

Fig. 1.—E.s.r. spectra of sodium fluorenone in DME: upper: spectrum of ketyl in absence of excess fluorenone; lower: spectrum after addition of fluorenone at 1.6 *M*.

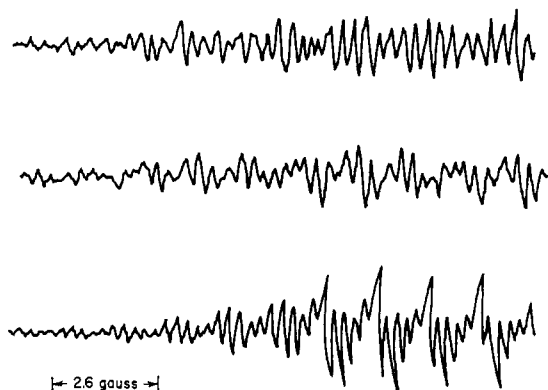


Fig. 2.—E.s.r. spectra of sodium benzophenone in Me THF: a (upper): in absence of excess benzophenone; b (middle): benzophenone added at 2×10^{-2} *M*; c (lower): benzophenone added at 1.5 *M*.

iodide, the e.s.r. lines of the ketyl first broaden, then narrow to a spectrum which displays only proton splittings. The spectral behavior is in accord with a simple ion-exchange process.

The second-order rate constants reported above extend over more than two orders of magnitude. For a given combination of alkali metal and ketone, two parameters—solvent and temperature—determine the rate constant. Similarly, the hyperfine coupling constant with the alkali metal ion is uniquely determined by temperature and solvent. Our results suggest a

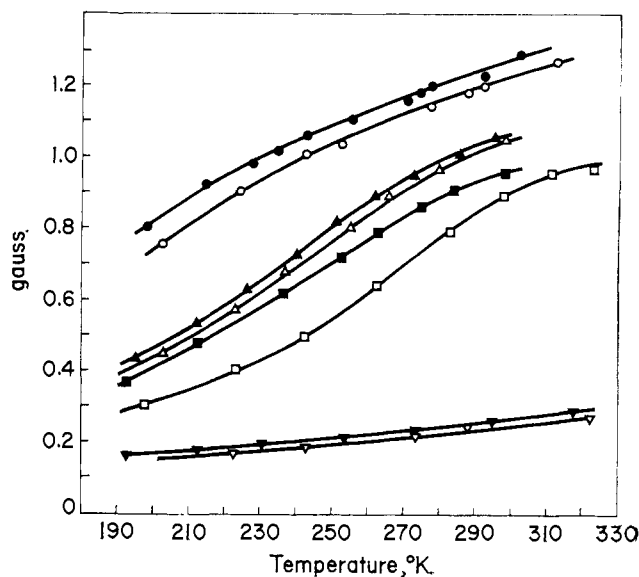


Fig. 3.—Dependence of alkali metal coupling constant on temperature: upper pair, sodium benzophenone: ●, THF; ○, DME. Central quartet, sodium xanthone: ▲, Me THF; △, tetrahydropyran; ■, THF; □, DME. Lower pair, potassium benzophenone: ▼, THF; ▽, DME.

one-to-one relationship between hyperfine coupling and rate constant. Dependence of hyperfine coupling constants of the cations on temperature, solvent, and ketyl are given in Fig. 3. The four temperatures at which the sodium coupling constant in sodium xanthone is 0.9 gauss are 37, 25, 7, and 0° in dimethoxyethane, tetrahydrofuran, tetrahydropyran, and methyl tetrahydrofuran, respectively. The rate constants at these temperatures are 4.56×10^8 , 4.48×10^8 , and 4.32×10^8 M^{-1} sec^{-1} . Although our data are not sufficient to determine whether the correlation is valid over a wider range of temperatures and solvents, they suggest that the binding of cation and anion is a determining factor in the rate. The hyperfine coupling constants of the cations are determined in part by the average conformation of the ion pair. The rates may be sufficiently sensitive to conformation to yield the correlations which we have noted.

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Electronic Interaction in Ketyl Radicals¹

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The existence of paramagnetic dimers of ketyls was confirmed from e.s.r. and optical absorption spectra. Spin-spin dipolar interactions in the dimers were studied from the e.s.r. spectra in rigid media and are discussed in connection with their structures. Slow spin exchange rates were found in the dimers. The equilibria among various forms of ketyls (paramagnetic monomer, paramagnetic dimer, and diamagnetic dimer) are discussed and several thermodynamic quantities are given for the paramagnetic monomer-dimer equilibrium. The factors which affect the equilibria are also discussed.

Introduction

The ketyls were discovered in 1891² and recognized as free radicals in 1911.³ Many experiments have since

(1) This work was supported by the National Science Foundation, the United States Air Force, and the Petroleum Research Fund of the American Chemical Society to whom grateful acknowledgment is made.

(2) F. Bechman and T. Paul, *Ann.*, **266**, 1 (1891).

been performed, not all with concordant conclusions, on the structures and chemical behavior of ketyls. We report here some of the results of our investigation of ketyls by electron spin resonance. Our experiments demonstrate that several forms of a ketyl may be in

(3) W. Schlenk and T. Weichel, *Ber.*, **44**, 1182 (1911); W. Schlenk and A. Thal, *ibid.*, **46**, 2840 (1913).

equilibrium with each other and that the equilibria depend on solvent, temperature, and cations. Some of the inconsistencies between conclusions drawn from earlier experiments arose because the various workers were dealing with different equilibrium mixtures.

In this paper we deal with the structures of the species which may be observed by e.s.r. spectroscopy and the equilibria between them. Rates of chemical processes in which the ketyls participate will be discussed elsewhere.

Experimental

Various ketyls of benzophenone, fluorenone, and xanthone were prepared by the reduction of ketones with alkali, alkaline, and rare earth metals in ether solvents such as dimethoxyethane (DME), tetrahydrofuran (THF), and methyltetrahydrofuran (Me THF). Alkali metal ketyls were reduced with alkali metal mirrors following procedures similar to those used in the preparation of hydrocarbon negative ions.^{4,5} Reduction with alkaline and rare earth metal ketyls was made with amalgams of the corresponding metals. All reactions were carried out in a sealed-off glass apparatus which included a cell for e.s.r. measurement and one for optical measurement when it was necessary. Reactions proceed almost instantaneously with alkali metals but are slower with alkaline earth metals. With rare earth metals the reaction is very slow and often a few days are required for formation of sufficient ketyl.

Preparations of ketyls in nonpolar solvent were made by transferring a desired nonpolar solvent into a sample tube containing solid ketyl which had been prepared in ether solution and freed of solvent by evacuation.

All of the e.s.r. measurements were made with a conventional X-band spectrometer with 100 kc. modulation.

Electron spin resonance spectra in rigid media were taken at the boiling point of liquid nitrogen in Me THF which forms a glass at that temperature. A sealed-off e.s.r. cell was placed in a quartz Dewar containing liquid nitrogen whose bottom tip was placed in the center of a cylindrical cavity of the spectrometer.

All of the optical measurements were made on a Cary spectrophotometer, Model 11M. The spectra at lower temperatures were taken by making use of a quartz dewar fitted to the spectrophotometer.

Results and Discussion

(I) **Optical Studies of the Formation of Paramagnetic Dimers.** (a) **Alkaline and Rare Earth Ketyls.**—Warhurst, *et al.*,⁶ found that the position of the maximum absorption shifts toward shorter wave length as the size of the positive ion becomes smaller. The phenomenon was interpreted by a molecular orbital treatment in terms of the electrostatic interaction between positive ion and electrons in the aromatic negative ion.⁷

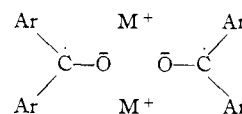
The results of more comprehensive experimental studies of the effect of the positive ion on the visible spectra including di- and trivalent metal ketyls are given in Table I for several ketyls in THF. It is clearly seen that generally the higher the charge and the smaller the size of the positive ion, the greater the shift of the maximum absorption toward shorter wave length. The strong dependence of the electronic spectra on the nature of the positive ion suggests that all these ketyls, including di- and trivalent metal ketyls are really associated to form the structure $\left(\begin{array}{c} \text{Ar} \\ \vdots \\ \text{C} \\ \vdots \\ \text{Ar} \end{array} \text{O}^- \right)_n \text{M}^{+n}$ in the solution. Ion pair formation in ether solution was also confirmed from the observation of var-

ious metal splittings^{8,9} (Na, K, Mg, and La) and the dependence of proton and C¹³ splittings on the metal in e.s.r. spectra in solution.⁸ Dissociation of the ion pair was found only in the highly polar solvents such as liquid ammonia or dimethylformamide.

TABLE I
ABSORPTION MAXIMA (m μ) OF KETYLs IN THF

	Benzophenone	Xanthone	Fluorenone
K	681	638	
Na	660	638	520 (monomer)
Na			450 (dimer)
Ba	637	610	451
Ca	620	590	449
Mg	605	565	446
La	595	555	
Sm	592	550	
Lu	598	541	

(b) **Alkali Metal Ketyls.**—Optical spectra of fluorenone alkali metal ketyls are remarkably dependent on the concentration of ketyls and the nature of the solvent as well as the nature of the positive ion. Figure 1a gives the concentration dependence of the optical spectra of Na fluorenone in Me THF. At high concentrations a strong absorption peak exists at 450 m μ and as the concentration decreases a peak begins to emerge at about 525 m μ . The change of the spectra with dilution suggests a monomer-dimer equilibrium between two species of similar electronic structure. The peak at 450 m μ belongs to the dimer and the one at 525 m μ to the monomer. The changes with concentration of sodium xanthone in Me THF are shown in Fig. 1b. The spectra are also dependent on the nature of the solvent and metal, as is illustrated in Fig. 2a. A dimer of structure



is suggested by the spectra.

Dependence on concentration of the optical spectra in the ketyls of xanthone and benzophenone is not so clear as for fluorenone ketyl because the spectra of the former are much broader than those of the latter. However, a shift of the maximum absorption with dilution was observed as shown in Fig. 1b. Therefore, it is supposed that the monomer-dimer equilibrium takes place quite generally in alkali metal aromatic ketyls in ether solution.

It must be noted that in aliphatic ketyls such as hexamethylacetone, e.s.r. studies showed that the stable radical species at room temperature is exclusively dimer in ether solution.¹⁰

(II) **E.s.r. Studies of the Paramagnetic Dimer. Spin-Spin Interaction and Spectra in Rigid Media.**—As was discussed in the previous section, optical studies suggest the existence of dimers. Since the optical spectra of the dimers are very similar to those of the monomers, it is likely that no changes in electron pairing accompany the dimerization. Whenever two

(4) D. E. Paul, Thesis, Washington University, 1954.

(5) T. R. Tuttle, Thesis, Washington University, 1957.

(6) H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960).

(7) B. J. McClelland, *ibid.*, **60**, 1458 (1961).

(8) N. Hirota, *J. Chem. Phys.*, **37**, 1884 (1962).

(9) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 3533 (1961)

(10) N. Hirota and S. I. Weissman, *ibid.*, **82**, 4424 (1960).

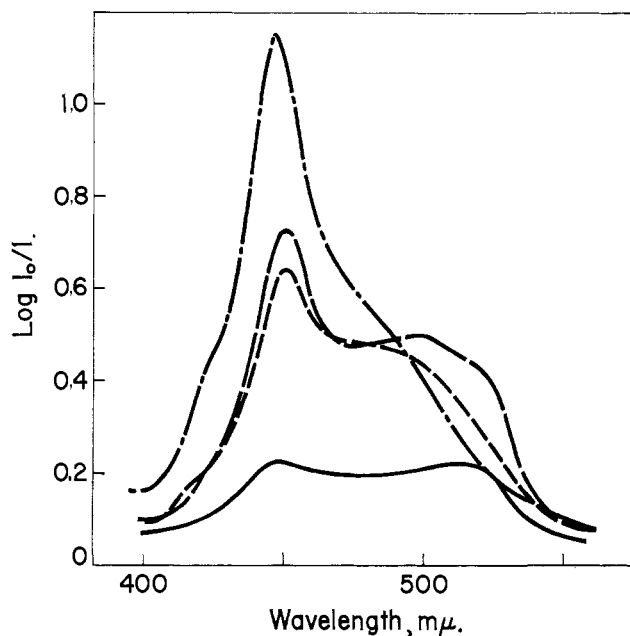


Fig. 1a.—Concentration dependence of optical absorption of sodium fluorenone in Me THF: — — —, $2.8 \times 10^{-2} M$; — · —, $3.5 \times 10^{-4} M$; · · · ·, $2.2 \times 10^{-4} M$; — — —, $5.8 \times 10^{-5} M$.

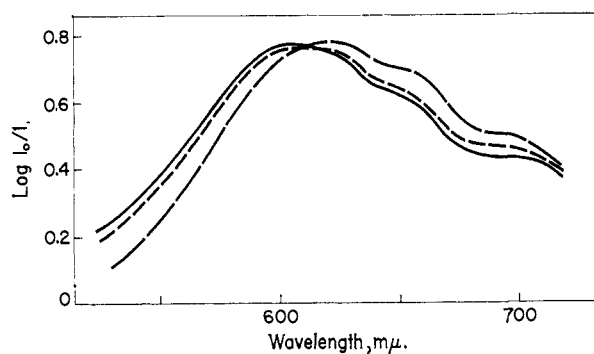


Fig. 1b.—Absorption spectra at three concentrations of sodium xanthone in Me THF. Product of optical path and concentration is constant: — — —, $10^{-4} M$; — · —, $10^{-3} M$; — — —, $10^{-2} M$.

spins exist in one system there is a magnetic dipolar interaction

$$\mathcal{H}_{ss} = \frac{g^2 \beta^2}{r_{12}^3} \left\{ \vec{S}_1 \cdot \vec{S}_2 - \frac{3(\vec{S}_1 \cdot \vec{r}_{12})(\vec{S}_2 \cdot \vec{r}_{12})}{r_{12}^2} \right\}$$

Here \vec{S}_1 and \vec{S}_2 are spin operators and r_{12} is the separation of the two spins. The effect of the dipolar interaction on the magnetic resonance spectra is well established. In triplet systems spectra may be analyzed in terms of the spin Hamiltonian

$$\mathcal{H} = g\beta H \cdot \vec{S} + DS_z^2 + E(S_x^2 - S_y^2)^{11,12}$$

where \vec{S} is the spin operator for the total spin and D and E are directly related to H_{ss} .¹³ Electron spin resonance spectra of randomly oriented triplet molecules have been studied recently in many cases.¹⁴ The analogous problem of a two-spin system is well known in n.m.r.,

(11) K. W. H. Stevens, *Proc. Roy. Soc. (London)*, **A214**, 237 (1952).

(12) A. D. Mochlachlan, *Mol. Phys.*, **6**, 441 (1963).

(13) M. Gouterman and W. Moffitt, *J. Chem. Phys.*, **30**, 1107 (1959).

(14) W. A. Yager, E. Wasserman, and R. M. R. Cramer, *ibid.*, **37**, 1148 (1962).

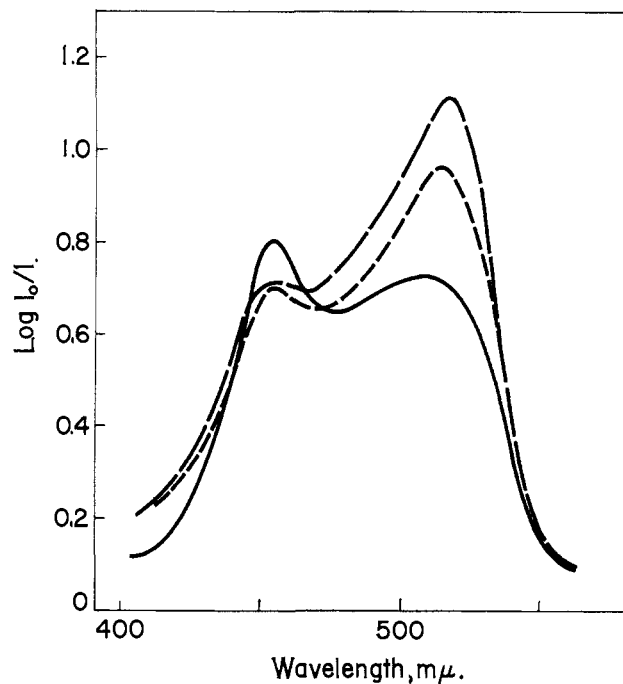


Fig. 2a.—Dependence of optical spectra on cations and solvent. Spectra in DME of alkali metal fluorenones: — — —, Na, $3.0 \times 10^{-2} M$; — — —, K, $2.5 \times 10^{-2} M$; — · —, Cs, $2.6 \times 10^{-2} M$.

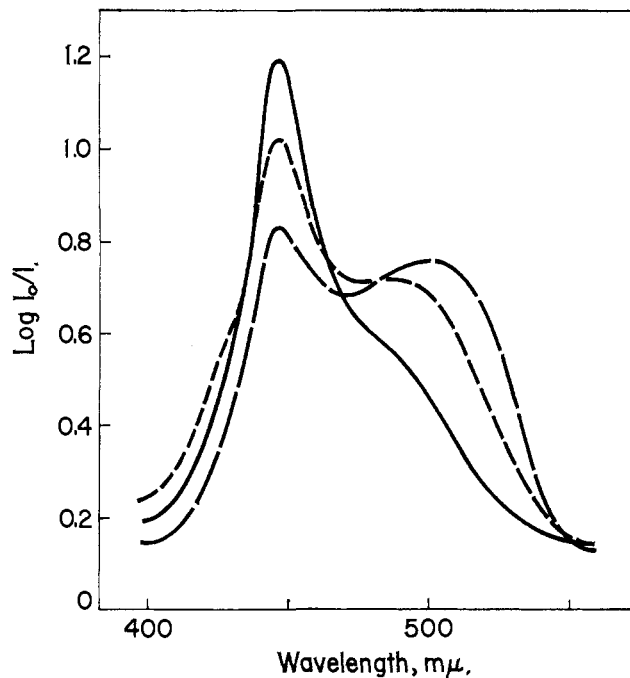


Fig. 2b.—Spectra of sodium fluorenone in various solvents: — — —, Me THF, $4.1 \times 10^{-2} M$; — — —, THF, $3.5 \times 10^{-2} M$; — · —, DME, $3.0 \times 10^{-2} M$.

where Pake¹⁵ first analyzed the proton resonance of powdered hydrated crystals as randomly oriented two-spin systems. The n.m.r. analog is simpler because the two protons are point spins with well-defined separation whereas spins are delocalized in the entire molecule in large organic triplet molecules.

(a) **Alkali Metal Ketyls.**—Electron spin resonance spectra due to the $\Delta M = 1$ and the $\Delta M = 2$ transitions in Me THF rigid media at 77° were taken for various fluorenone, xanthone and benzophenone ketyls. Rep-

(15) G. E. Pake, *ibid.*, **16**, 327 (1948)

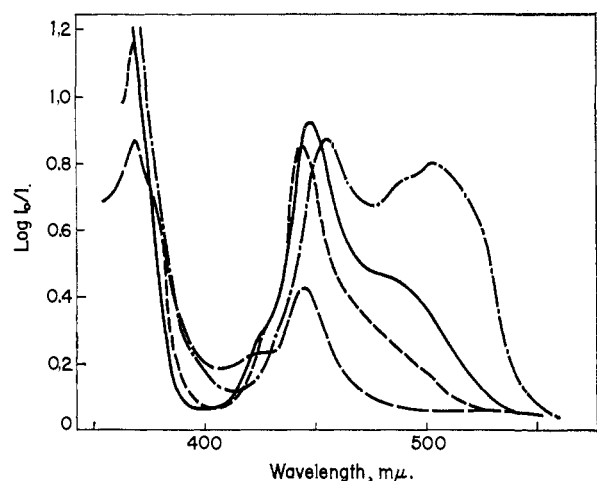


Fig. 2c.—Spectra of sodium fluorenone ion: ---, DME; —, Me THF; - · - ·, 1:1 Me THF and toluene; — — —, toluene.

representative spectra are shown in Fig. 3. The spectra due to the $\Delta M = 1$ transition consist of the superposition of two spectra, a central narrow single peak, and a widely separated doublet. The separation of the doublet decreases with increasing size of the alkali metal ion as shown in Table II. Optical spectra at 77°K. are similar to those obtained at room temperature and indicate the existence of both monomer and dimer at 77°K. Therefore, the assignment of the central peak to monomers and/or dimers with small dipolar interaction and the rest of the spectra to dimers with large dipolar interaction seems to be reasonable.

TABLE II
SPIN-SPIN DIPOLAR INTERACTION

	Doublet separation, gauss	D/hc , cm.^{-1}	r_{12} , Å.
Fluorenone	Li 118	0.0110	6.2
	Na 98	.0092	6.6
	K 82	.0077	7.0
Xanthone	Li 90	.0084	6.8
	Na 79	.0074	7.1
Hexamethylacetone	Na 163	.0152	5.6

Benzophenone ketyls showed a strong central peak of 15 gauss half-width and an extremely weak doublet. The aliphatic ketyl hexamethylacetone also showed a weak, widely separated doublet and a single central peak at 77°K. The integrated spectra of the dimer spectra of lithium and sodium fluorenone and xanthone agree very well with the theoretical curve for randomly oriented two-spin systems described by Pake; see Fig. 4.

(b) **Alkaline and Rare Earth Metal Ketyls.**—Barium and strontium fluorenone ketyls showed broad spectra whose tails extend over about 100 gauss. Calcium and magnesium fluorenone dimers and all benzophenone and xanthone alkaline earth metal ketyls showed absorption spectra of 10–15 gauss half-width. Lanthanum fluorenone and xanthone ketyls showed absorptions of about 25 gauss half-width which is appreciably broader than those of the alkaline earth metal ketyls. Representative spectra are shown in Fig. 3.

Whenever a large separated doublet spectrum or broadened spectrum of the dimer was observed in the $\Delta M = 1$ transition, the $\Delta M = 2$ transition was observed.¹⁶ The spectrum of the $\Delta M = 2$ transition is a

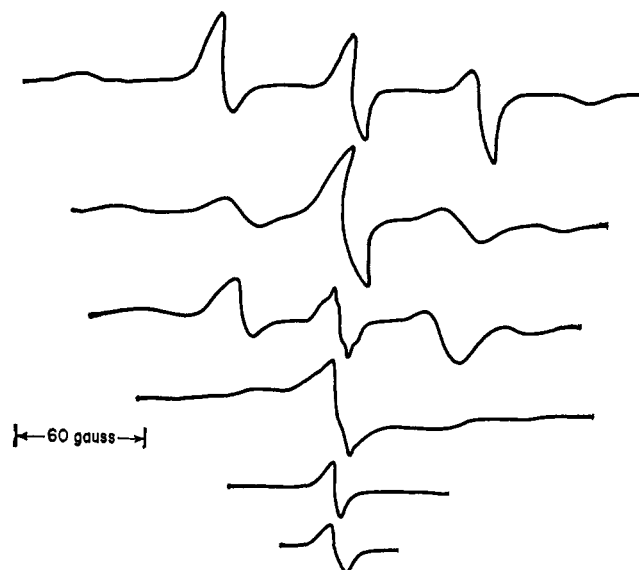


Fig. 3.— $d\chi''/dH$ vs. H for ketyls in Me THF at 77°K. Spectra are, reading from top down, $\Delta M = 1$ transition for lithium fluorenone, sodium fluorenone, lithium xanthone, barium fluorenone, magnesium fluorenone, and the $\Delta M = 2$ transition for lithium fluorenone. The latter is displaced and occurs at half the normal field.

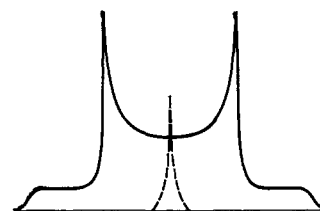
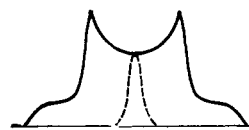


Fig. 4.—Integrated e.s.r. spectra in the $\Delta M = 1$ region of lithium xanthone (above) and lithium fluorenone (below) in Me THF at 77°K. The dotted spectra are those of the monomer.

single absorption peak of 10–15 gauss half-width at a field strength approximately half of the center of the $\Delta M = 1$ transition; see Fig. 3. The intensity of the $\Delta M = 2$ transition is of the order of 10^{-3} of the $\Delta M = 1$ transition.

In liquid solution the hyperfine splitting spectra of dimers with large dipole interactions is broadened by relaxation, while those with small dipole interactions such as most of the alkaline earth dimers showed well-resolved hyperfine structures. Sodium fluorenone dimer in Me THF showed a continuous change of the spectra with temperature starting from a single broad spectrum at higher temperatures to a doublet at lower temperature.

In the derivative curve of the $\Delta M = 1$ transition of a two-spin system characterized by the spin Hamiltonian written above, peaks should appear in three pairs whose separations are $2D$, $D + 3E_1$, and $D - E$, respectively.¹⁶ The observed spectra of dimers of lithium and

(16) J. H. Van der Waals and M. S. Groot, *Mol. Phys.*, **2**, 333 (1959).

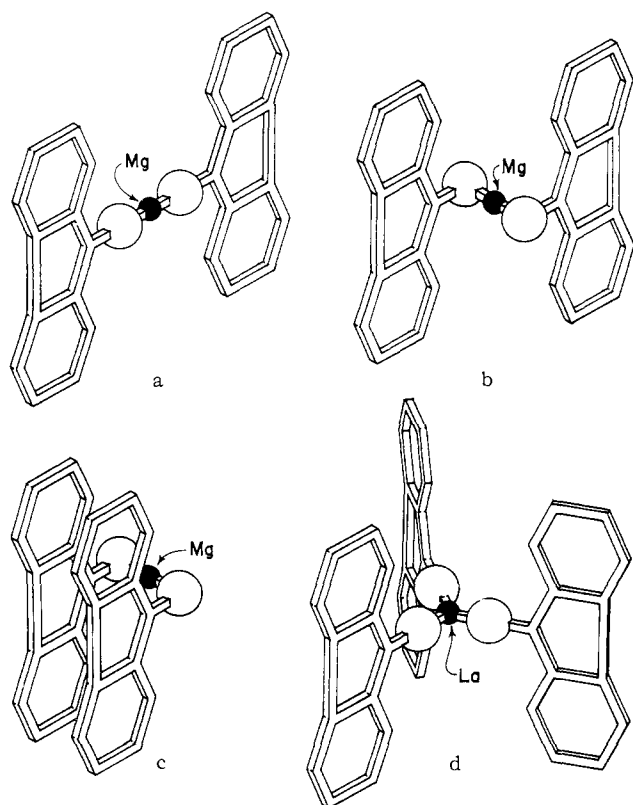


Fig. 5.—Possible structures of paramagnetic ketyls with polyvalent cations: a, b, c, dipositive ions; d, tripositive ion.

sodium fluorenone, and lithium and sodium xanthone ketyl can be analyzed by the above spin Hamiltonian, with E approximately zero. E is proportional to the expectation value of $(x_{12}^2 - y_{12}^2)r_{12}^{-5}$ for two spins with r_{12} as the distance between two spins and x_{12} and y_{12} as its x and y components.

The only reasonable structure which requires $E = 0$ by reason of symmetry has the point group D_{2d} with the planes of the aromatic systems perpendicular to each other. However, many other structures could yield the observed spectra through accidental cancellations. In the ketyls, most of the contribution to the spin-spin interaction probably comes from the spin densities in the carbonyl groups. As these carbonyl groups are separated by positive ions, the mutual separation of spins (r_{12}) would be rather large and favor reduction of E .

In randomly oriented two-point spin systems, the doublet separation is given by $3\beta r_{12}^{-3}$. For ketyl biradical systems as a first approximation we consider two spins separated by an average distance \bar{r}_{12} which can be calculated from the observed splittings; \bar{r}_{12} thus calculated and D are given for several systems in Table II. The broad spectra of barium and strontium fluorenone might be due to nonvanishing value of E or the superposition of different conformations with different magnitudes of dipolar interaction.

Dimerization and Electron Transfer Rate.—As stated in the last section, large dipolar interactions are not necessarily present in all paramagnetic dimers. In rigid media the spectra of dimers with small dipole interaction are not distinguishable from those of monomers. Other evidence for the existence of the two paramagnetic species in the alkali metal ketyls is demonstrated in a kinetic study of sodium benzophenone in

Me THF. The data will be presented in a subsequent publication on kinetics in ketyl systems.

Structure of Dimers and Spin-Spin Interaction.—From the magnitude of the observed splitting of the doublet or the magnitudes of the broadening in the rigid media spectra, we may consider possible structures of dimer ketyls. First, we notice that there is a large variation in the magnitude of the dipolar interaction, namely, from less than 10 to 160 gauss. Divalent ketyls except barium and strontium fluorenone and alkali metal ketyls of benzophenone showed single peaks with half widths of 10–15 gauss. Since there is no sign of dissociation in divalent ketyls, it must be concluded that the dipolar interaction in these ketyls would be equal to or less than 10 gauss. A possible structure of the complex with a dipositive ion in which two radicals are most separated is given in Fig. 5a. A recent theoretical study of the spin density in benzophenone free ion ketyl¹⁷ gives $\rho_c = 0.27$ and $\rho_o = 0.15$. For divalent ketyls ρ_c may be larger and ρ_o may be smaller than this value.⁸ Placing 0.3 spin density on the central carbon atom, 0.1 on the oxygen atom, and the rest on the rings, and taking $r_{cc} = 8.0 \text{ \AA}$. and $r_{oo} = 5.4 \text{ \AA}$., we obtain a crude estimate of the dipolar interaction of 30 gauss by the point spin approximation. In actual systems correlations between two spins and the angular distribution of the electron in a 2P orbital would decrease the magnitude of the interaction. Also the separations r_{cc} and r_{oo} , could be larger than estimated above because of the effect of solvation and vibration. Therefore, the observed small values of the dipolar interaction in most divalent ketyls and some alkali metal dimer ketyls are not surprising. In trivalent ketyls whose possible structures are given in Fig. 5b, mutual separation of the radicals is smaller and more dipolar interaction is expected. The observed 25 gauss half-width probably indicates a larger dipolar interaction.

In order to explain the observed large dipolar interaction in barium and strontium fluorenone and dimers of various alkali metal ketyls of fluorenone and xanthone, other structures with smaller mutual separation of spins must be considered. Although it is difficult to give definite structures for these dimers, structures as shown in Fig. 5c,d would possibly give the observed magnitude of dipolar interaction. There may be equilibria among different dimers shown in Fig. 5 and the most stable structure would be determined by several factors: the structure of the original ketone, the charge and size of the positive ion, and the nature of the solvent. The effect of the solvent in the equilibrium between the monomer and the dimer and the importance of the solvation in the dimer will be discussed in a later section.

Scalar Spin Exchange Interaction in Biradicals.—A Hamiltonian for a dimer in liquid solution which includes a scalar interaction between electron spin may be written as

$$\mathcal{H} = g\beta\vec{H} \cdot (\vec{S}_1 + \vec{S}_2) + \sum A_{1i} S_1 \cdot I_i + \sum A_{2j} \vec{S}_2 \cdot I_j + J \vec{S}_1 \cdot \vec{S}_2$$

where J is a scalar spin-spin interaction operator and

(17) G. K. Fraenkel and R. H. Rieger, *J. Chem. Phys.*, **37**, 2811 (1962).

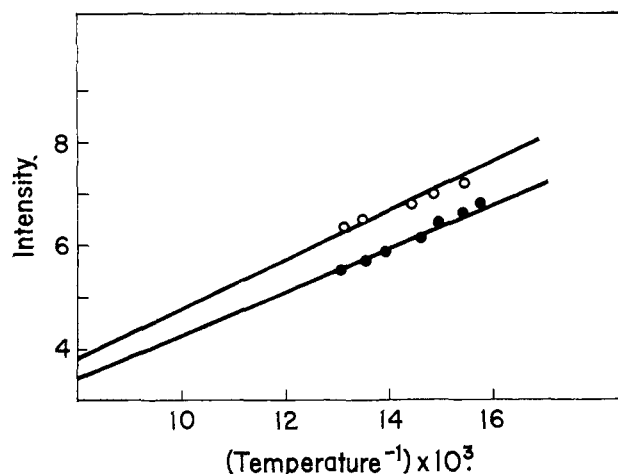


Fig. 6a.—Intensity of $\Delta M = 2$ transition vs. $1/T$ in Me THF for barium fluorenone (open circles) and lithium fluorenone (solid circles).

A_{ii} is nuclear spin isotropic hyperfine interaction between spin 1 and nucleus i . \vec{S} and \vec{I} are spin operators for electron and nuclear spin. Subscripts 1 and 2 refer to each half of the ion pair. The analysis of the hyperfine structure due to C^{13} splitting of the two-spin systems has been worked out in detail for C^{13} -labeled biradicals.¹⁸ In two limiting cases $A \gg J$ or $A \ll J$, the effect of the two terms are qualitatively easy to see. (1) $A \gg J$: the Hamiltonian is nearly the sum of the Hamiltonians for two independent spins which interact with one-half of the system. Hyperfine patterns are similar to those of the monomer. (2) $A \ll J$: each electron interacts with all nuclei in the entire system and the hyperfine pattern is quite different from that of the monomer.

The C^{13} and proton hyperfine patterns of the solution e.s.r. spectra of the divalent and trivalent ketyls correspond to the condition $A \gg J$. The rate of spin exchange between the two halves of the ion pair is, therefore, much slower than the hyperfine frequency, order of 10^6 sec.^{-1} .

The temperature dependence of the intensity of absorption is consistent with a small value of J . The intensity of the $\Delta M = 2$ resonance is proportional to reciprocal of temperature between 63 and 77°K. in lithium and barium fluorenones; see Fig. 6a. The $\Delta M = 1$ transition in magnesium and calcium xanthone follows the Curie law from 90 to 320°K.; see Fig. 6b.

III. Optical Studies of the Equilibrium. Extent of the Diamagnetic Dimer.—From the results of magnetic susceptibility measurements it is commonly believed that the diamagnetic dimer, pinacolate, exists in the solution of alkali metal ketyls. Most of these susceptibility measurements, however, were made in solutions of high ketyl concentrations.¹⁹ Since we are concerned with much lower ketyl concentrations ranging from 10^{-2} to $10^{-5} M$, and the solvents which we used are different from those used in the previous studies, it is doubtful whether the results of the former investigations are applicable. We studied, therefore, the equilibrium between the diamagnetic dimer and the paramagnetic species by a spectrophotometric method.

(18) D. C. Reitz and S. I. Weissman, *J. Chem. Phys.*, **33**, 700 (1960).

(19) G. W. Wheland and R. N. Doescher, *J. Am. Chem. Soc.*, **56**, 2011 (1934).

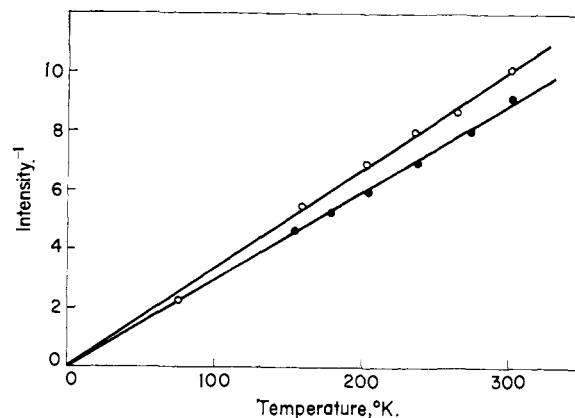
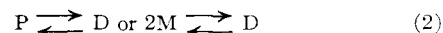


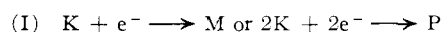
Fig. 6b.—Reciprocal of intensity of $\Delta M = 1$ transition of magnesium benzophenone (open circles) and calcium xanthone (closed circles) vs. T .

We consider two cases: (a) ether solvents (DME, THF, and Me THF) and (b) nonpolar solvents such as benzene, toluene, and cyclohexane.

(a) **Ether Solvent.**—The extent of the diamagnetic dimer was checked in the following way. Assume that the following equilibria exist in the solution



where M = monomer ketyl, P = paramagnetic dimer, and, D = diamagnetic dimer. Generally, two electrons can be added to one ketone molecule to form a dinegative ion in the presence of excess alkali metal. The reduction takes place stepwise.



Practically no dinegative ions are formed until all of the ketones are reduced to mononegative ions. Suppose that we have an appreciable amount of the diamagnetic dimer, pinacolate, in equilibrium with ketyl radicals. The transformation of the diamagnetic dimer into ketyl must take place as the formation of the dinegative ion proceeds. The total concentration of the absorbing species in the visible region given by $[S] = [M] + 2[P] + [N]$ will increase as the reduction proceeds. On the other hand, if the amount of the diamagnetic dimer is negligibly small, $[S]$ will be constant throughout the further reduction to form dinegative ions.

In sodium fluorenone in Me THF at $10^{-2} M$ of ketyl, the radical component is mostly dimer (as clearly seen from its optical and e.s.r. spectra) and the optical spectrum changes little in shape with the concentration from 4×10^{-2} to $5 \times 10^{-3} M$. We can assume, then, that $[S] = 2[P] + [N]$. If the concentration of the diamagnetic dimer is small, we should have isosbestic points in the course of the formation of the dinegative ion at the position where the extinction coefficients of the mononegative ion and the dinegative ion are equal. If the concentration of the diamagnetic dimer is large, there should be no such isosbestic points. Figure 7 shows the change of the optical spectrum with further reduction of sodium fluorenone in Me THF and two isosbestic points are seen at 480 and 360 $m\mu$. Therefore the concentration of the pinacolate type appears to

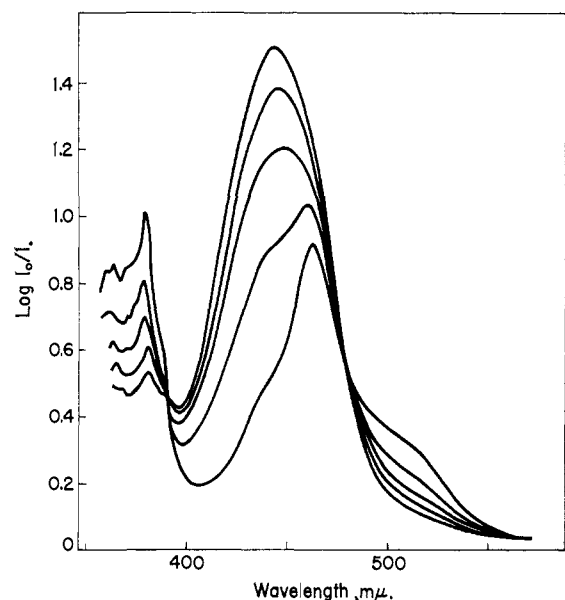
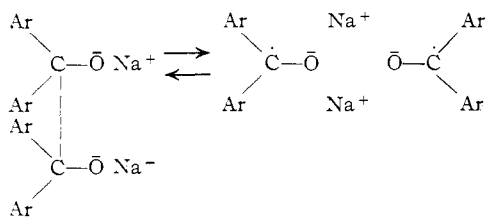


Fig. 7.—Optical spectra of sodium fluorenone in Me THF with increasing reduction.

be small in this case. Similar results were obtained where $[M] \gg [P]$. It is likely that in dilute ether (DME, THF, and Me THF) solutions of alkali metal ketyls the extent of pinacolate formation is small.

(b) **Nonpolar Solvents.**—The situation is quite different in nonpolar solvents. The transformation of the ketyl radical into the diamagnetic dimer and the complete reversibility of the equilibrium were demonstrated in the following experiments.

Ketyls were made in an ethereal solvent such as DME or THF and their optical spectra were taken. Then the ether solvent was pumped out and a nonpolar solvent was introduced. The intensity of the optical absorption was very much reduced in the nonpolar solvent. With the reintroduction of the ether solvent into the same sample cell most of the optical absorption was recovered. Representative examples are shown in Fig. 8 and Fig. 2c. The much reduced absorption in nonpolar solvents is consistent with Wheland and Doescher's observation that the paramagnetism of ketyls in benzene solution is very small.¹⁹ From the very slow electron transfer rate between radical and ketone and the small change of the spectrum with temperature in nonpolar solvents, the radical component is the paramagnetic dimer. Therefore, the equilibrium should be written as



Thermodynamic Quantities and the Nature of the Equilibrium between Monomer and Dimer.—The concentration of the monomer and dimer ketyls in solution was approximately determined under the assumption that the concentration of the diamagnetic dimer in ether solution is negligibly small. The ketyls are mostly in the dimer form at high concentration ($10^{-1} \sim 10^{-2} M$) in Me THF and the monomer form at

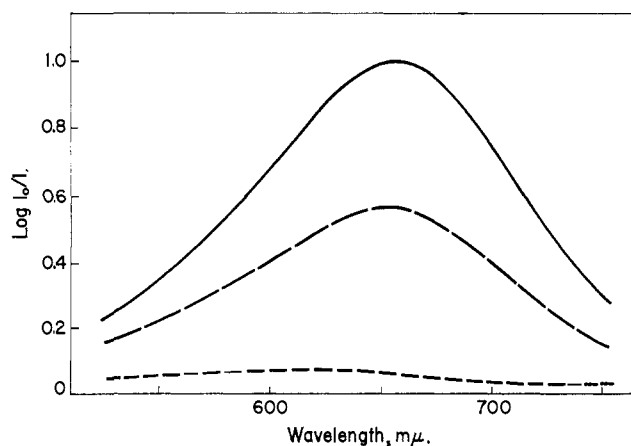


Fig. 8.—Spectra of sodium benzophenone ketyl in Me THF (above), toluene (below), mixed Me THF and toluene (center).

low concentration ($10^{-4} \sim 10^{-5} M$) in DME. Assuming that the effect of the solvent on each component of the spectrum is not large, we take the spectrum at high concentration in Me THF and at low concentration in DME as the standard spectrum for the pure dimer and monomer, respectively. The estimated molar extinction coefficients of the monomer of sodium fluorenone at 454 and 520 $m\mu$ are 2700 and 6060, respectively; the corresponding numbers for the dimer are 2700 and 450. From these extinction coefficients, dissociation constants for the equilibrium between the paramagnetic dimer and monomer were obtained at various concentrations. The temperature dependence of the spectrum was also studied. The thermodynamic quantities ΔF° , ΔH° , and ΔS° were estimated for the dissociation of the sodium fluorenone paramagnetic dimer into the paramagnetic monomer in ether solution. The data for the reaction $2M = D$ are given in Table III.

TABLE III
THERMODYNAMIC QUANTITIES FOR DISSOCIATION OF
Na FLUORENONE DIMER (23°)

Dissociation constant, mole per liter	ΔF° , kcal.	ΔH° , kcal.	ΔS° , cal. deg. ⁻¹
DME 2×10^{-3}	6.7	-2.5	-29
THF 5×10^{-4}	8.9	-1.3	-31
Me THF 2×10^{-6}	10.8	Small	-37

The spectroscopic determination of the dissociation constants is not accurate because of the several assumptions made in determining the concentration. Despite these assumptions, the obtained dissociation constants were fairly constant for a wide range of concentration.

With other metals qualitatively similar results were observed though quantitative measurements were not made. The order of the dissociation constants in different solvents and with different positive ions can be seen from the shape of the absorption spectra shown in Fig. 2 and are summarized as

$$\text{solvent: } K_{\text{DME}} > K_{\text{THF}} > K_{\text{Me THF}}$$

$$\text{metal: } K_{\text{Cs}} > K_{\text{Rb}} > K_{\text{K}} > K_{\text{Na}} > K_{\text{Li}}$$

From the values given in Table III, it is noticed that the nature of the equilibrium has many similarities to those found in the dissociation of sodium naphthalenide into sodium ion and naphthalene negative ion.²⁰ Large

(20) A. Mathias and E. Warhurst, *Trans. Faraday Soc.*, **59**, 345 (1960).

negative ΔS° and small negative ΔH° are characteristic in these cases.

The quantity of primary interest is the large negative ΔS° . Partial ordering of the solvent by the strong solvation of sodium ions in monomer ketyl could be primarily responsible for this change. The solvation of sodium ion in the ethereal solvent has been considered to be one of the main causes of the large entropy change in the dissociation of sodium naphthalenide ion pair.²¹ Mathias and Warhust²⁰ also mentioned the decrease in the solvent entropy due to the solvation in rationalizing a decreased value of the pre-exponential factor for the reaction of monosodium fluorenone and methyl iodide. Qualitatively this will be understood in the following way. As discussed in the previous section, two sodium ions are surrounded by two large ketyl anions and the solvation is greatly hindered in the paramagnetic dimer, while in the monomer more space is accessible for solvent molecules. The relative difference in the solvent ordering in the monomer and the

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dimer would result in the negative ΔS° for the dissociation. The small negative ΔH° would come mainly from the difference of two competing electrostatic interactions, namely, electrostatic interaction between positive ions and aromatic negative ions and that of solvation.

The dissociation constants increase as the size of the positive ion increases. The weakened electrostatic interaction between the positive ion and the negative charge of the ketyl and also the solvent molecules would weaken the solvation as well as the force which combines two ketlys. Dimers are predominant in aliphatic ketlys. This may be accounted for by the stronger electrostatic interaction due to the more localized charge on the carbonyl group.

While the equilibrium between the paramagnetic monomer and dimer is the major equilibrium in dilute ether solution, such as DME, THF, and Me THF, the major equilibrium in nonpolar solvents is the one between the paramagnetic and the diamagnetic dimer.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK AT STONY BROOK, STONY BROOK, L. I., N. Y.]

π -Complex Interactions. II.¹ Methyl Substituted Benzenes and Naphthalenes with Tetracyanoethylene²

BY ARTHUR R. LEPLEY

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The charge-transfer spectra of the π -complexes formed by a number of methyl substituted benzenes and naphthalenes with tetracyanoethylene have been measured. Comparison of the observed energy shifts with other spectroscopic shifts and energy level correlations shows that these π -complexes can be reasonably interpreted in terms of first-order perturbation theory using only inductive effects. The highest occupied Hückel molecular orbital relationship previously established for alternant and nonalternant hydrocarbons is used in evaluating the coulomb perturbation parameter for methyl shifts.

Introduction

A simple molecular orbital (MO) treatment has previously been successfully applied to the charge-transfer spectra of alternant^{3,4} and nonalternant¹ hydrocarbons. These hydrocarbons (D) containing only sp^2 -carbon atoms donate electrons from their highest occupied orbital (h.o.o.) to an interacting acceptor molecule (A) where it enters the lowest unoccupied orbital (l.u.o.). The energy, E_π , required for this transition is thus proportional to the difference in orbital energies m (eq. 1)

$$E_\pi = m_{A1^*} - m_{D1} \quad (1)$$

where the subscripts denote the molecule and the energy levels, numbering from the h.o.o. and l.u.o. (*), respectively. The individual orbital energies from the Hückel MO treatment are given by $\alpha + x_i\beta$. Here α and β are, respectively, the coulomb and exchange integrals. Since the hydrocarbons contribute only p-orbitals from sp^2 -carbon atoms to the energy matrix, the x_i and relative m_{D1} may be determined.⁵

The calculated x_i 's for the donor molecules have been used to determine the parameters m_{A1^*} for the acceptors

p-benzoquinone,⁶ chloranil,⁶ iodine,⁵ tetracyanoethylene,⁴ tetracyanoquinodimethane,⁶ trinitrobenzene,^{3,6} and trinitrofluorenone.¹ An example of such evaluation gives the relationship between E_π and x_1 for tetracyanoethylene (eq. 2)

$$x_{D1} = (E_\pi - 0.34)/3.06 \quad (2)$$

where E_π is in electron volts and x_{D1} is dimensionless.

In their classic work relating ionization potentials to the frequency of charge-transfer iodine complexes, McConnell, Ham, and Platt⁷ included a wide range of aromatic compounds. Among these were a number of methyl substituted aromatics. The general nature of the inclusion of such compounds has been adequately documented^{8,9} for a variety of acceptors. However, no attempt has been made to make specific comparisons of the influence of this group on the charge-transfer process.

The ionization potential relationship to methyl substituents has been explored.¹⁰ The MO h.o.o. which correlate¹¹ with the ionization potential has been used¹⁰

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