Interaction between the Carbonyl Group and a Sulphur Atom. Part 8.[1] Correlation between the Basicity Constants, corrected for Steric Effects, and Taft σ* Values for Some Ketones and Nitriles

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The basicity constants for a number of ketones, corrected for the steric effects of α-substituents, were plotted against the corresponding ionisation potentials of the carbonyl oxygen lone pair orbitals to give a linear relationship. A plot of log K_{as} + δE_s against Taft σ* values for the same ketones indicates an interaction for the α-sulphur and α-oxygen substituted ketones. A similar plot for a series of nitriles suggests an interaction in α-sulphur-substituted nitriles.

IN previous papers [2-9] the interacting systems $-S-CH_2-CO-$ and $-S-CH_2-CN$ were investigated by means of basicities, carbonyl or cyano-bond frequencies, and photoelectron and u.v. absorption spectral measurements. A decrease in basicity of the carbonyl or cyano-group in these systems was observed in comparison with the corresponding sulphur-free compounds. This was confirmed for the series of ketones by ionisation potential data, but was in disagreement with the decrease in carbonyl bond stretching frequencies. This anomalous relationship seemed to indicate that the inductive effect of the sulphur atom is not entirely responsible for the decrease in basicity, but that some interaction between the sulphur atom and the carbonyl group occurs.

This work provides some new evidence for the interaction between sulphur and the carbonyl group by investigation of the basicities of a larger number of compounds and by comparison of the effect of the sulphur atom to that of other heteroatoms, through correlations between basicity constants and ionisation potentials of the carbonyl oxygen lone pair and basicity constants and σ* Taft values of the substituents.

RESULTS AND DISCUSSION

The new data for the equilibrium constants K_{as} for association complexes between *p*-chlorophenol and ketones (1)—(10) are listed in Table 1. Inspection of the log K_{as} values indicates the following order of basicities for the ketones studied: unsubstituted > α-oxygen > α-sulphur > β-chloro > α-chloro. The larger decrease of basicity for the sulphur- than for the oxygen-substituted ketones is in disagreement with the order of electronegativity of the two heteroatoms.[10] The possibility that steric hindrance to hydrogen bonding, due to the bulky sulphur atom, could be responsible, partly, for a decrease in basicity, seemed unlikely, as a still larger decrease in basicity was reported for the thiacyclanones,[7] in which there is more favourable steric conditions for hydrogen bonding. Nevertheless, recalculation of log K_{as} values, taking into account the steric effects of α-substituents, was found to be necessary for comparative reasons. The literature data for Taft σ* and E_s values of the substituents [11,12] and the corrected equilibrium constants (log K_{as} + δE_s) are included in Table 1. It can be observed that the previous order of basicities is maintained.

TABLE 1

Basicity constants (log K_{as} and log K_{as} + δE_s), σ*, and E_s of the substituents and ionisation potentials of the carbonyl oxygen lone pair for ketones (1)—(10)

Ketone	log K_{as}	σ*	E_s	log K_{as} + E_s [a]	I.P. $n_{O(CO)}$ (eV)
(1)	1.029	0.00	0.00	1.029	
(2)	1.017	−0.100	−0.07	1.023	9.54 [b]
(3)	1.049	−0.115	−0.36	1.079	9.40 [b]
(4)	1.045	−0.190	−0.47	1.084	9.30 [b]
(5)	1.033	−0.300	−1.59	1.166	9.14 [b]
(6)	0.863	+0.42	−0.34	0.891	9.90 [c]
(7)	0.897	+0.56	−0.47	0.936	
(8)	0.978	+0.520	−0.19	0.994	9.62 [c]
(9)	0.339	+1.050	−0.24	0.359	
(10)	0.712	+0.385	−0.90	0.787	

[a] δ 0.083 7 (calculated from log K_{as} = log $K_{o\ as}$ + ρσ* + δE_s [11]). [b] B. J. Cocksey, J. H. D. Eland, and C. J. Danby, *J. Chem. Soc.* (*B*), 1971, 790. [c] Ref. 9.

RCOMe

(1) R = Me
(2) R = Et
(3) R = Pr^n
(4) R = Pr^i
(5) R = Bu^t
(6) R = CH_2SMe
(7) R = CH_2SEt
(8) R = CH_2OMe
(9) R = CH_2Cl
(10) R = $[CH_2]_2Cl$

The log K_{as} + δE_s values for ketones (2)—(6) and (8), plotted against the corresponding ionisation potentials

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[1] Part 7, B. T. Buzzi, M. T. Fabi, L. Marzorati, P. R. Olivato, R. Rittner, C. Trufem, H. Viertler, and B. Wladislaw, *Rev. Latinoamer. Quim.*, 1976, **7**, 58.

[2] B. Wladislaw, H. Viertler, and E. B. Demant, *J. Chem. Soc.* (*B*), 1971, 565.

[3] B. Wladislaw, A. Giora, and H. Viertler, *Anais Acad. brasil. Ceienc.*, 1971, **43**, 381.

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[6] B. Wladislaw, P. R. Olivato, and R. Rittner, *Rev. Latinoamer. Quim.*, 1974, **5**, 206.

[7] B. T. Buzzi, P. R. Olivato, R. Rittner, C. Trufem, H. Viertler, and B. Wladislaw, *J.C.S. Perkin II*, 1975, 1294.

[8] M. T. Fabi, L. Marzorati, P. R. Olivato, R. Rittner, H. Viertler, and B. Wladislaw, *J.C.S. Perkin II*, 1976, 16.

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[10] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, New York, 1948, p. 60.

[11] Y. Minamida, Y. Ikeda, K. Uneyama, W. Tagaki, and S. Oae, *Tetrahedron*, 1968, **24**, 5293.

[12] R. W. Taft, jun., in 'Steric Effects in Organic Chemistry,' ed. M. Newman, Wiley, New York, 1956, p. 598.

of the carbonyl oxygen lone pair orbitals (Table 1), give a straight line (Figure 1). This rules out any possibility that the high basicity constant in the oxa-ketone could be due to competitive hydrogen bonding to the α-oxygen.

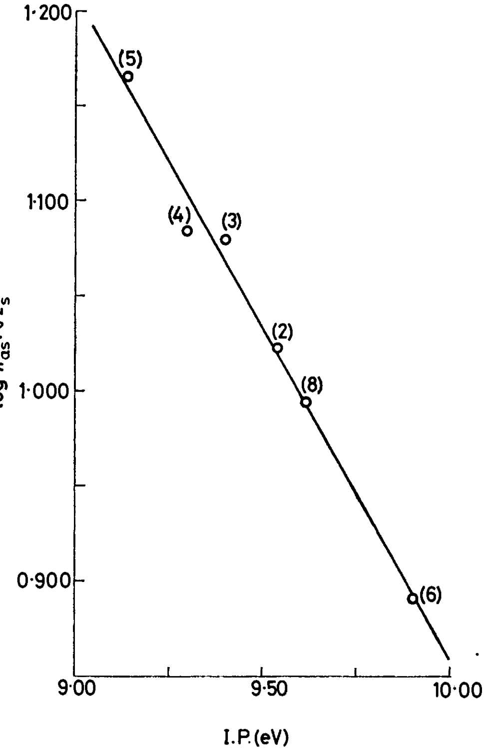

FIGURE 1 Correlation between log $K_{as} + \delta E_s$ and I.P. (r 0.994). The key to the numbering of the points is in Table 1

The order of basicity seems to suggest that the inductive effect of the heteroatom is not the only factor responsible for the extent of the decrease of basicity in the sulphur- and oxygen-substituted ketones, or at least in one of them. This was confirmed when the corrected basicity constants (log $K_{as} + \delta E_s$) were correlated with the corresponding Taft's σ^* values of the substituents. Figure 2 shows that the points for the sulphur- (6) and (7) and oxygen-substituted ketones (8) depart from linearity. Therefore, there may be an interaction between the heteroatom and carbonyl group.

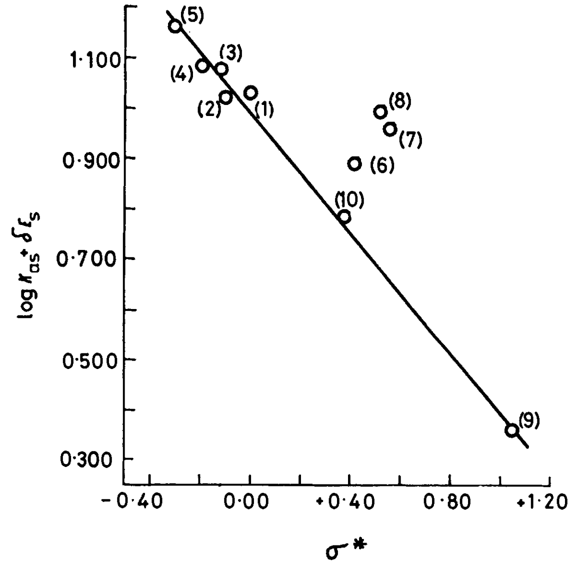

FIGURE 2 Correlation between log $K_{as} + \delta E_s$ and σ^* (r 0.996). The key to the numbering of the points is in Table 1

Some indication of the type of interaction which may occur in the sulphur-substituted ketone, is obtained by inspection of the energy level of the lone pair electrons on the sulphur atom (n_S) and carbonyl oxygen ($n_{O(CO)}$) in this compound, as compared with the corresponding sulphide and ketone (Figure 3). It shows that the ionisation potential values of $n_{O(CO)}$ in the ketone is higher than that of n_S in the sulphide and, that, apparently, stabilisation of both orbitals takes place in the sulphur-substituted ketone.

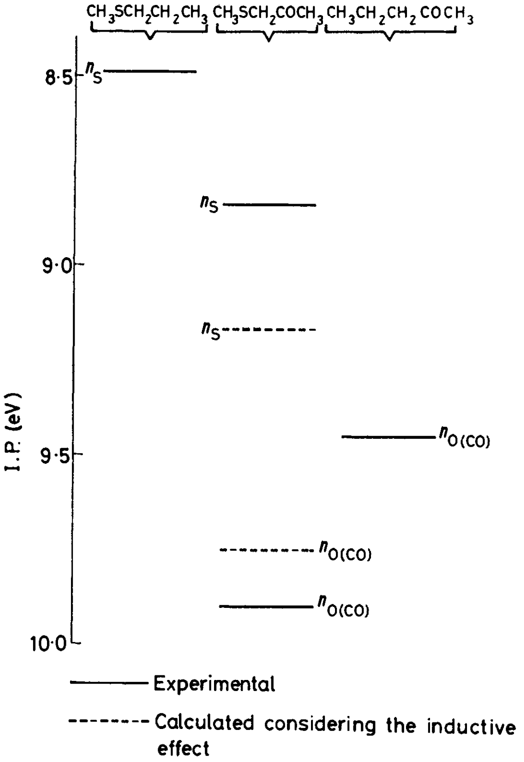

FIGURE 3 Energy levels of the lone pairs on the sulphur atom (n_S) and carbonyl oxygen ($n_{O(CO)}$) in 4-thiapentan-2-one, methyl n-propyl sulphide, and pentan-2-one

The comparison of the amounts of these stabilisations with those which can be estimated roughly for the mutual inductive effects of the carbonyl group and the sulphur atom may give some idea about the interaction between $n_{O(CO)}$ and n_S orbitals. The inductive effect of the carbonyl group, as estimated from the average ionisation potential of $n_{O(CO)}$ in cyclohexane-1,3-dione and that in cyclohexanone, was reported to be 0.68 eV.[13] The inductive effect of the sulphur atom may be similarly estimated from the mean value of n_S in 1,3-dithian

[13] K. N. Houk, L. P. Davis, G. R. Newkome, R. E. Duke, jun., and R. V. Nauman, *J. Amer. Chem. Soc.*, 1973, **95**, 8364.

(8.75 eV[14] and the n_S value in thiopyran (8.45 eV),[14] the latter being similar to that for methyl n-propyl sulphide.[9] The difference of 0.30 eV may be taken as a rough measure of the inductive effect which is produced when a methylene group is replaced by a sulphur atom.

Therefore, while the n_S level should be stabilised strongly (0.68 eV) due to the inductive effect of the carbonyl group, the $n_{O(CO)}$ would undergo only a slight stabilisation (0.30 eV) due to the weak inductive effect of the sulphur atom. This is in disagreement with the ionisation potential data, which show a reverse relationship. There is smaller stabilisation of n_S (0.35 eV) than of $n_{O(CO)}$ (0.45 eV). However, comparison of the n_S and $n_{O(CO)}$ data for the thia-ketone (8.84 and 9.90 eV) with those for sulphide and ketone, corrected for inductive effects (9.17 and 9.75 eV), indicates, clearly, that, in fact, the higher n_S level went up and the lower $n_{O(CO)}$ level went down. Although quantum mechanical calculations are necessary to draw any conclusion, a through space interaction[15,16] may be tentatively suggested on the basis of these data.

$RC{\equiv}N$

(11) $R = Me$
(12) $R = Et$
(13) $R = Pr^n$
(14) $R = Pr^i$
(15) $R = Bu^n$
(16) $R = Bu^t$
(17) $R = CH_2SMe$
(18) $R = CH_2SEt$
(19) $R = CHMeSEt$
(20) $R = CH_2OMe$
(21) $R = [CH_2]_2Cl$

Similarly to the ketones, the basicity constants for a large number of nitriles were corrected for the steric effects of the substituents to give $\log K_{as} + \delta E_s$ values (Table 2). The small value of δ(0.0367) compared with that for the ketones (0.0837) was expected due to the linearity of the cyano group.

TABLE 2

Basicity constants ($\log K_{as}$ and $\log K_{as} + \delta E_s$), σ^*, and E_s values of the substituents for nitriles (11)—(21)

Nitrile	$\log K_{as}$ [a]	σ^*	E_s	$\log K_{as} + \delta E_s$ [b]
(11)	0.785	0.00	0.00	0.785
(12)	0.895	−0.100	−0.07	0.898
(13)	0.890	−0.115	−0.36	0.903
(14)	0.946	−0.190	−0.47	0.963
(15)	0.899	−0.130	−0.39	0.913
(16)	0.974	−0.300	−1.59	1.032
(17)	0.612	+0.42	−0.34	0.624
(18)	0.674	+0.56	−0.47	0.691
(19)	0.740	+0.49	−1.53	0.796
(20)	0.342	+0.520	−0.19	0.349
(21)	0.477	+0.385	−0.90	0.510

[a] All data, with the exception of those for (16), (20), and (21), have been reported previously.[8] [b] δ 0.036 7.

The inspection of the $\log K_{as} + \delta E_s$ values indicates that the order of basicities of the nitriles studied is: unsubstituted > α-sulphur > β-chloro > α-oxygen. This order seems to follow that of the inductive effects of the substituents. However, a plot of the $\log K_{as} + \delta E_s$ against σ^* Taft's values (Figure 4) shows that the points for the sulphur-substituted nitriles (17—(19) deviate, strongly, from the linear correlation. This suggests that an interaction between sulphur and cyano-group occurs.

EXPERIMENTAL

Reagents.—Commercial unsubstituted ketones, t-butyl cyanide, chloroacetone, and 3-chloropropiononitrile were purified by distillation. 4-Thiapentan-2-one,[17] 4-oxapentan-2-one,[18] 4-chlorobutan-2-one,[19] and methoxyacetonitrile[20] were prepared by literature procedures. All compounds were analysed by g.l.c. to assess their purity.

N.m.r. Basicity Measurements.—The basicity measurements were performed using *p*-chlorophenol as proton donor.

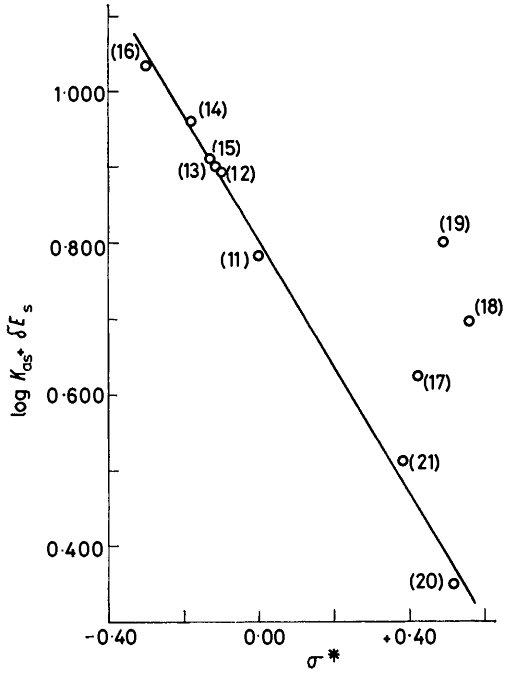

FIGURE 4 Correlation between $\log K_{as} + \delta E_s$ and σ^* (r 0.997). The key to the numbering of the points is in Table 2

The $\Delta\nu_{OH}$ values and the association constants K_{as} were obtained as previously reported.[7,8]

Calculation of δ Values and Treatment of Data.—The δ values for the ketones and nitriles studied were obtained from $\log K_{as} = \log K_{0\,as} + \rho\sigma^* + \delta E_s$, through an appropriate multiple linear regression analysis (three-variable). The points (6)—(8) (Table 1) and (17)—(19) (Table 2) were initially included, found to deviate, and then excluded for the determination of δ. The plots for $\log K_{as} + \delta E_s$ *versus* σ^* and ionisation potential data were treated by linear regression analysis to obtain the best straight lines which fit the results. All analyses of the data were performed with the aid of a Hewlett–Packard 9108A calculator, equipped with the Statistics 11214A block and a printer.

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