

[Acylium Ketene] Ion-Neutral Complexes in the Gas Phase

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Abstract: The gaseous metastable ion $\text{CH}_3\text{COCH}_2\text{CO}^+$ has been examined by mass spectrometry. Isotopic labeling shows that the dissociation, which produces the acylium fragment ion CH_3CO^+ , is preceded by atom exchange. Simple cleavage to an [acylium ketene] ion-neutral complex forms an intermediate that accounts for the data by means of a reversible proton transfer to a complex of identical structure in which the ion and neutral have exchanged rôles. Ab initio calculations predict the existence of several stable geometries for the [acylium ketene] ion-neutral complex. In the most stable structure, $[\text{CH}_2=\text{C}=\text{O}\cdots\text{HCH}_2\text{CO}^+]$, one hydrogen of the acylium ion is weakly bonded to the ketene oxygen. Despite the calculated stability of this structure (51 kJ mol⁻¹ relative to the separated components), it cannot lead to atom permutation and is an impasse on the potential energy surface. Another potential energy minimum, $[\text{O}=\text{C}=\text{CH}_2\cdots\text{HCH}_2\text{CO}^+]$ has one hydrogen of the ion weakly bonded to the sp² carbon atom of the neutral ketene. While that structure is less stable (25 kJ mol⁻¹ relative to the separate components), it can be involved in the proton transfer leading to the atom exchange process. The energy of the transition state of this H transfer lies only 4 kJ mol⁻¹ below that of the final state, $\text{CH}_3\text{CO}^+ + \text{CH}_2=\text{C}=\text{O}$, and agrees with the experimental results.

Introduction

The existence of ion-neutral complexes as intermediates in unimolecular ionic reactions in the gas phase has been well established by Bowen and Williams.¹ These authors have shown that protonated propionaldehyde reacts via a complex formed by an ethylene molecule and a formaldehyde molecule bonded by a proton (Scheme I).

Since this work, a great number of unimolecular reactions of closed-shell ions, as well as odd-electron ions, have been rationalized by supposing the intermediacy of such complexes and have been reviewed by several authors.^{2,3} Different kinds of ion-neutral complexes have been proposed in the literature according to their mode of stabilization.

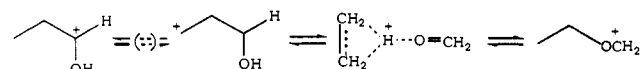
A complex can be stabilized by weak bonds: (i) hydrogen bonds,^{4,5} (ii) interaction between the charge of the ion and the π -system of the neutral,^{6,7} and (iii) stabilization by ion-dipole and ion-induced dipole attraction.^{2,3,9,10} For the case of (iii), Longevialle and Botter⁸ have shown that one partner can turn around with respect to the other and that the distances between the partners must be greater than one would expect for the equilibrium geometries corresponding to (i) or (ii).¹¹

Such loosely bound complexes may intervene when an initially covalently bonded ion undergoes an exothermic reaction to a weakly bonded complex. In such examples, the existence of the complex can be inferred from characteristic dissociations under collision or by neutralization reionization mass spectrometry (NRMS) experiments. Its structure and energy can be estimated by ab initio calculation or by semiempirical methods.

Many other transient complexes, e.g., H-bonded or ion-dipole complexes, which have been proposed, are often weakly stabilized and lie very close to the threshold for direct decomposition. In many experimental studies, the only justification for their existence is the reactions to which they lead: specific hydrogen exchange ($[\text{AH}^+ \text{B}] \rightleftharpoons [\text{A BH}^+]$) or rearrangement of the initial ion ($[\text{ABC}^+ \rightleftharpoons [\text{A}^+ \text{BC}] \rightleftharpoons [\text{ACB}^+]$).

Between these two extreme cases, a number of pathways have been suggested (endothermic isomerization of the initial ion to a stable complex, interconversion between a complex and a distonic ion, or existence of several successive complexes), and the interpretation of experimental results rests largely upon theoretical calculations. The energies of several proton-bridged intermediates, in which the proton lies between two oxygen atoms, have been evaluated experimentally¹² or calculated,^{13,14} but there is little

Scheme I



information concerning proton-bridged (or H-bonded) complexes such as $[\text{C}\cdots\text{H}^+\cdots\text{O}]$. To the best of our knowledge, only a few studies have been reported on the existence of $[\text{C}\cdots\text{H}^+\cdots\text{C}]$ complexes. In the gas phase the loss of CH_4 from ionized acetone^{15a} or the hydrogen atom transfer between neutral aldehydes and ionized enols^{15b} has been explained by the intermediacy of such a complex.

For these species, theoretical studies are more likely studied to provide information for structure and energy. For instance, Blanchette et al.¹⁴ have shown that among several hydrogen-

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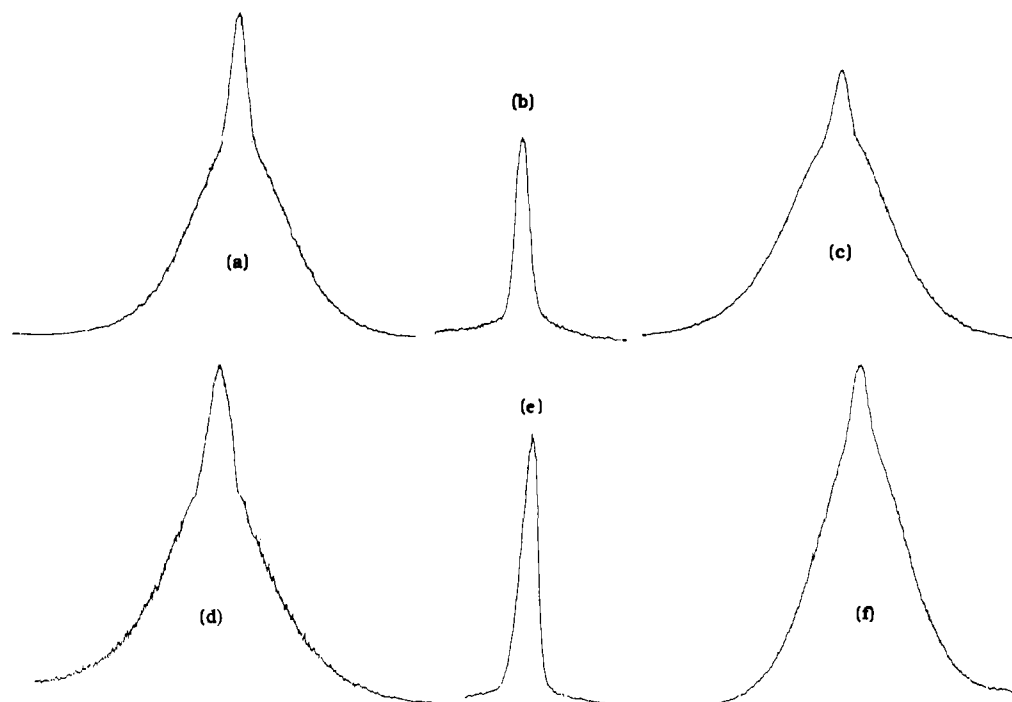


Figure 1. Peak shapes in MIKE spectra of ions 1: (a) $1 \rightarrow m/z$ 43, (b) $1a \rightarrow m/z$ 43, (c) $1a \rightarrow m/z$ 44, (d) $1b \rightarrow m/z$ 43, (e) $1b \rightarrow m/z$ 45, (f) $1c \rightarrow m/z$ 46.

bridged cations such as $[H_2C \cdots H^+ \cdots O=C]$, $[CH_2O \cdots H^+ \cdots O=C]$, and $[CH_2O \cdots H^+ \cdots C=O]$ located as minima on the $[C_2H_3O_2]^+$ potential surface, only the former appears to be a real stable intermediate, experimentally evidenced in the fragmentation pathways of CH_3OCO^+ . So, the difficult problem is to elucidate the relationship between the most stable forms obtained by calculation and the transient or reactive forms of the complexes leading to observed reactions (isomerizations or dissociations).

Here, we approach this issue by studying the complexes formed by cleavage of $CH_3COCH_2CO^+$ cations and pose the following questions: do the intermediates correspond to ion-dipole complexes $[CH_2=C=O \cdots CH_3CO^+]$, ketene proton-bound dimers $[CH_2=C=O \cdots H^+ \cdots O=C-CH_2]$, or weakly bonded complexes between an acylium and a neutral ketene $[CH_2=C=O \cdots HCH_2CO^+]$ and $[O=C=CH_2 \cdots HCH_2CO^+]$? Are there several stable forms for these complexes? What are the relationships between the most stable forms and the reactive forms?

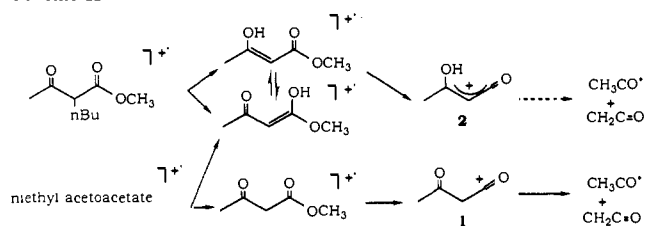
Experimental Section

The experiments were carried out on VG ZAB 2F double analyzer mass spectrometer. Typical instrument conditions were 150 °C source temperature, 8 kV acceleration voltage, and 70 eV ionizing energy. The $C_4(H,D)_5O_2^+$ cations were generated in the ion source by loss of a methoxy radical from labeled and unlabeled methyl acetoacetate radical cations. The metastable reactions of these ions were studied in the second field free region (FFR) by mass analyzed ion kinetic energy (MIKE) techniques.¹⁶ Collision induced dissociations (CID) were performed using helium as target gas. Helium was introduced into the collision cell until the precursor ion intensity was suppressed to 75%. The kinetic energy releases (KER) were calculated¹⁶ with correction of the width of the main beam. The β -keto esters used to produce the studied ions were commercially available (methyl 3-oxobutanoate and ethyl 3-oxo-[3-¹³C]butanoate) or were prepared by standard methods. Methyl 2-*n*-butyl-3-oxobutanoate was obtained from methyl 3-oxobutanoate in the usual manner¹⁷ for alkylation of β -keto esters. Methyl 3-oxo-[3-¹³C]butanoate was prepared by transesterification of the corresponding ethyl ester with methanol. Methyl 3-oxo-2,2-dideuteriobutanoate was obtained by treatment of methyl 3-oxobutanoate with K_2CO_3 in excess of D_2O . Methyl 3-oxo-4,4,4-trideuteriobutanoate was synthesized by acylation of Meldrum's acid with CD_3COCl followed by alcoholysis with methanol,

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Scheme II



as described¹⁸ in the literature. All compounds, except those obtained by D_2O exchange, were purified by gas chromatography (SE 30 column, 3 m), and their purity was checked by 1H and ^{13}C NMR spectroscopy.

The ab initio MO calculations were performed using the MONSTERGAUSS¹⁹ and GAUSSIAN 88²⁰ programs. Geometries were fully optimized at the SCF level using the 3-21G and 6-31G* basis sets. The harmonic vibrational frequencies were determined at the 3-21G level, by analytical second derivative calculations and used to characterize stationary and saddle points of the potential surface and to evaluate zero-point vibrational energies (ZPVE), which were scaled by the empirical factor 0.89. Single-point calculations were performed with the 6-31G* and 6-31+G** basis sets, which were used to gauge the effects of valence electron correlation by evaluating the energies at second-order Møller-Plesset theory (MP2). Thus, the levels of theory discussed within the text refer to MP2/6-31G**/3-21G + ZPVE and MP2/6-31+G**//6-31G*.

Experimental Results

Metastable Ions 1 and 2: $CH_3COCH_2CO^+$ and $CH_3C(OH)-CHCO^+$. In the gas phase methyl acetoacetate is a mixture of enol and keto forms.²¹ The corresponding radical cations can lose CH_3O^+ in the ion source to form two different $C_4H_5O_2^+$ cations, 1 and 2 (Scheme II).

Metastable $C_4H_5O_2^+$ ions (1 and 2) eliminate a ketene molecule spontaneously in the second FFR to yield $C_2H_3O^+$ (m/z 43) fragment ions, which have been shown to be CH_3CO^+ acylium

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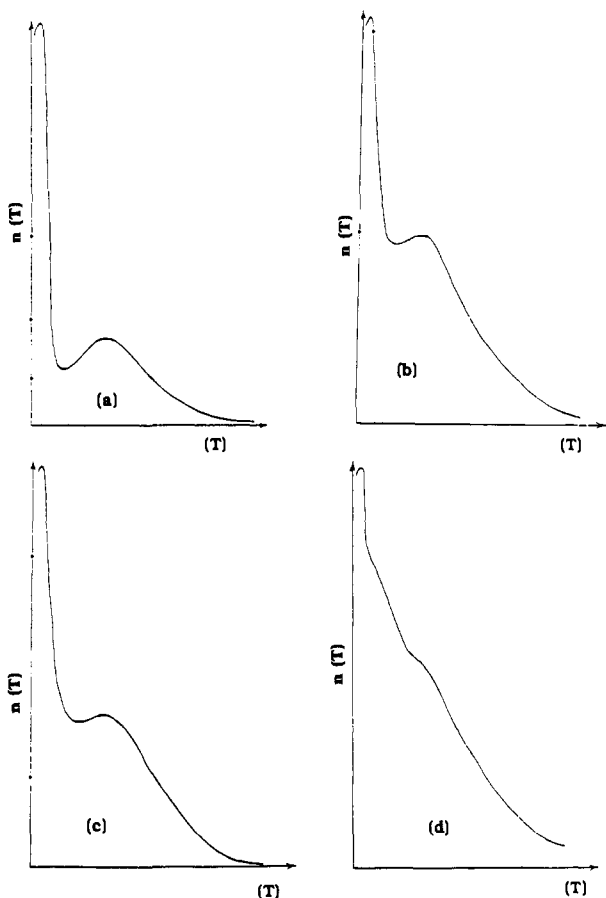


Figure 2. Kinetic energy release distribution $n(T)$ for the metastable ion decomposition processes: (a) $1 \rightarrow m/z 43$, (b) $1a \rightarrow m/z 44$, (c) $1b \rightarrow m/z 43$, (d) $1c \rightarrow m/z 46$.

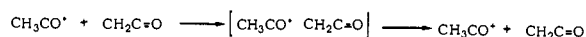
ion²² by collisionally activated dissociations (CAD) of the fragment formed in the first FFR.

In the MIKE spectrum of $1 + 2$ the $m/z 43$ peak is clearly composite (Figure 1). Deconvolution (Figure 2)²³ shows a broad component ($T_p = 60$ meV, $T_{0.5} = 35$ meV) and a very narrow component (T_p and $T_{0.5} < 0.5$ meV).

In order to determine the origin of both components, ions 2 have been specifically generated. By McLafferty rearrangement, the methyl 2-*n*-butyl-3-oxobutanoate radical cation yields two enol forms (Scheme II) in the ion source, which interconvert.²¹ These forms eliminate $\text{CH}_3\text{O}^\bullet$ leading to ion 2 . This ion produces CH_3CO^+ in the second FFR with a Gaussian KER distribution. The kinetic energy release associated with this fragmentation ($T_{0.5} = 25$ meV) is near the value measured for the broad component accompanying the CH_3CO^+ formation from $1 + 2$. This suggests that this broad component can be attributed to the fragmentation of enol form 2 .

This enol 2 may rearrange to eliminate a neutral ketene molecule. The energetically most feasible pathway corresponds to $2 \rightarrow 1$ isomerization via a 1,3 hydrogen atom migration. Thus, 1 generated from 2 by this pathway acquires a significant internal energy which is transformed into KER associated with the fragmentation. On the other hand, the reaction of acylium ion (generated by cleavage of acetone radical cation) with ketene yields an adduct ion $\text{C}_4\text{H}_5\text{O}_2^+$ in the ion source, which gives CH_3CO^+ in the second FFR with a very low KER ($T_p < 1$ meV) implying that there is no appreciable energy barrier for the reverse reaction (Scheme III). We therefore conclude that the narrow component observed in the CH_3CO^+ formation from $1 + 2$ corresponds to the dissociation of the keto form 1 .

Scheme III



In order to study the behavior of ion 1 we will consider here only the shifts of this narrow component in labeled ions $1 + 2$. Three isotopic analogues have been examined, giving evidence for transpositions in the metastable ions. In the CID spectra of labeled $1 + 2$ ions, the isotopic shifts of the acylium fragment show that the permutations of atoms preceding acylium formation do not take place in the stable ions.

Metastable Ion 1a: $\text{CH}_3^{13}\text{COCH}_2\text{CO}^+$. The MIKE spectrum of $^{13}\text{CC}_3\text{H}_5\text{O}_2^+$ ($m/z 86$) (formed by methoxy radical loss from methyl [3- ^{13}C]acetoacetate) shows a composite peak at $m/z 44$ (89%) and a narrow peak at $m/z 43$ (11%) (Figures 1 and 2). The area of the narrow component in the $m/z 44$ peak has been determined by deconvolution. From the area of both narrow components ($m/z 43$ and $m/z 44$), we estimate the ratio $\text{CH}_3\text{CO}^+/\text{CH}_3^{13}\text{CO}^+$ for ion $1a$ to be 45/55. This result indicates that the acylium formation from ion 1 is preceded by a carbon atom permutation.

Metastable Ion 1b: $\text{CH}_3\text{COCD}_2\text{CO}^+$. The MIKE spectrum of $\text{C}_4\text{H}_3\text{D}_2\text{O}_2^+$ ($m/z 87$) generated from methyl acetoacetate-2,2- d_2 shows two intense peaks: $m/z 43$ (composite, 78%) and $m/z 45$ (narrow, 13%), and a small peak at $m/z 44$ (composite 9%) (Figures 1 and 2). This last peak at $m/z 44$ comes partly from unselective labeling; the NMR spectrum shows that methyl acetoacetate-2,2- d_2 contains 3% of 2,4- d_2 derivative. There is also a small but nonnegligible H/D exchange within the molecular ion in the ion source prior to $\text{CH}_3\text{O}^\bullet$ loss.²¹ The sum of these two contributions can be estimated by the ratio ($m/z 44$)/($m/z 45$) obtained from fragmentation of the dideuterated methyl acetoacetate molecular ion in the first FFR. This correction and the deconvolution of the $m/z 43$ composite peak lead to the conclusion that metastable $1b$ yields $m/z 43$, 44, and 45 in the ratio 44/2/54. This result is also consistent with hydrogen atom permutations prior to acylium formation.

Metastable Ion 1c: $\text{CD}_3\text{COCH}_2\text{CO}^+$. The MIKE spectrum of $\text{C}_4\text{H}_2\text{D}_3\text{O}_2^+$ cation formed from methyl acetoacetate-4,4,4- d_3 shows a very intense $m/z 46$ peak (78%) and smaller ones at $m/z 45$ and $m/z 44$. The deconvolution curve $n(T)$ of the $m/z 46$ peak appears to be different from those obtained above (Figure 2). As above, broad and narrow components are observed, but an intermediate component also appears (Figure 2) which is explained further below by the simple cleavage of ion $1c$. The correction of $m/z 44$, $m/z 45$, and $m/z 46$ has been made using the same method as for $1b$, but the existence of a third component for the $m/z 46$ peak leads to lower precision for the ratio between the narrow components. It appears likely that in ion $1c$ the corresponding acetyl ion at $m/z 45$ (CD_2HCO^+) is not formed and that the narrow component at $m/z 46$ (CD_3CO^+) is at least five times greater than the corresponding component of the $m/z 44$ peak (CH_2DCO^+).

Calculations

The experimental data can be interpreted with the help of structures, relative energies, and isomerization barriers estimated by ab initio calculations. We have optimized geometries using SCF calculations with the 3-21G basis set (including vibrational frequency calculations) and have then explored the $\text{C}_4\text{H}_5\text{O}_2^+$ potential energy surface associated with the dissociation of ion 1 . Several potential energy minima corresponding to ion-neutral complexes were found in the course of examining incremental changes in the C(2)–C(3) bond length, which had been chosen as the reaction coordinate.

Except where otherwise specified, we report energies calculated at MP2/6-31G**//3-21G + ZPVE. Where appropriate we have reoptimized geometries at the SCF level using the 6-31G* basis set. Optimized geometries are displayed in Figure 3, a and b. Electronic energies for several points along the reaction coordinate were computed at MP2/6-31+G**//6-31G*. These are summarized in the potential energy profile shown schematically in Figure 4.

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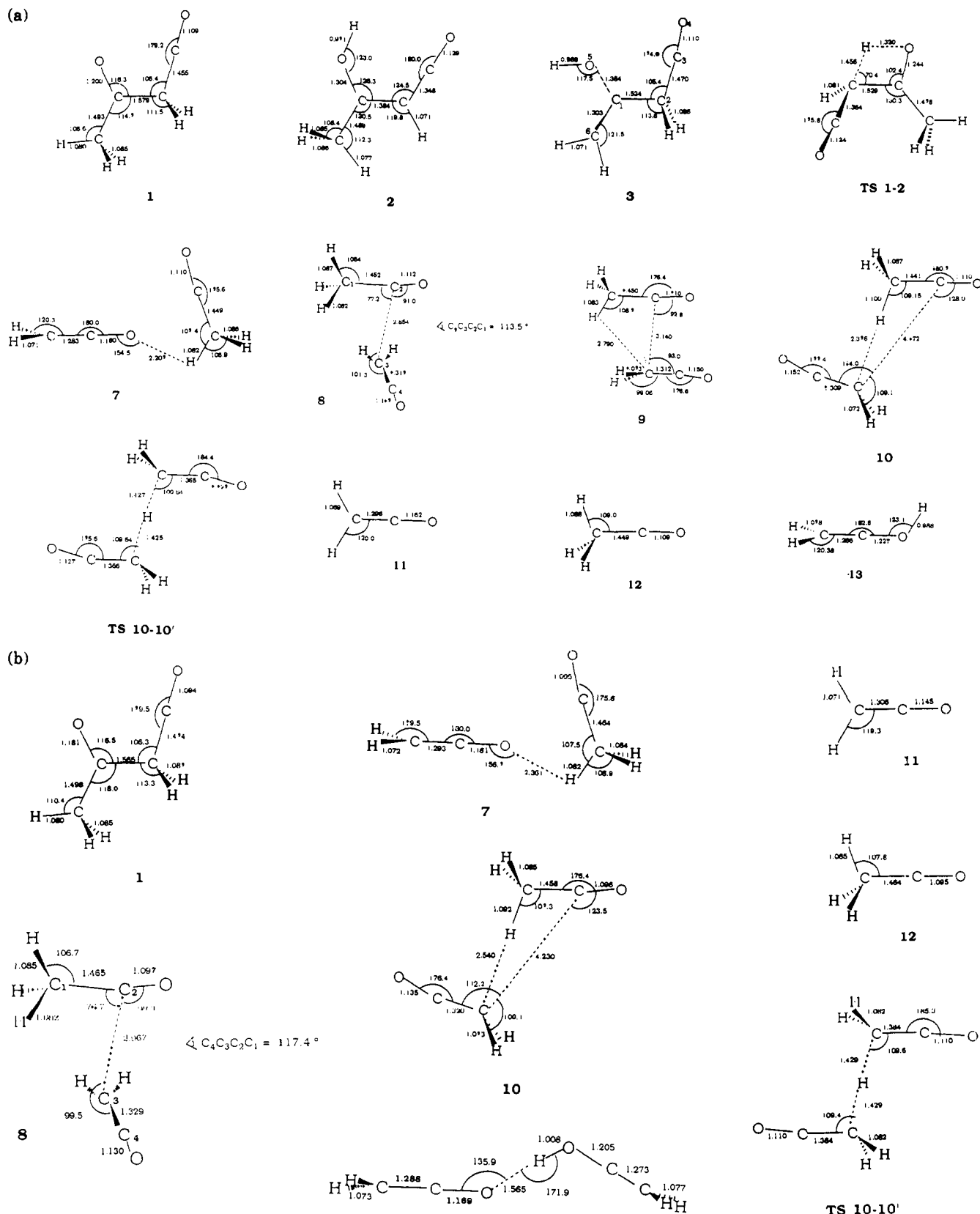


Figure 3. (a) Geometries of stationary and saddle points at 3-21G//3-21G level of theory (bond lengths in angstroms, angles in degrees). (b) Geometries of stationary and saddle points at 6-31G**//6-31G** level of theory (bond lengths in angstroms, angles in degrees).

Keto Structures. Two geometries for $\text{CH}_3\text{COCH}_2\text{CO}^+$ have been examined. The most stable conformer **1** has an unusually long (C(2)–C(3)) bond, 1.579 Å (Figure 3a), suggesting its easy rupture. Another conformer, in which the methyl is rotated by 60° , has one imaginary frequency and corresponds to a transition

state for internal rotation that is 2 kJ mol⁻¹ higher than **1**.

Enol Structures. The enol structure **2**, $\text{CH}_3\text{C}(\text{OH})\text{CHCO}^+$, is 13 kJ mol⁻¹ more stable than **1**. While the calculated electronic energy difference for this keto–enol pair depends upon the basis set (with a difference of 55 kJ mol⁻¹ at 3-21G//3-21G), **2** has

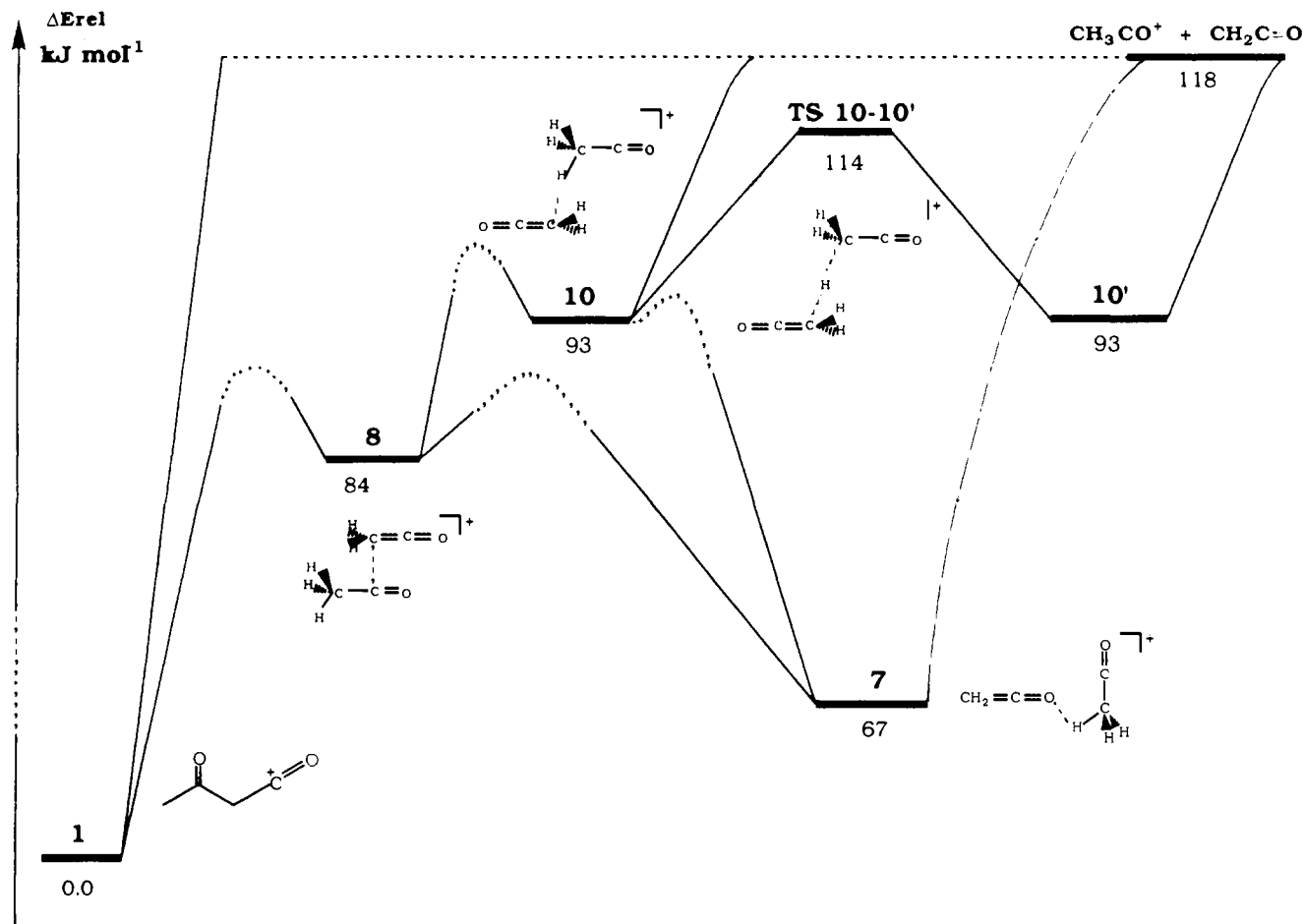


Figure 4. Schematic potential energy diagram for isomerization/dissociation processes of ion 1 (MP2/6-31+G**//6-31G*).

an energy below that of 1 at all levels, and its stability can be attributed to the charge delocalization between carbon atoms. This is mirrored in the C(1)–C(2) bond length which is shorter (1.348 Å) than in ion 1 (1.455 Å).

The other enolic form $\text{CH}_2\text{C}(\text{OH})\text{CH}_2\text{CO}^+$ (3) is less stable than 1 and 2. Neither enolic structure 2 nor 3 can yield CH_3CO^+ upon fragmentation by simple cleavage; they must first isomerize to ion 1 via a 1–3 H shift. It is well known that this kind of transfer is accompanied by a high energy barrier.²⁵ For 2 → 1 isomerization, the barrier is calculated to be 187 kJ mol^{-1} above 2 at the highest level examined.

Final State. The final state corresponding to acylium formation is calculated to be 118 kJ mol^{-1} above the initial state 1. The 1-hydroxyvinyl cation CH_2COH^+ is not the observed final state, and it has been calculated by Radom²⁶ to lie 181 kJ mol^{-1} (MP3/6-31G**//4-31G + ZPVE) above CH_3CO^+ . This is in agreement with the experimental findings showing that only acylium cation is formed.

Ion-Neutral Complexes. To simulate the minimal energy pathway for cleavage leading to CH_3CO^+ formation, we have elongated the C(2)–C(3) bond length (in steps of 0.1 Å while optimizing all other geometric parameters at 3-21//3-21G level) of the keto acylium ions 1. The elongation of the C(2)–C(3) bond length in ion 1 leads to a steep increase in the potential energy reflecting the loss of the covalent interaction. Between 2.5 and 3.5 Å, the energy stabilizes around 17 kJ mol^{-1} below the energy of decomposing fragments ($\text{CH}_3\text{CO}^+ + \text{C}_2\text{H}_2\text{O}$) and the potential surface becomes flat. After a small increase around 3.65 Å, a

subsequent descending phase leads to an energy minimum where the distance $d[\text{C}(2)\text{--C}(3)] = 4.8$ Å and the structure corresponds to the stable structure 7. In this structure, a hydrogen atom of the acylium is weakly bonded to the oxygen atom of the ketene (Figure 3a). The energy of 7 is 56 kJ mol^{-1} below that of the separated components.

The region between 2.5 Å and 3.5 Å appears at first to be a broad transition state for the 1 → 7 isomerization. However, more careful scrutiny reveals a series of shallow minima, corresponding to other stable [acylium ketene] geometries. For instance, during the elongation of C(2)–C(3) bond in 1, the interaction between C(2) and C(4) increases by rotation of the ketene moiety. After a transition state, the system stabilizes at structure 8 for $d[\text{C}(2)\text{--C}(3)] = 2.85$ Å. This intermediate 8 looks like a loose association corresponding to an electrophilic attack by the acylium ion on the more basic carbon of the neutral ketene (Figure 3a). Diagonalization of the force constant matrix of 8 gives all positive eigenvalues and the stabilization energy of 8 is 32 kJ mol^{-1} . A simple translation of the ketene in 8 leads to structure 9, which has one imaginary frequency and could serve as a transition state for hydrogen exchange. In 9, the hydrogen of the acylium is weakly bonded to the sp^2 carbon of ketene and the two carbonyl groups are syn. On the other hand, the anti conformer 10 can form 8 by rotation of the ketene.

The hydrogen-bonded structure 10 is characterized by an elongation of one C–H bond (1.10 Å versus 1.084 in 7) and corresponds to a potential energy minimum whose force constant matrix gives all positive eigenvalues. The stabilization energy of 10 is 26 kJ mol^{-1} as compared to that of 9 (31 kJ mol^{-1}).

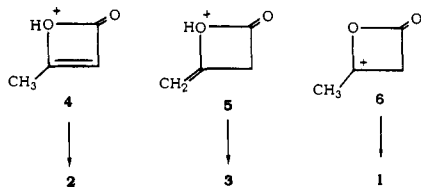
Much theoretical effort has been expended to provide a clear picture of the potential energy minima (7, 8, and 10) corresponding to ion-neutral complexes. Calculations at higher levels of theory do not significantly change the optimized geometries (e.g., bond lengths increase by only 4–7% in going from 3-21G to 6-31G* (Figure 3b), and the ordering of energies is not affected.

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Scheme IV



Following the experimental data, we have considered only the migration of hydrogen from the sp^3 - to the sp^2 -hybridized carbon atoms. Hydrogen transfer within **10** to form a symmetrical structure gives a transition state in which the two critical C-H bond lengths are 1.429 Å, showing a more covalent nature for this species.

The protonated ketene dimer **14** [$CH_2=C=O \cdots H^+ \cdots O=C=CH_2$] has been calculated to estimate its relative stability. In this respect, it must be mentioned that in this structure, which lies 111 kJ mol⁻¹ above the observed final state, the hydrogen atom is not equidistant to two oxygen atoms and must be considered as a complex formed by a 1-hydroxyvinyl cation CH_2COH^+ stabilized by a ketene moiety. The structure where H^+ is in the middle is not a minimum in the potential surface but a saddle point corresponding to the hydrogen atom transfer.

Discussion

In a first part, we will show that ion-neutral complexes are the only plausible intermediates in the atom exchange preceding the CH_3CO^+ formation. The existence and the interconversion of the stable forms of these ion-neutral complexes will be confirmed and described using ab initio calculations, and the relationships between stable and reactive structures will be then discussed.

Intermediacy of Ion-Neutral Complexes. The intermediacy of isomeric $C_4H_5O_2^+$ ions will first be examined both from experimental results and from calculations.

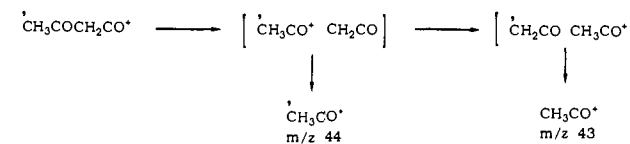
The enol structure **2** is the most stable among $C_4H_5O_2^+$ ions, but the data show that neither it nor enol **3** is an intermediate in the reaction pathway of ion **1**. First, calculations indicate that the isomerization of **2** or **3** to **1** involves a high energy barrier. Secondly, CH_3CO^+ formation from **2** occurs with a large kinetic energy release, whereas this value is extremely low for **1**. The same observation can be made for enol **3**, which is a valence isomer of protonated diketene **5**. If it were formed, **5** would ring open and lead to **3**, which yields CH_3CO^+ with a substantial kinetic energy release.

The cyclic structures **4**, **5**, and **6** (Scheme IV) can be discarded. Their planar geometries rule out hydrogen transfer prior to ring opening, and ring opening of **4** and **5** yields precisely the enols **2** and **3** previously ruled out. On the other hand, ion **6** is too high in energy to be a plausible intermediate; all attempts to optimize **6** lead to **1**, which indicates the great instability of this cyclic form. In any case the simple ring opening and ring closure of this ion cannot account for the atom permutation observed.

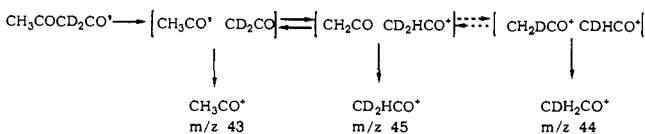
We now consider the ion-neutral complexes whose intermediacy appears highly probable. Using this hypothesis, the shifts of labeled ions **1** can be explained: (i) either by the existence of a symmetric, stable complex in which two neutral ketenes [one containing C(1) and C(2), and the other C(3) and C(4)] are bonded by a proton bridge; (ii) or by the isomerization via a hydrogen atom transfer of an [acylium ketene] ion-neutral complex to a complex of identical structure but in which C(1) and C(2) have been permuted with C(3) and C(4). The interpretation of the isotope effect favors the second hypothesis. In ¹³C-labeled ion **1a**, the fragments CH_3CO^+ (m/z 43) and $CH_3^{13}CO^+$ (m/z 44) have comparable intensities (Scheme V).

In the deuterated analogue **1b** $CH_3COCD_2CO^+$, the greater abundance of CD_2HCO^+ (m/z 45) compared to CH_3CO^+ (m/z 43) shows the existence of a nonnegligible secondary isotope effect. The very low intensity of CH_2DCO^+ (m/z 44) is the consequence of a large primary isotope effect. The isomerization [$CH_3CO^+ CD_2CO$] \rightleftharpoons [$CH_2CO CD_2HCO^+$] involves a H transfer, but [$CH_2CO CD_2HCO^+$] \rightleftharpoons [CH_2DCO^+CHDCO] requires a D-migration, which appears to be very difficult (Scheme VI).

Scheme V



Scheme VI



In ion **1c**, $CD_3COCH_2CO^+$, the operation of both the primary and secondary isotope effects inhibits the D transfer, CD_3CO^+ (m/z 46) dominates, and CH_2DCO^+ (m/z 44) is very small [$(m/z$ 46)/(m/z 44) > 5]. These pronounced isotope effects allow us to conclude that the transition state for the H-migration involved in the isomerization of the [acylium ketene] complex has an energy right below that of the final state.

The existence and the rôle of complexes such as [$(CH_3)_2CO \cdots HCH_2CO^+$] or [$CH_3CHO \cdots HCH_2CO^+$] in which a H of acylium is weakly bonded to the oxygen of a neutral has been already discussed in the literature.^{12,13} In the present case, there are no experimental data that exclude the intermediacy of such a complex [$CH_2CO \cdots HCH_2CO^+$]. However, even though its formation could be reversible, such an intermediate cannot account for atom permutation. Consequently, the experimental results suggest that the reactive form of the [acylium ketene] complex in the isomerization of **1** corresponds to structures in which a hydrogen atom of the acylium is weakly bonded to C(2) of the ketene.

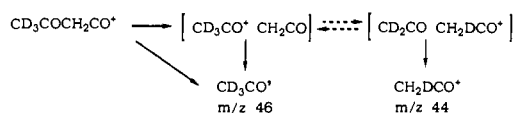
[Acylium Ketene] Complexes: Stable and Reactive Structures.

As shown by the calculations, the stretching of the C(2)-C(3) bond length in these structures gives **7**. This process involves first formation of an electrostatic complex **8**, hemmed in one side by a potential energy barrier corresponding to the point of covalent bond breaking and on the other side, by a series of translational and rotational barriers leading either to a more stable hydrogen-bonded complex **7** or to a hydrogen-bonded association **9**, or a stable species **10**. The chemical reaction (here hydrogen transfer) could take place within **9** and **10** before direct dissociation. After hydrogen permutation, structures **9** and **10** can also rearrange, to the same stable complex **7** which decomposes later. In all cases, the energy barriers of translations and rotations of the ketene with respect to the acylium ion, for **8** \rightarrow **9** \rightarrow **10** \rightarrow **7** should be very low. We summarize this part of the discussion by considering that several stabilization effects in the [acylium ketene] complex are evident. This means, as a consequence, that during the isomerization of one structure into another, the system is always stabilized by weak bonds: one stabilization effect is progressively substituted by another. For this reason, the potential wells determining the positions of the stable bridged-hydrogen forms **8** and **10** are very shallow. We have, therefore, a system in which one entity can turn easily with respect to the other.

We now turn to the problem of the reactive structures. Ion **7** corresponds to the most stable structure of the complex, but it has been shown that it cannot explain the atom permutation; **7** can only lead either to CH_3CO^+ [containing specifically the C(3) and C(4)] or to **1** via **8**, **9**, and **10**.

Proton transfer can take place from **9** without surmounting a substantial barrier if its geometry is permitted to adjust during the reaction. On the other hand, stable structure **10**, in which an hydrogen of the acylium is bonded to the ketene moiety, appears to be the direct precursor of the hydrogen atom exchange and can be taken to be the reactive form for the isomerization process. Ab initio calculations predict that the isomerization by H transfer of **10** to **10'** (in which the atoms are permuted) requires only 21 kJ mol⁻¹. The transition state of this reaction is completely symmetric: a proton is bonded to two neutral ketenes (Figure 3b) and lies in energy only 4 kJ mol⁻¹ (MP2/6-31+G**//6-31G*)

Scheme VII



under the final state. Moreover, by invoking tunnelling effects, described elsewhere^{15a} in this kind of linear C \cdots H \cdots C structure, the barrier of 21 kJ mol⁻¹ could be an upper limit for the hydrogen transfer.

The energy diagram elaborated at MP2/6-31+G**//6-31G* with these different data (Figure 4) is in accordance with the experimental results.

As the transition state for H transfer is below the final state, the isomerization leading to atom exchange is observed. However, its energy being very near that of the final state, the competition between the simple cleavage of **1** and the isomerization strongly depends on several parameters. On the one hand, this explains the low ratio of atom exchange in stable ions as previously shown in the CAD spectra of labeled ions **1**. This result accounts for the strong primary isotope effect when a deuterium atom is involved in the transfer **10** \rightarrow **10'**: the abundance of *m/z* 46 (CD₃CO⁺) peak in the MIKE spectrum of **1c** indicates that D transfer is inhibited, whereas the shape of this peak (existence of three components) shows that the direct cleavage of the initial ion becomes competitive in this case (Scheme VII).

Conclusion

Metastable CH₃COCH₂CO⁺ cation reacts via intermediate complexes. These complexes are not simply proton-bound dimers

of ketene [O=C=CH₂ \cdots H⁺ \cdots CH₂=C=O]. The symmetric structure in which a proton is bonded to two neutral ketene corresponds to a transition state. Instead, the intermediate corresponds to weakly bonded complexes of the form [acylium ketene].

Several stable structures have been considered. They are stabilized by different effects: weak bonding between a hydrogen atom of the acylium and the oxygen (or the carbon) of the ketene or interaction between a positive charge and a basic carbon. For this reason, the interconversion among structures is easy. One moiety can turn with respect to the other right below the threshold for dissociation, even though the intermolecular distances remain short.

Structure **7**, in which one hydrogen of the acylium is bonded to a ketene oxygen, is the most stable form of the [acylium ketene] complex but cannot lead to atom exchange reaction. The reactive structures are higher in energy and lie near the transition state. This implies that the calculation of a strongly stabilized structure cannot be the only argument to justify the intermediacy of a complex.

Only the energy variation has been discussed in this work. Entropy variation has been neglected in the first approximation. The study of substituted ions **1**, which will be published elsewhere, shows that this level of description is not always sufficient.

Supplementary Material Available: Tables of total energies (in hartrees) and relative energies (in kJ mol⁻¹) on selected levels of theory (2 pages). Ordering information is given on any current masthead page.

Experimental and Theoretical Studies of Alkaline-Earth Metal Coordination: X-ray Crystal Structures of Calcium, Strontium, and Barium Carbazoles and ab Initio Model Calculations

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Abstract: The solid-state structures of the aromatic alkaline-earth metal amides (*N*-carbazolyl)₂Ca(pyridine)₄ (**1**), (*N*-carbazolyl)₂Sr(NH₃)(DME)₂ (**2**) (DME = 1,2-dimethoxyethane), and (*N*-carbazolyl)₂Ba(DME)₃ (**3**) are compared. Compounds **1–3** crystallize as monomers with the M²⁺ cation (M = Ca, Sr, Ba) σ -bound to the carbazole nitrogen atoms. This is in contrast to the dimeric alkali metal carbazoles, which exhibit varying degrees of polyhaptic bonding to the carbazole π -system. While the metal coordination smoothly increases from six to seven to eight with M = Ca, Sr, Ba, respectively, the orientation of the anionic carbazole ligands changes from cisoid with M = Ca, Sr to transoid with M = Ba. Ab initio calculations on a series of solvated and unsolvated model complexes indicate this to be due to covalent Ba–N σ -bonding contributions involving metal d-orbitals and to cation polarization. These factors favor bent X–Ba–X arrangements, both in “naked” BaX₂ compounds and in solvated complexes BaX₂(L)_{*n*}. Anion–anion repulsion prevents cisoid structures for the complexes of the smaller Ca and Sr cations. Crystal data for **1**: monoclinic space group *P*2₁/*c*, *Z* = 4, *a* = 12.723 (6) Å, *b* = 18.169 (13) Å, *c* = 22.348 (10) Å, β = 105.82 (4)°. Crystal data for **2**: monoclinic space group *Cc*, *Z* = 4, *a* = 15.910 (9) Å, *b* = 13.040 (4) Å, *c* = 16.522 (7) Å, β = 116.83 (3)°. Crystal data for **3**: monoclinic space group *P*2₁/*c*, *Z* = 4, *a* = 9.785 (6) Å, *b* = 27.071 (7) Å, *c* = 14.370 (4) Å, β = 109.58 (4)°.

Introduction

What factors govern the coordination chemistry of the heavier alkaline earth metals? Theoretical studies of a large number of MX₂ compounds (M = Ca, Sr, Ba, Sm, Eu, Yb; X = H, Li, BeH,

BH₂, CH₃, NH₂, OH, Halogen, η -C₅H₅) demonstrate that, apart from pure Coulomb-type interactions, the influence of covalent bonding contributions involving metal d-orbitals, and the high polarizabilities of these heavy-metal cations are involved.^{1–5} While

[†]In memoriam (February 21, 1964 to February 16, 1992).

(1) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1991**, *94*, 1360.