

Spectra and Hydrogen Bonding of Diphenylcyclopropenone

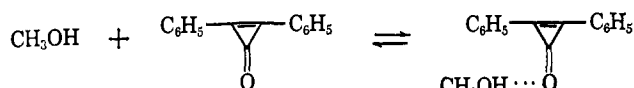
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Abstract: The effect of solvent on the two characteristic infrared absorption bands at 1850 and 1630 cm^{-1} of diphenylcyclopropenone is described. A new absorption band of this ketone in cyclohexane is found at 362 $\text{m}\mu$ (ϵ 1150) which might well be due to intramolecular charge transfer. The $-\Delta H$ of hydrogen bonding between this ketone and methanol in CCl_4 amounts to 8.1 kcal/mole.

In spite of increasing interest in the chemistry of cyclopropenones^{1,2} the physicochemical aspect of this highly polar, strained, and pseudoaromatic ketone has not yet been fully exploited. In this paper we describe the long-disputed problem of infrared band assignment, the observation of a new absorption band in the ultraviolet region, and the Lewis basicity as studied by the hydrogen-bonding method. This paper deals only with diphenylcyclopropenone, which is most easily accessible and stable.

Infrared Spectra. Two characteristic strong bands at *ca.* 1850 and 1630 cm^{-1} are considered to be concerned with both C=C and C=O stretching vibrations.^{1b,6,7} Application of Bellamy's method⁸ has shown that the solvent behavior of the 1630- cm^{-1} band is analogous to that of the $\nu_{\text{C=O}}$ absorption of a typical ketone.^{1g,9,10} Further support for the prevalence of the $\nu_{\text{C=O}}$ mode in this band is provided by the observation that, on addition of methanol to the solution of this ketone in carbon tetrachloride, the band moves about 10 cm^{-1} toward lower frequency. As shown in Figure 1, the appearance of an isosbestic point suggests the formation of a 1:1 hydrogen-bonded complex between the ketone and methanol.



On the other hand, the band at 1850 cm^{-1} is of a more complex nature. Scanning on an extended frequency scale revealed that this band was a doublet.

(1) (a) For a review see A. W. Krebs, *Angew. Chem.*, **77**, 10 (1965); (b) R. Breslow and L. J. Altman, *J. Am. Chem. Soc.*, **88**, 504 (1966); (c) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965); (d) R. Breslow, L. J. Altman, A. Krebs, E. Mochacs, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965); (e) D. G. Farnum, J. Chickos, and P. E. Thurston, *ibid.*, **88**, 3075 (1966); (f) J. Ciabattoni and G. A. Berchtold, *J. Org. Chem.*, **31**, 1336 (1966); (g) A. Krebs, *Z. Naturforsch.*, **21b**, 194 (1966).

(2) It should be noted that completely different products have been reported from the reaction of diphenylcyclopropenone with hydrogen on platinum^{1c,3}, 2,6-dinitrophenylhydrazine,^{1c,3} hydroxylamine,^{1c,4} and phosphorus pentasulfide.⁴⁻⁸

(3) D. N. Kursanov, M. E. Volpin, and Yu. D. Koreschkov, *J. Gen. Chem. USSR*, **30**, 2855 (1960); *Chem. Abstr.*, **53**, 21799 (1959).

(4) Y. Kitahara and M. Funamizu, *Bull. Chem. Soc. Japan*, **37**, 1879 (1964).

(5) B. Föhlisch and P. Buerge, *Tetrahedron Letters*, 2661 (1965).

(6) T. Eicher and G. Frenzel, *Z. Naturforsch.*, **20b**, 274 (1965).

(7) S. Andreades, *J. Am. Chem. Soc.*, **87**, 3941 (1965).

(8) For a review see H. E. Hallam in "Infrared Spectroscopy and Molecular Structure," M. Davies Ed., Elsevier, Amsterdam, 1963, Chapter 12.

(9) I. Agranat, and E. D. Bergmann, *Tetrahedron Letters*, 2373 (1966).

(10) We also obtained a nice linear Bellamy-Hallam-Williams plot between the 1630- cm^{-1} band and $\nu_{\text{C=O}}$ of acetophenone for nine solvents.

Increasing the amount of methanol added to the carbon tetrachloride solution of the ketone brought the two doublet peaks closer and closer, and finally they coalesced to one broad peak, as illustrated in Figure 2. During this change several isosbestic points appeared. The large influence of methanol would suggest that one of the coupled absorptions is again the carbonyl stretching.

The 1850- cm^{-1} band is also sensitive to the change of solvent as seen in Table I. Neither of the doublet peaks showed the same pattern of solvent shift with the

Table I. Frequency (cm^{-1}) of the Doublet Absorption Bands at *ca.* 1850 cm^{-1} of Diphenylcyclopropenone in Various Solvents

Solvent	A	B
Carbon tetrachloride	1852.5	1838.4
Carbon disulfide	1849.2	1835.4
Benzene	1851.3	1837.8
Dioxane	1851.1	1839.3
Nitromethane	1848.7	1840.8
Dichloromethane	1853.1	1840.1
Chloroform	1853.0 (sh)	1840.3
<i>sym</i> -Tetrachloroethane	1851.3 (sh)	1839.0
Bromoform	1851.5 (sh)	1838.4

typical carbonyl stretching absorption. The relative intensity of these peaks varies with the solvent: in carbon tetrachloride and carbon disulfide peak A is stronger than B, in benzene both peaks have about the same intensity, and in haloforms and tetrachloroethane peak B becomes much stronger than A. This behavior of the doublet toward the solvents indicates that Fermi resonance is probably involved.¹¹ Since no strong absorption is present at *ca.* 900 cm^{-1} , a resonance with a combination band will have to be considered.

Ultraviolet Spectra. As seen in Figure 3, the ultraviolet spectrum of diphenylcyclopropenone is similar to that of *trans*-stilbene. A new, low-intensity band was found at 362 $\text{m}\mu$ in cyclohexane (ϵ 1150). This band shifts to 333 $\text{m}\mu$ in acetonitrile. In methanol, it moves to below 300 $\text{m}\mu$. Figure 4 shows a gradual blue shift of this band on addition of more and more methanol to the solution of the ketone in cyclohexane. The wavelength, the relatively low extinction, and the response to

(11) We thank a referee for this suggestion. Fermi resonance in the carbonyl stretching bands of cyclopentanone [C. L. Angell, P. J. Krueger, R. Lauzon, L. C. Leith, K. Noack, R. J. D. Smith, and R. N. Jones, *Spectrochim. Acta*, **15**, 926 (1959)] and ethylene carbonate [L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959)] is known to be highly solvent sensitive.

Table II. Thermodynamic Data of Hydrogen Bonding between Ketones or Amines and Alcohols in Carbon Tetrachloride

Proton acceptor	Proton donor		K^{33° , l./mole	$-\Delta H$, ^a kcal/mole	$-\Delta S$, ^a cal/deg mole
Diphenylcyclopropenone	Methanol	A	6.55	5.31 ± 0.69	13.8 ± 2.4
		B	2.95	2.84 ± 0.72	7.2 ± 2.4
2,6-Dimethyl-4-pyrone	Methanol	A	8.94	5.57 ± 0.82	14.0 ± 2.8
		B	2.92	3.0 ± 0.9	7.6 ± 3
Pyridine	Methanol			3.88^b	
	<i>n</i> -Butyl alcohol			5.0^c	
	Isobutyl alcohol			4.1^c	
	<i>n</i> -Butyl alcohol			4.86^d	
Triethylamine	<i>n</i> -Butyl alcohol			4.98^d	
	Isobutyl alcohol				

^a Error limit given with 90% confidence. ^b E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961). ^c T. J. V. Findlay and A. D. Kindan, *Australian J. Chem.*, **18**, 521 (1965). ^d L. Lamberts and T. Zeegers-Huyskenes, *J. Chim. Phys.*, **60**, 435 (1963).

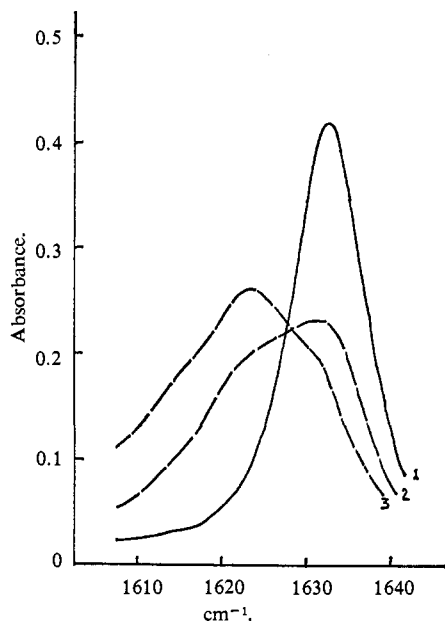


Figure 1. Diphenylcyclopropenone $2.67 \times 10^{-3} M$; methanol: 1, 0 M; 2, 0.321 M; 3, 0.610 M; solvent, CCl_4 ; 2-mm path length.

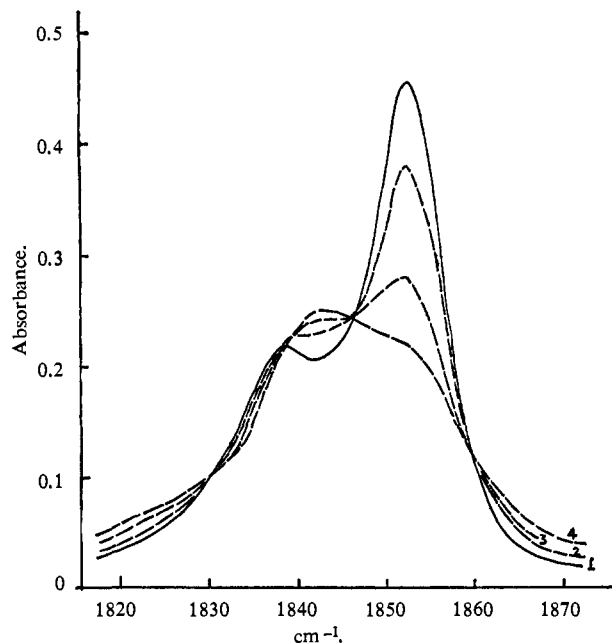
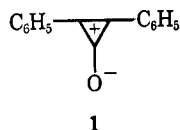


Figure 2. Diphenylcyclopropenone $2.22 \times 10^{-3} M$; methanol: 1, 0 M; 2, 0.078 M; 3, 0.321 M; 4, 1.56 M; solvent, CCl_4 ; 2-mm path length.

solvent suggest that this band might well be due to intramolecular charge transfer **1**.¹²



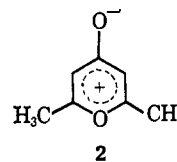
Hydrogen Bonding. Diphenylcyclopropenone is known to be a strong anhydro base.^{1c} The Lewis basicity of the ketone as measured by hydrogen bonding with methanol in carbon tetrachloride is given and compared with other organic bases in Table II. As with other ketones, diphenylcyclopropenone forms two types of hydrogen-bonded adducts A and B (see Experimental Section), which are believed to have slightly different configurations.¹³ Thermodynamic functions were obtained from the temperature variation of the intensities of the two bonded OH stretching absorption bands. Although the difference in the structure of species A and B is not yet clear, the over-all energy of hydrogen bonding, $-(\Delta H_A + \Delta H_B) = 8.1$ kcal/mole,

(12) The effect of substituents on the phenyl ring of diphenylcyclopropenone on the position of this weak band supports this assignment: R. West and E. Osawa, unpublished work.

(13) H. Fritzsche, *Spectrochim. Acta*, **21**, 199 (1965).

is the largest of the reported values¹⁴ for systems involving methanol as the proton donor.

2,6-Dimethyl-4-pyrone, which was reported to form very strong hydrogen bonding with phenol ($\Delta\nu_{OH}$ 350 cm^{-1} , $K^{20^\circ} = 196.4$ l./mole),¹⁵ gave a comparable $-\Delta H$ value (over-all 8.6 kcal/mole). The over-all $-\Delta H$ values of these anhydro bases surpass those of pyridine and triethylamine (Table II). This is striking because the apparent " pK_a " of diphenylcyclopropenone (-2.5)^{1c} is much smaller than the pK_a 's of pyridine (5) and triethylamine (10). The high Lewis basicity of these ketones is due to special electronic stabilization (formulas **1** and **2**) in the polar hydrogen-bonded state.



(14) G. C. Pimentel, and A. L. McClelland, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, Appendix.

(15) T. Gramstad, *Spectrochim. Acta*, **19**, 1698 (1963).

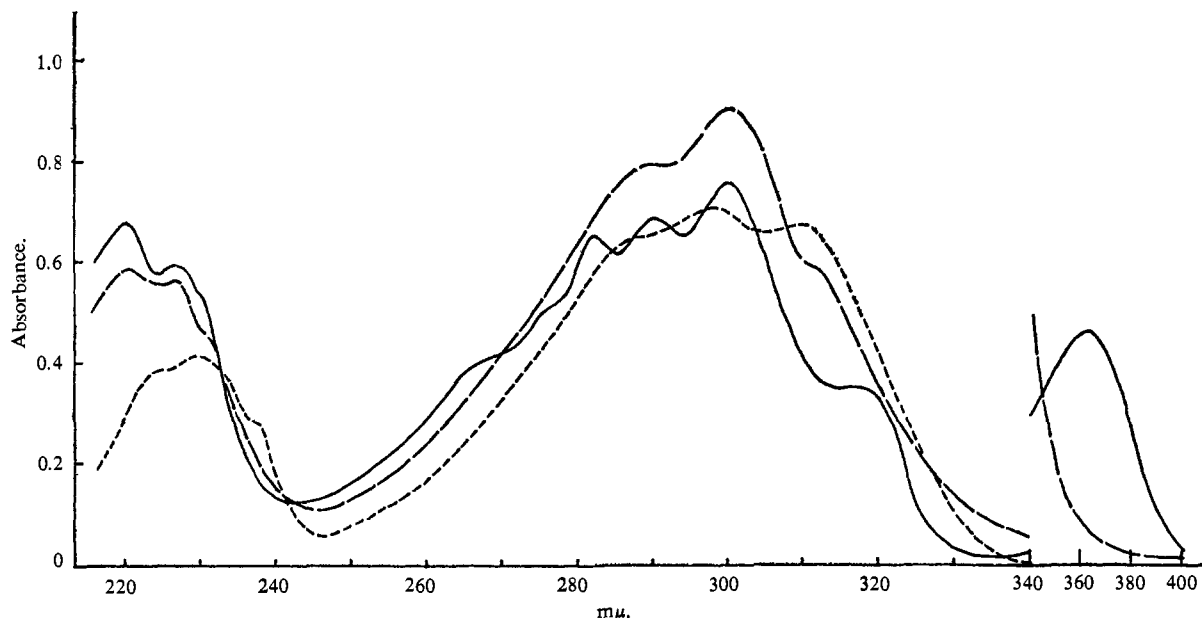


Figure 3. Ultraviolet spectra of diphenylcyclopropanone and *trans*-stilbene, 1-cm path length: DCP (cyclohexane) —, $2.95 \times 10^{-5} M$ ($>340 \text{ m}\mu$: $4.08 \times 10^{-4} M$); DCP (methanol) ---, $3.10 \times 10^{-5} M$ ($>340 \text{ m}\mu$: $4.65 \times 10^{-4} M$); *trans*-stilbene (cyclohexane) - · - · - ·, $2.50 \times 10^{-4} M$.

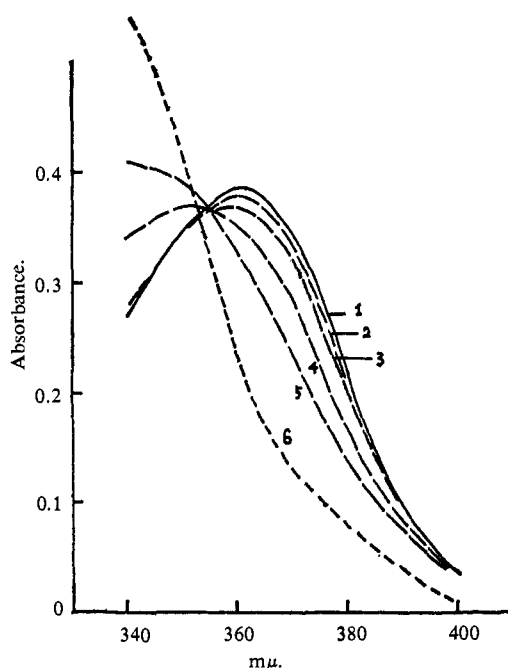


Figure 4. Effect of addition of methanol to the 362-m μ band of diphenylcyclopropanone; solvent, cyclohexane; 1-cm path length; concentrations: DCP $3.35 \times 10^{-4} M$; methanol: 1, 0 M ; 2, $1.34 \times 10^{-3} M$; 3, $2.68 \times 10^{-3} M$; 4, $1.34 \times 10^{-2} M$; 5, $2.68 \times 10^{-2} M$; 6, 0.124 M .

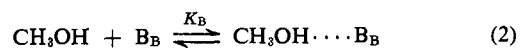
Experimental Section

Diphenylcyclopropanone was prepared according to the method of Breslow.¹⁰ Other compounds were commercially available and were purified by the usual methods. Merck Spectrograde solvents were used for spectroscopic measurements. Ultraviolet spectra were recorded on a Shimadzu spectrophotometer SV-50 A.

Infrared spectra were recorded on a grating spectrophotometer DS-402G of the Japan Spectroscopic Co., spectral slit width being kept at about 1.7 cm^{-1} between the 3700 and 3300- cm^{-1} region and 0.1 cm^{-1} in the 1900-1600- cm^{-1} region. The frequency was calibrated by gaseous ammonia and polystyrene film. The thickness of the sodium chloride prism was chosen between 0.2 and 10 mm depending on the solvent and concentration.

In hydrogen-bonding experiments, the initial concentrations of methanol and the proton acceptor were $8-9 \times 10^{-3}$ and $3-6 \times 10^{-2} M$, respectively. The temperature of the solution kept in the liquid cell was changed from 0 to 45° in an air bath thermostated with a thermomodule device ($\pm 0.1^\circ$).¹⁶

The OH stretching spectra of methanol in the presence of diphenylcyclopropanone is shown in Figure 5. The lower frequency band of the doublet is unsymmetrical, but could be resolved formally into two symmetrical bands, A and B (Lorentz function).¹⁷ According to Fritzsche,^{18,19} these two bands correspond to different 1:1 complexes formed by the following reactions



where B denotes the proton-accepting ketone. Equilibrium constants K_A and K_B were calculated from eq 3 and 4.

$$K_A = (\text{C})_A / (\text{CH}_3\text{OH})_f (\text{B})_f \quad (3)$$

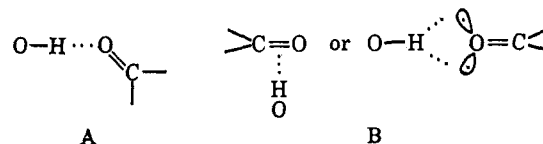
$$K_B = (\text{C})_B / (\text{CH}_3\text{OH})_f (\text{B})_f \quad (4)$$

where $(\text{C})_A$ and $(\text{C})_B$ are the concentrations of the complexes $\text{CH}_3\text{OH} \cdots \text{B}_A$ and $\text{CH}_3\text{OH} \cdots \text{B}_B$, which are obtained from the apparent integral intensities of the A and B bands divided by the absorption coefficients of these bands, which in turn are estimated from the $\Delta\nu$ vs. ΔA relationship given by Huggins and Pimentel.¹⁹ $(\text{CH}_3\text{OH})_f$ is the concentration of free methanol. The change of the absolute intensity of the methanol ν_{OH} band with temperature is taken into

(16) Z. Yoshida and N. Ishibe, to be published.

(17) Z. Yoshida and E. Ōsawa, *J. Am. Chem. Soc.*, **87**, 1467 (1965).

(18) Fritzsche proposed the following structure for the adducts



This hypothesis, however, cannot reconcile with the facts that acetonitrile gives a symmetrically bonded OH absorption contour (our own observation) and that di-*t*-butyl ether gives a bonded OH doublet band [L. J. Bellamy, *et al.*, *J. Chem. Soc.*, 4762 (1961)].

(19) C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).

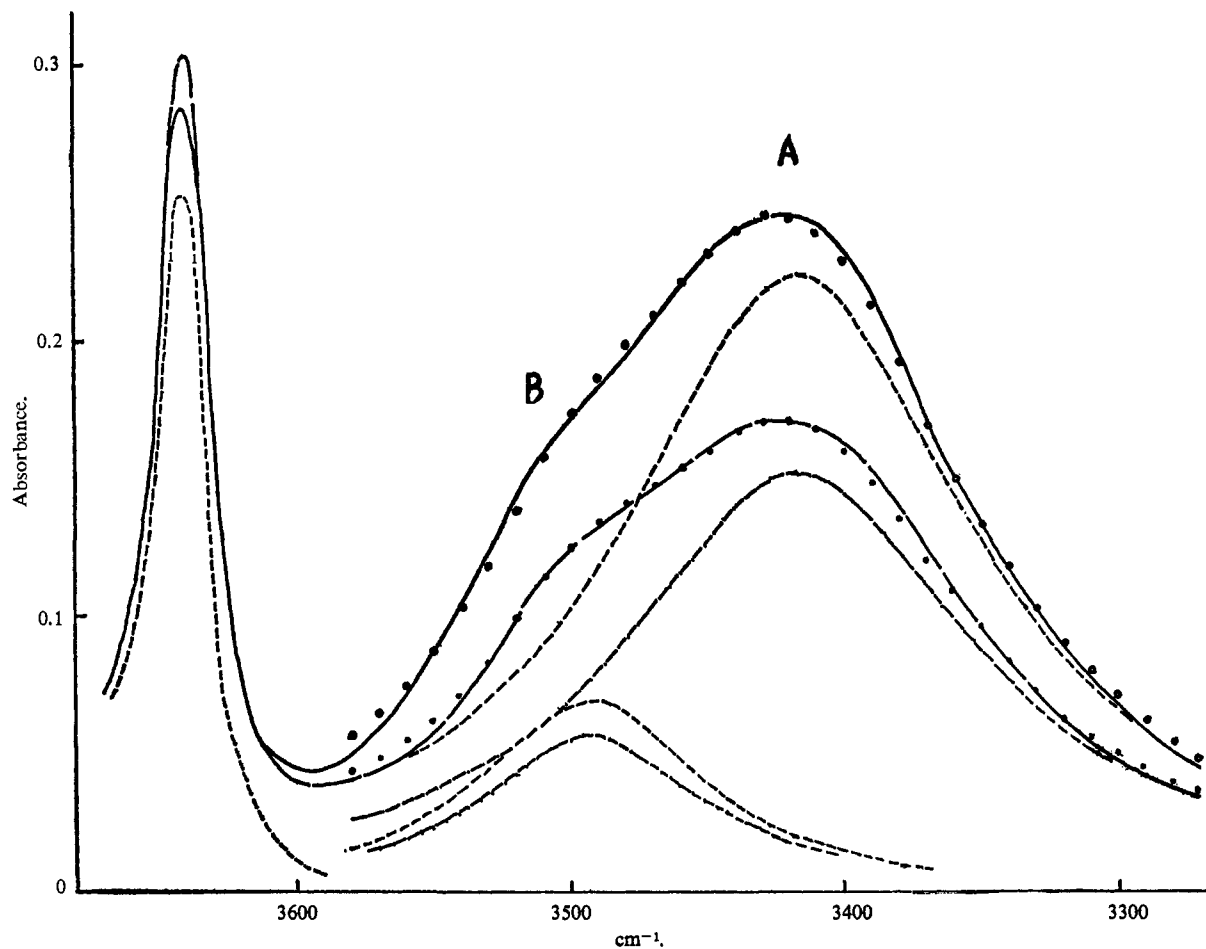


Figure 5. Hydroxyl stretching spectra of $8.24 \times 10^{-3} M$ methanol in the solution of diphenylcyclopropanone in carbon tetrachloride. Initial concentrations of the ketone: -----, $5.28 \times 10^{-2} M$; - · - · -, $3.54 \times 10^{-2} M$; temperature, 30° ; 1-cm path length.

account.²⁰ $(B)_f$ signifies the concentration of the free ketone. The temperature effect on the density of the solution was taken into consideration.

(20) U. Liddel, *J. Chem. Phys.*, **25**, 173 (1956).

Acknowledgment. The authors are grateful to Mr. F. Takabayashi for his experimental assistance and to Mr. Davis C. Zecker for his helpful advice on the manuscript.