Sum Rule Consideration of Molecular Photoelectron Spectra: s-Type Bands of Butenes

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(Received November 17, 1975)

The s-type photoelectron bands of *cis*-, *trans*-2-butene, and 2-methylpropene in the gaseous phase have been measured in the region 17—27 eV by a He(II) resonance lamp which was constructed for the present purpose. The vertical ionization energies obtained here from the s-type bands have been interpreted with the Hückel method involving the Coulomb integrals of carbon 2s atomic orbitals which were estimated on the basis of the idea of sum rule from the available He(II) data of many other hydrocarbons reported by Potts *et al.*

In previous He(I) photoelectron studies of many aliphatic compounds,[1–5] total and partial sums of vertical ionization energies in the p-type region have been interpreted by Kimura *et al.* in terms of the empirical energies selected on the basis of the photoelectron data of simple molecules. The sum rule has also been applied to all the ionization energies obtained in the p- and s-type regions in mono-, di-, and trimethylamines,[6] using Hall's equivalent orbitals.[7] From the sum rule considerations of various chloro-substituted compounds[4] and ethylene derivatives,[5] the following substitution effects have been pointed out on the total sums of the p-type vertical ionization energies: 1) The total sum increases approximately linearly with number of substituents. 2) The total sums of the isomers are nearly the same. 3) The total sum may be approximately reproduced with the sums of the p-type empirical ionization energies. In connection with our previous studies, we have attempted to extend our study to the s-type region of butenes in the present He(II) photoelectron study.

Potts *et al.*[8–10] have published He(II) photoelectron spectra of many saturated and unsaturated hydrocarbons, together with the resulting complete sets of vertical ionization energies in the s-type region. They have interpreted the s-type ionization energies in terms of the Coulomb integrals of carbon 2s atomic orbitals on the basis of a simple Hückel theory. In the present work, we tried to employ their experimental data for a test of our sum rule in the present work. We wish to point out here that: 1) the total sums of the available s-type vertical ionization energies in the individual hydrocarbons may be reproduced by the sums of Coulomb integrals associated with the carbon skeletons of the hydrocarbons and 2) the He(II) bands of butenes which have not been published so far may be interpreted by the Hückel method with the Coulomb energies estimated from other hydrocarbons.

Experimental

Measurements of He(II) photoelectron spectra were carried out in the region up to about 27 eV with a high-resolution photoelectron spectrometer previously used,[1,2] a DC discharge He lamp of hollow-cathode type being used as a He(II) resonance source (304 Å) which was constructed for the present purpose. The cathode of the He(II) lamp was made of aluminum. During the photoelectron measurements, the He lamp was discharged at a pressure of about 0.06 Torr at a voltage of 700 V (0.4 A). Calibrations of ionization energies were carried out with Xe and He as internal standards. In the region below about I_1+17 in eV units, where I_1 represents the first ionization energy, He(II) spectra may be observed without overlapping with He(I) spectra. In the higher region the ionization bands produced by He(I) lines (584, 537, 522 Å, *etc.*) are mixed with those produced by He(II) line. No filter films were used here for separating He(II) line from He(I) line. Commercial gaseous samples of propene and *cis*- and *trans*-2-butene, and 2-metyhlpropene were used without further purification.

Results and Discussion

The photoelectron spectra of propene and *cis*- and *trans*-2-butene, and 2-methylpropene obtained here in the region 17—27 eV are shown in Fig. 1, suggesting three ionization bands indicated by vertical lines with the numbering. The propene spectrum in Fig. 1(a) is essentially the same as that reported by Potts *et al.*[10] It may be pointed out from the photoelectron spectra of butenes that the separations of the second and third

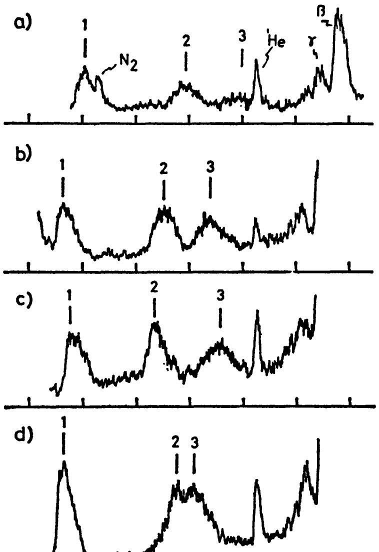

Fig. 1. The He(II) photoelectron spectra of (a) propene, (b) *cis*-2-butene, (c) *trans*-2-butene, and (d) 2-methylpropene in the region 17—27 eV. The peaks indicated by He are due to the ionization of helium gas by a He(II) line and those indicated by β and γ are due to the ionization of the samples by the 537- and 522-Å lines of He(I), respectively.

Table 1. Vertical ionization energies of propene and *cis*- and *trans*-2-butenes, and 2-methylpropene in the s-type region, together with the theoretical Koopmans' theorem ionization energies with orbital assignments

Propene		*cis*-2-Butene		*trans*-2-Butene		2-Methylpropene	
Expt$^{a)}$	Calcd	Expt	Calcd	Expt	Calcd	Expt	Calcd
18.30	18.30(a′)	17.5	17.42(a_1)	17.8	17.77(b_2)	17.5	17.77(b_u)
21.88	21.84(a′)	21.1	21.72(a_1)	20.8	20.60(a_1)	21.6	20.60(a_g)
24.16	24.18(a′)	22.9	22.17(b_2)	23.1	22.97(b_2)	22.2	22.97(b_u)
		[24.3]	24.46(a_1)	[24.1]	24.42(a_1)	[24.5]	24.42(a_g)

a) Ref. 10.

s-type bands remarkably differ from one another among the three isomers. The first s-type bands of the isomers are located approximately at the same position. The vertical ionization energies obtained from these photoelectron bands are summarized in Table 1. For *cis*- and *trans*-2-butene, and 2-methylpropene there are no available He(II) spectra for comparison.

In the previous He(I) photoelectron studies,[3,5)] it has been indicated that all the p-type bands of methyl-substituted ethylenes appear below about 17 eV and may be interpreted in terms of p-type localized MO's. In the present work, we discuss only s-type bands in the photoelectron spectra. The number of such s-type MO's in a hydrocarbon is equal to that of carbon atoms. Propene has three carbon s-type MO's which probably correspond to the three bands in Fig. 1(a). Butene isomers show three bands, the remaining bands being not clear in Fig. 1(b—d). The theoretical treatments mentioned later suggest that the fourth bands may be located at about 24.5 eV.

Potts *et al.*[8—10)] have indicated in their He(II) photoelectron studies that the s-type bands of hydrocarbons may be interpreted in terms of carbon 2s atomic orbitals. They estimated the Coulomb integrals of the C-2s orbitals on the basis of the He(II) data, and suggested that the Coulomb integrals depend on the number of hydrogen atoms attached to the carbon atoms. However, no formulas have been given for correlating the Coulomb integrals to the number of hydrogen atoms.

Using the ionization energy data of Potts *et al.*,[9,10)] we found that there may be an approximately linear relationship between the Coulomb integrals ($\alpha_{\mathrm{CH}_{4-m}}$) and the number ($m$) of hydrogen atoms lost from CH_4,

$$\alpha_{\mathrm{CH}_{4-m}} = a + bm \qquad (1)$$

$$m = 0\text{—}4$$

where a means the Coulomb integral of CH_4 and bm a correcting term due to the change of CH_4 to CH_{4-m}. The Coulomb integrals α_{CH_i} (i=0—4) are hereafter represented by α_i for simplicity.

In the present work, we first estimated Coulomb integrals α_i's from the available s-type ionization energies of several hydrocarbons; $CH_{4-m}(CH_3)_m$ (m=0—4), ethylene, and butadiene. From least squares calculations, we found that $a=-22.90$ eV and $b=0.73$ eV. The Coulomb energies thus determined are summarized in Table 2, which are used in the present study of propene and butenes. Before going into the analysis of the He(II) spectra of the compounds studied, we examined how the α_i's in Table 2 can reproduce the experimental total sums of s-type vertical ionization energies for various other hydrocarbons.

Table 2. Coulomb integrals (in eV) of the carbon s-type orbitals in CH_i (i=0—4), estimated from the sum rule

α_0	α_1	α_2	α_3	α_4
−19.98	−20.71	−21.44	−22.17	−22.90

The traces of the Hückel determinants and their numerical values for fourteen hydrocarbons are given in Table 3, compared with the corresponding experimental sums (T_{expt}) based on the s-type ionization energies reported by Potts *et al.*[9,10)] As seen from Table 3, excellent agreements are obtained between calculation and experiment, except for cyclopropane and benzene.

Applying the above sum rule to butenes, we may

Table 3. The traces of the Hückel determinants and the calculated and experimental total sums for various hydrocarbons (in eV units)

Compound	Trace	$-T_{\mathrm{calcd}}$	$-T_{\mathrm{expt}}^{9,10)}$
CH_4	$\alpha_4=a$	22.9	22.9
CH_3-CH_3	$2\alpha_3=2a+2b$	44.3	44.3
$CH_3CH_2CH_3$	$2\alpha_3+\alpha_2=3a+4b$	65.8	65.8
CH_3-$(CH_2)_2$-CH_3	$2\alpha_3+2\alpha_2=4a+6b$	87.2	87.2
$(CH_3)_3CH$	$3\alpha_3+\alpha_1=4a+6b$	87.2	87.0
CH_3-$(CH_2)_3$-CH_3	$2\alpha_3+3\alpha_2=5a+8b$	108.7	108.8
$(CH_3)_2CHCH_2CH_3$	$3\alpha_3+\alpha_2+\alpha_1=5a+8b$	108.7	108.9
$(CH_3)_4C$	$4\alpha_3+\alpha_0=5a+8b$	108.7	108.6
$[CH_2]_3$	$3\alpha_2=3a+6b$	64.3	65.6
$[CH_2]_6$	$6\alpha_2=6a+12b$	128.6	128.9
CH_2=CH_2	$2\alpha_2=2a+4b$	42.9	42.8
CH_3-CH=CH_2	$\alpha_3+\alpha_2+\alpha_1=3a+6b$	64.3	64.3
CH_2=CH-CH=CH_2	$2\alpha_2+2\alpha_1=4a+10b$	84.3	84.7
C_6H_6	$6\alpha_2=6a+12b$	124.4	125.3

Table 4. The traces of the Hückel determinants and the calculated total sums (eV) for *cis*- and *trans*-2-butene, and 2-methylpropene

Compound	Trace		$-T_{\mathrm{calcd}}$
cis-CH_3-CH=CH-CH_3	$2\alpha_3+2\alpha_1$	$=4a+8b$	85.7
trans-CH_3-CH=CH-CH_3	$2\alpha_3+2\alpha_1$		
$(CH_3)_2C$=CH_2	$2\alpha_3+\alpha_2+\alpha_0$		

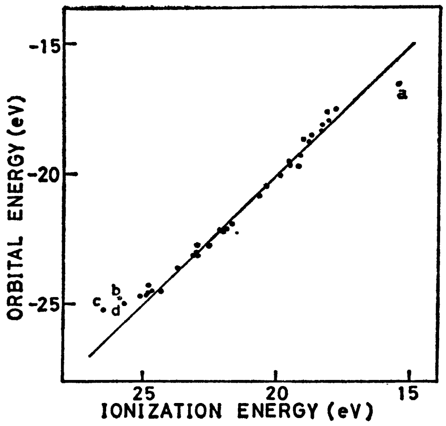

Fig. 2. A plot of the calculated (Hückel) orbital energies against the experimental vertical ionization energies in the s-type region for fourteen hydrocarbons given in Table 3. The solid line is drawn to show Koopmans' theorem. Points a and b are for the benzene b_{1u} and a_{1g} MO's, respectively; point c for the cyclopropane a_1 MO; and point d for the cyclohexane a_{1g} MO.

predict that the remaining s-type bands may appear at about 24.1—24.5 eV as shown in brackets in Table 1. The traces of the Hückel determinants of *cis*- and *trans*-2-butene, and 2-methylpropene are summarized in Table 4 which may be given simply by $4a+8b$.

In addition to the sum rule considerations mentioned above, we also calculated orbital energies by solving secular equations containing off-diagonal elements given by resonance integrals

$$\beta_{\mu\nu} = kS_{\mu\nu}(\alpha_\mu + \alpha_\nu) \quad (2)$$

where $S_{\mu\nu}$ is the overlap integral between the nearest neighboring C-2s atomic orbitals and $k=0.12$ is used which was selected so as to reproduce the separation (3.48 eV) between two s-type vertical ionization energies of ethane. In order to test the validity of the parameter value (k) in Eq. (2), we calculated the orbital energies of s-type MO's for all the hydrocarbons given in Table 3. The resulting orbital energies are plotted against the available experimental ionization energies in Fig. 2, from which it may be seen that agreements between the orbital energies and the negative ionization energies are excellent except a few cases.

Similarly, solving secular equations, we also calculated the orbital energies of s-type MO's for *cis*- and *trans*-2-butene and 2-methylpropene. The calculated Koopmans' theorem ionization energies are also shown in Table 1, compared with the experimental ionization energies. Good agreements may be seen between experiment and theory.

The most interesting conclusions obtained in the present work are the following. 1) The sum rule of ionization energies approximately holds in the s-type region for the various hydrocarbons studied. 2) The s-type ionization energies in each of the hydrocarbons may well be interpreted in terms of the constant parameters a, b, and k. 3) The separation between the second and third s-type bands of 2-methylpropene is much smaller compared with that of *cis*-2-butene (or *trans*-2-butene) and such difference may be explained mainly with the difference in the Coulomb integrals of the C-2s atomic orbitals between the two isomers.

Further applications of the sum rule to many other organic compounds not only in the p-type region but also in the s-type region will be interesting subjects to be studied.

We would like to express our gratitude to Professor S. Kiyono, Dr. N. Ueno, and Dr. Y. Hayashi of Tohoku University for their valuable suggestions for the design of the He(II) lamp.

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