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SUBSTITUENT EFFECTS ON IONIZATION ENERGIES IN SOME 4R-SUBSTITUTED CYCLOHEXANONES.

CARLA CAULETTI[a*], GIORGIO DI MAIO[a*], WEIMIN LI[b], ELISABETTA VECCHI [a] and TOMAS VONDRÁK[c].

a) Dipartimento di Chimica, Università "La Sapienza" di Roma
Piazzale A. Moro 5, 00185 Rome, Italy.
b) On leave from East China Engineering Institute, Nanjing.
c) On leave from J. Heyrovský Institute of Physical Chemistry
and Electrochemistry,Czechoslovak Academy of Sciences,Prague.

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Abstract - A series of 4R-substituted cyclohexanones were investigated by gas-phase UV photoelectron spectroscopy in order to study the influence of the substituent in the ionization energy of the carbonyl non-bonding orbital. A plot of the IE_s vs. the substituent's Taft's σ_I indicated a different behaviour of the alkyl substituted compounds with respect to the others. A sharp linear correlation between IE_s and conformational energies for the former compounds is found and discussed in terms of ring flattening and angle deformation along the series -H, -Me, -Et and -t-Bu. Conjugative interactions between polar substituents and the $n_O(C=O)$ orbital can explain the departure from linearity of the IE_s vs. σ_I's correlation.

Considerable attention has been devoted in recent years to the study of problems concerning "long-range" interactions, but much remains still to be understood about the mechanism of transmission of the effects induced on reactivity by remote substituents. Several theories have been put forward to explain the experimental available data [1-3].

In the case of nucleophylic addition reactions on substituted cyclohexanones,the existence of anchimeric effects, the conformational flexibility of substrates, the choice of the experimental conditions are a few examples of the complicating phenomena which are involved.

Recent kinetic and stereochemical studies on reactivity of 4R-substituted cyclohexanones[4-6] showed that the reactivity of the ketonic group is influenced by "long-range" induction effects of substituents. Satisfactory linear free energy correlations between Taft's σ_I's of substituents and reactivity were obtained as an evidence of their direct influence upon the electron density of the reaction center.

RESULTS

We tested by gas-phase UV photoelectron spectroscopy a series of 4R-substituted cyclohexanones in order to investigate whether the changes in IE_s of carbonyl non-bonding orbital correlate with the substituent electronegativity or with any substituent's parameters.

Both He I (21.22 eV) and He II (40.81 eV) spectra were recorded for each compound but no significant differences in band intensities were observed. The spectra of all the compounds display a band around 9 eV, arising from ionization of the oxygen lone pair of the carbonyl group. This is the ionization phenomenon of main interest to follow possible influence of the substituents on the ionization energies along the series. In the spectra of the simplest members of the series (R=-H, -Me, -Et, -t-Bu, -OMe, -Cl) a vibrational structure appears. Beyond 12 eV the spectra show an unresolved band-envelope related to several σ--type orbitals (mainly σ_{C-C} and σ_{C-H}) with IE_s very close to each other. In the intermediate spectral region some compounds present one or more bands arising from ionization of orbital localized on the substituent group. The assignment is quite straightforward in all cases and is supported by comparison with known UP spectra of parent molecules.

Representative He I spectra are reproduced in Fig. 1 and the measured ionization energies are reported in Table 1 together with the assignments and the references to literature data. The IE_s values are averages of the results of several measurements for each compound. The He I spectra of the compounds with R=H ^{7,10}, -Me ^{9}, -t-Bu ^{9} were already known but were repeated during the present investigation for comparison purposes.

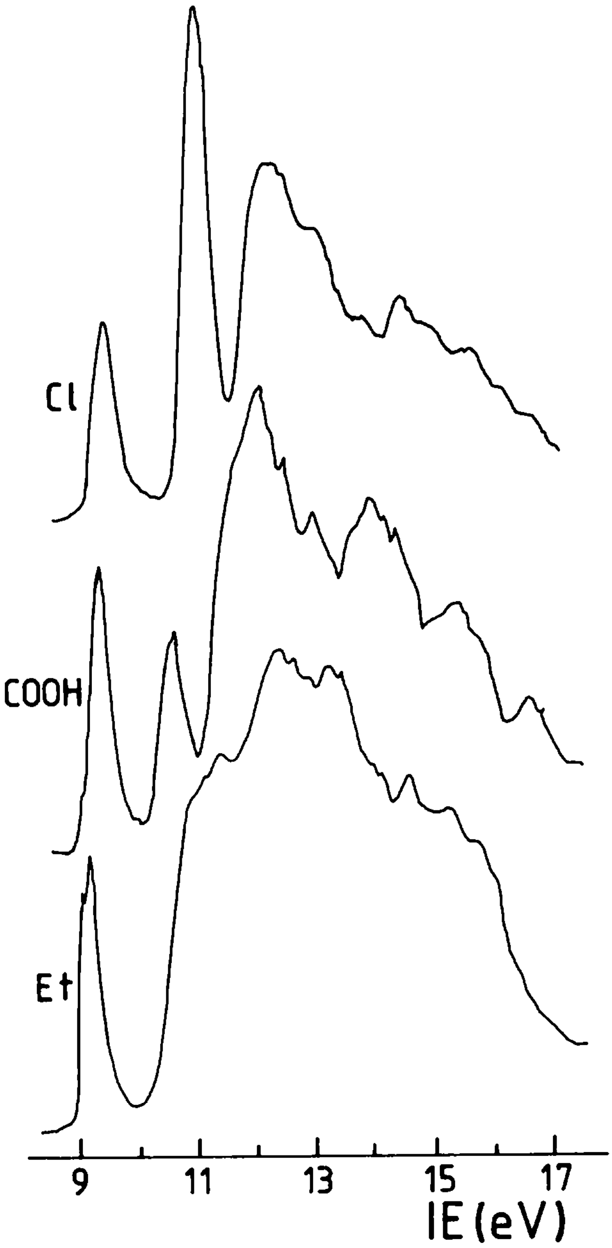

Fig. 1. Gas-phase He I photoelectron spectra of some 4R-substituted cyclohexanones (R= -Et, -COOH, -Cl).

Table 1. Ionization energies for some 4R-substituted cyclohexanones

Substituent	σ_I	IE (eV)		
		$n_{O(C=O)}$	n_X, π_X	
-Et	-0.03	9.07 9.20[a]		
-H	0.00	9.12 9.27[a]		
-t-Bu	0.02	8.95 9.09[a]		
-Me	0.03	9.08 9.21[a]		
-Ph	0.11	9.21[b]		
-OH	0.25	9.31	10.55 $n_{O(OH)}$[c]	
-OMe	0.25	9.06 9.17[a] 9.26	9.85 $n_{O(OMe)}$[d]	
-NHCOMe	0.28	9.48[e]		
-COOMe	0.30	9.27	10.33 $n_{O(C=O)}$[f]	11.26 $n_{O(C-O-C)}$[f]
-COOH	0.32	9.37	10.60 $n_{O(C=O)}$[g]	
-OCOMe	0.41	9.32	10.58 $n_{O(C=O)}$[h]	10.84 $\pi_{C=O}$, n_O[h]
-OCOPh	0.47	9.46[i]	10.25 $n_{O(COOH)}$[j]	10.67 $\pi_{O(COOH)}$[j]
-Cl	0.47	9.31 9.46[a] 9.57	10.98 n_{Cl}[k]	11.06 n_{Cl}[k]

a) Vertical IE.
b) Accounting also for π_{Ph}^{-1} ionization.IE(e_{1g}^{-1}) in benzene 9.25 eV[11].
c) Corresponding IE in MeOH 10.94 eV[12].
d) Corresponding IE in MeOMe 10.04 eV[13].
e) Accounting also for $n_{O(NHCOMe)}^{-1}$ ionization. IE (n_O^{-1}) in MeCONH$_2$ 9.96 eV[14].
f) Corresponding IE$_s$ in HCOOMe 10.99 and 11.53 eV[15].
g) Corresponding IE in HCOOH 10.99 eV[16].
h) Corresponding IE$_s$ in HOCOMe 10.87 and 12.05 eV[17].
i) Accounting also for π_{Ph}^{-1} ionization. IE$_s$(π_{Ph}^{-1}) in C_6H_5COOH 9.6 eV[18].
j) Corresponding IE$_s$ in C_6H_5COOH 10.6 and 11.4 eV[18].
k) Corresponding IE$_s$ in Chloro-2-Cyclohexanone 11.02 and 11.38 eV[9].

DISCUSSION

The IE$_s$ values we obtained were tentatively plotted in Fig.2 against the substituent's Taft σ_I's. We can observe that the ionization energies roughly increase with increasing the electronegativity of substituents. The line through the points has a low correlation coefficient (ϱ =0.754). One can observe that groups having very close Taft σ_I's (as the -OMe and -NHCOMe groups for instance) have very different IE$_s$. What is more surprising is the high dispersion in IE$_s$ values for non polar substituents which is not accounted for with any σ scale. Actually IE$_s$ for the alkyl-substituted compounds show a completely different behaviour with respect to the other molecules: an interesting observation is that a plot of IE values vs. conformational energies[19] of -H , -Me, -Et and -t-Bu in the cyclohexane system, shown in Fig. 3, gives a sharp line (ϱ =0.997). We are observing a single conformation for the 4-alkyl substituted cyclohexanones, that is the one possessing the alkyl group equatorially conformed (and, of course, a single species is observed for the cyclohexanone itself). One must therefore conclude that the group conformational energy represents an indirect measure of geometrical changes in the molecules, namely the flattening of the cyclohexane ring and the consequent widening of the C-CO-C bond angle which must be considered the ultimate factor influencing the n-MO energy. This behaviour parallels that of cycloalkanones whose IE_s change with the ring size and linearly correlate with IR ν_{CO} bands[7]. The vibrational structure of the spectra shows half band widths of the $n_{O(C=O)}$ band that accordingly decrease in the order -H(0.38 eV), -Me (0.38 eV), -Et (0.36 eV) and -t-Bu (0.32 eV) from cyclohexanone to the 4-t-Bu derivative.

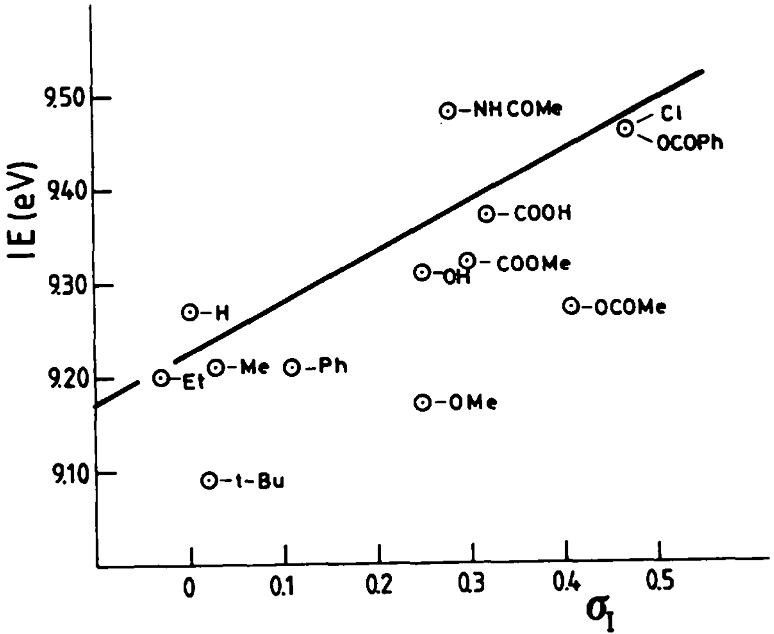

Fig. 2. Plot of IE vs. σ_I of some 4R-substituted cyclohexanones.

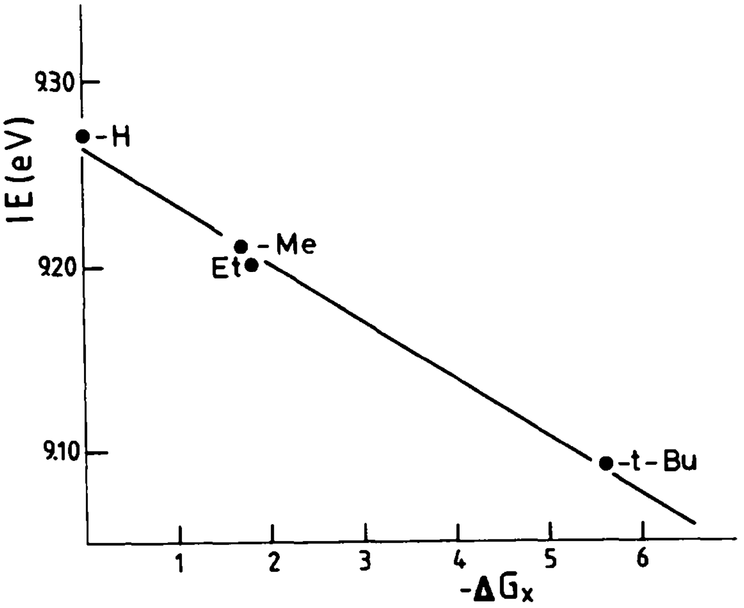

Fig. 3. Plot of IE_s vs. conformational energies of 4-alkyl substituted cyclohexanones (-H, -Me, -Et and -t-Bu).

The above discussion leads to the conclusion that the position of each point in Fig. 2 can result from a balance of electronic and conformational factors. Any attempt to handle IE_s of the polar substituted cyclohexanones in the same way described above for the non polar ones can not but fail. Actually too few data on conformational energies of 4R-substituted cyclohexanones in the gas-phase are known and, for polar substituents,it is by no means safe to use in the cyclohexanone system the conformatinal energies determined for the cyclohexane systems as we did for the alkyl substituents. Recent data[20] confirm, for instance, that due to electrostatic interactions, 4-Cl and 4-OMe cyclohexanones are axially conformed. It is plausible to foresee that the carbonyl group experiences different molecular orbital interactions with the polar substituent in the 4-axial or 4-equatorial conformation and the $n_{O(C=O)}$ ionization could consequently be differently affected. These conjugative interactions are not accounted for by the Taft σ_I's, and this could also cause the failure of the IE_s vs. σ_I's correlation for these molecules. It is meaningful that linear relationships were found for some series of aromatic molecules between IE_s and Hammett σ_p constants[21-26], which take into account both inductive and resonance effects.

EXPERIMENTAL

Cyclohexanone (Carlo Erba) and 4-t-Butylcyclohexanone (Merck) were used without further purification.
4-Methylcyclohexanone, 4-Methoxycyclohexanone and 4-Carbomethoxycyclohexanone were synthesized according to Carlson and Zey[27].
4-Ethylcyclohexanone was synthesized according to Plant, Rogers and Williams[28].
4-Phenylcyclohexanone was synthesized according to Ugnade[29].
4-Hydroxycyclohexanone was synthesized according to Haslanger and Lawton[30].
4-Acetamidocyclohexanone was synthesized according to Nelson and Mortimer[31].
4-Carboxycyclohexanone was synthesized by hydrolysis of 4-Carbomethoxycyclohexanone according to known methods: m.p. 65-66°C; lit. [32] 66-67°C.
4-Acetoxycyclohexanone was synthesized according to Aldersley, Burkhardt, Gillman and Hindley[33].
4-Benzoyloxycyclohexanone was synthesized according to Jones and Sondheimer[34].
4-Chlorocyclohexanone was synthesized according to Owen and Robins[35] and Grewe[36].
The gas-phase photoelectron spectra were recorded on a Perkin Elmer PS 18 spectrometer equipped with a He I/He II lamp (Helectros Development). The spectra of the liquid samples were run at room temperature, those of the solid ones at temperatures ranging between 30 and 120°C. Calibration was performed by N_2 and self-ionizing He as internal standard.

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