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Ionic Dissociation. III. An Extended Hückel Treatment of the Dissociation of Cyclohexanone

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It is said that the more stable its anion, the more easy is the dissociation of an acid.[1] As for the intermediate of the aldol condensation, Ingraham mentioned[2] that the ionization of the α-hydrogen will be aided: (1) if it is sterically in a favorable position and (2) if the anion can be stabilized. We have discussed these problems in our previous two papers.[3] In this note we will give another example, one concerning the dissociation of cyclohexanone, which should support the above description of the relative stability of a molecule and its anion.

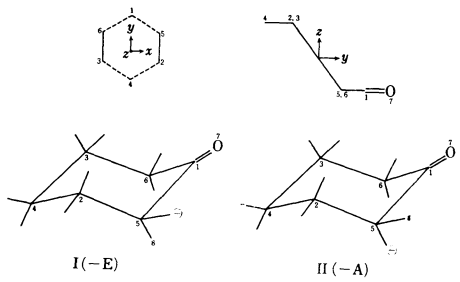

Fig. 1. Coordinate axes adopted and numbering of atoms.

It has been reported by Corey and Sneen[4] that the axial hydrogen of cyclohexane dissociates more readily than the equatorial one, since the former anion is stabilized by the σ-π delocalization. The resonance structure in the transition state is stabi-

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1) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," The Clarendon Press in the University of Oxford (1949), Chapter VI.

2) L. L. Ingraham, "Biochemical Mechanics," John Wiley and Sons, Inc., New York (1962), Part Two, Condensation.

3) H. Yamabe, T. Yonezawa and H. Kato, "Ionic Dissociation I, and II" (to be published in this Bulletin).

4) E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.*, **78**, 6269 (1950).

TABLE 1. TOTAL ELECTRONIC ENERGY AND POPULATION OF SOME ATOMS

I. Dissociation of the equatorial H(−E)

		1C	5C	7O	8H	5C(H.O)*
Atomic orbital population	*S*	1.054	1.274	1.768	0.853	0.018
	x	0.894	1.565	1.967	—	1.097
	y	0.551	1.308	1.730	—	0.386
	z	0.403	0.991	1.766	—	0.002
Atom population		2.902	5.137	7.230	0.853	—
Total electronic energy (eV)				−721.052		

II. Dissociation of the axial H (−A)

		1C	5C	7O	8H	5C(H.O)*
Atomic orbital population	*S*	1.052	1.269	1.767	0.874	0.029
	x	0.900	1.028	1.967	—	0.006
	y	0.552	1.218	1.727	—	0.552
	z	0.624	1.316	1.815	—	0.757
Atom population		3.127	4.831	7.276	0.874	
Total electronic energy (eV)				−721.701		

* 5C(H.O) is an abbreviation of the highest occupied orbital of the 5th carbon.

TABLE 2. ATOMIC ORBITAL BOND POPULATION BETWEEN THE ATOMS 1C AND 5C

(I) Dissociation of the equatorial H (−E)

		1C			
		S	*x*	*y*	*z*
5C	*S*	0.111	0.098	0.038	0.000
	x	0.115	0.111	0.094	0.000
	y	0.079	0.146	−0.006	0.000
	z	0.000	0.000	0.000	0.056

(II) Dissociation of the axial H (−A)

		1C			
		S	*x*	*y*	*z*
5C	*S*	0.105	0.099	0.043	0.000
	x	0.136	0.131	0.096	0.000
	y	0.066	0.106	−0.005	0.000
	z	0.000	0.000	0.000	0.204

(III) Cyclohexanone

		1C			
		S	*x*	*y*	*z*
5C	*S*	0.052	0.043	0.019	0.000
	x	0.067	0.065	0.047	0.000
	y	0.035	0.063	−0.003	0.000
	z	0.000	0.000	0.000	0.028

lized when there is the conjugation between the orbital of the α-carbon, made available by the leaving hydrogen, and the orbital of the carbonyl group is possible. We confirmed their assertion by the Hoffmann's Extended Hückel calculation. The values of the parameters used have been given in a previous paper[3] and will not be repeated here.

In Fig. 1, the coordinate axes adopted and the numbering of the atoms are shown. The 2C, 3C, 5C, and 6C atoms are placed on the X-Y plane. The dissociations of the equatorial and the axial protons are indicated by (-E) and (-A), respectively. Table 1 gives the total energy of the anion, which is derived from the dissociation of a proton from cyclohexanone, and the atomic orbital populations and the atom populations of the several atoms close to the α carbon. From Table 1, it can be seen that anion (II) is more stable than the anion (I) which is in agreement with the experimental suggestion.[4] The atomic orbital population of the P_z AO of the 1C, 5C, and 7O atoms and that of the S orbital of 8H of the anion (II) are larger than the corresponding values of the anion (I). This relation is most prominent in the atomic orbital population of the P_z AO of the 5C atom in the highest occupied MO given in the 7th column of Table 1. That is the conjugation of the anion II is more prevalent than that of the anion I. This also agrees with the previous experimental suggestion.[4] This conclusion can also be deduced from Table 2. In Table 2 the atomic orbital bond populations between the 1C and 5C atoms are given for cyclohexanone and the anions I and II. The atomic orbital bond population in the Z direction increases in the order of cyclohexanone (0.028), the anion I (0.056), and the anion II (0.204). This means that the anion II is more highly conjugated than the anion I.

The calculation was carried out on a HITAC 5020 computer at the computation center of the University of Tokyo.