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Solvent and Substituent Effects. The Neopentyl and Other β-Branched Alkyl Groups and their Effect on the "Principal" Ultraviolet Transition[1]

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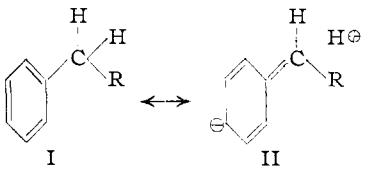
It has been found that in the principal ultraviolet transition of *p*-alkylnitrobenzenes (gas phase), 4-alkylpyridinium ions and 4-alkyl-1-hydroxypyridinium ions, the neopentyl group is inherently a considerably better electron donor than *t*-butyl or methyl. The observed excitation energies are in the order: neo-P < *i*-Bu < Pr < Et < Me. A detailed examination of the solution data indicates that steric hindrance to solvation may be a factor in the apparent effect of these substituents.

For alkyl substituents of the type RCH_2, it has been found that increased branching at the β-carbon atom leads to a lowering of the rate constant for a number of reactions in solution in which the transition state is electron demanding relative to the ground state. These reactions include (1) bromine addition to ethylenes, in which neopentylethylene is about ten times less reactive than *n*-butylethylene[3]; (2) bromination of alkylbenzenes,[4] and solvolysis of *p*-alkylbenzhydryl halides,[5] in which the order of rates is: Et (fastest) > *n*-Pr > isoBu > neoP; and (3) the reaction of $RCHBrCH_3$ in ethanol containing 1 *N* sodium ethoxide, for which both substitution and elimination rates are in the order: Et (fastest) > *n*-Pr > isoBu > neoP.[6] In addition, it has been found that the retardation of rate accompanying α-deuterium substitution is less for the neopentyl than the ethyl group.[7] Similarly, ratios of solvolysis rates of α-deutero-*p*-alkylbenzhydryl chlorides compared to the corresponding protium analogs fall off in the order $CD_3 > CH_3CD_2 > (CH_3)_2CHCD_2 > (CH_3)_2CD$. The isotope effects are positive (*i.e.*, $k_H/k_D > 1$) and of the order of 6% or less.[8]

The retarding effect of increased branching at the β-position, observed in the above reactions, has been attributed to a number of different factors: (1) second-order hyperconjugation[4]; (2) steric hindrance to bond shortening[9]; (3) steric shielding of the reaction center[10]; (4) steric interference with solvent enhancement (by hydrogen bonding with the α-hydrogens of the alkyl group) of hyperconjugation[8]; (5) steric hindrance to solvation of electron deficient sites near the alkyl substituent, coupled with inherent release by alkyl substituents in the inductive *order*[11a,b,c]; and (6) steric inhibition of hyperconjugation.[7,12]

With regard to steric inhibition of hyperconjugation, Arnold and Truett,[12a] and Baddeley and Gordon,[12b] consider hyperconjugation to be a maximum when the conformation of the molecule is such that the formal contributing valence bond structure with a double bond between the alkyl group and the unsaturated system can make its maximum contribution; *e.g.*, when R in structure I⟷II is in the plane of the ring. Thus when R is large, as in the neopentyl group, steric interference with coplanarity of the R and phenyl groups leads to a lessened contribution by II. An essentially similar



I II

viewpoint is that maximum hyperconjugative release by an α-C–H of the alkyl group occurs when the C–H bond lies parallel to the adjacent π-orbital of the unsaturated system[13]; and that the end methyl groups of the neopentyl substituent hinder the approach of the methylene group to the proper orientation for this.[7] On the other hand, Jaffé has concluded that hyperconjugation is relatively insensitive to the conformation of the alkyl group.[14]

Because of the recent demonstration that inherent alkyl substituent effects may be masked or considerably modified by solvent,[7,8,11] it was considered desirable to study the effect of branching in the β-position in a gas phase reaction in which a large demand for electron release is placed upon the substituent. As in a previous study of other alkyl substituents, the "reaction" chosen for convenient study was the gas phase ultraviolet excitation of *p*-alkylnitrobenzenes that results in the so-called principal ultraviolet band in the spectrum.[11c] This band has been identified as due to a dipolar transition, with the transition moment lying in the long axis of the molecule.[15] The valence bond depiction of this excitation, equation 1, is only an approximate representation of the excitation process. However, it at least conveys the idea that on excitation there is an increase in polarity in the direction of the nitro group.[11c]

To determine the perturbing influence of solvent

(1) Presented in part at the 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 8–13, 1957.

(2) Du Pont Fellow, 1955–1956.

(3) P. W. Robertson, J. K. Heyes and B. E. Swedlund, *J. Chem. Soc.*, 1014 (1952).

(4) E. Berliner and F. Berliner, THIS JOURNAL, **72**, 222 (1950).

(5) V. J. Shiner, Jr., and C. J. Verbanic, *ibid.*, **79**, 369 (1957).

(6) V. J. Shiner, Jr., M. J. Boskin and M. L. Smith, *ibid.*, **77**, 5525 (1955).

(7) V. J. Shiner, Jr., *ibid.*, **78**, 2654 (1956).

(8) V. J. Shiner and C. J. Verbanic, *ibid.*, **79**, 373 (1957).

(9) A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954).

(10) C. C. Price and W. J. Belanger, THIS JOURNAL, **76**, 1014 (1954).

(11) (a) W. A. Sweeney and W. M. Schubert, *ibid.*, **76**, 4265 (1954); (b) *J. Org. Chem.*, **21**, 119 (1956); (c) W. M. Schubert, J. Robins and J. L. Haun, THIS JOURNAL, **79**, 930 (1957).

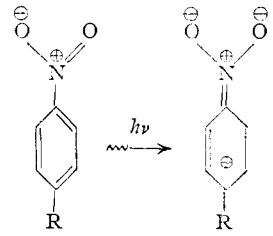
(12) (a) R. T. Arnold and W. L. Truett, *ibid.*, **73**, 5508 (1951); (b) G. Baddeley and M. Gordon, *J. Chem. Soc.*, 2191 (1952).

(13) See, *e.g.*, C. A. Coulson, "Valence," Oxford Press, Oxford, 1952, p. 312.

(14) H. H. Jaffé and J. L. Roberts, THIS JOURNAL, **79**, 391 (1957).

(15) A. G. Albrecht and W. T. Simpson, *J. Chem. Phys.*, **23**, 1480 (1955); THIS JOURNAL, **77**, 4455 (1957).

on the excitation energy, the position of the principal band of *p*-neopentylnitrobenzene also has been measured in a variety of solvents. In addition, solution spectra of certain 4-alkylpyridinium perchlorates and 4-alkyl-1-hydroxypyridinium ions were studied.



(1)

Experimental

p-Alkylnitrobenzenes.—Neopentylbenzene was prepared by the method of Berliner.[16] The procedure of Nelson and Brown was applied in the nitration of propylbenzene, isobutylbenzene and neopentylbenzene.[17] Purification of the nitro compounds was achieved by steam distillation, then fractionation through a 40-plate spinning band column followed by five low temperature recrystallizations from methanol. The infrared spectra, in the strong out of the plane bending frequencies of aromatic C–H bonds, showed the absence of *o*- or *m*-isomers.[18]

The following physical properties were observed: *p*-propylnitrobenzene, b.p. 141.5–142° (10 mm.), $n^{25}D$ 1.5362, m.p. −14° (lit.[19] b.p. 154° (20 mm.)); *p*-isobutylnitrobenzene, b.p. 141–141.5° (8 mm.), $n^{25}D$ 1.5290, m.p. −34° (lit.[20] b.p. 125° (3 mm.), $n^{25}D$ 1.5299[21]). *p*-Neopentylnitrobenzene, a new compound, had m.p. 29°.

Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.38; H, 7.83. Found: C, 68.52; H, 7.85.

Oxidation of a 1-g. sample of *p*-neopentylnitrobenzene by hot sodium dichromate in sulfuric acid gave a 70% yield of *p*-nitrobenzoic acid, m.p. 239°, identical with an authentic sample.

Pyridinium Perchlorates.—Pyridine and γ-picoline were commercially available (C.P., Baker Chemical). The method of Osuch and Levine[22] was applied to the preparation of the other 4-alkylpyridines. Purification was achieved by fractionation through a 40-plate spinning band column: 4-ethylpyridine, b.p. 110° (130 mm.), $n^{25.5}D$ 1.4997 (lit.[23] b.p. 168° (751 mm.), $n^{20}D$ 1.5020); 4-propylpyridine, b.p. 74° (12 mm.), $n^{25.5}D$ 1.4935 (lit.[22] b.p. 79–84° (22 mm.)). The new compound, 4-neopentylpyridine, was obtained in 20% yield, b.p. 134° (101 mm.), $n^{25.5}D$ 1.4902. The parent peak in the mass spectrum (Consolidated Engineering Co. mass spectrometer, model no. 21–103) occurred at mass 149; calcd. mol. wt. 149.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13. Found: C, 80.57; H, 9.93.

The new compound, 4-(2,2-dimethylbutyl)-pyridine, was obtained in 20% yield, b.p. 156° (103 mm.), $n^{25.5}D$ 1.4958. The perchlorate salt was analyzed.

The perchlorate salt of each pyridine was prepared by the addition of the pyridine to cold 50% perchloric acid. Water was removed under reduced pressure and the resulting white precipitate separated by suction filtration and recrystallized several times from methanol–ether. Pyridinium perchlorate melted at 288–289° uncor. (lit.[24] m.p. 287–288°). The γ-picoline perchlorate melted at 99.8–100.2°.

Anal. Calcd. for $C_6H_8NO_4Cl$: C, 37.50; H, 4.17. Found: C, 37.50; H, 4.28.

The 4-ethylpyridinium perchlorate melted at 78–78.5°. *Anal.* Calcd. for $C_7H_{10}NO_4Cl$: C, 40.79; H, 4.85. Found: C, 40.60; H, 4.79.

The 4-propylpyridinium perchlorate melted at 50–50.5°. *Anal.* Calcd. for $C_8H_{12}NO_4Cl$: C, 43.67; H, 5.46. Found: C, 43.45; H, 5.39.

The 4-neopentylpyridinium perchlorate melted at 120.7–121.2°. *Anal.* Calcd. for $C_{10}H_{16}NO_4Cl$: C, 48.10; H, 6.46. Found: C, 48.05; H, 6.45.

The 4-(2,2-dimethylbutyl)-pyridinium perchlorate melted at 79.0–79.3°. *Anal.* Calcd. for $C_{11}H_{18}NO_4Cl$: C, 50.46; H, 6.88. Found: C, 50.01; H, 6.79.

Pyridinium-1-oxides.—These hygroscopic compounds were prepared from the corresponding pyridines by the method of Ochiai.[24a] Pyridine-1-oxide was fractionally distilled through a 40-plate spinning band column, b.p. 142° (14 mm.), then repeatedly sublimed under reduced pressure, m.p. 66–67° (lit.[25] m.p. 67°). The γ-picoline oxide was recrystallized three times from ethyl acetate–methanol, m.p. 165–165.5°.

Anal. Calcd. for C_6H_7NO: C, 66.03; H, 6.47. Found: C, 66.22; H, 6.43.

The 4-neopentylpyridine-1-oxide was distilled, b.p. 169° (6 mm.), recrystallized from hexane, and then twice sublimed under 1 mm. pressure, m.p. 97–98°.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.68; H, 9.15. Found: C, 72.82; H, 9.12.

Spectral Determinations.—Spectral measurements were made as previously described, using a Beckman DU spectrophotometer equipped with a fused quartz prism and a photomultiplier.[11c] An air-thermostated cell compartment was used for the gas phase spectral determinations rather than the water-bath as previously. Values of ν_{max} were determined in the graphical manner already described.[11c]

Results

The principal band of the nitrobenzenes was structureless and quite symmetrical about the peak, even in the gas phase.[11c] Some remnants of the so-called B-band ($A_{1g} - B_{2u}$) were observed around 270 mμ, but this in no way seemed to influence the position of the principal band. Also, transitions occurring at shorter wave lengths did not interfere. Consequently, the generally accepted practice of using the absorption maximum to indicate the entire band position has been followed. The gas phase and solution data are summarized in Tables I and II.

TABLE I

VALUES OF ν_{max} IN CM.$^{-1}$ FOR THE PRINCIPAL BAND OF *p*-$RC_6H_4NO_2$ IN GAS AND IN HEPTANE[a,b]

R	Gas phase,[c,d] λ_{max}, mμ	Gas phase,[c,d] ν_{max}	Heptane ν_{max}
NeoP	253.2	39490	37410
i-Bu	252.5	+110	+140
Pr	251.6	260	260
Et[e]	251.0	350	330
Me[e]	250.2	480	460
H[e]	239.1	2330	2290

[a] Absolute values of ν_{max} are given for neopentyl; the others are relative to neopentyl. [b] Values of ν_{max} are averages of three determinations, duplicatable in gas to ±30 cm.$^{-1}$; in heptane, to ±20 cm.$^{-1}$. [c] Measurements at 80°. Measurements made at 150° were within the experimental error of those at 80°. [d] For *t*-butyl, ν_{max} was 39,760.[11c] [e] Previously reported.[11c]

The principal band for pyridinium perchlorates appears at around 210 mμ and has an ϵ_{max} of about 8,000. The peaks were very symmetrical and rather sharp. The results for these compounds are listed in Table III.

(16) E. Berliner, THIS JOURNAL, **71**, 1195 (1949).
(17) K. L. Nelson and H. C. Brown, *ibid.*, **73**, 5605 (1951).
(18) N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).
(19) G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303 (1935).
(20) T. E. Zalesskaya, *J. Gen. Chem. (U.S.S.R.)*, **17**, 489 (1947).
(21) We are indebted to Mr. Richard B. Murphy for preparing these compounds and determining their spectra.
(22) C. Osuch and R. Levine, THIS JOURNAL, **78**, 1723 (1956).
(23) H. C. Brown and W. A. Murphey, *ibid.*, **73**, 3308 (1951).
(24) A. I. Popov and R. T. Pflaum, *ibid.*, **79**, 570 (1957).
(24a) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).
(25) E. P. Linton, THIS JOURNAL, **62**, 1945 (1940).

TABLE II

VALUES OF ν_{max} IN CM.$^{-1}$ FOR THE PRINCIPAL BAND OF *p*-$RC_6H_4NO_2$ IN SOLVENTS[a,b]

R	*n*-C_7H_{16}	*t*-BuOH	*n*-$BuNH_2$	HOAc	CH_3OH	70% $HClO_4$[c]
NeoP	37410	36450	36300	36180	36060	32580
Me	460	320	270	300	400	440
H	2290	2340	...	2410	2480	3140

R	95% EtOH	CH_3CN	HCO_2H	H_2O	60% $HClO_4$[c]
NeoP	36090	35800	35070	34670	33580
Me	360	380	410	430	390
H	2440	2480	2660	2770	2920

[a] Absolute values of ν are given for neopentyl; the others are relative to neopentyl. Values for nitrobenzene and *p*-nitrotoluene previously reported.[11c] [b] Values of ν_{max} are average of three separate determinations; ν_{max} duplicatable to ±20 cm.$^{-1}$. [c] No detectable amount of conjugate acid present.

TABLE III

VALUES OF ν_{max} IN CM.$^{-1}$ FOR THE PRINCIPAL BAND OF 4-ALKYLPYRIDINIUM PERCHLORATES[a]

4-Group	1% $HClO_4$[b]	CH_3OH[c]	95% EtOH[c]
2,2-Dimethylbutyl	44210	...	...
NeoP	44440	44520	44580
Pr	45320	...	...
Et	45680	45660	45680
Me	46080	45980	46020
H	49700	49080	48340

[a] Average of two determinations; accuracy estimated at ±20 cm.$^{-1}$. [b] The ν_{max} value for 4-*t*-butylpyridinium perchlorate in this solvent was 45,310 cm.$^{-1}$. [c] These solvents contained 1% $HClO_4$.

The principal band of the conjugate acid of the pyridine-1-oxides was to the red of that of the free base and occurred around 220 mμ with an ϵ_{max} of about 5,000. The spectral envelope was symmetrical and did not change in shape upon variation of the 4-substituent. The ν_{max} results for the 1-hydroxypyridinium ions are given in Table IV.

TABLE IV

VALUES OF ν_{max} (CM.$^{-1}$) FOR THE PRINCIPAL BAND OF 4-ALKYL-1-HYDROXYPYRIDINIUM IONS[a,b]

4-Group	70% $HClO_4$	9% $HClO_4$[c]	Acidic CH_3OH[d]	95% EtOH[d]
NeoP	43030	42840	42890	42550
Me	44400	44000	43670	43560
H	46530	45680	45090	44850

[a] Average of two runs; estimated accuracy, ±20 cm.$^{-1}$. [b] The pyridinium oxides were completely in the conjugate acid form in these media. [c] The value for *t*-butyl in this solvent is 43,520 cm.$^{-1}$. [d] These media contained 10% concentrated H_2SO_4 by weight.

Discussion

The Inherent Effect of Neopentyl and Other β-Branched Alkyl Groups.—As noted previously, the effect of *p*-alkyl substitution is to considerably lower the energy of the principal ultraviolet transition of nitrobenzene. This indicates that there is considerably more electron release by the *p*-substituent in the excited state than in the ground state. In comparing *p*-alkyl compounds, it had been found that *in the gas phase* stabilization of the excited state relative to the ground state is in the inductive order: *t*-Bu > *i*-Pr > Et > Me >> H.[11c] The gas phase data of Table I reveal that for *p*-alkyl groups of the type RCH_2 a change in R has qualitatively the same effect as when R is directly attached to the aromatic ring; that is, stabilization of the excited state relative to the ground state decreases regularly in the order: neoP > *i*-Bu > Pr > Et > Me. The results in heptane parallel those in gas (Table I), except, of course, that the principal band position of the entire series has been shifted to the red (*i.e.*, lower energy or frequency). A surprising feature of these results is the relatively large activating effect of the neopentyl group. Thus stabilization of the excited state over the ground state is 480 cm.$^{-1}$ (or 1400 cal.) greater for *p*-neopentyl than for *p*-methyl, whereas *p*-*t*-butyl lowered the excitation energy by a lesser amount, 210 cm.$^{-1}$ (or 600 cal.), relative to *p*-methyl. In addition, the spreads in excitation energy in the series Et to neoP are somewhat larger than found in the series Me to *t*-Bu.[11c] The neopentyl compound retains its position of lowest excitation energy in all the solvents studied, although the $\nu_{NeoP}-\nu_{Me}$ spread is modified (Table II).

For the 4-alkylpyridinium ions in solution (Table III) the effect of changing the alkyl group is qualitatively the same as for the *p*-alkylnitrobenzenes in gas and heptane; *i.e.*, the excitation energies are in the order: neoP (lowest excitation) < Pr < Et < Me; also, *t*-Bu < Et < Me. In addition, the 2,2-dimethylbutyl group has a somewhat greater activating effect than neopentyl in the 4-alkylpyridinium ion series.[26] Fewer alkyl groups are compared in the solution spectra of 4-alkyl-1-hydroxypyridinium ions, but the general trends are the same as for the 4-alkylpyridinium ions (Table IV). It is to be noted that the spreads between excitation energies are greater for the 4-alkylpyridinium ions and 4-alkyl-1-hydroxypyridinium ions than for the *p*-alkylnitrobenzenes. Presumably this reflects a greater demand for electron release placed upon the alkyl group in the excited state (relative to the ground state) of the ions.

It is concluded from the above results that the neopentyl group is *inherently* a more efficient electron-releasing group than either methyl or *t*-butyl, at least in these spectral excitations. Furthermore, the order of electron release by RCH_2 groups is: 2,2-dimethylbutyl (greatest release) > neoP > *i*-Bu > Pr > Et > Me. Therefore, if steric inhibition of hyperconjugation is a factor in determining the electronic effects of these groups, it is not a sufficiently important factor to reduce their inherent electron release tendencies below that of methyl. If inherent substituent effects in spectral excitation reactions are no different in principle from those in ordinary chemical reactions, then one must look elsewhere for an explanation of the apparent relative retarding effect of β-branched groups such as neopentyl in the chemical reactions cited in the Introduction.

In a previous publication it has been suggested that substituent effects may be qualitatively "understood" and perhaps quantitatively correlated by assuming that electron release or accept-

(26) The spectra of the free pyridines were not measured because the wave length of the principal band is so low that accurate measurement of its position is difficult.

ance by a substituent is merely a function of the electronegativity difference between it and the group to which it is attached (in ground or excited states) and the "polarizabilities" of the two portions.[27] In these terms, if one assumes the electronegativity difference between alkyl groups to be relatively small, then the "extra" activating effect of the neopentyl substituent (and to a lesser extent, of isobutyl and propyl) relative to say ethyl would in the main be attributed to its greater "polarizability." The "extra" polarizability of the neopentyl substituent conceivably may be due to the close proximity of the terminal methyl groups to the aromatic ring.[28] Thus, on excitation of the molecule, the terminal portion of the substituent may be polarized directly across space, by the ring as well as *via* the bond to the substituent; *i.e.*, the terminal portion of the substituent which overhangs the ring may be acting in much the same way as would an adhering hydrocarbon solvent molecule.

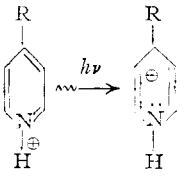
Another factor leading to increased activation by the branched alkyl groups may be the relief of strain on spectral excitation. It has been proposed previously, in connection with the spectra of α,β-unsaturated carbonyl compounds, that the excitation energy will be lowered when the electron displacement in the spectral excitation is away from a site of angle strain, even though no movement of the atomic nuclei is allowed in the short time of the electronic excitation (Franck–Condon Principle).[29] If increased branching of the alkyl groups does lead to any angle strain at or near the substituent (this is not evident from molecular models), then the excitation energy should be lowered since the electron displacement on excitation is away from this region.

Solvent Effects.—For the neopentyl substituent, the solvent effect on the $\nu_R-\nu_{Me}$ spread in the nitrobenzene series is qualitatively not as dramatic in its appearance as for the series Me, Et, *i*-Pr, *t*-Bu in which the effect of more basic solvents was to tend to invert the inductive order of excitation energies found in the gas phase, giving a jumbled order of excitation energies tending toward a complete Baker–Nathan order.[11c] On the other hand, the neopentyl compound retains its position of lowest excitation energy in all the solvents studied. However, there is an experimentally significant reduction in $\nu_{neoP}-\nu_{Me}$ in the basic solvents (Table II) that is comparable to the reduction in $\nu_{t\text{-}Bu}-\nu_{Me}$. The $\nu_{neoP}-\nu_{Me}$ spread is lowest in *n*-butylamine while the $\nu_{tBu}-\nu_{Me}$ spread is lowest in water.[11c] The decrease in spread is qualitatively consistent with the operation of either steric hindrance to ring solvation or steric hindrance to solvent enhancement of C–H hyperconjugation (for a more complete discussion see reference 11c).[30]

A plot of $\nu_{neoP}-\nu_H$ *vs.* ν_H shows a scatter similar to that found in the corresponding plot for *p*-*t*-butylnitrobenzene.[11c] As in the case of the *t*-butyl compound, the scatter can be interpreted as indicating disproportionate solvation effects between the neopentyl compound and nitrobenzene and is consistent with the operation of steric hindrance to ring solvation.[31]

The contrasting fact that *p*-neopentylnitrobenzene has a lower excitation energy than *p*-nitrotoluene in solution whereas in certain reactions (Introduction) the rate constant for the neopentyl compound is less than for the corresponding methyl compound, may be attributable, in part at least, to the operation of the Franck–Condon principle in spectra. Thus, in the spectral excitations, solvent stabilization of the excited state depends in part on the position of solvent molecules *as fixed by the ground state;* whereas the transition states of ordinary chemical reactions are maximally solvated. Thus steric hindrance to solvation would be expected to be an even more important factor in "ionic" reactions in solution.

The shifts in the position of the principal band brought about by changing solvent are small for the pyridinium ions and 1-hydroxypyridinium ions (Tables II and III), in contrast to the large shifts in the nitrobenzene series. This is not surprising since the excitation of the ions, crudely represented by equation 2, involves a redistribution of a positive charge. Thus some sites, *e.g.*, the protonated group, become less positive in the excited state than in the ground state; other sites, *e.g.*, the ring and the substituent, become more positive in the excited state. Solvent stabilization at sites becoming less positive on excitation (*e.g.*, by hydrogen-bonding at the N–H hydrogen) will be *less* in the excited than in the ground state. Approximately balancing this will be *greater* solvent stabilization in the excited state than in the ground state (*e.g.*, of the ring and possibly the substituent) at the sites becoming more positive on excitation.



(2)

The red shift for the unsubstituted pyridinium ion in proceeding from 1% aqueous perchloric acid to 1% perchloric acid in ethanol indicates that,

(27) W. M. Schubert, J. M. Craven, H. Steadly and J. Robins, *J. Org. Chem.*, **22**, 1285 (1957).

(28) In the molecular model of *p*-neopentylnitrobenzene the substituent is constrained in such a manner that a terminal portion of it closely overhangs one side of the aromatic ring in the neighborhood of the *p*-position. This is true to a lesser extent in the models of the isobutyl and propyl compounds. The fact that *p*-neopentylnitrobenzene and 4-neopentylpyridinium perchlorate have a noticeably higher melting point than the corresponding propyl or isobutyl compounds (see Experimental) may be a reflection of the additional conformational restraint placed upon the neopentyl group.

(29) W. M. Schubert and W. A. Sweeney, THIS JOURNAL, **77**, 2297 (1955).

(30) In the *absence* of steric hindrance to solvation effects it would be reasonable to expect a solvent red shift in the spectrum to be accompanied by an *increase* in $\nu_{neoP}-\nu_{Me}$, particularly in hydrogen bonding solvents. In other words, hydrogen bond solvation of the nitro group would be stronger for the neopentyl compound than for the methyl in the ground state (greater inherent electron release by neopentyl). In view of the Franck–Condon principle, this would contribute to an even greater solvent stabilization of the excited state of the neopentyl compound relative to the methyl compound, acting to increase the spread in excitation energies. Witness the increased observed $\nu_{Me}-\nu_H$ spread accompanying solvent red shifts.

(31) In the Fisher–Taylor–Hirschfelder model of *p*-neopentylnitrobenzene part of one side of the ring is effectively shielded by terminal methyl groups of the substituent; the other side of the ring remains exposed.

with this solvent change, solvation at sites acquiring increasing positivity on excitation becomes relatively *more* important than solvation at sites that decrease in positivity on excitation. For the neopentyl compound, by contrast, there is actually a slight blue shift accompanying this solvent change. This indicates that solvation at sites acquiring increased positivity on excitation is becoming relatively somewhat *less* important than solvation at sites that decrease in positivity on excitation. Thus the importance of ring solvation relative to functional group solvation appears to be greater for the hydrogen compound than for the neopentyl compound. A factor in this could be steric hindrance to ring solvation or, alternatively, steric hindrance to hydrogen bonding solvation of the substituent.

The differing solvent shifts for the 1-hydroxypyridinium ions in proceeding from 70% perchloric acid to 9% perchloric acid to acidic methanol could be rationalized similarly. However, a complicating factor is the question of just how solvation at various sites on these ions is affected by the different dispersal of charge induced by the inherent substituent effect. It is clear that considerably more experimental data on the spectra of the ions in various solutions would have to be amassed before a definite pattern allowing clear-cut decisions about solvation effects in such species could emerge.

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Benzyl Tosylates. IV. Halogen Substituent Effects[1]

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All eight *m*- and *p*-halobenzyl tosylates have been prepared. The rates of solvolysis of these compounds have been determined in 55.6% aqueous acetone at 25° and correlation with the Hammett equation has been attempted. The magnitude of deviations of the *p*-halogen substituents from their normal σ-constants follow the order *p*-F > *p*-I > *p*-Cl > *p*-Br, whereas the *m*-halogen substituents all have negative $\Delta\sigma$-values. These observations are discussed in terms of transition-state resonance and by comparison with similar systems. The unusual rate-enhancing influence of iodine has been further ascertained by solvolysis of the two iodobenzyl tosylates in dioxane–water and acetone–water mixtures of varying composition.

Recent work in this Laboratory showed that the solvolysis of *m*- and *p*-substituted benzyl tosylates gives a limited correlation with the Hammett equation.[2,3] Donor substituents such as methoxyl and methyl in the *p*-position provide exceptionally large driving forces above those to be expected from their normal σ-constants. That these deviations are due to important contributions of transition-state resonance is shown by the relatively normal behavior of *m*-methoxy- and *m*-methylbenzyl tosylates. This is reminiscent of the deviations of acceptor substituents such as *p*-nitro in the reactions of substituted phenols and anilines. These are reactions which involve the freeing of an electron-pair whereas in the solvolysis of benzyl tosylates the vacating of an orbital is important in stabilizing the transition state.

The sensitivity of the solvolysis of benzyl tosylates to substituent effects as indicated by the large negative ρ-values[2,3] has prompted an investigation of the behavior of the *m*- and *p*-halogenated compounds. There has been substantial disagreement in the literature as to the relative effects of halogen substituents. It was felt that the solvolysis of halobenzyl tosylates would make a good case for the evaluation of the polar effects of these substituents. The deviation from the Hammett σ-constant can be taken as a measure of the ability of a substituent to accommodate a positive charge in the transition state regardless of the origin of the stabilizing influence. Since the completion of our work the results of a similar study of halogen substituent effects on the solvolysis of phenyldimethylcarbinyl chlorides has been published.[4]

Previous work in this Laboratory included the solvolysis of *p*-fluoro- and *p*-chloro-,[3] *m*- and *p*-bromobenzyl tosylates[2] in various solvent systems. In order to ensure a fair correlation, all eight *m*- and *p*-halobenzyl tosylates have been prepared and their rates of solvolysis have been determined in the same mixed solvent, namely, 55.6% aqueous acetone. In addition, the rates of solvolysis of the two iodobenzyl tosylates have been measured in five other dioxane–water and acetone–water mixtures of low dielectric constants and varying composition.

Experimental[5]

Preparation and Purification of Materials. Benzyl Alcohol.—The commercial alcohol (Matheson, Coleman and Bell, chlorine-free) was distilled under reduced pressure through a glass helices packed column, b.p. 91.9–92.4° (11.5 mm.).

Halobenzyl Alcohols.—All except *m*-fluorobenzyl alcohol were prepared from the corresponding benzoic acids by reduction with lithium aluminum hydride.[6] Most of the commercial acids were purified by recrystallization from ethanol followed by vacuum sublimation. This procedure was found to increase the ease of purification of the benzyl alcohols. The liquid alcohols were purified by distillation under

(1) Presented in part before the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

(2) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

(3) G. S. Hammond, C. E. Reeder, F. T. Fang and J. K. Kochi, *ibid.*, **80**, 568 (1958).

(4) H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957).

(5) All melting and boiling points are uncorrected.

(6) W. G. Brown, in R. Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 491.