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Electronic Structures and Reactivities of Aliphatic Small Membered-Ring Compounds. II[*1]

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Extended Hückel MO investigations of the physico-chemical properties of cycloalkanes have been carried out. The calculated total energies of protonated cyclopropane and cyclopentane show that the most stable configuration of protonated cycloalkanes is the one with the conformation in which a proton exists in the ring plane. In cyclopropane, the changes in the total electronic energies and in the charge distributions caused by the protonation are almost the same as those in ethylene, while no remarkable changes in these quantities can be observed in protonated cyclopentane. It may be concluded that cyclopropane has unsaturated properties similar to those of the π-electron system in its ring plane. Further, the reaction mechanism and the reactivities of halogenocycloalkanes in the S_N2-type reaction are discussed. It is shown that the theoretical results can successfully explain their chemical reactivities.

It has been shown in the previous paper¹⁾ that the distinctive physico-chemical properties of cyclopropane and its derivatives, such as the large electron affinities, the high conjugative powers, and the abundant s-characters of the C–H bond, can be interpreted fairly successfully by the extended Hückel treatment.

In the present paper, the chemical reactivities of cycloalkanes are elucidated. The electronic structures of protonated cycloalkanes are investigated in order to discuss the olefinic character

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[*1] Presented at the Meeting on the Electronic Structure of Molecules, October, 1965.

1) T. Yonezawa, K. Shimizu and H. Kato, This Bulletin, **40**, 456 (1967).

of cycloalkanes. Hoffmann[2] has also studied energetically the stable molecular configurations of protonated benzene and cyclopropane; here further investigations are made by population analysis of the protonated configurations of ethylene,[3] cyclopropane, and cyclopentane. Here cyclopentane is chosed for comparison, since the electronic structure of cyclopentane has been shown to be similar to those of saturated *n*-hydrocarbons.[1] Further, some theoretical discussions of the reaction mechanism are presented, and the relative reactivities of halogenocycloalkanes in the S_N2-type reaction are explained.

Theoretical

The extended Hückel method is used for the elucidation of the electronic structures. The parameters adopted in the present treatment are the same as those used in the previous paper.[1] The atomic orbital population, $N(p)$; the partial atomic orbital population, $N^i(p)$, of the ith MO; the atomic population, M_X; the atomic orbital bond population, $N(pt)$; the partial atomic orbital bond population, $N^i(pt)$, of the ith MO, and the atomic bond population, M_{XY}, are defined as follows:[4]

$$N(p) = \sum_i^{\text{occ}} \sum_t^{\text{all}} \nu_i C_p{}^i C_t{}^i S_{pt} \tag{1}$$

$$N^i(p) = \sum_t^{\text{all}} \nu_i C_p{}^i C_t{}^i S_{pt} \tag{2}$$

$$M_X = \sum_p^{\text{onX}} N(p) \tag{3}$$

$$N(pt) = 2 \sum_i^{\text{occ}} \nu_i C_p{}^i C_t{}^i S_{pt} \tag{4}$$

$$N^i(pt) = 2\nu_i C_p{}^i C_t{}^i S_{pt} \tag{5}$$

$$M_{XY} = \sum_p^{\text{onX}} \sum_t^{\text{onY}} N(pt) \tag{6}$$

where ν_i denotes the number of occupied electrons in the ith molecular orbital, $C_p{}^i$ is the coefficient of the pth atomic orbital belonging to the ith MO, and S_{pt} is the overlap integral between the pth and tth atomic orbitals.

Results and Discussion

Electronic Structures of Protonated Cycloalkanes. Figure 1 shows the three possible configurations of a protonated cyclopropane, where [A] denotes the configuration in which H^+ exists in the ring plane; [B], the structure where H^+ remains above the center of the C–C bond, and [C], the conformation in which H^+ stays above the center of gravity of the ring. The suffix in Fig. 1 indicates the ring-constituting carbon number*2.

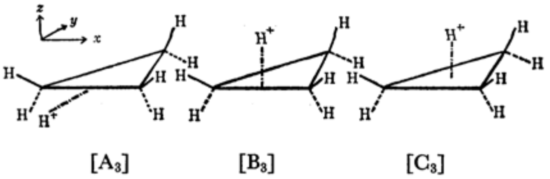

Fig. 1. Configurations of protonated cyclopropanes.

For cyclopropane, the total electronic energies in these three protonated configurations seem to be lower than those of isolated molecules,*3 as may be seen by the magnitude of the total electronic energy cited in Table 1. Among these three structures, the [A] configuration is the most stable. To facilitate the further study of the nature of these orbitals of the protonated cyclopropanes in Fig. 1, the energies of the occupied orbitals for these structures are shown in Fig. 2.

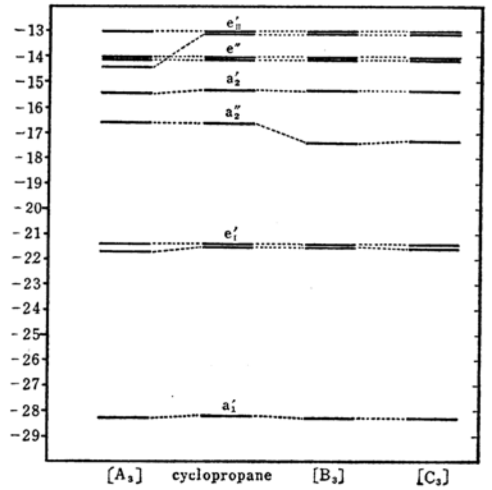

Fig. 2. Energy diagram of the occupied levels for cyclopropane and protonated cyclopropanes.

One of the doubly-degenerate molecular orbitals of cyclopropane, e'_{II} in Fig. 2, is remarkably stabilized in the [A] configuration, while in neither the [B] or [C], conformation is there any variation in these orbitals, the π-type molecular orbital,

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[2] R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).
[3] T. Yonezawa, H. Konishi, H. Kato, K. Morokuma and K. Fukui, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 869 (1966).
[4] K. Morokuma, H. Kato, T. Yonezawa and K. Fukui, This Bulletin, **38**, 1263 (1965).

*2 Ethylene is regarded as a two-membered ring as a matter of convenience, so its suffix in Table 1 is 2.

*3 More exactly, however, the discussion should be made using the total energy, including the core repulsion. Therefore, it may not be valid to conclude that protonated compounds are more stable than isolated molecules.

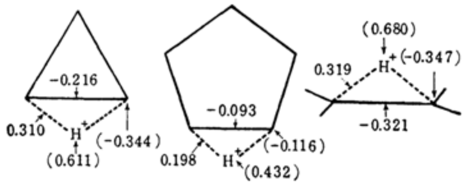
TABLE 1. CALCULATED RESULTS OF PROTONATED CYCLOALKANES

Compound	Total electronic energy eV	Atomic bond population $M_{\mathrm{C'C}}$	$M_{\mathrm{CH^+}}$	Net charge Q_{C}	$Q_{\mathrm{H^+}}$
Ethylene	−210.8297	1.2592	—	−0.2445	—
[A$_2$]	−212.8639	1.0652	0.1833	−0.0925	+0.5499
[B$_2$]	−214.7465	0.9378	0.3186	+0.1021	+0.3201
Cyclopropane	−314.6568	0.6285	—	−0.2236	—
[A$_3$]	−317.9406	0.4129	0.3097	+0.1203	+0.3894
[B$_3$]	−316.7118	0.5488	0.1746	−0.0819	+0.5597
[C$_3$]	−316.2924	0.5943	0.0669	−0.1409	+0.6177
Cyclopentane	−521.3967	0.7011	—	−0.2320	—
[A$_5$]	−523.2667	0.6084	0.1976	−0.1166	+0.5684
[B$_5$]	−522.7464	0.6757	0.0712	−0.1841	+0.6574

a_2'', being stabilized.*4 The lowering of the energies of the a_2'' MO in [B] and [C] is smaller than that of the e'_{II} orbital in the configuration [A].

In Table 1, the total electronic energies, together with the atomic bond populations and the net charges of ethylene, cyclopropane, cyclopentane, and their protonated configurations, are shown collectively. For cyclopentane, the total electronic energy is the minimum in the structure [A], the same as in the case of cyclopropane, while in ethylene, the conformation [B] in which a proton exists in the direction of the π-atomic orbitals,*5 is the most stable.

The differences in atomic-bond populations and in atomic populations between protonated and original molecules are shown in Fig. 3 for ethylene and cycloalkanes.*6



[A$_3$] [A$_5$] [B$_2$]

Fig. 3. Differences of atomic bond populations and of atomic populations between protonated molecules and original ones.

The atomic-bond population between the C–C bond diminishes upon protonation, and that

TABLE 2. POPULATIONS IN ETHYLENE AND CYCLOPROPANE

Atomic orbital population

	$N(\mathrm{S_C})$*	$N(\mathrm{X_C})$**	$N(\mathrm{Y_C})$	$N(\mathrm{Z_C})$
Ethylene	1.2043	0.9722	1.0704	1.0000
[B$_2$]	1.1959	0.9238	1.0637	0.7145
Cyclopropane	1.1799	0.9018	1.0678	1.0741
[A$_3$]	1.1590	0.8211	0.8997	1.0741

Atomic orbital bond population

Ethylene

	$\mathrm{S_C}$	$\mathrm{X_C}$	$\mathrm{Y_C}$	$\mathrm{Z_C}$
$\mathrm{S_{C'}}$	0.1446	0.1934	—	—
$\mathrm{X_{C'}}$	0.1934	0.3363	—	—
$\mathrm{Y_{C'}}$	—	—	−0.0514	—
$\mathrm{Z_{C'}}$	—	—	—	0.4035

[B$_2$]

	$\mathrm{S_C}$	$\mathrm{X_C}$	$\mathrm{Y_C}$	$\mathrm{Z_C}$
$\mathrm{S_{C'}}$	0.1088	0.1652	—	—
$\mathrm{X_{C'}}$	0.1652	0.3245	—	—
$\mathrm{Y_{C'}}$	—	—	−0.0410	—
$\mathrm{Z_{C'}}$	—	—	—	0.2152

Cyclopropane

	$\mathrm{S_C}$	$\mathrm{X_C}$	$\mathrm{Y_C}$	$\mathrm{Z_C}$
$\mathrm{S_{C'}}$	0.0571	0.1049	—	—
$\mathrm{X_{C'}}$	0.1049	0.3491	—	—
$\mathrm{Y_{C'}}$	—	—	0.0466	—
$\mathrm{Z_{C'}}$	—	—	—	−0.0340

[A$_3$]

	$\mathrm{S_C}$	$\mathrm{X_C}$	$\mathrm{Y_C}$	$\mathrm{Z_C}$
$\mathrm{S_{C'}}$	0.0429	0.0722	—	—
$\mathrm{X_{C'}}$	0.0722	0.2849	—	—
$\mathrm{Y_{C'}}$	—	—	−0.0254	—
$\mathrm{Z_{C'}}$	—	—	—	−0.0340

* $\mathrm{S_C}$; s orbital belonging carbon atom C
** $\mathrm{X_C}$; $\mathrm{P_x}$ orbital belonging carbon atom C

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*4 The electronic structure of cyclopropane belonging to D_{3h} is described as $(a_1')^2(e_1')^4(a_2'')^2(a_2')^2(e'')^4(e'_{\mathrm{II}})^4$, where a_2'' and e'' are the π-type MO's and where the other orbitals are constructed by 1s, 2s, $2P_x$ and $2P_y$ AO's.

*5 In the case of ethylene, the configuration in which H^+ exists in the molecular plane is expressed as the structure [A], and the one in which a proton exists above this plane, as [B].

*6 Protonated structures of the three kinds of compounds having the most stable configuration are adopted.

between C$\cdots$H$^+$ indicates only a weak interaction. Further, the atomic-orbital population of the carbon and the atomic-orbital-bond population of the carbon-carbon bond participating in the protonation in ethylene and cyclopropane are summarized in Table 2, together with those of isolated molecules.

The atomic orbital populations of π-orbitals in ethylene are reduced by about 50% by the protonation. In cyclopropane, the atomic-orbital-bond population between P_y orbitals, which is 0.0466 (bonding) in the original, becomes -0.0254 (antibonding) upon the protonation.

From the atomic populations, it may be seen that the electrons of the carbon atoms flow towards the proton, and that the formal charge of the carbon becomes positive in all cases. For cyclopropane, the electrons occupying the e'_{II} orbital seem to be delocalized toward the proton, while the atomic orbital population $N(P_y)$ varies from 1.0678 to 0.8997. The variation in the atomic population is almost the same in ethylene as in cyclopropane, but it is smaller in cyclopentane than in the above two compounds.

It may be concluded that the π bond in ethylene is weakened by the protonation; in cyclopropane, however, P_z orbitals of the carbon atom are not concerned in the variation of the electronic distributions and P_x and P_y orbitals in the ring plane participate in the electronic delocalization by the protonation. Further, the magnitude of the stabilization energy due to the protonation is of the same order in ethylene (3.9 eV) and cyclopropane (3.3 eV), but it is small in cyclopentane (1.8 eV).

Lawrence and Tipper⁵⁾ have studied the decomposition reaction of some hydrocarbons with strong acids and have reported that the rate of proton addition in cyclopropane is about five times as fast as that of propylene.

From this experimental result, it may be seen that the stabilization energy due to the protonation is almost the same in olefin and cyclopropane, but the cyclopropane is attacked by protons in more positions.

In conclusion, it may be pointed out that the cyclopropane ring has unsaturated properties similar to those of the π-electron system in its ring plane and that the π-type hydrogen bond will occur in the molecular plane, if at all, as the [A] configuration, not as the configuration [B] or [C], in ordinary aromatic compounds.

The Electronic Structures and Reaction Mechanisms of the S$_N$2-Type Substitution Reaction of Halogeno-Cycloalkanes. *Experimental Evidence.* The S$_N$2-type substitution reaction is expressed as:

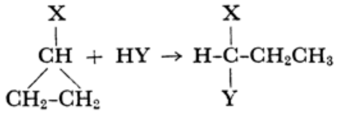
$$RX + Y^- \rightarrow \underset{\text{intermediate}}{[Y\cdots R\cdots X]^-} \rightarrow RY + X^- \qquad (7)$$

Many experimental results on this reaction with cycloalkanes⁶⁻⁸⁾ have been reported in which the relations between the ring-constituting carbon numbers and their relative reaction velocities have been made clear. For example, Fierens and others⁷⁾ have reported that the relative reaction velocities in the reaction of cycloalkylbromides with L_iI or KI are:

Compound	Isopropyl	3-Membered	4-Membered
Relative velocity	1.00	0	0.0075
Compound	5-Membered	6-Membered	
Relative velocity	1.6	0.0099	

while Brown and Borkowski⁸⁾ have obtained a similar result with 1-chloro-1-methyl-cycloalkanes.

In a summary, the relative velocities of cycloalkanes in this reaction are in the order: cyclopentyl $>$ cyclohexyl $\sim$ cyclobutyl $\gg$ cyclopropyl compounds. In the cyclopropane ring, the substitution reaction hardly ever takes place; rather, its ring is cleaved⁶⁾ by the addition of an anion, Y^-, as in the chemical formula Eq. (8);



(8)

Theoretical Results. Here a theoretical study of the reactivity as to cycloalkyl-chlorides in the S$_N$2 reaction will be made, assuming the structure [T] in Fig. 4 to be a transition state of Eq. (7). In Fig. 4, the hybridization of the carbon atom (with the suffix 1) bonded directly to the substituted group is that of the SP^2 type,*7 the hydrogen atom bonded to this carbon atom is on the ring plane (the direction of the y axis), and the bond of C$_1$–Cl is perpendicular to the ring plane.

In this type of reaction, the electrons of the nucleophilic reagent, Y^- will enter into the lowest vacant level of the [T] structure. Figure 5 shows the partial atomic populations*8 in the lowest vacant orbital of the intermediate [T]. Their

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5) C. D. Lawrence and C. F. H. Tipper, *J. Chem. Soc.*, **1955**, 713.

6) See, for example, E. Imoto and H. Shinohara, *Kagaku (Chemistry Japan)*, **16**, 241 (1961); S. Nishida and T. Tsuji, *J. Soc. Org. Syn. Chem. Japan*, **22**, 272 (1964); M. Murakami, "Advance in Organic Chemistry.," Vol. 9, Kyoritsu Shupan, Tokyo (1954). p. 31.

7) P. J. C. Fierens and P. Verschelden, *Bull. Soc. Chim. Belges*, **61**, 427, 609 (1952); L. Schotsmans, P. J. C. Fierens and T. Verlie, *ibid.*, **68**, 580 (1959).

8) H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).

*7 However, the bond angle of the ring-constituting carbons is assumed to be invariable.

*8 The position where this distribution is at its maximum is most reactive. The distrbutions at the hydrogen atoms are omitted in Fig. 5 since they are small.

TABLE 3. VALUES OF AO BOND POPULATIONS OF C_1 ATOM AT THE LOWEST VACANT IN THE INTERMEDIATE [T] OF CHLORO-CYCLOALKANES

Cycloalkyl chloride	$N^{l.v.}(S_{C_1})$*	$N^{l.v.}(X_{C_1})$**	$N^{l.v.}(Y_{C_1})$	$N^{l.v.}(Z_{C_1})$
Cyclopropyl-	0	0.346	0	0
Cyclobutyl-	−0.002	0	0.037	0.465
Cyclopentyl-	−0.002	0	0.021	0.435
Cyclohexyl-	−0.001	0	0.006	0.508

* S_{C_1}; S orbital belonging carbon atom C_1
** X_{C_1}; P_x orbital belonging carbon atom C_1

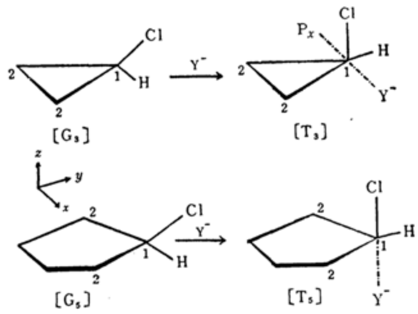

Fig. 4. Structures of cycloalkyl chlorides and their intermediates in S_N2 reaction.

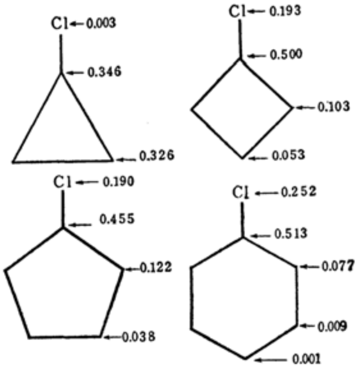

Fig. 5. Partial atomic populations of the lowest vacant MO in cycloalkyl chlorides.

largest values are always found on the C_1 atoms which directly bind the chlorine atom in each compounds.

The partial atomic orbital populations of the lowest vacant level belonging to the C_1 atom are cited in Table 3. The mode of this electronic distribution in cyclopropane is different from that of other compounds; that is, the value of the AO populations is largest on the P_x orbital and is zero on the P_z orbital. On the other hand, in four-, five- and six-membered rings, they are negligibly small on the P_x and P_y orbitals lying in the ring plane, while the atomic orbital populations of P_z orbitals (participating in the C–Cl bond formation) become the largest.

That is, in the cyclopropane ring, the direction of the x axis on the ring plane is the most susceptible to a nucleophilic attack, while in other compounds a nucleophilic reagent may approach the carbon atom along the direction of the z axis (from the opposite side of the C–Cl bond).

The partial atomic-bond populations of the lowest vacant level are shown in Table 4. In the cyclopropane ring, the bond having the largest absolute value is between the C_1–C_2 bond in the ring and is antibonding, resulting in a weakening of this bond by the interaction with the anion. On the other hand, in the other cyclic compounds, it is between the C_1–Cl bond, not the C_1–C_2 bond, in the ring, and it is antibonding.

TABLE 4. PARTIAL ATOMIC BOND POPULATIONS MATRIXES OF THE LOWEST VACANT LEVEL IN THE INTERMEDIATE [T] OF CYCLOPROPYL AND CYCLOPENTYLCHLORIDE

Cyclopropylchloride

	S_{C_1}	X_{C_1}	Y_{C_1}	Z_{C_1}
S_{C1}	—	—	—	—
X_{C1}	—	−0.018	—	—
Y_{C1}	—	—	—	—
Z_{C1}	—	—	—	—
S_{C2}	—	0.002	—	—
X_{C2}	—	−0.038	—	—
Y_{C2}	—	−0.241	—	—
Z_{C2}	—	—	—	—

Cyclopentylchloride

	S_{C_1}	X_{C_1}	Y_{C_1}	Z_{C_1}
S_{C1}	0.010	—	—	−0.236
X_{C1}	—	—	—	—
Y_{C1}	—	—	−0.001	—
Z_{C1}	0.016	—	—	−0.344
S_{C2}	−0.002	—	−0.007	—
X_{C2}	−0.003	—	−0.011	—
Y_{C2}	−0.008	—	0.002	—
Z_{C2}	—	—	—	0.033

As to the S_N2-type reaction of cycloalkanes, it may be seen from the above discussions that, even when the cyclopropane ring is in the [T] structure, the P_x orbital within the ring plane and the reagent anion interact most easily; consequently, the C_1–C_2 bond in the ring is easily cleaved and a 1, 3-addition compound is formed. On the other hand, when other cycloalkanes are in the same transition state [T], a reagent interacts with the P_z orbital from the opposite side of the C_1–Cl bond and the C_1–Cl bond ionically dissociates; *i. e.*, a typical S_N2-type substitution takes place.

Reactivity in the S_N2 Reaction. The difference in the total electronic energies between the assumed transition state [T] and the ground state [G] may be a reactivity index for the S_N2 reaction; this energy difference, ΔE, is written as Eq. (9):

$$\Delta E = E_T - E_G \qquad (9)$$

where E_T and E_G are the total electronic energies in the [T] and [G] structures respectively.

The net charge, Q, of the C_1 atom is also a reactivity index for this reaction.

In Table 5, the reactivity indices, ΔE and Q_{C_1}, of cycloalkanes are listed. These indices can explain the experimental relative velocities stated above.

TABLE 5. RELATIVE REACTION VELOCITIES OF CYCLOALKYL COMPOUND IN S_N2 TYPE SUBSTITUTED REACTION

Cycloalkyl chloride	ΔE, eV	Q_{C_1}
Cyclopentyl-	3.97	0.121
Cyclohexyl-	4.35	0.118
Cyclobutyl-	4.10	0.112
Cyclopropyl-	4.37	0.089

The calculations were carried out on the IBM 7090 at the Japan IBM Co., with the permission of the UNICON Committee, whose kindness we hereby acknowledge.