defined charge-transfer band was observed and whenever there was little distortion of the spectrum owing to reaction-product formation. Only absorbance data from the first two increments of donor could be used because significant amounts of reaction product had accumulated by the time the third addition of donor was made. Considering these limitations, the equilibrium constants obtained are questionable. Results for the complexes are given in Table I.

Although valid comparisons cannot be made from the equilibrium constants, some qualitative differences are evident from the optical spectra. There certainly appears to be some hindrance to complex formation by methyl substitution in the positions adjacent to the nitrogen atom, and the effect is more pronounced with disubstitution than with monosubstitution. Also, if the assumption is made that all of the complexes have approximately equal extinction coefficients, the amount of complexation may be estimated from the intensity of the charge-transfer band after the initial addition of donor, since the concentrations of reactants were the same for each system. The initial spectrum was used, since only small amounts of reaction products had distorted the spectrum and consumed TCNE at this point. The peaks decreased in intensity in the order 3,4-lutidine > 3,5-lutidine > 4-picoline > pyridine. Using this method of analysis, the intensities of the complex bands of the donors which are not sterically hindered parallel closely their basicities. Although comparisons of the steric effect and order of donor strength are not conclusive, these data indicate that the donors act as n-electron donors toward TCNE.

Esr investigations of the TCNE–pyridine systems showed the nine-line spectrum of the TCNE anion radical, but no evidence was found for any other paramagnetic species. The lack of evidence for the presence of the pyridine cation radical implies that the formation of the TCNE anion radical may not be due to the dissociation of the charge-transfer complex.

The radical anion is formed in good yields by the reaction of TCNE with cyanide ion,[14] and this method was used to synthesize the potassium salt of the anion radical in this laboratory. Since the formation of both pentacyanopropenide and tricyanoethenolate ions in the donor–TCNE systems liberates cyanide ion, this ion is very likely responsible for the reduction of TCNE to the anion radical. This possibility is supported by our finding that the concentration of radical increased slowly over a period of hours.

Registry No.—TCNE, 670-54-2; pyridine, 110-86-1; 4-picoline, 108-89-4; 3,4-lutidine, 583-58-4; 3.5-lutidine, 591-22-0.

Deuterium Isotope Effects in the Principal Electronic Transition of Nitrobenzene and Aniline and Their *p*-Alkyl Derivatives

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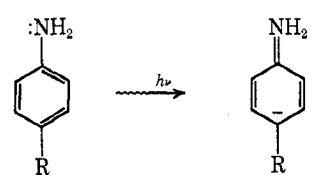
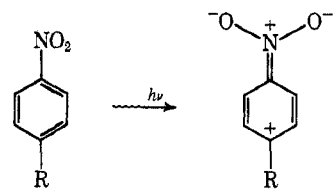
A study has been made of the effect of *p*-D *vs.* *p*-H, *p*-CD_3 *vs.* *p*-CH_3, and *p*-$CH_2C(CD_3)_3$ and *p*-$CD_2C(CH_3)_3$ *vs.* *p*-$CH_2C(CH_3)_3$ on the principal electronic transition of nitrobenzene and aniline in the gas phase and in heptane solvent. In all but one instance, that of *p*-neopentylnitrobenzene *vs.* *p*-neopentylnitrobenzene-γ-d_9, deuterium substitution shifted the principal band to slightly higher energies. These results are consistent with the polarizability–electronegativity treatment of substituent effects.

It has been reported that *p*-alkyl substituents substantially lower the energy of the "principal" electronic transition of compounds of the type aniline, phenol, and anisole, the excitation energy order in the gas phase and in heptane being neopentyl (neop) < *t*-Bu, Me < H.[1] It is known that in the principal electronic transition of *p*-disubstituted benzenes (also known as the E band or K band), there is a migration of electronic charge in the long axis of the molecule.[2] For *para*-substituted anilines, phenols, and anisoles it has been amply demonstrated by solvent studies that the electron migration takes the expected direction, *i.e.*, away from the heteroatom substituent, toward the *para* substituent.[3–5] Thus it may be symbolized by eq 1, in which the formulas I and II are understood to be only approximately representative of ground and



I II (1)



III IV (2)

excited states.[6,7] To anyone holding the static viewpoint that alkyl substituents invariably should act as if electron releasing relative to hydrogen, these results are

(1) W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962).

(2) W. T. Simpson and C. W. Looney, *J. Amer. Chem. Soc.*, **76**, 6293 (1954), and references cited therein.

(3) W. M. Schubert and J. M. Craven, *ibid.*, **82**, 1357 (1960).

(4) N. S. Bayliss and L. Hulme, *Aust. J. Chem.*, **6**, 257 (1953); N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

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

(6) More accurately, dipolar structures of type II are said to contribute to a much greater extent to the excited state than to the ground state.

(7) For a justification, in quantum mechanical terms, of such a structural depiction of the excitation process see ref 2 and 8.

(8) W. T. Simpson, *J. Amer. Chem. Soc.*, **75**, 597 (1953).

somewhat of a surprise. However, the conclusion that under a sufficiently high influx of negativity alkyl substituents exert a stabilizing effect in the polarizability order has been recently verified by the finding of Brauman and Blair that the relative gas-phase stabilities of alkoxide ions are neopo$^-$ (most stable) > *t*-BuO$^-$ > *i*-PrO$^-$ > EtO$^-$ > MeO$^-$ > HO$^-$.[9]

In the principal electronic transition of nitrobenzene, acetophenone, and similar compounds, in which the electron migration is in the opposite direction, *i.e.*, away from the substituent (eq 2), alkyl substituents have the expected effect of lowering the excitation energy. However, the excitation-energy order in the gas phase and in nonpolar solvents is also in the polarizability order, not in the hyperconjugative order: neop < *t*-Bu < *i*-Pr < Et < Me < H.[10] To account for the alkyl substituent effect, which is to lower the energy of transitions in which the electron migration is toward the substituent as well as those of the opposite sense, it was proposed that the substituent response was a function of its polarizability and its electronegativity (relative to the moieties to which it is bonded in ground and excited states).[1] The postulate had earlier been introduced to account for the effect of *para* halogen substituents, which also gave the polarizability order of excitation energies for both compounds of type I and type III.[3,11] The failure generally of alkyl substituents to respond as apparent electron acceptors relative to hydrogen in nucleophilic *chemical* transitions was attributed to the relatively low demand of the chemical compared with the electronic transitions. In other words, in transitions of lower demand, substituent response is qualitatively governed by relative substituent electronegativity.

To test the polarizability–electronegativity concept and to gain a further insight into the nature of the substituent polarization in the two types of electronic transitions, the effect of *p*-D, *p*-CD_3, *p*-$CD_2C(CH_3)_3$, and *p*-$CH_2C(CD_3)_3$ has now been studied.

Experimental Section

Compounds were purified with great care and thoroughness, to assure constancy of spectra. Vpc purification was followed by *ca.* five low-temperature recrystallizations, usually from pentane.

Nitrobenzene-*p*-*d*.—The reduction of *p*-nitrobenzenediazonium sulfate with hypophosphorus acid-d_3 according to the method of Hammond yielded nitrobenzene-*p*-*d*.[12] Analysis on the mass spectrometer (Consolidated Engineering Corp., type 21-103) showed d_0, 4%; d_1, 96%; d_2 and d_3, 0%.

Aniline-*p*-*d*.—The reduction of nitrobenzene-*p*-*d* was carried out by the method of Pietra[13] on the following scale: nitrobenzene-*p*-*d* (1.19 g), hydrazine hydrate (1.8 ml), 5% Pd on charcoal (52 mg), and ethyl alcohol (5 ml). Only 5 ml of water was used in the isolation procedure. The yield of purified aniline-*p*-*d* was 0.5 g. Analysis on the mass spectrometer showed d_0, 6%; d_1, 94%; d_2 and higher, 0%.

p-**Nitrotoluene-α-d_3.**—Nitration of toluene-α-d_3 (d_0, 0%; d_1, 0.7%; d_2, 14.0%; d_3, 85.3%), kindly furnished by Professor K. B. Wiberg,[14] yielded *p*-nitrotoluene-α-d_3: mp 50.2–50.8°; bp 146° (76 mm); $n^{25.5}$D 1.5462. The isotopic composition by mass spectral analysis was d_0, 0%; d_1, 0.7%; d_2, 13.9%; d_3, 85.4%.

p-**Toluidine-α-d_3.**—The method of Smith,[15] applied to the reduction of 1.1 g of *p*-nitrotoluene-α-d_3, yielded 0.37 g of purified *p*-toluidine-α-d_3. Mass spectral analysis follows: d_0, 0%; d_1, 0.9%; d_2, 15.5%; d_3, 83.6%.

Reduction of *p*-nitrotoluene-α-d_3 by the method of Pietra[13] yielded *p*-toluidine containing very little deuterium. Mass spectral analysis follows: d_0, 93%, d_1, 6%; d_2, 1%; d_3, 0%.

p-**Methylanisole-α-d_3.**—The isotopic composition of a sample of *p*-methylanisole-α-d_3, kindly furnished by Professor K. B. Wiberg, by mass spectral analysis follows: d_0, 4.5%; d_1, 0.7%; d_2, 9.8%; d_3, 85.0%.

p-**Neopentylnitrobenzene-α-d_2.**—Reduction of ethyl benzoate (17.3 g) with $LiAlD_4$ (3 g) in purified tetrahydrofuran (200 ml) yielded benzyl alcohol α-d_2 (11.7 g), bp 100° (13 mm). The benzyl chloride was prepared by refluxing with thionyl chloride. The Grignard reagent was treated with *t*-butyl chloride according to the method of Berliner[16] to yield *p*-neopentylbenzene-α-d_2, bp 75° (18 mm). Nitration was carried out as before,[10d] yielding *p*-neopentylnitrobenzene-α-d_2, mp 30.0–30.1°. The isotopic composition by mass spectral analysis follows: d_0, 1.9%; d_1, 24.7%; d_2, 73.4%.

Isobutylene-d_8 and *t*-Butyl Chloride-d_9.—A mixture of isobutylene (0.23 mol) and 30% D_2SO_4–D_2O (98.5% *d*) was shaken for 72 hr at room temperature in a sealed tube. After 12 hr the mixture was homogeneous. The solution was cooled to −80° and transferred to a 200-ml, round-bottom flask which was attached in series to an efficient water-cooled condenser, a Drierite tube, a trap cooled in ice, a Dry Ice–acetone trap, and a Drierite tube. The isobutylene was driven from the solution by gentle heating followed by more vigorous heating until reflux temperature. Refluxing was continued for 12 hr. The liquid that collected in the Dry Ice–acetone trap was bulb to bulb distilled. A total of three equilibrations were run in this manner, yielding finally 6.1 g of deuterated isobutylene. The deuterated isobutylene was distilled through a Drierite tube into a liquid nitrogen trap, the entry tube of which, at the end of the distillation, extended just below the surface of the liquid. Anhydrous ferric chloride (0.2 g) was added to the trap. Deuterium chloride, prepared according to the method of Brown,[17] was slowly passed into this entry tube and the mixture was allowed to stand for 30 min after the addition was complete. The trap was allowed to warm to room temperature in order to enable DCl to escape. The liquid then was distilled bulb to bulb, washed twice with 5 ml of water, dried over anhydrous magnesium sulfate, and distilled, bp 51°, yield 8.0 g. A comparison of the nuclear magnetic resonance spectrum with that of normal *t*-butyl chloride indicated that the *t*-butyl chloride-d_9 contained less than 4% protium.

p-**Neopentylnitrobenzene-γ-d_9.**—The reaction of *t*-butyl chloride-d_9 with the Grignard reagent of benzyl chloride, according to the procedure of ref 16, gave *p*-neopentylbenzene-γ-d_9, which was nitrated as above. The isotopic composition of the resulting *p*-neopentylnitrobenzene-γ-d_9, by mass spectral analysis, follows: d_7, 5%; d_8, 28%; d_9, 67%.

p-**Neopentylaniline-γ-d_9.**—The reduction procedure of Pietra,[13] applied to 0.915 g of *p*-neopentylnitrobenzene-γ-d_9, yielded 0.653 g of purified *p*-neopentylaniline-γ-d_9. Mass spectral analysis follows: d_6, 6%; d_7, 7%; d_8, 27%; d_9, 60%.

Spectral Measurements.—Measurements of gas-phase and solution spectra were made by multirepeated scanning with a Beckman DU instrument as described previously.[10c-e] The values of ν_{max} were determined graphically as described previously.[10c-e] Values of ν_{max} in heptane also were determined from spectral data obtained by means of a Cary Model 14 instrument, run at a slow chart speed with 5 Å/1 cm of chart paper. Both spectrophotometers were in top condition, the latter brand new. For spectra on the Cary, the base line was carefully balanced, air *vs.* air. Solvent *vs.* solvent showed no

(9) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 5636 (1968).

(10) (a) W. M. Schubert and W. A. Sweeney, *ibid.*, **76**, 4625 (1954); (b) W. M. Schubert and W. A. Sweeney, *J. Org. Chem.*, **21**, 119 (1956); (c) W. M. Schubert, J. Robins, and J. L. Haun, *J. Amer. Chem. Soc.*, **79**, 910 (1957); (d) W. M. Schubert and J. Robins, *ibid.*, **80**, 559 (1958); (e) W. M. Schubert, J. Robins, and J. M. Craven, *J. Org. Chem.*, **24**, 943 (1959).

(11) W. M. Schubert, J. M. Craven, H. Steadly, and J. Robins, *ibid.*, **22**, 1285 (1957); W. M. Schubert, J. M. Craven, and H. Steadly, *J. Amer. Chem. Soc.*, **81**, 2695 (1959); W. M. Schubert, H. Steadly, and J. M. Craven, *ibid.*, **82**, 1353 (1960).

(12) G. S. Hammond and E. Grundemeier, *ibid.*, **71**, 2444 (1955).

(13) S. Pietra, *Justus Liebigs Ann. Chem.*, **45**, 850 (1955).

(14) K. B. Wiberg and L. H. Slaugh, *J. Amer. Chem. Soc.*, **80**, 3033 (1958).

(15) L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 225.

(16) E. Berliner and F. Berliner, *J. Amer. Chem. Soc.*, **71**, 1195 (1949).

(17) H. C. Brown and C. Groat, *ibid.*, **64**, 2223 (1942).

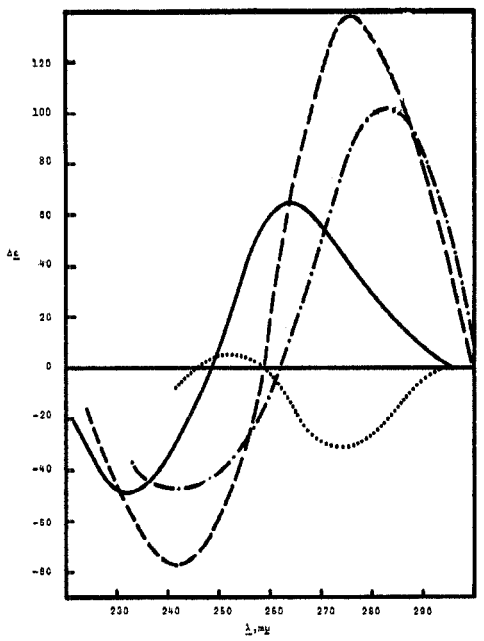


Figure 1.—Difference spectra for *para*-substituted nitrobenzenes, H compound (sample cell) *vs.* D compound (blank cell): D, ——; CD_3, – –; $CD_2C(CH_3)_3$, ·–·–; $CH_2C(CD_3)_3$, ·····.

deviation from the base line except at λ values lower than those used in the spectral determinations. A special cell holder was constructed to assure precise alignment of the cells each time.

The double-beam instrument was used to determine relative spectra of H and D compounds in heptane. Samples of *ca.* 5 mg were weighed on an analytical balance and diluted to 100 ml, and these solutions ($2–4 \times 10^{-4} M$) were used directly. Hydrogen and corresponding deuterium compounds were of the same molarity to an estimated precision of 0.05%. Difference spectra, in which the solution of hydrogen compound was in the sample cell and that of the deuterium compound in the blank cell, were recorded. The maximum slit width, occurring at *ca.* λ_{max}, was usually below 1.0.

Results

The general appearance of the principal band spectra of the *p*-alkyl nitrobenzenes, anisoles, and anilines has been described.[1,10c,d] Table I lists the values of the

TABLE I

GAS-PHASE VALUES OF ν_{max} (cm^{-1}) FOR p-RC_6H_4X AND DIFFERENCES IN ν_{max} BETWEEN DEUTERIUM AND PROTIUM ANALOGS[a]

	NO_2	NH_2	OCH_3
ν_H	41,820	43,590	46,510
$\nu_D - \nu_H$	160	150	...
ν_{CH_3}	39,970	42,790	45,500
$\nu_{CD_3} - \nu_{CH_3}$	80	70	130
$\nu_{CH_2C(CH_3)_3}$	39,490	42,280	44,880
$\nu_{CD_2C(CH_3)_3} - \nu_{CH_2C(CH_3)_3}$	30	60	...
$\nu_{CH_2C(CD_3)_3} - \nu_{CH_2C(CH_3)_3}$	−30	40	...

[a] Average of three determinations at 150° on a Beckman DU, duplicable to ±20–30 cm^{-1}.

difference in ν_{max} between deuterium and protium analogs in the gas phase, as determined at elevated temperatures in a Beckman DU instrument. The ν_{max} differences for averages of three determinations for each compound were reproducible to ±20–30 cm^{-1}. Table II lists ν_{max} differences obtained in heptane. Two sets of values are reported. One set of values was obtained with the Beckman DU instrument and is

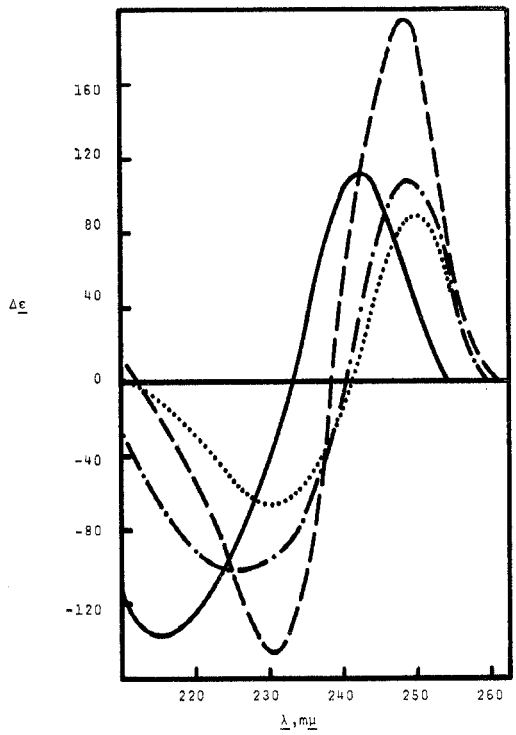


Figure 2.—Difference spectra for *para*-substituted anilines, H compound (sample cell) *vs.* D compound (blank cell): D, ——; CD_3, – –; $CD_2C(CH_3)_3$, ·–·–; $CH_2C(CD_3)_3$, ·····.

reproducible to ±20 cm^{-1} or less. The other set of values was obtained with the Cary Model 14 instrument and is reproducible to ±15 cm^{-1} or less.

TABLE II

VALUES IN HEPTANE OF ν_{max} (cm^{-1}) FOR p-RC_6H_4X AND DIFFERENCES IN ν_{max} BETWEEN DEUTERIUM AND PROTIUM ANALOGS[a,b]

	NO_2	NH_2
ν_H	39,700	42,740
$\nu_D - \nu_H$	50,[a] 30[b]	70,[a] 60[b]
ν_{CH_3}	37,870	42,230
$\nu_{CD_3} - \nu_{CH_3}$	50, 40	50, 50
$\nu_{CH_2C(CH_3)_3}$	37,410	41,170
$\nu_{CD_2C(CH_3)_3} - \nu_{CH_2C(CH_3)_3}$	30, 30	30, 40
$\nu_{CH_2C(CD_3)_3} - \nu_{CH_2C(CH_3)_3}$	0, −20	40, 30

[a] The first number reported is the average of three to five determinations at room temperature made on a Beckman DU, reproducible to ±20 cm^{-1} or better. [b] The second number reported is the average of two or three determinations at room temperature made on a Cary, Model 14, duplicable to ±15 cm^{-1} or better.

The plots of Figures 1 and 2 are experimental difference spectra of H compound against corresponding D compound. The experimental definition of $\Delta\epsilon$ is given by eq 3, where A is absorbance, positive or negative, that was determined as a function of wavelength. The quantity $\Delta\epsilon$ is related by eq 4 to $\epsilon_H - \epsilon_D$, the true difference between molar absorptivity of H and D compound. Only in the event that the concentration ratio of H to D compound ([H]/[D]) is exactly unity is $\Delta\epsilon$ at each wavelength *exactly* the molar absorptivity difference, $\epsilon_H - \epsilon_D$. Inherent weighing and volumetric areas impart an unavoidable uncertainty of 0.05% to the ratio [H]/[D]. Thus, if the H compound (sample cell) is in slight excess, $\Delta\epsilon$ is algebraically greater than $\epsilon_H - \epsilon_D$ at all wavelengths.

If the D compound (blank cell) is in slight excess, $\Delta\epsilon$ is algebraically less than $\epsilon_H - \epsilon_D$.[18] It can be shown that for broad, smooth, nearly symmetrical spectral peaks of the type being dealt with here, a slight excess of H or D compound will shift the whole $\Delta\epsilon$ *vs.* λ curve up or down without appreciably changing its shape. Thus the sum of the areas of positive absorption (where $\Delta\epsilon > 0$) and negative absorption (where $\Delta\epsilon < 0$) is practically unaffected, and the algebraic difference $\Delta\epsilon_{max} - \Delta\epsilon_{min}$ is practically unchanged. In other words, for compounds whose peaks are smooth and lie close to each other, the effect of a slight excess of, say, the H compound is to subtract about as much from the intensity of negative absorption as it adds to the intensity of positive absorption. Raising or lowering the $\Delta\epsilon$ curve does appreciably change the point of intersection with the wavelength axis, however.

$$\Delta\epsilon = A/[H] \tag{3}$$

$$\Delta\epsilon = \frac{\epsilon_H[H] - \epsilon_D[D]}{[H]} = \epsilon_H - \epsilon_D\frac{[D]}{[H]} \tag{4}$$

Discussion

Except for *p*-neopentylnitrobenzene-d_9, all the deuterium compounds have experimentally significant higher ν_{max} values than the corresponding hydrogen compounds, though the differences are quite small. The maximum observed $\nu_H - \nu_D$, 160 cm^{-1}, corresponds to 460 cal/mol (Tables I and II). It would, of course, be desirable to be able to measure directly the effect of deuterium on the 0–0* component of the band, which would give the energy difference between zero vibrational levels of ground and excited states. Since the intense principal spectral bands are characteristically smooth, continuous, and nearly bell shaped,[1,10] the 0–0* transition is experimentally inaccessible. However, Figures 1 and 2 show that deuterium substitution does shift the entire spectral band envelope, within the wavelength range of an observable difference spectrum. Thus the differential absorption (H *vs.* D compound) reaches a maximum on one side of the isoabsorptive wavelength and a minimum on the other side. Since the range of 0–n* transitions that contribute to the spectrum is shifted by substitution of D for H,[19] the inference is clear that the 0–0* transition is similarly shifted.

In the interpretation of the results obtained, two assumptions will be made. One is that inherent electronic effects exerted by substituents are qualitatively the same for electronic as for chemical transitions, though quantitatively different, of course. The second assumption is that, although secondary deuterium isotope effects "are vibrational in origin, . . . they can be regarded as genuine substituent effects for all practical purposes." The quotation is from p 123 of the review on secondary deuterium isotope effects by Halevi,[20a] who develops the common ground between formal theory and the language and concepts familiar to the physical organic chemist. Indeed, Halevi suggests that the physical organic chemist's approach may be the more meaningful and productive one in many instances of interpretation of secondary isotope effects.

From the magnitude of the experimental ν_{max} differences of Tables I and II, there is not much to choose in the way of deciding where deuterium substitution has its greatest effect. However, there is a trend toward greater magnitudes of $\nu_H - \nu_D$ in *p*-CD_3 and *p*-D compounds than in *p*-$CH_2C(CD_3)_3$. The difference spectra of Figures 1 and 2 are more definitive in this regard. They indicate that for both anilines and nitrobenzenes, the magnitude of the band shift takes the order $CD_3 > D$, $CD_2C(CH_3)_3 > CH_2C(CD_3)_3$.[21]

p-**D** *vs.* *p*-**H**.—The substitution of *p*-D for *p*-H leads to a significant increase in the principal electronic transition energy of both nitrobenzene and aniline in both the gas phase (Table I) and in heptane solution (Table II and Figures 1 and 2). Since the electron migration is away from the substituent in the excitation of nitrobenzene and toward the substituent in the excitation of aniline, the effect is not governed by a relative inductive effect, in a fixed direction, between H and D. The results are consistent with the electronegativity–polarizability concept.[1,11] There is ample physical evidence that D is less electronegative than H, and that the C–D bond is less polarizable than the C–H bond.[20b] The effect of *p*-D *vs.* *p*-H on the principal transition of aniline corresponds to both the electronegativity and polarizability order. However, the effect on the principal electronic transition of nitrobenzene corresponds only to the polarizability order, in agreement with the hypothesis that when the transition places a very high electron demand on the substituent, as it does here, a greater polarizability (*i.e.*, a greater response *per increment* of demand) can overcome the retarding effect of a greater electronegativity.[1,11]

The results here are not necessarily in contradiction to the apparent greater activating effect of D than H in certain electron-demanding chemical transitions. Examples in which H (or D) is bonded to trigonal carbon in both states include the ionization of tris-*p*-deuteriophenylmethyl chloride in SO_2 at 0°, for which $K_H/K_D = 0.969 \pm 0.003$ (the corresponding *m*-*d* compound has $K_H/K_D = 0.957 \pm 0.007$),[22] and the solvolysis of bis(pentadeuteriophenyl)methyl chloride in 80% acetone at 25°, for which $k_H/k_D = 0.85$.[23] While these reactions are electron demanding of the substituent, the demand is not nearly comparable with that in the principal electronic transition of nitrobenzene.[24] In other words, the demand may be sufficiently low in the chemical transitions to allow the electronegativity difference between H and D to predominate in the combined polarizability–electronegativity "product."[25]

(18) At the ϵ_{max} of the hydrogen compounds ($\epsilon \cong 10{,}000$), $\Delta\epsilon$ could be as much as 50 units greater (excess H compound) or less (excess D compound) than $\epsilon_H - \epsilon_D$.

(19) For the spectral data in heptane, at room temperature, it may be assumed that the ground state largely occupies the zero vibrational level. Upper levels of the ground state may be somewhat populated in the gas-phase measurements, which were carried out at 150° to avoid adsorption of compound on cell windows.[10c]

(20) (a) E. A. Halevi, "Physical Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1963, pp 109–221; (b) pp 114–123.

(21) For the *para* hydrogen through neopentyl derivatives of the nitrobenzenes and anilines, the spectral band retains the same shape and increases only a little in intensity. Therefore, the change with substituent in the integrated areas of Figure 1 (sum of areas above and below $\Delta\epsilon = 0$) or Figure 2 is qualitative measure of the relative magnitude of the λ shift produced by D replacing H.

(22) (a) A. J. Kresge, K. N. Rao, and N. N. Lichtin, *Chem. Ind.* (London), **53** (1961); (b) ref 20, p 158.

(23) H. S. Klein and A. Streitwieser, Jr., *Chem. Ind.* (London), 180 (1961).

(24) From the effect of *para* substituents with negative σ^+ only, the "reaction" constant, ρ, has been estimated to be -13 ± 1.2.[1]

Reactions that result in negativity at or near trigonal carbon appear generally to be "activated" by H relative to D, in correspondence with both the electronegativity and polarizability order. Examples include the ionization of formic acid (k_{HA}/k_{DA} = 1.06[26] or 1.12[27]) and the ionization of pentadeuteriophenol (k_{HA}/k_{DA} = 1.12).[23]

CD_3 and $CD_2C(CH_3)_3$.—The substitution of α deuterium in either *p*-methyl or *p*-neopentyl raises the energy of both the electron-removing (nitrobenzene) and electron-donating transition (aniline). The effect is greater in methyl than in neopentyl derivatives, as shown especially by the H *vs.* D difference spectra of Figures 1 and 2. However, it is risky to surmise whether this is more or less than a statistical difference owing to three α deuteriums compared with two. Shiner has found a somewhat more than statistical difference, which he attributes to inhibition of C–H hyperconjugation, in the solvolysis of $CD_3CCl(CH_3)_2$ (k_H/k_D = 1.40) and $(CH_3)_3CCD_2CCl(CH_3)_2$ (k_H/k_D = 1.08).[28]

From the facts that H is more electronegative than D and the C–H bond is more polarizable than the C–D,[20] it can be presumed that CH_3 and $CH_2C(CH_3)_3$ are somewhat more electronegative and polarizable than the corresponding α-D substituents. Thus, as with *p*-D compared with *p*-H, the ν_{max} shift on α-D substitution corresponds to both the electronegativity and polarizability order for *p*-methyl and *p*-neopentylaniline, but only to the polarizability order for the nitrobenzenes.

In electron-demanding chemical transitions, CD_3 has been found to sometimes have a retarding effect relative to CH_3, and sometimes an accelerating effect. Deuterium substitution slightly decreases the rate of solvolysis of *p*-methylphenyl-1-chloroethane: $k_{p\text{-}CD_3}/k_{p\ CH_3}$ is 1.08 (30 cal/mol per D) in acetic acid at 50° and only 1.01 in "80%" acetone at 38°.[29] A greater isotope effect is found in the α-methyl substituent, which is under greater electron demand: $k_{\alpha\text{-}CH_3}/k_{\alpha\text{-}CD_3}$ = 1.28 in acetic acid at 50°.[29] Deuterium substitution in the α position of *para* alkyl substituents also reduces solvolysis rates of *p*-alkylbenzhydryl chloride; *e.g.*, $k_{p\text{-}CH_3}/k_{p\text{-}CD_3}$ = 1.06 in "80%" acetone at 0°.[30] The basicity of acetophenone is greater than that of its CD_3 analog, $k^H_{SH^+}/k^D_{SH^+}$ = 0.775 (−51 cal/mol per D).[31] Aromatic substitution gives varied effects. Nitration of CD_3Ph apparently shows no significant effect;[32–34] *e.g.*, k_H/k_T = 1.002 ± 0.002 per tritium.[32] In the more electron-demanding bromination a retarding effect was observed: k_H/k_T = 1.046 ± 0.009 per tritium in 85% acetic acid at 25°.

The β-deuterium isotope effect in solvolysis of purely aliphatic halides and inorganic esters also appears to be demand dependent. Methyl inorganic esters hydrolyze slower in water than the CD_3 esters (*e.g.*, $\Delta F_D^{\ddagger} - \Delta F_H^{\ddagger} = -25$ cal/mol for the bromide).[35] As the SN1 contribution to hydrolysis increases, *i.e.*, as the electron demand in the transition states increases, k_H/k_D increases. Thus the isotope effect for ethyl-α-d_2 derivatives is borderline, and that of isopropyl-α-d_1 is positive (*e.g.*, $\Delta F_D^{\ddagger} - \Delta F_H^{\ddagger} = 22$ for the bromide).[35] With tertiary halides and inorganic esters, β D invariably has a retarding effect.[20,28,36,37] For example, k_H/k_D = 1.40 (64 cal/mol per D) in the solvolysis of $CD_3CCl(CH_3)_2$ in "80%" ethanol at 25°.[28] A somewhat smaller retardation was observed in the hydrolysis of α-deuterio ketals.[38]

The general pattern that emerges from the results of the electron-demanding chemical transitions is that k_H/k_D per deuterium tends to increase as the electron demand on the substituent increases, and has a value less than unity for weakly electron-demanding reactions. This is in agreement with the electronegativity–polarizability hypothesis.[1,11] However, it also agrees with the often advanced argument that inductive electron release (CD_3 better than CH_3) predominates at low demands and that C–H hyperconjugative release (CH_3 better than CD_3) predominates at higher electron demands.

In reactions that place negative charge at the alkyl substituent, deuterium seems generally to exert a retarding effect, but the studies are fewer in number.[20] Deuterium substitution in the α position reduces the acidity of carboxylic acids; *e.g.*, K_H/K_D = 1.06 (12 cal/mol per D) for (CD_3COOH).[20,39] This has been attributed to greater inductive electron release by α-CD than by α-CH substituents, leading to a greater destabilization of the CD_3COO^- anion.[39] A larger effect was encountered in the rate of α proton abstraction from CD_3CH_2Ph by lithium cyclohexylamide in cyclohexylamine at 50°, k_H/k_D = 1.11 ± 0.03.[40] This also was attributed to greater inductive electron release by CD_3,[40] but the suggestion has been made that there may be a contribution by anionoid hyperconjugation.[20]

The fact that in both electron-donating and electron-demanding electronic transitions the ease of substituent polarization takes the order alkyl > deuterioalkyl ≫ H > D requires that any assigned specific mechanism or mechanisms of the substituent role be one that allows the alkyl substituent to respond favorably either to an electron-rich or an electron-poor attached moiety. Thus, if hyperconjugation is of prime importance, it must be cationoid (classical hyperconjugation) at high electron demand and anionoid toward high electron richness. If the effects are largely a consequence of unequal sharing of σ electrons (inductive effect), then the unequal sharing must be able to take either direction. If polarization occurs through space (internal dispersion force), this is by definition operable in either "direction."[41]

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p-$(CD_3)_3CCH_2$.—The effect that γ-deuterium substitution exerts on the principal band of *p*-neopentylnitrobenzene and *p*-neopentylaniline is the smallest one observed. However, in each successive determination on H and D compounds, ν_{max} for neopentylaniline was consistently less than that for its γ-d_4 derivative. The difference spectrum of Figure 2 shows this even more clearly. For neopentylnitrobenzene in heptane, no difference was found in the average of determinations on a Beckman DU, but, in determinations on the Cary Model 14 spectrometer, ν_{max} for the γ-d_9 derivative was consistently smaller by a tiny amount. The differential absorption curve of Figure 1 shows a rather weak maximum and minimum, but has the shape required for a shift to lower energy of the transition of the D compound.

In previous articles, it has been pointed out that the lowest energy conformation of neopentylbenzenes is probably one in which a portion of two of the terminal methyl groups somewhat overhang one side of the ring (see also ref 28).[10d,e] It was suggested that part of the enhanced effectiveness of the *p*-neopentyl substituent in electronic transitions, both of the type represented by eq 1 and that represented by eq 2, may be due to a polarization across space of these terminal methyl groups (the $h\nu$ order in both instances is neop < *t*-Bu, CH_3 < H). However, the observed opposite effect of γ deuterium on the principal band of *p*-neopentylnitrobenzene and *p*-neopentylaniline is difficult to reconcile with this suggestion. If the effect of γ-D substitution is transmitted through the bonding electrons, then the effect would be expected to be very small in any event.

As regards the effect of γ-D substitution on chemical transitions, γ-d_9 neopentyl methanesulfonate hydrolyzes somewhat slower than the normal compound in water: k_H/k_D = 1.017.[42,43] On the other hand, γ-d_9 may slightly increase the rate of solvolysis of α-methylneopentyl brosylate: k_H/k_D = 0.979 ± 0.017 in 43% ethanol at 40°; k_H/k_D = 0.986 ± 0.014 in 95% trifluoroacetic acid at 10°.[44]

Registry No.—Nitrobenzene, 98-95-3; aniline, 62-53-3; nitrobenzene-*p*-*d*, 13122-36-6; aniline-*p*-*d*, 13122-28-6; *p*-nitrotoluene-α-d_3, 23346-24-9; *p*-toluidine-α-d_3, 23346-25-0; *p*-methylanisole-α-d_3, 23346-26-1; *p*-neopentylnitrobenzene-α-d_2, 23346-27-2; isobutylene-d_8, 20762-54-3; *t*-butyl chloride-d_9, 918-20-7; *p*-neopentylnitrobenzene-γ-d_9, 23346-29-4; *p*-neopentylaniline-γ-d_9, 23359-82-2.

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Kinetics and Stereochemistry of the Gas-Phase Addition of HBr to Methyl-Substituted Allenes

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The kinetics and stereochemistry of the gas-phase, photocatalyzed addition of HBr to allene, methylallene, 1,1-dimethylallene, 1,3-dimethylallene, and tetramethylallene have been investigated. The rate expression is the same for all: rate of adduct formation = $k[HBr]I_0^{1/2}$. Reactivities relative to allene are 1:1.36:1.31:1.56:1.65 for the compounds as listed. The products, with one minor exception, involve addition of the bromine atom to the center carbon of the allenic system.

The free-radical addition of HBr to simple olefins reaction has been investigated in both solution and gas phases for many years. The general picture that has emerged is that the bromine atoms add to that carbon of the olefinic bond which will yield the most stable radical. In the gas-phase reaction, this radical contains the energy of the new carbon–bromine bond, and may readily dissociate to starting olefin and bromine atom, or be collisionally deactivated to thermal equilibrium, whereupon it may abstract a hydrogen from HBr to give the alkyl bromide product.[1,2]

The situation is more complex with cumulative bond systems. The addition of a radical or atom to the terminal (more electronegative[3]) carbon of an allene produces a vinyl radical. If addition of a radical takes place at the center carbon, however, the radical structure can acquire allylic resonance stabilization by rotation through 90°.[4] The question arises as to whether this rotation can occur fast enough so that this stabilization becomes kinetically important. An examination of the kinetics of the reaction of allene with HBr demonstrated that the initial reaction of the bromine atom with the allene is at the center carbon, and is apparently irreversible.[5] The kinetics does not disclose whether there may be a reversible terminal carbon attack, but only that all of the product of kinetic importance is from reaction at the center carbon.

The stereochemistry of free-radical attack on allene and alkyl-substituted allenes has been investigated for other radials than bromine atoms. Methyl radicals,[6] trifluoromethyl radicals,[6] and trichloromethyl[7] attack exclusively at the terminal carbon, while fluorine

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