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A Theoretical Approach to the Rearranged Ion in the Mass Spectrum of Methyl Formate

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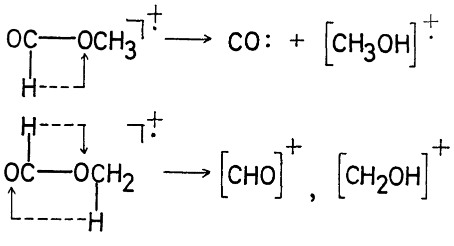
The hydrogen-migration mechanism of the fragmentation of the methyl formate under electron impact has been discussed from the standpoint of the all-valence electron semi-empirical SCF-MO theory (CNDO/2-Unrestricted Hartree Fock), assuming the following models:



$$[\mathrm{OC{-}OCH_3}]^{+\cdot} \longrightarrow \mathrm{CO}: + [\mathrm{CH_3OH}]^{+\cdot}$$

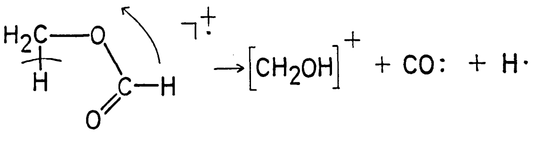
$$[\mathrm{OC{-}OCH_2}]^{+\cdot} \longrightarrow [\mathrm{CHO}]^{+},\ [\mathrm{CH_2OH}]^{+}$$

The model for the hydrogen migration and the possible driving force are presented based on the partition method. The localized MO calculation has been carried out, by the "energy localization" method of the MINDO MO's, for the origin and the terminus of the migration as an aid to the understanding of the migration. Although the possibility of the hydrogen migration in other models can not always be neglected, the hydrogen migration via Model 1 may be estimated to be energetically favorable, judging from the variation in the total energy and the conformation influence.

It is interesting to disclose the migration processes[1] involved in the fragmentation from the standpoint of the molecular orbital theory (MO theory), although the empirical speculations of the migration mechanisms based on a variety of mass spectral data have been presented by many investigators. The analyses of the mass spectral data of organic compounds has not been completely established because of the complexity of the driving factors governing the cleavage of the molecular ion $M^{+\cdot}$ on electron-impact collision. In order to establish the rules governing fragmentation, it is important to clarify the mechanism of the intramolecular migration of hydrogen.

In a previous paper,[2] models for the hydrogen migration in butyl alcohol were reported. The results have been related to the ease of the cleavage of the $M^{+\cdot}$ ion to the $[M-H_2O]^{+\cdot}$ ion in the rearrangement process. This simple model employed was able to explain the mechanism.

In the mass spectrum of methyl formate, the peak thought to be the ion formed by the rearrangement was observed. Production of the ion with a m/e 32 involves hydrogen rearrangement from the formyl carbon to the oxygen atom. The base peak corresponds to the CH_2OH ion with a m/e 31 due to the loss of hydrogen[3] on the methyl group. The $[CH_2OH]^+$ ion is probably formed by the following mechanism:[4]



$$\longrightarrow [\mathrm{CH_2OH}]^{+} + \mathrm{CO}: + \mathrm{H}\cdot$$

This migration mechanism has however not been fully elucidated, but only speculated from the mass spectral data.[5]

The present paper is concerned with the hydrogen-migration mechanism in methyl formate and the variation of energy in terms of the MO theory. In the model-process simulated, the migration points, the driving force in the hydrogen migration and the energy profiles obtained from the CNDO and MINDO calculations are reported. The bonding interaction along the migration path has also been examined.

Computation and Geometry

Computation. All computations were carried out on a NEAC 2200 Model 700 computer at Osaka University. The semi-empirical SCF-MO wave functions were computed with the CNDO-UHF method developed by Pople and coworkers.[6] The AO parameters used for CNDO were those originals[7] reported by the authors. The energy partitioning was obtained from the method reported by Fischer[8] and Gordon.[9] The LMO calculation was carried out using the "energy localization" method of Edmiston-Reudenberg.[10]

Geometry. The starting geometry for the migration requires a minimization of the total energy of the system with respect to all its independent internal coordinates, and the generation of a complete potential energy surface for the chemical reaction requires a path in the energy minimum. The problem is that the conformation and the electronic state of the $M^{+\cdot}$ ion absorbing energy in the ionizing chamber have stable geometries and the migrating hydrogen has a path in the energy minimum.

For the rearrangement model, it is, therefore, important to clearly decide the geometry. However, under electron impact, it is difficult to absolutely determine the reaction coordinate passing through the equilibrium geometry. The instantaneous conformation of the $M^{+\cdot}$ ion which had absorbed the energy could not be established. According to Franck-Condon,[11] it may be assumed that the geometry of the M^{+} ion is in the ground state. Consequently, the assumed models in the migration process are as shown in Fig. 1.

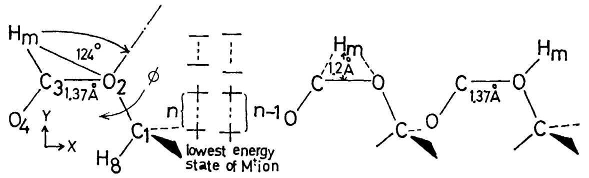


Fig. 1. Schematic representation of hydrogen-migration from carbon to oxygen.
n represents a number of the occupied MO and the numbering system of the atoms is that used in this paper.

Five points were chosen to form a path representing the hydrogen migration from the formyl carbon(C_3) to Oxygen(O_2). The terminus structure employed here was decided from the stability of the conformation of the CH_3OH. Point 3 in which angle $\angle C_3H_mO_2$ is 60° was also available for the intermediate structure and then the other points were situated in the middle of these points. The distance between the center of the C–O bond and the migrating hydrogen at Point 3 was assumed to be 1.2 Å; 1.2 Å was defined judging from the energy minimum state in which the conformation is energetically stable with 1.1 and 1.3 Å. The length of the O_2–C_3 bond with 1.37 Å was chosen as the terminus of the migration. As shown in Fig. 2, the total energy changed with the length of the O_2–C_3 bond at Points 4 and 5; thus the total energy was a minimum at 1.37 Å.

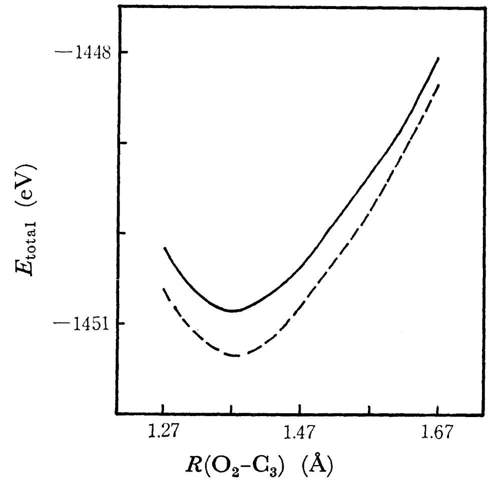


Fig. 2. Variation of the total energy with O-C bond length for Points 4 and 5.
——: Point 4, ----: Point 5.

The bond lengths and bond angles for the origin of the migration, with the exception of the C_2–O_3, were taken from the standard tables.[12]

The migrating hydrogen in the terminus is then situated in the XY plane as shown in Fig. 1 and the hydrogen atom migrates in this plane. The conformations in Models 1 and 2 were chosen to be planar with $\phi=0°$ and $\phi=180°$, respectively. The form of the CH_3OH in the terminus of the migration is an eclipsed one in Model 1, while in Model 2 it is a staggered one.

Table 1. Molecular geometries[a)] for the migrating points

Parameter[b)]	1 Origin	2	3	4	5 Terminus
$\angle O_2C_3H_m$(°)	118.5	86.5	60.0	38.8	27.7
$R(O_2\text{-}H_m)$(Å)	2.119	1.736	1.382	1.052	0.960

a) The other parameters were described in Fig. 1.
b) Application of the law of cosines for a triangle.

In Model 3, the path synchronously representing the two hydrogenes (H_m and H_8) in the following figure was selected, in which the movement of H_8 was chosen with respect to the least-motion path from C_1 to the lone pair of O_4. The lengths between O_4 and H_8 in each point are 2.920, 1.753, 1.457, 1.184, and 0.960 Å, and then the others are the same as Model 1.

Finally, the electronic states of the M^{+} ion are not the only states that loses an electron in the highest occupied orbital; the states in any part of the lower orbitals also lose electrons. However, the demotion step of an electron from the higher energy levels to the lower vacant level may occur before fragmentation.[13] Therefore, the electronic state of the M^{+} ion employed has been the lowest energy state, as found in butyl alcohol.[2]

Results and Discussion

Energy Profile. The results of the CNDO calculation in methyl formate are summarized in Table 2. This treatment was found to give a good description of the cleavage of the C–H bond during the migration.

It is apparent from the shape of the curve in Fig. 3 that the transition state lies in the latter half of the reaction. Both the total energy profiles which were obtained from Models 1 and 2 show a maxima at Point 3 along the coordinate representing migration of the hydrogen from C_3 to O_2. The total energy tends to decrease after the transition state. These results suggest that the small potential energy easily

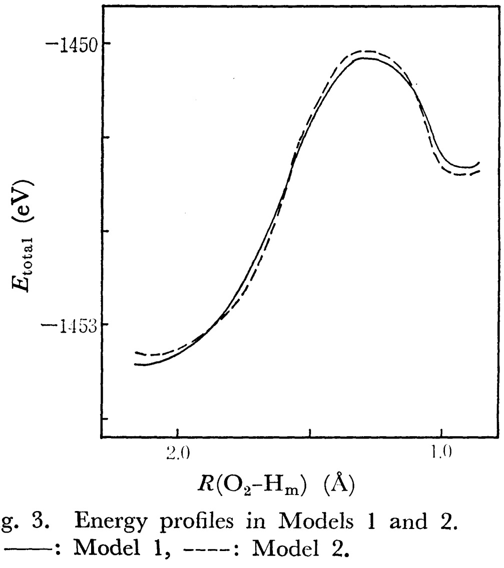


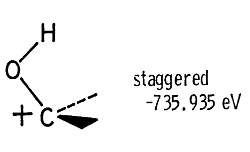
Fig. 3. Energy profiles in Models 1 and 2.
——: Model 1, ----: Model 2.

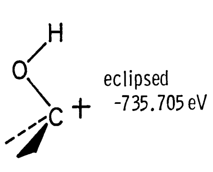
TABLE 2. VARIATION OF THE TOTAL ENERGY AND E_{AB}[a,b)]

	1	2	3	4	5
			Model 1		
$R(O_2\text{-}H_m)$ (Å)	2.119	1.736	1.382	1.052	0.960
E_{total}	−1453.416	−1452.608	−1450.156	−1450.829	−1451.319
E^U+E^R c)	−2372.164	−2372.885	−2385.868	−2392.275	−2388.718
	(−187.390)	(−185.609)	(−182.173)	(−185.234)	(−188.203)
E_{AB} $C_1\text{-}O_2$	−24.706	−24.700	−24.121	−23.190	−23.666
$O_2\text{-}C_3$	−33.145	−31.465	−28.468	−26.954	−27.597
$C_3\text{-}O_4$	−33.782	−40.256	−45.030	−45.837	−46.099
$C_3\text{-}H_m+O_2\text{-}H_m$	−18.677	−17.982	−15.552	−18.597	−18.501
			Model 2		
E_{total}	−1453.313	−1452.537	−1450.090	−1450.898	−1451.375
E^U+E^R	−2371.368	−2372.165	−2385.088	−2391.368	−2388.072
E_{AB} $C_1\text{-}O_2$	−24.752	−24.751	−24.129	−23.222	−23.648
$O_2\text{-}C_3$	−33.118	−31.388	−28.004	−23.062	−27.633
$C_3\text{-}O_4$	−39.004	−40.529	−45.042	−45.948	−46.214
$C_3\text{-}H_m+O_2\text{-}H_m$	−18.661	−17.874	−15.544	−18.584	−18.433

a) Energy in eV. b) The total energy, E, in the CNDO scheme, can be partitioned into chemically useful terms, $E=\sum_{A}E_A+\sum_{A<B}E_{AB}$; in which $E^U=\sum_{r}^{A}P_{rr}U_{rr}$ and $E^R=2\sum_{r}\sum_{s}P_{rs}S_{rs}\beta_{AB}^{\circ}$. There is a qualitative correspondence between E_{AB} and the bond length; thus the values of E_{AB} for the strong bonding interaction are very large and negative one.[14)] c) Values in parentheses correspond to E^R.

initiated the migration. The potential energy, 3.3 eV in Model 1, is small in comparision with the ionization potential. Moreover, the variation of the total energy of the system is small in comparison with the appearance potentials of the fragment ions. The difference between the total energy of the ground state of the molecule and that of the M^{+} ion is also smaller than the appearance potentials in the simple fragmentation. The potential energy, 3.3 eV, is thus small in comparision with the minimum energy required to bring about scission of the bonds. Then, the variation of the total energy in the origin of the migration in both Models, which is 2.4 kcal/mol, is the small difference. The difference in the terminus energies of both Models is smaller than that in the origin and this indicates that the migration by both Models is energetically favorable and that Model 1 is more favorable.





In the fragment ion, *i.e.*, CH_3OH ion, the calculation of methyl alcohol[15)] in the cation radical state predicts the staggered form to be more stable energetically. In the calculation on the fragment ion, it is predicted that the CH_2OH ion in the cation state has the lower energy in the staggered form. The difference in the total energy is 5.3 kcal/mol. It seems that the terminus of the migration is favorable in the staggered form.

Here, the driving force in the hydrogen migration was interpreted using the partitioned energy. The variation of the one-center term $\Delta\sum E_A$, is 1.67 eV and that the two-center term $\Delta\sum E_{AB}$, 0.426 eV. The driving force from the origin to the terminus form is, therefore, found principally in the two-center term. As is shown in Table 2, it was found that the partitioned energy contributing to this migration was the resonance energy in which there was proportionality between the total energy and the E^R value. The resonance energy term (E^U+E^R) decreases with the hydrogen migration in both Models. It has been suggested that the decrease in energy is due to the resonance effect and that the decrease in total energy results from the steric effect.

The sum of the E_{AB} values of the two bonds ($C_3\text{-}H_m+O_2\text{-}H_m$) decreases along the latter half of the reaction. This decrease implies that the bonding interaction between oxygen and the approaching hydrogen becomes

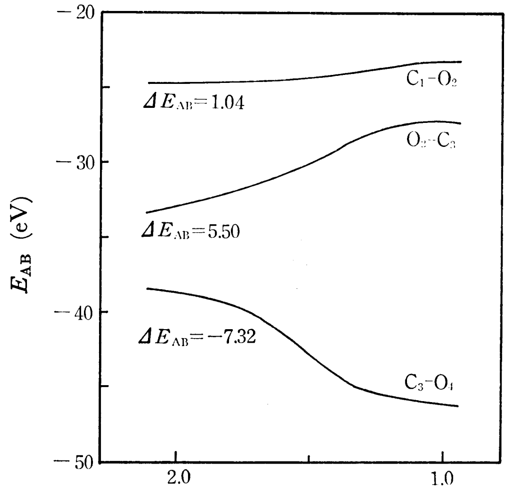


Fig. 4. Variation of E_{AB} of each bond to migration in Model 1.

stronger in this process. As shown in Fig. 4 the bonding interaction energy of the O_2–C_3 bond increases remarkably with the approach of hydrogen to O_2; this shows that the interaction between O_2 and C_3 is weakened by the hydrogen migration in Model 1. The variation of the E_{AB} value of the C_1–O_2 bond is smaller than that of the O_2–C_3 bond, whereas the E_{AB} value for the C_3–O_4 bond decreases remarkably. These results may be related to the ease of the cleavage from the M^{+} ion to the CH_3OH ion.

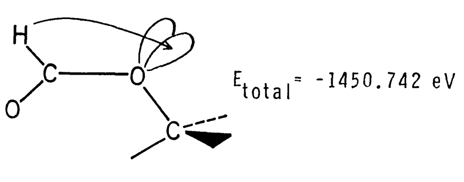
Table 3 shows the energy profile calculated by the MINDO calculation in the hydrogen migration in Model 1; both predict the decrease of the E_{AB} value of the sum of the two bonds and the resonance energy, although there are some differences between the CNDO and MINDO. The total energy and the E_{AB} of the O_2–C_3 bond are more stable at the terminus of the migration. It is also shown that investigation for hydrogen should be esitmated from MINDO.[16]

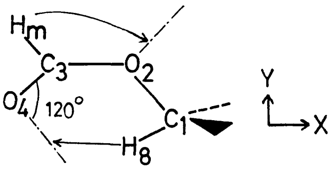
TABLE 3. VARIATION OF E_{AB}[a]

	Origin	Terminus
$R(O_2$-$H_m)$ (Å)	2.119	0.960
E_{total}	−933.858	−933.619
E_{AB} O_2-C_3	−22.392	−17.001
E_{AB} C_3-H_m+O_2-H_m	−10.617	−13.809

a) Geometries are same as CNDO and energy in eV.

The energy barrier by rotation of the O_2–C_3 bond is 1.2 kcal/mol, which is small in comparison with that of the CH_3 group. So, the hydrogen migration in Model in such a conformation was considered. Consequently, the total energy changes from −1453.279 to −1443.630 eV in the CNDO and this variation is larger than in the models discussed previously. There are then, as many conformations existing as migration processes, but the most likely conformation is the planar form. In the terminus form in the model the migration hydrogen is out of the molecular plane in the figure. The angle between the two lone pairs and the O_2–H_m bond is 61.8°[17] in this model. As a results, the variation of the total energy is 61.7 kcal/mol which compared with Model 1 decreases by more than 10 kcal/mol. It has been concluded this model that for the migration toward the lone pair of O_2 is energetically less favorable than Model 1. The formation of the CH_2OH ion has been discussed in terms of the synchronized migration model, *i.e.*, Model 3 in which the migration of hydrogen on the CH_3 group in the molecular plane was employed.





The movement of H_m is the same as in Model 1 and H_8 synchronously migrated to O_4. Table 4 shows the variation of the energies with the migration. The total energy increases remakably with the migration, though there is a slight decrease at the end of the migration. The change of the bonding interaction of the O_2–C_3 bond shows the remarkably increasing trend. The sum of the E_{AB} values of the two bonds for H_m changes randomly, implying that the migration of H_m is prevented by H_8. Convertly, the length between O_4 and H_8 at the origin and the terminus of the migration, 2.920 Å, is larger than that for H_m. However, the E_{AB} value decreases during the migration from Point 3 to Point 4. Consequently, the migration of H_8 may be possible, judging from the variation of the E_{AB} value. These results are energetically in agreement with regard to the mass spectral data; the peaks of the CH_2OH ion and the CHO ion are in abundance, which shows that this process is possible.

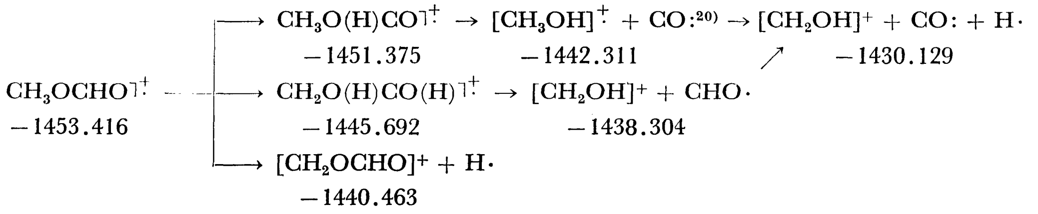
It may be possible that H_8 migrates from C_1 to O_4 just like protonated formaldehyde.[18] Thus, the process which H_8 migrates to the lone pair of O_4 was calculated, in which H_m was fixed at the origin of the migration. The variation of the sum of the two bonds was similar to that in Model 3. The total energy increases with the migration, but in the latter half tends to decrease. The E_{AB} values of the O_2–C_3 bonds in the origin and the terminus were −33.145 and −33.572 eV, respectively, implying that the bonding interaction of the O_2–C_3 bond does not weaken by the migration of H_8 alone. These results show that the peaks of HCO(H)[19] ion and CH_2O ion with a *m*/*e* 30 is in less abundance. These peaks are, in fact, in less abundance in the mass spectrum of methyl formate.

Considering the variation of the total energy, the profile is as follows, (the values are the total energies of the systems). The variation of the toatl energy in each system predicts that the fragmentation

TABLE 4. VARIATION OF THE TOTAL ENERGY AND E_{AB}[a]

	Model 3				
	1	2	3	4	5
$R(O_4$-$H_8)$ (Å)	2.920	1.753	1.457	1.184	0.960
E_{total}	−1453.416	−1451.120	−1445.164	−1445.323	−1445.690
E_{AB} O_2-C_3	−33.145	−32.054	−29.739	−26.036	−21.962
E_{AB} C_3-H_m+O_2-H_m	−18.677	−17.968	−16.097	−18.919	−16.178
E_{AB} C_1-H_8+O_4-H_8	−20.513	−19.248	−15.913	−17.508	−19.073

a) Energy in eV.



reaction in methyl formate would be *via* the $CH_3O(H)CO]^{+\cdot}$; the fragment ion, $[CH_3OH]^{+\cdot}$, is produced by the elimination of CO from the terminus of the migration. Judging from the variation of the total energy the CH_2OH ion results from the elimination of hydrogen from the CH_3OH ion in methyl alcohol. In the case of methyl formate, the CH_3OH ion decomposes further, and one of the energetically most favorable paths appears to be α-cleavage[21] to give the stable CH_2OH ion. The bonding character of the particular bond, *i.e.*, the O_2–C_3 bond varies from bonding to antibonding with the migration. Moreover, the bonding character of the O_2–C_3 bond changed from bonding(0.232) to antibonding(−0.143), as the electron was excited from the single occupied MO to the lowest unoccupied MO; thus the O_2–C_3 bond was weakened by the migration and then by the excitation in the origin of the migration. There is then the possibility that hydrogen migrates to O_2 before scission of the O_2–C_3 bond.

Charge Distribution. The changes of the electron densities of the atoms along the reaction coordinates have been examined and the results of the calculation for Model 1 are summarized in Table 5. It is immediately apparent from the densities that the most significant electron density changes observed are on the atoms: *viz.* C_3 and O_4. There is an increase in the atomic population on C_3. This electron flow to C_3 and O_4 implies that the CO has a stabilizing radical in the migration process. There is the charge on the CHO side in the origin of the migration. However, when H_m migrates to O_2, the charge moves to the CH_3OH side;

$$[OHC]^+\text{-}OCH_3 \rightarrow CO\text{-}[HOCH_3]^+.$$

Thus, the elctron density of H_m decreases with the migration as is shown in Table 5. It seems the migrating hydrogen moves like a proton, judging from the variation of the density of H_m. From the results of the hydrogen migration, it appears that the charge of the system remains on the CO, suggesting the formation of the $[M-CO]^{+\cdot}$ ion with a *m/e* 32. A decrease of electron on H_8 and an increase on O_4, was seen, *i.e.*, H_8 in the methyl group is a movable hydrogen and in the same way as the rearrangement of hydrogen to oxygen in aldehydes, there is a good chance of migration from C_1 to O_4. The increase of the electron on O_4 interacts with H_8 and may be considered as a driving force. Therefore, the influence of the synchronized migration of H_8 on the migration of H_m should be discussed.

Table 5. Atomic populations

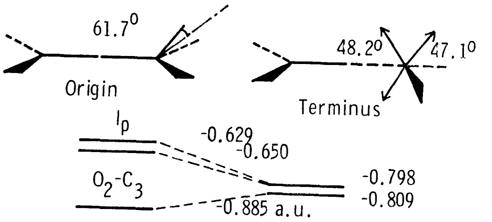
Atoms	1	2	3	4	5
C_1	3.8851	3.8864	3.8676	3.8287	3.8634
O_2	6.0781	6.0931	6.1412	6.0924	6.0460
C_3	3.5172	3.5537	3.6226	3.7396	3.6905
O_4	5.9044	5.8951	5.9679	6.0230	6.0233
H_m	0.8374	0.7855	0.6192	0.5938	0.6607
H_6	0.9162	0.9196	0.9227	0.9111	0.9114
H_7	0.9162	0.9196	0.9227	0.9111	0.9114
H_8	0.9453	0.9471	0.9360	0.9005	0.8933

Localized MO. The simplest relation between the origin and the terminus of the migration by the LMO representation is as follows. In the terminus of the migration the O_2–C_3 bond becomes the lone pair of oxygen and the radical orbital of carbon.The increase of LMO energy of the O_2–C_3 bond due to the migration results from the change to the weak C–O bond due to the conversion of the O_2–C_3 bond to the lone pair. However, the increase of this MO energy is considerably offset by the lone pairs.

Table 6. % s nature[a)] in Model 1

	Origin	Terminus
C_3–O_2	34.12	7.98
O_2–C_3	16.25	25.37
O_2–C_1	23.09	21.21
C_3–O_4	18.47	20.05

a) Percent s nature determined by summing the squares of the coefficients of the AO contribution to the LMO and dividing this by the 2s AO coefficient.



In Table 6, the values of the % s nature of the hybrid orbitals contributing to the localized orbitals are given. From this data, it seems that there is a remarkable decrease in % s in the C_3–O_2 bond. The % s of the C_3–O_2 bond decreases by 7.98 with the migration. This indicates that the electrons are highly localized in the C_3–O_4 bond and in the shape as the C_3 radical orbitals; since the s AO energy is lower than the p AO, the lower value of s nature leads to the more unstable state. This picture is more directly attainable than from the set of LMO.

Conclusion

There are many configurations in the $M^{+\cdot}$ ion produced by electron impact. The fragment ions and the rearranged ions result from the fission of the M† ion produced. Therefore, it is difficult to absolutely determine the geometry and the electronic state of the M† ion which has absorbed the energy and the path of the hydrogen migration. As a model, the lowest energy state of the M† ion in the planar form and the terminus form of the migration which has the lower energy in the staggered form were employed . This indicates that the hydrogen on the formyl carbon migrates to O_2. This simple model gives a fairly good feature with respect to the CH_3OH ion and the CH_2OH ion in the mass spectrum. The treatment of the M† ion using the partitioning energy yielded results in the rearrangement reaction.

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