and a radical) is generally favored over the regeneration of a dicoordinated and tetracoordinated species (the reactants). However, two possible cation/radical pairs can be formed upon fragmentation of the intermediate. One of the pairs is that associated with halide abstraction, and the other with halogen-atom abstraction. Since the two fragment pairs can interconvert by electron transfer, the relative ionization energies (IE) of the fragments (Table 2) provide a convenient index of the relative stability of each pair and thus the extent to which they should be expected to be produced. In cases of significant IE differences, the fragment with the lower IE retains the charge and dominates the mass spectrum in accordance to Stevenson's Rule.[33] Thus, both halide and halogen-atom abstraction pathways can be explained by a single mechanism involving a common reaction intermediate. The strong thermodynamic control over the competition between halide and halogen-atom abstractions is a direct consequence of this common intermediate. For example, iodide abstraction from allyl iodide is not observed because, though exothermic, it is the less exothermic of the two competing reaction pathways sharing the same dialkylhalonium ion intermediate.

Fig. 2 shows the potential energy surface for a net-chlorine-atom abstraction: the case of CH_2Cl_2. This reaction was observed to proceed by exclusive chlorine-atom abstraction, as predicted by the ionization energies of $CCl_3^{\bullet}$ (8.1 eV) and $CH_2Cl^{\bullet}$ (8.8 eV). The overall reaction is rapid, with 24% of collisions resulting in product formation. It is interesting to note that, according to the calculations, the separated chlorine-atom abstraction products ($CH_2Cl^{\bullet}$ and CCl_3^{+}) are actually lower in energy than the intermediate formed by addition of CH_2Cl_2 to $CCl_2^{+\bullet}$. This situation departs from the halide abstraction potential energy surface shown in Fig. 1, in which the intermediate lies below both products and reactants in energy, and strongly favors the homolytic fragmentation of the intermediate to form $CH_2Cl^{\bullet}$ and CCl_3^{+}. This driving force is ample to overcome the non-negligible barrier[30] associated with the cleavage of what is effectively a 2-center-3-electron bond. After initial formation of the products within the collision complex, they may reform a covalent association before eventually escaping the complex, but such an association is likely to take the form of addition of the chlorine from $CH_2Cl^{\bullet}$ to the cationic center of CCl_3^{+} (an intermediate 6 kcal mol^{-1} lower in energy than the initial adduct). This second intermediate can only fragment to form $CH_2Cl^{\bullet}$ and CCl_3^{+}, and it is likely only a resting point on the path to exit from the collision complex.

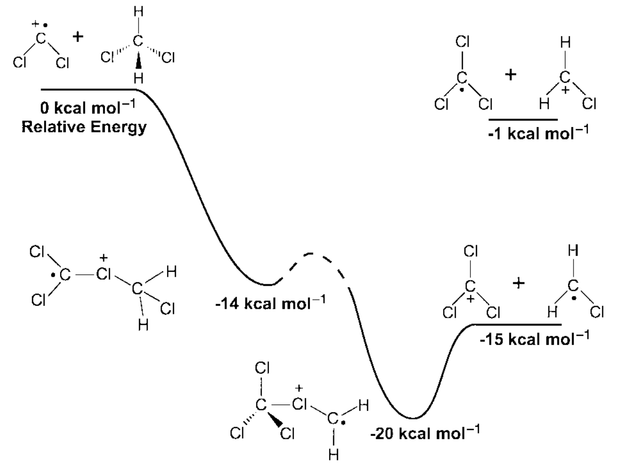

Fig. 2 The potential energy surface calculated (MP2/6-31G(d,p)//HF/6-31G(d,p) + ZPVE) for the reaction of the dichlorocarbene radical cation with dichloromethane (the dotted line indicates an unknown barrier height).

The reaction of $CCl_2^{+\bullet}$ with carbon tetrachloride provides an interesting test of the dual addition–elimination mechanism. Both halide and halogen-atom abstraction products have the same molecular formula: CCl_3. Indeed, observation of the product ion gives no information on whether the reaction is a net chloride or chlorine-atom abstraction. The above mechanism predicts that both reactions will take place to an equal extent, since both fragments have the same ionization energy. This hypothesis was examined by isolating the $CCl_2^{+\bullet}$ isotopomer corresponding to one ^{35}Cl and one ^{37}Cl (*m*/*z* 84) by ejection of all other isotopomers (*m*/*z* 82 and *m*/*z* 86) from the mass spectrometer and allowing the isolated ion to react with CCl_4 (Fig. 3). Comparison of the observed ratio of CCl_3^{+} isotopomers with the predictions made for the three limiting cases reveals a nearly equal partitioning of charge between the two CCl_3 fragments—strong evidence in favor of a common reaction intermediate.

The reaction of $CCl_2^{+\bullet}$ with dibromodichloromethane provides another example similar to that of carbon tetrachloride.

Table 3 Reactions of the dichlorocarbene radical cation with various oxygen-containing compounds

Neutral reagent (mol. wt)	Ionization energy of the neutral reagent/ eV[a]	Observed product ions[b] m/z (%)	Reaction
Diethyl ether (74)	9.5	74 (38)	Electron abstraction
		127 (62)	$^{\bullet}OCH_2CH_3$ abstraction
Methyl acetate (74)	10.3	43 (100)	$^{-}OCH_3$ abstraction
Acetic acid (60)	10.6	43 (100)	^{-}OH abstraction
Trimethyl phosphate (140)	10.7	113 (110)	$^{\bullet}OCH_3$ abstraction
Methanol (32)	10.8	99 (100)	$^{\bullet}OH$ abstraction
Dimethyl carbonate (90)	11.0	59 (60)	$^{-}OCH_3$ abstraction
		113 (18)	$^{\bullet}OCH_3$ abstraction
		74 (22)	$O^{\bullet -}$ abstraction
Formic acid (46)	11.3	99 (100)	$^{\bullet}OH$ abstraction

[a] Ref. 25. [b] Only primary reaction products are listed.

Table 4 Reactions of the dichlorocarbene radical cation with selected carbonyl compounds

Neutral reagent (mol. wt)	Ionization energy of the neutral reagent/ eV[a]	Observed product ions[b] m/z (%)	Reaction
Cyclopentanone (84)	9.3	67 (61)	^{-}OH abstraction
		84 (49)	Electron abstraction
Benzaldehyde (106)	9.5	90 (100)	$O^{\bullet -}$ abstraction
Butan-2-one (72)	9.5	56 (37)	$O^{\bullet -}$ abstraction
		72 (63)	Electron abstraction
Acetone (58)	9.7	42 (100)	$O^{\bullet -}$ abstraction
Acetone-d_6 (64)	9.7	48 (100)	$O^{\bullet -}$ abstraction
Nitrobenzene (123)	9.9	77 (12)	$^{-}NO_2$ abstraction[c]
		107 (88)	$O^{\bullet -}$ abstraction

[a] Ref. 25. [b] Only primary reaction products are listed. [c] This product may also be explained as unimolecular loss of NO from m/z 107.

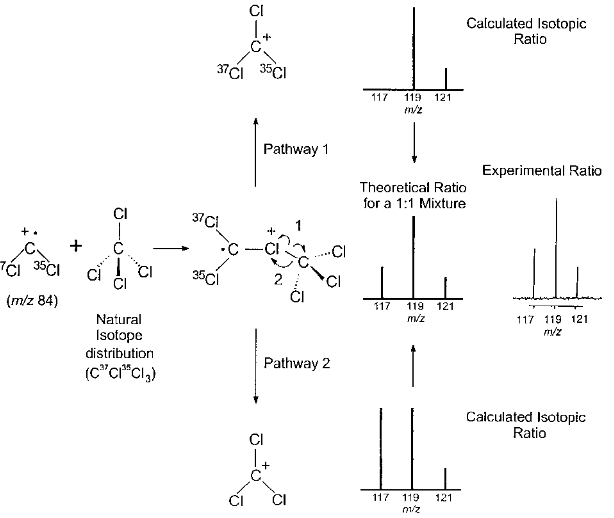

Fig. 3 Comparison of theoretical and observed CCl_3^+ isotope ratios for the reaction of $C^{35}Cl^{37}Cl^{+\bullet}$ (m/z 84) with carbon tetrachloride.

Electrophilic attack by $CCl_2^{+\bullet}$ at one of the bromine substituents results in equal division of the charge between the two resultant CCl_2Br fragments. Attack at a chlorine substituent can result in two distinct ionic products which are both observed as minor products. This is a departure from the usual exclusivity of one of the two abstraction channels. It is, however, consistent with the calculated IE values of the two ions (Table 2) which differ by only 0.1 eV, making them similar within the probable error of the calculation.

$^{\bullet}$OR and $^{-}$OR abstraction

The electrophilic addition–elimination mechanism that rationalizes the reactions of the dichlorocarbene radical cation with alkyl halides can be extended to reactions with other classes of organic compounds, including alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, and phosphates (Tables 3 and 4). In principle, any compound that contains a heteroatom is likely to readily add to the cationic center of $CCl_2^{+\bullet}$. The heteroatom-bridged intermediate then fragments to form either net-radical or net-anion abstraction products depending on their relative stabilities. For example, the dichlorocarbene radical cation reacts with methanol and formic acid by net $^{\bullet}OH$ abstraction, which is consistent with the addition to the hydroxyl moiety to form an oxygen-bound adduct and subsequent homolytic C–O bond cleavage to form Cl_2COH^+ and a neutral radical ($CH_3^{\bullet}$ and $HCO^{\bullet}$, respectively). Just as in the case of alkyl halide reactions, the distribution of charge between the product fragments is consistent with the relative ionization energies of the fragments (Table 2). The reaction with acetic acid also appears to proceed *via* the oxygen-bound carbene ion adduct. However, the charge remains on the acetyl fragment to produce the hydroxide abstraction product (CH_3CO^+). The significant differences in the ionization energies of the formyl and acetyl radicals (8.1 and 6.4 eV respectively) explain the different products observed for the reaction with formic and acetic acids. Alkoxy radicals and alkoxides are also readily abstracted by $CCl_2^{+\bullet}$. Ethyl ether and trimethyl phosphate react with $CCl_2^{+\bullet}$ by net-alkoxy radical transfer, and methyl acetate reacts by methoxide transfer.

All the observations reported above are in agreement with the formation of the most stable abstraction product by the addition–elimination mechanism. However, $CCl_2^{+\bullet}$ abstracts the methoxide ion as well as the methoxy radical from dimethyl carbonate. Unlike in the case of carbon tetrachloride and dibromodichloromethane, where both abstraction products have the same or similar ionization energies, our calculations predict a substantial difference in the ionization energies (0.4

eV) of the two abstraction products of dimethyl carbonate, with the major reaction product (60% methoxide abstraction) having the *larger* ionization energy. The barrier to homolytic dissociation discussed above in the context of Fig. 2 may be partially responsible for the dominance of the methoxide abstraction channel, but this seems insufficient to explain such a large divergence from the generally observed pattern. It is possible that this discrepancy is merely an artifact of the computational method, as experimental IE measurements do not exist for either product. Whatever the cause of the higher-than-expected methoxide abstraction rate, the reaction deserves special examination due to a third product that corresponds to formal $O^{\bullet-}$ abstraction. The simplest explanation for this product is the formation of an adduct at the carbonyl oxygen and fragmentation to form a new carbene radical cation: the dimethoxy carbene radical cation. This structural assignment is supported by the observation that this ion reacts further with ambient dimethylcarbonate by methoxy-radical abstraction.

$O^{\bullet-}$ abstraction

The formation of a new carbene radical cation by $O^{\bullet-}$ abstraction from carbonyl compounds is a tantalizing prospect. However, the absence of such products for the reactions of formic and acetic acids demonstrates that this is not a reaction that will be observed for every carbonyl compound. Addition of the carbonyl oxygen to $CCl_2^{+\bullet}$ produces what is effectively two carbene radical cations bridged by an oxygen. Fragmentation of this intermediate will therefore be controlled by the stability of the two possible sets of products. If the reactants are more stable than the new carbene ion and phosgene, the intermediate will fragment to regenerate the reactants, and no net $O^{\bullet-}$ abstraction reaction is observed. Due to the instability of phosgene relative to other carbonyl compounds, this is the most common situation. However, there appear to be cases—such as that of dimethyl carbonate—in which the stability of the new carbene ion ameliorates the formation of phosgene. $O^{\bullet-}$ abstraction is favorable in this case, although outside-competition from methoxide abstraction renders it a minor product. However, competition from other reaction channels is minimized for reactions of aldehydes and ketones (Table 4) in which the carbonyl oxygen is the only site capable of bond formation with the carbene radical cation. For example, the dichlorocarbene radical cation reacts with acetone by rapid and exclusive $O^{\bullet-}$ abstraction to produce an ionic product of *m*/*z* 42 with the formula $C_3H_6^{+\bullet}$. Reaction with d_6-acetone confirms this formula assignment. The same reaction was observed for a number of other carbonyl compounds (Table 4), as well as for nitrobenzene.

If $O^{\bullet-}$ abstraction from acetone produces the dimethyl carbene radical cation it is likely to isomerize by a 1,2-hydrogen (or hydride) shift to yield the more stable propene radical cation. The barrier to this isomerization has been calculated by others to be 8 kcal mol^{-1} at the G2 level of theory.[15] *Ab initio* molecular orbital calculations were carried out to depict the potential energy surface for abstraction of $O^{\bullet-}$ from acetone by the dichlorocarbene radical cation (Fig. 4). The initially formed, covalently bonded adduct lies 54 kcal mol^{-1} below the energy level of the separated reactants—a significantly larger stabilization of the adduct than in the case of CH_2Cl_2. Formation of the dimethylcarbene radical cation is 18 kcal mol^{-1} exothermic, and the collision complex thus contains more than enough energy for the incipient product ion to overcome the small barrier to hydride shift to form the significantly more stable propene radical cation. A similar isomerization is likely to occur for the carbene radical cation formed upon abstraction of $O^{\bullet-}$ from butan-2-one.[34]

Unlike acetone, the $O^{\bullet-}$ abstraction product of benzaldehyde does not have a stable isomer with an ionized alkene structure. The most plausible structures for the product ion in this case are those of the phenylcarbene radical cation and the dehydrotropylium cation. Both of these ions can be seen as carbene radical cations with delocalized charge sites. The chemical nature of the $C_7H_6^{+\bullet}$ was investigated by allowing it to react with acetone and dichloromethane. The observation of $O^{\bullet-}$ abstraction from acetone and chlorine atom abstraction from dichloromethane is in qualitative agreement with a carbene radical cation structure for the ion $C_7H_6^{+\bullet}$, although it is not clear which of the two isomeric carbene structures predominates.

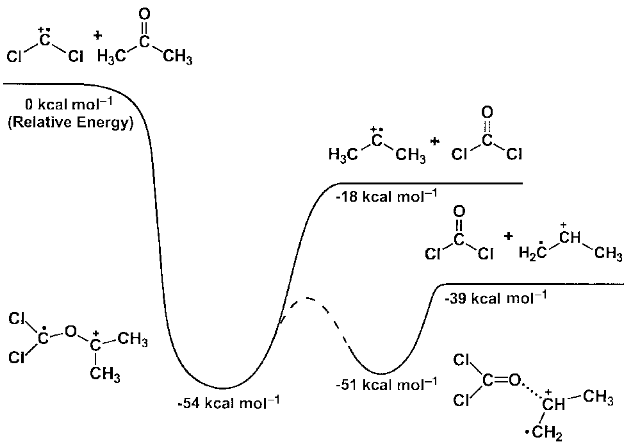

Fig. 4 The potential energy surface calculated (MP2/6-31G(d,p)//HF/6-31G(d,p) + ZPVE) for the reaction of the dichlorocarbene radical cation with acetone (the dotted line indicates an unknown barrier height).

Conclusion

The gas-phase reactions of the dichlorocarbene radical cation are dominated by electrophilic reactivity, in qualitative agreement with solution studies of carbene radical cations.[2,6] Addition of this species to a nucleophilic center and subsequent elimination produces a cation/radical pair. This addition–elimination reactivity is conceptually quite similar to anion abstractions by carbocations. However, due to the odd-electron nature of the carbene radical cation and its addition intermediate, a net-radical abstraction can also result *via* this electrophilic mechanism. The final reaction product is under strong thermodynamic control. The occurrence of net-radical reactions by a decidedly non-radical mechanism illustrates the competitive advantage of electrophilic reactions in the gas phase. The lack of solvation in the gas phase makes cations inherently more aggressive electrophiles than in solution. Further studies will explore whether radical reactivity is competitive with electrophilic reactivity for carbene radical cations of less electrophilicity than the dichlorocarbene radical cation.

The electrophilic addition–elimination reactions observed for $CCl_2^{+\bullet}$ provide a route to gas-phase synthesis of new carbene radical cations by $O^{\bullet-}$ abstraction from carbonyl compounds. While carbene ion formation is probably impractical in many cases due to competing reactions, endothermicity, or instability of the new carbene ion with respect to unimolecular isomerization, this reaction nevertheless broadens the range of carbene ions accessible for gas-phase studies.

Acknowledgements

The National Science Foundation (CHE-9710456) is acknowledged for financial support of this work. S. E. T. wishes to thank R. A. J. O'Hair for a strong recommendation to study at Purdue University. K. K. Thoen and J. Heidbrink are thanked for their help with some experiments. Finally, Joe Campana and the Finnigan FT/MS are thanked for donation of the permanent magnet-based FT/ICR.

References

1 (*a*) W. Kirmse, *Carbene Chemistry*, Academic Press, New York, 1971; (*b*) M. S. Platz, *Kinetics and Spectroscopy of Carbenes and Biradicals*, Plenum Press, New York, 1990; (*c*) W. Kirmse, *Advances in Carbene Chemistry*, U. H. Brinker, Ed., JAI Press, Greenwich, CT, 1994; Vol. 1.

2 (*a*) D. Bethell and V. D. Parker, *Acc. Chem. Res.*, 1988, **21**, 399; (*b*) V. Parker and D. Bethell, *J. Am. Chem. Soc.*, 1987, **109**, 5066.

3 1 kcal = 4.18 kJ.

4 W. Reuter and S. D. Peyerimhoff, *Chem. Phys.*, 1992, **160**, 11.

5 T. Bally, S. Matzinger, L. Truttman, M. S. Platz, A. Admasu, F. Gerson, A. Arnold and R. Schmidlin, *J. Am. Chem. Soc.*, 1993, **115**, 7007.

6 D. G. Stoub and J. L. Goodman, *J. Am. Chem. Soc.*, 1997, **119**, 11110.

7 (*a*) J. Berkowitz, *J. Chem. Phys.*, 1978, **69**, 3044; (*b*) C. Wesdemiotis and F. W. McLafferty, *Tetrahedron Lett.*, 1981, **22**, 3479.

8 P. C. Burgers, A. A. Mommers and J. L. Holmes, *J. Am. Chem. Soc.*, 1983, **105**, 5976.

9 P. C. Burgers, G. A. McGibbon and J. K. Terlouw, *Chem. Phys. Lett.*, 1994, **222**, 129.

10 F. A. Wiedmann, J. Cai and C. Wesdemiotis, *Rapid Commun. Mass Spectrom.*, 1994, **10**, 804.

11 G. A. McGibbon, C. A. Kingsmill and J. K. Terlouw, *Chem. Phys. Lett.*, 1994, **222**, 539.

12 J. K. Terlouw, J. Wezenberg, P. C. Burgers and J. L. Holmes, *J. Chem. Soc., Chem. Commun.*, 1983, 1121.

13 J. M. Buschek, J. L. Holmes and J. K. Terlouw, *J. Am. Chem. Soc.*, 1987, **109**, 7321.

14 D. Sülzle, T. Drewello, B. L. M. van Baar and H. Schwarz, *J. Am. Chem. Soc.*, 1988, **110**, 8330.

15 C. Aubry, M. J. Polce, J. L. Holmes, P. M. Mayer and L. Radom, *J. Am. Chem. Soc.*, 1997, **119**, 9039.

16 The reactivity of carbene radical anions has been examined. See for example: M. Born, S. Ingemann and N. M. M. Nibbering, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2537.

17 K. K. Thoen, R. L. Smith, J. J. Nousiainen, E. D. Nelson and H. I. Kenttämaa, *J. Am. Chem. Soc.*, 1996, **118**, 8669.

18 L. C. Zeller, J. M. Kennedy, H. I. Kenttämaa and J. E. Campana, *Anal. Chem.*, 1993, **65**, 2116.

19 (*a*) A. G. Marshall, T. C. L. Wang and T. L. Ricca, *J. Am. Chem. Soc.*, 1985, **107**, 7893; (*b*) A. G. Marshall, T. L. Ricca and T. C. L. Wang, U.S. Patent 4,761,545, 1988.

20 (*a*) P. Lin and H. I. Kenttämaa, *Org. Mass Spectrom.*, 1992, **27**, 1155; (*b*) R. L. Smith, L. J. Chyall, K. M. Stirk and H. I. Kenttämaa, *Org. Mass. Spectrom.*, 1993, **28**, 1623; (*c*) D. T. Leeck, K. M. Stirk, L. C. Zeller, L. K. M. Kiminkinen, L. M. Castro, P. Vainiotalo and H. I. Kenttämaa, *J. Am. Chem. Soc.*, 1994, **116**, 3028; (*d*) R. Li, R. L. Smith and H. I. Kenttämaa, *J. Am. Chem. Soc.*, 1996, **118**, 5056.

21 T. Su and W. J. Chesnavich, *J. Chem. Phys.*, 1982, **76**, 5183.

22 J. E. Bartmess and R. M. Georgiadis, *Vacuum*, 1983, **33**, 149; (*b*) K. J. Miller and J. A. Savchik, *J. Am. Chem. Soc.*, 1979, **101**, 7206.

23 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzwewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Repongle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordan, C. Gonzalez and J. A. Pople, Gaussian Inc., Pittsburgh PA, 1995.

24 A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502.

25 S. G. Lias, *Ionization Energy Evaluation* in *NIST Chemistry WebBook*, *NIST Standard Reference Database Number 69*, Eds. W. G. Mallard and P. J. Linstrom, March 1998, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).

26 See for example: K. B. Wiberg, C. M. Hadad, P. R. Rablen and J. Cioslowski, *J. Am. Chem. Soc.*, 1992, **114**, 8644.

27 This result suggests that the ionization energy value of 9.27 eV reported in reference 23 understates the adiabatic ionization energy of $CCl_2^{+\bullet}$ by 0.2–0.3 eV.

28 N. A. McAskill, *Aust. J. Chem.*, 1970, **23**, 893.

29 (*a*) R. B. Sharma, D. K. S. Sharma, K. Hiraoka and P. Kebarle, *J. Am Chem. Soc.*, 1985, **107**, 3747; (*b*) J. H. J. Dawson, W. G. Henderson, R. M. O'Malley and K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.*, 1973, **11**, 61; (*c*) D. K. S. Sharma, S. W. de Höjer and P. Kebarle, *J. Am. Chem. Soc.*, 1985, **107**, 3757.

30 P. C. Burgers, J. L. Holmes and J. K. Terlouw, *J. Chem. Soc., Chem. Commun.*, 1982, 642.

31 J. Fossey, D. Lefort and J. Sorba, *Free Radicals in Organic Chemistry*, Wiley, New York, 1995, Chapter 6.

32 Based on the relative hydride affinities of CF_3^+ (which is similar to $CCl_2^{+\bullet}$) and the allyl cation from A. G. Harrison, *Chemical Ionization Mass Spectrometry*, 2nd edition, CRC, Ann Arbor, 1992, p. 21; hydride affinities generally correlate well with halide affinities.

33 A. G. Harrison, C. D. Finney and J. A. Sherk, *Org. Mass Spectrom.*, 1971, **5**, 1313.

34 W. J. van der Hart, *J. Am. Soc. Mass Spectrom.*, 1999, **10**, 575.

Paper 9/03936H