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INDUCTIVE EFFECTS ON MOLECULAR IONIZATION POTENTIALS—VI*

ALKENES

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Abstract—The experimental ionization potentials, E_I, of fourteen alkenes have been correlated with the sum of the inductive substituent constants, $\Sigma\sigma_I$, of the corresponding alkyl substituents attached to the C=C group of the alkene, and a good correlation obtained. Models of alkenes were treated by the simple HMO method using the heteroatom model for the alkyl groups. A good correlation between the experimental ionization potentials, E_I, of the alkenes and the corresponding energies of their highest occupied π-molecular orbitals was found.

INTRODUCTION

WE HAVE SHOWN recently that the ionization energies of the alcohols,[1] ethers,[2] amines,[3] thiols,[4] and thioethers[5] are linear functions of both the polar substituent constants, σ^*, and the inductive substituent constants, σ_I. Thus it becomes possible, from the simple single-parameter correlation equations, to calculate, to a good approximation, values of ionization potentials of compounds which are difficult to obtain in a pure state, or which yield the primary radical cation only in very low abundance. This has considerably augmented the large number of structure and reactivity data which had previously been successfully correlated by the Hammett and Taft equations.[6] The ionization potentials of alkyl free radicals, R·, have also been correlated[7] with σ^*.

The purpose of this paper is to demonstrate that the ionization energies of alkenes, $R_2C{=}CR_2$ (where R=H or alkyl) are a linear function of σ_I, and can be calculated theoretically by means of the simple HMO method.

Ionization potentials are very important theoretically. According to Koopmans' theorem, the first ionization potential can be identified with the energy of the highest occupied orbital.[8–11] In the case of π-electron-containing systems, it is assumed that the electron being ionized is lost from a π-molecular orbital and this assumption is not unreasonable if the only other alternative is a bonding σ-molecular orbital. Thus, the gas-phase expulsion of an electron from the π-bond of an olefin is in accord with the equation:

$$\mathrm{RCH{=}CH_2} \rightarrow \mathrm{e^-} + \mathrm{R\overset{+}{C}H{-}\dot{C}H_2} \leftrightarrow \mathrm{R\dot{C}H{-}\overset{+}{C}H_2} \qquad \Delta H = E_I \qquad (1)$$

Good to excellent linear correlations of ionization potentials with the energies of the highest occupied π-molecular orbitals (HOMO) have already been obtained,

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[*] Part V. See Ref. 5.

mainly for hydrocarbons,[12, 13] but in other cases, even with some systems containing exo- or endocyclic heteroatoms.[12–14]

Electron-releasing alkyl groups bonded to the olefinic C-atoms of a molecule should increase the π-electron density and thus facilitate electron removal, thereby lowering the value of E_I. On the other hand, the presence of electron-withdrawing groups should cause an increase in the required ionization energy.*[15]

METHODS

Ionization potentials

The experimental values of the photoionization potentials for various olefinic hydrocarbons were taken from the literature.[16, 17]

HMO treatment

Models of alkenes were treated using the simple HMO method. Calculations were performed by the standard procedure on a CDC 3100 computer.†

On the basis of previous success with the heteroatom model[12, 18] of the methyl and ethyl groups, which proved to be much more satisfactory than the strictly inductive or hyperconjugation model, the heteroatom model for the methyl, ethyl, and isopropyl groups was used in these calculations. Larger alkyl groups were approximated as ethyl or isopropyl groups. No explicit inductive effect on the C═C carbon atoms was considered since the inductive effect of the alkyl groups is correctly reflected by the choice of the Coulomb and resonance integrals. Thus, the following empirical parameters were adopted:

$$\begin{aligned} \alpha_{\text{Me}} &= \alpha + 2\beta; & \beta_{\text{C-Me}} &= 0{\cdot}7\beta \\ \alpha_{\text{Et}} &= \alpha + 1{\cdot}5\beta; & \beta_{\text{C-Et}} &= 0{\cdot}6\beta \\ \alpha_{\text{i-Pr}} &= \alpha + 1{\cdot}2\beta; & \beta_{\text{C-i-Pr}} &= 0{\cdot}5\beta \end{aligned}$$

where α_X is the Coulomb integral of the p_z atomic orbital of the group X, α is the same quantity for the $2p_z$ atomic orbital of carbon, β_{XY} is the resonance integral of the XY bond, and β is the same quantity for the C—C π-bond in planar conjugated hydrocarbons.

Regression lines

The least squares method was used to calculate the regression lines and the corresponding correlation coefficients.

RESULTS AND DISCUSSION

Table 1 presents the experimental values of the photoionization potentials for various olefinic hydrocarbons along with the corresponding σ_I values[19] and the HMO energies of their highest occupied π-molecular orbitals.

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* The same effect should manifest itself in a greater basicity, the greater the electron density at the double bond of the alkene molecule, similar to that recently demonstrated for alcohols.

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Correlation with σ_I

It can be seen from Fig. 1 that a very good correlation is obtained when the experimental E_I values are plotted against σ_I. The regression line* obtained for the plot is expressed by eq. (2):

$$E_I = 10{\cdot}260 + 11{\cdot}586\Sigma\sigma_I \qquad (2)$$

The E_I values calculated for the compounds 1–14 using eq. (2) are summarized in Table 1 and are in good agreement with the experimental data. An estimated E_I value is also given for diisopropylethylene, for which the experimental value is not yet available.

TABLE 1. EXPERIMENTAL AND CALCULATED IONIZATION POTENTIALS OF ALKENES

No.	Compound	$\Sigma\sigma_I$[a]	HOMO (β)[b]	E_I(eV)[c] (Exptl.)	E_I(eV) (Calcd., Eq. 2)	E_I(eV) (Calcd., Eq. 3)
1	Ethene	0	1·00000	10·51	10·26	10·36
2	Propene	−0·046	0·81447	9·73	9·73	9·70
3	1-Butene	−0·055	0·78061	9·58	9·62	9·58
4	2-Methylpropene	−0·092	0·69305	9·23	9·19	9·28
5	*cis*-2-Butene	−0·092	0·63977	9·13	9·19	9·09
6	*trans*-2-Butene	−0·092	0·63977	9·13	9·19	9·09
7	1-Pentene	−0·058	0·78061[d]	9·50	9·59	9·58
8	2-Methyl-1-butene	−0·101	0·67508	9·12	9·09	9·21
9	3-Methyl-1-butene	−0·064	0·75692	9·51	9·52	9·50
10	2-Methyl-2-butene	−0·138	0·51771	8·67	8·66	8·66
11	1-Hexene	−0·060	0·78061[d]	9·46	9·56	9·58
12	2,3-Dimethyl-2-butene	−0·184	0·39095	8·30[e]	8·13	8·21
13	Cyclopentene	−0·101[f]	0·61874[g]	9·01	9·09	9·01
14	Cyclohexene	−0·110[h]	0·60000[i]	8·95	8·98	8·95
15	3,5-Dimethyl-3-hexene	−0·128	0·59010	—[j]	8·78	8·91

[a] Taken from ref. 19.
[b] The energy of the highest occupied π-molecular orbital.
[c] Taken from ref. 16.
[d] Approximated as 1-butene.
[e] This value of E_I from ref. 17.
[f] Calculated as a methyl and an ethyl substituent.
[g] Approximated as 2-pentene.
[h] Calculated as two ethyl substituents.
[i] Approximated as 3-hexene.
[j] Experimental value not yet available.

This correlation indicates that the effect of alkyl substituents on the π-electron density is primarily an inductive one. This is particularly evident in the case of the three isomeric dimethylethylenes whose ionization potentials appear to depend little on chain isomerism, and not at all on geometric isomerism. Further confirmation of this is found in the ionization potentials of the two isomeric dichloroethylenes[16] whose *cis* and *trans* isomers have, again, identical E_I's.

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[*] Number of points n = 14, correlation coefficient $r = 0{\cdot}981$; all data are significant on 1% probability level.

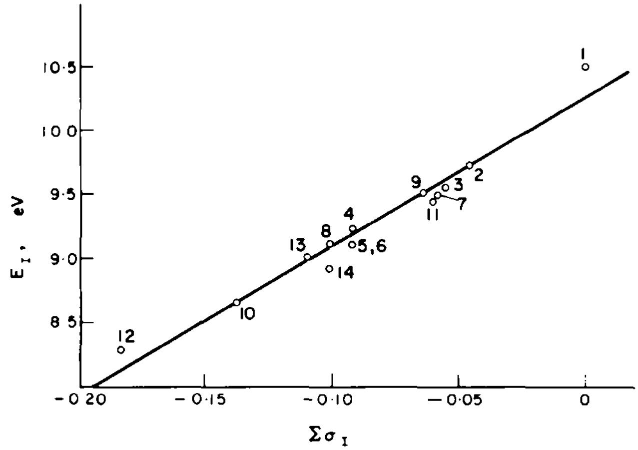

FIG. 1. Plot of the experimental ionization potentials, E_I, of alkyl substituted ethylenes *vs.* the sum of the inductive substituent constants, $\Sigma\sigma_I$, of the corresponding R-group substituents. The corresponding regression line is given by eq. (2).

The slope of the regression line is, of course, analogous to the reaction constant, ρ_I, and is a measure of the susceptibility of the reaction site (π-bond) to substituent effects. The value of 11·59 obtained here may be compared to those observed in the correlations of E_I's of alcohols (37·5),[1] ethers (28·0),[2] amines (13·8),[3] thiols (22·2),[4] and thioethers (18·8).[5] These comparisons show that the π-electrons of an alkene are considerably *less* sensitive to inductive effects than the non-bonding lone pairs on O or S, and are more comparable to that of N.

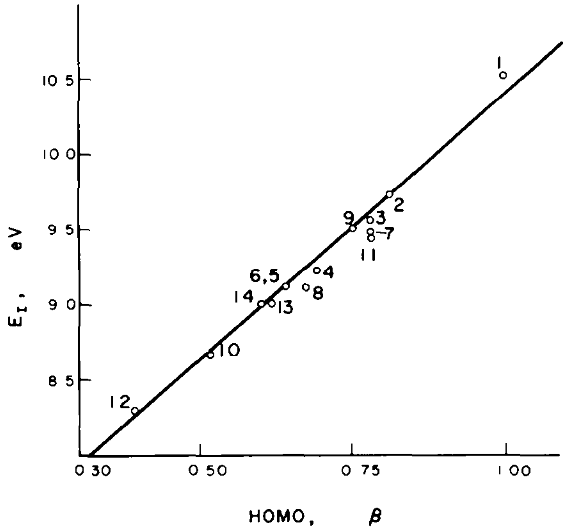

FIG 2. Plot of the experimental ionization potentials, E_I, of alkyl substituted ethylenes *vs.* the energy of their highest occupied π-molecular orbital. The regression line is given by eq. (3).

Correlation with HOMO

Figure 2 shows a plot of the experimental E_I values *vs.* the HMO energies of the highest occupied π-molecular orbitals, HOMO. The corresponding regression line* is given by

$$E_I = 6{\cdot}831 + 3{\cdot}528 \text{ HOMO } (\beta) \tag{3}$$

A comparison of the experimental ionization energies and those calculated using eq. (3) shows that the agreement is quite good (Table 1). Thus, a significant correlation is obtained even without the inclusion of σ-electrons and σ-bonds in the calculation, which would require the use of more sophisticated methods.

The regression lines (2) and (3) can be conveniently used to predict the ionization potentials of alkenes for which the experimental value is not yet available, as shown in Table 1 for diisopropylethylene (compound 15).

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* Number of points n = 14; correlation coefficient $r = 0{\cdot}990$; all data are significant on 1% probability level.