more effect on the rate than does the term containing the entropy of activation. The *m*-substituents however produce a real effect on activation energy, although even here the changes in log *PZ* may be significant. Since it can thus be shown that entropy of activation terms are not all the same and can in fact account for an important part of the rate changes, it is not fruitful to discuss the other two alternative explanations which are based on modifications of the potential energy effects alone. Assignment of effects to potential energy terms alone is especially unjustified in cases of this sort where the variations in rate are small.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NEW MEXICO HIGHLANDS UNIVERSITY]

The Effect of Solvents on the Absorption Spectra of Aromatic Compounds

BY HERBERT E. UNGNADE[1]

RECEIVED MAY 19, 1952

Solvent shifts have been determined for benzene derivatives with electron-donor and electron-acceptor substituents. It is proposed that the direction of the shifts of the high-intensity bands depends on the solvent-solute interaction.

Solvents can affect the fine structure of absorption curves as well as the intensities and wave lengths of the maxima. From the standpoint of fine structure solution spectra of aromatic compounds in paraffin solvents most nearly resemble those in the vapor state. With increasing solvent polarity the spectra suffer a loss in vibrational fine structure which may perhaps serve as a measure of the extent of the solvent interaction.

The absorption spectrum of benzene is only very slightly affected by solvents.[2] Aromatic hydrocarbons more complex than benzene undergo definite shifts of their absorption curves when the polarity of the solvent is changed. Still larger solvent shifts are observed in substituted benzenes with polar substituents.

The direction of the solvent shifts is not always the same for all absorption bands of the same compound and it is therefore necessary to classify the bands. Above 200 mμ most benzene derivatives possess two types of bands which are distinguishable by their relative absorbancies.[3] The high intensity bands, also called K-bands,[3] primary bands[4] or E-bands,[5] are usually displaced to longer wave lengths with increasing polarity of the solvent. The low intensity bands are known as secondary bands[4] or B-bands[3] and are shifted toward higher frequencies when the dielectric constant of the solvent is increased.

In mono-substituted benzene derivatives with electron-acceptor substituents such as COOH, $COCH_3$, CHO and NO_2 the high intensity bands become identical with the red-shift bands of McConnell.[6] When measurements are omitted in solvents where association occurs (*e.g.*, benzoic acid dimer in hydrocarbons, chloroform, etc.),[7] the shifts are progressive from hydrocarbon solvents to water and, for a given solvent pair, roughly proportional to the shift of the corresponding benzene band due to the particular substituent (Table I).

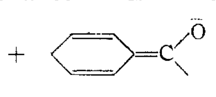
TABLE I

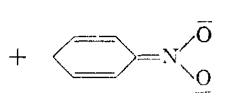
PRIMARY BANDS OF BENZENE DERIVATIVES WITH ELECTRON ACCEPTOR SUBSTITUENTS

Compound	λ_{max} (H_2O)	λ_{max} (EtOH)	$\Delta\lambda^a$	$\Delta\lambda^b$
Benzoic acid	230[c]	228[g]	26.5	+2
Acetophenone[d]	245.5[c]	241[e]	42.0	+4.5
Benzaldehyde	249.5[c]	243[h]	46.0	+6.5
Nitrobenzene[f]	268.5[c]	260[i]	65.0	+8.5

[a] Wave length shift of the benzene band at 203.5 mμ due to the substituent.[c] [b] λ_{max} (H_2O) − λ_{max} (EtOH). [c] Reference (4). [d] In hexane λ_{max} 235 mμ[e] and $\lambda_{H_2O} - \lambda_{HC} + 10.5$ mμ. [e] G. Scheibe, F. Backenköhler and A. Rosenberg, *Ber.*, **59**, 2617 (1926). [f] In isoöctane λ_{max} 252 mμ and $\lambda_{H_2O} - \lambda_{HC} + 16.5$ mμ (W. G. Brown and H. Reagan, THIS JOURNAL, **69**, 1032 (1947)). [g] Reference (7). [h] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1349 (1940). [i] H. E. Ungnade, V. Kerr and E. Youse, *Science*, **113**, 601 (1951).

These findings are in accord with the conclusions reached by Doub and Vandenbelt,[4] that the absorption bands in mono-substituted benzene derivatives are displaced benzene bands and that the displacements are due to electronic interaction of the group with the nucleus. Polar solvents, such as water, would tend to stabilize polar quinoid resonance forms of the types





The stabilization of the arrangement of the solvent molecules in the excited states would be greater in molecules with strong interaction between substituent and nucleus.

Literature data for monosubstituted benzene derivatives with electron donor groups (OH,[8] OMe,[4,9] SH,[10,11] SR,[11–13] NH_2,[4,9–11,14] NMe_2[14c,15,5]

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TABLE II

PRIMARY AND SECONDARY BANDS OF BENZENE DERIVATIVES WITH ELECTRON DONOR SUBSTITUENTS[b]

Compounds	Water				Alcohol				Cyclohexane			
	λ_{max}[c]	log ε	λ'_{max}	log ε	λ_{max}	log ε	λ'_{max}	log ε	λ_{max}	log ε	λ'_{max}	log ε
Anisole	217[f]	3.80	269[f]	3.17	220	3.85	270	3.24	222	3.86	271	3.33
Diphenyl ether	220[a]	3.94	270	3.17	225[a]	4.01	271	3.31	226[a]	3.05	273	3.31
Acetanilide	238	4.02	..[a]	..	242	4.12	...[a]	..	(238)[d]	4.12	(274)[d]	2.92
Dimethylaniline	244	3.94	284[a]	3.11	251	4.11	298	3.28	251	4.16	298	3.37
Iodobenzene	227	3.93	254[a]	2.82	227	4.06	256	2.82	228.5[e]	4.12	258	2.83

[a] Shoulder. [b] The author is indebted to J. McDowell, S. Lee and J. Mundzak for some of the measurements. [c] λ_{max} = first primary band and λ'_{max} = most intense absorption in the secondary band.[4] [d] Associated. [e] The second maximum in this band is located at 233.5 mμ (log ε 4.10). [f] The data of Doub and Vandenbelt[4] have been in excellent agreement with the best values obtained with our instrument. The new measurements permit an extension of their Δλ values (in their Table I, p. 2716) to give 34.5 mμ for acetanilide, 40.5 mμ for dimethylaniline and 23.5 mμ for iodobenzene (in aqueous solution).

and X[4,5,10,16]) indicate that these substances fail to give red shifts for non-polar → polar solvent changes if associated states are disregarded. The maxima of the absorption curves appear to be unaffected by solvents in some cases or may undergo blue shifts with increasing solvent polarity. In either event the extinction values are decreased. The changes in wave lengths and extinctions, however, are often small and exceeded in many cases by the discrepancies between instruments and methods.

In the present work absorption spectra have been obtained for identical specimens with the same instrument in three different solvents. The measuring technique has been described previously.[7] The experimental results for five selected compounds appear in Table II.

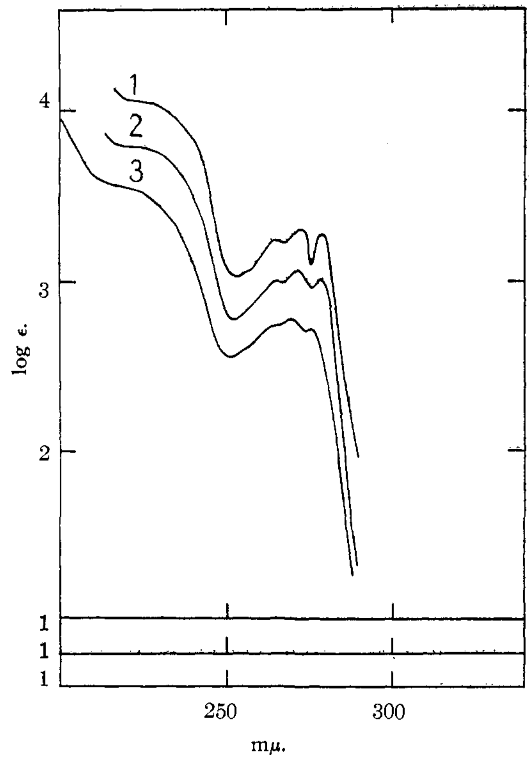

Fig. 1.—Diphenyl ether in: 1, cyclohexane; 2, 95% ethanol; 3, water containing a minimum amount of methanol.[4] The measurements were carried out in 1-cm. silica cells at 25° in concentrations of 2 × 10^{-4} mole per liter. Curves 2 and 3 in each figure are dropped 0.2 and 0.4 unit of log ε, respectively, to avoid overlapping with curve 1. The intensities are plotted as logarithms of the molecular extinction coefficients.

The curves for anisole and diphenyl ether (Fig. 1) show decreases in fine structure and intensity and blue shifts of both bands when the solvent is changed from cyclohexane to alcohol to water. Acetanilide behaves abnormally in hydrocarbon solvents in which it is believed to be associated. Dimethylaniline cannot form intermolecular hydrogen bonds and therefore has a normal (blue shift) solvent sequence for both bands (Fig. 2). It has very similar curves in alcohol and cyclohexane which may indicate a shielding effect of the methyls toward the approach of the alcohol molecules. This is evidently not true to the same extent

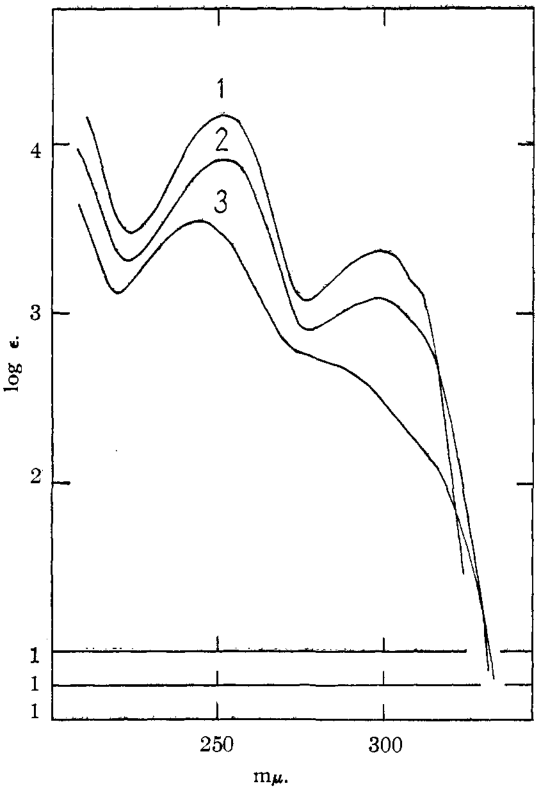

Fig. 2.—Dimethylaniline in: 1, cyclohexane; 2, 95% ethanol; 3, water containing a minimum amount of methanol.[4] Concentration at the maxima 1 × 10^{-4} mole per liter.

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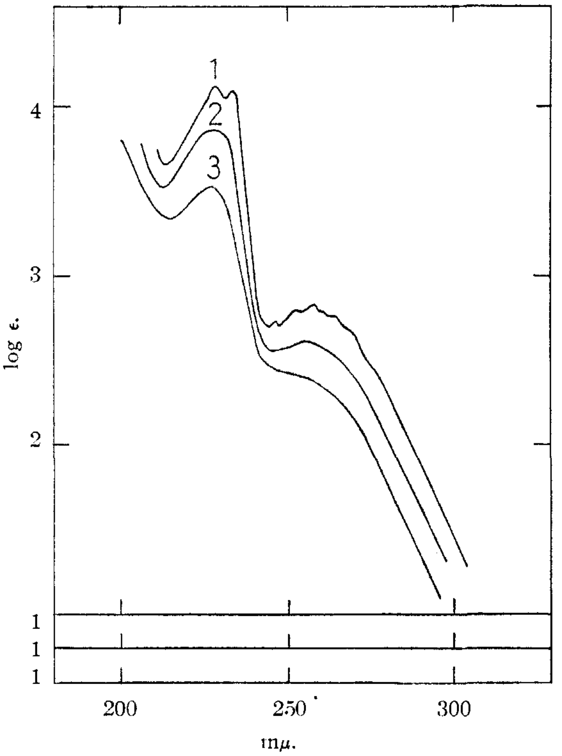

Fig. 3.—Iodobenzene in: 1, cyclohexane; 2, 95% ethanol; 3, water containing a minimum amount of methanol.[4] Concentration at the primary band 3-5 × 10^{-5} mole per liter, at the secondary band 3-6 × 10^{-4} mole per liter. The fine structure bands required measurements at 0.5 mμ intervals.

for the smaller water molecules.[17] The blue shifts in iodobenzene are actually more pronounced than the values for λ_{max} would indicate because the primary band shows asymmetric broadening in alcohol and appears as a doublet in cyclohexane (Fig. 3).

A tentative explanation of the experimental results is offered on the basis of the present data. A blue shift of the primary band caused by increasing the polarity of the solvent implies a decrease in the polar quinoid resonance forms. The benzene substituents in these compounds are electron donors, characterized by unshared electron pairs, which may interact with the respective nuclei and partake in hydrogen bonds with the solvent (solvation) or with other molecules (association). Blue shifts would be accounted for by assuming that the solvation with polar solvents contributes to the stability of the ground states more than it does to the excited states.[18] Barring other effects, the blue shifts should increase progressively with the solvent polarity. This appears to be the case for phenyl ethers, dimethylaniline and iodobenzene, while abnormal solvent sequences are observed for phenol, aniline and acetanilide, *i.e.*, in substances in which association is known to occur.

The effect of a solvent is apparently dependent on the degree and type of solvent bonding (or dipole association), or, particularly in non-polar solvents, on the degree of association. It is well known that such molecular interaction is sensitive to steric effects. A more detailed study would be indicated in order to establish what other factors need to be considered in order to evaluate solvent effects.

Acknowledgment.—The author is indebted to Dr. J. R. Platt for valuable suggestions.

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[17] It is necessary to assume a hydrate involving the unshared electron pair in aromatic amines in order to account for the basic properties of these substances. The formation of such hydrates is also subject to steric effects (H. C. Brown, *Science*, **103**, 385 (1946); THIS JOURNAL, **67**, 374, 378 (1945)).

[18] The suggestion of a ground state stabilization is not original since it was proposed by L. G. S. Brooker and R. H. Sprague (*ibid.*, **63**, 3215 (1941)) to explain the lack of color in Michler ketone "even in strongly polar solvents."

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Consecutive Constants for the Association of Cadmium with Imidazole[1,2]

BY CHARLES TANFORD AND MYRON L. WAGNER

RECEIVED AUGUST 14, 1952

The successive association constants of the cadmium-imidazole complex have been determined potentiometrically by the method of Bjerrum. At 25° log k_1 = 2.80, log k_2 = 2.10, log k_3 = 1.55 and log k_4 = 1.13. From measurements at other temperatures ΔH_1 is estimated to be -5 ± 2 kcal./mole. The value of log k_1 is identical with the logarithm of the intrinsic association constant of cadmium with the imidazole groups of serum albumin.

Recent work from this Laboratory and elsewhere[3,4] has indicated that in the combination of metals with serum albumin the principal binding sites are the imidazole groups of the protein molecule. If this is so the binding constant for the reaction of a metal with imidazole itself should be of the same order of magnitude as the intrinsic constant found for the association of the same metal with serum albumin. The present paper verifies this conclusion for cadmium. A similar verification for zinc has been made by Gurd and Goodman.[4]

Experimental

The reaction was studied potentiometrically by the method of Bjerrum.[5] A Beckman model G *p*H meter with external electrodes was used, and the procedure employed

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[1] This investigation was supported by a research grant from the National Institutes of Health, Public Health Service.

[2] Abstracted from a thesis by Myron L. Wagner in partial fulfillment of the requirements for the M.S. degree, State University of Iowa, June, 1952.

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