Figure 6. Comparison of spectral shifts with solvent for betaines[7] and sodium benzophenone ketyl.

pletely detailed description of these phenomena would require the further specification of the roles of various kinds of ion pairs.[6]

Polarity of Ethers and Chemical Reactions. Aside from a considerable quantity of data which compare only two or three ethers (all of which comparisons seem consistent with the above ideas), data on chemical reactions are rather limited. Even so, in the extant examples the order of apparent polarity of ethers toward organosodium compounds is consistent with the benzophenone ketyl spectra.

The formal equilibrium constants for the disproportionation of monosodium tetraphenylethylene parallels E_T(sodium benzophenone ketyl) through five ethers.[26] The equilibrium constants for the dissociation of paramagnetic sodium fluorenone ketyl dimers decreases with solvent in the following order: 1,2-dimethoxyethane > tetrahydrofuran > 2-methyltetrahydrofuran > dioxane > diethyl ether, again paralleling the ketyl spectral shifts.[27] Also paralleling E_T(so-

dium benzophenone ketyl) are the relative positions of equilibria 1 and 2 among seven ethers.[28] Further, the rates of air oxidation of the carbanion derived from Koelsch's radical[29] by one-electron reduction with sodium parallel E_T(sodium benzophenone ketyl) among several ethers, pyridine, and N,N-dimethylformamide.[30]

Solvent Effect on Betaines. Dimroth has kindly communicated to the authors some unpublished results which extend the range of solvents through which the spectral shifts of certain betaines can be compared with those of sodium benzophenone ketyl.[31] As Professor Dimroth points out, the reasonably linear correlation between the two E_T values suggests the operation of similar solvation mechanisms (Figure 6). Since the betaines have quaternary nitrogen cationic sites, rather than sodium ions, this conclusion further suggests the absence of very specific sodium ion–solvent molecule interactions. Alternatively, the specific effects parallel the nonspecific effects.

Summary. The order of polarity of ethers toward organosodium compounds is consistent over the available data. This suggests that the ionic aggregates which have been considered are rather loose, so that specific solvent–anion interactions do not appreciably interfere with cationic solvation. The appearance of a little more scatter in the data for less polar ethers suggests the possibility that in these solvents the aggregates may be approaching sufficient tightness that such effects are beginning to appear.

(26) J. F. Garst, E. R. Zabolotny, and R. S. Cole, *J. Am. Chem. Soc.*, 86, 2257 (1964). See also ref. 21.

(27) Results of Hirota and Weissman[16] extended by our own observations.

(28) A. I. Shatenstein, E. S. Petrov, M. I. Belousova, K. G. Yanova, and E. A. Yakovleva, *Dokl. Akad. Nauk SSSR*, 151, 353 (1963).

(29) C. F. Koelsch, *J. Am. Chem., Soc.*, 79, 4439 (1957).

(30) J. G. Pacifici, J. F. Garst, and E. G. Janzen, *ibid.*, 87, 3014 (1965).

(31) Private communication from Professor Dimroth. See ref. 7.

Spectra of Alkali Phenoxides in Aqueous Dioxane

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The apparent energy of transition (E_T) of the A_{1g}–B_{2u} band of phenoxide ion varies with metal ion (among alkali metals) in aqueous dioxane less than 50 mole % rich in water. At the same time, E_T is linear with dielectric constant in media more highly aqueous than about 50 mole %, but deviates in less aqueous media. These facts are interpreted as reflections of ionic aggregation in the less aqueous solvent mixtures. The addition of water to pure dioxane solutions of lithium phenoxide results in a decrease in E_T, while similar treatment of sodium and potassium phenoxides leads to increases in E_T. These results can be rationalized in terms of competing anion (hydrogen bonding) and cation solvation effects on the spectra of the ionic aggregates.

Introduction

There is a pronounced metal ion effect on E_T (alkali phenoxide) in dioxane and 1,2-dimethoxyethane.[2] Such situations are frequently accompanied by pro-

nounced solvent effects among rather nonpolar solvents.[2-6]

While most of the organoalkali salts previously investigated in this regard could not exist in aqueous media, the alkali phenoxides can, enabling an investigation of the variation of E_T with metal ion and solvent through a series of dioxane–water mixed solvents, reported in the present paper. Such an investigation was of interest in connection with the possibilities of spectrally detecting ionic aggregation and competing anion and cation solvation effects in these media, both of which were realized. The results may bear on the recent considerations of Kornblum and co-workers in connection with the alkylation of phenoxides and naphthoxides.[7]

Experimental

The spectra of alkali phenoxides in pure dioxane were determined as described previously.[2] In highly aqueous media, the spectra can be obtained simply by neutralizing phenol with the appropriate alkali hydroxide. The positions of the phenoxide maxima so obtained are in agreement with those obtained by other workers for all three alkali cations.[8-10] Thus, the positions of the spectral bands are firmly established in pure dioxane and in the more highly aqueous dioxane–water mixtures. These points alone are sufficient to establish the general nature of the curves shown in Figure 1.

The spectra of the phenoxides in sparsely aqueous media are more difficult to obtain. In these media, addition of excess base is required to suppress the hydrolysis of the phenoxides. The spectra of the phenoxides in the region 1–20 mole % water in dioxane were obtained in a rather crude fashion described below. The requirement of varying amounts of excess alkali hydroxide in these media would seem to justify not attempting more intricate procedures.

For the spectra in the 1–20-mole % region, alkali phenoxides were prepared by refluxing recrystallized phenol and the appropriate alkali metal in benzene for several days. The precipitate was collected, recrystallized from dioxane, heated *in vacuo* to drive off solvent, and stored in a vacuum desiccator. The lithium phenoxide so prepared and stored contain a dioxane-insoluble material, perhaps lithium hydroxide or carbonate, which dissolved in slightly aqueous dioxane. Solutions of approximately 20 mg. of phenoxide in 25 ml. of dioxane were prepared. One-milliliter aliquots were diluted to 25 ml. with appropriate quantities of *ca.* 0.025 M aqueous alkali hydroxide and dioxane. Spectra of the *ca.* 3 × 10⁻⁴ M (in phenoxide) solutions thus prepared were obtained on a Cary Model 14 spectrophotometer. These operations were carried

(3) J. F. Garst, C. Hewitt, D. Walmsley, and W. R. Richards, *J. Am. Chem. Soc.*, **83**, 5034 (1961); J. F. Garst, D. Walmsley, C. Hewitt, W. R. Richards, and E. R. Zabolotny, *ibid.*, **86**, 412 (1964).
(4) D. G. Powell and E. Warhurst, *Trans. Faraday Soc.*, **58**, 953 (1962).
(5) R. Waack and M. A. Doran, *Chem. Ind.* (London), 1290 (1962); *J. Phys. Chem.*, **67**, 148 (1963).
(6) A. Streitwieser, Jr., and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963).
(7) N. Kornblum, P. J. Berrigan, and J. le Noble, *ibid.*, **85**, 1141 (1963); **82**, 1257 (1960); N. Kornblum, R. Selzer, and P. Haberfield, *ibid.*, **85**, 1148 (1963).
(8) H. E. Zaugg and A. D. Schaefer, *ibid.*, **87**, 1857 (1965).
(9) J. Jortner, M. Ottolenghi, and G. Stein, *ibid.*, **85**, 2712 (1963).
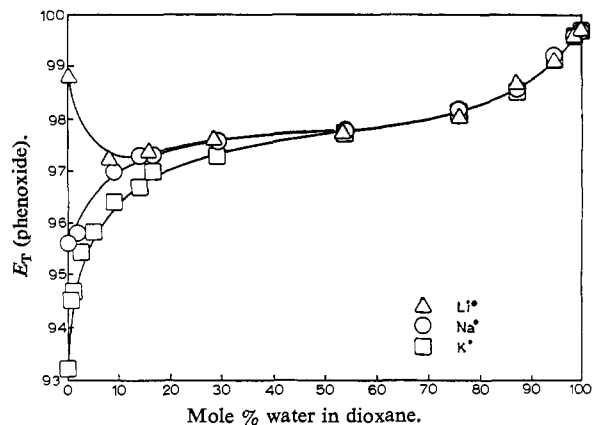(10) L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947).

Figure 1. Dependence of E_T(alkali phenoxides) on solvent composition in aqueous dioxane.

out using ordinary laboratory techniques, but excluding the atmosphere as much as possible. The three alkali phenoxides gave bands with the same position and shape in highly aqueous media, in agreement with the literature, suggesting suitable purity.

Results

In aqueous dioxane the phenoxide spectrum is not influenced by the nature of the cation in the region *ca.* 50–100 mole % water, while the cation effect is in the same direction as in the pure ethers for the more sparsely aqueous solvent mixtures. The dependence of the *ca.* 3000-Å. bands of lithium, sodium, and potassium phenoxides on solvent constitution is given in Figure 1. While the quantitative values for points in the sparsely aqueous media are not to be taken too seriously, since relatively large amounts of other salts (hydroxides) were present, and since the phenoxides used were crudely prepared, the points in the pure ethers *and* in the more highly aqueous media are meaningful. These points span the doubtful region. The points in the sparsely aqueous regions derive some support from the fact that they form smooth curves with the more significant points.

It is noteworthy that the addition of water to a lithium phenoxide solution in dioxane results in a *decrease* in E_T, while addition of water to sodium and potassium phenoxides in dioxane leads to an increase.

Discussion

The ca. 3000-Å. Transition. Since the spectra of the phenoxides are very similar to that of phenol itself,[11] and since the variations in the phenoxide spectra between nonaqueous media (in which the ions are highly associated) and highly aqueous media (dissociated ions) involve only band shifts, and not changes in the form of the spectra, the transition at *ca.* 3000 Å. (95 kcal./mole) must be an internal transition of the phenoxide ion, not a charge-transfer transition. A similar conclusion has been reached by Jortner, Ottolenghi, and Stein, who investigated the effects of large concentration of additives which usually shift charge-transfer-to-solvent transitions.[9] The corresponding transition of phenol has been designated A_{1g}–B_{2u} (a $\pi \rightarrow \pi^*$
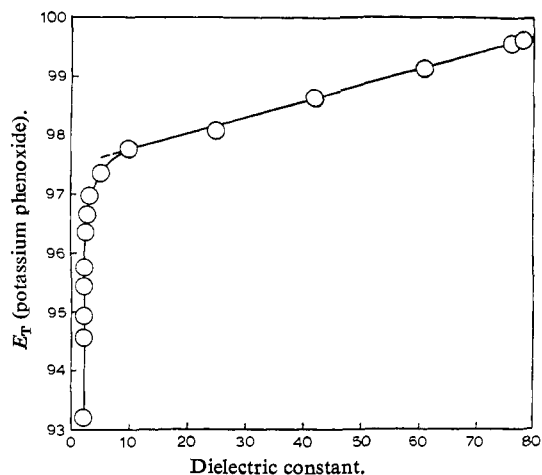
(11) See Figure 1 of ref. 2.

Figure 2. Dependence of E_T(potassium phenoxide) on dielectric constant in aqueous dioxane.

transition),[12] which must apply with equal propriety to the *ca.* 3000-Å. band of phenoxides. The loss of fine structure in the A_{1g}–B_{2u} band in going from phenol to its salts is probably a consequence of Franck–Condon orientation strain.[13,14]

Spectral Effects in Aqueous Dioxane. If hydrogen bonding or other modes of anionic aquation affect the energy of the A_{1g}–B_{2u} phenoxide transition in the same direction as does association with a cation,[2] which should be the case if aquation interactions occur principally at the oxygen atom of phenoxide, then it is to be expected that among the factors influencing E_T should be two which operate in opposing directions as water is added to dioxane solution: (1) increasing cation solvation and/or cation–anion charge separation should cause red shifts,[15] and (2) increasing aquation of

the anion should cause blue shifts. Effect 1 should be largest for small, very polarizing ions such as lithium, for which the change in the cationic electric field at the anion is greatest in going from a tight ionic aggregate to dissociated ions. On this basis it is expected that dE_T/dX, where X is the mole fraction of water in the solvent mixture, should, in the vicinity of $X = 0$, be algebraically increasing in the order lithium, sodium, potassium. This is the observed order. For potassium, effect 2 dominates effect 1, leading to a trend in E_T with increasing solvent polarity opposite from that found in pure ethers.[2] The same is true but to a lesser extent for sodium, and for lithium, effect 1 dominates effect 2, inverting the sign of dE/dX with respect to the other cations.

Kornblum and co-workers have presented evidence indicating that phenoxide ion is "selectively" solvated at the oxygen atom and that solvation by hydrogen-bonding solvents is more effective in preventing O-alkylation than is ionic aggregation in aprotic solvents.[7] Our spectral data are consistent with these conclusions, since selective aquation accounts for the blue shift attributed to increasing amounts of water in water-dioxane mixtures, and since the relative magnitudes of the spectral shifts due to phenoxide aquation and cation aquation, and/or ionic aggregate loosening with added water, are consistent with a rather strongly energetic interaction between water and phenoxide ion.

It is interesting to note that E_T(phenoxide) correlates linearly with the dielectric constant of the medium in the region of free ions, but begins to deviate strongly from this correlation at about $D = 10$–12 (Figure 2).[16] This point corresponds to about 50 mole % water, in good agreement with the region in which cation effects begin to be noticed (Figure 1).

(12) See F. A. Matsen in "Techniques of Organic Chemistry," Vol. IX, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 674. The transition in question is viewed, in this designation, as a transition of benzene perturbed by a substituent group. The corresponding transition of the unperturbed molecule is symmetry forbidden.

(13) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002, 1006 (1954).

(14) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, and references cited therein.

(15) Whether the solvation effects refer to ion pairs, higher aggregates, or mixtures of these with dissociated ions, the directions of these effects are presumed to be the same. Undoubtedly at least a portion of the shifts in E_T reported here is due to variations in the aggregation

equilibria. Dissociation is one means of increasing cation–anion charge separation.

(16) There seems to be no theoretical reason to expect E_T to be linear with D for a transition of a molecule, but such correlations are sometimes noted, at least over limited ranges.[5,17] On the other hand, deviations from linearity in solvents of low dielectric constant, where the present deviations occur, have been noted for molecular species which cannot be ionic aggregates.[17]

(17) C. J. Timmons, *J. Chem. Soc.*, 2613 (1957).