Structure–Basicity Relationships in Carbonyl Compounds

C. Laurence,* G. Guiheneuf, and B. Wojtkowiak

Contribution from the Laboratoire de Spectrochimie Moléculaire, U.E.R. de Chimie, Université de Nantes, 44072 Nantes Cedex, France. *Received January 3, 1979*

Abstract: Substituent effects on the basicity of 39 carbonyl compounds X_iX_jCO were studied by measuring $\Delta H°$ and $\Delta G_c°$ for the formation of iodine complexes in heptane, the solvent sensitivity α, the infrared shift $\Delta\nu(OH)$ of phenol complexes, and the carbonyl stretching vibration wavenumber. The iodine enthalpic basicity scale is well correlated with the $SbCl_5$ and protonation scales and, provided that comparison is made with the n band maximum, with $\Delta\nu(OH)$. α parallels roughly $\Delta G_c°$ indicating localized association of solvent on the oxygen lone pair. The carbonyl vibrator is not isolated, so no general correlation between basicity and carbonyl frequency exists. The formation of iodine complexes follows the isoequilibrium relationship and, in terms of linear free energy relationships, carbonyl compounds from ureas to acid halides are considered to form a homogeneous series. The cumulative effect of the two substituents X_i and X_j follows the additive relationship for $\Delta H°$ and $\Delta G_c°$ and the simplest nonadditive relationship for α. The dual substituent parameter equation is obeyed using σ_R^+, which shows that inductive effects are the dominant factor controlling the basicity of the carbonyl group toward iodine.

Introduction

The basicity of the carbonyl group has been measured in diverse ways in the literature, e.g., (1) the pK_a of protonation equilibrium in aqueous solution;[1] (2) the thermodynamic data, ΔG or ΔH, for the formation of addition compounds with various Lewis acids such as FSO_3H,[2] I_2,[3,4] BF_3,[5] $SbCl_3$,[6] $SbCl_5$,[7] and ROH[4,8-11] in nonaqueous solution; (3) the infrared shifts $\Delta\nu(XH) = \nu^{free}(XH) - \nu^{bound}(XH)$ of a reference proton donor;[12,13] (4) the proton affinities[14] and the ionization potentials[13] in the gas phase; (5) the solvent sensitivities of the carbonyl vibrator or α slopes of the Bellamy–Hallam–Williams (BHW) lines[15,16] (in the same way that α for $\nu(XH)$ vibrators was adopted as a measure of acidity of the XH link[15]).

The inadequacy of the first approach already has been outlined.[2] Previous work with the second method suffers from using noninert solvents such as CH_2Cl_2[5] or 1,2-dichloroethane[7] or from dealing with a sample not sufficiently numerous[4-6] or diverse.[17] Results of the third approach must be considered with caution because the associated $\nu(XH)$ band is unsymmetrical owing to two stereoisomeric complexes, probably π and n.[18] The fourth method is experimentally and theoretically difficult. Finally, not enough advantage has been taken of the last approach except for some ketones,[19] aldehydes,[16] esters,[20] and carbonates.[21]

Literature data for the thermodynamic quantities referring to iodine complexes with carbonyl compounds are scarce and the variety of solvents and temperatures makes them difficult to compare (see Table I). Consequently, in this work we have determined the ΔG and ΔH values of the equilibrium

$$X_iX_jCO + I_2 \rightleftarrows [X_iX_jCO, I_2] \qquad (1)$$

in heptane at 298 K for about 40 carbonyl compounds belonging to various series (HCOX, MeCOX, ArCOX, ROCOX, R_2NCOX) with electronically diversified X substituents (Ar, alkyls, halogens, OR, NR_2, CX_3, CH_2X, SR, H). In spite of having low equilibrium constants and enthalpy values, iodine was chosen as the reference Lewis acid because of its role as a standard in the Drago double-scale enthalpy equation[22] and of decisive experimental advantages.[23]

We also report the α slopes of the so-called BHW plots[15] for about 60 carbonyl compounds. Bellamy and Williams have shown[24] that the $\nu(CO)$ frequencies of two carbonyl compounds when measured in several solvents and plotted against each other are linearly correlated. We chose acetone as the reference compound and 11 solvents, apolar (pentane, heptane, cyclohexane, Freon 113, C_2Cl_4, CCl_4, CS_2), polar aprotic (dioxane, acetonitrile), and polar protic (CH_2Cl_2, $CHCl_3$), in order to determine the solvent sensitivity of the carbonyl vibrator according to the equation

$$\nu_{CO}{}^{X_iX_jCO} = \nu_0 + \alpha\nu_{CO}{}^{MeCOMe} \qquad (2)$$

The basicity scales so obtained (iodine scale and α scale) will be compared to the protonation scale[2] and $SbCl_5$ scale[7] (the so-called "donor number"[25]) already proposed for carbonyl compounds. Then structural effects on the basicity will be discussed in terms of a frequency–basicity relationship, isoequilibrium relationship,[26] additivity rule,[27] and dual single parameter equation.[28]

Experimental Section

Materials. Carbonyl compounds, iodine, and solvents are commercial products purified by standard procedures.

Method. Equilibrium constants at 298 K have been obtained by the spectrophotometric method of Rose and Drago[29] (eq 3) from absorbance measurements on the visible transition of iodine:

$$\frac{1}{K_c} = \frac{A - A_0}{\epsilon_C - \epsilon_I} - C_D° - C_I° + \frac{C_D°C_I°(\epsilon_C - \epsilon_I)}{A - A_0} \qquad (3)$$

$A - A_0$ is the difference in absorbance between a sample cell (l = 1 cm) containing iodine at concentration $C_I°$ and carbonyl compound at concentration $C_D°$ and a reference cell of the same optical path containing iodine at the same concentration as the sample cell. $\epsilon_C - \epsilon_I$ is the difference between the molar extinction coefficients of complexed and free iodine. The unknown quantities K_c and $\epsilon_C - \epsilon_I$ are calculated from the $A - A_0$ values measured at the maximum of the curve $A - A_0 = f(\lambda)$[30] for a series of solutions with varying $C_I°$ (from 10^{-3} to 4×10^{-3} M) and $C_D°$ (from 10^{-2} to 1 M depending on the strength of the base). The error in K_c is calculated from the standard deviation of the mean at the 95% confidence level.

The enthalpy $\Delta H°$ is calculated from the temperature dependence (273–303 K) of the $A - A_0$ absorbance at 550–560 nm of a single mixture of iodine ($C_I°$) and carbonyl compound ($C_D°$) against a reference cell containing iodine at the same concentration $C_I°$.[31] If $\epsilon_C - \epsilon_I$ were temperature independent, its values when determined jointly with that of K_c (298) would permit calculation of the equilibrium constant at any temperature $K_c(T)$ from eq 3. Actually $\epsilon_C - \epsilon_I$ is temperature dependent but at 550 nm it is sufficient to make allowance for the temperature dependence only of ϵ_I ($d\epsilon_I/dT$ = 2 L mol^{-1} cm^{-1} K^{-1}) because ϵ_C at this wavelength is low and its variation affects the slope of the van't Hoff plot only slightly.[32] The error in $\Delta H°$ is calculated from the standard deviation of the slope at the 95% confidence level.

A few values of K_c and $\Delta H°$ also have been verified or determined by a differential method perfected in our laboratory.[33] The tests carried out on iodine complexes with various carbonyl compounds have shown that this method can be applied when the ratio of the constants is near unity or when the difference of enthalpy is near zero and the electron donors have similar structures. It was used to compare K_c and $\Delta H°$ values of ethyl acetate with methyl acetate, 1-acetyl- with 2-

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Table I. Literature Values for the Thermodynamic Data of Several Iodine Complexes with Carbonyl Bases

no.	compd	K_c[a]	solvent	$-\Delta H^\circ$[b]	ref
17	benzophenone	<0.2	C_6H_{12}		*c*
		0.76 ± 0.05 (25)	CCl_4	2 ± 0.5	*d*
			CCl_4	2.41 ± 0.07	*e*
20	benzaldehyde	0.6 ± 0.05 (30)	CS_2		*f*
21	methyl acetate	0.52 ± 0.03 (25)	CCl_4	2.5 ± 0.1	*g*
		~0.35 (30)	CS_2		*h*
22	4-chloroacetophenone	0.48 ± 0.10 (33)	CCl_4		*i*
24	acetophenone	0.83 ± 0.04 (33)	CCl_4		*i*
		0.4 (25)	C_6H_{12}		*c*
26	2-butanone	0.7 (25)	C_6H_{12}		*c*
27	4-methylacetophenone	1.02 ± 0.07 (33)	CCl_4		*i*
29	3,3-dimethyl-2-butanone	1.6 (25)	C_6H_{12}		*c*
31	2-acetylnaphthalene	1.20 ± 0.13 (33)	CCl_4		*i*
32	acetone	0.85 ± 0.1 (25)	CCl_4		*g*
		0.8 (25)	C_6H_{12}		*c*
		1.7 (20)	Freon	5.8	*j*
		0.29 (30)	CS_2		*h*
35	*N,N*-dimethylbenzamide	3.8 ± 0.1 (25)	CCl_4	4.0 ± 0.2	*k*
36	*N,N*-dimethylformamide	2.9 ± 0.2 (25)	CCl_4	3.7 ± 0.3	*l*
37	*N,N*-dimethylacetamide	6.8 ± 0.2 (25)	CCl_4	3.9 ± 0.1	*m*
38	tetramethylurea	19 ± 2 (20)	C_7H_{16}	5.0 ± 0.4	*n*
		6.5 ± 0.2 (25)	CCl_4	4.3 ± 0.1	*g*

[a] L mol^{-1}, temperature in °C in parentheses. [b] kcal mol^{-1}. [c] K. R. Bhaskar, S. N. Bhat, A. S. N. Murthy, and C. N. R. Rao, *Trans. Faraday Soc.*, **62,** 788 (1966). [d] I. G. Murgulescu, V. E. Sakim, and A. Greff, *Proc. Int. Symp. Mol. Struct., Tokyo,* D 108 (1962). [e] H. P. Sieper and R. Paetzold, *Z. Phys. Chem.* (*Leipzig*), **255,** 1125 (1974). [f] E. Augdahl and P. Klaboe, *Acta Chem. Scand.*, **19,** 1637 (1962). [g] Reference 4. [h] H. Yamada and K. Kozima, *J. Am. Chem. Soc.*, **82,** 1543 (1960). [i] J. Foster and M. Goldstein, *Spectrochim. Acta, Part A*, **24,** 807 (1968). [j] D. Wobschall and D. A. Norton, *J. Am. Chem. Soc.*, **87,** 3559 (1965). [k] Reference 32. [l] Reference 3. [m] Reference 31. [n] R. P. Lang, *J. Phys. Chem.*, **72,** 2129 (1968).

acetylnaphthalene, and substituted acetophenones with acetophenone.

Infrared Data. Carbonyl frequencies have been measured from 1600 to 1800 cm^{-1} with 0.1-cm cells for 0.01 M solutions in CCl_4.

The spectra of phenol complexes with carbonyl compounds were recorded from 3100 to 3650 cm^{-1}. The concentration of the carbonyl compound stock solution in CCl_4 was adjusted so that the absorbance of the solution in a 2-cm cell did not exceed 0.8 at the maximum of the $2\nu(CO)$ band. Then quantities of phenol were added to the stock solution until the associated $\nu(OH)$ band was intense enough. The phenol concentration never exceeded 0.01 M. Sample and reference cells were matched. Doing so, we avoided abnormalities in the shape of the associated $\nu(OH)$ bands caused by the $2\nu(CO)$ absorption (loss of energy or bad compensation).

Apparatus. Visible spectra were recorded on a Beckman DK2A or Acta III instrument. The solutions were thermostated to ±0.2 K. Temperature was measured within the cells with a chromel-alumel thermocouple. A dry-nitrogen purge of the sample compartment avoided condensation of water vapor on the cell windows when the cell temperature was below room temperature. However, temperatures lower than 0 °C could not be employed.

Infrared spectra were recorded on a Beckman IR 9 spectrophotometer.

Solutions were prepared and cells were filled in a drybox (under dry nitrogen for benzaldehyde).

Results and Discussion

Table II lists the thermodynamic data for iodine complexes with 39 carbonyl bases. This extends our previous tabulation.[34]

Concerning the Choice of Heptane as Solvent. Weak complexes of low K_c and ΔH require a medium of very low polarity since there is a general trend to higher association constants with decreasing polarity of the solvent.[35] This was the reason why we chose heptane as the solvent, which is considered to give a small solvation contribution. Comparing the data in Tables I and II for compounds 21, 32, 37, and 38 shows that the values of K_c and ΔH° are significantly higher for heptane than for CCl_4. The use of hydrocarbons has been questioned, however, by Drago and co-workers,[36] who hold the opinion that they should be avoided as solvents for studies of the interaction of Lewis acids with polar oxygen donors because such donors are more highly associated through dipole-dipole interaction in hydrocarbons than in CCl_4. Comparison of $\log K_c$ for adduct formation in heptane with the values obtained in CCl_4 yields the least-squares equation

$$\begin{gathered}\log K_c\ (\text{heptane}) = 1.24 \log K_c\ (CCl_4) + 0.38 \\ n = 7 \text{ points; correlation coefficient } R = 0.995 \\ \text{standard deviation of the estimate } s = 0.14\end{gathered} \qquad (4)$$

Considering the large variation in dipole moments of carbonyl bases (from 3.85 D for DMF to 1.6 D for MeCOOMe), the linear relationship (4) excludes irregular dipolar aggregation effects in heptane, and the disadvantages of using hydrocarbons as solvents are not critical for spectrophotometric results.[37] On the contrary, the slope of 1.24 of eq 4 shows a greater sensitivity to structural effects in heptane than in CCl_4.

Comparison with Other Basicity Scales. Enthalpimetric Scales. Gutman[25] has established an order of base strengths from the enthalpy of the reaction of the base with the reference acid $SbCl_5$ and assumed that this order remains constant for all other acids, or alternatively that two acids must give a linear enthalpy plot with each other. Comparison of the iodine scale with the $SbCl_5$,[7,25] BF_3,[5] and protonation[2,38] scales yields the least-squares eq 5-7 exemplified in Figure 1.

$$\begin{gathered}\Delta H^\circ(I_2) = 0.16\Delta H^\circ(SbCl_5) + 0.41\ (\pm 0.41) \\ n = 18 \quad R = 0.963 \quad s = 0.4 \text{ kcal mol}^{-1}\end{gathered} \qquad (5)$$

$$\begin{gathered}\Delta H^\circ(I_2) = 0.12\Delta H^\circ(BF_3) + 0.82\ (\pm 0.44) \\ n = 7 \quad R = 0.88 \quad s = 0.15 \text{ kcal mol}^{-1}\end{gathered} \qquad (6)$$

$$\begin{gathered}\Delta H^\circ(I_2) = 0.14\Delta H^\circ(\text{protonation}) + 0.55\ (\pm 0.23) \\ n = 16 \quad R = 0.963 \quad s = 0.3 \text{ kcal mol}^{-1}\end{gathered} \qquad (7)$$

We consider the iodine scale to be well correlated to the other basicity scales, even to the BF_3 scale for which the standard deviation of the estimate is within the limits of precision of $\Delta H^\circ(I_2)$, the poor correlation coefficient being partly

Table II. Structural Parameters and Thermodynamic Data for Iodine Complexes with Carbonyl Bases in Heptane at 25 °C

no.[a]	compd	formula	K_c, L mol^{-1}	$\Delta G_c°$,[b] kcal mol^{-1}	$-\Delta H°$,[c] kcal mol^{-1}	$\nu_{C=O}$,[d] cm^{-1}	$\Delta\nu_{OH}$,[e] cm^{-1}
1	benzoyl bromide	PhCOBr	~0.1	~1.4	0.7 ± 0.2	1779.6	39
2	acetyl bromide	MeCOBr	0.13 ± 0.06	1.2 ± 0.3	0.7 ± 0.2	1813.6	
3	ethyl trifluoroacetate	$EtOCOCF_3$	~0.1	~1.4	0.8 ± 0.2	1788.5	54
4	α,α,α-trifluoroacetophenone	$PhCOCF_3$	~0.1	~1.4	0.9 ± 0.2	1724.1	60
5	acetyl chloride	MeCOCl	0.12 ± 0.07	1.26 ± 0.35	0.9 ± 0.3	1806.3	
6	benzoyl chloride	PhCOCl	0.1 ± 0.05	1.4 ± 0.5	1.1 ± 0.2	1763.5[k]	56
7	ethyl trichloroacetate	$EtOCOCCl_3$	0.24 ± 0.09	0.85 ± 0.25	1.25 ± 0.1	1769.1	68
8	ethyl bromoacetate	$EtOCOCH_2Br$	[f]	[f]	1.7[f]	1742.5, 1761.7[g]	115
9	ethyl fluoroacetate	$EtOCOCH_2F$	[f]	[f]	2.0[f]	1746.2, 1774.1[g]	110
10	ethyl chloroacetate	$EtOCOCH_2Cl$	[f]	[f]	1.95[f]	1742.7, 1767.1[g]	108
11	ethyl formate	EtOCOH	0.49 ± 0.06	0.42 ± 0.09	2.15 ± 0.2	1730.9	124
12	dimethyl carbonate (DMC)	MeOCOOMe	0.56 ± 0.03	0.34 ± 0.03	2.2 ± 0.15	1756.7	146
13	methyl benzoate	PhCOOMe	0.61 ± 0.02	0.29 ± 0.02	2.3 ± 0.05	1728.4	156
14	ethyl benzoate	PhCOOEt	0.71 ± 0.03	0.20 ± 0.03	2.4 ± 0.15	1722.1	174
15	diethyl carbonate (DEC)	EtOCOOEt	0.62 ± 0.05	0.28 ± 0.04	2.55 ± 0.2	1746.1	159
16	3-trifluoromethylacetophenone	$3\text{-}CF_3\text{-}C_6H_4COMe$	0.58 ± 0.02[h]	0.32 ± 0.02	2.6 ± 0.15[j]	1698.0	176
17	benzophenone	PhCOPh	0.86 ± 0.11	0.09 ± 0.02	2.6 ± 0.1	1664.8	174
18	isobutyrophenone	PhCO-*i*-Pr	0.73 ± 0.04	0.20 ± 0.03	2.6 ± 0.1	1688.7	165
19	propiophenone	PhCOEt	0.79 ± 0.05	0.14 ± 0.04	2.7 ± 0.1	1694.1	170
20	benzaldehyde	PhCOH	0.53 ± 0.04	0.38 ± 0.04	2.8 ± 0.1	1708.9	173
21	methyl acetate	MeCOOMe	0.76 ± 0.03	0.16 ± 0.02	2.9 ± 0.07	1748.2	154
22	4-chloroacetophenone	$4\text{-}Cl\text{-}C_6H_4COMe$	0.86 ± 0.02[h]	0.09 ± 0.01	2.95 ± 0.2[j]	1691.6	190
23	ethyl acetate	MeCOOEt	0.94 ± 0.03	0.04 ± 0.02	3.0 ± 0.08	1742.6	165
24	acetophenone	PhCOMe	1.15 ± 0.05	−0.08 ± 0.02	3.2 ± 0.12	1691.2	202
25	3-methylacetophenone	$3\text{-}Me\text{-}C_6H_4COMe$	1.29 ± 0.02[h]	−0.15 ± 0.01	3.25 ± 0.15[j]	1689.7	208
26	2-butanone	MeCOEt	1.03 ± 0.09	−0.02 ± 0.05	3.35 ± 0.15	1722.0	216
27	4-methylacetophenone	$4\text{-}Me\text{-}C_6H_4COMe$	1.44 ± 0.03[h]	−0.22 ± 0.02	3.4 ± 0.15[j]	1687.3	215
28	1-acetylnaphthalene	1-NaphCOMe	0.65 ± 0.1	0.26 ± 0.14	3.4 ± 0.2	1685.9[k]	210
29	3,3-dimethyl-2-butanone	MeCO-*t*-Bu	1.14 ± 0.08	−0.08 ± 0.03	3.4 ± 0.1	1709.8	165
30	3-methyl-2-butanone	MeCO-*i*-Pr	1.08 ± 0.04	−0.05 ± 0.02	3.45 ± 0.1	1718.6	204
31	2-acetylnaphthalene	2-NaphtCOMe	0.85 ± 0.12[i]	0.10 ± 0.08	3.6 ± 0.2	1686.7	210
32	acetone	MeCOMe	1.12 ± 0.06	−0.07 ± 0.03	3.65 ± 0.15	1718.0	236
33	ethyl thioacetate	MeCOSEt	0.86 ± 0.14	0.09 ± 0.09	3.65 ± 0.15	1695.2	140
34	tetraethylurea (TEU)	$N(Et)_2CON(Et)_2$	11 ± 1	−1.42 ± 0.07	4.5 ± 0.2	1647.5	323
35	*N,N*-dimethylbenzamide (DMBz)	$PhCON(Me)_2$	8.1 ± 0.7	−1.24 ± 0.05	4.85 ± 0.15	1645.2	302
36	*N,N*-dimethylformamide (DMF)	$HCON(Me)_2$	6.45 ± 0.6	−1.10 ± 0.05	5.0 ± 0.25	1687.0	289
37	*N,N*-dimethylacetamide (DMA)	$MeCON(Me)_2$	15 ± 0.4	−1.60 ± 0.10	5.15 ± 0.1	1661.7	344
38	tetramethylurea (TMU)	$N(Me)_2CON(Me)_2$	14.3 ± 0.9	−1.58 ± 0.08	5.2 ± 0.2	1654.7	340
39	*N,N*-diethylacetamide (DEA)	$MeCON(Et)_2$	18.8 ± 0.5	−1.74 ± 0.08	5.25 ± 0.15	1651.9	345

[a] Numbered according to increasing enthalpy. [b] Calculated for standard states of 1 M solutions. [c] $\Delta H° = RT^2(\mathrm{d}\log K_c/\mathrm{d}T) - \alpha RT^2$. The last term involves the thermal expansion coefficient of heptane α and equals 220 cal at 298 K. [d] CCl_4 as solvent. [e] Infrared shift of the 3612-cm^{-1} band of phenol by hydrogen bonding with carbonyl bases in CCl_4. [f] Enthalpy was measured from one solution of ester and iodine at several temperatures by assuming a value for $\epsilon_c - \epsilon_I$ not so different from $\epsilon_c - \epsilon_I$ of methyl acetate. Of course no reliable value of $K_c(298)$ could be so obtained. [g] The two bands corresponding to cis and gauche isomers were mathematically decomposed. [h] Values determined by the differential method of ref 33 using acetophenone as reference. [i] Value determined by the differential method of ref 33 using 1-acetylnaphthalene as reference. [j] Values determined by the differential method of ref 31 using acetophenone as reference. [k] Corrected for Fermi resonance.

explained by a too limited sample. At the 95% confidence level only the nonzero intercept of eq 7 is significant. Two points deviate twice as much as the standard deviation: TMU in the protonation scale and HCOOEt in the $SbCl_5$ scale. A serious disadvantage of the iodine scale is its much lower sensitivity to structural effects than the other scales for the stronger Lewis acids.

These correlations are not in conflict with the Drago–Wayland equation[22]

$$-\Delta H = E_A E_B + C_A C_B \qquad (8)$$

because carbonyl bases have an almost constant E_B/C_B ratio (0.50 for DMF, 0.51 for DMA, 0.56 for MeCOOMe and MeCOOEt, 0.42 for MeCOMe).

$\Delta\nu$(OH) Scale. We did not compare literature enthalpy data for proton donors with $\Delta H°(I_2)$ because, in solution, carbonyl compounds form two types of 1:1 hydrogen-bonded complexes and the measured enthalpy is an average of both adducts. In the same way the ν(XH) infrared band of proton donors associated to carbonyl bases is unsymmetrical[18] and, since resolution into the two component bands is possible only in a few favorable cases, the infrared shift $\Delta\nu$(XH) is measured traditionally at the point of maximum absorption and is a composite quantity. But keeping in mind that the more shifted band (attributed to an n complex[18,39]) is generally more intense (Figure 2), or that in some cases the two component bands are located near the same frequency, thereby leading to almost symmetrical bands (Figure 2), apparent maxima may furnish $\Delta\nu$(XH) data of good reliability for establishing the basicity of a lone pair toward a proton donor. If iodine is associated to this lone pair, a correlation is expected between $\Delta H°(I_2)$ and $\Delta\nu$(XH). This expectation is verified in Figure 3 by the infrared shifts $\Delta\nu$(OH) of the 3612-cm^{-1} band of phenol in CCl_4 listed in the eighth column of Table II. The deviating points 33 (MeCOSEt), 29 (MeCO-*t*-Bu), 21 (MeCOOMe), and 23 (MeCOOEt) correspond to the high-frequency component band of higher intensity (Figure 4). Excluding these four more deviating points leads to

$$-\Delta H°(I_2) = 0.0149\Delta\nu(\mathrm{OH}) + 0.15\ (\pm 0.08) \qquad n = 33 \quad R = 0.989 \quad s = 0.2\ \mathrm{kcal\ mol^{-1}} \qquad (9)$$

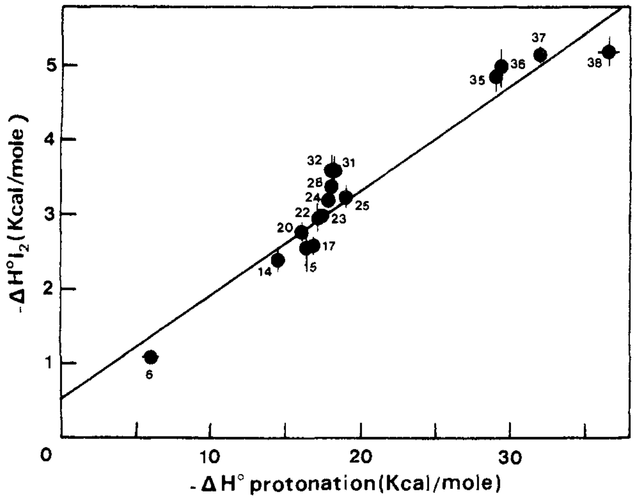


Figure 1. Plot of the enthalpy of iodine complexes with carbonyl bases vs. heat of protonation of the bases in FSO_3H. Numbers refer to Table II.

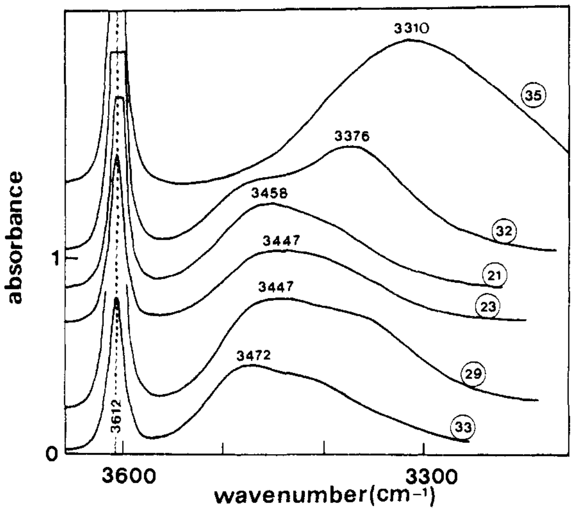


Figure 2. Hydroxyl region infrared spectra of phenol complexes with carbonyl bases in CCl_4. Examples of an almost symmetrical associated band (*N,N*-dimethylbenzamide 35) and two components bands with the more shifted band being the more intense (acetone 32) and with the less shifted band being the more intense (methyl acetate 21; ethyl acetate 23; 3,3-dimethyl-2-butanone 29; methyl thioacetate 33).

The good correlation coefficient and the reasonable value of the intercept, not significantly different from zero at the 95% confidence level, give support to the reliability of the iodine enthalpy scale.

α **Scale.** Results of a least-squares analysis of eq 2 are reported in Table III. Solvent effects on the carbonyl stretching vibration of 55 compounds are well related to solvent effects on acetone, the correlation coefficients varying from 0.8 to 0.998 with most values greater than 0.95. No break or change in slope of the regression line is found on passing from a strongly interacting solvent such as $CHCl_3$ to a weakly interacting solvent such as pentane. This indicates that similar factors operate in both cases or, since the interaction is well recognized with chloroform, that localized association is a controlling factor in determining the frequency shifts. Relative values of α seem independent of the model: for the compounds R_2NCOX, for which the slopes and also the standard deviations of the slopes are high, α was calculated by choosing DMA instead of MeCOMe as the reference compound and an excellent correlation ($R = 0.99$) is found between α (model MeCOMe) and α' (model DMA). Thus the quantity α seems a good intrinsic property of the carbonyl bond.

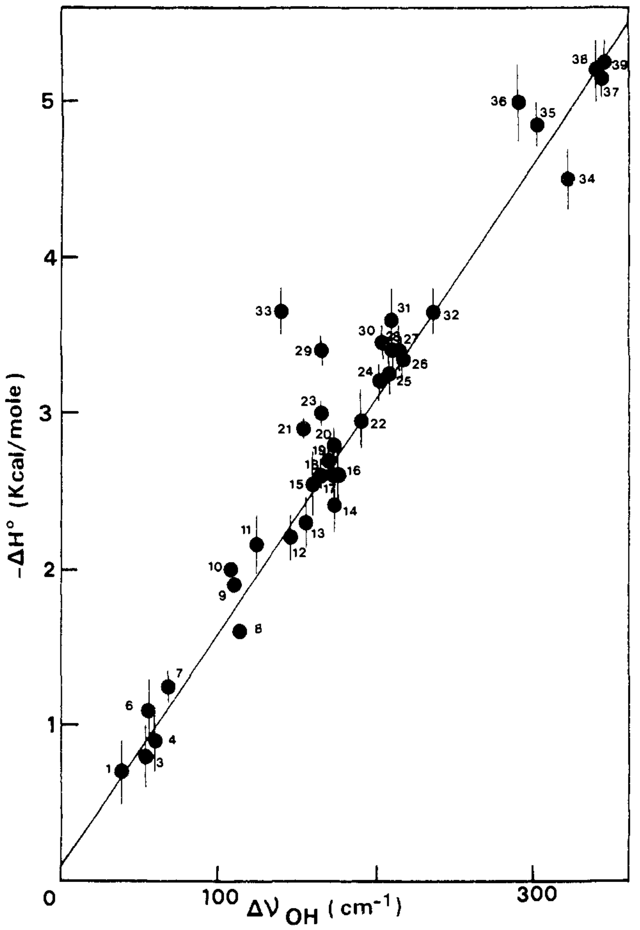


Figure 3. Plot of $\Delta H°$ for iodine complexes with carbonyl bases vs. the OH frequency shifts for the association of phenol with the bases in CCl_4. Numbers refer to Table II.

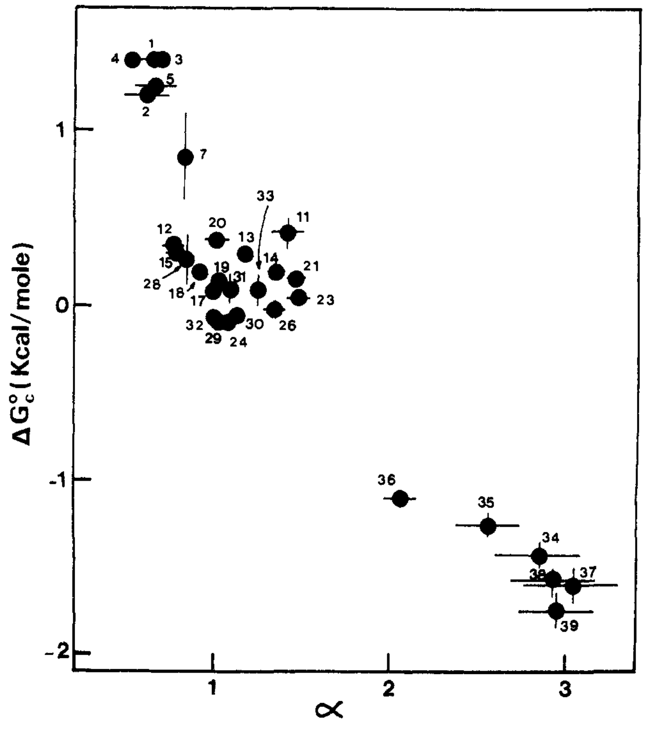


Figure 4. Plot of $\Delta G_c°(298)$ for iodine complexes with carbonyl bases vs. solvent sensitivity α of the carbonyl vibrator. Numbers refer to Tables II and III.

Table III. Solvent Sensitivity of Carbonyl Bases or α Slope of BHW Plots

no.[a]	compd	α[b]	*R*[c]
	MeCOCN	0.31 ± 0.08	0.80
	PhCOCN[d]	0.40 ± 0.08	0.92
	EtOCOCN	0.44 ± 0.08	0.89
4	PhCOCF$_3$	0.53 ± 0.05	0.964
	MeCOI	0.57 ± 0.09	0.950
	MeCO-9-anthryl[e]	0.58 ± 0.05	0.972
2	MeCOBr	0.61 ± 0.13	0.87
5	MeCOCl	0.66 ± 0.13	0.86
1	PhCOBr	0.66 ± 0.08	0.93
3	EtOCOCF$_3$	0.68 ± 0.03	0.993
12	MeOCOOMe (DMC)	0.76 ± 0.06	0.970
15	EtOCOOEt (DEC)	0.78 ± 0.06	0.974
	MeOCOCCl$_3$	0.80 ± 0.04	0.991
7	EtOCOCCl$_3$	0.83 ± 0.03	0.995
28	MeCO-1-naphthyl[d,e]	0.84 ± 0.04	0.992
18	PhCO-*i*-Pr	0.91 ± 0.04	0.993
	MeCOH	0.98 ± 0.07	0.978
17	PhCOPh	0.99 ± 0.04	0.994
32	MeCOMe[f]	1	
29	MeCO-*t*-Bu	1.01 ± 0.03	0.995
20	PhCOH	1.01 ± 0.06	0.983
19	PhCOEt	1.02 ± 0.03	0.997
	MeCO-3-phenanthryl[d]	1.02 ± 0.02	0.998
	PhOCOOPh[d] (DPC)	1.03 ± 0.06	0.986
	MeOCOC≡CH	1.03 ± 0.06	0.986
24	PhCOMe	1.07 ± 0.02	0.998
31	MeCO-2-naphthyl	1.09 ± 0.05	0.989
	HCO-1-naphthyl	1.12 ± 0.06	0.987
30	MeCO-*i*-Pr[g]	1.13 ± 0.04	0.995
	HCO-2-naphthyl[d]	1.16 ± 0.06	0.985
13	PhCOOMe	1.18 ± 0.03	0.996
	PhCOOPh	1.24 ± 0.06	0.988
33	MeCOSEt	1.24 ± 0.04	0.994
26	MeCOEt[g]	1.34 ± 0.06	0.990
	HCOOMe	1.36 ± 0.10	0.997
14	PhCOOEt	1.37 ± 0.05	0.994
	HCOO-*i*-Pr	1.40 ± 0.08	0.987
11	HCOOEt	1.41 ± 0.09	0.982
	PhCOOH[h]	1.44 ± 0.07	0.993
21	MeCOOMe	1.46 ± 0.05	0.995
23	MeCOOEt	1.47 ± 0.05	0.995
	ClCON(Ph)$_2$[d]	1.48 ± 0.11	0.975
	MeCOOPh[d]	1.54 ± 0.08	0.988
	ClCON(Me)$_2$	1.55 ± 0.11	0.978
	ClCON(Et)$_2$	1.56 ± 0.12	0.974
	MeCOOH[h]	1.56 ± 0.06	0.995
	MeCOOPr	1.58 ± 0.07	0.991
	EtOCON(Ph)$_2$	1.60 ± 0.09	0.986
	MeCOO-*i*-Pr[i]	1.74 ± 0.12	0.978
36	HCON(Me)$_2$ (DMF)	2.06 ± 0.09	0.991
	HCON(Ph)$_2$[d]	2.17 ± 0.12	0.986
	EtOCON(Et)$_2$	2.24 ± 0.21	0.962
	PhEtNCONEtPh	2.27 ± 0.26	0.95
	HCON(Et)$_2$	2.28 ± 0.12	0.987
	MeCON(Ph)$_2$	2.34 ± 0.19	0.972
	PhCONH$_2$[j]	2.45 ± 0.18	0.986
35	PhCON(Me)$_2$ (DMBz)	2.56 ± 0.18	0.979
34	N(Et)$_2$CON(Et)$_2$ (TEU)	2.85 ± 0.26	0.964
38	N(Me)$_2$CON(Me)$_2$ (TMU)	2.93 ± 0.26	0.967
39	MeCON(Et)$_2$ (DEA)	2.95 ± 0.21	0.977
37	MeCON(Me)$_2$ (DMA)	3.04 ± 0.26	0.979

[a] Numbering is the same as in Table II. [b] Slope ± standard deviation of the slope. [c] Correlation coefficient with 11 points unless stated. [d] Carbonyl frequencies are corrected for Fermi resonance (see ref 61). [e] Abnormally low value of α due to steric effects of peri hydrogen(s) (see ref 61). [f] Reference compound. [g] Unsymmetrical band due to rotational isomerism. Stabilization of the more polar rotamer in polar solvents makes the α slope artificially high. [h] Acetonitrile and dioxane are excluded from the BHW plot due to strong hydrogen bonding. [i] Fermi resonance not corrected owing to too great overlap between the bands. Correction would lower α. [j] Four apolar solvents are excluded of the BHW plot owing to lack of solubility.

The correlation between the ΔG° values of Table II and α is illustrated in Figure 4. The correlation coefficient is 0.92 (n = 31 points). The correlation is worse with ΔH° (R = 0.83). The correlation between ΔG° and α is certainly not linear and inversion occurs between ketones and esters. However, the rough parallelism between α and the lone-pair basicity indicates that nonspecific and specific interactions (sometimes called "contacts" or weak "complexes") are a controlling factor of the solvent sensitivity of CO links. The occurrence of such interactions is to a considerable extent governed by entropy effects.[40] Thus, to some extent, the better correlation with ΔG° than with ΔH° of α is understood.

Carbonyl Frequency–Basicity Relationship. A relation between basicity and carbonyl stretching frequency is expected[41] because an increase in basicity means an increase of the negative charge on the oxygen atom, and this in turn means an increase in bond polarity—or a decrease in bond length[42]—leading to a decrease in bond force constant. Bellamy and Pace[12] found such a correlation provided that strained rings, conjugated systems, and thioesters are excluded. Later, Liler reported[43] the same correlation for aromatic carbonyl compounds, except benzamide. Arnett et al. found[2] no general correlation but they do not exclude separate correlations within each class of carbonyl compounds.

A plot of $\Delta H^\circ(I_2)$ vs. carbonyl frequency listed in the seventh column of Table II is shown in Figure 5.[44] Although a definite trend (R = 0.85, n = 39) toward decreasing frequency with increasing basicity is evident, no precise general relationship exists: the standard deviation of the estimate is 0.7 kcal mol^{-1}, and the deviation reaches as high as 1.7 kcal mol^{-1} for PhCOCF$_3$. Enthalpy values cannot be evaluated from vibrational spectra. The reason is that the carbonyl stretching frequency in X_iX_jCO molecules is determined not only by the CO force constant, but also by the masses of X_i and X_j (or their first atom), the X_iCX_j angle, and the remaining force constants.[45] Correlations for separate families do exist only for very similar compounds where mechanical effects are constant or vary in the sense of electronic effects. Ring-substituted acetophenones constitute such a family (R = 0.967, n = 5). With the above criteria, the compounds EtOCOX (R = 0.78, n = 7) and ArCOX (R = 0.92, n = 16, ArCOAr excluded) do not constitute homologous families. An apparently excellent correlation is found for MeCOX compounds (R = 0.998, n = 11, MeCOAr excluded).

Remembering the good correlations found[46] between the ΔG° values of the molecular complexes of $X_1X_2X_3PO/I_2$, X_1X_2SO/I_2, and X_1X_2SeO/I_2 and the PO, SO, and SeO stretching frequencies, the CO group may be considered to be a worse case of an isolated vibrator than the PO, SO, and SeO groups, partly due to the higher masses of phosphorus, sulfur, and selenium compared to carbon.

Isoequilibrium Relationship. In Figure 6, ΔH° is plotted against $\Delta G_c{}^\circ$. Several points deviate more than the experimental error (for instance, 1- and 2-acetylnaphthalene, ethyl thioacetate, acetone, and TEU) but the overall linear correlation cannot be doubted (R = 0.963, n = 36).[47]

Another expression for the isoequilibrium relationship relates two equilibrium constants measured at two tempera-

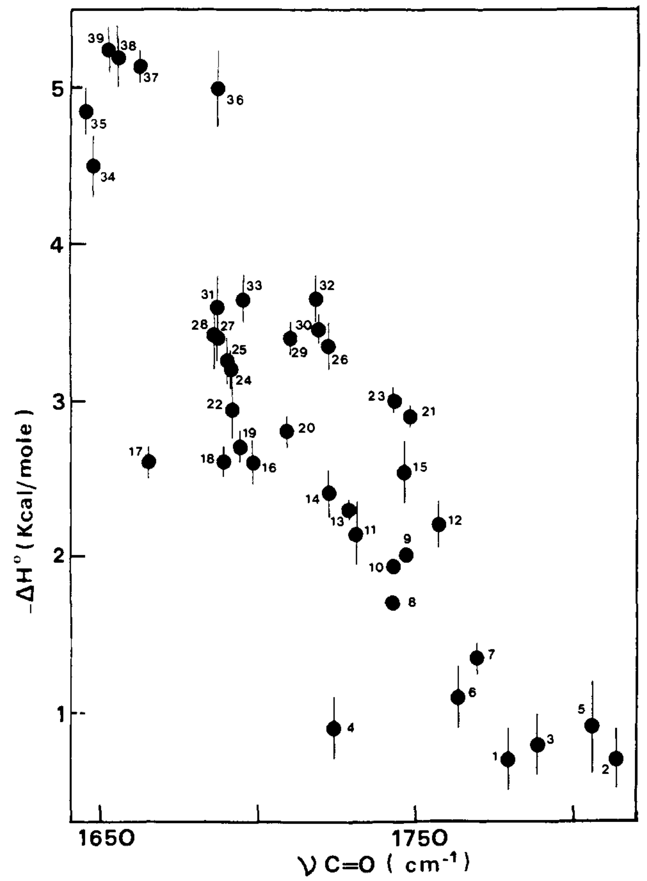


Figure 5. Enthalpy of iodine complexes with carbonyl bases vs. carbonyl stretching frequencies. Numbers refer to Table II.

tures.[26] Some values of K_c (283) have been determined independently.[34] They yield

$$\log K_c(298){-}0.108 + 0.911 \log K_c(283) \qquad n = 14 \quad R = 0.9989 \tag{10}$$

An estimated value of the isoequilibrium temperature near 650 K is calculated[26] from the slope 0.911.

Although the interval of experimental temperatures is narrow,[48] we conclude that the isoequilibrium relationship holds for the formation of iodine complexes with carbonyl bases. In spite of the fact that the carbonyl group acts both as the transmitting and as the functional group, the term "reaction series" probably applies to ureas, amides, aldehydes, ketones, esters, carbonates, and acid halides, and there is a presumption of a linear free energy relationship (such as eq 13).

Additive and Nonadditive Behavior of Substituents. Exner recently examined[27] thoroughly the behavior of two substituents adjacent to the reaction center and found that their effects are generally not additive. On the contrary, Katritzky et al.[49] found that the integrated intensity of the ethylenic double bond stretching vibration in compounds $X_iX_jC{=}CH_2$, which are very similar to $X_iX_jC{=}O$, depends additively on the π-delocalization parameter $\sigma_R°(X)$.

Following the procedure described by Exner[27] we have tested graphically the equations

$$Y_{ij} = C_i + C_j + \epsilon_{ij} \tag{11}$$

$$Y_{ij} = Y_0 + C_iC_j + \epsilon_{ij} \tag{12}$$

where Y is the property tested for additivity ($Y = \Delta H°, \Delta G_c°$, or α), C_i and C_j are empirical constants for substituents i and j, and ϵ_{ij} is a random variable expressing both the experimental error and the imprecision of the correlation equation. Equation 11 is the additive relationship and eq 12 is the simplest possible type of nonadditive relationship. By plotting on the abscissa axis the Y_{ij} values of a selected series ($PhCOX_j$ for $\Delta G_c°$ and $\Delta H°$, and $MeCOX_j$ for α) and on the ordinate axis the Y_{ij} values of other series $HCOX_j$, $EtOCOX_j$, $(Me)_2NCOX_j$, etc., one obtains a family of straight lines, one for each value of i. The lines are parallel in the case of eq 11 and intersect in one point in the case of eq 12. Figures 7-9 show that $\Delta H°$ and $\Delta G_c°$ are correlated by eq 11 and α by eq 12 provided that ureas (TEU and TMU) are excluded for $\Delta H°$, $\Delta G_c°$, and α and that carbonates (DEC, DMC, and DPC) and urethanes ($(Ph)_2NCOOEt$ and $(Et)_2NCOOEt$) are excluded for α.[50]

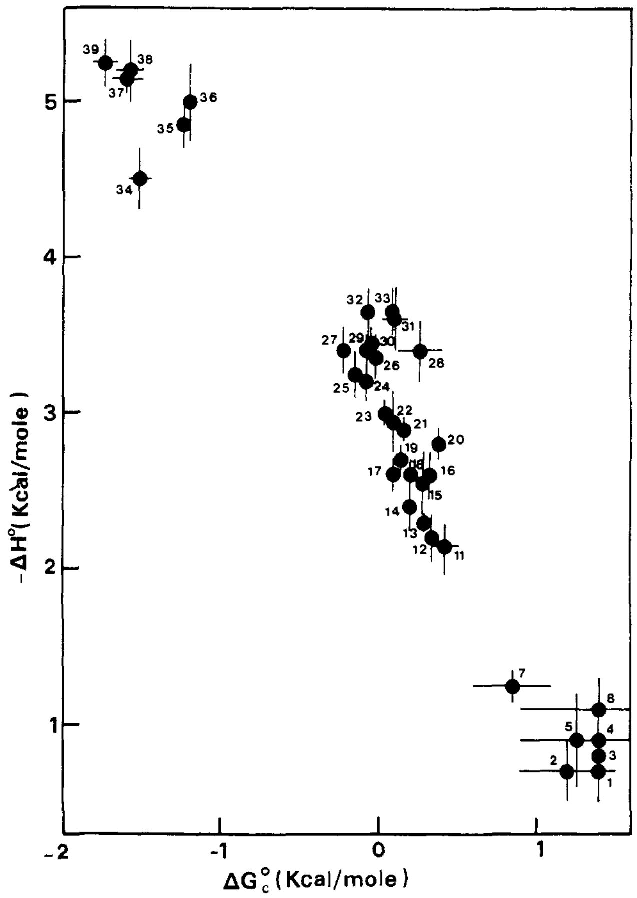
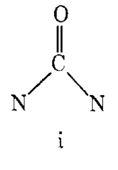


Figure 6. Plot of ΔH° for iodine complexes with carbonyl bases vs. $\Delta G_c°(298)$ for iodine complexes with the bases. Numbers refer to Table II.

In the case of the thermodynamic data $\Delta H°$ and $\Delta G_c°$, the nonadditive behavior of $N(Me)_2$ was already noticed by Drago et al.[4] and attributed to the nonplanarity of NNC=O in ureas compared to the planarity of NCC=O in DMA because of steric interaction of the methyl groups. Contrastingly, Filgueiras and Huheey[52] attribute it to the low ability of the oxygen atom to accept charge. The dramatic nonadditivity observed in TEU compared to TMU[53] seems to favor the steric explanation. In any case, TMU and TEU have to be excluded in any correlation equation assuming additivity such as eq 13 below.

The nonadditive effect of substituents on α prevents its use in eq 13. It is striking that all compounds containing the frameworks i-iii, where nonbonded interactions between lone



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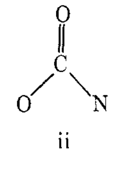

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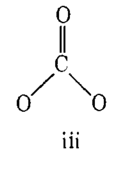

iii

Table IV. Application of the DSP Equation 13 to Thermodynamic Data of Iodine Complexes with Carbonyl Bases

quantity	ρ_{I}	ρ_{R}	h	s_{est}[a]	% I[b]	R	n[c]
$\Delta G_c°$	2.63 ± 0.19	0.94 ± 0.08	0.51	0.25	54	0.959	28
$\Delta H°$	4.55 ± 0.33	1.30 ± 0.13	2.46	0.43	60	0.951	30

[a] Standard deviation of the estimate in kcal mol^{-1}. [b] Percentage contribution of inductive effects. [c] Number of data points, TMU and TEU being excluded.

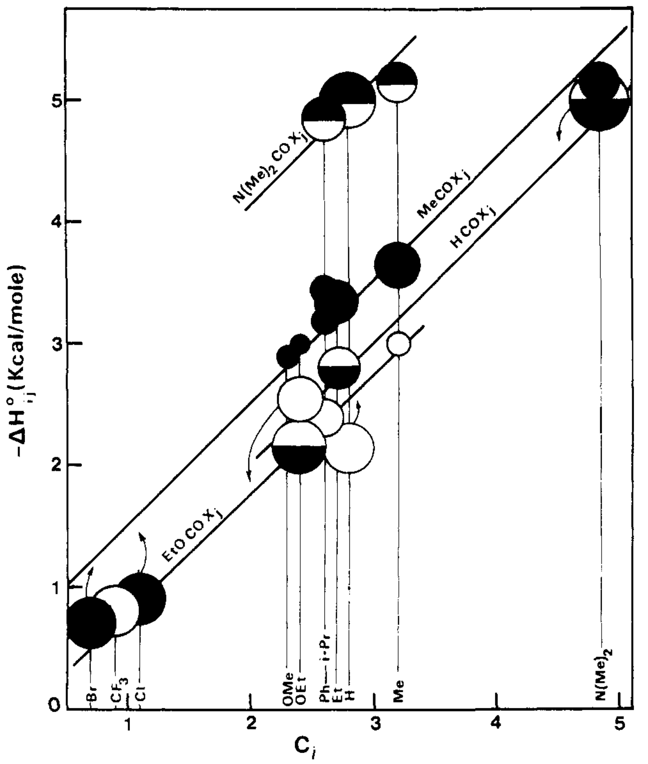

Figure 7. Correlation of $\Delta H_{ij}°$ for iodine complexes with carbonyl bases X_iX_jCO according to eq 11. Numbers refer to Table II: (◐) $N(Me)_2COX_j$, (●) $MeCOX_j$, (◒) $HCOX_j$, (○) $EtOCOX_j$.

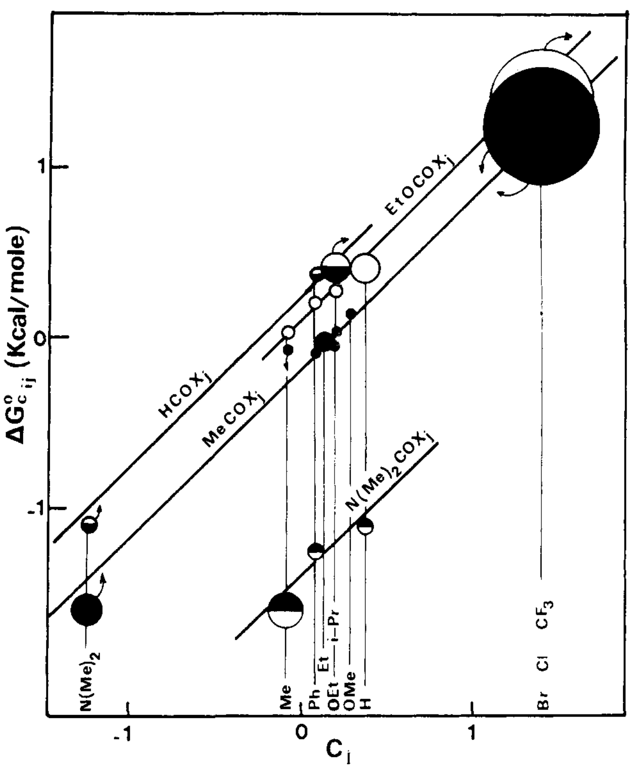

Figure 8. Correlation of $\Delta G_{c,ij}°(298)$ for iodine complexes with carbonyl bases X_iX_jCO according to eq 11. Numbers refer to Table II: (◐) $N(Me)_2COX_j$, (●) $MeCOX_j$, (◒) $HCOX_j$, (○) $EtOCOX_j$.

pairs on the oxygen and nitrogen atoms seem important, do not obey the simplest nonadditive eq 12. In fact the quantity α seems very sensitive to the influence of lone pairs; by varying their orientation α increases from 0.67 for DMC to 1.76 for ethylene carbonate and to 2.08 for propylene carbonate.[21,54]

Analysis by the Dual Substituent Parameter (DSP) Equation. It is well-known[55] that, relative to H_2CO, inductive withdrawal by X in X_iX_jCO stabilizes the lone pair while π donation, which increases the negative charge on the carbonyl oxygen, causes the oxygen lone-pair orbital to be less tightly bound. The basicity of the carbonyl group results from a balance between these inductive and π-delocalization effects. Two points bear witness to the great sensitivity of the basicity to inductive effects in the enthalpic scale: (1) the seven least basic compounds are those substituted by halogens and trihalogenomethyl groups and (2) the π donation of alkoxy and phenyl substituents is overcome by their $-I$ effect causing the sequences (> for "more basic than")

ketones > esters and MeCOMe > PhCOMe > PhCOPh

However, π-delocalization effects are also of importance since the six most basic compounds are amides and ureas in the order

DEA > TMU > DMA > DMF > DMBz > TEU

The sequence of the effect of alkyl groups Me, Et, i-Pr, and t-Bu is not systematic between the two series PhCOX and MeCOX, but note that OEt substitution always leads to a greater basicity than OMe substitution as shown by the inequalities

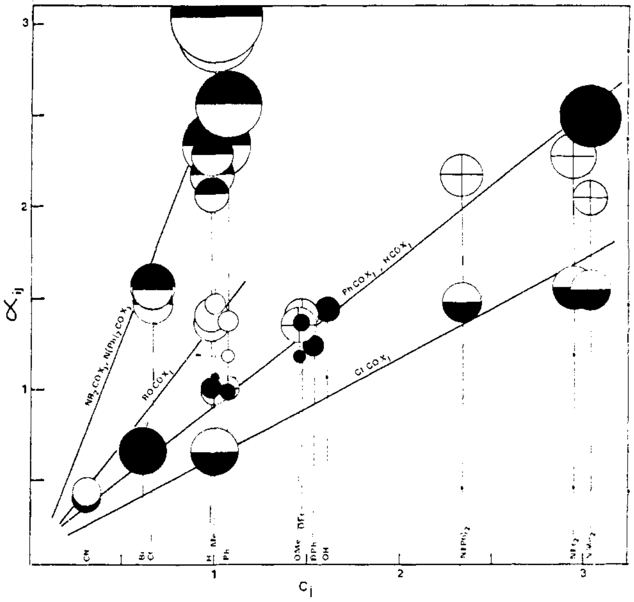

Figure 9. Correlation of the solvent sensitivity α_{ij} on the X_iX_jCO compounds' carbonyl vibrator according to eq 12. Numbers refer to Table III: (◐) NR_2COX_j with R = Et, Me, Ph, (○) $ROCOX_j$ with R = Et, Me, (●) $PhCOX_j$, (⊕) $HCOX_j$, (◒) $ClCOX_j$.

$$\mathrm{PhCOOEt} > \mathrm{PhCOOMe},\ \mathrm{MeCOOEt} > \mathrm{MeCOOMe},\ \mathrm{EtOCOOEt} > \mathrm{MeOCOOMe}$$

Comparison of SEt and OEt substitution is puzzling since SEt substitution makes ΔH° more negative, in accordance with the greater gas-phase basicity of thioesters than esters,[56] but equilibrium constants are stronger with OEt substitution,[57] in accordance with solution results.[56]

The relative importance of inductive and π-delocalization effects[58] can be estimated quantitatively by the equation[28]

$$\Delta G^\circ \text{ or } \Delta H_c^\circ = \rho_I \sum_{i,j} \sigma_I + \rho_R \sum_{i,j} \sigma_R + h \qquad (13)$$

The intercept h is the ΔG_c° or ΔH° statistical value for formaldehyde. Parameters σ_I and σ_R measure respectively inductive and π-delocalization effects. σ_R^+, σ_R^{BA}, or σ_R° scales may be used,[28] according to the electronic demand of the reaction center. The regression coefficients ρ_I and ρ_R are the sensitivity of the property to these effects. Successive correlations with 16 substituents for which σ_R^+, σ_R^{BA}, and σ_R° are known[28] give the best fit with σ_R^+ ($R = 0.966$, 0.957, and 0.86, respectively). Thus the equilibrium investigated belongs to the σ_R^+ type which corresponds to greater polarization of the carbonyl group in the complex than in the free state. The definitive correlation was recalculated for all substituents after completing the σ_I and σ_R^+ scales.[59] Results are listed in Table IV.

The percentage contributions $\% I$ and $\% R$ of inductive and π-delocalization effects to the observed variation of the property are calculated according to the procedure of Swain and Lupton[60] to take into account the difference in variance of σ_I and σ_R^+

$$\%I = 100 \frac{|\rho_I| \Sigma |\sigma_I - \bar{\sigma}_I|}{|\rho_I| \Sigma |\sigma_I - \bar{\sigma}_I| + |\rho_R| \Sigma |\sigma_R - \bar{\sigma}_R|} \qquad (14)$$

$$\%R = 100 - \%I$$

Inductive effects are found (Table IV) to contribute the most to the variation of basicity of carbonyl compounds toward iodine, in accordance with the above qualitative discussion.

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(54) These values are not directly comparable to those of Table III as they refer to methyl acetate.

(55) See, for instance, R. Ditchfield, J. E. Del Bene, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 703 (1972).

(56) J. R. Grunwell, D. L. Foerst, F. Kaplan, and J. Siddigui, *Tetrahedron*, **33**, 2781 (1977).

(57) Drago et al.[4] also found K_c (MeCOOMe) > K_c (MeCOSMe) for iodine complexes in CCl_4.

(58) Previous conclusions by Charton (ref 28, p 81) concerning the importance of inductive and π-delocalization effects on the basicity of carbonyl compounds are uncertain because both the number and kind of substituent data within the series are open to criticism.

(59) σ_I values for Et, *i*-Pr, *t*-Bu, and CH_2Cl come from R. W. Taft and C. A. Grob,

J. Am. Chem. Soc., **96**, 1236 (1974). σ_I and σ_R^+ values of SEt and $N(Et)_2$ have been supposed equal to those of SMe and $N(Me)_2$. σ_I for OEt and CCl_3 and σ_R^+ for CCl_3 come from ref 28, p 189. σ_I for CH_2Br has been calculated from $\sigma^*(\sigma_I = \sigma^*/6.23)$. σ_R^+ for Et, *i*-Pr, *t*-Bu, OEt, and SEt have been calculated from ν(CO) of para-substituted acetophenones and benzoic acids [C. Laurence and M. Berthelot, *J. Chem. Soc., Perkin Trans. 2*, in press] according to the equations

$$\sigma_R^+ = 0.012 + 0.0949(\nu - \nu_0) - 1.1505\sigma_I$$

(acetophenones $R = 0.989$, $n = 14$)

$$\sigma_R^+ = 0.049 + 0.1092(\nu - \nu_0) - 1.3664\sigma_I$$

(benzoic acids $R = 0.994$, $n = 13$)

(60) C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, **90**, 4328 (1968).

(61) G. Guiheneuf and C. Laurence, *Spectrochim. Acta, Part A*, **34**, 15 (1978).

Acidity Function of Solid-Bound Acids[1,2]

Paul Rys* and Werner J. Steinegger

Contribution from the Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology ETH, ETH-Zentrum, CH-8092 Zurich, Switzerland.

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Abstract: A new method has been developed to determine the acidity of acids bound to solids and hence compare their acidity with that of homogeneous acid systems. A model was set up to relate the sorption of indicators onto proton-carrying solids with the protonation of these indicators in acid solutions. The resulting relationship allows calculation of the acidity function of solid-bound acids. For a strongly acidic ion exchanger, e.g., Amberlyst-15, dispersed in water, the calculated acidity corresponds to an acidity of 35 wt % aqueous sulfuric acid.

The proton-donating ability (Brønsted acidity) of solid materials is an important consideration concerning their behavior in ion-exchange processes and in heterogeneous acid catalysis. The most useful measure of the acid strength of concentrated acid solutions is Hammett's H_0 function[3-7] which relates to primary aromatic amines, and is defined as

$$H_0 = -\log (a_{H^+} f_B / f_{BH^+}) = pK_{BH^+} - \log ([BH^+]/[B]) \quad (1)$$

where a_{H^+} is the activity of the hydrogen ion, f_B and f_{BH^+} are the activity coefficients for a neutral (i.e., uncharged) base and its conjugate acid, respectively, pK_{BH^+} is the negative logarithm of the acidity constant of the protonated base, and [B] and $[BH^+]$ are the concentrations of the neutral base and its conjugate acid, respectively. Analogous functions, such as H_R, H_-, and so on, have been developed for other families of acids and bases.[4]

Acidity functions have been an enormous aid in the study of the rates and mechanisms of organic reactions in solution. Various attempts have also been made to determine the H_0 values of acidic solids. Such an H_0 scale for solid-bound acids is important not only for investigations of the mechanisms of heterogeneous acid-catalyzed reactions but also in the determinations of possible reactivity differences between solid-bound and dissolved acids caused by the solid matrix. The present methods[8,9] to determine surface acidities of cracking catalysts, clays, and a variety of acids mounted on silica gel allow only a semiquantitative estimation of H_0. These methods consist of bringing separate samples of the solid under study into contact with various indicator solutions and noting the resulting colors of the adsorbed indicators.

The present study introduces a new method for an improved quantitative determination of H_0 in solid materials. This method is based on the sorption model SINA (sorption of indicators for the determination of the acidity of solid materials). It enables $f_B f_{H^+} / f_{BH^+}$, and therefore H_0, to be determined from the sorption isotherms of indicator bases onto acidic solid materials. The applicability and usefulness of this new method for determining the H_0 of a sulfonated polystyrene ion-exchange resin in its acidic form (Amberlyst-15) are shown.

Experimental Section

Indicators. The following compounds were obtained from Fluka AG, Switzerland, and were used without further purification (mp, pK_{BH^+}): 2-nitroaniline (70-72 °C, −0.29); 3-nitroaniline (112-113 °C, 2.47); 4-nitroaniline (148-149 °C, 1.00); 2,4-dinitroaniline (179-181 °C, −4.53); 4-chloro-2-nitroaniline (114-116 °C, −1.03). Commercially available (Fluka AG and Aldrich Chemical Co.) samples of the following compounds were recrystallized from ethanol/water mixtures to constant melting point (mp, pK_{BH^+}): 2-methyl-5-nitroaniline (103-105 °C, 2.32); 2-methyl-4-nitroaniline (130-132 °C, 1.04); 4-methyl-2-nitroaniline (114-115 °C, 0.43); 2,6-dichloro-4-nitroaniline (190-192 °C, −3.27); 2-chloro-6-nitroaniline (73-75 °C, −2.46). All melting points were obtained on a FP61 melting point apparatus from Mettler AG, Switzerland, and are uncorrected. The pK_{BH^+} values are taken from the literature.[10]

Solid Substrates. The acidic solid material used was Amberlyst-15 (Rohm and Haas Co.), a sulfonated polystyrene ion-exchange resin in its H^+ form, having[11,12] an exchange capacity of 4.3 equiv/L of imbibed water, a porosity of 0.36, an inner surface area of 54 m^2/g, an apparent density of the dried resin bead of 1.012 g/cm^3, a true density of the polystyrene matrix of 1.513 g/cm^3, and an average pore size of 8×10^{-7} cm.

The ion-exchange resin for the sorption experiments was prepared by successive washing with methanol, ethanol, and distilled water until each wash was colorless. Afterwards, the resin was converted into its H^+ form by treating it with a 2 M hydrochloric acid solution. The excess acid was removed by extensive washing with distilled water. For the sorption experiments from organic solvents the resin was first predried in air and then at 90 °C under vacuum at 0.1 mmHg. The remaining water content was determined using the method of Karl Fischer. Before the sorption experiments the resin was carefully preconditioned with the appropriate solvent.

The solid substrates used as reference materials were Amberlite XAD-2 (Rohm and Haas Co.), a nonsulfonated polystyrene resin, and Amberlyst-15 in its partial or its total exchanged Na^+ form.

Solvents. The solvents were the purest grade products from Merck AG, West Germany. They were used without further purification.

Technique. The sorption isotherms were determined by adding between 0.1 and 1 g of the preconditioned ion-exchange resin to a solution of the appropriate indicator. After the sorption equilibrium was established at 25 °C (24 h), the resin beads were filtered. The amount of the sorbed indicator was then determined spectrophotometrically either by measuring the decrease in the concentration of the indicator in the remaining solution or by extracting the resin with

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