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JMS Letters

Dear Sir,

Methyl Transfer Within Complexes in the Gas Phase: the [Ketene, H_3COCO^+] System

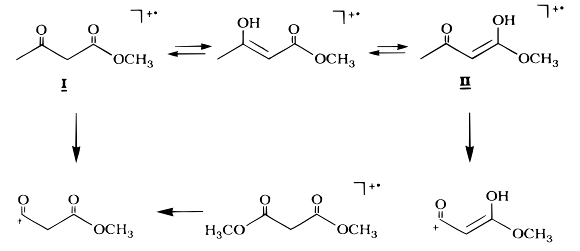
The $H_3COCH_2^+$ and H_3COCO^+ ions are good methyl cation donors in the gas phase.[1–6] The methylation process occurs within an ion–neutral complex formed either (i) by reaction of these cations with a neutral species or (ii) by simple cleavage of a larger cation giving a complex containing one of these cations. For instance, CO_2 elimination from the $(H_3CO)_3C^+$ cation has been explained by such a mechanism.[4] The methylation site of bifunctional compounds can be controlled *a priori* either by the relative stabilities of the methylated product ions or by the geometries and the relative stabilities of the intermediate complexes through which the CH_3^+ transfer takes place. This problem was studied in this work on the [ketene, H_3COCO^+] system generated by the cleavage of the $H_3COC(O)CH_2CO^+$ cation **1**. In addition, an interesting permutation of the carbonyl groups, occurring prior to dissociation, is demonstrated.

The $H_3COC(O)CH_2CO^+$ cation **1** was generated by loss of a methyl radical from methylacetoacetate radical cation in the ion source of a VG ZAB-2F double-focusing mass spectrometer. However, it is known that ionization of methylacetoacetate leads to a mixture of the keto and enol structures **I** and **II**.[7] therefore, in the ion source, the loss of $CH_3^{\bullet}$ yields a mixture of cations **1** and **2** (Scheme 1 which dissociate in the second field-free region (2nd FFR) to give the *m/z* 57 (24%), 59 (3%) and 69 (73%) fragment ions.

Ions **1** and **2** can be specifically generated as follows: Ion **1** was formed by loss of a $CH_3O^{\bullet}$ radical from ionized methylmalonate. In the 2nd FFR, **1** mainly leads to the $C_3H_5O^+$ fragment ion (*m/z* 57, 98%), but also to CH_3OCO^+ (*a*, *m/z* 59, 1%) and $C_3O_2H^+$ (*b*, *m/z* 69, 1%) cations. The $H_3COC(OH)CHCO^+$ ion **2** was formed by loss of $CH_3^{\bullet}$ from ion **II**, which was generated by a McLafferty rearrangement from ionized propyl 2-methylacetoacetate. Ion **2** eliminates mostly CH_3OH to give protonated carbon suboxide $C_3O_2H^+$ (*m/z* 69, 80%).

Since these two spectra are completely different, we conclude that interconversion of metastable ions **1** and **2** is very slow. It is therefore possible to study the behavior of each of them by fragmentation of specifically labeled methylacetoacetate.

The structures of the fragment ions were studied by collision-induced dissociation (CID), while their energies were calculated at the BLYP/6–31G* level by using density functional theory.[8,9] The *m/z* 59 fragment *a* leads to the same CID spectrum as the CH_3OCO^+ ion formed by $Cl^{\bullet}$ loss from methylchloroformate. The CID spectrum of the *m/z* 69 fragment ion *b* matches that of protonated carbon suboxide, $C_3O_2H^+$.[10] The CID spectrum of the *m/z* 57 ion, $C_3OH_5^+$, formed in both the 1st and 2nd FFR (CID spectra in the 2nd FFR were performed on a ZAB-qQ mass spectrometer), shows a strongly dominant *m/z* 42 peak (ionized ketene) formed by loss of $CH_3^{\bullet}$ and a smaller *m/z* 15 peak (CH_3^+), in agreement with the ionization energies of ketene (9.61 eV) and $CH_3^{\bullet}$ (9.84 eV).[11] The *m/z* 60 ion, generated by fragmentation of $D_3COCOCH_2CO^+$, only eliminates $CD_3^{\bullet}$ upon collision. This indicates that the *m/z* 57 ion, $C_3OH_5^+$, is formed by a methyl cation transfer to a ketene moiety and therefore its structure can only be $CH_3CH_2CO^+$ (*c*) or $CH_3OCCH_2^+$ (*d*). Ion *c* is 148 kJ mol^{-1} more stable than ion *d* but, upon collision, this ion only loses CO. The CID spectrum of ion *d* has not been published, but it is noteworthy that loss of a methyl radical is the only simple cleavage of *d* leading to a stable final state.



Scheme 1

Theoretical calculations reveal three stable structures for the initial ion **1**. The most stable is shown in Fig. 1. When the C(1)—C(2) bond is stretched, the length of the O—CH_3 bond also increases while the CH_3OCO^+ moiety rotates with respect to the ketene in order to increase the interaction between the CH_3 group and the oxygen of the ketene. This process leads to the [CH_2CO, H_3COCO^+] ion–neutral complex **4** (Fig. 1), in which the CH_3 group of the ion is close

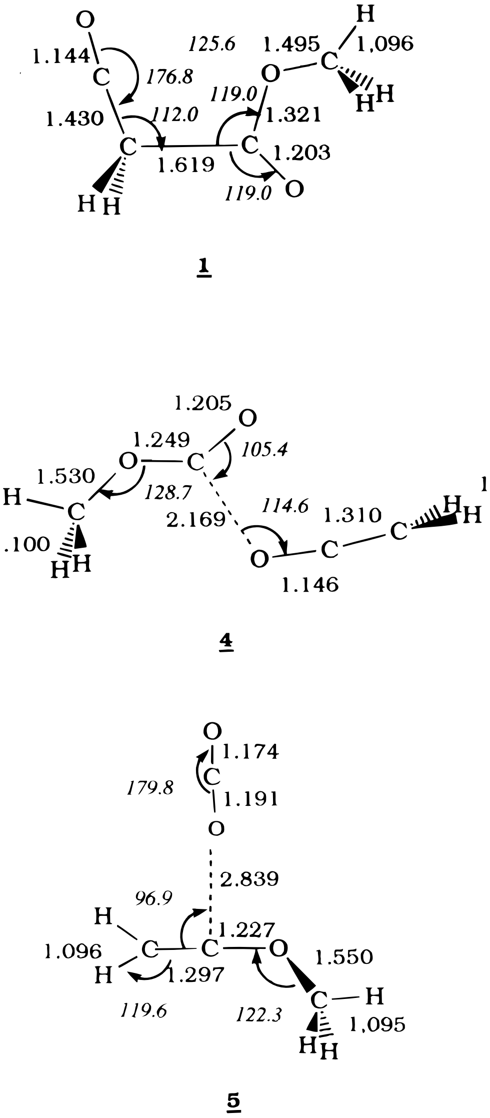


Figure 1. Geometries of stationary structures **1**, **4** and **5** at the BLYP/6–31G* level (bond lengths in Å, angles in degrees).

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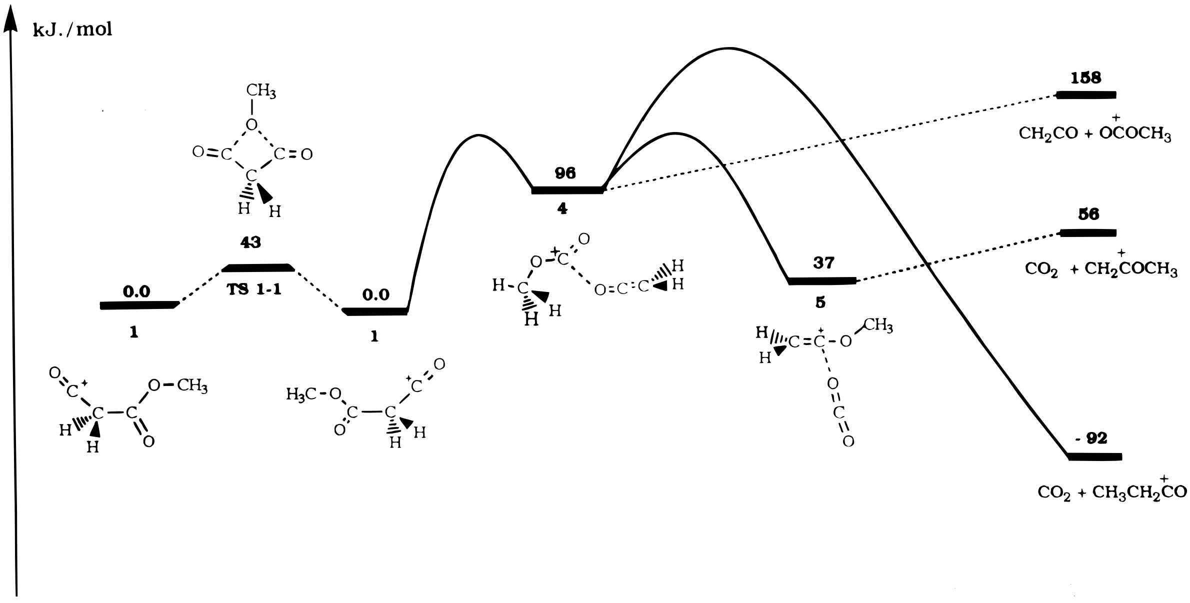

Figure 2. Schematic potential energy diagram for isomerization/dissociation processes of ion **1** at the BLYP/6–31G* + ZPE level.

to the oxygen of the neutral species. The complex **4**, which lies 96 kJ mol^{-1} above **1** (Fig. 2), is the key intermediate in the reaction of ion **1**.

A small proportion of the most energetic complexes **4** dissociate by simple cleavage to give the CH_3OCO^+ (*m/z* 59) fragment ion. Significantly, the abundance of this fragment strongly increases upon collision. The dominant phenomenon is $CH_3{}^+$ transfer from the CH_3OCO^+ ion to the ketene moiety to give the isomer complex [$CH_3OCCH_2{}^+$, CO_2] (**5**) and then the $CH_3OCCH_2{}^+$ product ion *d* by elimination of CO_2. The absence of the $CH_3CH_2CO^+$ fragment ion *c*, corresponding to the most stable final state, should be noted. Starting from **4**, both reactions giving either *c* or *d* are exothermic (Fig. 2) and the reaction pathway will be determined by the relative energies of the corresponding transition states. The absence of ion *c* shows that the complex [CH_2CO, H_3COCO^+] (**4**) does not isomerize into the [$OCCH_2$, H_3COCO^+] complex which would give *c* by $CH_3{}^+$ transfer; the rotation of the ion with the respect of the neutral species, within the complex **4**, may then implicate an important energy barrier (Fig. 2).

The reactions of labeled ions show that the isotope effects are not significant and that hydrogen exchange prior to dissociation is negligible. However, the ^{13}C and ^{18}O labelings indicate that complete permutation of both carbonyl groups takes place in ion **1** prior to the formation of the *m/z* 57 and 59 fragment-ions. The permutation of the carbonyl groups is also observed for long-living methyl acetoacetate molecular ions;[7] however, this process is negligible in the ion source and, therefore, prior to formation of ion **1**. This permutation occurs via a cyclic transition state whose calculated energy lies far below those of the final states corresponding to the *m/z* 57 and 59 fragments (Fig. 2).

In conclusion, the $C_3H_5O^+$ cation, formed by loss of CO_2 from the $H_3COC(O)CH_2CO^+$ cation **1** does not correspond to the most stable structure $CH_3CH_2CO^+$ but to $CH_2COCH_3{}^+$, whose ΔH_f is 148 kJ mol^{-1} higher. This is a consequence either of the existence of an energy barrier for the C—C bond formation or of the energy barrier which separates the [CH_2CO, H_3COCO^+] complex **4** and the [$OCCH_2$, H_3COCO^+] complex. This behavior contrasts with that of similar systems such as [$H_3COCH_2{}^+$, ketone][12] and [CH_3CO^+, CH_2CO][13] leading to methylation or protonation of the neutral species. In the present case, the absence of reorientation of the ion within the complex **4** may be due to two complementary factors: exothermicity of the dissociation of the complex **4** and great flexibility of H_3COCO^+, which is in fact a weakly bonded species between CO_2 and a methyl cation.[4]

Yours,

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