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

Solvent and Substituent Effects. Concerning the Baker–Nathan Effect and the Influence of Solvent on the Principal Ultraviolet Spectral Band of Some *p*-Alkylnitrobenzenes and *p*-Alkylacetophenones[1]

BY W. M. SCHUBERT, JANIS ROBINS[2] AND J. L. HAUN

RECEIVED JULY 10, 1956

The "principal" band in the ultraviolet spectrum (due to excitation to a dipolar state) has been measured for nitrobenzene and acetophenone and their *para* methyl, ethyl, isopropyl and *t*-butyl derivatives in the gas phase and in a wide variety of solvents. The gas phase excitation energies are in the inductive order, with the alkyl groups responding in linear proportion to the change in electron demand in proceeding from the acetophenone to the nitrobenzene series. The effect of solvent, particularly basic solvents, is to tend to invert the order of excitation energies. Quantitative treatment of the data indicates that this effect is consistent with the operation of steric hindrance to solvation.

Introduction

The Baker–Nathan effect, *i.e.*, apparent "activation" by alkyl groups in the order Me > Et > *i*-Pr > *t*-Bu, is generally found for reactions in which a large demand for electron release by alkyl attached to an unsaturated system is created. In the electron-demanding state of such systems, C–H hyperconjugation has been presumed to be the predominant mode of electron release by alkyl (*i.e.*, with increasing electron demand, C–H hyperconjugative release is presumed to increase more rapidly than inductive release).[3] However, it has been pointed out recently that certain data, particularly ionization potential and ultraviolet spectral data, appear to contradict the concept that C–H hyperconjugation can be predominant. Sweeney and Schubert have suggested that alkyl substituents release electrons in the inductive order (though not necessarily by the inductive mechanism) regardless of demand and that steric hindrance to solvation of electron-deficient sites near the alkyl substituent tends to give an opposite experimentally observed order of *apparent* "activation."[4,5] Shiner has suggested that the role of the solvent is to enhance C–H over C–C hyperconjugation by hydrogen bonding with the α-hydrogens of the alkyl substituent.[6] Burawoy and Spinner consider alkyl groups to release electrons by the inductive mechanism only and have neglected the role of solvation. According to their view, steric hindrance to bond contraction accompanying inductive release acts to invert the order of electron release as the electron demand is increased.[7]

In order to determine the inherent electron release tendencies of alkyl substituents in the face of a large electron demand, *and in the absence of solvent effects*, we have studied the so-called principal band of the gas-phase ultraviolet spectra of some *p*-alkylnitrobenzenes and *p*-alkylacetophenones. The spectra of these compounds in a wide variety of solvents also was studied in order to determine what influence solvent may have on the apparent activating effect of the alkyl substituents.

Experimental

Compounds.—The *p*-alkylnitrobenzenes were prepared by nitration of the corresponding hydrocarbons using known procedures. Purification was achieved by the following procedures, in order: (1) steam distillation, (2) ordinary distillation under reduced pressure, (3) distillation twice through a 40-plate spinning band column under reduced pressure (from 40 to 100 mm.), (4) recrystallization up to five times from methanol (the compounds that were liquids were recrystallized below room temperature), (5) drying in a vacuum desiccator over calcium chloride and finally, (6) an ordinary distillation to remove possible last traces of methanol.

The infrared spectrum of each of these compounds, checked several times during the purification procedure, was constant during the latter stages of the purification, as were the index of refraction and ultraviolet spectrum. The strong aromatic C–H "out of the plane" bending frequencies, characteristic for each isomer, were used as a criterion for the presence of *o*- and *m*-isomers.[8] The infrared spectra indicated that no *o*-isomer and only a trace of *m*-isomer were present after the second fractional distillation. No trace of *m*-isomer was discernible after about one recrystallization, although the compounds were usually recrystallized five times. The properties of the compounds prepared are listed in Table I.

TABLE I

OBSERVED PHYSICAL PROPERTIES OF COMPOUNDS PREPARED

Compound	B.p. °C.	B.p. Mm.	M.p., °C.	$n^{25.5}D$	Ref.[a]
Nitrobenzene	100	20	.....	1.5509	9
p-Methyl-	..	..	51.8–52.0	....	10
p-Ethyl-	172	95	.....	1.5440	11
p-Isopropyl-	164	53	.....	1.5352	12
p-*t*-Butyl-	..	45	28.4 ± 0.1	....	13
Acetophenone	127	70	+20	1.5310	14
p-Methyl-	146	76	−19	1.5316	15, 16
p-Ethyl	150	49	.....	1.5272	17
p-Isopropyl-	158	49	.....	1.5213	18
p-*t*-Butyl-	166	46	.....	1.5191	19

[a] Reference to preparative method and recorded properties.

(1) Presented at the 129th National Meeting of the American Chemical Society, Dallas, Texas, April 8–13, 1956.

(2) Du Pont Fellow, 1955–1956.

(3) J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1953.

(4) W. A. Sweeney and W. M. Schubert, THIS JOURNAL, **76**, 4625 (1954).

(5) W. M. Schubert and W. A. Sweeney, *J. Org. Chem.*, **21**, 119 (1956).

(6) V. J. Shiner, Jr., THIS JOURNAL, **76**, 1603 (1954).

(7) (a) A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954); (b) 2557 (1955).

(8) N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).

(9) G. W. Luckey, A. B. F. Duncan and W. A. Noyes, *J. Chem. Phys.*, 407 (1948).

(10) W. W. Jones and M. Reissel, *J. Chem. Soc.*, 921 (1947).

(11) E. L. Cline and E. E. Reid, THIS JOURNAL, **49**, 3150 (1927).

(12) C. Hansch and G. Helmkamp, *ibid.*, **73**, 3080 (1951).

(13) K. LeRoi, L. Nelson and H. C. Brown, *ibid.*, **73**, 5605 (1951).

(14) J. W. Bruehl, *J. prakt. Chem.*, **49**, 201 (1894).

(15) C. R. Noller and R. Adams, THIS JOURNAL, **46**, 1889 (1924).

(16) P. H. Groggins and R. H. Nagel, *Ind. Eng. Chem.*, **26**, 1313 (1934).

(17) J. F. Norris and P. Arthur, Jr., *ibid.*, **62**, 874 (1940).

(18) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1943.

(19) M. S. Newman and H. V. Zahn, THIS JOURNAL, **65**, 1097 (1943); A. Verley, *Bull. soc. chim.*, [3] **19**, 73 (1898).

The acetophenones were purified by ordinary distillation under reduced pressure followed by distillation through a concentric tube column under pressures ranging from 46 to 76 mm. The infrared spectra showed no traces of *m*- or *o*-isomer.[8] Acetophenone and *p*-methylacetophenone were further purified by two low temperature recrystallizations from isopentane. The ultraviolet spectra of these compounds were identical with those from the twice-distilled samples. The acetophenones deteriorated slowly on standing (autoöxidation?) and hence were used freshly after purification.

Purification of Solvents.—Large solvent batches were prepared in order that each particular solvent would be constant for all comparisons made in it. Cyclohexane and *n*-heptane (C.P., Matheson) were passed through a column of activated basic aluminum oxide.[20] *t*-Amyl alcohol was dried over potassium carbonate and distilled through a 10-plate column.[21] *t*-Butyl alcohol was fractionally distilled from sodium.[22] *n*-Butylamine was distilled through a spinning band column. Dioxane was fractionally frozen after purification by the method described by Vogel.[21] Acetic acid was fractionally distilled under 20-mm. pressure from chromic acid, to contain 0.2% water (Karl Fischer method). Absolute methanol (reagent grade, Allied Chemical and Dye) and C.P. 95% ethanol were used without further purification. Acetonitrile was dried over potassium carbonate and fractionally distilled. Formic acid (C.P., Allied Chemical and Dye), sulfuric acid (C.P. du Pont) and 60 and 70% perchloric acid (Allied Chemical and Dye) were not purified further. Water was purified by simple distillation.

Gas phase ultraviolet spectra were determined in 20-cm. Aminco cells in a water-thermostated cell compartment at 70°, using a finely adjusted Beckman DU instrument containing a fused quartz prism and equipped with a photomultiplier. The sample was introduced into the cell by either of two methods. In one method the cell and a weighed amount of compound were placed in a stoppered 5.5-l. flask and kept at 90° for a period of at least 12 hr. to assure complete vaporization of the compound. The cell was then quickly removed, stoppered, sealed with high melting wax and placed in the thermostated cell compartment. The amount of sample used was regulated to keep the compound below saturated vapor pressure and below a pressure that would give noticeable adsorption on the walls of the vessel. A plot of optical density *versus* cell temperature showed adsorption to be noticeable (in a lowering of the optical density) below 50°. The amount of sample was usually such that the absorbancy at the peak was around 0.4. With this method of introducing the sample, the blank cell was filled with air. The extinction coefficient was calculated from the known volume of the 5.5-l. flask and the sample weight. The other method of introducing the sample was to place a drop of compound in the cell and evacuate the cell with an oil-pump until the drop just evaporated. A bit of trial and error was needed with this method before the correct amount of sample was present in the cell. An evacuated cell was used as a blank. After the gas phase spectrum was run, the extinction coefficient was determined by allowing alcohol to be drawn into the evacuated cells and repeating the spectral determination. Both methods were used on the nitrobenzenes and gave identical results. Only the latter method was used on the acetophenones.

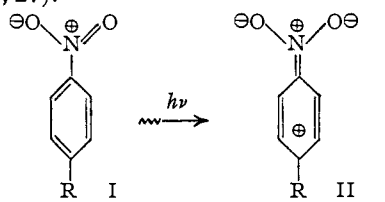
To accurately determine the absorption maximum of the principal band, the entire spectrum was first scanned and then repeated readings were made 0.5 mμ apart over a 10–20 mμ range at the peak. The usual extra precautions were taken, including standardizing the cells against each other and approaching the wave length positions and absorbancy readings from the same side.[23] The slit width was kept at a constant value of 0.2 over the peak for each compound. Absorbancy was plotted *versus* wave number and the peak maximum determined graphically according to the method of Bayliss and Hulme.[24] An alternative method, less frequently used, involved first finding two wave lengths 3–5 mμ on each side of the peak having the same absorbancy with great accuracy by averaging 5 to 7 measurements. This was repeated several times at successively smaller wave length spreads. The midpoint average was taken as λ_{max}. Differences in maxima were determined by different workers to within ±20 cm.$^{-1}$, usually to about ±10 cm.$^{-1}$. Results are summarized in Table II.

Solution Spectra.—The spectra of solutions about 10^{-4} *M* in sample were determined in carefully standardized 1-cm. stoppered quartz cells. Two instruments, calibrated against mercury lines, were used. One of these was a Beckman DU spectrophotometer containing a fused quartz prism and a photomultiplier; the other, an ordinary Beckman DU. A constant slit width was maintained over the peak in all comparisons (0.1 with the former instrument, 0.3–0.5 with the latter instrument). The slit width was not critical except for the acetophenones in heptane, for which the peak was somewhat unsymmetrical and a change in slit width from 0.1 to 1.0 caused about a 0.2 mμ change in the observed maximum. However, differences between members of the acetophenone series in heptane showed no discernible dependence on slit width.

Spectral measurements (cells at a temperature of 25 ± 1°) and determination of peak maxima were done as described above, mainly by the first method. Differences in λ_{max} between compounds and solvents were duplicated by three workers to ±0.1 mμ (10–20 cm.$^{-1}$), although absolute values depended somewhat on the instrument used. Results are summarized in Tables III and IV. The absolute values of ν reported are those obtained using the ordinary Beckman DU spectrophotometer.

Discussion

Attention here is centered on the "principal band" in the ultraviolet spectrum (also called E-band, K-band, etc.) which occurs at around 2100 Å. for alkylbenzenes and 2300–2700 Å. for benzene substituted by such groups as NH_2, COR, NO_2. This band is due to a π- to π^*-transition to a dipolar excited state and is represented crudely by the valence bonds structures I and II for ground and excited states, respectively (see *e.g.*, references 24, 25, 26, 27).[28]



(1)

For the nitrobenzenes the principal band was structureless, even in the gas phase, and was quite symmetrical about the peak. Furthermore, general band width and shape did not change as the *p*-alkyl substituent or solvent was changed, although there was some flattening at the very peak in polar solvents. For the acetophenones in the gas phase and in heptane, the spectrum was slightly unsymmetrical at the peak and showed a small shoulder at about 7 mμ to the red of the peak. In all other solvents, the peak was symmetrical and the shoulder was absent. In view of these consid-

(20) G. Nesse and H. Schildknecht, *Angew. Chem.*, **67**, 737 (1955).

(21) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1951.

(22) M. Pestemer, *Angew. Chem.*, **63**, 118 (1951).

(23) L. S. Goldring, R. C. Hawes, G. H. Hare, A. O. Beckman and M. E. Stickney, *Anal. Chem.*, **25**, 869 (1953).

(24) N. S. Bayliss and L. Hulme, *Aus. Chem. J.*, **6**, 257 (1953).

(25) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

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

(27) For a discussion in quantum mechanical terms of the "validity" of such a structural depiction of the excitation process see W. T. Simpson, THIS JOURNAL, **75**, 597 (1953); W. T. Simpson and C. W. Looney, *ibid.*, **76**, 6293 (1954).

(28) An alternative theory, which is qualitatively in agreement with structures I and II for ground and excited states and which would lead to the same interpretation of the results, is the charge-transfer absorption theory as expounded particularly by S. Nagakura and associates: S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, *ibid.*, **23**, 1441 (1955); J. Tanaka, S. Nagakura and M. Kobayashi, *ibid.*, **24**, 311 (1956).

TABLE II

GAS PHASE SPECTRA

Compound	λ_{max}, mμ	ν_{max}, cm.$^{-1}$ [a,b]	ϵ_{max} [c]
Acetophenone	231.3	43,230	7,800
p-Methyl-	238.9	41,860	13,200
p-Ethyl-	239.5	41,750	14,000
p-Isopropyl-	239.7	41,720	14,800
p-*t*-Butyl-	239.8	41,700	15,600
Nitrobenzene	239.9	41,680	7,600
p-Methyl-	250.2	39,970	9,000
p-Ethyl-	251.0	39,840	9,300
p-Isopropyl-	251.3	39,790	9,100
p-*t*-Butyl-	251.5	39,760	9,600

[a] Differences duplicated to ±20 cm.$^{-1}$ (approx. ±0.1 mμ). [b] Average of three separate runs. [c] Only approximate.

TABLE III

VALUES OF ν_{max} (CM.$^{-1}$) AND ϵ_{max} FOR *p*-ALKYLNITROBENZENES IN VARIOUS SOLVENTS[a]

	ν [b]	$\epsilon \times 10^{-2}$ [c]	ν	$\epsilon \times 10^{-2}$	ν	$\epsilon \times 10^{-2}$
	Heptane		Cyclohexane		*t*-AmOH	
t-Bu	37670	114	37510	113	36700	105
i-Pr	+30	109	10	108	0	103
Et	70	100	50	102	20	99
Me	200	98	190	97	80	95
H	2030	86	2030	85	2100	80
	t-BuOH		n-BuNH$_2$		Dioxane	
t-Bu	36710	103	36490	..	36480	104
i-Pr	−20	106	10	..	−10	105
Et	0	100	30	..	10	99
Me	60	94	80	..	70	97
H	2080	80	...	..	2170	86
	HOAc		MeOH		95% EtOH	
t-Bu	36420	103	36400	104	36400	102
i-Pr	−10	99	−30	104	−50	100
Et	+10	99	0	98	−30	95
Me	60	97	60	97	50	93
H	2170	82	2140	82	2130	81
	CH$_3$CN		2/1 HOAc/ H_2SO_4		HCO_2H	
t-Bu	36130	103	35580	..	35370	99
i-Br	−30	99	...	..	−30	99
Et	−10	98	...	..	−10	95
Me	50	95	80	..	110	94
H	2150	80	2310	..	2360	82
	1/1 HOAc/ H_2SO_4		H_2O		60% $HClO_4$	
t-Bu	35250	..	35090	95	33840	93
i-Pr	...	..	−70	95	−30	96
Et	...	..	−70	92	30	92
Me	90	..	10	90	130	87
H	2410	..	2350	76	2660	76
	70% $HClO_4$ [d]					
t-Bu	32880	95				
i-Pr	−40	97				
Et	20	93				
Me	140	89				
H	2840	76				

[a] The absolute values of ν are given for *t*-butyl; the others are relative to *t*-Bu. [b] Estimated precision in differences, ±20 cm.$^{-1}$ or less. [c] Estimated precision in ϵ, 3–5%. [d] No detectable amount of solute conjugate acid present.

TABLE IV

VALUES OF ν_{max} (CM.$^{-1}$) AND ϵ_{max} FOR *p*-ALKYLACETOPHENONES IN VARIOUS SOLVENTS[a]

	ν [b]	$\epsilon \times 10^{-2}$ [c]	ν	$\epsilon \times 10^{-2}$	ν	$\epsilon \times 10^{-2}$
	Heptane		Cyclohexane		CH$_3$CN	
t-Bu	40290	176	40230	174	39970	163
i-Pr	30	164	10	168	−10	160
Et	60	162	40	162	30	151
Me	160	151	150	150	110	148
H	1690	123	1710	120	1740	126
	t-BuOH		95% EtOH		HOAc	
t-Bu	39610	168	39480	171	39340	158
i-Pr	−10	156	−10	157	0	153
Et	40	158	30	155	30	148
Me	120	149	120	148	110	144
H	1810	122	1810	120	...	..
	H_2O		50% $HClO_4$ [d]			
t-Bu	38950	156	38200	137		
i-Pr	−30	155	−10	132		
Et	−20	150	30	126		
Me	70	142	100	123		
H	1870	119	2020	115		

[a] Absolute values of ν given for *t*-butyl; the others are relative to *t*-butyl. [b] Estimated precision, ±20 cm.$^{-1}$. [c] Estimated precision, ±3–5%. [d] No conjugate acid present.

erations, the general and accepted practice of using the absorption maximum to indicate the entire band position has been followed.[26]

Gas Phase Spectra.—The observed absorption maxima are listed in Table II. The excitation energy of each *p*-alkyl compound is considerably lower than that of the unsubstituted member of the series; *i.e.*, the effect of a *p*-alkyl substituent in place of *p*-hydrogen is to stabilize the more highly electron-demanding excited state II to a greater extent than the ground state I.[29] The differences in excitation energies among the *p*-alkyl compounds of each series are, of course, much smaller than those between alkyl and hydrogen, but are nevertheless significant. The smallest differences, those between the *p*-isopropyl and *p*-*t*-butyl compounds, are just outside the experimental error. The largest difference, that between nitrotoluene and *p*-*t*-butylnitrobenzene, is equivalent to 600 cal./mole. The data show that among the alkyl compounds of each series, stabilization of excited over ground state is in the inductive order, despite the presumed large demand for electron release placed upon alkyl in the excited state. Furthermore, the spread between *t*-butyl and methyl compounds is significantly greater for the nitrobenzenes than for the acetophenones. Presumably this is due to the greater electron demand of the nitro group (in excited *versus* ground state). It is to be noted that for the conjugate acids of the acetophenones and nitrobenzenes measured in acidic solution, the spread in excitation energies in the inductive order is further increased.[4,5]

In Fig. 1 are plotted the excitation energy maxima in wave numbers for the acetophenones against those of the nitrobenzenes. The line drawn includes the point for *p*-hydrogen which lies at a

(29) The *p*-alkyl group affords an additional source, besides the ring, from which the excess charge on the nitro or acetyl group can be drawn. Presumably, *most* of this charge *still* comes from the ring.

considerable distance removed from the points for the *p*-alkyl substituents. By use of the Hammett free energy relationship, $\log k_R - \log k_H = \sigma\rho$, with ν-values being substituted for $\log k$, it readily can be shown that the slope of the line is the ratio of the "reaction" constants for the acetophenone to the nitrobenzene series. The term reaction is used here to include spectral excitation processes. It can be concluded from the linearity of this plot that, within the experimental error, of course, and within the change in electron demand in proceeding from the acetophenone to the nitrobenzene series, the alkyl groups studied are responding in linear proportion to the demand. Thus for this gas phase system, there is no evidence that one mode of electron release by alkyl (*e.g.*, C–H hyperconjugation) is becoming more predominant over others as the electron demand is increased.

The fact that the inductive order was observed for the gas phase excitation energies may mean that C–C hyperconjugation is here more effective than C–H hyperconjugation. On the other hand, the release may be entirely inductive. It could be maintained that the large red shift produced when an alkyl group is substituted for *p*-hydrogen indicates that an alkyl group is a conjugating group. It has been stated by some that the inductive effect has little influence on spectral excitation energies. The basis for this statement is the fact the introduction of $-NH_3^{\oplus}$ and similar substituents usually causes little shift of the principal band of benzene derivatives in solution[30] (see, however, reference 7b). The $-NH_3^{\oplus}$ substituent presumably cannot conjugate (although hyperconjugation structures can be written), but has a powerful inductive effect. However, the conclusion that the inductive effect is unimportant in electronic excitation by light should be accepted with reservation, in view of the possibly strong solvation effects brought into play by the introduction of this ionic group.

Solution Spectra.—A classification of solvent effects on the principal band has been made recently by Bayliss and McRae.[26] For solutes such as nitrobenzene, in which the dipole moment increases during light excitation (equation 1), there is a general shift to the red (higher wave length, lower excitation energy) of the principal band, in solution as compared to gas. The ground state is viewed as being stabilized by the solvent, by dipole–polarization and dispersion forces in non-polar solvents and, in addition, by more powerful dipole–dipole and hydrogen bonding forces in polar solvents. According to the Franck–Condon principle, crudely stated, the solvent nuclei (as well as solute nuclei) have no time to move in the time of light excitation although electronic polarization of solvent molecules is allowed. However, solvent molecules in position to solvate polar sites in the ground state of solutes such as nitrobenzene are in a position to solvate more strongly the sites of increased polarity in the excited state. Thus the excited state is stabilized more than the ground state, and a solvent red shift is observed.[26] Solvation of the ground state is presumed relatively strong at the polar substituent (nitro or acetyl)

(30) L. Doub and J. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

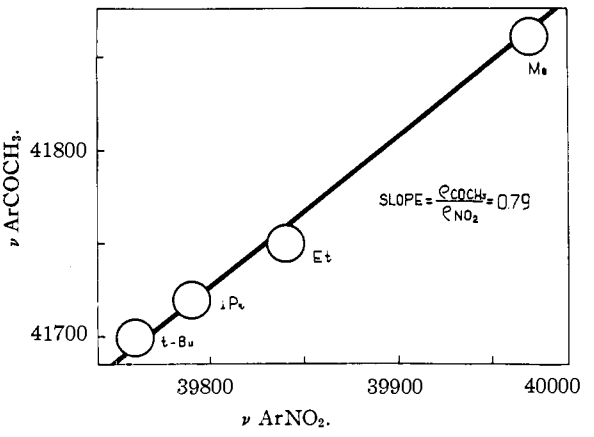


Fig. 1.—Plot of maximum frequencies (cm.$^{-1}$) for *p*-alkylacetophenones against *p*-alkylnitrobenzenes.

and relatively weak at partially positive sites at or near the *p*-alkyl substituent. However, changes in solvation at the alkyl substituent as the substituent is changed (due, for example, to either the changing bulk or the changing number of α-hydrogens) would be reflected in a change in the *relative* excitation energies of the alkyl compounds.[31]

Turning attention to the data of Tables III and IV, it is seen that the general solvent red shift with respect to gas is least in the non-polar, hydrocarbon solvents. This is in agreement with the observations on nitrobenzene by Bayliss and McRae.[32] In the hydrocarbon solvents, as in the gas, the inductive order of excitation energies is observed for both the nitrobenzenes and acetophenones. In fact, the spreads in excitation energies are about the same in the hydrocarbon solvents as in the gas, for both series. This result is not unexpected, since in these solvents solvation of the ground state, and hence also excited state, would be expected to be negligibly weak at R.

In polar solvents, two effects are to be noted. Firstly, there is a greater red shift with respect to the gas for all the compounds of each series. This has been observed previously for nitrobenzene and is attributed to a further increase in solvent stabilization of the excited over the ground state.[32] Secondly, the red shift is not the same for each alkyl compound, particularly in the basic solvents. This is illustrated in Fig. 2, in which is plotted the ν_{max} values for *p*-alkylnitrobenzenes *relative to* *p*-*t*-butylnitrobenzene. The greatest effect observed is that in water. In going from gas phase to water solution, solvent stabilization of excited over ground state, *relative to* that of *p*-*t*-butylnitro-

(31) The Franck–Condon excited state, *i.e.*, the state attained in *observed* light absorption, is not an equilibrium state. The equilibrium excited state, a lower energy state than the Franck–Condon state, is reached only after the solvent molecules have had time to reorient most favorably to the new disposition of charge in the excited state. It is apparent that operation of the Franck–Condon principle would make the appearance of a Baker–Nathan effect much less frequent in spectral than in rate studies. Energy differences between ground and equilibrium excited states should show the Baker–Nathan effect more frequently. Such energy differences could perhaps become accessible by a study of both adsorption and emission spectra on suitable systems. A complicating feature is that the emission energy observed would be that to a Franck–Condon ground state.

(32) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1006 (1954).

benzene, is 200 cm.$^{-1}$ (600 cal./mole) for nitrotoluene, 150 cm.$^{-1}$ for *p*-ethylnitrobenzene and 100 cm.$^{-1}$ for *p*-isopropylnitrobenzene. The order of solvent stabilization of excited state over ground is: CH_3 > Et > *i*-Pr > *t*-Bu. As a net result the excitation energies in water show a "jumbled" order tending toward the C–H hyperconjugative order. The trend in the other basic solvents is similar, though not as pronounced. In the strongly acidic solvents such as 70% perchloric acid, the excitation energies tend to revert back to the inductive order, despite the increased electron deficiency of the ring brought about by strong acidic solvation of the nitro group. Apparently, the weakly basic properties of the solvent result in less efficient solvation of the electron-deficient aromatic ring and/or alkyl group.

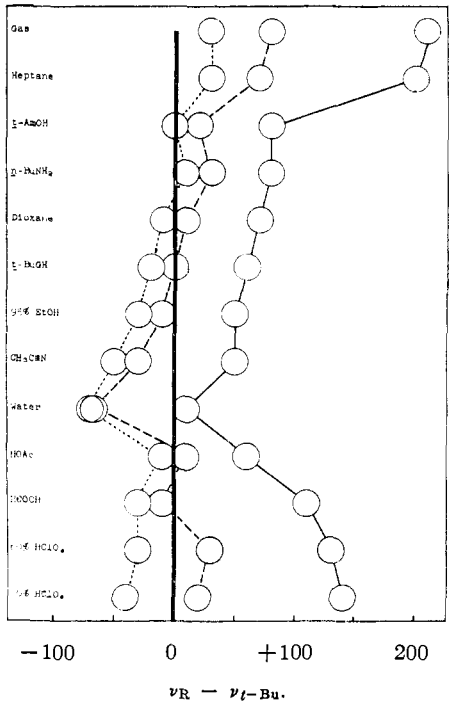


Fig. 2.—Plot of differences $\nu_R - \nu_{t\text{-Bu}}$ for the nitrobenzenes in various solvents: zero line, *t*-Bu; —, Me; — —, Et; ---, *i*-Pr.

The effects observed in the acetophenone series parallel those found in the nitrobenzene series. However, they are less pronounced, presumably because solvation at or near R by basic species is called upon less strongly with the more weakly electron-demanding acetyl group. The maximum intensities for the two series, not accurately measured, appear very roughly to follow the same trends as the maximum frequencies.

The first conclusion to be reached is that the solvent has a considerable influence on the apparent relative activating effect of the alkyl groups in these systems and probably in other systems as well. Therefore, the explanation of alkyl group effects advanced by Burawoy and Spinner[7] must be regarded as incomplete, at best. Their explanation ignores the role of the solvent, except possibly insofar as the solvent may change the electron demand on alkyl.[33]

The second conclusion that can be made from a *qualitative* consideration of the results is: *either* steric hindrance to solvation *or* hydrogen bonding to the α-hydrogens of the alkyl group can be responsible for the solvent effect. This follows from (1) the fact that the order of solvent stabilization of excited over ground state is CH_3 > Et > *i*-Pr > *t*-Bu and that the greatest effect is exerted generally in basic solvents and (2) the observation that the solvent stabilization order is both the order of increasing bulk and of decreasing numbers of α-hydrogens. Of course, the degree of solvation of acidic sites (in the aromatic ring and, possibly, the alkyl substituent) is not a simple function of solvent basicity but also depends on a number of other closely interrelated factors such as (1) the extent to which acidic solvation of the nitro or acetyl group affects the electron deficiency, *i.e.*, acidity, of the aromatic ring and thus changes the *demand* for basic solvation as well as for electron release by alkyl; and, (2) the size and shape of the basic solvating species as well as of substrate species. The fact that the Baker–Nathan effect is less pronounced in *n*-butylamine than in some of the less basic solvents such as ethanol is attributable to the greater acidity of the aromatic ring (in the ground state) in the latter solvent. The stronger over-all solvation of the substrate in ethanol as compared to *n*-butylamine is reflected in the fact that the excitation energies are lower in ethanol than in *n*-butylamine. The fact that the Baker–Nathan effect is apparently slightly more pronounced in *t*-butyl or *t*-amyl alcohol than *n*-butylamine could also be attributed in part to greater sensitivity of the former solvents to the changing bulk of the *p*-alkyl substituent.

A quantitative treatment of the data is made in the next section in an effort to determine if the experimental results can lead to a choice between the explanations of steric hindrance to solvation and solvent enhancement of C–H hyperconjugation.

Quantitative Treatment.—The following related linear free energy equations, 2, 3 and 4, were applied to the spectral data.

$$\log \frac{k_x}{k_x^\circ} = Q_x \log \frac{k_H}{k_H^\circ} \quad (2)$$

$$\log \frac{k_x}{k_x^\circ} - \log \frac{k_H}{k_H^\circ} = \gamma_x \log \frac{k_H}{k_H^\circ};\ \gamma_x = Q_x - 1 \quad (3)$$

$$\log \frac{k_x}{k_x^\circ} - \log \frac{k_H}{k_H^\circ} = \beta_x \log \frac{k_x}{k_x^\circ};\ \beta_x = \frac{Q_x - 1}{Q_x} = \frac{\gamma_x}{Q_x} \quad (4)$$

$$\log \frac{k_x}{k_x^\circ} - \log \frac{k_H}{k_H^\circ} \equiv \log \frac{k_x}{k_H} - \log \frac{k_x^\circ}{k_H^\circ} = \sigma_x(\rho - \rho_0) \quad (5)$$

(33) In a polar solvent there is presumably an increased demand for electron release placed upon the *p*-alkyl substituent, due, for example, to increased hydrogen bonding at the polar substituent. It could be maintained that this gives more opportunity for the operation of steric hindrance to bond shortening in the alkyl group. However, a necessary part of the argument of Burawoy and Spinner, in comparing spectral and rate data, is the invoking of the Franck–Condon principle for spectral excitation; *i.e.*, movement of atomic nuclei of the solute is negligible in the time of electronic excitation, therefore steric hindrance to bond shortening is not operative. Furthermore, in the acidic solvents (*e.g.*, 70% perchloric acid), in which the demand placed upon release by alkyl is greatest, the inductive order of excitation energies tends to be restored.

The quantities Q_x, γ_x β_x are defined as substituent constants for a *m*- or *p*-substituent, X, in a benzene derivative. For X = H, Q_x has the value unity, and γ_x and β_x have the value zero. Values of these substituent constants could be obtained in either of two ways. Firstly, the reaction can be kept constant and the solvent varied. In that case, k_H° and k_x° are rate or equilibrium constants (or for spectral data, ν is used instead of log k) for the unsubstituted and substituted compounds for a particular reaction in a standard solvent; k_H and k_x are values obtained for the same reaction in any other solvent. Alternately, the solvent can be kept constant and the reaction varied.

Equations 2, 3 and 4 resemble the linear free energy relationships of Grunwald and Winstein, Gutbezahl and Grunwald, and Swain[34-36] but differ from the latter in their application and in the fact that they define substituent constants. As seen from equation 5, equations 2, 3 and 4 are related to the Hammett equation; *i.e.*, either (1) γ_x or β_x is equal to $\pm$ σ_x, or a proportionality exists between σ_x and either γ_x or β_x or between σ_x and both γ_x and β_x.

In Fig. 3 is shown a plot of equation 3 for nitro-

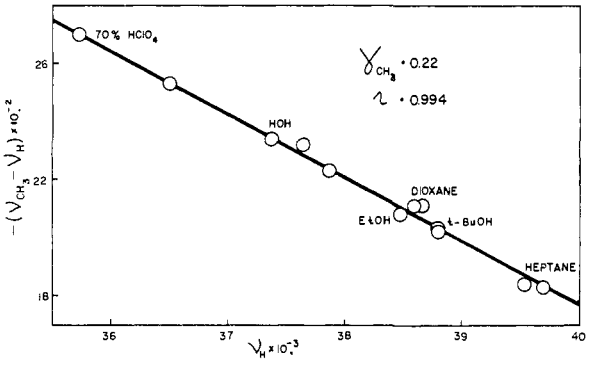


Fig. 3.—Plot of $\nu_{CH_3} - \nu_H$ against ν_H for nitrotoluene in various solvents.

toluene, using solution data in Table III, and substituting ν_{max} values for log k values. The least squares slope, γ_{CH_3}, is 0.22 with a correlation coefficient r = 0.994. For the *p*-methylacetophenone data of Table III, γ_{CH_3} is 0.20, with r = 0.996. Over the wide range of solvents used, the decrease in ν_{max} for nitrotoluene in proceeding from heptane to 70% perchloric acid amounts to 13,900 cal./mole. If it is granted that the linearity of the γ-plot for nitrotoluene (or *p*-methylacetophenone) is a result of a linearity between the response of the excitation energies of the methyl and unsubstituted compounds to solvent change, then it follows that the methyl substituent is releasing electrons in linear proportion to changing electron demand (ρ changing with solvent) over a very considerable change in medium. Thus it would appear that either: (1) the methyl group is releasing electrons by a single mechanism or (2) if more than one mechanism is operative, these are acting in constant proportion with changing solvent. Therefore, the concept of solvent enhancement of C–H hyperconjugation (which should be greatest with the basic hydrogen-bonding solvents) does not satisfactorily explain the results for this system. It follows also that steric hindrance to solvation is negligible with the methyl substituent.

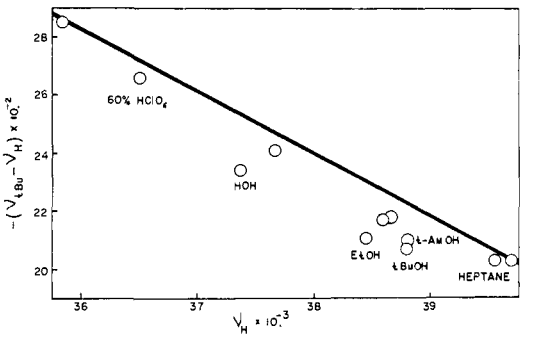


Fig. 4.—Plot of $\nu_{t-Bu} - \nu_H$ against ν_H for *t*-butylnitrobenzene in various solvents.

In Fig. 4 is shown a γ-plot for *p*-*t*-butylnitrobenzene in the same solvents. An arbitrary line has been drawn between the two points for the least basic solvents at the two extremes, heptane and 70% perchloric acid. This plot and the one for *p*-*t*-butylacetophenone show considerably more scatter than those for the corresponding methyl compounds, the scatter being much greater than the experimental error. The *p*-isopropyl and ethyl compounds show intermediate scatter. The scatter could be attributed either to a non-constancy of γ_{tBu}, or to a disproportionate change with solvent of the "reaction" constant for *p*-*t*-butylnitrobenzene as compared to nitrobenzene. It is considered unlikely that the scatter is due to direct solvation of the *t*-butyl group bringing about a change in the substituent constant with solvent. However, if the "reaction site" is considered to be the entire molecule (with its adhering solvent) except for the substituent, then the scatter is consistent with the view that steric hindrance to solvation of the aromatic ring is causing a disproportionate change, with changing solvent, of the reaction constant for *t*-butylnitrobenzene as compared to nitrobenzene.[37]

It is to be noted that γ_{CH_3} has about the same magnitude as σ_{CH_3} (σ_{CH_3} = −0.17)[38] but is opposite in sign. A rationalization of the sign of γ_{CH_3} can be made in terms of equations 3 and 5. The alternate use of equation 3 for a series of "reactions" in a constant solvent was applied to the gas phase spectra. Although values based on only two points (for electronic excitation of acetophenones and of nitrobenzenes) could hardly be considered valid, the values obtained are γ_{CH_3} = 0.21; γ_{tBu} = 0.25. The β-plot (equation 4), applied to the solution data for *p*-nitrotoluene, gives β_{CH_3} = 0.18. The possible general usefulness of equations

(34) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).
(35) B. Gutbezahl and E. Grunwald, *ibid.*, **75**, 559 (1953).
(36) C. G. Swain, D. C. Dittmer and L. E. Kaiser, *ibid.*, **77**, 3737 (1955).

(37) The effect of the bulky substituent could be viewed as one of "prying" away the solvent layer adhering to the electron deficient aromatic ring.
(38) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

2, 3 and 4 and the relationship between the various substituent constants and σ is being actively explored.

Acknowledgment.—The authors wish to thank Dr. W. T. Simpson for helpful discussions of ultraviolet spectra and for his examination of the manuscript in advance of publication.

SEATTLE 5, WASHINGTON

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

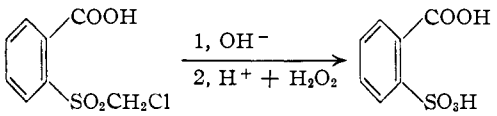
Participation of the Carboxylate Group in the Displacement of Chlorine in *o*-(Chloromethylsulfonyl)-benzoic Acid[1]

BY F. G. BORDWELL AND GLENN D. COOPER

RECEIVED SEPTEMBER 10, 1956

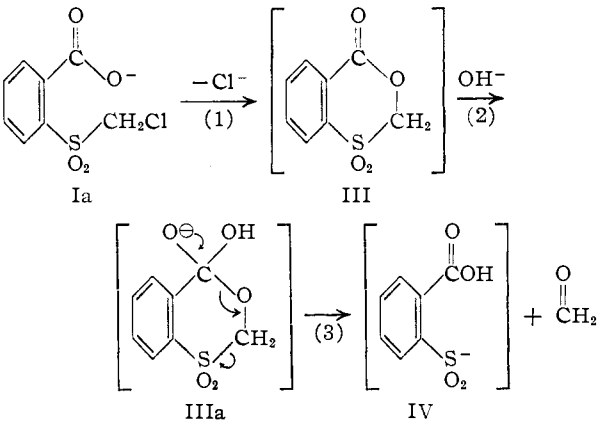
The fairly rapid release of chloride ion, at 100°, in neutral solution from *o*-(chloromethylsulfonyl)-benzoic acid, in contrast to the failure of release of any chloride ion from the *para* isomer under comparable conditions is interpreted as evidence for participation of the carboxylate ion in the reaction. Evidence from approximate rate data indicates that participation of the carboxylate ion may be increased by hydroxide ion.

The inertness of the halogen in chloromethyl phenyl sulfone to nucleophilic displacement[2] and the stereoselective sodium borohydride reduction of 2-(*p*-tolysulfonyl)-cyclohexanone[3] indicate that the phenylsulfonyl group is capable of exerting a large steric effect. In view of this, the observation[4] that the halogen could be released almost quantitatively from *o*-(chloromethylsulfonyl)-benzoic acid (I) by heating at 100° for 4 hr. in alkaline medium aroused our interest. *o*-Carboxybenzenesulfinic acid and formaldehyde are the initial products of this reaction, and *o*-sulfobenzoic acid (II) may be produced in high yield by mild oxidation of the reaction mixture.[4]



I II

The halogen in I is considerably more reactive than that in phenyl chloromethyl sulfone itself,[2] whereas models suggest that the *o*-carboxyl group should greatly increase the hindrance to attack by hydroxide ion, particularly since the group would bear a negative charge in neutral or alkaline solution. This suggested the probability of an intramolecular displacement,[5] with the carboxylate anion participating in the displacement in the manner shown in step 1. The rough kinetic measurements presented herein confirm this viewpoint.



Ia III IIIa IV

The participation by the carboxylate group in Ia was made evident by the fairly rapid release of chloride ion at 100° in *neutral solution*, whereas no reaction was observed for the *p*-isomer, *p*-$HOOCC_6H_4SO_2Cl$, under comparable conditions.

The pK_a's for the *o*- and *p*-chloromethylsulfonylbenzoic acids were found to be 2.38 and 3.44, respectively, at 25°.[6] The σ-constant for the *p*-$ClCH_2SO_2$ group is slightly greater than that for the *p*-CH_3SO_2 group[7] (+0.78 *vs.* +0.72), which is to be expected, since substitution of a Cl for H in CH_3SO_2 should lead to slightly more electron attraction.

Chloride ion is released from 0.16 *N* aqueous solutions of *o*-chloromethylsulfonylbenzoic acid at a rate about one-fourth that in neutral solution. This is the order of magnitude expected for intramolecular displacement by the carboxylate anion, since the acid is about 15% dissociated at this concentration.

In 2 *N* sodium hydroxide solution the release of chloride ion from Ia was about twice that observed in neutral solution. The increase in rate does not appear to be due to a salt effect, since an equivalent

(1) This investigation was supported by the Office of Naval Research under Contract No. N7-onr-45007.

(2) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **73**, 5184 (1951).

(3) J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3468 (1956).

(4) B. B. Lampert, Ph.D. Dissertation, Northwestern University, June, 1951.

(5) Sterically hindered halides are known to undergo intramolecular displacements. For example, 1,1-dimethylcyclopropane is formed by the reaction of sodium and neopentyl chloride [F. C. Whitmore, A. H. Popkin, H. I. Berstein and J. P. Wilkins, *ibid.*, **63**, 124 (1941)], and the halogen is released readily from alkyl α-haloalkyl sulfones by an intramolecular mechanism [F. G. Bordwell and G. D. Cooper, *ibid.*, **73**, 5187 (1951)].

(6) We wish to thank Dr. Pierre J. Boutan for making these determinations.

(7) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952).