Hyperconjugative Interactions in Halogen-substituted Carbonyls: Ultraviolet Photoelectron Spectroscopy of ω-Halogenoacetophenones

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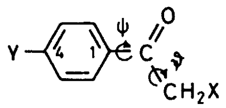
The He^I and He^{II} photoelectron spectra of the *para*-substituted ω-halogenoacetophenones Y-C_6H_4-$COCH_2X$ [Y = NO_2, CN, H, OCH_3, $N(CH_3)_2$; X = H, Cl, Br, I] are assigned on the basis of the composite-molecule approach, substituent effects, and intensity variations observed on changing the wavelength of the ionizing radiation. *Ab initio* minimal basis set calculations using the pseudo-potential method have been used to calculate the most stable conformation of acetophenone and its ω-bromo and ω-iodo derivatives. The first band of the iodine derivatives shows peculiar energy and intensity variations on changing the *para*-substituent. These findings have been ascribed to an easier interaction of the iodine lone-pair orbitals with the substrate owing to their lower ionization energy values and larger size with respect to the other halogens.

I.r., u.v., and n.m.r. spectroscopic evidence as well as theoretical analyses have shown [1–8] that hyperconjugative interactions are present in cyclic and open-chain α-halogen-substituted carbonyls R^1-CO-CHX-R^2 (X = hydrogen or halogen) between the two functions. These interactions are responsible for the stabilization of axial or *gauche* conformers with respect to equatorial or *cis* ones. The hyperconjugative interaction, which increases with the size of the halogen, alters the electronic distribution and, as a consequence, MO energies, ν_{CO} stretching frequencies, $n \longrightarrow \pi^*_{CO}$ transition energies, n.m.r. chemical shifts, and dipole moment values are modified with respect to the parent compounds where X = H.[1–8]

U.v. photoelectron (p.e.) spectroscopy, measuring the ionization energy (IE) of bands related to various valence MOs, offers, in principle, the possibility of isolating components of the total electronic effect of a substituent. This technique, therefore, is well suited for investigating substituent effects. Applications of p.e. spectroscopy to the study of hyperconjugative interactions between halogen and unsaturated adjacent groups ($\pi_{C=C}$, $\pi_{C=O}$, and π_{aryl}) have been reported. Using this technique, Schmidt and Schweig have shown that allyl halides[9] and benzyl halides[10] adopt a *gauche* conformation. In the benzyl series, the interaction between the σ_{C-X} and the benzene π-MOs results in the loss of degeneracy of the filled e_{1g} orbital of benzene giving rise to the π_s and π_a MOs.† In the allyl halides the ionization energy of the $\pi_{C=C}$ MO increases (Br, 10.18; Cl, 10.34; F, 10.56 eV) or decreases (I, 9.75 eV) with respect to propene (H, 9.88 eV).[9] These energy shifts have been ascribed to the combined effects of the variation of the halogen electronegativity and the ability of the C–X bond to hyperconjugate with the π-MOs.[9,10]

In halogenoacetones,[11] the energy trend of the MOs mainly localized at the carbonyl group (π_{CO}, π^*_{CO}, and n_O) has been discussed in terms of the various electronic interactions with the substituent orbitals. Experimental and theoretical evidence indicated that the hyperconjugative interactions $\pi_{CO} - \sigma_{C-X}$ and $\pi^*_{CO} - \pi^*_{C-X}$ and the mixing between the n_O and the halogen lone pair (X_{1p}) orbitals increase with the size of the heteroatom.

As an extension of previous work on halogen-substituted acetones[11] we present here the results of a He^I and He^{II} p.e. spectroscopic study of some *para*-substituted ω-halogenoacetophenones (**1**)—(**5**).



(**1**) Y = NO_2
(**2**) Y = CN
(**3**) Y = H
(**4**) Y = OCH_3
(**5**) Y = $N(CH_3)_2$
a ; X = H
b ; X = I
c ; X = Br
d ; X = Cl

In these compounds, the *para*-substituent affects the interaction between the CH_2X and CO groups by modifying the electronic structure of the latter without varying its steric environment. I.r. measurements in solution on these compounds indicate[12] that the C–X bond preferentially (≥80%) assumes a *gauche* conformation which allows hyperconjugative interaction.

Pseudo-potential *ab-initio* calculations[13] have been used to investigate their gas-phase conformation.

Experimental

The He^I and He^{II} p.e. spectra were recorded using a Perkin-Elmer photoelectron spectrometer equipped with a Helectros He^{II} lamp. The spectra were calibrated with noble gas lines. The

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† In monosubstituted benzenes π_s and π_a are the benzene ring π-MOs symmetric and antisymmetric, respectively, to a plane perpendicular to the ring plane and passing through C-1 and -4.

Table 1. *Ab initio* psuedopotential theoretical results on conformational preferences of ω-halogenoacetophenones. Total energies of absolute minima in a.u., relative energies in kJ mol^{-1}

Torsion angle	Y = H			Y = OMe		Y = NO$_2$
φ^a (°)	X = H	X = Br	X = I	X = Br	X = I	X = I
0	−63.485 719	1.46	4.52	1.46	4.44	4.85
30	7.45	7.20	9.37	7.16	9.29	9.73
60	16.86	12.76	13.26	12.72	13.18	13.62
90	7.45	−75.910 478	−74.104 918	−98.058 695	−96.253 076	−114.202 122
120	0.00	12.39	17.45	12.01	16.99	16.66
150	7.45	*b*	*b*	*b*	*b*	*b*

^{a} Torsion angle ψ 0°. ^{b} Relative energy larger than 250 kJ mol^{-1}.

error in the quoted IE values is ±0.05 eV if two decimal places are given and ±0.1 eV in other cases.

The halogen-substituted dimethylamino derivatives were unstable under vacuum at the lowest temperature needed to obtain suitable vapour pressure (50—70 °C). In particular, (**5b**) decomposed completely, while (**5c**) decomposed largely producing mainly CH_3Br (whose sharp X_{1p} lines have been used to calibrate the first three bands in the He^I spectrum). For the same reason, it was not possible to record the He^{II} spectra of the (**5b**—**d**) derivatives.

To compute preferential conformations of some of the investigated compounds, *ab-initio* LCAO-MO-SCF calculations were carried out using the non-empirical pseudo-potential method of Bartelat *et al.*[13] This method offers the advantage of a consistent level of accuracy along the series of halogen derivatives. All calculations were carried out using the PSHONDO program.*

Owing to the molecular complexity, minimal basis sets were employed. It is well known that this level of accuracy is sufficient to provide reliable torsional barriers. In contrast theoretical IEs need extended basis sets. For this reason, no attempt has been made to relate theoretical and experimental IEs.

Geometrical parameters were taken from available *X*-ray structures.[15–17] The angle ψ is equal to 0° when the O and the C_{CH_2} atoms lie in the benzene ring plane. The *cis* conformer has φ 0°. In the calculations ψ was taken as constant at 0° on the basis of experimental evidence.

Results

Conformation.—It is well established[15,16,18–22] that acetophenone and its *para*-substituted derivatives are planar (or nearly planar) in the solid, solution, and gas phase (ψ 0, φ 0°). The barrier to internal rotation around the C(1)–CCO bond (variation of ψ) in the gas phase has been found to be *ca.* 3.2 kcal mol^{-1} by i.r. measurements,[22] or 3.9—4.4 kcal mol^{-1} by theoretical calculations.[23,24]

Less information is available on the conformation of halogen derivatives. In the computations ψ was taken to be 0° by analogy with acetophenones. As far as the torsion angle φ is concerned, the compounds studied are present in solution in two conformations, *cis* and *gauche*, the latter being the more abundant (≥80%).[12] In the solid state, ω-chloro- and ω-bromoacetophenone have a *cis* conformation. By contrast, the iodo-analogue assumes a *gauche* conformation where the dihedral angle φ is 93°. This peculiarity has been ascribed to steric hindrance.[17]

The computed total energy for the most stable conformation and the energy differences at selected φ values are reported in Table 1.

The most stable conformer of acetophenone has one C–H bond of the methyl group in the molecular plane pointing away from the ring (φ 0°). The energy barrier to internal rotation is 16.86 kJ mol^{-1} (4.03 kcal mol^{-1}) and the energy difference between φ 0 and 90° is 7.45 kJ mol^{-1} (1.78 kcal mol^{-1}). These results are in agreement with previous theoretical computations[23,24] and (n.m.r.) oriented-molecule[19] and *X*-ray studies.

In contrast, the total energy of the halogen derivatives shows a minimum for φ 90° in all cases. The φ 0° conformation is 1.46 kJ mol^{-1} (0.45 kcal mol^{-1}) higher in energy in the bromine derivatives (Y = OCH_3 and H) and *ca.* 4.5 kJ mol^{-1} (1.1 kcal mol^{-1}) higher in the iodine derivatives (Y = OCH_3, H, and NO_2). The barrier to internal rotation is 12.75 kJ mol^{-1} (3.05 kcal mol^{-1}) in the bromine compounds, while it slightly increases from 13.18 to 13.62 kJ mol^{-1} (3.15 to 3.26 kcal mol^{-1}) in the iodine derivatives on going from Y = OCH_3 to NO_2.

According to the present calculations and in agreement with i.r. data in solution,[12] therefore, in *para*-substituted ω-halogenoacetophenones the carbon–halogen bond assumes in preference a *gauche* conformation with respect to the C=O bond. This conformation is not influenced by the nature of Y.

One could speculate that the similarity of the barrier to internal rotation around the C(1)–C_{CO}[22,24] and C_{CO}–C_{CH_2X} bonds indicates that the assumption regarding the mutual independence between the variation of ψ and φ is inadequate. However, the nearly constant values for the barrier related to the change of φ indicates that its influence on the ψ value should be rather similar in all the halogenoacetophenones considered [(**1b**), (**3b**), (**3c**), (**4b**), and (**4c**)]. Therefore, it is unlikely that the unusual findings in the p.e. spectra of the iodine compounds, discussed later, are related to unusual conformations of these compounds.

Photoelectron Spectra.—The He^I photoelectron spectra of a variety of ring-substituted acetophenones have previously been reported by a number of investigators.[25] Nevertheless, we have preferred to record all the spectra under the same conditions to have a homogeneous set of data and a better comparison with the He^{II} spectra. The He^I and He^{II} spectra of the (**1b** and **c**) and (**4b** and **c**), as examples, as shown in the Figure, and the experimental IE values are presented in Table 2.

Five bands are expected, and indeed found, in the low-IE region of the p.e. spectra of halogenoacetophenones due to ionization from the π_s and π_a ring orbitals, the carbonyl lone pair MO, n_O, and, at slightly higher energy,[26] from the two halogen lone pairs, X_{1p}. In the *para*-substituted derivatives, one [Y = OCH_3 at *ca.* 11 eV; Y = $N(CH_3)_2$ below 8 eV][27] or two additional bands (Y = NO_2 at *ca.* 11 eV; Y = CN at *ca.* 12 eV)[27] contribute to the initial part of the spectrum.

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* PSHONDO Is a modified version of the HONDO program[14] which includes pseudopotentials.

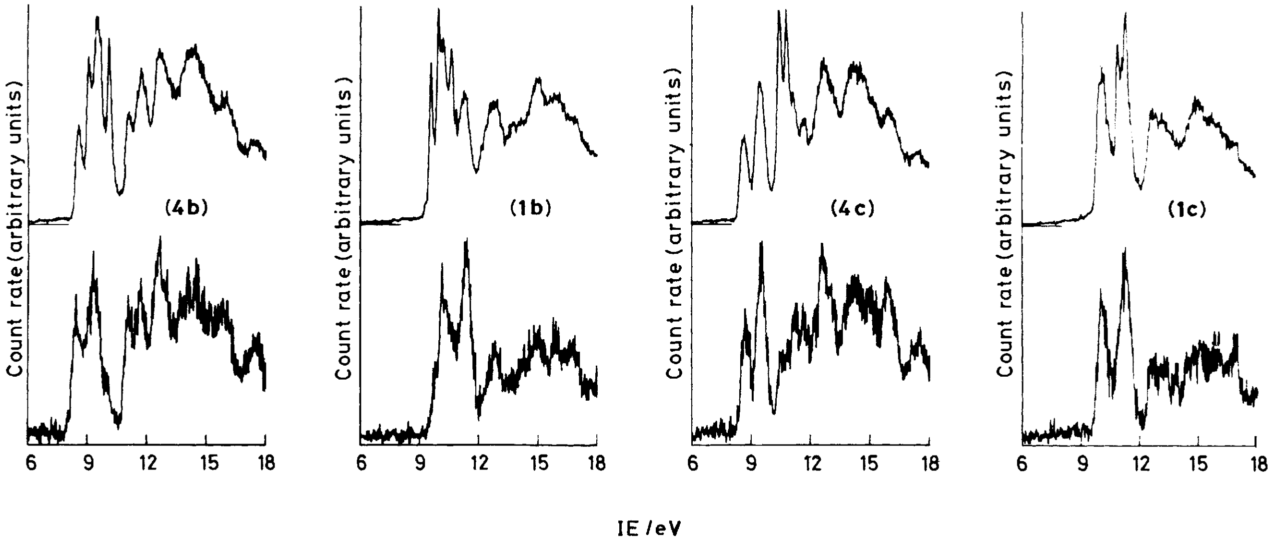

Figure. He^I and He^{II} (lower) u.v. p.e. spectra of selected *para*-substituted ω-halogenoacetophenones. The approximate intensity is *ca.* 2 000 and 200 counts s^{-1} for the He^I and He^{II} spectra, respectively

Table 2. Ionization energy values (eV) of the photoelectron bands related to the π-ring (symmetric and antisymmetric) orbitals, the carbonyl lone pair (n_O), the halogen lone pairs (X_{1p}), and the Y-based MOs in *para*-substituted ω-halogenoacetophenones (**1**)—(**5**)

Compd.	π_s	n_O	π_a	X_{1p}	Y
(**1a**)	10.05	10.05	10.05		11.26
(**1b**)	9.59	9.97	10.20	10.2 10.64	11.28
(**1c**)	10.10	10.10	10.10	10.91 11.31	11.31
(**2a**)	9.9	9.78	10.2		11.92 12.14
(**2b**)	9.54	9.88	10.15	10.15 10.64	11.97 12.21
(**2c**)	10.1	9.9	10.4	10.92 11.32	12.04 12.25
(**2d**)	10.1	10.0	10.4	11.55 11.98	11.98 12.24
(**3a**)	9.38	9.57	9.8		
(**3b**)	9.21	9.54	9.84	9.84 10.32	
(**3c**)	9.7	9.6	10.0	10.62 11.0	
(**3d**)	9.6	9.6	9.6	11.19 11.60	
(**4a**)	8.52	9.36	9.19		11.05
(**4b**)	8.60	9.10	9.53	9.53 10.11	11.13
(**4c**)	9.65	9.46	9.46	10.42 10.76	11.11
(**5a**)	7.69	9.15	9.15		9.97
(**5c**)	7.7	9.2	9.2		10.1
(**5d**)	7.69	9.24	9.24		10.06

An accurate analysis of the experimental IE values has been carried out following three different approaches which agreed in supporting the assignment proposed in Table 2.

A comparison of the p.e. spectrum of each *para*-substituted acetophenone with those of the relevant substituted benzene[27] and halogenoacetone[11] supplies information for band assignment as well as ionization shifts and splittings related to the electronic interaction between the two components of the acetophenone molecule. This composite-molecule approach to p.e. spectra analysis has received wide application.[28]

Further information on the assignment was obtained by observing IE trends for the various bands on changing X or Y, taking into account the known[26,27] electronic properties of the substituents.

The assignment of ionization bands has been confirmed by the analysis of the intensity variations of corresponding bands on changing the ionization radiation. On going from He^I to He^{II} spectra, the bands corresponding to MOs rich in nitrogen and oxygen 2*p* atomic orbitals increase in relative intensity with respect to those related to MOs of mainly carbon 2*p* character, while the intensity of those rich in chlorine, bromine, and iodine *p*-orbitals decreases.[29]

In several cases, mainly when $X \neq I$ and $Y \neq OCH_3$ and $N(CH_3)_2$, no obvious splitting among the π_s, π_a, and n_O bands is observed indicating that the resonance capability of the $COCH_2X$ group is small. As proposed by Peel and co-workers for benzoyl halides,[30] a mechanism similar to the Jahn–Teller effect, which broadens the first p.e. band of benzene, could contribute to the width of the observed composite band.

As stated before, minimal basis set computations are not suitable for reproducing experimental IE values. Nevertheless, the calculations confirm that in the initial part of the p.e. spectra only the bands taken into account on an experimental basis are present and that their IE values decrease on increasing the electron-releasing capacity of Y.

Discussion

As mentioned above, the cross-section of halogen *np* orbitals decreased on going from He^I to He^{II} radiation.[29] This effect is evident also in the spectra of the halogen derivatives investigated here. For example, the intensity of the sharp peaks at 10.42 and 10.76 eV in the He^I spectrum of (**4c**) is drastically reduced in the He^{II} spectrum (see Figure).* Similar intensity variations are shown by iodine (see Figure) and chlorine derivatives.

In the He^{II} spectra of the iodine compounds (**1b**)—(**3b**) a large intensity decrease is also shown by the first band. This effect is not present in the spectrum of (**4b**) nor in any of the chlorine or bromine compounds (see Figure). The HOMO is a π-MO which derives from the benzene π_s orbital and contains contributions from the π-orbital(s) of the Y substituent and the π_{CO} MO. Even the halogen *np* atomic orbitals contribute to the HOMO *via* hyperconjugative interaction of the C–X bond. In the φ 90° conformation, in addition, a through-space mixing between the halogen lone pairs and the MOs localized at C(1) and C_{CO} is possible,[11,31]

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* The corresponding bands in the spectrum of (**1c**) apparently do not decrease sizeably in the He^{II} spectrum (see Figure). This is due to the accidental degeneracy with the band related to ionization from two nitro group orbitals whose intensity increases in the He^{II} spectrum.

A likely explanation of the above experimental observations is that the halogen–substrate hyperconjugative and through-space interactions are more effective in the iodine compounds than in the corresponding chlorine and bromine analogues, and that they are reduced by a powerful electron-releasing Y substituent. The higher capability of iodine to take part in hyperconjugation is related to the lower IE[27] (better energy matching with the acetophenone π_s orbital), while the larger size (better overlap with distant centres) of the iodine orbitals with respect to those of other halogens is responsible for the larger through-space interaction.

Further support for the proposed interpretation of the intensity variation of the first p.e. band of the iodine derivatives and an explanation for the effect of Y is supplied by IE data. In fact, the lowest IE (IE_1) value of the bromine derivatives is slightly higher (0.2 ± 0.1 eV) than that of the corresponding hydrogen derivatives, while the difference between the IE_1 of hydrogen and iodine derivatives changes significantly with Y. In particular, IE_1 is reduced by iodine when Y = NO_2 (−0.46 eV), CN (−0.36 eV), and H (−0.17 eV), but increased when Y = OCH_3 (+0.08 eV). The IE difference can be considered to derive from a balance among the stabilizing inductive effect of the halogen, its destabilizing hyperconjugative interaction, and the through-space mixing.

The variation of the interaction between halogen and substrate on changing Y can be rationalized by the following argument. Electron-withdrawing Y substituents lower the energy of the highest occupied and lowest unoccupied MOs, while electron-releasing groups have a destabilizing effect.[32,33] Both the hyperconjugative $\pi_s - \sigma_{C-X}$ and the charge transfer $\pi_s^* - X_{1p}$ interactions are improved by the former and rendered more difficult by the latter substituents.

It appears that there is competition between the two electron-releasing substituents, CH_2X and YC_6H_4, to conjugate with the CO group which shows a sort of saturation effect: the less powerful electron-releasing group, CH_2I, cannot fully exert its donating capability when that of the substituted ring increases. It is to be noted that a similar saturation effect has been reported by Gal *et al.*[25] These authors found that in *para*-$YC_6H_4COCH_2X$ [X = H, CH_3, $N(CH_3)_2$], the conjugative effect of Y is weaker the greater the electron-releasing ability of X.

Support for the interpretation of the p.e. results comes from the analysis of other spectroscopic data. The competition between the YC_6H_4 and CH_2X groups in donating charge to the carbonyl group is also shown by ^{13}C n.m.r. data.[12] In addition, a low IE_1 allows a large electron migration from the aryl group towards the carbonyl π^*_{CO} orbital which reduces the carbonyl bond order and therefore the ν_{CO} frequency.[34] For this reason, a low IE value of the uppermost π_s MO corresponds to a low ν_{CO} value (see Table 3). At the same time, the increase of negative charge at the carbonyl group steadily reduces the n_O IE value (for constant X) from Y = NO_2 to $N(CH_3)_2$ (see Table 3). Similar trends have been reported for 3-substituted cyclohex-2-enone[35] and benzamides.[36] The ring $\longrightarrow$ CO charge migration also influences the ^{18}O isotope shifts[34] and $\lambda_{max.}$ for the $n_O \longrightarrow \pi^*_{CO}$ transition[37] (see Table 3).

A final comment on the IE values related to the halogen lone pair orbitals is worthwhile. The X_{1p} IEs increase with respect to those of the corresponding acetones[11] when Y has a prevailing electron-withdrawing effect (Y = CN and NO_2), and decreases when Y is H or an electron-releasing group. In the chlorine and bromine derivatives the splitting between the two X_{1p} MOs is constant and equal to that observed in the corresponding acetones. In the iodine derivatives, instead, this splitting decreases (OCH_3, 0.6; H, 0.5; CN and NO_2, 0.4 eV) indicating a variation of the interaction of the halogen lone pairs with the rest of the molecule by changing the electron-withdrawing capability of X.

Table 3. Photoelectron π_s and n_O ionization energy values, ν_{CO} stretching frequencies in n-hexane,[12] ^{18}O isotope shift, and $\lambda_{max.}$ for the $n \longrightarrow \pi^*$ transition of *para*-substituted ω-halogenoacetophenones, $YC_6H_4COCH_2X$

Compound	π_s/ eV	n_O/ eV	ν_{CO} [a]/ cm^{-1}	^{18}O [b] (p.p.m.)	$\lambda_{max.}$ [c]/ nm
(1a)	10.05	10.05	1 703.1	0.0485_6	335
(2a)	9.9	9.78	1 700.9	0.0476_3	
(3a)	9.38	9.57	1 694.6	0.0471_2	320
(4a)	8.52	9.36	1 686.9	0.045_8	308
(5a)	7.69	9.15	1 680.1		
(1b)	9.59	9.97	1 694.1		
(2b)	9.54	9.88	1 692.2		
(3b)	9.21	9.54	1 686.5		
(4b)	8.60	9.10	1 679.5		
(1c)	10.10	10.10	1 700.2		
(2c)	10.1	9.9	1 698.1		
(3c)	9.7	9.6	1 692.1		
(4c)	8.65	9.46	1 683.6		
(5c)	7.7	9.2	1 672.8		
(2d)	10.1	10.0	1 702.8		
(3d)	9.6	9.6	1 697.2		
(5d)	7.69	9.24	1 676.6		

[a] From ref. 12. [b] From ref. 34. [c] From ref. 37.

Acknowledgements

G. D. thanks the C.N.R., Rome, for the use of the facilities at the Institute of Ozzano.

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Received 29*th August* 1986; *Paper* 6/1747