

Ion Aggregate Spectra and Solvent Polarity

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The positions of certain electronic spectral bands of disodium benzophenone and sodium phenoxide vary with the nature of the solvent. For these and a number of similar systems, ethereal solvents appear in a consistent order in their influence on the spectra. This order is the same for the effect of solvent on several equilibria and a reaction rate, so long as the cation involved is sodium. Deviations for other cations suggest rather specific effects. Factors influencing the positions of spectral bands in ionic aggregates are discussed.

Introduction

For several ionic or ionoid compounds, shifts in the positions of electronic spectral bands with solvent, among relatively nonpolar solvents (particularly ethers), have been interpreted as reflections of solvation phenomena.²⁻⁷ It has been suggested that such shifts might provide useful indices, at least qualitative, to the polarities of these solvents toward organometallic compounds.²

The spectral behavior of both disodium benzophenone and sodium phenoxide has been examined in ethers (and, in the latter case, a few amines). In order to test the previous interpretations and suggestions, the spectral data for disodium benzophenone, sodium phenoxide, sodium *p,p'*-diphenylbenzophenone ketyl,² and 1,1-diphenylhexyllithium,⁴ and equilibrium data for several reactions, as well as rate data for one, are compared with the spectral shifts for sodium benzophenone ketyl in the same solvents, primarily ethers.

Experimental

Solvents. All ethers and amines were purified by prolonged refluxing over sodium or sodium-potassium alloy, followed by fractional distillation and storage over sodium adducts of benzophenone on a vacuum manifold. They were distilled through the vacuum manifold from storage vessels to solution preparation vessels as needed.

Alkali Phenoxides. Phenoxide solutions in the desired solvents were prepared on a vacuum manifold by essentially the same techniques as described for benzophenone ketyls.² In reaction vessels attached to optical cells, solutions of phenol in the desired solvent were allowed to react with alkali metal mirrors created

by distillation of the appropriate alkali metal through several constrictions in a side arm (lithium mirrors were created by evaporation of ammonia from lithium-ammonia solutions in a similar side arm). The phenol solutions and metal mirrors were allowed to react at room temperature, with contact between the two being interrupted for the determination of intermediate spectra. The contact time between the solution and mirror was on the order of a day beyond that at which the spectrum stopped changing, a total of one to a few days. As shown in Figure 1, the near-ultraviolet spectrum of phenol is readily distinguishable from that of any of the phenoxides, due to the fact that the phenoxide band corresponding to the *ca.* 2700-Å band of phenol is considerably displaced to the red and does not have the vibrational fine structure of the phenol. The occurrence of sharply defined vibrational fine structure in the phenol permits the detection of small quantities of phenol in the presence of large quantities of phenoxide, since corresponding shoulders appear on the short wave length side of the phenoxide band in most cases. In all ethers a sharp, well-defined isosbestic point appeared when the progress of the reaction of phenol with alkali metal was monitored spectrophotometrically. A typical case is shown in Figure 1. The position of the maximum of the phenoxide band is seen to be independent of concentration over the range studied for each ether. In some cases, this extends from 10⁻² to 10⁻⁴ M, and in all cases covers at least a range of a factor of 10 in this region.

The extinction coefficient of phenol at the maximum of the *ca.* 2750-Å band is the same in all ethers (2.15 ± 0.02) $\times 10^3$ l. mole⁻¹ cm.⁻¹. Extinction coefficients for the phenoxides were evaluated by estimation from the initial and final spectra of data such as that of Figure 1, followed by slight adjustments until the best fit was obtained for *all* spectra (including the intermediate curves) of the type shown in Figure 1. The extinction coefficients at the maxima of the phenoxide peaks (*ca.* 3000 Å.) were the same, within probable experimental error, in all solvents (3.8×10^3 l. mole⁻¹ cm.⁻¹).

The occurrence of isosbestic points, the lack of concentration effects on band maxima, and the consistency of the extinction coefficients confirm our *a priori* assumption that this method of preparing dilute phenoxide solutions is a particularly clean one. In addition, Dr. Harold Zaugg has kindly communicated to us some of his results on the spectra of alkali phenoxides in 1,2-dimethoxyethane.⁸ Our results are in good agreement with his, both as to band positions and extinction coefficients, for lithium, sodium, and potassium salts.

Disodium Benzophenone. Solutions of disodium benzophenone were prepared employing techniques pre-

(1) Part of the experimental work reported herein was performed at the University of California, Riverside, Calif.

(2) (a) J. F. Garst, C. Hewitt, D. Walmsley, and W. Richards, *J. Am. Chem. Soc.*, **83**, 5034 (1961); (b) J. F. Garst, D. Walmsley, C. Hewitt, W. R. Richards, and E. R. Zabolotny, *ibid.*, **86**, 412 (1964).

(3) D. G. Powell and E. Warhurst, *Trans. Faraday Soc.*, **58**, 953 (1962).

(4) R. Waack and M. A. Doran, *J. Phys. Chem.*, **67**, 148 (1963); *Chem. Ind. (London)*, 1290 (1962).

(5) A. Streitwieser, Jr., and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963).

(6) T. E. Hogen-Esch and J. Smid, *ibid.*, **87**, 669 (1965).

(7) K. Dimroth, C. Reichardt, T. Seipmann, and F. Bohlman, *Ann.*, **661**, 1 (1963); K. Dimroth, C. Reichardt, and A. Schweig, *ibid.*, **661**, 95 (1963).

(8) H. E. Zaugg and A. D. Schaeffer, *J. Am. Chem. Soc.*, **87**, 1857 (1965).

viously described for the preparation of benzophenone ketyls, except that the reaction with the sodium mirror was allowed to proceed to the point that the ketyl spectrum had entirely disappeared and had been replaced by that of a second species.

General. All spectra reported were determined using a Cary Model 14 spectrophotometer. Room temperature was *ca.* 23°. Concentrations were usually *ca.* 10⁻⁴ M.

Results

The visible spectrum of the disodium adduct of benzophenone consists of a single band with a maximum between 4800 and 5800 Å., depending on the solvent.

The alkali phenoxides exhibit a structureless band at about 3000 Å., the exact position of which depends on the metal ion and solvent.

Figure 1 and Tables I–III detail these results.

Table I. Solvent Effect on the Visible Spectrum of Disodium Benzophenone

Solvent	E_T , kcal./ mole ^a
Di- <i>n</i> -propyl ether	59.0
Methyl <i>n</i> -propyl ether	57.6
Methyl isopropyl ether	57.5
Diethyl ether	57.1
1,1-Dimethoxyethane	56.4
1,4-Dioxane	52.2
Tetrahydrofuran	50.7
1,2-Dimethoxyethane	50.4

^a Energy of transition of the visible band (from the position of its maximum) in *ca.* 10⁻⁴ M solution. Estimated limits of error, ±0.2 kcal./mole.

Table II. Metal Ion Effect on Phenoxide Spectra

Solvent	$E_T(\text{Li})^a$	$E_T(\text{Na})^a$	$E_T(\text{K})^a$
1,4-Dioxane ^b	98.8	95.4	93.2
1,2-Dimethoxyethane	96.6	94.7	91.1

^a Apparent energy of the *ca.* 3000-Å. transition of phenoxide ion in kcal./mole. The limits of error are estimated at ±0.2 kcal./mole. ^b In dioxane, E_T (benzophenone ketyl) is as follows: Li, 46.0 kcal./mole; Na, 44.3; Cs, 41.7 (H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960)).

Table III. Electronic Spectra of Sodium Phenoxide in Solution

Solvent	E_T^a	$E_T(\text{ketyl})^b$
Di- <i>n</i> -butyl ether	95.9	45.5
Diethyl ether	96.2	45.1
1,1-Dimethoxyethane	95.9	44.4
1,4-Dioxane	95.4	44.3
Tetrahydrofuran	95.1	42.2
1,2-Dimethoxyethane	94.7	40.9
Triethylamine	95.9	45.4
<i>t</i> -Butylamine	94.6	43.0
<i>n</i> -Butylamine	92.8	

^a Apparent energy of transition of the *ca.* 3000-Å. band of sodium phenoxide in kcal./mole. The uncertainty is estimated at ±0.2 kcal./mole. ^b Apparent energy of transition of the *ca.* 6500-Å. band of sodium benzophenone ketyl, kcal./mole. See ref. 2.

Discussion

General Interpretation of Solvent Effects. Current interpretations of solvent effects on electronic spectra

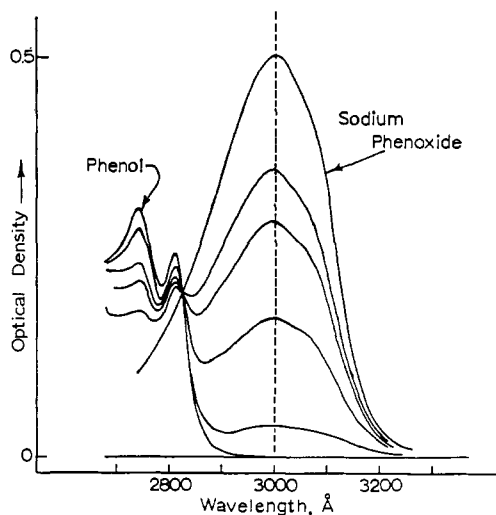


Figure 1. Example of isosbestic point obtained in the conversion of phenol to phenoxide by reaction with a sodium mirror in an inert atmosphere. Most of the experiments were run on more concentrated solutions than this one. It was typical, however, and convenient for tracing. The solvent here was 2-methyltetrahydrofuran and the metal sodium.

of anions associated with alkali cations share one feature of importance to the present considerations: all agree that the shifts constitute reflections of some kind of solvent polarity.²⁻⁸ Details and emphasis have varied. Two theoretically distinct classes of potential effects have been recognized: (1) variations with solvent in ground-state ion aggregate structure (including the kinds of aggregates present and the interionic geometry in a given class of aggregate), and (2) for aggregates of fixed geometry, variation among solvents in the differential between ground- and excited-state solvation energies. The relative roles of these effects is not well established, but recent data suggest that 1 may be the only effect of importance.⁶ The role of cation solvation has been emphasized relative to the role of anion solvation.

If specific and tight solvent-cation interactions are involved, the apparent order of solvent polarity might be expected to vary with the metal ion, for steric reasons. For similar reasons, if the ionic aggregates involved are tight, the apparent order of solvent polarity might vary with the anion.⁹ The latter point is tested in this paper, with some attention being given the former.

When monotonic, but not linear, correlations between apparent energies of transition (E_T values), for anions with the same counterion and among the same solvents are found, the direction of curvature can be given a simple, but naive, interpretation: concave up curvature in plots such as Figure 2 implies that the species plotted along the ordinate tends to exist in looser aggregates than the one plotted along the abscissa. Concave down curvature implies the converse situation. The basis of this interpretation is the expecta-

(9) As used here with regard to ionic aggregates, "tight" describes aggregates which are coulombically at a lower potential energy (gas phase, neglecting solvation) than a collection of equal numbers and kinds of ions in "looser" aggregates. Thus, ion quadrupoles and higher aggregates are tighter than others. From tight to loose, the order of other aggregates is triple ions, ion pairs, dissociated ions. Within a given kind of aggregate tightness may vary, so that contact ion pairs are tighter than solvent separated ion pairs.

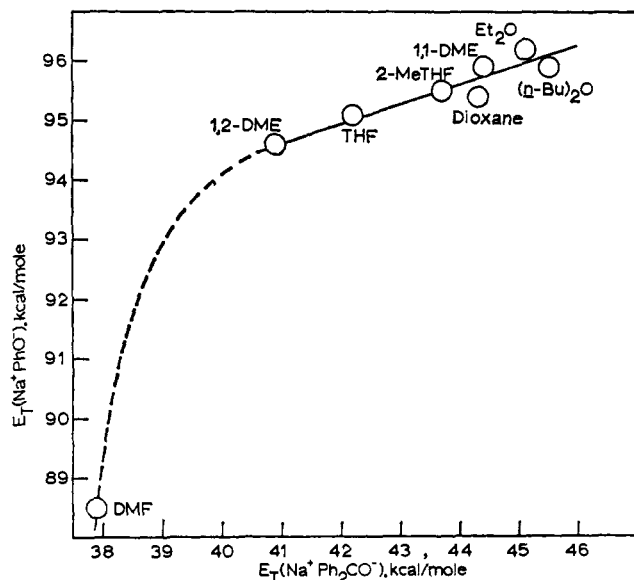


Figure 2. Comparison of spectral shifts with solvent for sodium phenoxide and sodium benzophenone ketyl. The values in DMF are from ref. 3 and 8.

tion that sufficiently tight, and sufficiently loose, aggregates will not exhibit spectral responses to solvent polarity changes, the latter because a distant metal ion and its solvation sphere will only slightly perturb the anion, the former because sufficiently tight aggregates will not effectively orient solvent molecules in the ground state (or, alternatively, sufficiently tight aggregates will not respond with ground state structural changes to changes in solvent polarity).¹⁰ This discussion of the situation may neglect other factors which might contribute to curvature in these plots, but it is simple and seems to apply reasonably to the cases at hand.

Reasons for assigning the major solvation effects to the cations include the poor anion solvation capacity usually ascribed to ethers,¹¹ the large size of the anions employed here, and the steric and electrostatic shielding of the prime anion solvation sites by the cation of the aggregates involved (for all aggregates except free ions). Ethers are often thought of as Lewis bases which coordinate metal ions. Some data considered later suggest that they have considerable solvation capacity even in the absence of the ability to directly coordinate with a cationic site.

Sodium Phenoxide. The *ca.* 3000-Å. bands of alkali phenoxides are due to $\pi \rightarrow \pi^*$ transitions of the phenoxide ion.^{12,13}

The fact that the metal ion effect on E_T (phenoxide) in dioxane and 1,2-dimethoxyethane is similar in magnitude to that found for the benzophenone ketyls suggests that the spectra of the two anions are comparably sensitive to coulombic perturbations. The

(10) It is here assumed that the cation plays the major role in solvation, so that direct anion-solvent interactions can be neglected.

(11) Even the "dipolar aprotic solvents," such as dimethylformamide and dimethyl sulfoxide, have been presumed to be poor anion solvators. Ethers, with their smaller dipole moments, must be even more certainly in this class. See A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962), and references therein.

(12) J. Jortner, M. Ottolenghi, and G. Stein, *J. Am. Chem. Soc.*, **85**, 2712 (1963).

(13) J. F. Garst and W. R. Richards, *ibid.*, **87**, 4084 (1965), and references cited therein.

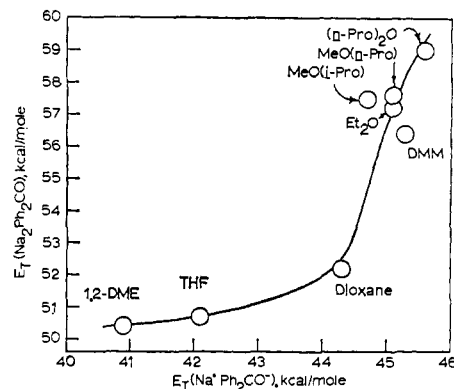


Figure 3. Comparison of spectral shifts with solvent for disodium benzophenone and sodium benzophenone ketyl. DMM is dimethoxymethane.

smaller solvent sensitivity, among ethers, of E_T (sodium phenoxide) then points to the presence of tighter aggregates for the phenoxide than for the ketyl.^{14,15} The concave down curvature of the plot when dimethylformamide is included is consistent with this idea, as is the smaller size of the phenoxide ion.

The larger sensitivity of E_T (sodium phenoxide) to solvent variation among amines may be due to the presence of ion pairs in the amines, as opposed to ion quadrupoles or higher aggregates in the ethers, or it may be due to special effects involving hydrogen bonding of the primary and secondary amines to the phenoxide and ketyl anions.

The monotonic trend in the E_T plot for ethers indicates the applicability of a consistent solvent polarity scale to these species, both of which contain sodium ions.

Disodium Benzophenone. The results of Hoijtink and co-workers suggest that hydrocarbon dianions are usually associated with two cations in ethers.¹⁷ The monotonic trend in E_T (disodium benzophenone) vs. E_T (sodium benzophenone ketyl) (Figure 3) is consistent with the applicability of a mutual solvent polarity scale.

The concave up curve suggests that disodium benzophenone exists in looser aggregates than sodium benzophenone ketyl. This unexpected result could be rationalized as being a consequence of an asymmetric triple ion structure, in which one sodium ion is very

(14) Waack and Doran have proposed this explanation for the lack of sensitivity of the spectrum of benzyl lithium to solvent.⁴

(15) Some of the data of Garst, *et al.*,^{2b} fit very well with the suggestion of Hirota and Weissman that the observed solvent shifts may reflect nothing other than the position of the ion pair-ion quadrupole equilibrium, the spectra of each of these species being considered to be solvent independent.¹⁶ Thus, E_T (sodium benzophenone ketyl) approaches a maximum in nonpolar solvents which is the same for a number of solvents, reflecting, possibly, the presence of a preponderance of ion quadrupoles in these solvents.

However, construction of composite bands from those observed near the extremes of position for sodium benzophenone ketyl demonstrate that the solvent shifts must reflect more than this since the band in tetrahydrofuran, for example, is predicted on this basis to be quite different in shape and much wider than is actually observed. Lack of apparent band shape changes could be preserved in a similar theory if several more kinds of aggregates, say, different kinds of ion pairs, were included in the scheme.⁶

(16) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2538 (1964).

(17) G. J. Hoijtink, E. deBoer, P. H. van der Meij, and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956); A. C. Aten, V. Dieleman, and G. J. Hoijtink, *Discussions Faraday Soc.*, **29**, 182 (1960).

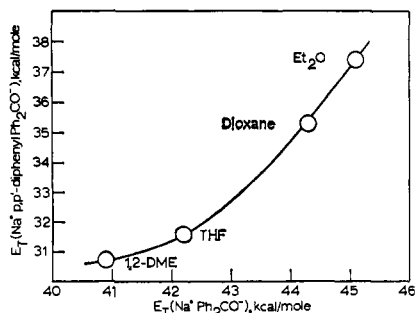


Figure 4. Comparison of spectral shifts with solvent for sodium *p,p'*-diphenylbenzophenone ketyl and sodium benzophenone ketyl.

tightly bound and the other very loosely bound, as has been previously suggested.¹⁸ The unit might then behave as a rather loose ion pair (Ph_2CONa^- , Na^+).

Sodium *p,p'*-Diphenylbenzophenone Ketyl.^{2b} The concave up curvature of the monotonic plot of Figure 4 indicates looser aggregates for this species than for the benzophenone ketyl, consistent with the larger size of the former anion.

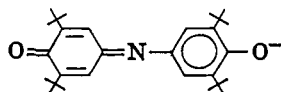
Sodium 2,3',5',6-Tetra-*t*-butylindophenoxide.¹⁹ This salt also exhibits E_T shifts with solvent which parallel those obtained for sodium benzophenone ketyl. In tetrahydrofuran and 1,2-dimethoxyethane the visible band at *ca.* 6500 Å. shows a distinctly measurable concentration dependence, so that in these solvents some ionic dissociation is apparent. In less polar solvents the concentration dependence is not apparent.

1,1-Diphenylhexyllithium. A linear correlation with sodium benzophenone ketyl is obtained if 1,2-dimethoxyethane is omitted, a concave up correlation if it is included, but in the latter case the curvature is rather abrupt (Figure 5). One of two conclusions seems to be in order. Either 1,1-diphenylhexyllithium exists as very loose aggregates (perhaps dissociated ions) in both tetrahydrofuran and 1,2-dimethoxyethane,²⁰ or the relative polarities of these solvents toward the two organoalkali compounds involved are not the same. Since the two metal ions are not the same, the latter possibility deserves serious consideration.

Two other examples for which the combination lithium 1,2-dimethoxyethane shows aberrant behavior are the "cationic plots"¹¹ of Warhurst and co-workers³ and the formal equilibrium constants for the disproportionation of monoalkali tetraphenylethylenes at room temperature.^{21,22} It is tempting to associate the lithium 1,2-dimethoxyethane deviations with the steric

(18) B. M. Mikhailov and N. G. Cheronova, *Dokl. Akad. Nauk SSSR*, **85**, 341 (1952).

(19) Studied in these laboratories by G. Pacifici and S. C. Chadha, unpublished results. The solutions were prepared in a manner similar to the ketals² by the one-electron reduction of the stable free radical over a sodium mirror. The structure of the anion is



(20) As suggested by R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 4042 (1963).

(21) J. F. Garst and E. R. Zabolotny, *ibid.*, **87**, 495 (1965).

(22) In 1,2-dimethoxyethane the equilibrium constants for the disproportionation of monoalkali tetraphenylethylenes vary in the order $\text{Cs} > \text{K} > \text{Li} > \text{Na}$, while in tetrahydrofuran the order is $\text{Cs} > \text{K} > \text{Na} > \text{Li}$. Either sodium or lithium is out of line in 1,2-dimethoxyethane with respect to decreasing radius. All such deviant cases considered here become consistent if Li is viewed as the culprit. Further, the disproportionation

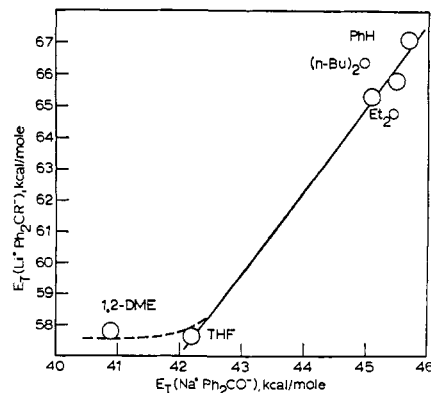
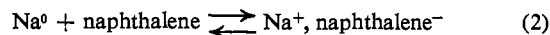
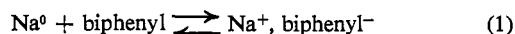


Figure 5. Comparison of spectral shifts with solvent for 1,1-diphenylhexyllithium and sodium benzophenone ketyl.

requirements of the ligands and the lithium and sodium ions, particularly with reference to the bidentate coordination possibilities of 1,2-dimethoxyethane.²³ Since all the deviations for lithium compounds in 1,2-dimethoxyethane are in the direction indicating that it is a less polar solvent than is predicted from data on organosodium compounds, a reasonable speculation for the origin of this effect is that tetracoordinate Li^+ can be coordinated (in a contact ion pair) in bidentate fashion by only one 1,2-dimethoxyethane molecule (since one coordination position is occupied by the organic anion), while the larger Na^+ may be hexacoordinate, thereby being able to enjoy the bidentate attentions of two 1,2-dimethoxyethane molecules.²⁴ If especially favorable energetic factors are associated with this type of chelation, the change in coordination number could have a greater effect on the solvation energies for bidentate solvents than for monodentate solvents. Other specific steric solvation effects are also imaginable.

Shatenstein, Petrov, and Belousova have noted differences in the order of apparent solvent polarity, for sodium and lithium, judged from equilibria 1 and 2.²⁵ For example, relative to 1,2-dimethoxyethane, they find that 1,3-dimethoxypropane is a very poor solvent for Na^+ , but a very good solvent for Li^+ . Further, potassium and lithium react with biphenyl and naph-



thalene to a greater extent in 1,2-dimethoxyethane than does sodium, although in tetrahydrofuran the order of metals is $\text{Li} > \text{Na} > \text{K}$.

While these considerations suggest the importance of solvation steric requirements of a rather specific nature, some such variations could alternatively be accounted for in general terms through competitive interionic coulombic and ion solvation factors.²¹ These, in turn, probably depend on specific solvation effects. A com-

parison of the equilibrium constants for lithium tetraphenylethylene are the same for tetrahydrofuran and 1,2-dimethoxyethane, as one might construe they should be from the 1,1-diphenylhexyllithium spectra.

(23) Many authors have previously noted the potential bidentate behavior of 1,2-dimethoxyethane and dioxane, and the similar potential bi- or tridentate behavior of diglyme. Reference 2b contains some spectral data which can be construed as evidence for such behavior, but is not compelling.

(24) For free ions, or for solvent-separated ion pairs, the number of coordinating bidentate 1,2-dimethoxyethane molecules would be two and three for lithium and sodium, respectively, on this basis.

(25) A. I. Shatenstein, E. S. Petrov, and M. I. Belousova, *Organic Reactivity*, Tartu State University, Estonian SSR, **1**, 191 (1964).

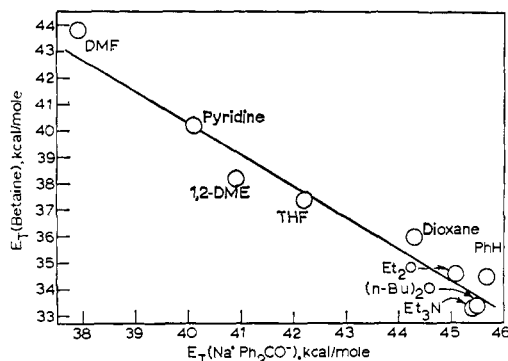


Figure 6. Comparison of spectral shifts with solvent for betaines⁷ and sodium benzophenone ketyl.

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-

(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 Weissman¹⁸ extended by our own observations.

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 radical²⁹ 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.

Acknowledgments. This work was supported by grants from the National Science Foundation. We are grateful to Dr. Harold Zaugg, Professor Nathan Kornblum, and Professor Karl Dimroth for providing us with unpublished information.

(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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Contribution from the Department of Chemistry, The University of Georgia, Athens, Georgia.¹ Received August 10, 1964

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 com-

peting 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-

(1) A portion of the experimental work reported herein was performed at the University of California, Riverside, Calif.

(2) J. F. Garst, R. A. Klein, E. R. Zabolotny, and D. Walmsley, *J. Am. Chem. Soc.*, **87**, 4080 (1965).