A Theoretical Treatment of the Difference in the Fragmentation of Urea and Acetamide

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The difference in the hydrogen migration in urea and acetamide under electron impact has been discussed from the standpoint of the all-valence electron semi-empirical SCF-MO theory (CNDO/2). The features of the molecular ion in the ground state and the hydrogen-migration models for both compounds were estimated based on the variations in the total and the partitioned energies. The variation in the total energy with the hydrogen migration in urea was smaller than that in acetamide. Moreover, the bonding interaction between carbon and nitrogen becomes weak; the cleavage of the migrated molecular ion to NH_3 was predicted. On the other hand, the weak bonding interaction between carbon and carbon in acetamide does not change through the migration of hydrogen. It is predicted that the α-cleavage in the C–C bond will occur in preference to the migration of hydrogen. Finally, in acetamide, it was found that the possibility of the migration of hydrogen is lower than that in urea, judging from the variations in the total and the partitioned energies.

It is interesting to ascertain the hydrogen-migration process involved in fragmentation from the standpoint of the molecular orbital (MO) theory. The analyses, by MO theory, of the mass spectral data of the organic compounds have not been completely established because of the complexity of the driving factors governing the cleavage of the molecular ion (M^{+}) on electron-impact collision.

The mass spectra of urea[1] and acetamide[2] have been reported. In the mass spectrum of urea, a peak thought to be the ion formed by the migration of hydrogen has been observed. This shows that the NH_3 ion with *m/e* 17 is richly abundant, accompained by the migration of hydrogen from one nitrogen to another nitrogen. On the other hand, in acetamide the most important fragmentation arises from α-cleavage, resulting in the formation of an ion with a mass of 44. The migration of hydrogen from carbon to nitrogen does not appear as clearly as that of urea. This fragmentation of acetamide has, however, not been fully elucidated, but only speculated from the mass spectral data.

This paper will describe an attempt to analyze the hydrogen migration in urea and the possibility of the migration of hydrogen in acetamide by calculations based on the CNDO/2 method.

Method and Calculations

Interaction Energies. These discussions were supported by unrestricted open-shell SCF calculations with a CNDO/2 approximation. The total molecular energy, E, can be expressed by the sum of one- and two-center terms:[3]

$$E_{\text{total}} = \sum_{\text{A}} E_{\text{A}} + \sum_{\text{A<B}} E_{\text{AB}}$$

where

$$E_{\text{A}} = \sum_{r}^{\text{A}} p_{rr} U_{rr} + \frac{1}{2} \sum_{r}^{\text{A}} \sum_{s}^{\text{A}} \{p_{rr} P_{ss} - (p_{rs}^{\alpha})^2 - (p_{rs}^{\beta})^2\} \gamma_{\text{AA}}$$

$$E_{\text{AB}} = \sum_{r}^{\text{A}} \sum_{s}^{\text{B}} 2 p_{rs} \beta_{\text{AB}}^{\circ} S_{rs} - \sum_{r}^{\text{A}} \sum_{s}^{\text{B}} \{(p_{rs}^{\alpha})^2 + (p_{rs}^{\beta})^2\} \gamma_{\text{AB}} + (Z_{\text{A}} - P_{\text{AA}})(Z_{\text{B}} - P_{\text{BB}}) \gamma_{\text{AB}}$$

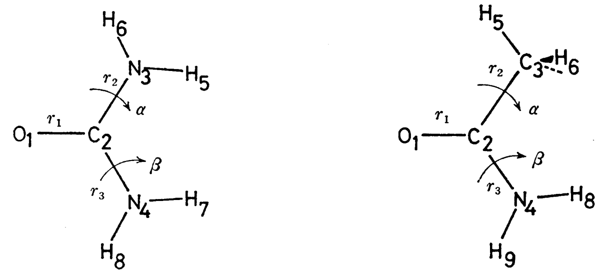
E_{AB} is the contribution to the total energy from all the two-center integrals involving A and B centers; it can be partitioned into covalent binding, core repulsion, and ionic terms. The total E_{AB} is used for discussing the nature of each bond with a hydrogen migration.

TABLE 1. MOLECULAR GEOMETRIES[c] FOR THE M^{+} IONS

Urea		Acetamide	
r_1	1.2875[a]	r_1	1.220
r_2	1.375[a]	r_2	1.540
r_3	1.375	r_3	1.3675[b]
∠OCN	121.5°	∠OCN	125.0°

a) The total energy shows minimum at 1.2875 Å and 1.375 Å. b) This value was decided from the minimum total energy as a function of r_3. c) Lengths in Ångström.

Geometry. It is difficult to determine absolutely the reaction coordinate in the hydrogen-migration process under electron impact.[4] Consequently, the parameters for the geometry of the M^{+} ion employed here were decided as is shown in Table 1. These values of the bond lengths and the bond angles for the starting geometry, with the exception of the r_1, r_2, and r_3, were taken from the standard tables.[5]



Urea　Acetamide

Fig. 1. Representation of the geometries of urea and acetamide.

The basic conformations in the M^{+} ions of urea and acetamide are shown in Fig. 1. As the lengths of the N–H bonds in urea and acetamide we employed 1.000 Å, and as that of the C–H bonds in acetamide, 1.080 Å.

Migration Model. The total energy contour

TABLE 2. E_{AB} VALUES[a)] BETWEEN NITROGEN AND HYDROGEN IN UREA

	$\beta(\alpha=0°)$			
	0°	30°	60°	90°
E_{total}	−1399.511	−1399.300	−1398.843	−1398.600
N_4-H_5	−0.168	−0.202	−0.282	−0.311
		$\beta(\alpha=30°)$		
		30°	60°	90°
E_{total}		−1399.052	−1398.563	−1398.316
N_4-H_5		−0.222	−0.305	−0.335

a) Energies in eV.

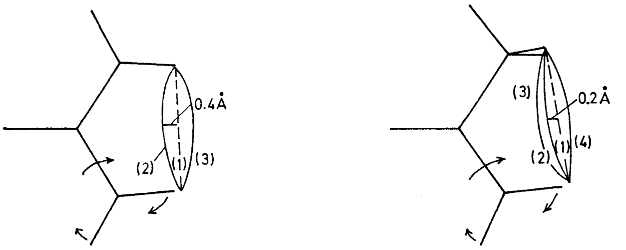
TABLE 3. E_{AB} VALUES[a)] BETWEEN NITROGEN AND HYDROGEN IN ACETAMIDE

	$\alpha(\beta=0°)$		
	0°	90°	180°
E_{total}	−1295.831	−1278.794	−1295.797
N_4-H_5		0.011	0.057
N_4-H_6	−0.031	−0.079	
	$\beta(\alpha=0°)$		
	30°	60°	90°
E_{total}	−1295.577	−1294.967	−1294.644
N_4-H_6	−0.071	−0.062	−0.121
N_4-H_7	−0.025	−0.117	−0.121

a) Energies in eV.

diagram[6)] of the M^+ ion for the origin of the migration shows the deep energy minima at $\alpha=0°$ and $\beta=0°$ in both compounds, adopting the values in Table 1. The variation in the E_{AB} of the N_4H_5 by the rotation by β is shown in Table 2 for urea. The bonding interaction between N_4 and H_5 is strong at $\beta=90°$. These results suggest that the possibility of the migration of hydrogen to N_4 is large in this conformation. However, in this conformation the variation in the total energy with the hydrogen migration in the first stage was large. On the other hand, in acetamide the bonding interaction in the possible conformation of the hydrogen migration was weak, as is shown in Table 3. Consequently, as a model of the hydrogen migration, the planar geometries shown in Fig. 2 were employed, judging from the E_{AB} values and the total energies.

Models of both compounds, in which the migration of hydrogen was assumed to follow the curve path(2), show that the migrating hydrogen moves to N_4. The deviations from the least-motion path[7)] at the transition state are at 0.4 Å in urea and 0.2 Å in acetamide. The variations in the total energies with the hydrogen migration in the models, caused by the least-motion path(1) and the other paths, were large in comparison with that caused by the curve path. The curve-path model was, therefore, chosen for the hydrogen migration in both compounds.

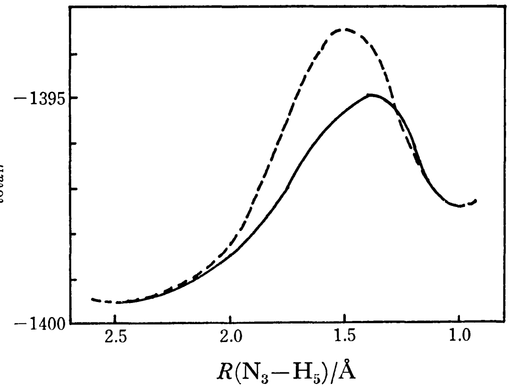


Urea Acetamide

Fig. 2. Migration model and paths.

Results and Discussion

Urea. The results calculated by using the curve path are shown in Table 4 and Fig. 3. It is apparent from the shape of the curve that the total energy of the transition state, in which the N_3–H_5 distance is 1.306 Å, was low in the curve path. The potential energy was 4.736 eV. The total energy tends to decrease in the latter half of the migration of hydrogen. It is thought that a comparatively stable state results from the hydrogen migration. In this case, the variation in the total energy between the origin and the terminus of the migration was 2.105 eV.



Reaction coordinate for hydrogen migration

Fig. 3. Variation of the total energies in urea.
——: The curve path (1). ----: The least-motion path (2).

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

	Point	1	3	5
E_{total}		−1399.511	−1394.775	−1397.406
$R(N_4$-$H_5)$/Å		2.494	1.359	1.000
E_{AB}	O_1-C_2	−34.266	−33.787	−37.462
	C_2-N_3	−36.436	−37.299	−37.607
	C_2-N_4	−36.436	−30.561	−26.857
	N_3-H_5+N_4-H_5	−20.934	−18.056	−19.843

a) Energies in eV.

The increase in the total energy results from the increases in the E_{AB} value of the C_2–N_4 and the sum of the E_{AB} values of the two bonds (N_3–H_5 and N_4–H_5), as is shown in Table 4.

Although it is thought that the slight increase in the sum of the E_{AB} values of the two bonds hinders the migration of hydrogen, there is a tendency to decrease near the terminus of the migration.

The tendency of the E_{AB} value of the C_2–N_4 bond to increase with the approach of H_5 to N_4 shows that the interaction between C_2 and N_4 is weakened; this results from the change in the bond length of this bond through the hydrogen migration. On the other hand, the variations in the E_{AB} values of the C_2–N_3 and the O_1–C_2 were small; this shows a slight tendency to decrease, after which these values were large and negative. This phenomenon may be related to the cleavage of the migrated M^+ ion to the fragment ion, *m/e* 17 or *m/e* 42.

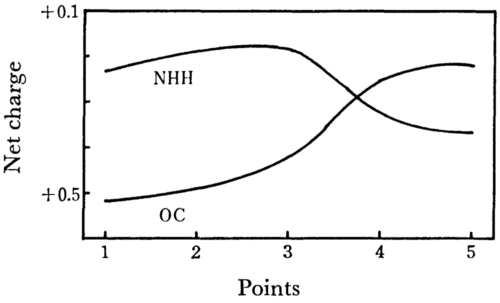


Fig. 4. Variation of the net electric charges.

Next, the variation in the net electric charge is shown in Fig. 4. The charge of the CO tends to be positively small with the hydrogen migration, while that of the N_4HH is large and positive. In the OCN_3H, after the migration of hydrogen, the density increases. These results may be reflected in the intense peak height of the NH_3 ion.

Acetamide. The most apparent fragmentation arises from cleavage, resulting in the formation of the ion with a mass of 44. If the migration of hydrogen as well as urea occurs, the hypothetical process for the migration of hydrogen can be expected to be energetically favored.

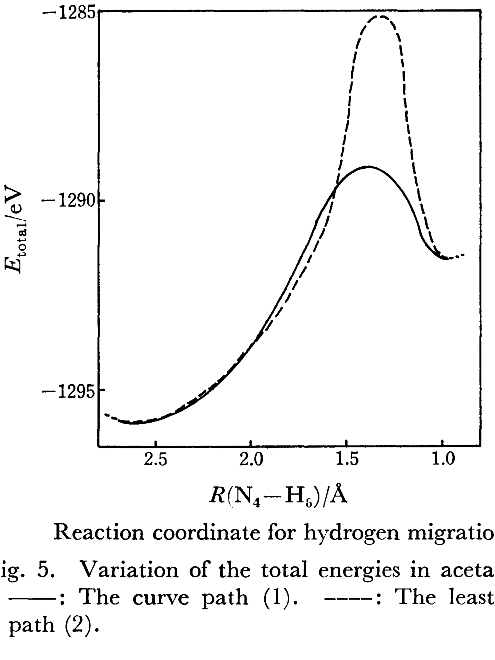


Fig. 5. Variation of the total energies in acetamide.
——: The curve path (1). ----: The least-motion path (2).

The variation in the total energy in the model was larger than that in urea, as is shown in Fig. 5. This variation in the least-motion path was larger than that in the curve path. The potential energy in this curve-path process was 6.675 eV, which is larger by 2.0 eV than that in urea. Moreover, the variation in the total energy between the point of origin and the terminus of the migration was 4.075 eV, which is large. The variation in the total energy with the hydrogen migration at the conformation at $\alpha=180°$ and $\beta=0°$ was also large, similar to that at $\alpha=0°$ and $\beta=0°$, which was 11.284 eV.

Difference in Urea and Acetamide. The values of the E_{AB} of the N_4–H_6 in $\alpha=0°$ and of the N_4–H_5 in $\alpha=180°$ were −0.031 and 0.057 eV respectively, as is shown in Table 3. The values of the resonance interaction were positive (0.097 and 0.144 eV) in acetamide, while in urea this value of the N_4–H_5 was −0.168 eV. Therefore, the bonding interaction between hydrogen and nitrogen in urea is strong; this may be related to the ease of the migration of hydrogen. It may be predicted that the chance of the migration of hydrogen in urea is fairly strong.

Although the decrease in the E_{AB} values of the two bonds is not smooth, the variation in this energy in urea is smaller than that in acetamide. In acetamide, the increase (from −20.185 to −16.561 eV) shows the hindrance of the migration of hydrogen.

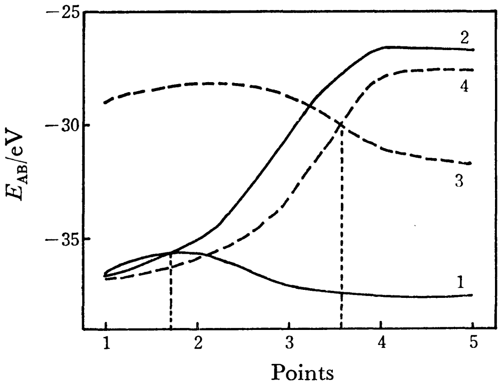


Fig. 6. Variation of the E_{AB} values of the skeletal bonds with the hydrogen migration.
——: Urea, 1: C_2–N_3, 2: C_2–N_4. ----: Acetamide, 3: C_2–C_3, 4: C_2–N_4.

Fig. 6 shows the variations in the E_{AB} values of the C–C and C–N bonds. The E_{AB} value of the C_2–N_4 decreases smoothly. In acetamide, that of the C_2–C_3 is negatively small in comparision with the other bonds, including that of urea, in the origin of the migration. Moreover, the variation in this value is small, as in the case of the C_2–N_4 bond in urea.

It is found that the bonding interaction between C_2 and N_4 in acetamide is weaker than that of the C_2–C_3 bond after Point 3. However, the interaction in the first stage is strong. These features in acetamide show a great difference from urea. It may be thought that, even if the hydrogen migration occurs, the cleavage of the C_2–C_3 bond will occur preferentially to that of the C_2–N_4.

Conclusion

The estimation of the CNDO scheme provides fairly good information with respect to the fragmentation, including the migration of hydrogen in urea and acetamide. The treatment for the M^{+} ion in the ground state shows a different profiles for the hydrogen migrations in the two compounds. As for the variation in the total energy in acetamide, the potential energy is large; therefore, there are large differences in the changes in E_{AB} values of the skeletal bonds. It is, therefore, found that the possibility of the migration of hydrogen is undoubtedly large in urea.

Finally, the quantitative discussion was unsatisfactory; the precise relation between the relative intensity of the rearranged ion and the estimation of the energy by the migration process has not been established. However, the possibility of the migration of hydrogen was qualitatively predicted by this treatment with respect to urea and acetamide, based on the partitioned energy and the migration model.

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