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Electronic Structures of Some Olefins and Their Radical Cations*

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CNDO/2 calculations of the electronic properties of the series of isomeric butenes and pentenes yield ionization potentials which reproduce the observed trends. These are interpreted in terms of the charge distribution effects of the alkyl groups.

CNDO/2 Rechnungen für die Butan- und Penten-Isomeren ergeben die richtigen Trends für die Ionisierungspotentiale. Sie werden im Zusammenhang mit der Änderung der Ladungsverteilung infolge Methylsubstitution diskutiert.

Des calculs CNDO/2 des propriétés électroniques des séries d'isomères du butène et du pentène fournissent des potentiels d'ionisation qui reproduisent les tendances observées. Les distributions de charge calculées pour les molécules sont utilisées pour interpréter les propriétés observées en termes d'effet du substituant alkyle.

Introduction

CNDO/2 calculations [1] have been carried out on the series of isomeric butenes and pentenes and their radical cations in order to investigate theoretically the effects of molecular structure on the electronic properties of these molecules. Semi-empirical calculations have been reported previously on the methyl-substituted ethylenes [2–4] but a study of the effects of larger alkyl groups on the olefinic properties had not been included. That the size of the alkyl group may itself be the determining influence on molecular properties has been demonstrated in the photoelectron spectra of alkyl halides [5] and the gas-phase acidities of alcohols and amines [6].

The present calculations use the parametrization of Pople and Segal [1] since these parameters have been chosen to yield charge distributions comparable to those of *ab initio* calculations and have been shown to reliably predict charge distribution effects in a wide variety of molecules [4]. The geometries used assume that all carbon atoms lie in a plane, with the exception of the iso-propyl group in 3-methyl-1-butene. Bond lengths and angles are as follows: $d(\mathrm{C=C}=1.33\,A$; $d(\mathrm{C-C})=1.54\,A$; $d(\mathrm{C-H})=1.10\,A$; olefins bond angles $=120°\,54'$.

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Results and Discussion

Table 1 gives the calculated ionization potentials according to Koopmanns' theorem and also as the difference in total energies of the parent olefin and the radical cation, $\Delta E(M, M^+)$. Since the geometry is held fixed upon ionization, both values refer to the vertical IP. The experimental IP's are adiabatic photoionization values and would be expected to be different, generally, from the vertical ones (but see [7]); however, the trends observed upon alkyl substitution would probably not be affected, and the IP's calculated here correlate very well with the observed ones, as shown in Fig. 1.

Net charges for the olefins in their ground configurations are summarized in Table 1. The net π-electronic charge, $q^{\pi}_{C=C'}$ is summed over the two doubly-bonded carbon atoms, as is the net total olefinic electronic charge, $q^{\text{total}}_{C=C} \cdot \Sigma q_{\text{alkyl}}$ represents the sum over the net total charges of the alkyl groups. (Detailed net charges for some representative molecules are given in Fig. 2). Although $q^{\pi}_{C=C}$ becomes more negative as the number of alkyl groups increases, thus paralleling the decrease in IP as a function of the number of substituents, $q^{\pi}_{C=C}$ becomes less negative as the size of the alkyl group increase and thus cannot account for the decreasing IP as a function of substituent size. Conversely $q^{\text{total}}_{C=C}$ becomes more negative as the size of the alkyl group becomes larger, but becomes increasingly more positive as the number of alkyl substituents increases, and therefore also fails to account for the trends in IP.

The sum over the changes in the net charge of the alkyl groups upon ionization, $\Sigma \Delta q_{\text{alkyl}}$, is given for each olefin in Table 1 and is plotted versus observed IP in

Table 1. Ionization potentials, net charges, and change in net charges upon ionization.

Olefin	Ionization potential (eV)			Ground configuration			$\Sigma \Delta q_{\text{alkyl}}$ on Ionization
	Koopmanns	$\Delta E(M, M^+)$	Exp.[a]	$q^{\pi}_{C=C}$	$q^{\text{total}}_{C=C}$	Σq_{alkyl}	
Ethylene	16.18	15.30	10.52	0.0000	−0.0530	–	–
Propene	14.42	13.58	9.73	−0.0133	−0.0313	+0.0095	+0.2996
1-Butene	14.08	13.32	9.58	−0.0124	−0.0348	+0.0140	+0.3837
cis 2-Butene	13.35	12.53	9.13	−0.0256	−0.0094	+0.0098	+0.4600
trans 2-Butene	13.24	12.32	9.13	−0.0226	−0.0102	−0.0008	+0.4928
2-Me Propene	13.57	12.51	9.23	−0.0270	−0.0168	+0.0124	+0.4482
1-Pentene	14.15	13.28	9.50	−0.0119	−0.0394	+0.0228	+0.3784
3-Me-1-Butene	14.07	13.18	9.51	−0.0259	−0.0428	+0.0214	+0.3896
2-Me-1-Butene	13.37	12.35	9.12	−0.0232	−0.0206	+0.0269	+0.4776
cis 2-Pentene	13.21	12.39	9.11	−0.0250	−0.0132	+0.0170	+0.4903
trans 2-Pentene	13.10	12.18	9.06	−0.0219	−0.0139	+0.0031	+0.4928
2-Me-2-Butene	12.57	11.60	8.68	−0.0354	+0.0048	−0.0035	+0.5901
2, 3-DiMe-2-Butene	11.95	10.93	8.30	−0.0442	+0.0202	−0.0200	+0.6836

[a] Bralsford, R., Harris, P. V., Price, W. C.: Proc. Roy. Soc. (London) A **258**, 459 (1960); and Watanabe, K., Nakayama, T., Mottl, J.: J. Quant. Spectrsc. Radiat. Transfer **2**, 369 (1962); as quoted in Franklin, J. L. *et al.*: Ionization potentials, appearance potentials, and heats of formation of gaseous positive ions U. S. National Bureau of Standards 1969.

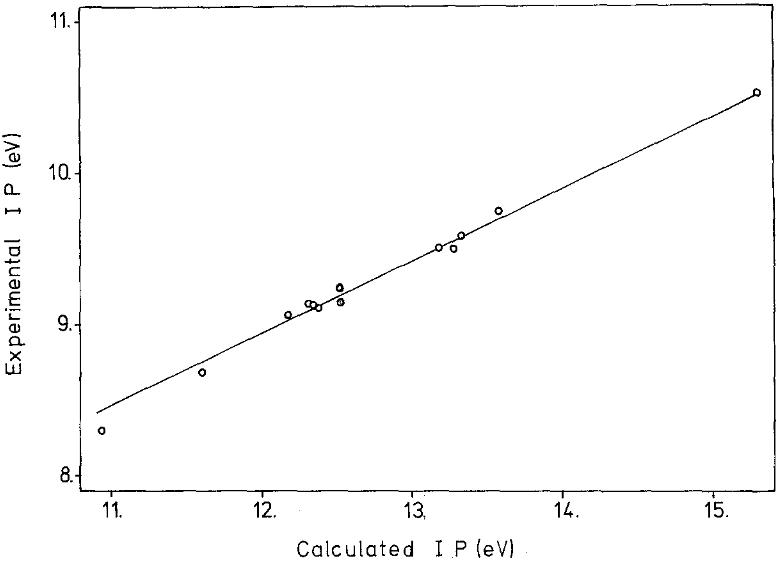

Fig. 1. Correlation between experimental and calculated ionization potentials, in electron volts

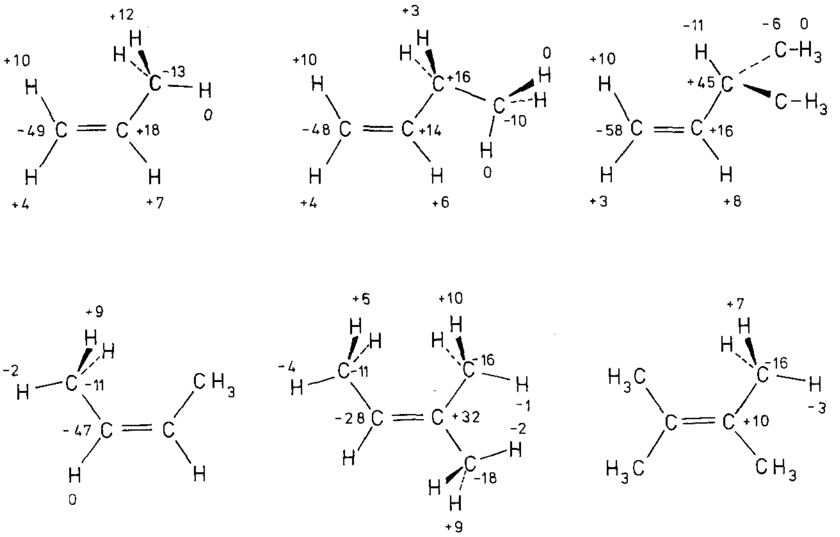

Fig. 2. Net charge densities, in units of 10^3 e^-, in (top:) propene, 1-butene, and 3-methyl-1-butene, (bottom:) *cis* 2-butene, 2-methyl-2-butene, and 2, 3-dimethyl-2-butene

Fig. 2. This shows the good, but not quite linear, correlation obtained between the decrease in the observed IP and the increase in $\Sigma \Delta q_{\mathrm{alkyl}}$ upon ionization, which depends upon (1) the increase in the size of the alkyl substituent and (2) the increase in the number of alkyl substituents.

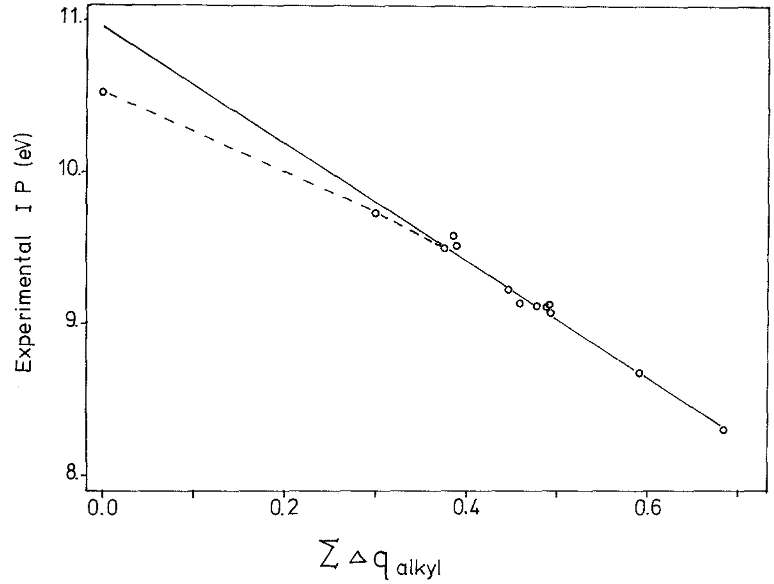

Fig. 3. Correlation between observed ionization potential (eV) and the change in the alkyl group charge density, $\Sigma \Delta q_{\text{alkyl}}$, upon ionization

Thus the observed trends in ionization potentials in these olefins may be explained on the basis of the relative ability of the alkyl substituents to donate charge to the positive hole left by the ionized electron, this ability increasing with size or complexity and also with number of alkyl groups. In discussing the effects of alkyl substituents on the gas-phase acidities of alcohols and amines and on the gas-phase basicities of amines, Brauman and Blair [6] have stated that the greater polarizability of the larger groups enhances their ability to stabilize a positive or negative charge in the molecule. However, Brogli and Heilbronner

Table 2. Extent of hyperconjugation as evidenced by the alkyl group contribution to the highest occupied π molecular orbital.

	Ground configuration			Radical cation		
	% H	% C	% Total	% H	% C	% Total
Propene	16.5	8.8	25.3	21.3	15.6	36.9
cis 2-Butene	22.8	9.2	32.0	26.4	14.2	40.6
2-Me-2-Butene	26.4	9.6	36.0	28.6	14.3	42.9
2,3-DiMe-2-Butene	30.0	9.1	39.1	31.1	13.0	44.1
1-Butene	27.7	13.7	41.4	45.4	28.6	74.0
1-Pentene[a]	26.3	12.7	39.0	28.8	26.2	55.0
3-Me-1-Butene	4.9	35.1	40.0	19.0	60.1	79.0

[a] Not the highest π but that containing a higher percentage of C = C character has been chosen.

have found in the photoelectron spectra of the alkyl halides that there is also an increasing conjugative effect with increasing alkyl group size [5].

That hyperconjugation plays a rôle in the stabilization of the radical cations may be seen from an inspection of the wavefunctions. The extent of hyperconjugation is indicated by the relative contribution of alkyl H and C atomic orbitals to the highest occupied π molecular orbital; this is given in Table 2 as % H, % C, and % total alkyl contribution for representative molecules and their radical cations. It is seen that the alkyl contribution increases with number of alkyl groups and also with size of the group, although the ethyl, n-propyl, and isopropyl groups have about the same extent of hyperconjugation in the parent olefins. As Mulliken has discussed, hyperconjugation increases in the cation [8]. In fact, the present calculations indicate that, in the cations with the larger substituents, the wavefunction for the singly-occupied π MO is considerably delocalized over the entire molecule. To what extent this is influenced by the assumed planarity of the alkyl chains, and by the strong interactions between π and σ MO's common to the CNDO method, is a serious question.

Baird [9] has reported hyperconjugation energies for propene, 1-butene, and 2-methylpropene calculated by the MINDO method and has found these energies to be an additive function of alkyl substitution. This additivity is not apparent in the CNDO/2 wavefunctions or in the charge distributions reported here. The present results do support the suggestion of Radom *et al.* [10] that C – C hyperconjugation may be more important than C–H hyperconjugation (compare 1-petene and 3-methyl-1-butene).

Although the correlation obtained here between ionization potential and charge distribution effects is good, the dependence of the quantities on the geometry used in the calculations is being investigated.

Charge distribution effects in alkyl-substituted fulvenes and their radical cations will be discussed in connection with the interpretation of the photoelectron spectra of these molecules [11].

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