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A Theoretical Model for the Hydrogen Migration of Butyl Alcohol

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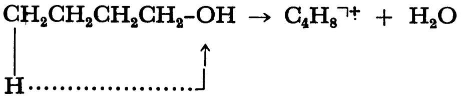
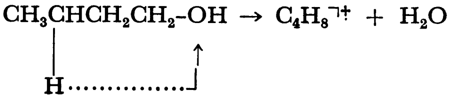
Synopsis. The hydrogen-migration mechanism of the fragmentation of *n*-butyl alcohol in a mass spectrometer is discussed from the standpoint of the bonding interaction energy, as estimated by an all-valence electron semi-empirical SCF-MO treatment (CNDO/2-UHF), assuming the following models I and II:



$$CH_2CH_2CH_2CH_2\text{-}OH \rightarrow C_4H_8^{\urcorner +} + H_2O \qquad (I)$$

(I)



$$CH_3CHCH_2CH_2\text{-}OH \rightarrow C_4H_8^{\urcorner +} + H_2O \qquad (II)$$

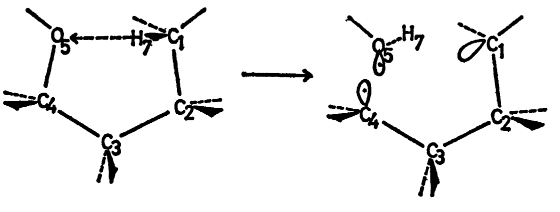
(II)

Finally, Model I is suggested to be energetically favorable.

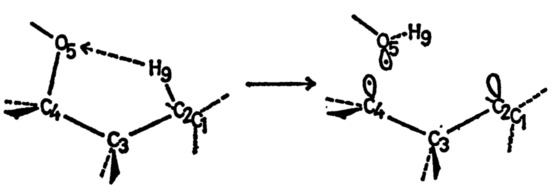
The elimination of H_2O from *n*-butyl alcohol[1)] in the fragmentation by electron impact was suggested to be due to the intramolecular migration of a hydrogen atom from the γ- or δ-carbon to oxygen. However, the precise mechanism of the migration has not yet been elucidated, but only speculated from the mass spectra data.

The present paper is concerned with a discussion of the hydrogen migration mechanism in a mass-spectrometric fragmentation of *n*-butyl alcohol from the standpoint of the theory of the partition of the total energy.[2)]

The models in the hydrogen migration are schematically represented in view of the least-motion path from the origin of migration to the terminus. It should be considered that the lengths and angles of each bond change with the migration steps of the hydrogen migration, and that the breaking of the carbon-oxygen bond requires more precise electronic structure calculations. However, in the calculations, the conformation of the molecule was already assumed to be the optimal ground state, as determined from the standard table.[3)] Four steps were also chosen to form a path representing the hydrogen migration. The bond distances between the migration hydrogen (H_7 or H_9 in the two models respectively) and oxygen (O_5), and the energy profile along the migration steps, which was estimated by CNDO calculations, have also been listed in Table 1.



Model I



Model II

TABLE 1. COMPUTED TOTAL ENERGY AND PARTITION TERMS[a)] WITH HYDROGEN MIGRATION

	Model I			
	1	2	3	4
R (H_7-O_5) (Å)	1.503	1.377	1.252	1.127
E_{total}(eV)	−1473.298	−1472.947	−1472.434	−1471.689
E^U+E^R	−2328.056	−2328.093	−2328.659	−2330.827
E^J	2954.263	2959.952	2965.194	2969.319
E^K	−75.930	−75.981	−76.068	−76.163
E^V	−6111.083	−6123.297	−6135.238	−6146.378
E^N	3243.770	3250.860	3258.260	3266.421
	Model II			
	1	2	3	4
R (H_9-O_5) (Å)	1.619	1.406	1.193	0.980
E_{total}(eV)	−1470.946	−1448.610	−1447.723	−1446.309
E^U+E^R	−2338.007	−2355.283	−2360.017	−2362.120
E^J	2755.547	2797.674	2793.019	2792.099
E^K	−75.246	−74.752	−74.962	−75.549
E^V	−5714.770	−5814.251	−5814.445	−5820.285
E^N	3043.687	3126.999	3131.315	3141.743

a) E^U is the total one electron AO energy of the electrons on atom A. E^R is the contribution of the resonance integral to the energy of the AB bond and is the main feature of the covalent bond. E^J is the repulsion of the electrons of the atoms A and B. E^K is the corresponding term of the electronic exchange interactions. E^V is the potential energy of the electrons on atom A in the field of nucleus B plus that of the electrons on atom B in the field of nucleus A. E^N represents the nuclear repulsion energy of the nuclei A and B.

Here, the driving factor for the migration was interpreted by using the partition method for the total energy. The total energies of both models increase with the hydrogen migration. The variation in the total energy in Model I is, however, smaller than that in Model II. The resonance energy term (E^U+E^R) decrease with the hydrogen migration in both models. It can be suggested that the decrease in the energy is due to the resonance effect and that the increase in the total energy results from the steric effect.

Now, the changes of the E_{AB} of each bond due to migration will be employed to estimate the bond length and the bond order.[4)] The E_{AB} of the C_1-H_7

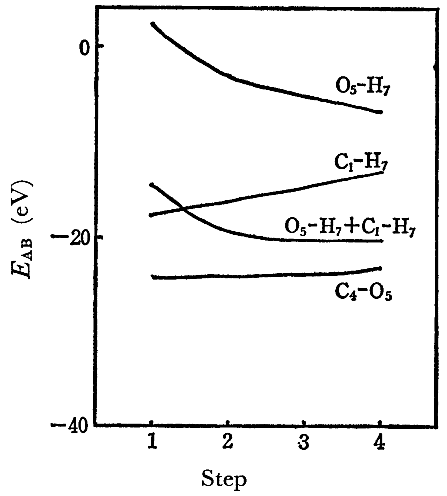


Fig. 1. Variation of E_{AB} of each bond due to migration through the least motion path in the model I.

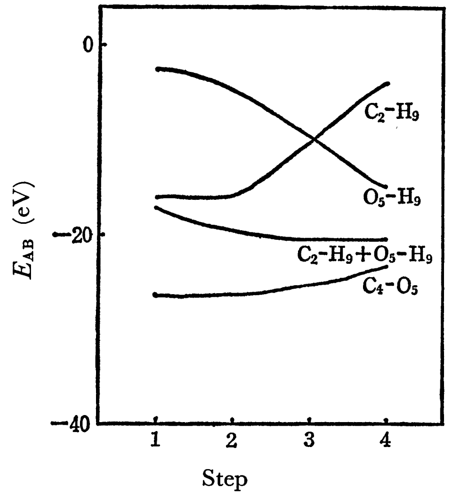


Fig. 2. Variation of E_{AB} of each bond due to migration through the least motion path in the model II.

bond becomes smaller and the E_{AB} of the O_5–H_7 bond becomes larger in Model I, as is shown in Fig. 1. Therefore, the sum of the E_{AB} values of the two bonds is significant. The sum of the E_{AB} values of the two bonds decreases along the migration steps. On the other hand, in Model II, as is shown in Fig. 2, the C_2–H_9 bond also becomes smaller, while the O_5–H_9 bond becomes larger. In the case of Model II, the sum of the E_{AB} values of the two bonds decreases with the hydrogen migration, the same tendency as in Model I. The decrease in the sum of the E_{AB} values of the two bonds implies that the bonding interaction between O_5 and the leaving hydrogen becomes strong along the coordinates representing the migration of hydrogen to O_5.

As is shown in Figs. 1 and 2, the bonding interaction energies of the C_4–O_5 bonds decrease with the approach of hydrogen to oxygen. In other words, the bonding interaction between C_4 and O_5 is weakened by the hydrogen migration. The variation in the bonding interaction of the C_4–O_5 bond in Model I was, however, smaller than that in Model II. Also, the E_{AB} values of the other carbon-carbon bonds are larger than that of the C_4–O_5 bond; the E_{AB} values of the C_4–O_5 bonds of Step 4 in Models I and II were calculated to be −23.753 eV and −23.376 eV respectively. Moreover, the E_{AB} values of the C_1–C_2, C_2–C_3, and C_3–C_4 bonds were found to be −29.124 eV, −28.497 eV, and −29.260 eV in Model I.

On the other hand, the E_{AB} values of the C_1–C_4 and C_2–C_4 non-bonds were found to change from 0.147 eV to 0.041 eV and from −0.015 eV to −0.255 eV respectively. The interaction between non-bonded carbon atoms (between C_1 and C_4 in Model I and between C_2 and C_4 in Model II) tends to change from the non-bonding to a weakly bonding state, *i.e.*, the sequence of ring formation.

Thus, these results may be related to the ease of the cleavage from the molecular ion (M ion) to the M-H_2O ion in the rearrangement reaction. Moreover, although the possibility of the hydrogen migration in Model II can not always be eliminated, the hydrogen migration *via* Model I may be estimated to be energetically favorable, judging from the variation in the total energy and the small steric effect compared with those of Model II. The simple models described in the present paper can provide sufficient information as the rearrangement reaction of *n*-butyl alcohol.

All the calculations were performed using a NEAC 2200 MODEL 700 computer at Osaka University.

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