

Fig. 1.—Apparatus employed for Beer's law studies.

Di-(*p*-anisyl)-nitrogen oxide was prepared employing the methods of Kehrman and Schmajewski¹⁷ and Meyer and Reppe¹⁸; m.p. 150–153°.

Commercially obtained 1,2-dimethoxyethane, 1,1-dimethoxyethane, 1,1-dimethoxymethane, bis-(2-methoxyethyl) ether (diglyme), dioxane, and di-*n*-butyl ether were purified by refluxing over sodium or sodium-potassium alloy and distilling, a middle fraction of constant boiling point being used. The amines were similarly treated. 2-Methyltetrahydrofuran and tetrahydrofuran were purified by the method recommended for tetrahydrofuran by Fieser.¹⁹ Absolute reagent diethyl ether was used without further purification (except as noted below in storage).

Benzene was purified by the method recommended by Fieser,¹⁹ dried over Drierite, refluxed over sodium-potassium alloy, and distilled therefrom through an 80 cm. glass helices packed column; b.p. 81.6° (730 mm.).

N,N-Dimethylformamide was Matheson Coleman and Bell spectroquality solvent.

General Considerations.—All visible, ultraviolet, and infrared electronic transitions were recorded on a Cary Model 14 spectrophotometer using matched quartz cells (2.00, 1.00, and 0.118 cm. light paths) at room temperature (21 ± 3°) in an air conditioned room. Fluctuations in the room temperature did not affect the spectra.

Alkali metal adducts were prepared on a vacuum manifold in small (*ca.* 30 ml.) Pyrex reaction vessels attached to quartz optical cells by means of graded seals, attached to quartz e.s.r. tubes which could be sealed off *in vacuo*, or attached to the double cell apparatus for Beer's law studies, described below. Spectra obtained in apparatus employing Teflon tipped stopcocks were identical with those obtained with greased stopcocks, even though solutions prepared in the presence of stopcock grease often faded slightly after preparation, whereas those prepared in the absence of grease usually exhibited no fading.

The reaction vessels were attached to the vacuum manifold, degassed, baked out by flaming repeatedly, and briefly reopened for the addition of a small quantity (*ca.* 2–4 mg.) of the organic substrate. Alkali metal was added either at this time, as an amalgam, or, later, by distillation into the vessel from a side arm. The vessel was degassed and 5 to 20 ml. of the chosen solvent were distilled into it from storage in a reservoir on the vacuum manifold as a solution of the sodium or potassium adduct of benzophenone, tetraphenylethylene, or phenanthrene.

Preparation of the adducts was carried out in such a manner as to lead to solutions containing a small excess of the organic parent compound. The spectra so obtained were identical with those obtained in experiments in which such an excess was carefully avoided, but in experiments in which the concentration of excess benzophenone was on the order of 1 *M*, the visible band was often shifted to higher energies.

Concentrations of the resulting ketyl solutions were not carefully determined, but the optical densities (1-cm. cell) at the benzophenone ketal visible maximum ranged from 0.4 to about 1.8, corresponding to ketyl concentrations from 3×10^{-4} to 10^{-5} *M*, the exact values being dependent on the extinction coefficient employed for the calculation. In the cases of the sodium benzophenone ketyls in diethyl ether and dioxane, the spectra were examined in 0.118-cm. cells at concentrations corresponding to optical densities as high as 0.5, or about 6×10^{-4} *M*.

(17) F. Kehrman and C. Schmajewski, *Ber.*, **54**, 2438 (1921).

(18) K. H. Meyer and W. Reppe, *ibid.*, **54**, 327 (1921).

(19) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 285 (dioxane) and p. 282 (benzene).

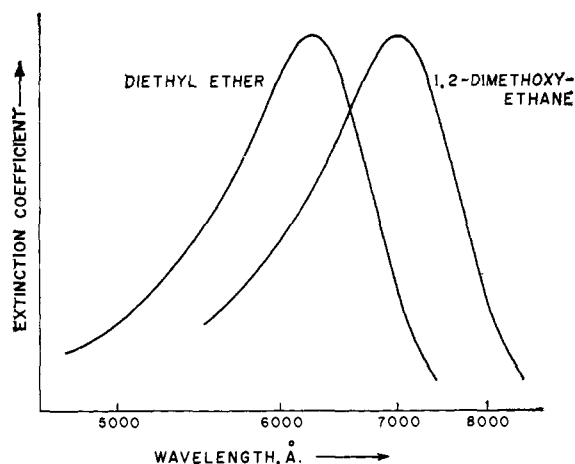


Fig. 2.—Solvent effect on the *ca.* 6500-Å band of sodium benzophenone ketyl. The ordinate contains an arbitrary multiplicative factor, the relative shapes of the bands being correctly given.

Variations in the position of the maximum with concentration were within the estimated experimental error (±50 Å).

For the mixed solvent ketyl preparations, a 15-ml. graduated tube which could be read to 0.05 ml. was substituted for the Pyrex reaction vessel. A small quantity of one solvent was distilled into the graduated tube, measured, and diluted to the desired concentration with the other solvent. In selected cases the composition of the mixed solvents were later verified by vapor phase chromatography.

Beer's Law Tests.—Tests of Beer's law employed the apparatus shown in Fig. 1, consisting of two 1.00- or 0.118-cm. matched quartz cells assembled in such a manner as to enable all of a solution of a ketyl to be tipped into one side of the apparatus. Solvent was then distilled into the other side until the volumes of liquid in both sides were the same (adjusted *via* calibration marks). Beer's law runs were made by progressively pouring some of the ketyl solution into the cell containing pure solvent, then equalizing the volumes in the two arms by pouring some of the more dilute solution back into the other side. After each such operation, the apparatus was gently shaken to assure thorough mixing in each arm, and the optical density through each cell measured. The optical density when all the solution was thoroughly mixed could be checked before and after each run, as a check on possible fading of the solution during the run. The fading during runs was negligible, usually immeasurable, although with the more dilute solutions up to 30% of the original optical density was lost in a period of a few hours after sealoff from the reaction vessel in which the solution was prepared. Beer's law runs were not attempted until such fading had ceased. Fading was not observed in the more concentrated solutions.

If Beer's law is followed, the sum of the optical densities (*A* and *B*) through the cells (1 and 2, Fig. 1) will be a constant. If, on the other hand, a reaction of the type of $nM \rightleftharpoons M_n$, where the monomer absorbs but the polymer does not, is responsible for deviation from Beer's law, the following equation should be obeyed

$$A + B = (-nK/\epsilon^{n-1}l^{n-1})(A^n + B^n) + 2T\epsilon l$$

where *K* is the equilibrium constant for the polymerization, *l* is the path length of the cells, ϵ is the molar extinction coefficient for the monomer, and *T* is the over-all formal concentration of *M* (*T* is half the sum of the formal concentrations of *M* in the two cells, if they are of equal volume). We assume the deviations observed in diethyl ether to be due to dimerization; thus, the appropriate plot for the extraction of information is (*A* + *B*) vs. (*A*² + *B*²), shown in Fig. 3.

E.s.r. Measurements.—A Varian Associates X-band e.s.r. apparatus with 100-Kc. field modulation and a 12-in. magnet system was used.

Spin resonance intensity measurements employed the method of Lindblom,²⁰ using a solution of MnCl₂ in MgO of cubic crystalline structure sealed into a Teflon sheet formed into a cylinder which could be placed in the cavity along with the unknown or with a primary reference material. Primary reference compounds used were diphenylpicrylhydrazyl and di-(*p*-anisyl)-nitrogen oxide. The values obtained for the effective concentration of spins in the Mn secondary reference were 1.97×10^{-8} and 2.19×10^{-8} *M*, respectively.

(20) R. O. Lindblom, University of California Radiation Laboratory Report No. UCRL-8910, October 19, 1959; R. O. Lindblom, R. M. Lemmon, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 2484 (1961).

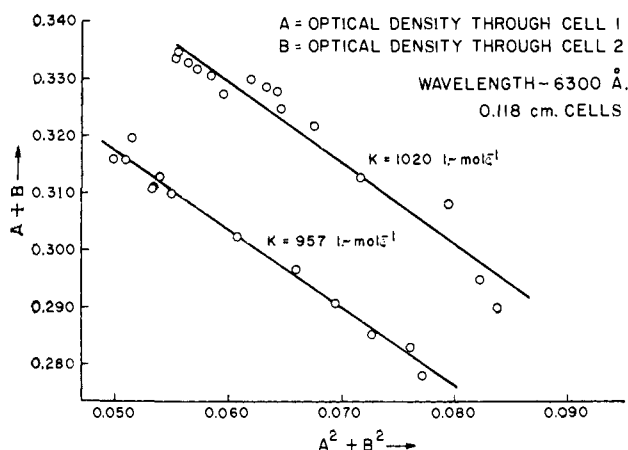


Fig. 3.—Deviations of sodium benzophenone ketyl from Beer's law at 6300 Å. (room temperature). In the calculation of dimerization constants (K) the extinction coefficient employed was 12,000.

A sodium benzophenone ketyl solution in diethyl ether was prepared in a vessel attached to both a 1-cm. quartz optical cell and an e.s.r. tube. The optical density at 6300 Å. was 0.720; e.s.r. intensity measurements on the same solutions then permitted calculation of the extinction coefficient. The two values so obtained were 12,700 (diphenylpicrylhydrazyl primary standard) and 11,400 (di-(*p*-anisyl)-nitrogen oxide primary standard). A value of 12,000 was employed for further calculations pertinent to the Beer's law runs. In spite of the good agreement between the two primary standards, the value of the extinction coefficient given should be viewed as subject to the usual uncertainty of such e.s.r. intensity measurements.

Low temperature e.s.r. spectra were taken of a sample of sodium benzophenone ketyl in diethyl ether (estimated concentration: $10^{-3} M$). The sample was quickly frozen in a Varian low temperature quartz Dewar cavity insert at liquid nitrogen temperature. When the sample was scanned in the region of the field corresponding to a g -value of two, a spectrum very similar to that displayed by Hirota and Weissman was obtained,²¹ although we did not detect resonance at half that field.

Results

Figure 2 shows the visible spectral band of sodium benzophenone ketyl in diethyl ether and 1,2-dimethoxyethane. The band progresses from high energy to lower through the solvents reported here with no discernible change in shape. The half-width at half-height is constant at 5.65 ± 0.15 kcal./mole.²² The behavior of the spectrum of sodium *p,p'*-diphenylbenzophenone ketyl is similar. Concentration effects on the position and shape of the *ca.* 6500-Å. band were within experimental error in the range of concentrations investigated.

The cyclohexanone $n \rightarrow \pi^*$ transition is much less sensitive to variation among the ethers and other "nonpolar" solvents considered here than are the ketyl spectra. In spite of this, a directional trend of the energy of transition (E_T) of the $n \rightarrow \pi^*$ band among the ethers is detectable, in a direction opposite to that of the ketals.

Table I summarizes the spectral data on sodium benzophenone ketyl, sodium *p,p'*-diphenylbenzophenone ketyl, and cyclohexanone in various solvents.

It is found that Beer's law is obeyed by sodium benzophenone ketyl in 1,2-dimethoxyethane. The report of Bent and Harrison that Beer's law is not obeyed by the latter compound in diethyl ether is also confirmed.¹⁴ The quantitative aspects of these variations are shown in Fig. 3. The quantitative agreement with Bent and Harrison is not particularly good. Recalculations of their data show that their determinations of K lead to values from 0.32 to 0.51 ϵ ,

²¹ N. Hirota and S. I. Weissman, *Mol. Phys.*, **5**, 537 (1962).

²² The "width at half height" previously given was the full width.¹

TABLE I

SOLVENT EFFECTS ON KETYL AND CYCLOHEXANONE SPECTRA	$E_T(B)^a$	$E_T(P)^b$	$E_T(C_6H_{10}O)^c$
Benzene	45.7 ^d	..	99.0
Diethyl sulfide	45.6	..	99.4
Di- <i>n</i> -propyl ether	45.6	..	98.8
Di- <i>n</i> -butyl ether	45.5	..	98.7
1,1-Dimethoxymethane	45.3
Diethyl ether	45.1	37.4	98.7
Methyl <i>n</i> -propyl ether	45.1	..	99.0
Methyl isopropyl ether	44.7	..	99.1
Methyl <i>t</i> -butyl ether	44.4
1,1-Dimethoxyethane	44.4	..	99.1
1,4-Dioxane	44.3	35.3	99.1
2-Methyltetrahydrofuran	43.7
Tetrahydrofuran	42.2	31.6	99.1
1,2-Dimethoxyethane	40.9	30.7	99.6
Diglyme	40.5	..	99.3
Triethylamine	45.4	..	98.3
<i>tert</i> -Butylamine	43.0	..	99.2
<i>n</i> -Propylamine	41.9	..	98.0
Pyridine	40.2
Dimethylformamide ^e	37.9	..	99.3
1,4-Dioxane (Li ⁺) ^f	46.0
1,4-Dioxane (Na ⁺) ^f	44.3
1,4-Dioxane (Cs ⁺) ^f	41.7

^a Energy of transition corresponding to *ca.* 6500-Å. band of sodium benzophenone ketyl (measured at the maximum), kcal./mole. ^b Energy of transition of *ca.* 8500-Å. band of sodium *p,p'*-diphenylbenzophenone ketyl. ^c Energy of $n \rightarrow \pi^*$ transition of cyclohexanone. ^d Small deviations of a few of these values from those previously reported are the result of averaging more determinations. The variations are all well within the estimated experimental error of ± 0.2 kcal./mole except for the value for benzene, previously reported as 45.4 kcal./mole.¹ ^e From ref. 15. ^f From ref. 13.

the average being 0.44 ϵ . Our values range from 0.066–0.084 ϵ in 0.118-cm. cells (no detectable fading) to 0.16–0.24 ϵ in 1-cm. cells (fading after seal-off). In the latter cases, which we consider less trustworthy than the former, our values begin to approach those obtained from the data of Bent and Harrison.

Sodium benzophenone ketyl does not give visibly detectable dissolution in cyclohexane containing no excess benzophenone, although the addition of a trace of 1,2-dimethoxyethane leads to obvious dissolution. Figure 5 shows the further changes in E_T for the admixture of more 1,2-dimethoxyethane. The change is very sharp for the first few per cent 1,2-dimethoxyethane added.

Discussion

In the following paragraphs the origin and potential significance of the shifts of the visible band of sodium benzophenone ketyl are discussed. After a brief presentation of arguments pertaining to the degree and nature of ionic aggregation in ethereal ketyl solutions, the nature of the transition corresponding to the visible band, and the origin of the metal ion effect, the solvent effect is considered.

Ionic Aggregation.—Recently presented evidence leaves little room for doubt that the accepted structure for ketals is proper.^{23,24} Many studies have demonstrated that the ions of I are appreciably associated in ethers and amines, metal ion effects on e.s.r. and electronic spectra being particularly direct evidence.^{13,21,23–27}

(23) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **82**, 4424 (1960).

(24) P. B. Ayscough and R. Wilson, *Proc. Chem. Soc.*, 229 (1962).

(25) F. C. Adam and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 1518 (1958).

(26) A. C. Aten, J. Dieleman, and G. J. Hoijtink, *Discussion: Faraday Soc.*, **29**, 182 (1960).

(27) N. B. Keevil and H. E. Bent, *J. Am. Chem. Soc.*, **60**, 193 (1938).

Presently available data on the specific system consisting of sodium benzophenone ketyl in 1,2-dimethoxyethane indicate that in the region 10^{-5} – 10^{-3} *M* ion pairs are dominant, with free ions or higher aggregates present in minor quantities, if at all. Thus, the total e.s.r. spectrum can be analyzed in terms of coupling with one sodium nucleus in addition to the ring hydrogen atoms²⁴; the e.s.r. spectrum shows no distinct variation with temperature²⁴; Beer's law is obeyed in the region of the visible band, and the position of the maximum is independent of concentration over the range studied (*ca.* 10^{-4} – 10^{-5} *M*).

While the deviation of sodium benzophenone ketyl from Beer's law in diethyl ether (Fig. 3) was originally attributed to dimerization to the pinacolate,¹⁴ a recent communication suggests the possibility that at least a portion of the dimeric species may be paramagnetic.²¹ On the basis of the presently available data such a species would probably best be described as an ion quadrupole.^{28,29} Resonance due to a two-spin species was detected at lower temperatures in a diethyl ether solution of the ketyl.

Although the pinacolate would be expected to show no adsorption in the visible or near-ultraviolet regions, a paramagnetic dimer might. Visible absorption due to such a species in the fluorenone ketyl system has been reported.²¹ It is important to consider the possibility that the corresponding band of the sodium benzophenone ketyl (dimer) in ethers is a component of the visible band upon which our attention is focused.

If the bands due to ion pairs and ion quadrupoles were both present in the spectrum of sodium benzophenone ketyl in ethers, it would be expected that their relative intensities would be a function of the solvent.²¹ If the two bands are components of the 6500-Å. band, band shape changes from one solvent to another might be expected. Such changes are not observed (Fig. 2). Moreover, Beer's law studies in diethyl ether at 3670 Å., where a distinct shoulder appears in the spectrum, showed deviations in the opposite direction from those observed at 6300 Å. Such behavior would be expected if a material absorbing in the former region were a dimer of a material absorbing in the latter region. Further, shifts in the position of the maximum with concentration, which are not observed, would be expected.

The lack of band shape changes with solvent and the lack of concentration effects on the position of the band also suggest, on similar grounds, that ion pairs and free ions do not both absorb at *ca.* 6500 Å.,³⁰ since the fact that a metal ion effect exists suggests that it would be unlikely that the ion pair and the free radical-anion would show coincident absorptions in all solvents.

The data are consistent with the hypothesis that the visible band is due to ion pairs, not to ion quadrupoles or free ions.

The *ca.* 6500-Å. Transition.—The intensity, breadth, and lack of fine structure of the visible band suggest that a charge-transfer transition ought to be considered as a possible assignment. Such a transition would reasonably involve "transfer" of the antibonding elec-

tron of the radical-anion to the associated metal ion or to a solvent cavity.²⁹

If the transfer were to the metal ion, the direction of the variation of band position with metal should be the opposite of that observed.³² If the transfer were to either metal ion or solvent cavity, the band would be expected to appear at higher energy in the sodium *p,p'*-diphenylbenzophenone ketyl than in the corresponding ketyl from benzophenone, while the transition appears, in fact, at a lower energy in the *p,p'*-diphenylbenzophenone case. The latter argument presumes that the energy of an electron in a solvent cavity or about a metal ion in solution is not drastically affected by the nature of a nearby ketone molecule, and that the electron affinity of *p,p'*-diphenylbenzophenone is greater than that of benzophenone, an assumption that is supported by Hückel MO calculations on the two ketones. In view of these data, assignment of the band as a charge-transfer band does not appear tenable.

Warhurst and co-workers view the *ca.* 6500-Å. band as a $\pi \rightarrow \pi^*$ transition of the organic radical-anion.^{13,31} We concur. The extinction coefficient is consistent with this assignment.³³ E_T is also consistent with other experimental data. The electronic spectrum of crystalline benzophenone shows intense maxima at about 39,000 and 49,500 cm^{-1} .³⁴ On a simple orbital basis, the ketyl would therefore be expected to absorb at about 10,500 cm^{-1} . The actual absorption is in the vicinity of 15,000 cm^{-1} , but McClelland has offered a theoretical extrapolation of the data for counterions Li^+ , Na^+ , and K^+ , the result being that in the absence of a counterion absorption is expected to occur at about 10,900 cm^{-1} , in good agreement with his molecular orbital calculations as well as with the benzophenone spectrum.³¹

The complete lack of vibrational fine structure is readily understood as a consequence of the Franck-Condon principle as applied to solutes in media with which they strongly interact on a molecular basis.^{35–37}

Metal Ion Effect.—Ion pairing effects on spectra have long been noted in connection with complex ions, but the existence of such effects in simple ionic systems has been disputed.³⁸ It is not difficult to imagine geometric relations between paired ions such that for certain internal transitions of one ion (polarized, say, perpendicular to the general line of centers between the two ions) the electric field of the counterion interacts nearly equally with the ground and excited states.

It is clear, however, that this situation may not be general.³⁹ If a transition results in the net movement of electronic charge away from a positive counterion, that counterion will interact more strongly with the ground than with the excited (Franck-Condon)³⁵ state, and a blue shift with ion pairing might be expected,¹³ provided that direct solvation of the free anion does not generate an overriding spectral shift.⁴⁰ On similar

(32) The basis of this statement is a consideration of the ionization potentials of the metals. Both solvation and ion pair coulombic factors would be expected to tend to reverse the assumed direction of the metal ion effect. Such factors could negate this argument.

(33) Reference 14 gives ϵ 7000. Our value (see Experimental) is 12,000. Considering the methods employed, this is probably satisfactory agreement.

(34) D. S. McClure and P. S. Hanst, *J. Chem. Phys.*, **23**, 1772 (1955).

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

(36) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 186–195.

(37) See ref. 31 and citations listed therein for an alternative suggestion.

(38) See literature cited in ref. 29.

(39) A recent publication makes this point quite clearly. Calculations predict and experiments confirm the fact that one electronic transition of the alkali metal adducts of anthracene is metal ion dependent while another is not: N. S. Hush and J. R. Rowlands, *Mol. Phys.*, **6**, 201 (1963).

(40) Preliminary studies suggest that the alkali phenoxides in dioxane-

(28) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, pp. 302–303.

(29) T. R. Griffiths and M. C. R. Symons, *Mol. Phys.*, **3**, 90 (1960), assigned various ultraviolet bands of tetraalkylammonium iodides in nonpolar solvents to "solvent shared, solvent separated, and contact" ion pairs. It is at least equally reasonable to assign one of these bands to ion quadrupoles.

(30) The calculations of McClelland indicate, by extrapolation, that the free radical-anion in dioxane should absorb in the vicinity of 9000 Å.³¹ It is not clear, however, that this extrapolation takes proper account of the solvent effect.

(31) B. J. McClelland, *Trans. Faraday Soc.*, **57**, 1458, 2073 (1961).

grounds, a decreasing metal ion radius would lead to a blue shift (in an ion pair). The ketyls provide examples of the latter behavior.^{13,41}

The Origin of the Solvent Effect.—A number of possibilities ought to be considered in connection with the origin of the rather pronounced shifts of the *ca.* 6500-Å. band among the various ethers and other solvents (Table I and Fig. 2). The factors contributing to these possibilities can be divided into two classes: (a) those in which the solvent effect is considered to operate *via* direct interaction of the solvent and the radical-anion, the effects being independent of the metal ion; and (b) those in which the solvent effect is considered to arise from the interaction of the ion pair with the solvent, the effect being possibly quite dependent on the metal ion involved.

If factors of the former class are operative, and those of the latter class are inoperative, one might expect to find correlations of the shifts with certain solvent properties, the nature of the correlation being determined by the particular kind of solute-solvent interaction which is dominant.

Red shifts (with increasing polarity of the solvent) of π - π^* transitions due to changes in the polarizability of the solvent are often observed. However, there is no correlation whatsoever of the observed ketyl shifts with the refractive index function of Bayliss and McCrae.³⁵

Differences in the direct solvation energies of the radical-anion in its ground and excited states could account for the shifts, which would then be expected to parallel the shifts of $n \rightarrow \pi^*$ transitions of ketones in the same solvents.⁴² While the variations in the position of the $n \rightarrow \pi^*$ transitions of cyclohexanone⁴³ shown in Table I are much smaller than those for the ketyl, a trend among the ethers in the *opposite* direction is discernible.⁴⁴

A more satisfactory theory than either of the above incorporates the cation in a major role in determining the ion pair spectral shifts with solvent. It is tempting to assign to the cation the major solvation effects. While this may be a dangerous procedure, the idea is of long standing in the field of organometallic chemistry,⁵⁻¹⁰ is attractive for its simplicity and intuitive chemical basis (Lewis acid-base interaction), and will be adopted here in further discussion.

If the *effective* separation of the ionic charges in the ketyl ion pair can be influenced by the solvent, the shifts are readily interpreted in terms of the same theory cited above for the metal ion effect, since changing the radius of the cation is but one way to bring about charge separation.^{31,45}

To some extent, the abilities of ethers to disperse cationic charge through solvation, thereby increasing charge separation in an ion pair, should reflect variations in their basicities.⁴⁶ However, no monotonic

water mixtures may provide an example of competing ionic aggregation and solvent-anion interaction effects on the spectrum of an anion: W. R. Richards, unpublished work in this laboratory.

(41) Warhurst and co-workers have listed other systems behaving similarly.¹² In addition, the benzyl alkalis (F. J. Hopton and N. S. Hush, *Mol. Phys.*, **6**, 201 (1963)) and the alkali phenoxides¹⁰ show parallel effects.

(42) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(43) The cyclohexanone $n \rightarrow \pi^*$ shifts correlate well with Kosower's Z-values: E. M. Kosower and G. S. Wu, *J. Am. Chem. Soc.*, **83**, 3142 (1961). See also E. M. Kosower, *ibid.*, **80**, 3253 (1958), and later papers of the series.

(44) The data recently presented by K. Dimroth, C. Reichardt, T. Seipmann, and F. Bohlmann, *Ann.*, **661**, 1 (1963), on the variations with solvent of certain bands in the spectra of conjugated betaines provide better grounds for this argument, since the shifts are larger, should depend on the same arguments as for the $n \rightarrow \pi^*$ shifts, and again are in the opposite direction from the ketyl shifts. The betaine shifts correlate well with Z-values. Further discussion of the relation of the betaine and ketyl spectra is reserved for later presentation.

(45) See ref. 15 for further evidence in favor of a similar theory.

relationship between the proton basicities and the ketyl solvent shifts is found. In view of the very different steric requirements and covalent bonding abilities of protons and alkali metal ions, this lack of correlation is not disturbing.

In addition to the intrinsic basicity of the solvent, various other factors can play a role in determining the effective separation of charge in an ion pair, and hence the position of an anionic absorption band. Steric factors may well be important, since the solvating molecules must be brought into close proximity with the anion. In addition, the energy of the transition may be more sensitive to variations in the amount of effective charge separation at some interionic distances (smaller) than others (larger). Furthermore, there may be effects arising from gross considerations of the effects of the dielectric constant (D) of the medium. For example, not only might the equilibrium separation of the ions be affected by D , but also the force constant for vibration along the interionic axis, leading possibly to variations with solvent in the average charge separation. It may be impractical or impossible to separate the general dielectric effects from the more specific ones mentioned earlier.

The structural variations described in the two paragraphs above have been termed variations in the "detailed structure" of the ion pairs.¹ The fact that e.s.r. coupling constants vary with solvent for the ketyls and other alkali metal adducts of unsaturated organic compounds confirms the view that there are variations in the ground state structures of ion pairs with solvent.²⁴

Spectral solvent effects similar to those observed for the ketyls have been recently reported by Waack and Doran for 1,1-diphenylhexyllithium.¹⁶ The shifts were accounted for in terms of the general theory of Bayliss and McCrae³⁵ relating to polar molecules in polar solvents. If the dipole moment of such a solute increases upon transition to an excited state, a red shift can be expected with increasing polarity of the solvent, since the molecules of the solvent will be properly oriented in the ground state for enhanced solvation of the more polar excited state. Waack and Doran also suggested that variations with solvent in the amount of ionic character of the carbon-lithium bond could account for the shifts. When analyzed in detail, these theories are seen to incorporate the same effects as those mentioned above, differing primarily in viewpoint and emphasis.⁴⁷

Although Waack and Doran demonstrated a reasonably linear relationship between E_T (1,1-diphenylhexyllithium) and solvent D , the ketyl data do not conform to a similar relationship. Figure 4 shows a plot of E_T (sodium benzophenone ketyl) *vs.* $(D - 1)/(2D + 1)$, the latter quantity being related to the electrostatic free energy of a dipole in a cavity immersed in a continuous dielectric medium.⁴⁸ The data appear to be badly scattered, but a close examination reveals several ways in which deviations from an assumed "normal" relationship can be made rational. The solid line of Fig. 4 gives one such "normal" relationship, the

(46) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **84**, 1680, 1683 (1962).

(47) We have taken the viewpoint of the anion, as perturbed by the cation and its environment, whereas Waack and Doran took the viewpoint of the entire molecule or ion pair. We emphasize the role of the cation and ground state structural changes more than do Waack and Doran, although the introduction of possible variations in the ionic character of the carbon-lithium bond into their theory permits ground state structural changes.¹⁶

(48) We have chosen to discuss all such compounds as if they were ion pairs, realizing that in some cases this may be an inadequate representation, but also that for our present purposes the effects of increased ionic character parallel the effects of increased effective charge separation.

(49) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

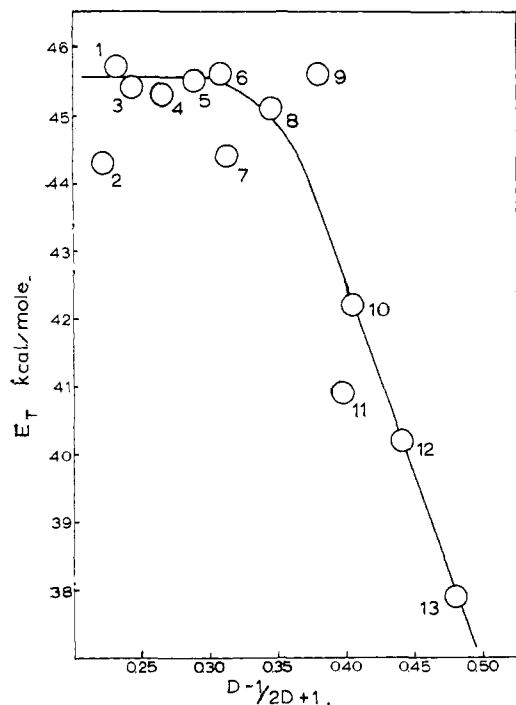


Fig. 4.—Variation of E_T (sodium benzophenone ketyl) with dielectric constant of the solvent. A plot in which the abscissa is $1/D$ rather than $(D - 1)/(2D + 1)$ is of nearly identical form. Unless otherwise noted here, the values of D are taken from A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," N. B. S. Circ. 514 (1951), where further references are given, and were determined at temperatures of 20–26°. Waack and Doran have noted the disagreement between J. L. Downs, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 1367 (1959), and F. E. Critchfield, J. A. Gibson, Jr., and J. L. Hall, *J. Am. Chem. Soc.*, **75**, 6044 (1953), over D for tetrahydrofuran (former workers: 6.00; latter workers: 7.39 (25°), but chose the higher value.¹⁶ G. Wittig and E. Stahnecker, *Ann.*, **605**, 69 (1957), agree with the higher value (7.3). Wittig and Stahnecker also obtained a higher value for 1,2-dimethoxyethane (6.8) than did Downs, *et al.* (5.50). It would appear that the balance of evidence is in favor of the higher values, which we have employed. In view of the apparent errors in their values for tetrahydrofuran and 1,2-dimethoxyethane, we have chosen not to employ the values given by Downs, *et al.*, for any solvents.

Key to solvents: (1) benzene, (2) 1,4-dioxane, (3) triethylamine, (4) 1,1-dimethoxyethane, (5) di-*n*-butyl ether, (6) di-*n*-propyl ether, (7) 1,1-dimethoxyethane, (8) diethyl ether, (9) diethyl sulfide, (10) tetrahydrofuran, (11) 1,2-dimethoxyethane, (12) pyridine, and (13) N,N-dimethylformamide.

deviant solvents being diethyl sulfide and some which are potentially bidentate ligands in their coordination to a metal ion.

The "deviant" points of Fig. 4 can be rationalized as follows: (a) Since bidentate coordination for dioxane, and possibly for 1,1- and 1,2-dimethoxyethane, involves conformations corresponding to higher dipole moments than those of conformations prevailing in the bulk of these solvents, over which D is measured, deviations in the observed directions are expected.⁵⁰ (b) Although diethyl sulfide has a higher D than, say, diethyl ether, its basicity is notably smaller, as evidenced by studies of its coordination with BF_3 ,⁵¹ thus accounting for its poorer specific solvation properties.

In rationalizing the relative positions of the various solvents in Fig. 4, other "normal" curves could have been chosen (e.g., a line through points 1, 3, 4, 7, 10,

(50) J. B. Hyne, *J. Am. Chem. Soc.*, **85**, 304 (1963), has recently utilized this point in connection with specific solvation in dioxane–water.

(51) H. E. Wirth and P. I. Slick, *J. Phys. Chem.*, **66**, 2277 (1962):

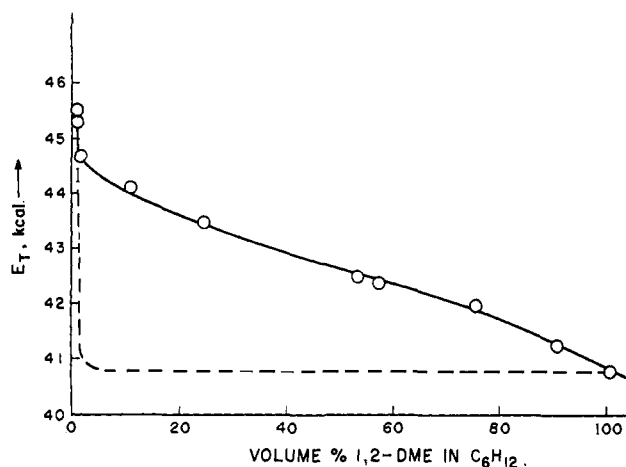


Fig. 5.—Effect of 1,2-dimethoxyethane on the visible spectrum of sodium benzophenone ketyl in cyclohexane. The "volume %" of the abscissa relates to the relative volumes of the two components at room temperature before mixing. The volume change on mixing is very small. Since the two components have similar molecular weights and densities, "volume %" is approximately the same as mole %. The dashed curve would be expected if the local environment were the sole factor contributing to variations in E_T and local 1,2-dimethoxyethane molecules were very tightly bound.

12, and 13) and other specific interactions (such as steric solvation effects) invoked. We believe that such factors must play roles in the determination of E_T which are at least as important as those played by bulk properties. Although the latter reflect the former, the reflection is not entirely satisfactory for the considerations at hand.

Differential Solvation in Mixed Solvents.—In order to assess the degree to which the ketyl shifts reflect purely local environment, and/or the degree to which local environment changes with the composition of a binary solvent consisting of one "inert" and one ethereal component, we investigated the variation of the position of the visible sodium benzophenone ketyl band with the amount of 1,2-dimethoxyethane in cyclohexane.

No dissolution of the ketyl in cyclohexane could be visually detected.⁵² Upon momentarily opening a stopcock connecting a cyclohexane–ketyl mixture with a 1,2-dimethoxyethane reservoir, enough of the ether was transferred to result in visually noticeable dissolution of ketyl. The resulting solvent mixture was estimated to be much less than one mole per cent 1,2-dimethoxyethane. This small amount of impurity in the cyclohexane could make no measurable difference in the dielectric constant of the medium. It is clear, therefore, that one or more ether molecules must be intimately associated with the ketyl ion pairs.⁵³

Figure 5 shows the variations of the position of the visible band of the ketyl with the amount of 1,2-dimethoxyethane present in cyclohexane. As would be expected if ether molecules are strongly bound to the ketyl ion pairs, the position of the band is a very sensitive function of the amount of 1,2-dimethoxyethane present when there is but little present.⁵⁴ The

(52) In cyclohexane containing a substantial quantity of benzophenone, the ketyl does dissolve, giving solutions with a greenish cast. The green color is a consequence of the enhanced intensity of a band in the near-ultraviolet, tailing into the visible, which is present with a lesser intensity in the pure ether.

(53) Solid diethyl etherates of ketyls have, in fact, been reported: B. M. Mikhailov and N. G. Cheronova, *Doklady Akad. Nauk S.S.S.R.*, **85**, 341 (1952).

(54) The ratio of intensities at ca. 6500 and ca. 3500 Å. also varies with solvent composition, favoring (relatively) the 6500-Å. material in the more

position of the band is less sensitive to the amount of 1,2-dimethoxyethane when there is a substantial amount present. It is concluded that local environmental factors play an important role in determining the energy of the visible transition of the ketyl ion pairs.

Solvent Polarity.—It is possible that the ketyl spectral shifts reflect solvent properties to a greater extent than solute properties or properties which depend on both solvent and solute (such as the degree of solute-solvent steric interaction). If this should be the case, these spectral variations might have value as measures of the "polarity" of ethereal solvents toward ionic or ionoid species, particularly organometallic compounds. In order to be empirically useful and possibly theoretically significant, such a measure of polarity would have to be shown to correlate, qualitatively or quantitatively, with other chemical phenomena dependent on the same kind of "polarity." The fact that spectral shifts in another solvent dependent system have been successful in correlating spectra and reaction parameters

ethereal solvents. We have not attempted the extraction of quantitative information on this point.

in a wide range of solvents is justification for seeking a similar application of the present results.⁵⁵ Moreover, it is possible that deviations from otherwise consistent correlational behavior may be significant in establishing the details of theories related to ionic aggregation and ethereal solvent effects in organometallic systems.

Data against which to make quantitative tests of correlations are not plentiful, but those which are available are, for the most part, consistent, and will be discussed in detail later.

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(55) See papers cited in footnote 43.

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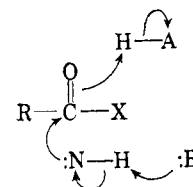
The Compensation in ΔH^\ddagger and ΔS^\ddagger Accompanying the Conversion of Lower Order Nucleophilic Displacement Reactions to Higher Order Catalytic Processes. The Temperature Dependence of the Hydrazinolysis and Imidazole-Catalyzed Hydrolysis of Substituted Phenyl Acetates

BY THOMAS C. BRUCE AND STEPHEN J. BENKOVIC¹

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The hydrazinolysis and imidazole-catalyzed hydrolysis of a series of substituted phenyl acetates were found to be dependent on the concentration of the conjugate acid and base species of the nitrogen bases in the following manner: $-d(\text{ester})/dt = [k_n(\text{H}_2\text{NNH}_2) + k_{rb}(\text{H}_2\text{NNH}_2)^2 + k_{ra}(\text{H}_2\text{NNH}_2)(\text{H}_2\text{NNH}_3^{\oplus})](\text{ester})$ and $-d(\text{ester})/dt = [k_n(\text{C}_3\text{H}_4\text{N}_2) + k_{rb}(\text{C}_3\text{H}_4\text{N}_2)^2](\text{ester})$, respectively. The terms k_n are second-order rate constants for nucleophilic displacement at the ester bond, and the k_{rb} and k_{ra} terms are third-order rate constants for general-base and general-acid assisted nucleophilic displacement reactions at the ester bond. The $k_n - \rho$ value for hydrazine is considerably greater than that for ammonia, so that the α -effect is greatest with the best leaving group. Also, the α -effect is of greater importance in k_{rb} and in k_{ra} than in k_n . The ρ -values for the k_{rb} and k_{ra} terms are very much smaller than those for the k_n terms, as previously found for general base-catalyzed ammonolysis reactions. The consistent finding that the ρ -values for the third-order, generally assisted reactions are always much less than the ρ -values for the simple unassisted bimolecular reactions has the result that the assisted reactions are always of much greater importance for nucleophilic displacement reactions on esters with poorer leaving groups. The k_{rb} term for hydrazine, as previously found for ammonia, exhibits no deuterium solvent kinetic isotope effect; however, the k_{rb} term for imidazole does. Unlike the k_{rb} term, the k_{ra} term for hydrazine does exhibit a deuterium solvent isotope effect. The ΔH^\ddagger for the k_n term does not appear to be simply related to the nature of the nucleophile nor the substituent on the phenyl ester. With change in the electronic nature of substituent groups on the ester, the $T\Delta S^\ddagger$ term may follow a consistent pattern of decrease, of increase, or a random variation. The electronic effects on $T\Delta S^\ddagger$ may be considered to be secondary perturbations of that value determined by the nucleophile and the kinetic order of the reaction. By averaging the $T\Delta S^\ddagger$ values for the series of esters for a particular term (*i.e.*, k_n , k_{rb} , or k_{ra}) with a particular nucleophile, the electronic effects of substituent groups may be compensated for. The kinetic order of the reaction when multiplied by 5 ± 1 kcal. mole⁻¹ provides in each case (eleven reactions) the value of $T\Delta S^\ddagger_{av}$. This result is discussed on the basis of the arbitrary division of $T\Delta S^\ddagger$ into a component ($T\Delta S^\ddagger_{t.r.}$) determined by the number of species which must be brought to a position of close approach in order to enter the transition state and a component ($T\Delta S^\ddagger_e$) which relates to the kinetic energy terms in taking the reactants from a position of close approach to the transition state. The expected lowering of ΔH^\ddagger and $T\Delta S^\ddagger$ accompanying the conversion of a lower order displacement reaction to a higher order catalytic process has been examined. The values of ΔH^\ddagger and $T\Delta S^\ddagger$ for k_n , k_{rb} , and k_{ra} for the hydrazinolysis reactions are found to behave in a compensatory manner so that ΔF^\ddagger becomes only slightly more negative for the catalytic reactions.

The displacement of a leaving group ($-X$) by a nucleophile ($:\text{NH}$) may be assisted by general-acid (AH) and by general-base (BH) catalysis.^{2,3} It is anticipated that the conversion of a bimolecular nucleophilic attack by $:\text{NH}$ into one of the higher order catalytic processes (*i.e.*, general acid or general base) should be accompanied by a compensatory change in potential and kinetic energy terms. Assuming that



ΔH^\ddagger and $T\Delta S^\ddagger$ reflect simply potential energy and kinetic energy parameters, respectively, it is reasonable to suppose that the necessity of incorporating extra species into the transition state should decrease $T\Delta S^\ddagger$.

(1) Predoctoral Fellow of the National Institutes of Health (1960-1963). A portion of the Ph.D. thesis of S. J. B.

(2) T. C. Bruce, *Brookhaven Symposia in Biology*, No. 15, 52 (1962).

(3) M. L. Bender, *Chem. Rev.*, 60, 53 (1960).