A Theoretical Approach to the Possible Hydrogen Migration in Butadiene under Electron Impact

Tsutomu TAKAGI* and Masayoshi OIWA

Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564

(Received July 13, 1978)

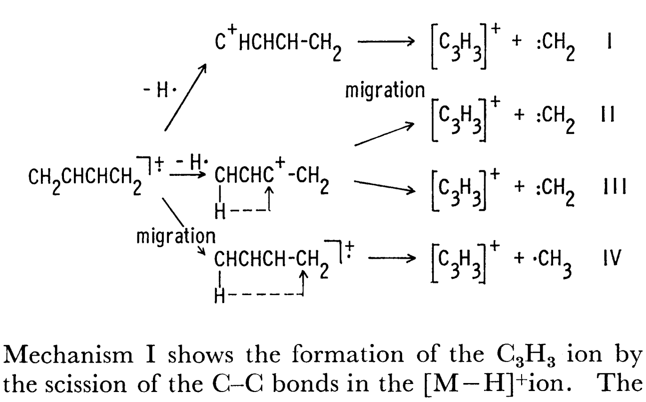
The hydrogen migration in butadiene under electron impact was studied by means of the calculated potential energy surfaces. The all-valence electron semi-empirical SCF-MO(MINDO/2-Unrestricted Hartree Fock) theory was employed. The possibility of the migration of hydrogen has been discussed. Moreover, the mechanisms (I—IV) including the hydrogen migration for the formation of the C_3H_3 ion have been discussed. The hydrogen-migration models are presented based on the variations in the total and the partitioned energies. It is very probable that the hydrogen on C_1 in the M^{+} ion migrates to the other carbon, C_4, *via* Models 1 and 2 in Mechanism IV. It was predicted that the formation of the C_3H_3 ion occurs by means of the fragmentation of the migrated M^{+} ion, although the other mechanisms can not always be ignored. Finally, for the hydrogen-migration models, the theoretical predictions were found to be in good agreement with the available experimental results.

The fragmentation in the unsaturated hydrocarbons is more complex than in the case of the saturated hydrocarbons. The hydrogen migration in the molecular ion(M^{+}) can be expected to be essentially prevalent if the M^{+} ion possesses a large amount of excess vibrational energy. In this case, it is thought that the hydrogen migration proceeds *via* the four- or six-ring transition state.[1,2]

The possibility of the migration of hydrogen in butadiene can not always be neglected, judging from the mass number of the produced fragment ions. In butadiene, the C_3H_3, C_2H_3, and C_4H_5 ions are found in the mass spectrum in rich abundance. The precise mechanisms for the formation of these fragment ions, especially the C_3H_3 ion, have, however, not yet been elucidated, but only speculated from the mass spectral data.

By the way, the Woodward-Hoffmann rule is very useful in discussing the migration of hydrogen. However, with respect to the mechanism of the formation of the C_3H_3 ion including the hydrogen migration, the contribution of the hydrogen migration to the cleavage of the C–C bond can not be discussed in terms of the W-H rule. Therefore, it is necessary that the role of the M^{+} ion for the hydrogen migration be discussed in terms of energy.

The mechanisms for the C_3H_3 ion with *m/e* 39 are thought to be as follows:



Mechanism I shows the formation of the C_3H_3 ion by the scission of the C–C bonds in the $[M-H]^{+}$ion. The mechanism with the hydrogen migration to the carbon atom loses a hydrogen atom as is shown in II. In Mechanism III, this process shows the simple fragmentation of the $[M-H]^{+}$ion. If the existence of the five-ring transition state in Mechanism IV is real, *i.e.*, if it is estimated that the hydrogen-migration process is energetically favorable, Mechanism IV should not be ignored. Mechanism IV shows the process with the migration of hydrogen.

The present paper is concerned with a discussion of the migration of hydrogen and with the treatment by the simple models for the formation of the C_3H_3 ion in order to gain a better understanding of the fragmentation in butadiene from the standpoint of the MO theory.

Method and Conformation

Computations. All the computations were carried out on a FACOM 230-48 computer at Kansai University. The wave functions were calculated by means of the MINDO method, with the original parameterization.[3] The MINDO calculation of the open shell-configuration was carried out using the method reported by Dewar.[3]

The total energy, E, can be partitioned into these chemically useful terms:[4,5]

$$E=\sum_{\mathrm{A}} E_{\mathrm{A}}+\sum_{\mathrm{A}<\mathrm{B}} E_{\mathrm{AB}}$$

E_{A} is the energy due to the atom A. E_{AB} is the contribution to the total energy from all two-center integrals involving A and B centers, and can be partitioned into covalent binding, core repulsion, and ionic terms.[6]

Geometry. The starting geometry for the hydrogen-migration model requires a minimization of the total energy of the system with respect to all its independent internal coordinates, as has been discussed in a previous paper.[7] Moreover, it is difficult to determine absolutely the reaction coordinate passing through the equilibrium geometry. A full optimization of the

TABLE 1. MOLECULAR GEOMETRIES FOR THE M^{+} ION

Parameter		Parameter	
r_1	1.37 Å	α	122°
r_2	1.47 Å	β	125°
r_3	1.06 Å	θ	119°

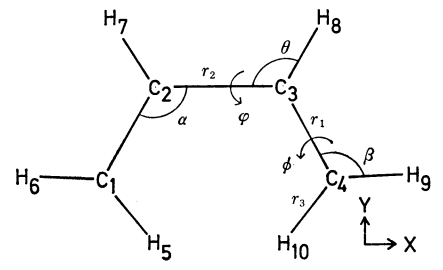


Fig. 1. Definition of the geometrical parameters for the M^+ ion.

geometries at each point in the migration process is thus quite impractical. Consequently, we employed the parameters[8] for the geometry of the M^+ ion as shown in Fig. 1 and Table 1.

The geometries were chosen by assuming the same valence angles for the hydrogen atoms on the CH_2 groups and by neglecting the changes in the C–C bond lengths in the migration process. The twisting of the carbon frame is expressed by φ, the dihedral angle between the $C_1C_2C_3$ and $C_4C_3C_2$ planes; $\varphi=0°$ for *cis*. The CH bond length was changed from 1.06 Å in the starting geometry to 1.09 Å in the terminus of the migration. At the terminus of the hydrogen migration, the angles of β and φ are 109.5° and 90° respectively.

Rotation. The variation in the total energy of the M^+ ion, as a function of the angle, φ, keeping the other internuclear distances and angles constant, is shown in Table 2.

The bond distance between C_4 and H_5 is 2.691 Å in *cis*($\varphi=0°$) and 2.812 Å in $\varphi=30°$, while the bond distance between C_4 and H_7 is 2.720 Å in *trans*($\varphi=180°$). Upon the rotation in φ from 0° to 180°, the chance of the migration of H_7 to C_4 becomes large. The resonance interaction (E^R) between C_4 and H_5 is slightly stronger at 30° than at 0°. Therefore, as a starting conformation, it seems reasonable to adopt that one at $\varphi=30°$ with respect to the migration of H_5 to C_4.

By the way, the net electric charge on C_4 is 0.2048, which is larger and more positive than that as C_3. If the migration of hydrogen is induced by the positive charge, it can be predicted that the migration of hydrogen to the end carbon atom is possible. One findings are, of course, as yet insufficient for us to discuss the possibility of the migration of hydrogen.

Energy Contour. In order to ascertain the migration path, a two-dimensional energy surface was generated by calculating the energy minimum as a function of the α angle, as well as of φ, assuming the other parameters in Table 1. The calculations were carried out with the φ angle increased from 0° to 90°, and at each value of φ, with α varying from 60° to 122°.

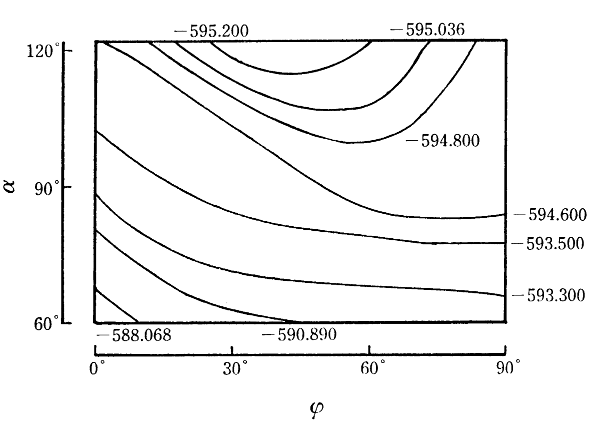


Fig. 2. Energy contours (in eV) of the M^+ ion of the origin of the migration of bent and twisted butadiene, as a function of the angles α and φ. Note that the contours are not separated by equal intervals of energy.

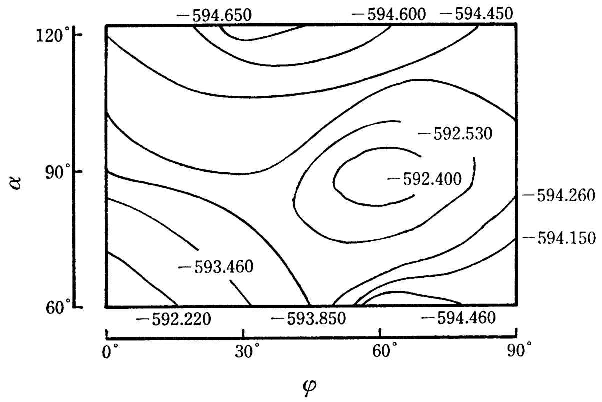


Fig. 3. Energy contours (in eV) of the M^+ ion of the terminus of the migration of bent and twisted butadiene, as a function of the angles α and φ. Note that the contours are not separated by equal intervals of energy.

The total energy-contour diagram for the origin of the migration is given in Fig. 2. The most obvious feature was the deep energy minimum at $\varphi=30°$ and $\alpha=122°$. It can be predicted that this feature results from the electron deficiency; the rotation of the C_2–C_3 bond is comparatively more favorable than a neutral molecule. On the other hand, the total energy-contour diagram calculated for the terminus of the migration is given in Fig. 3. The energy minimum was situated

Table 2. Variations in the total energy and the physical parameters

Angle/φ	0°	30°	60°	90°	120°	150°	180°
E_{total}[a]	−594.560	−595.270	−595.203	−594.702	−595.150	−595.301	−594.716
$R(C_4$–$H_5)$[b]	2.691	2.812	3.118	3.494	3.833	4.063	4.144
$R(C_4$–$H_7)$	3.422	3.379	3.260	3.091	2.911	2.773	2.720
C_3[c]	0.0506	0.0324	0.0422	0.0555	0.0138	−0.0091	0.0355
C_4	0.2048	0.1559	0.1386	0.1576	0.1572	0.2020	0.2372
$E^R(C_4$–$H_5)$[d]	−0.031	−0.033	−0.019	0.009	−0.004	0.001	0.000

a) Energies in eV. b) Distances in Ångströms. c) Net electric charge. d) $E^R=2\sum_r^A\sum_s^B p_{rs}\beta^\circ_{AB}S_{rs}$ in E_{AB}.

Table 3. Variations in the total energy and E_{AB}[a] in Model 1

	Points	1	2	3	4	5
$R(C_4\text{–}H_5)/\text{Å}$		2.812	2.320	1.849	1.422	1.090
E_{total}		−595.270	−595.476	−594.186	−594.664	−594.966
E_{AB}	$C_1\text{–}C_2$	−19.984	−20.377	−21.365	−21.157	−21.367
	$C_2\text{–}C_3$	−16.164	−17.114	−16.756	−17.255	−17.094
	$C_3\text{–}C_4$	−21.135	−20.304	−19.599	−17.556	−17.207
	$C_1\text{–}H_5+C_4\text{–}H_5$	−12.507	−12.284	−9.634	−10.772	−12.520

a) Energies in eV.

at $\varphi=30°$ and $\alpha=122°$, while the local minimum energy was -594.662 eV at $\varphi=60°$ and $\alpha=60°$. If this local minimum-energy state is formed by the hydrogen migration, an interesting feature emerges: the formation of the C_3H_3 ion with a three-memberd ring will be accelerated by the fragmentation of the M^{+} ion after the hydrogen migration.

Results and Discussion

Migration Models. Mechanism IV was also discussed assuming several models for the hydrogen migration. Model 1, in which the starting and final geometry are $\varphi=30°$ and $\alpha=122°$, is the migration process of H_5 to C_4. The C_4 carbon atom was then changed from sp^2 to sp^3 hybridization by means of the C_3–C_4 bond through the hydrogen migration, as is shown in the following figure. The other parameters were kept constant.

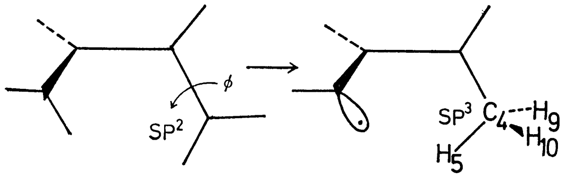


Table 3 shows the variation in the total and the partitioned energies. It is apparent from the variation in the total energy that the transition state lies at Point 3 along the coordinate representing the migration of hydrogen from C_1 to C_4. The potential energy in this process in Model 1 was 1.290 eV, smaller than the minimum energy required for the scission of the C–C bond. The total energy in the first stage shows a tendency to decrease. This results from the decrease in the sum of the two-center energies of the C–C bonds. The increase in the total energy from Point 2 to the transition state results from the increase in the sum of the E_{AB} values of the two bonds (C_1–H_5 and C_4–H_5).

The variation in the bonding interaction of each C–C bond is shown in Fig. 4. The variation in the E_{AB} value of the C_3–C_4 bond increases remarkably with the approach of H_5 to C_4; this shows that the interaction between C_3 and C_4 is weakened by the hydrogen migration, while the variations in the E_{AB} values of the C_1–C_2 and C_2–C_3 bonds are small, which shows a slight decreasing trend. These results may be related to the fragmentation of the migrated M^{+} ion to the $[M-CH_3]^{+}$ ion.

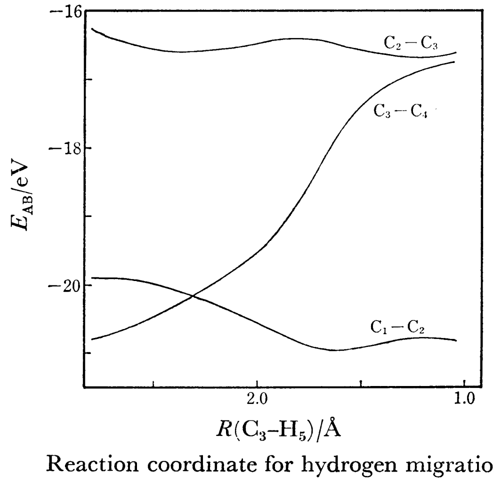


Fig. 4. Variation of E_{AB} of the C–C bonds due to the hydrogen migration in Model 1.

Table 4. Charge distribution of the M^{+} ion

	Origin			Terminus	
	0°	30°	180°	0°	30°
C_1	0.2048	0.1699 (0.2465)[a]	0.2372	0.1791	0.1453
C_2	0.0506	0.1210 (0.1535)	0.0356	−0.0966	−0.0541
C_3	0.0506	0.0324 (0.0109)	0.0356	0.3551	0.3220
C_4	0.2048	0.1559 (0.2803)	0.2372	−0.0267	−0.0190

a) The values in parentheses correspond to the net electric charge on the p_z orbital.

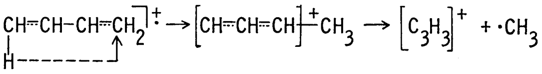
The sum of the E_{AB} values of the C_1–H_5 and C_4–H_5 bonds decreases in the latter half of the reaction. This implies that the bonding interaction between C_4 and H_5 becomes strong through the migration process.

The net electric charge of the C_4 atom is large and positive, as is summarized in Table 4. The net electric charge on the p_z orbital on C_4 at $\varphi=30°$ is very positively large. It seems, therefore, that the possibility of the migration of hydrogen to C_4 is certainly large. There is also an electron flow of the $C_1C_2C_3$ moiety, changing from $+0.3233$ to $+0.4132$ by the migration of hydrogen. Consequently, it is apparent that the charge on the migrated M^{+} ion remains on the CH_3 moiety, suggesting the formation of the $[M-CH_3]^{+}$ ion with m/e 39. These features are shown in the following process:

TABLE 5. VARIATIONS IN THE TOTAL ENERGY AND E_{AB}[a] IN MODEL 2

	Points	1	2	3	4	5
$R(C_4\text{–}H_5)$/Å		2.691	1.948	1.716	1.322	1.090
E_{total}		−594.560	−594.824	−594.151	−594.382	−594.662
E_{AB}	$C_1\text{–}C_2$	−20.359	−19.619	−19.354	−19.154	−18.519
	$C_2\text{–}C_3$	−17.059	−16.971	−16.580	−15.479	−14.109
	$C_3\text{–}C_4$	−20.359	−20.928	−19.905	−16.143	−14.423
	$C_1\text{–}H_5+C_4\text{–}H_5$	−12.484	−11.426	−11.738	−11.660	−12.396

a) Energies in eV.



$$\left.CH{=}CH{-}CH{=}CH_2\right]^{+\cdot} \rightarrow \left[CH{=}CH{=}CH\right]^{+}CH_3 \rightarrow \left[C_3H_3\right]^{+} + \cdot CH_3$$

In the simple model employed here, these results indicate that the migration of H_5 to C_4 is very probable. Moreover, the hydrogen migration gives fairly good information with respect to the formation of the C_3H_3 ion.

In Model 2, the calculations were carried out with the $C_1C_2C_3$ chain bent at C_2 with the α values varying from 122° to 60° in 15.5° increments; then, at each value of α, the calculations were made by increasing φ from 0° to 60° in 15° increments. For the other parameters we adopted the same values as in Model 1.

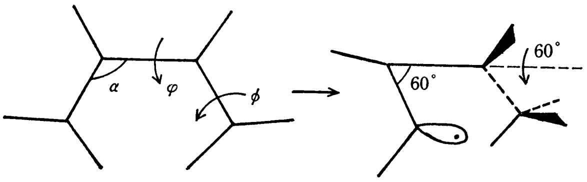
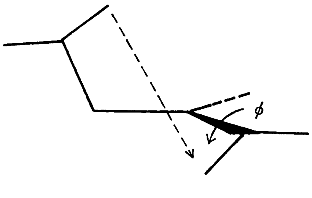
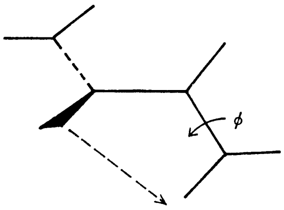


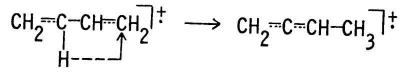
Table 5 shows the variations in the total and the partitioned energies in Model 2. The energy profile is depicted by the curve, as in Model 1. The total energy at the terminus of the migration is −594.662 eV, nearly equal to that in Model 2. The most remarkable difference from Model 2 is that the bonding interaction between C_1 and C_3 becomes strong. These results indicate that the hydrogen-migration process in Model 2 is energetically favorable, as in Model 1.

Next, the starting geometry at $\varphi=90°$ and $\alpha=122°$, in which H_5 migrates to C_4, is shown as Model 3. The migration path of H_5 was chosen as the least-motion path[9] from C_1 to C_4. This release of H_5 from C_1 requires more energy than in Models 1 and 2; the potential energy in this process was 1.367 eV. This is related to the increase in the sum of the E_{AB} values of the $C_1\text{–}H_5$ and $C_4\text{–}H_5$ bonds; this remarkable increase shows that the migration of H_5 is prevented in this process. The bonding interaction between C_2 and C_3 was almost unchanged with the hydrogen migration. The value of the $C_2\text{–}C_3$ bond is larger than that of the $C_3\text{–}C_4$ bond; it may be thought, therefore, that the scission of the $C_2\text{–}C_3$ bond occurs in preference to that of the $C_3\text{–}C_4$ bond. As a result, judging from this variation, it may be predicted that the C_2H_3 ion is formed.





In Model 4, the variation in the total energy between the origin and terminus of the migration was 0.276 eV; the potential energy was, then, 1.448 eV. It is possible to form the resonance structure by the migration of H_7 as follows:



$$\left.CH_2{=}C{-}CH{=}CH_2\right]^{+\cdot} \longrightarrow \left.CH_2{=}C{=}CH{-}CH_3\right]^{+\cdot}$$

TABLE 6. VARIATIONS IN THE TOTAL ENERGY AND E_{AB}[a] IN MODELS 3 AND 4

	Points	1	2	3	4	5
				Model 3		
E_{total}		−594.702	−594.527	−593.335	−593.751	−594.435
E_{AB}	$C_2\text{–}C_3$	−16.852	−14.973	−14.812	−16.074	−16.233
	$C_3\text{–}C_4$	−20.536	−21.849	−20.733	−17.049	−17.392
	$C_1\text{–}H_5+C_4\text{–}H_5$	−12.621	−11.539	−5.804	−10.106	−12.476
				Model 4		
E_{total}		−595.301	−595.561	−593.853	−594.323	−595.025
E_{AB}	$C_2\text{–}C_3$	−17.273	−15.259	−15.080	−16.683	−16.993
	$C_3\text{–}C_4$	−21.016	−21.046	−20.021	−17.374	−17.174
	$C_1\text{–}H_7+C_4\text{–}H_7$	−12.657	−12.136	−9.734	−10.693	−12.434

a) Energies in eV.

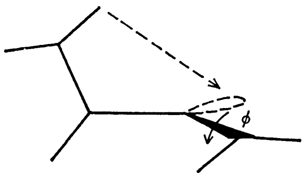
The bonding interaction energy between C_2 and C_3 was larger than that between C_3 and C_4. This is the same as in Model 3. On the other hand, the variation in the sum of the E_{AB} values of the C_2–H_7 and C_4–H_7 bonds in Model 4 was similar to that in Model 1. Therefore, the possibility of the migration of H_7 to C_4 is larger than in Model 3.

Table 7. The total energies and the net electric charges in the $[M-H]^+$ ions

	$[M-H_5]^+$	$[M-H_6]^+$	$[M-H_8]^+$
		Trans	
E_{total}/eV	−578.031	−578.196	−578.219
C_3			0.3138
C_4			0.0118
		Cis	
E_{total}/eV	−578.034	−575.796	−578.191

$[M-H]^+$ Ion. In order to discuss Mechanism II, the calculations for the $[M-H]^+$ ion were carried out using the same parameters as in Model 1. The stable structure of the $[M-H]^+$ ion was in a state which lost H_7 and H_8 in *trans*; this phenomenon is estimated to be more energetically favorable than in *cis*. Table 7 shows the total energies of the several structures for the $[M-H]^+$ ion and the net electric charges on the carbon atoms. The net electric charge of the C_3 which had lost H_8 was +0.3138, which is large and positive. If the driving force is this positive charge, as much as in the M^+ ion, in the $[M-H]^+$ ion it can be predicted that the possibility of the migration of hydrogen to C_3 is large. Therefore, as a model, the migration process of H_5 to C_3 was discussed.

The total energy in the $[M-H]^+$ ion upon the rotation of the C_2–C_3 bond was the energy minimum at 90°. Therefore, this starting geometry for the migration of H_5 from C_1 to C_3 at 90° was chosen:



The variation in the total energy in this process is shown in Table 8. The position of the H_5 atom at Point 3 was decided on the basis of the energy-minimum state; the position of H_5, in which the $C_1H_5C_3$ angle is 90°, was chosen.

The potential energy in this process was 3.251 eV, larger than those in the models of the M^+ ion. Moreover, the bonding interaction between C_2 and C_3 was weakened, contrary to the case of the C_2–C_3 bond in the M^+ ion. Therefore, it can be predicted that this bond is easy to cleave in the $[M-H]^+$ ion. The bonding interaction of this bond at 180° was also weakened from −17.257 to −15.210 eV by the loss of the hydrogen atom; in other $[M-H]^+$ ions this trend also appeared. Consequently, it seems that it is more difficult for the

Table 8. Variations in the total energy and E_{AB}[a] in the $[M-H]^+$ ion

	Points	1	2	3	4	5
$R(C_3$–$H_5)$/Å		2.783	2.301	1.716	1.313	1.060
E_{total}		−578.563	−578.069	−575.312	−577.413	−578.028
E_{AB}	C_2–C_3	−16.286	−16.222	−16.316	−14.079	−14.788
	C_3–C_4	−23.761	−23.689	−22.937	−22.831	−22.910

a) Energies in eV.

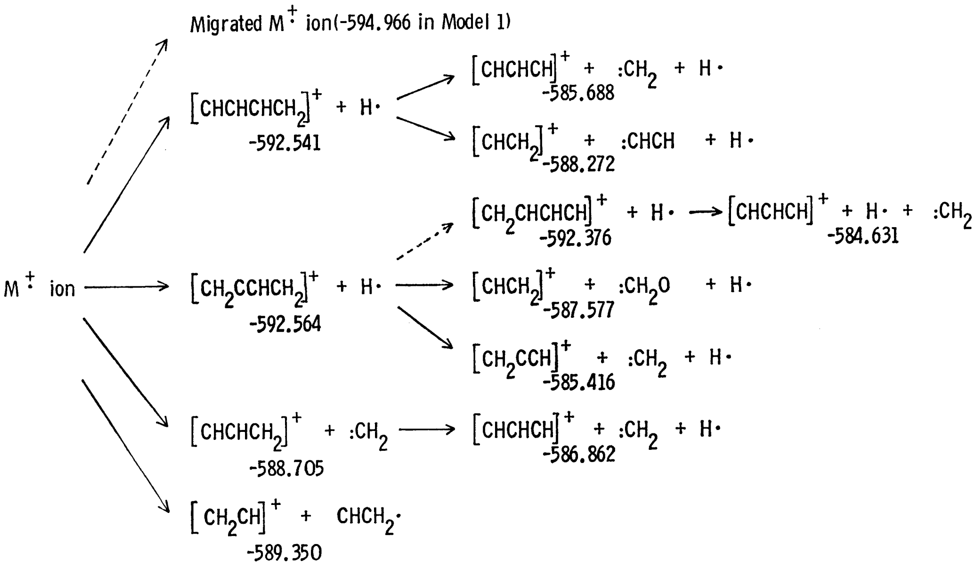


Fig. 5. Fragmentation pattern of butadiene. The dotted arrow shows the hydrogen-migration process. The total energies of the fragments are the sum of the fragments.

migration of H_5 to occur in the $[M-H]^+$ ion than in the $M^{\dagger}$ ion.

Fragmentation Pattern. Considering the variation in the total energies in the fragmentation process, the energy relations are shown in Fig. 5. It is apparent from the total energies that the variation for the hydrogen migration is smaller than that for the simple fragmentation. The variation for the C_3H_3 ion which is produced from the $[M-H]^+$ ion is larger than that for the C_2H_3 ion. The fragmentation of the $M^{\dagger}$ ion to the C_3H_4 ion is energetically less favorable than the direct cleavage to the C_2H_3 ion; it may, then, be asserted that the formation of the C_3H_4 ion by the direct release of the CH_2 radical is energetically less favorable. This tendency causes the $[M-H]^+$ ion to appear. Moreover, by the fragmentation of the migrated $[M-H]^+$ ion, the scission of the C_2–C_3 bond occurs in preference to that of the C_3–C_4 bond.

Conclusion

Calculations have been presented in support of a discussion of the possibility of the hydrogen migration in butadiene, taking account of the variations in the total and the partitioned energies with respect to the migration of hydrogen in the $M^{\dagger}$ ion.

This treatment is not absolutely essential, but it is a very convenient starting point.

The following features were postulated: (1) The net electric charges on the C_1 and C_4 atoms were large and positive in the $M^{\dagger}$ ion. The positive charge on the carbon atom was one of the driving factors in the migration of hydrogen. (2) It is very probable that the hydrogen atom migrates *via* Models 1 and 2 in Mechanism IV, judging from the variation in the total energy. (3) The migration of hydrogen from C_1 to C_4 migrates in the $M^{\dagger}$ ion, and then the C_3H_3 ion is produced by the hydrogen migration. (4) It was found that the positive charge remains in the $C_1C_2C_3$ moiety after the hydrogen migration. (5) It can be predicted that the formation of the C_3H_3 ion results from the fragmentation of the $M^{\dagger}$ ion. (6) The fragmentation of the $[M-H]^+$ ion leads to the formation of the C_2H_3 ion. Finally, this treatment for the migration of hydrogen gives fairly good information as the mass spectrum of butadiene.

References

1) F. W. McLafferty, *Appl. Spectrosc.*, **11**, 148 (1957).

2) F. W. McLafferty, *Anal. Chem.*, **31**, 82, 2072 (1959).

3) M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590, 3854 (1970).

4) a) H. Fischer and H. Kollmar, *Theoret. Chim. Acta*, **16**, 163 (1970); b) M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.*, **93**, 7201 (1971).

5) M. S. Gordon, *J. Am. Chem. Soc.*, **91**, 3122 (1969).

6) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

7) T. Takagi and M. Oiwa, *Bull. Chem. Soc. Jpn.*, **51**, 1931 (1978).

8) a) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1958); b) "Table of Interatomic Distances," Chem. Soc., Spec. Publs., No. 11 (1958); No. 18 (1965).

9) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).