

anilinium ions in 50% aqueous ethanol, ~ 3.5 ,³⁴ and that for the exchange reaction in this paper, 4.0, we would anticipate that a plot of $\log k$ for the exchange reaction of polycyclic methylarenes with lithium cyclohexylamide *vs.* the pK values for the corresponding amines would have a slope of ~ 1.1 . In such a plot, Fig. 4,

- (34) Jaffé (ref. 35) gives $\rho = 3.435$ in 30% aq. ethanol and 3.535 in ethanol.
 (35) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

the non-*peri*-positions do give a good straight line but with a slope of 1.8. The difference in slopes is undoubtedly due to the prevailing importance of inductive effects in the substituted anilines and toluenes and to the enhanced importance of conjugative charge distribution in the polycyclic systems. We conclude that for other than broad qualitative purposes, amines are not good models for carbanions.

[CONTRIBUTION NUMBER 1175 FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH, PITTSBURGH 13, PENNA.]

Solvent Effects in Organic Chemistry. II. Sulfolane¹—A Weakly Basic Aprotic Solvent of High Dielectric Constant²

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Indicator and cryoscopic studies have been performed on solutions of sulfuric acid in sulfolane.¹ All of the evidence presented here indicates that this is a very weakly basic solvent in which ions are poorly solvated so that highly acidic solutions are obtained even at low acid concentration. In spite of ion-pair complications, a fairly good H_0 acidity function scale is developed in this solvent. In all of these ways sulfolane is very similar to nitromethane^{3,4} but has the great advantage of being far easier to handle.

Introduction

The three most important properties of a solvent that determine its behavior as a medium for acid-base reactions are: (1) its acidity and basicity; (2) its ability to function as a hydrogen bond donor, especially through hydroxyl groups; (3) its dielectric constant. Interesting effects have been observed by the shrewd variation of these properties. One of the most enlightening studies of this kind is that of Hammett and his students on nitromethane as a diluent for sulfuric acid.^{3a,b} Nitromethane is an aprotic dipolar solvent of very low basicity^{4,5} and relatively high dielectric constant (38). Hammett found it to be an extraordinarily poor medium for the solvation of ions^{3b} although a reasonably good acidity function could be developed in nitromethane solutions of sulfuric acid. Furthermore, because nitromethane is such a poor proton acceptor, sulfuric acid itself acts as the acid in this medium instead of the protonated solvent serving in this role as is usually the case. The result is that sulfuric acid solutions in nitromethane have an enormously greater effective acidity at low acid concentrations than do aqueous ones of the same acid concentration.

In the course of an investigation of ion solvation which will be described at a later time we were prompted to examine the properties of sulfolane.¹ Although our study is by no means as complete as that of Hammett for nitromethane, we believe that it will be of value to other workers.

Sulfones are almost as weakly basic as aliphatic nitro compounds⁶ and since sulfolane has a dielectric constant of 44 one might expect that if Hammett's conclusions are correct it should behave in a way similar to nitromethane as an acid-base medium. There are other properties of sulfolane that make it even more at-

tractive than nitromethane for such studies: it is much more easily purified and also has a large cryoscopic constant⁷ with a melting point close to room temperature so that dissociation or association measurements in it are especially convenient to perform. In the work to be described here we will show that sulfolane is probably not protonated by sulfuric acid and that its behavior is very similar to that found for nitromethane by Hammett and his students.

Experimental

Sulfolane was supplied through the generosity of the Shell Development Company of Emeryville, Calif. It was vacuum distilled repeatedly from sodium hydroxide pellets⁸ until a 1-ml. sample in a small test tube did not show development of visible color within 5 min. after the addition of an equal volume of 100% sulfuric acid. This usually required two or three distillations. It was then distilled again from calcium hydride to remove traces of water, which it holds tenaciously, and stored briefly under vacuum or dry air. Following the use of a batch of sulfolane for the cryoscopic or indicator studies to be described, it was usually found possible to remove most of this valuable solvent from the less acidic solutions by neutralization of the sulfuric acid content with sodium hydroxide pellets. The high viscosity of the solutions prevented the reaction from becoming violent and, after cooling, the remaining sulfolane could be decanted from the residual salts to produce material with the desired physical properties (freezing point 28.37°⁹ and optically clear) after several distillations.

Sulfuric acid (100%) was prepared by mixing Baker and Adamson 96% sulfuric acid (C.P. reagent) with Baker analyzed reagent 21% oleum until a maximum freezing point was reached. A small excess of oleum, corresponding to 0.02% sulfur trioxide, was then added to assure the use of anhydrous material. All glassware was baked out prior to use.

Cryoscopic Measurements in Sulfolane.—A sealed freezing point apparatus of the Beckmann type was attached through a ground glass joint to the fraction collector of the vacuum distillation apparatus used for purification of the sulfolane. It could thereby be filled to a suitable level with solvent without exposure to the atmosphere. Material that was handled in this way maintained a steady freezing point of 28.37° over a number of hours, but when the apparatus was vented to the atmosphere the freezing point dropped to 28.23° within an hour due to absorbance of atmospheric moisture. The thermometer used could be estimated to the nearest 0.01° and was calibrated against a National Bureau of Standards one.

A small side arm fitted with a silicone rubber serum plug was attached to the freezing point tube in such a way that solute

(1) Tetramethylene sulfone; thiophene, tetrahydro-1,1-dioxide.

(2) This work was generously supported by the National Institutes of Health through Grant Number G. M. 10872-04 in the Division of General Medical Sciences.

(3) (a) L. C. Smith and L. P. Hammett, *J. Am. Chem. Soc.*, **67**, 23 (1945);

(b) H. Van Looy and L. P. Hammett, *ibid.*, **81**, 3872 (1959).

(4) E. M. Arnett, "Quantitative Comparisons of Weak Organic Bases," in "Progress in Physical Organic Chemistry," A. Streitwieser, Jr., R. W. Taft, Jr., and S. G. Cohen, Eds., Interscience Publishers, Inc., New York, N. Y., 1963.

(5) For an extensive discussion of the physical properties of dipolar aprotic solvents and their applications to organic chemistry see A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962).

(6) R. J. Gillespie and J. A. Leisten, *ibid.*, **8**, 40 (1954).

(7) R. L. Burwell, Jr., and C. H. Langford, *J. Am. Chem. Soc.*, **81**, 3799 (1959).

(8) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **83**, 4571 (1961).

(9) S. F. Birch and D. T. McAllan, *J. Chem. Soc.*, 2556 (1951), report a melting point of 28.86°, but this was based on an estimate which led them to the erroneous conclusion that the cryoscopic constant of sulfolane was very low.

could be easily introduced with a calibrated microsyringe. In order to bring the apparatus to atmospheric pressure, air was admitted which had been carefully dried by passage through a silica gel tower.

Spectral Measurements.—Even under the best conditions, solutions of sulfuric acid in sulfolane show detectable coloration and the development of this color is rather erratic during the first few hours. It was found that reproducible measurements with indicators were best achieved using solutions that had aged for a day before addition of the indicator. To prepare a solution, a suitable quantity of sulfuric acid was weighed into a 25-ml. volumetric flask. The flask was then filled to the mark with sulfolane, stoppered tightly, and, after reweighing, was allowed to stand at room temperature for 24 hr. before use.

The Hammett indicators were purchased from the Aldrich Chemical Co. and were used with no further purification after careful checking of the melting points. 2,5-Dichloro-4-nitroaniline¹⁰ was also purchased from the same company. It was carefully recrystallized and then vacuum sublimed until it melted cleanly in the range 156.8–157.4° (lit.¹⁰ 157–158°). Stock solutions were prepared by weighing the appropriate number of milligrams into a 25-ml. volumetric flask and filling to the mark with dry sulfolane. They were stored in ampoules capped with serum stoppers. The final solutions of indicator in sulfolane-sulfuric acid were prepared 5 to 10 min. before observation by the addition with a microsyringe of 200 μ l. of the stock solution to a 10-ml. volumetric flask which was then filled immediately with the acid solution and shaken. A 1-cm. quartz spectrophotometer cell was filled from it and placed in the cell holder (thermostated at 30 \pm 0.1°) of a Beckman DU spectrophotometer, the cell in the reference beam being filled with the same acid solution. It was established through a series of six replica runs that an optical density of 0.375 could be reproduced with a standard deviation of \pm 0.005 by this technique.

Results and Discussion

The *i*-Factor of Sulfuric Acid in Sulfolane.—Presented in Table I below are the freezing point depressions produced by the addition of various small quantities of sulfuric acid to anhydrous sulfolane.

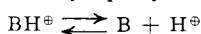
TABLE I
FREEZING POINT DEPRESSIONS OF DILUTE SOLUTIONS OF
SULFURIC ACID IN SULFOLANE^a

Moles of H ₂ SO ₄ added $\times 10^4$	Freezing point depressions, °C.	<i>i</i> -Factor ^b
1.87	0.47	1.34
2.06	.33	0.85
3.36	.68	1.06
3.74	.78	1.10
3.74	.71	1.00
3.93	.62	0.84

^a For a 34.95-g. sample of sulfolane. ^b $K_f = 66.2 \pm 0.6$ deg. kg./mole.

The average value of the *i*-factor for this compound is 1.03. When the values shown above for added moles of H₂SO₄ are plotted against freezing point depression, a straight line is obtained from whose slope a cryoscopic constant of -64.8 deg. kg./mole is obtained compared to the literature value of -66.2 deg. kg./mole.⁷ The apparent unit *i*-factor for sulfuric acid may be interpreted to mean either that the acid is dissolving as molecular units of "naked" sulfuric acid or that it is protonating the solvent to give very tight ion pairs of sulfonium bisulfate. Burwell and Langford⁷ found quite different ion pair dissociation constants for different kinds of salts in sulfolane, but salts of large cations were completely dissociated. Therefore, the cryoscopic results suggest (inconclusively) nonprotonation of the medium.

The H_0 Acidity Scale in Sulfolane.—Hammett's acidity function H_0 is an operational measure of the ability of a strongly acidic solution to protonate Brønsted bases.¹¹ It is properly defined to refer to the



(10) M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963).

(11) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

equilibrium for a dilute solution in water, the solvent and counterion not being shown. H_0 may be defined by the equations

$$H_0 = \text{p}K_a + \log Q$$

or

$$H_0 = -\log (a_{\text{H}^{\oplus}} f_{\text{B}} / f_{\text{BH}^{\oplus}})$$

where $\text{p}K_a$ refers to the thermodynamic dissociation constant of the conjugate acid of the indicator at the standard state, $\log Q$ is the indicator ratio, and the activity coefficient terms refer to the free energy required to transfer the ions from the standard state to the particular medium in question. Using the overlap method¹¹ it is possible in principle to derive acidity functions even for strong oleum solutions in which no free water exists at all. The development of acidity functions for poorly solvating nonaqueous media is theoretically a dubious matter¹² and in cases such as that under consideration here where very few free ions exist their use would seem to be unjustified.¹³ Nonetheless, Hammett^{3,4} found that a rather good acidity function could be developed for nitromethane; the relative basicities of the series of indicator bases remained nearly the same as in water and the variation of $\log Q$ with changing acidity was essentially the same for adjacent indicators. This was true despite the fact that this is one of the poorest solvating media known and complicated ion-pairing phenomena occur in it. It appears that sulfolane is indeed similar to nitromethane in these respects.

Our results are based on two completely different sets of measurements done several months apart with different batches of solvent. The only difference between them is that in the second series particular precautions were taken to protect against moisture. Except for the most dilute solutions of acid where the presence of traces of water is crucial, there is little difference in the results, showing that for most purposes the sulfolane-sulfuric acid system can be used effectively without elaborate precautions. In contrast, we have found extreme difficulty in handling the nitromethane-sulfuric acid system. This was also the experience of Van Looy and Hammett.^{3b}

As is customary in dealing with nonaqueous solvents, we arbitrarily fix our standard state by assigning 4-chloro-2-nitroaniline a $\text{p}K_a$ of -1.03; the $\text{p}K_a$'s of the other indicator bases are then determined by the overlap method. It is clear from Fig. 1 that for the most part the overlap method may be applied with impunity in this case, the slopes for $\log Q$ vs. % H₂SO₄ being quite similar for adjacent indicators with the exception of 6-bromo-2,4-dinitroaniline. A serious gap exists in the region of $H_0 = -7$ which is not bridged well by the data for 6-bromo-2,4-dinitroaniline and anthraquinone and beyond 70% H₂SO₄ we have no meaningful data. However, in contrast to the aqueous H_0 scale, that in sulfolane changes very little in strong acid; therefore, the effect of poor overlap in this region is not so serious here and the 70–100% region only represents 0.85 H_0 unit change. As shown in Table II, even the least basic indicators in this series give $\text{p}K_a$'s in sulfolane which parallel rather well the relative basicities in water. This is another graphic demonstration of the fact that *in most*,¹⁴ but by no means in all¹⁵ cases the apparent relative strengths of a series of bases are roughly maintained through drastic changes in solvent, even when there are complications from ion pairing.

(12) B. Gutbezahl and E. Grunwald, *J. Am. Chem. Soc.*, **75**, 559 (1953).

(13) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 277.

(14) H. K. Hall, Jr., *J. Phys. Chem.*, **60**, 63 (1956).

(15) J. F. Coetzee and G. R. Padmanabhan, *Talanta*, in press.

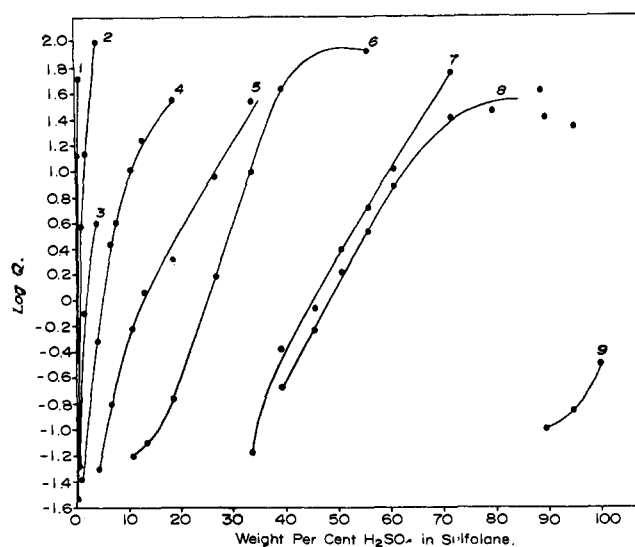


Fig. 1.—Test of overlap principle for Hammett indicators in sulfolane-sulfuric acid solutions: 1, 4-chloro-2-nitroaniline; 2, 2,5-dichloro-4-nitroaniline; 3, 2,4-dichloro-6-nitroaniline; 4, 2,4-dinitroaniline; 5, benzalacetophenone; 6, 6-bromo-2,4-dinitroaniline; 7, anthraquinone; 8, 2,4,6-trinitroaniline; 9, nitrobenzene.

Part of the evidence presented by Van Looy and Hammett for solvation of the protonated indicator bisulfate ion pair by two molecules of sulfuric acid was derived from the fact that a plot of log molarity of sulfuric acid *vs.* H_0 had a slope of almost exactly 3 between 0.1 and 1.0 *M*. We have made a similar plot of our results and find the slope to be 2.8, suggesting once again that the ion-pairing situation in the two solvents is very similar.

TABLE II
BASICITIES IN SULFOLANE AND WATER

Indicator base	pK_a in sulfolane	pK_a in water ¹¹	pK_a in nitromethane ^a
4-Chloro-2-nitroaniline	-1.03	-1.03	-1.03
2,5-Dichloro-4-nitroaniline	-2.12	-1.78	
2,4-Dichloro-6-nitroaniline	-3.37	-3.32	-3.34
2,4-Dinitroaniline	-4.36	-4.53	-4.17
Benzalacetophenone	-5.55	-5.73	
6-Bromo-2,4-dinitroaniline	-6.55	-6.71	-6.46
Anthraquinone	-8.64	-8.27	
Trinitroaniline	-8.82	-9.41	
Nitrobenzene	-11.11	-11.38	

Turning now to the acidity function itself, our measurements for the sulfolane-sulfuric acid system are presented in Table III.

TABLE III

H_0 VALUES FOR SOLUTIONS OF SULFURIC ACID IN SULFOLANE					
Weight % H_2SO_4	H_0	Weight % H_2SO_4	H_0	Weight % H_2SO_4	H_0
0	0	8	-5.00	40	-8.05
1	-2.80	9	-5.15	45	-8.50
2	-3.30	10	-5.30	50	-8.95
3	-3.70	15	-5.75	55	-9.35
4	-4.05	20	-6.20	60	-9.65
5	-4.35	25	-6.65	65	-9.90
6	-4.60	30	-7.15	70	-10.10
7	-4.85	35	-7.60	100	-10.95

These are best compared with acidity scales in other solvents through reference to Fig. 2. Sulfuric acid in sulfolane clearly gives solutions of very high acidity for relatively low acid concentrations, although nitro-

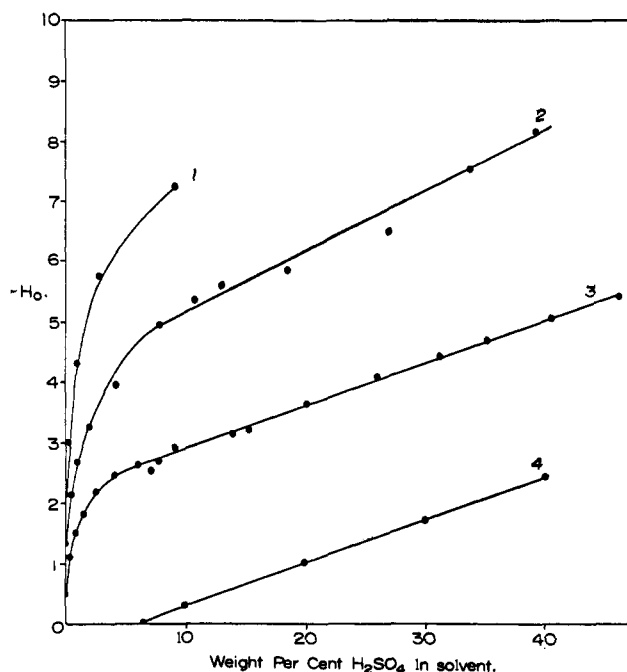


Fig. 2.—Comparison of apparent H_0 acidity scales in solvents of varying basicity: 1, nitromethane^a; 2, sulfolane^a; 3, acetic acid^a; 4, water. ^a Based on an arbitrary assignment of $pK_a = -1.03$ for 4-chloro-2-nitroaniline, its value in water.

methane excels it in this respect. A similar plot was constructed for the same four H_0 scales *vs.* mole fraction of acid present. The resulting curves had quite similar shapes and relative positions except that the curve for the aqueous solution crossed that for acetic acid close to $H_0 = -4$. The points for nitromethane solutions are in doubt since Hammett prepared his solutions by volume and there are no density figures for nitromethane-sulfuric acid solutions. Accordingly, we assumed a linear relation between mole fraction and weight per cent for interpolation of intermediate solutions.

The Effect of Added Water on Acidity.—A further close similarity between the behavior of sulfuric acid in nitromethane and in sulfolane is observed when small quantities of water are deliberately added to a 0.354% solution of sulfuric acid in the latter solvent. This solution was chosen since it contains enough sulfuric acid so that the concentration is well characterized and the concentration of adventitious water is relatively low, but it is still in a region of the acidity curve where H_0 is very sensitive to acid concentration. The results shown in Table IV indicate clearly the powerful in-

TABLE IV

EFFECT OF ADDITION OF SMALL QUANTITIES OF WATER TO 0.354% H_2SO_4 IN SULFOLANE USING 4-CHLORO-2-NITROANILINE ($pK_a = -1.03$) AS INDICATOR

Vol., μ l.	Amount of H_2O added		Absorbance	Q $D_{BH^+ 0.676}$ $D_B 0.006$	$\log Q$	$-H_0$
	Moles per mole of H_2SO_4	Weight %				
0	0	0	0.061	0.0894	-1.05	2.08
2.1	0.25		.099	.161	-0.79	1.82
4.8	0.50		.144	.259	-.59	1.62
6.2	0.75		.180	.351	-.45	1.48
8.2	1		.220	.469	-.33	1.36
12.3	1.5		.292	.745	-.13	1.16
16.4	2.0		.351	1.062	.03	1.00
24.7	3		.441	1.851	.27	0.76
33.0	4		.507	2.964	.47	.56
42.2	5		.551	4.36	.64	.39

fluence that water exerts for the solvation of protonated indicator ions. Alternatively, it could be said that the operational acidity of the solution is greatly reduced as the very strong acid H_2SO_4 in a nonbasic solvent is replaced by the weaker acid $\text{H}_{2n+1}\text{O}_n^+$, or that water is competing as a base with the indicator for protons from the sulfuric acid—at our present stage of understanding these descriptions are probably equivalent.

In conclusion we may cite the following evidence that sulfolane, like nitromethane, is a very weakly basic solvent with a very feeble ability for solvating cations: (1) Sulfones give nearly unit i -factors in sulfuric acid.⁶ (2) Sulfuric acid gives a unit i -factor in sulfolane. (3) Sulfuric acid solutions in both of the above solvents have very high acidities at low acid concentrations compared to aqueous solutions of mineral acids.¹⁶ (4) Small

quantities of water sharply reduce the acidities of sulfuric acid solutions in these solvents. (5) The relationship of acidity to sulfuric acid concentration in the 0.1 to 1.0 M region is strongly indicative of solvation of the bisulfate ion by sulfuric acid molecules rather than by the solvent.

In view of the fact that sulfolane is an extremely weak acid^{16,17} as well as being a very weak base it must indeed have one of the lowest autoprotolysis⁷ constants of all useful organic media.

Acknowledgment.—This paper was prepared in part while E. M. A. was a Visiting Lecturer at the University of Illinois. He expresses herewith his appreciation for the facilities placed at his disposal.

(16) C. H. Langford and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **82**, 1503 (1960).

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIF., AND THE UNIVERSITY OF GEORGIA, ATHENS, GA.]

The Solvent Effect on the Electronic Spectra of Ion Pairs. Ketyls in Ethers¹

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The position of the *ca.* 6500 Å. band of sodium benzophenone ketyl, a $\pi-\pi^*$ transition of the radical-anion, varies with solvent in a pronounced fashion among a series of rather nonpolar solvents. Sodium *p,p'*-diphenylbenzophenone ketyl behaves similarly. These spectral shifts are interpreted as reflections of the polarities of the solvents toward organometallic solutes. Cationic solvation may be especially important, but other considerations may also affect the spectra.

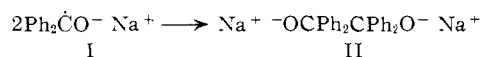
Introduction

Among ethereal solvents, dramatic solvent effects on the behavior of ionic and ionoid³ systems, such as those involving organometallic compounds, have often been observed.⁴⁻⁸ It is generally accepted that the proper explanation for these effects must involve considerations of the interactions among ions, ionic aggregates, and solvent. Lewis acid-base solvation of the metal cation is often given a dominant role in the theories advanced to account for the solvent effects.^{1,5-9}

Some ethers are clearly more polar than others.¹⁰ Among the more polar ethers, judging from usage in the literature, are tetrahydrofuran, 1,2-dimethoxyethane, and diethylene glycol dimethyl ether (diglyme). Diethyl ether appears rather nonpolar, while the status of dioxane on this scale appears indeterminate.

The present paper deals with alkali metal adducts of diaryl ketones (ketyls),¹¹ in particular, those derived

from benzophenone (I) and *p,p'*-diphenylbenzophenone with sodium. The ketyls are presumed to be in equilibrium with their dimers, the pinacolates (II),¹² although



recent reports have indicated that many 10^{-3} – 10^{-5} M solutions follow Beer's law, suggesting that the association to pinacolate is not significant in this concentration range.^{15,14}

We are primarily concerned here with the solvent effect on the electronic spectrum of the ketyl from sodium and benzophenone. The data may have application to the problem of the polarities of ethers in their interactions with organometallic compounds. Related work from two other groups has recently appeared.^{15,16}

Experimental

Preparation and Purification of Materials.—Diaryl ketones were either commercially obtained or prepared by standard methods and recrystallized until their melting points corresponded to literature values with a range of 1° or less. Commercially obtained cyclohexane was dried over Drierite and distilled through a 5 × 60 cm. spinning-band column, a middle fraction of constant boiling point (152.8°, 732 mm.) being retained for use.

Diphenylpicrylhydrazyl (Aldrich Chemical Co.) was recrystallized from carbon disulfide a few hours before use and stored in a vacuum desiccator.

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(13) H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960), and earlier papers of the series.

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(1) Part of this work has been reported in preliminary form, *J. Am. Chem. Soc.*, **83**, 5034 (1961).

(2) Department of Chemistry, The University of Georgia, Athens, Ga.

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