[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

Halogen Substituents. II. Solvent Effects on the Principal Electronic Transition of *p*-Halonitrobenzenes and *p*-Haloacetophenones

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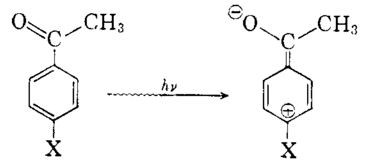
RECEIVED JULY 6, 1959

The principal ultraviolet band excitation energies of the *p*-halonitrobenzenes and *p*-haloacetophenones take the same order in solvents as in the gas phase: I < Br < Cl < F < H. Transition moment lengths in heptane take the order I > Br > Cl > F, H, in support of the conclusion that substituent polarization in these transitions is in the order I > Br > Cl > F. The gas to non-polar solvent red shifts grossly reflect the increase in total polarity on excitation, being I > Br, Cl > F for the *p*-halonitrobenzenes and I > Br, Cl, F for the *p*-haloacetophenones. The sensitivity of the excitation energy to solvent change (red shift with increasing solvent polarity) is H, F > Cl > Br > I for the nitrobenzenes and H, F > I > Cl > Br for the acetophenones. These orders are rationalized in terms of solvent orientation effects arising from the fact that the Franck-Condon principle is operative. Plots of solvent shifts for substituted compound against unsubstituted are linear. The relationship between the slopes of these plots and Hammett σ-constants is discussed.

In Part I it was reported that for *p*-halonitrobenzenes and *p*-haloacetophenones the energy order for the principal electronic transition is I < Br < Cl < F < H and for *p*-haloanisoles it is I < Br < Cl < H < F. In other words, stabilization of the excited state relative to the ground state by *p*-halogen substituents takes the polarizability order in both an electronic transition in which the electron migration is away from the substituent (represented approximately by equation 1) and one in which the electron migration is apparently toward the substituent (equation 2). It was further found that a decrease in excitation energy was paralleled by an increase in molar refraction for each of the three series of compounds. An explanation of these results in terms of the polarizability and electronegativity of the substituent was advanced.[2,3] It was with the hope that solvent spectral shifts would give a clue as to whether polarization of the substituent occurs through its bonding electrons or through space (dispersion force) that the studies reported herein and in the following paper[4] were made.



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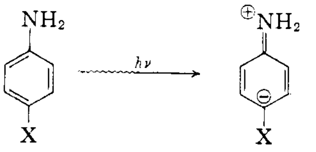

(2)

Experimental

Preparation and purification of compounds and solvents have been described.[2,5] The solution spectra were measured and ν_{max} values determined as before.[5] A constant slit width (0.1–0.2) was maintained in scanning the spectral peaks.

Transition moment lengths, q, defined by equation 3, were obtained from plots of ϵ (molar extinction coefficient) *vs.* log λ.[6] In each case, the area under the principal band was measured up to the generally low minimum between the principal band and the lower wave length transition. In

$$q^2 = 1.09 \times 10^{-19} \int \epsilon \, d \log \lambda \qquad (3)$$

the case of acetophenone in 51% $HClO_4$, the low intensity longer wave length B band merged into the principal band somewhat. Therefore the total area under both bands was measured and then corrected by subtracting from it the B-band area found in dioxane. The correction amounted to only 0.02 Å. in q.

Results

The nitrobenzenes had an isolated and structureless principal band in all solvents. The band also was symmetrical about the peak except for *p*-iodonitrobenzene, which gave an unsymmetrical band in non-polar solvents. The acetophenones also had a generally structureless principal band free from overlap by other bands in all solvents. The band was somewhat narrower than that of the nitrobenzenes and was slightly unsymmetrical in most solvents. Values of ν_{max} are listed in Table I for the nitrobenzenes and in Table II for the ace-

TABLE I

VALUES OF $\nu_{max} \times 10^{-1}$ (CM.$^{-1}$) FOR p-$XC_6H_4NO_2$[a]

Solvents	H	F	Cl	Br	I[b]
Gas[c]	4182	4080	3979	3928	3786
Isopentane	3998	3917	3795	3739	3491
Heptane	3970	3896	3778	3718	3477
Cyclohexane	3954	3885	3762	3700	3448
t-BuCl	3889	3830	3721	3656	3427
t-BuOH	3879	3806	3705	3649	3414
95% EtOH	3853	3786	3686	3625	3394
29% $NaOCH_3$	3846	..[d]	3674	3610	3376
CH_3CN	3828	3771	3677	3618	3404
H_2O	3744	3667	3583	3524	3316
20.6% $HClO_4$	3722	3651	3564	3516	3303
40.6% $HClO_4$	3696	3629	3538	3483	3286
70.9% $HClO_4$	3566	3505	3418	3366	3172
λ_{max}, heptane, mμ[c]	251.8	257.1	264.7	269.0	287.6

[a] All values average of two or more determinations, duplicable to ±2–3 × 10^{-1} cm.$^{-1}$. [b] Values for the iodo compound in gas and in non-polar solvents not as reliable due to the fact that the band was asymmetric. [c] Taken from reference 2. [d] Spectrum changed with time, possibly because of nucleophilic aromatic substitution.

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[1] National Science Foundation predoctoral fellow, 1956–1959.

[2] W. M. Schubert, J. M. Craven and H. Steadly, THIS JOURNAL, **81**, 2695 (1959).

[3] W. M. Schubert, J. M. Craven, H. Steadly and J. Robins, *J. Org. Chem.*, **22**, 1285 (1957); see also A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 4314 (1956).

[4] W. M. Schubert and J. M. Craven, THIS JOURNAL, **82**, 1357 (1960).

[5] W. M. Schubert, J. Robins and J. L. Haun, *ibid.*, **79**, 910 (1957).

[6] G. S. Levinson, W. T. Simpson and W. Curtis, *ibid.*, **79**, 4314 (1957); G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., Inc., New York, N. Y., 1950, pp. 381–383.

tophenones. Values of transition moment length, q, in three solvents are given in Table III, along with values of ϵ_{max}.

TABLE II

VALUES OF $\nu_{max} \times 10^{-1}$ (CM.$^{-1}$) FOR p-$XC_6H_4COCH_3$[a]

Solvent	H	F	Cl	Br	I
Gas[b]	4346	4286	4144	4085	3942
Isopentane	4211	4169	4028	3970	3804
Heptane[b]	4198	4162	4013	3954	3795
Cyclohexane	4194	4153	4009	3937	3782
t-BuCl	4178	4152	4022	3957	3809
CH_3CN	4171	4149	4028	3962	3818
t-BuOH	4142	4100	3982	3913	3764
95% EtOH	4129	4101	3985	3916	3768
26% $NaOCH_3$	4117	4078	3959	3894	3745
H_2O	4082	4040	3927	3866	3705
20.6% $HClO_4$	4069	4033	3919	3857	3693
40.6% $HClO_4$	4036	4006	3896	3836	3665
52.5% $HClO_4$	4003	3965	3857	3807	3610
λ_{max}, heptane, mμ[b]	238.1	240.3	249.2	252.9	263.5

[a] All values average of two or more determinations, duplicable to ±2–3 × 10^{-1} cm.$^{-1}$. [b] Taken from reference 2.

TABLE III

VALUES OF TRANSITION MOMENT LENGTHS, q (Å.), AND $\epsilon_{max} \times 10^{-3}$ IN VARIOUS SOLVENTS[a]

	H	F	Cl	Br	I
		p-Halonitrobenzenes			
q in:					
Heptane	0.81	0.78	0.94	0.98	0.99
Dioxane	.83	.81	.96	1.01	1.03
51% $HClO_4$	.86	.86	.98	0.99	1.04
$\epsilon_{max} \times 10^{-3}$ in:					
Heptane	8.7	8.4	12.2	13.3	12.4
Dioxane	8.0	7.8	10.8	11.8	12.3
51% $HClO_4$	7.6	7.5	10.1	10.5	10.5
		p-Haloacetophenones			
q in:					
Heptane	0.75	0.77	0.92	0.97	1.00
Dioxane	.77	.75	0.96	1.01	1.03
51% $HClO_4$	.88	.88	1.04	1.05	1.09
$\epsilon_{max} \times 10^{-3}$ in:					
Heptane	12.4	11.9	17.4	19.2	19.4
Dioxane	12.1	10.9	17.0	19.0	16.4
51% $HClO_4$	12.0	11.6	15.8	16.2	14.3

[a] Values of q duplicable to ± 0.02 Å., ϵ_{max} to ±3%.

Discussion

In any discussion of the effect of solvent on electronic spectra it should be recalled that the Franck–Condon principle applies.[7] In other words, in the short time of the electronic excitation (about 10^{-16} sec.) the solvent as well as solute atomic nuclei suffer practically no change in position, although electronic polarization of the solvent is allowed. However, for solutes in which the dipole moment is greater in the excited state than in the ground state and in the same direction, solvent stabilization is generally greater for the excited than for the ground state. This is because solvent molecules in a position to solvate the polar sites of the ground state are in a generally favorable position, though not the most favorable one, to solvate the sites of increased polarity in the excited state.[5,7]

Spectral Shifts, Gas to Non-Polar Solvent.—Judging from the gas phase excitation energies, the increase in total solute polarity on excitation for the p-halonitrobenzenes and p-haloacetophenones is in the order I > Br > Cl > F > H. However, the solvent spectral shifts will not necessarily reflect this, particularly since orientation of the solvent atomic nuclei remains the same for the excited state as for the ground state. Specific solvent orientation effects should be least in a nonpolar solvent since the interactions between solute and solvent are primarily dispersion and dipole–polarization forces.[7] Therefore, the degree to which the excitation energy is lowered in proceeding from gas to non-polar solvent might be expected to reflect primarily, though not wholly, the degree to which solute polarity is increased in the excitation. In agreement with this conclusion is the observation that for the p-halonitrobenzenes the red shift in proceeding from gas to, say, isopentane is I > > Br, Cl > F (Table I), and for the acetophenones it is I > Br, Cl, F (Table II). The fact that the orders are somewhat jumbled may indicate the superposition of a solvent orientation effect acting in the direction of giving solvent stabilization of the excited state relative to the ground state in the order F > I.

Spectral Shifts, Changing Solvent.—The order of excitation energy of the nitrobenzenes and acetophenones observed in the gas phase is maintained in all the solvents used. Furthermore, there is a general red shift of all the spectra with increasing polarity of solvent, in agreement with the nature of the transition.[7,8] However, the magnitudes of the solvent shifts differ according to the nature of the substituent. This is graphically illustrated in Fig. 1 for the nitrobenzenes and Fig. 2 for the acetophenones. These figures contain plots of ν_X, the frequency maximum for a particular halogen compound, against ν_H, the frequency maximum for the parent compound, in the various solvents. It is seen that the effect of changing solvent on ν_X is approximately linear with the effect on ν_H. The slope (called the Q_x value[5]) of the plot for a particular halogen compound is thus a measure of the sensitivity of its excitation energy to solvent change, relative to that of the parent compound. Values of Q_x for each series are given in Table IV, together with the probable error in Q_x and the value of the correlation coefficient, r.

Consider first the fact that the sensitivity of the excitation energy of the halogen compounds of each series, except possibly fluoro, is less than that of the parent compound. From the dipole moments of the nitrobenzenes and acetophenones (see Table IV) it can be deduced that, in the ground states, the p-halogens act as strongly electron-withdrawing substituents relative to a p-hydrogen.[9] If it is

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[7] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

[8] While solvent stabilization of the excited and ground states is related in a general way to solvent polarity, it is clear that more specific solvent properties enter in. These factors include the size and orientation of solvent molecules and their specific ability to solvate electron-rich sites on the one hand, and electron-deficient sites on the other.

[9] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 323, 239, 253.

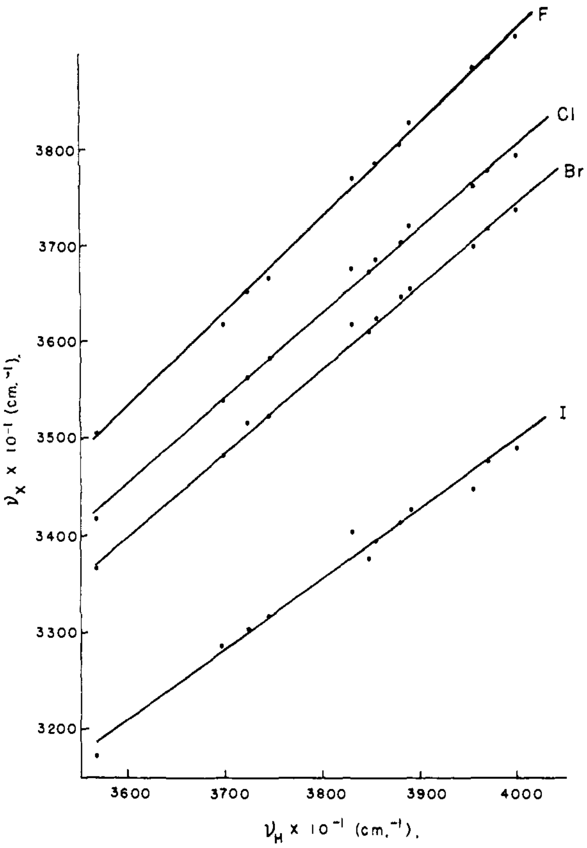

Fig. 1.—Plot of ν_{max} in various solvents for *p*-halonitrobenzenes *vs.* nitrobenzene. Reading from right to left on the ν_H axis, the points correspond to the descending order of solvents listed in Table I.

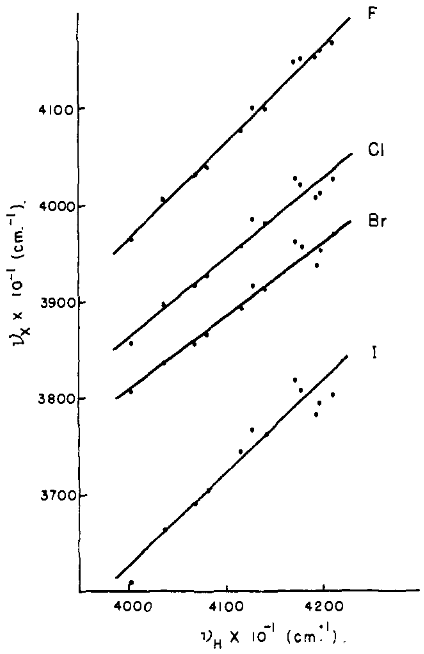

Fig. 2.—Plot of ν_{max} in various solvents for *p*-haloacetophenones *vs.* acetophenone. Reading from right to left on the ν_H axis, the points correspond to the descending order of solvents listed in Table II.

assumed that a *p*-halogen thereby reduces the negativity of the oxygen of the functional group in the ground state, then specific solvation of this site, *e.g.*, by hydrogen bonding, will be reduced. On the other hand, halogen substitution presumably also increases the electron deficiency of the aromatic ring of the ground state, leading to greater specific solvation of this site. In view of the Franck–Condon principle and the nature of the transition, the former solvent orientation effect would act to lower (relative to the parent compound) solvent stabilization of the excited less that of the ground state, whereas the latter effect would act to increase solvent stabilization of the excited state relative to the ground state. Since specific solvation of the negative oxygen of the functional group would be expected to be generally stronger than solvation of the more diffuse positive charge of the ring, a change in solvent polarity might be expected to produce less of a change in the excitation energy of the *p*-halogen compound than of the hydrogen compound.

TABLE IV

VALUES OF DIPOLE MOMENTS, Q_X AND σ_X

	H	F	Cl	Br	I	Me[5]
			p-Halonitrobenzenes			
μ (D.) in C_6H_6[a]	3.98	2.63	2.5	2.55	2.8	4.42
Q_X	1.00	0.98	0.88	0.86	0.72	1.22
s[b]	..	.02	.02	.02	.03	0.006
r[c]	..	.999	.997	.997	.991	.9998
$Q_X - 1$	0	− .02	− .12	− .14	− .28	.222
σ_X[d]	0	.062	.227	.232	.276	− .170
			p-Haloacetophenones			
μ (D.) in C_6H_6[a]	2.89	..	2.29	2.29	2.23	3.23[e]
Q_X	1.00	1.01	0.83	0.78	0.92	1.21
s[b]	..	0.03	.05	.05	.08	0.01
r[c]	..	.995	.979	.980	.961	.9997
$Q_X - 1$	0	.01	− .17	− .22	− .08	.21

[a] Dipole moment values taken from ref. 9, pp. 323 and 325. [b] Standard deviation of the slope Q_X.[12] [c] Correlation coefficient of the slope Q_X.[12] [d] Taken from ref. 12. [e] J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949).

Turning attention now to the effect of changing halogen substituents on the solvent spectral shifts, it is seen that Q_x takes the order F > Cl > Br > I for the nitrobenzenes and F > I > Cl > Br for the acetophenones. These are not the orders to be expected were solvent stabilization of excited state less that of ground state solely determined by the increase in total polarity on excitation. The results suggest that there are solvent orientation effects acting in the direction of giving solvent stabilization of the excited state relative to the ground state in the order F > I. A tentative explanation of these results can be advanced if it is assumed that the lowering of the excitation energy by *p*-halogen substituents is due mainly to direct polarization of the substituent through its bonding electrons, rather than to polarization through space (dispersion force). In that event the electron deficiency on the substituent in the excited state would be in the order I > F. Hence the polarity increase on excitation could take the order F > I for the *p*-nitrophenyl or *p*-acetylphenyl portion of the molecule although the polarity increase in the *entire* molecule is in the order I > F.

Insofar as the solvent shifts would be expected to be governed more by solvation of the *p*-nitrophenyl or *p*-acetylphenyl moiety than by solvation of the substituent, this factor could act in the direction of giving solvent red shifts in the order F > I.

Transition Moment Lengths.—The transition moment length of an electronic transition, *q*, is determined from the integrated intensity of the transition (see Experimental). It is considered to be a measure of the length of oscillation of the dipole *during* the absorption of light energy. The oscillation is set into motion by the electric vector of the light and corresponds in frequency to the frequency of the light absorbed.[6,10] It is seen in Table III that for each series the order of increasing transition moment length, H, F < Cl < Br < I, corresponds to the order of decreasing excitation energy. Since the relative values of *q* are a measure of the degree of polarization of the substituent electrons in the oscillation of the solute dipole during the interaction with the electric vector of the light, these results are in support of the conclusion reached on the basis of the excitation energies, namely, that polarization of the substituent in going from ground to excited state is in the order I > Br > Cl > F. However, they give no clue as to whether the substituent is polarized through space (dispersion force) or through the bonding electrons to the substituent.

There is a tendency for the transition moment lengths to increase in proceeding from heptane to dioxane to 51% $HClO_4$, although ϵ_{max} is decreased (Table III).[11] This is a reflection of the fact that the principal band of these compounds becomes flatter and broader as solvent polarity is increased. This broadening may be due to variations in specific dipolar solvation from one solute molecule to another. For example, in perchloric acid, the functional group of some solute molecules may be hydrogen-bonded to H_3O^+, that of others to H_2O.

Relationship between Q_x and σ_x, the Hammett Substituent Constant.—The "lines" in Figs. 1 and 2 are plots of the linear relationship of equation 4, in which ν_x and ν_H refer to the excitation energies in various solvents of the substituted and unsubstituted members of a particular series. The slope,

$$\nu_x = Q_x\nu_H + \text{const.} \tag{4}$$

Q_x, may be considered to be a solvent-independent substituent constant, although it is also dependent on the structure of the remainder of the substrate.[5] The constant of equation 4 can be given the value $\nu_x^0 - Q_x\nu^0_H$, where ν_x^0 and ν_H^0 refer to measurements made in some particular standard solvent. Equation 4 then becomes

$$\nu_x - \nu_x^0 = Q_x(\nu_H - \nu_H^0) \tag{5}$$

The Hammett linear free energy relationship as applied to rate and equilibrium constant data is given by equation 6.[12] In the application to spectral excitation energies, the Hammett equation takes the form of equation 7, in which the value of ρ depends on the units of energy used in the quantity $\nu_x - \nu_H$ (ref. 12, p. 241).

$$\log k_x - \log k_H = \sigma_x\rho \tag{6}$$

$$-(\nu_x - \nu_H) = \sigma_x\rho, \text{ and for std. solvent } -(\nu_x^0 - \nu_H^0) = \sigma_x\rho^0 \tag{7}$$

By simple manipulation of equations 5 and 7 one obtains equation 8, which relates $Q_x - 1$ to σ_x.

$$Q_x - 1 = -\sigma_x\frac{\rho - \rho^0}{\nu_H - \nu_H^0} \tag{8}$$

A similar relationship is derived between $Q_y - 1$ and σ_y for any other substituent Y. Making the usual assumption that the "reaction" constants ρ and ρ^0 are substituent independent leads to equations 9, 10 and 11.

$$\frac{Q_x - 1}{Q_y - 1} = \frac{\sigma_x}{\sigma_y} \tag{9}$$

$$Q_x - 1 = C\sigma_x \tag{10}$$

$$C = \pm\frac{\rho - \rho^0}{\nu_H - \nu_H^0} \tag{11}$$

Equations 9 and 10 state that values of $Q_x - 1$ are proportional to values of σ_x. Equation 11 states that $\nu_H - \nu_H^0$ is a measure of the change with solvent of the "reaction" constant, ρ.

A comparison is made in Table IV of the values of σ_x and $Q_x - 1$ for both the nitrobenzenes and acetophenones, including the previously determined $Q_{CH_3} - 1$ values for the *p*-methyl compounds.[5] It is seen that there is a qualitative correspondence between the absolute magnitudes of the σ_x and $Q_x - 1$ values, except for *p*-iodoacetophenone. Evidently the proportionality constant has a value in the neighborhood of −1 for each series.

The effect of solvent on the energy of the principal electronic transition of a particular nitrobenzene (*e.g.*, nitrotoluene) could be used as an empirical measure of solvent "polarity," much in the manner that Kosower has used the effect of solvent on the charge transfer band of 1-ethyl-4-carbomethoxypyridinium iodide to define solvent *Z*-values.[13] However, the principal band of the nitrobenzenes is not as sensitive to solvent change as is the charge transfer band of 1-ethyl-4-carbomethoxypyridinium iodide. On the other hand, the spectrum of the nitrobenzenes can be measured in a much wider variety of solvents, particularly in non-polar solvents in which the pyridinium iodide is insoluble.

Acknowledgment.—We are grateful to the Office of Ordnance Research, U. S. Army, for their financial support, and to Mr. Rodney H. Quacchia for measuring some of the transition moment lengths.

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[10] E. V. Bowen, "Chemical Aspects of Light," Oxford University Press, New York, N. Y., 1946, pp. 78, 123.

[11] There are other instances in Table III in which ϵ_{max} values do not correspond to *q*-values. For instance, values of ϵ_{max} for the acetophenones are much greater than for the nitrobenzenes, although the *q*-values are comparable. Also, the change in ϵ_{max} with substituent does not always parallel the change in *q*. This reaffirms that differences in ϵ_{max} do not necessarily correspond qualitatively to differences in integrated intensities and therefore ϵ_{max} is not a completely reliable measure of transition probability.

[12] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[13] E. M. Kosower, THIS JOURNAL, **80**, 3253, 3261, 3267 (1958).