Basicity of the Carbonyl Group. Part 12.[1] Correlations between Ionization Potentials and Lewis Basicities in Aromatic Carbonyl Compounds

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Linear relationships between ionization potentials of the carbonyl oxygen lone pair and enthalpies of complexation (ΔH°) of the carbonyl group with boron trifluoride are established for three series of *para*-substituted aromatic carbonyl compounds: benzaldehydes (**1**), acetophenones (**2**), and *NN*-dimethylbenzamides (*3*). The predictive value of these correlations is explored and the variation of their slopes is discussed in terms of a saturation effect of the direct conjugative interaction between the *para*-substituents and the variable carbonyl function in the complexed state.

Although the photon probes the electron-binding energy of a basic molecule B and the proton probes its ability to share electron density in the formation of a B–H$^+$ bond, there have been attempts to use valence shell ionization potentials to predict the proton affinity or the Brønsted and Lewis basicities of oxygen-, nitrogen-, or phosphorus-containing molecules.[2,3] Indeed it is of great interest to attempt to correlate various basicity parameters with some molecular property which is amenable to unambiguous determination. For instance, Davis and Rabelais,[2] and Benoit and Harrison,[4] have observed correlations between proton affinity (P.A.s) and valence shell vertical ionization potentials (I.P.s) for oxygen-containing molecules, especially carbonyl compounds. Recently, we have established similar relationships between ionization potentials of the oxygen lone pair (n_O I.P.) of the carbonyl group of a series of 3-substituted cyclohex-2-en-1-ones and the enthalpies of complex formation, ΔH° (Lewis basicity), between these ketones and boron trifluoride in dichloromethane.[5,6] These relationships have enabled us to propose that (i) in the free ketone direct conjugative interaction between the substituent, X, and the carbonyl group is weak, but becomes very strong in the complexed (or protonated) state and (ii) such correlations cannot be used for the comparison of Lewis basicities of different types of ketone, but they do permit the comparison of the relative basicities of the same type.

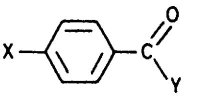
In this paper we report the results of investigations to ascertain whether, in three homogeneous series of *para*-substituted aromatic carbonyl compounds (1)—(3), each series requires a separate correlation of ΔH° *versus* n_O I.P. and also whether such correlations can yield information on the transmission of substituent effects through the aromatic ring when the group Y directly bonded to the carbonyl function varies.

Experimental

Valence shell vertical ionization potentials were derived from u.v. photoelectron spectra (He^I) obtained from a Perkin-Elmer PS18 photoelectron spectrometer operating with an electron energy resolution of 0.03 eV. The energy scale was calibrated by admitting argon and xenon together with the relevant sample.

The microcalorimetric method for ΔH° measurements has been previously reported.[7,8]

All the acetophenones and benzaldehydes were commercially available and gave satisfactory microanalysis after purification.


(1) Y = H
(2) Y = CH_3
(3) Y = $N(CH_3)_2$
X = variable substituent

NN-Dimethylbenzamides were prepared by reaction of the aroyl chloride with dimethylamine.[9]

Results and Discussion

(a) *Vertical Ionization Potentials and Assignment.*—Although the photoelectron spectra of a wide variety of substituted benzaldehydes[4,10–14] and acetophenones[4,13,15–17] has previously been published by a number of investigators (see also refs. 18—20), we have preferred to record all spectra under the same conditions in order to obtain three series of homogeneous values suitable for comparison. The I.P. values for the $\mathrm{Ph_s}$ and $\mathrm{Ph_A}$ orbitals of the aromatic moiety and for the oxygen lone pair orbital n_O are listed in Table 1.

The three I.P. values ($\mathrm{Ph_s}$, $\mathrm{Ph_A}$, and n_O) of *NN*-dimethylbenzamide have been assigned from the numerous data for disubstituted benzenes available in the literature, from the results of Houk for benzamides[21] and those of McGlynn concerning the effects of methyl, amino, and dimethylamino substituents on the n_O ionization of carbonyl compounds.[22] Compared with the $\mathrm{Ph_s}$, $\mathrm{Ph_A}$, and n_O ionizations of benzaldehyde (9.71, 9.71, and 9.89 eV) amino substitution to give benzamide lowers $\mathrm{Ph_s}$ and n_O ionization, further to 9.45 and 9.78 eV whereas the $\mathrm{Ph_A}$ level is not significantly affected (9.78 eV). In the case of *NN*-dimethylbenzamides the effect of the two methyl groups is greatly to destabilize the n_O level because the carbonyl function is directly conjugated with the dimethyl amino group Y; however, the $\mathrm{Ph_s}$ and $\mathrm{Ph_A}$ levels of the aromatic ring are only slightly affected. The observed values agree with these considerations and we obtained 9.04, 9.41, and 9.74 eV respectively for n_O, $\mathrm{Ph_s}$, and $\mathrm{Ph_A}$. The three orbital energy levels of these compounds are reported in Table 1, as are the $\mathrm{Ph_s}$ and $\mathrm{Ph_A}$ energy levels of monosubstituted benzenes.

For the three series of carbonyl compounds, the value of slopes of $\mathrm{Ph_s}$ I.P. or $\mathrm{Ph_A}$ I.P. (*para*-substituted aromatic carbonyl compound) *versus* $\mathrm{Ph_s}$ I.P. or $\mathrm{Ph_A}$ I.P. (monosubstituted benzene) confirms the $\mathrm{Ph_s}$ and $\mathrm{Ph_A}$ level assignments. Indeed the values of the slopes of the relationships between the

Table 1. Ph$_s$, Ph$_A$, and n_O vertical ionization potentials for series (**1**)—(**3**) and for monosubstituted benzenes

Substituent	Series (1)			Series (2)			Series (3)			Monosubstituted benzenes		
X	Ph$_s$	Ph$_A$	n_O	Ph$_s$	Ph$_A$	n_O	Ph$_s$	Ph$_A$	n_O	Ph$_s$	Ph$_A$	ref.
NO_2	10.37	10.37	10.37	10.20	10.58	9.98	10.21	10.21	9.46	9.99	10.32	18
CN	10.10	10.10	10.35	9.82	10.26	9.82				9.72	10.14	15
CF_3							10.05	10.05	9.38	9.70	9.90	10
$COCH_3$				9.61	9.61	9.61				9.51	9.51	This work
Br				9.22	9.88	9.55	9.09	9.74	9.09	9.05	9.67	19
Cl	9.57	10.05	10.05	9.25	9.90	9.52	9.16	9.81	9.16	9.06	9.69	19
F	9.60	10.17	9.85				9.13	9.82	9.13	9.19	9.82	19
H	9.71	9.71	9.89	9.51	9.51	9.51	9.41	9.74	9.04	9.23	9.23	20
CH_3	9.34	9.78	9.78	9.42	9.56	9.38	8.90	9.39	8.90	8.85	9.34	20
OCH_3	8.88	9.75	9.75	8.65	9.47	9.20	8.40	9.35	8.88	8.39	9.22	15
NH_2				8.27	9.43	9.08				8.05	9.21	15
$N(CH_3)_2$	7.81	9.40	9.40	7.55	9.10	8.75	7.40	8.95	8.70	7.37	8.96	15

Table 2. Relationships between Ph$_s$ or Ph$_A$ [for series (**1**)—(**3**)] and Ph$_s$ or Ph$_A$ (monosubstituted benzenes) {expressed as *e.g.* Ph$_s$ [series (**1**)] = ρ•Ph$_s$ (C_6H_5X) + h}

Series	I.P.	ρ	h	r^a	s^b	n^c
(1)	Ph$_s$	0.972	0.702	0.9982	0.051	8
(1)	Ph$_A$	0.615	4.021	0.9512	0.104	8
(2)	Ph$_s$	0.977	0.404	0.9969	0.065	10
(2)	Ph$_A$	0.933	0.268	0.9901	0.065	10
(3)	Ph$_s$	1.099	−0.785	0.9926	0.109	9
(3)	Ph$_A$	0.833	1.703	0.9111	0.170	9

[a] Correlation coefficient. [b] Standard deviation (eV). [c] Number of points.

Table 3. $-\Delta H^\circ$ (kJ mol^{-1}) values of series (**1**)—(**3**) at 295.15 ± 0.1 K[a]

Substituents	Series (1)	Series (2)	Series (3)
NO_2	62.32 ± 0.18	67.07 ± 0.50	94.20 ± 0.57
CN	65.06 ± 0.44	67.08 ± 0.25	
CF_3			98.38 ± 0.40
$COCH_3$		70.58 ± 0.18	
Br		73.09 ± 0.40	98.78 ± 0.59
Cl	73.51 ± 0.54	73.03 ± 0.31	
F	76.14 ± 0.36		100.08 ± 0.35
H	74.88 ± 1.00	74.52 ± 0.15	101.75 ± 0.24
CH_3	79.62 ± 0.56	77.82 ± 0.33	102.70 ± 0.60
OCH_3	84.81 ± 0.42	83.01 ± 0.43	103.19 ± 0.57
$N(CH_3)_2$	103.21 ± 0.38	98.84 ± 0.23	108.76 ± 0.34

[a] Errors quoted are at the 95% confidence level.

Ph$_s$ I.P. values are almost constant and close to unity (Table 2). Houk,[21] who made parallel observations, noted that in *para*-disubstituted benzenes, electron-releasing groups such as CH_3, OCH_3, NH_2, and NMe_2 have a direct influence on the value of Ph$_s$ I.P. of the benzene, whereas electron-withdrawing groups such as $COCH_3$, CN, or NO_2 do not display this effect and show slopes close to unity.

An interesting feature of the plots of Ph$_s$ I.P. values of these disubstituted benzenes *versus* those of monosubstituted benzenes is that they can aid in assignment of ionization potentials of some of these compounds. For instance, a conflicting assignment (9.60, 9.90, and 9.38 eV for Ph$_s$, Ph$_A$, and n_O, respectively) has been reported by McAlduff[17] for the photoelectron spectrum of *p*-chloroacetophenone. Indeed, it appears that the Ph$_s$ level (9.25 eV) is lower than the n_O level (9.52 eV) and that this new assignment then becomes consistent with the direction and magnitude of the Cl substituent effect (9.23 eV to 9.06 eV) observed between benzene and chlorobenzene.[15,19,21]

(b) *Photoelectron Spectra Correlations with Lewis Basicity Data*.—As we have recently shown with αβ-unsaturated ketones,[5] a linear correlation exists between the I.P. of the oxygen lone pair of the carbonyl group and the enthalpies of complexation, ΔH°, with boron trifluoride in dichloromethane. These enthalpies of complexation (Table 3) are an adequate and relevant estimation of the Lewis basicity of carbonyl compounds.[8] In Figure 1 the ΔH°–I.P. correlations obtained using the data from Tables 1 and 3 are shown.

Three separate correlations are obtained as follows:

$$\text{Series (1)}\quad \Delta H^\circ = (37.67 \pm 4.68)n_O\,\text{I.P.} - 451.48 \quad r\ 0.9567,\ s\ 3.99\ \text{kJ mol}^{-1}$$

$$\text{Series (2)}\quad \Delta H^\circ = (27.08 \pm 2.39)n_O\,\text{I.P.} - 332.87 \quad r\ 0.9738,\ s\ 2.40\ \text{kJ mol}^{-1}$$

$$\text{Series (3)}\quad \Delta H^\circ = (15.74 \pm 2.31)n_O\,\text{I.P.} - 243.81 \quad r\ 0.9410,\ s\ 1.56\ \text{kJ mol}^{-1}$$

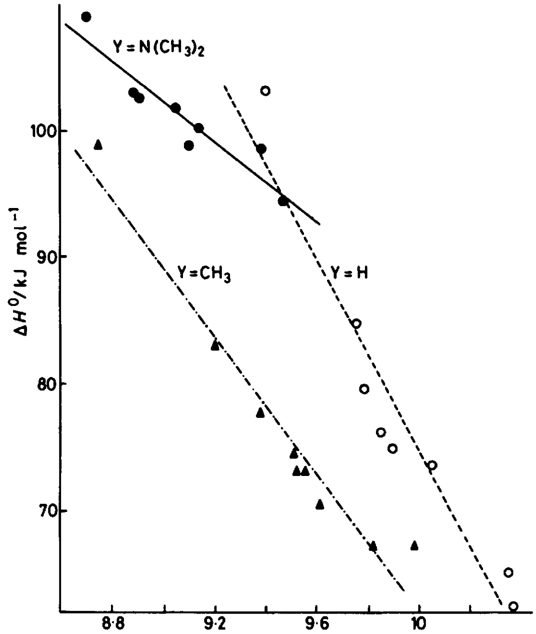


Figure 1. Relationships of ΔH° and n_OI.P. for benzaldehydes (○), acetophenones (▲), and *NN*-dimethylbenzamides (●).

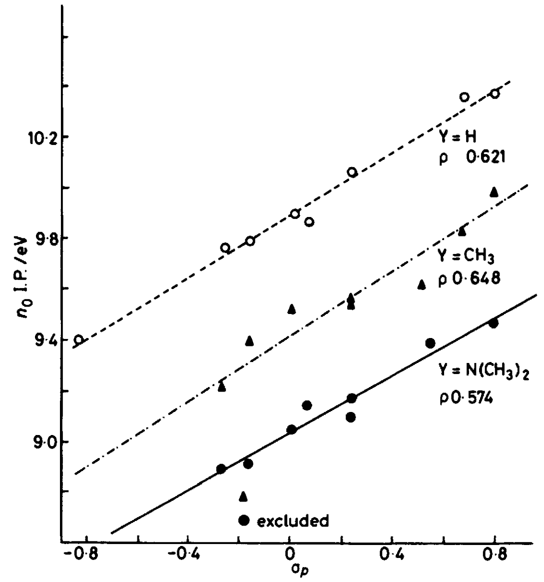


Figure 2. Relationships of n_OI.P. and σ_p for benzaldehydes (○), acetophones (▲), and *NN*-dimethylbenzamides (●)

There appears to be little doubt that each homogeneous class of compounds requires a separate correlation. These expressions (ΔH° *versus* n_O I.P.) do permit the comparison of relative basicities of the same type of carbonyl function.

Interestingly, these plots are not mutually parallel; accordingly it appears that the influence (*via* transmission) of substituent effects on the ionization of oxygen lone pairs and on the Lewis basicities of the carbonyl groups differs for each class of aromatic carbonyl compound. This observation and the values of the slopes can be interpreted from the n_OI.P.–σ Hammett-type relationships. Although we consider that correlations of ionization potentials with Hammett-type substituent constants must be made with caution because these parameters are generally estimated from kinetic or equilibrium data obtained in solvating media, such correlations have frequently been attempted.[13,17,23,24] The substituent effects on the n_O orbitals of series (1)—(3) are shown in Figure 2 where values of the ionization potential are plotted against the relevant Hammett substituent parameter, σ_p.[25]

Thus it seems that the transmission of substituent effects is the same irrespective of the nature of the group Y [H, CH_3, or $N(CH_3)_2$] which is directly linked to the electron-withdrawing carbonyl function. In addition, correlations are achieved with the classical σ_p Hammett constant, rather than the $\sigma_p{}^+$ constant of Brown and Okamoto,[26] and this shows that the direct conjugative interaction between the *para*-electron-releasing substituents and the electron-withdrawing side-chain is similar in the ground state and in the positively ionized final state. This observation is in agreement with our previous results[5] and the application of Koopmans' theorem.[27]

The variation of the slope of the ΔH°–n_O I.P. relationships allows us to propose that the direct conjugative interaction is different in the free carbonyl compound and in the complexed state and also that the importance of this interaction in the complexed form is a function of the electron-withdrawing power of the substituent Y linked to the carbonyl group. The slopes [38 for Y = H, 27 for Y = CH_3, and 16 for Y = $N(CH_3)_2$] decrease as the electron-withdrawing power of Y increases.

We conclude that the Y group directly linked to the carbon of the carbonyl function inhibits the direct conjugative effect of X through the aromatic ring and that the weight of this inhibition depends on the electron-releasing power of Y. This saturation effect of the resonance with the carbonyl group in the final complexed state can also be interpreted as a 'buffer' effect of Y with respect to effects of substituents X; the conjugative effects of X are weakened the greater the electron release of Y*. This conclusion relates to the observation from the Hammett-type treatment of substituent effects upon the pK_{BH^+} of benzaldehydes, acetophenones, benzoic acids, and benzamides (Table 4).

Table 4. ρ and σ values for the relationships $pK_{BH^{+X}} - pK_{BH^{+H}} = \rho^i\sigma^i$ for benzaldehydes (Y = H), acetophenones (Y = CH_3), benzoic acids (Y = OH), and benzamides (Y = NH_2)

Y	$-\rho^i$	$\sigma^{i\,a}$	$H_i{}^b$	Ref.
H	1.85	σ^+	H_0	28
CH_3	2.17	σ^+	H_0	29
	1.21	σ^+	H_A	30
OH	1.09	σ^+	H_0	31
NH_2	0.92	σ	H_A	32

[a] Substituent constants: σ values from Exner;[25] σ^+ values from Brown and Okamoto.[26] [b] Acidity function: Hammett acidity function H_0;[33] acidity function H_A for amides.[34]

Although these pK_{BH^+}–σ relationships illustrate the influence of electronic effects of Y on the transmission of the substituent effects of X, it is difficult to ascertain the origin of this influence. Indeed, it is known that the slopes depend on the acidity function involved and that the thermodynamic validity of pK_{BH^+} values is not established; in this respect acetophenones do not follow the conventional acidity function H_0 nor the amide acidity function H_A but rather an acidity function

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* An alternative explanation for the decrease of the slopes of plots of ΔH° *versus* n_O I.P. could be steric inhibition of resonance when the bulky BF_3 moiety is added to a Y side-chain of progressively increasing size: H, CH_3, $N(CH_3)_2$, if present.

intermediate between these two.[30,35]. The correlated quantity pK_{BH^+} depends on two parameters *viz.* the enthalpy and the entropy of protonation. The latter is essentially a measure of solvation for an ionization reaction in aqueous medium [36,37] and this solvation is known to vary with the nature of the lateral side-chain Y.[38] Accordingly the slopes of pK_{BH^+}–σ (or σ^+) relationships not only reflect the electronic effects of substituents on the carbonyl group, and their values include a significant contribution from solvation effects contrary to the slopes of $\Delta H°$–n_O I.P. relationships.

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