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PHOTOELECTRON SPECTROSCOPY OF CYCLOHEXANE, CYCLOPENTANE, AND SOME RELATED COMPOUNDS

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Photoelectron spectra of cyclohexane, cyclopentane, n-hexane and n-pentane have been studied. The vibrational structures of cyclohexane parent ion were clearly observed. The vibrational spacing is about 1160 cm^{-1} which can be assumed due to the C-C stretching vibrations. This spectrum was compared with the breakdown curves by charge exchange.

Photoelectron spectroscopy has been widely utilized to study molecular electronic structures of various substances. The helium resonance line of 21.22 eV is useful as the light source to obtain information about electrons of the molecular orbitals. Turner and coworkers[1] extensively studied the energetics of the molecular ions involving electronically excited state.

It has also been recognized that knowledges obtained from this spectroscopy is quite helpful in interpreting fragmentation of molecular ions produced by charge exchange of molecules with various ions. Lindholm[2] compared the appearance potentials of the fragment ions of organic substances such as benzene produced in the double mass spectrometer with the (adiabatic) ionization potentials obtained by photoelectron spectroscopy, and pointed out the existence of the fragmentation of the molecular ion involving electronically excited state, and stressed that the quasi-equilibrium theory which was proposed by Rosenstock et al.[3] was questionable because the supposition of fragmentations from the electronically ground states was not adequate.

In the present paper we have studied photoelectron spectra of some alkanes and cycloalkanes, and checked whether Lindholm's idea could apply to these substances or not by comparing these spectra with the fragmentation patterns which were studied by a double mass spectrometer in our previous papers.[4,5]

The photoelectron spectrometer used in this experiment was of a deflexion-type with parallel plates, and the details of the apparatus was already described.[6] Calibration of the energy scale was done by introducing xenon in the sample gas taking standard lines of Xe $2P_{3/2}$ (I.P. = 12.130 eV) and Xe $2P_{1/2}$ (I.P. = 13.436 eV).

Cyclohexane, cyclopentane, n-hexane and n-pentane were reagent grade products of Tokyo Kasei Co.

The photoelectron spectra of cyclohexane[7,8,9] and cyclopentane[8] were already studied. However, they were all measured with low resolution spectrometers, and, therefore, were not suitable for discriminating vibrational structure as well as overlapping bands.

In Fig.1 the lower energy bands of cyclohexane are shown. The vibrational structure of the first band indicates that vibrational spacing is about 1160 cm^{-1}, which could be due to the C-C stretching vibrations. This value may be compared with that of about 1170 cm^{-1} for ethane which is caused by the C-C stretching mode.[10] It is very interesting that the vibrational structure has been discovered in a relatively large hydrocarbon molecule such as cyclohexane.

The ionization potentials of cyclohexane obtained from the results of Figs.1 and 2 are shown in Table 1. We can see the adiabatic transition (transition to the v'=0 level) in the first band occurs at 9.87 eV which is very close to the value of the ionization potential (9.88 ± 0.02 eV) obtained by Watanabe.[11] The vertical transition in the first band occurs at 10.30 eV (v'=3) which is almost equal to the ionization potential (10.3 ± 0.2 eV) obtained by electron impact.[12] From these results it is clear that the first band structure is important to consider ionization phenomena in cyclohexane. The photoelectron sepctra also revealed that there exist at least two bands between the first band and the band which Demeo et al. considered to be next to the first band.

The breakdown curve of cyclohexane using the double mass spectrometer of a perpendicular type is shown in Fig.3. The appearance potentials of the fragment ions ($C_4H_8^+$ and $C_5H_9^+$) involving the scission of the ring of the parent ion are at about 11.0 eV. Although it is difficult to determine the appearance potentials of the fragment ions in the breakdown graph accurately, this value is approximately the same as those of the electronically excited levels (10.60 eV and 11.62 eV). So far as we are concerned with the scission of the cyclohexane molecule to the fragment ions ($C_4H_8^+$ and $C_5H_9^+$), it is reasonable to argue that the electronically excited levels play an important role in producing the fragment ions. This arguement is in agreement with the study of benzene by Lindholm.

We have already pointed out that the parent ion of cyclohexane is more stable than that of n-hexane. These

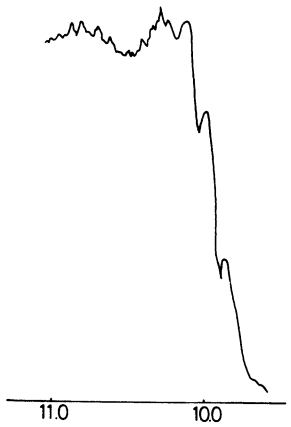

Fig.1 Lower energy bands of cyclohexane.

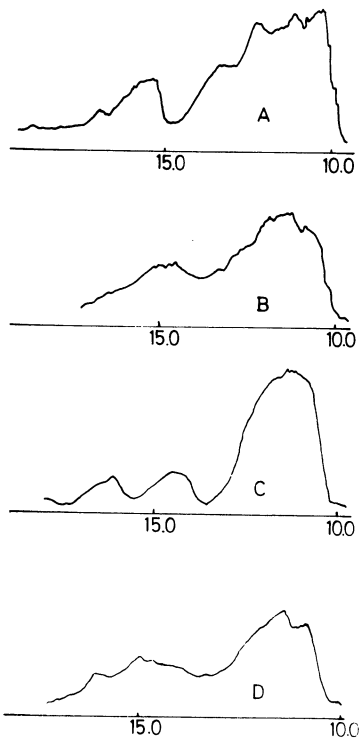

Fig.2 Photoelectron spectra of cyclohexane(A), n-hexane(B), cyclopentane(C) and n-pentane(D)

Table 1. Ionization potentials (in eV) of cyclohexane.

Band number	Adiavatic i.p.	Vertical i.p.	Vibrational progression	Demeo et al.[9] Adiavatic i.p.
1	9.87	10.30	9.87	9.89
			10.02	
			10.16	
			10.30	
2	10.26*	10.45		
3	10.60	10.86		
4	11.62	11.88		11.9
5	12.58	12.84		12.8
6	14.28	14.81		14.4
7	15.83	16.13		16.0
				16.8
8	17.78	18.01		18.0

* Owing to overlapping of vibrational components of the first and the second bands, the value is provisional.

Table 2. Ionization potentials (in eV) of cyclopentane.

Adiavatic i.p.	Vertical i.p.	Dewan et al.[8] Adiavatic i.p.
10.40	10.96*	10.49
13.73	14.28	13.89
15.33	15.96	15.91
18.17	18.28	18.27

* The first maximum of spectra

findings are now further confirmed by the presence of vibrationally excited components of the first band in cyclohexane, in comparison with the absence of such components in n-hexane.

Contrary to the case of cyclohexane, we have failed to find fine structures in the bands in cyclopentane as shown in Fig.4. The ionization potentials of cyclopentane are given in Table 2. In the region above approximately 14 eV the spectrum is similar to that in cyclohexane. Below this energy, however, it is simpler than the latter. The adiabatic ionization potential in this work is 10.40 eV which is somewhat lower than the value (10.53 eV) obtained by Lossing.[13]

The photoelectron spectra for cyclohexane, n-hexane, cyclopentane and n-pentane are shown in Fig.2. It is obvious that the spectra of n-alkanes are more complicated than those of the corresponding cycloalkanes. The adiabatic ionization potentials are 10.22 and 10.36 eV for n-hexane and n-pentane, respectively. Because of the complexity of the spectra of n-alkanes, comparison of photoelectron emission with breakdown phenomena in charge exchange does not bring any clear conclusion. Perhaps there may be some relationship between these, especially in certain energy regions, and the arguement done in cyclohexane may be applicable too, if more elaborate technique of measurements will develop.

In conclusion, it is reasonable to consider the presence of electronically excited states in the breakdown phenomena of alkanes such as cyclohexane.

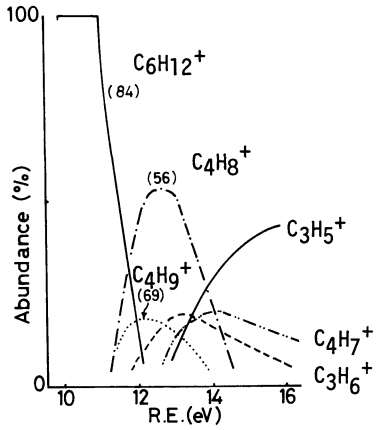

Fig.3 Breakdown curve of cyclohexane.

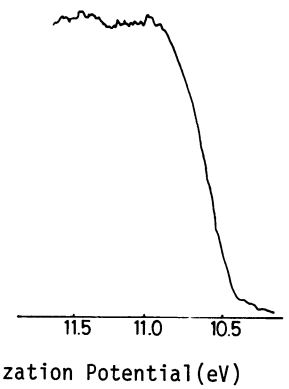

Fig.4 Lower energy bands of cyclopentane

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