Electron Paramagnetic Resonance and Optical Studies of the Structures of Ion Clusters of Radical Ions and Electronic Interactions in Ion Clusters

S. W. Mao, K. Nakamura, and N. Hirota*

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. Received December 3, 1973

Abstract: Detailed epr and optical studies of the alkali and alkaline earth metal fluorenone ketyls were made under various conditions. From the analyses of the solution epr spectra it was shown that the anions and cations are in contact with each other in the alkaline earth metal ketyls. It was shown, however, that they form higher ion clusters $(R^-M^{2+}R^-)_n$ in ethereal solutions. In more polar solvents they dissociate into biradical triple ions $(R^-M^{2+}R^-)$. In the case of alkali metal ketyls it was shown that the biradical triple ion $(R^-M^+R^-)$ exists in solution as well as ion quadruplets. Besides these paramagnetic species, diamagnetic ion clusters $(R^-M^+)_n$ are shown to exist. The assignments of the absorption peaks to the different ionic species were made from the comparisons of the epr and the visible spectra taken at the same concentration and temperature. Possible structures of the ionic species to explain the results of epr and optical studies are suggested. Paramagnetic ion clusters were also found in the solutions of other radical anions such as quinoxaline, terephthalonitrile, and p-chloronitrobenzene.

Radical anions in solution are known to exist in various forms of ionic species ranging from the free ion and ion pairs to various forms of clusters and aggregates.[1,2] The dominant forms of the ionic species existing in a given solution depend on the anion, the cation, the solvent, the concentration, and the temperature. Ion cluster formation is known to be important in the ethereal solutions of radical anions containing heteroatoms.[3-9]

Although earlier epr studies established the presence of paramagnetic ion clusters, there have been several observations which needed further clarifications. First, rigid media epr spectra of fluorenone ketyls showed the existence of at least two different paramagnetic ion clusters, but their origins were not clear.[10] Second, low-temperature visible spectra of fluorenone ketyls showed striking concentration dependence, which indicates the existence of several different ionic species in solution. Third, well resolved solution epr spectra of alkaline earth metal ketyls are not consistent with simple biradical structures.[11] These observations clearly indicate that these systems are far more complex than were thought in the earlier studies and further studies are needed to clarify their structures. Accordingly, we have made more detailed epr and spectroscopic studies of the alkali and alkaline earth metal ketyls and other related systems.

Experimental Section

Solutions of radical anions were prepared by the reduction of aromatic molecules with alkali and alkaline earth metals in a vacuum sealed glass apparatus. The alkali metal reduction was made following the standard procedure already described elsewhere.[8] The alkaline earth metal reduction was made by using a Hg amalgam of alkaline earth metals prepared under vacuum. The solvents used in this study were 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), 2,6-dimethyltetrahydrofuran (DMTHF), dioxane, diethyl ether (DEE), N,N'-dimethylformamide (DMF), and their mixtures. For making samples in the mixtures of ethereal solvents and DMF, desired amounts of DMF were added to the ethereal solutions of radical anions through vacuum lines.

All epr measurements were made by following the standard procedure.[8] Rigid media epr spectra in MTHF and mixtures of MTHF and DMF were obtained at about 120°K unless otherwise stated. In most cases rigid media spectra do not change much by lowering the temperature from 120°K. Hyperfine and fine structure splittings were determined by using a proton gauss meter. The fine structure splittings were determined as one-half of the separation between the two outside peaks (z axis peaks), whenever these peaks are clearly observed. Otherwise, they were estimated from the inside peaks (x and y peaks). MTHF and mixtures of other solvents with MTHF form good glass at our measuring temperatures. However, other solvents form only polycrystalline samples at 120°K.

Visible absorption spectra were obtained on a Cary 14 spectrometer. The visible spectra at low temperatures were obtained by inserting the sample cells into a hole of an aluminum block fitted into a dewar. The aluminum block was first cooled down to the boiling nitrogen temperature and then was allowed to warm up slowly. The optical path lengths of the cells used in this work were 0.2, 2, 20, and 50 mm depending on the concentration.

The approximate value of the extinction coefficient ($\epsilon \sim 9000$) of the 530-mμ peak was estimated from the maximum intensity of the absorption peak of dilute DME solutions of ketyls and the initial concentration of fluorenone. This value can be used to estimate the concentration of ion pairs. However, the complexities due to the existence of various paramagnetic species discussed in this paper make it impossible to determine the concentrations of radicals very accurately. Hence the concentrations given in this paper are very approximate ones. Uncertainties could be as large as a factor of 2.

Results and Discussions

(I) Natures of the Ketyls of Divalent Cations. When anions are combined by a divalent cation, a biradical ketyl may be formed.[12] It is then expected that strong dipole interactions between two unpaired electrons in biradicals broaden the solution epr spectra and characteristic rigid media biradical epr spectra are observed.

(1) N. Hirota, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Wiley, New York, N. Y., 1967.
(2) M. C. R. Symmons, "Ions and Ion Pairs in Organic Reactions," M. Szwarc, Ed., Wiley, New York, N. Y., 1972.
(3) T. Takeshita and N. Hirota, *J. Chem. Phys.*, **58**, 3745 (1973).
(4) N. Hirota and S. I. Weissman, *Mol. Phys.*, **5**, 537 (1962); *J. Amer. Chem. Soc.*, **86**, 2358 (1964).
(5) I. M. Brown, S. I. Weissman, and L. C. Snyder, *J. Chem. Phys.*, **42**, 1105 (1965).
(6) P. Biloen, R. Prins, J. D. W. Van Voorst, and G. J. Hoijtunk, *J. Chem. Phys.*, **42**, 1105 (1967).
(7) H. van Willigen and S. I. Weissman, *Mol. Phys.*, **11**, 101 (1966).
(8) N. Hirota, *J. Amer. Chem. Soc.*, **89**, 32 (1967).
(9) G. W. Canters, Thesis, University of Nigmegen, 1969.
(10) K. Nakamura and N. Hirota, *Chem. Phys. Lett.*, **3**, 134 (1969).
(11) S. W. Mao and N. Hirota, *Chem. Phys. Lett.*, **22**, 26 (1973).
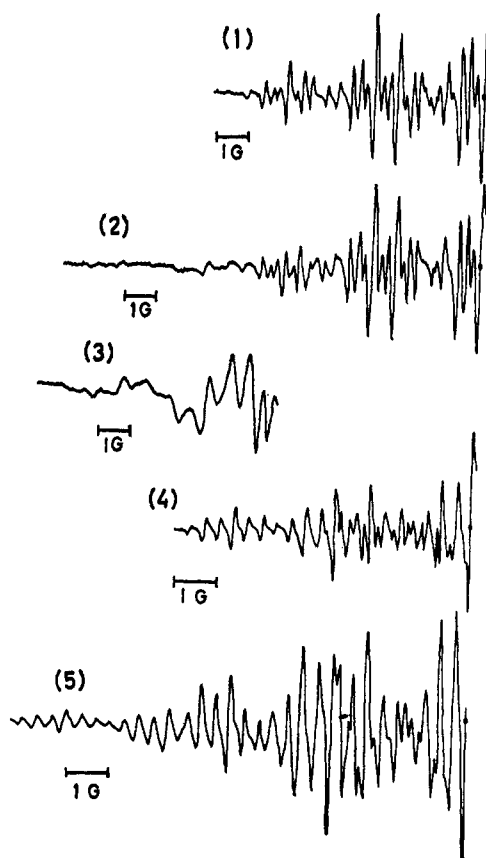(12) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **83**, 3533 (1961).

Figure 1. Solution epr spectra of fluorenone ketyls with alkaline earth metal ions. (1) magnesium fluorenone in THF at 25°; (2) magnesium fluorenone (59.5% enriched ^{13}C at the carbonyl carbon) in THF at 25° (obtained with the same experimental conditions as used in obtaining spectrum 1); (3) tail of spectrum 2 obtained with higher 100 kc field modulation amplitude; (4) calcium fluorenone in DME at 25°; (5) calcium fluorenone (59.5% enriched ^{13}C) in DME at 25°.
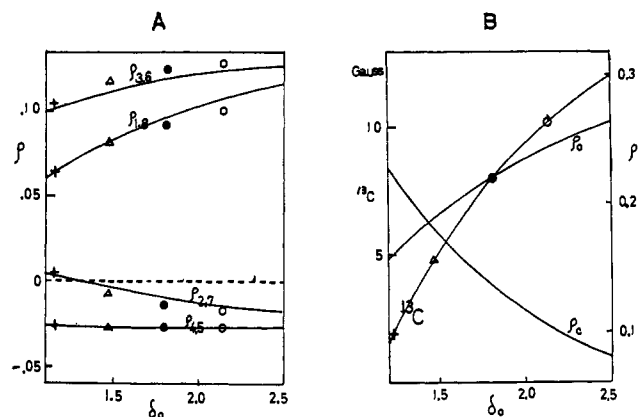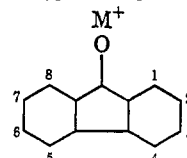

Figure 2. (A) Experimental and calculated spin densities in the rings of fluorenone ketyls. Curves give the calculated spin densities as a function of δ_0. Points indicate the experimentally estimated spin densities: (△) Na, (●) Ca, (○) Mg, (+) free ion (HMPT solvent). (B) Calculated spin density on C=O and the experimental and calculated ^{13}C splitting of the carbonyl carbon. Curves indicate the calculated spin densities and the ^{13}C splitting as a function of δ_0. Points give the experimental values of ^{13}C splitting: (△) Na, (●) Ca, (○) Mg, (+) free ion (HMPT solvent).

Table I. Comparison of Hyperfine Splittings (G) of Fluorenone

Metal	Solvent	^{13}C	$H_{1,8}$	$H_{2,7}$	$H_{3,6}$	$H_{4,5}$
Na	THF	4.8	2.17	0.17	3.13	0.67
Ca	DME	8.0	2.43	0.35	3.30	0.68
Mg	THF	10.3	2.64	0.44	3.38	0.68

Contrary to this expectation, many of the divalent metal ketyls show well resolved solution epr spectra but do not show rigid media biradical spectra.[4,11,12] Therefore, simple biradical structure does not seem correct for many ketyls of divalent cations. In the following we consider the possible structures of these ketyls.

(A) Solution Epr Spectra of Alkaline Earth Metal Ketyls and the Natures of the Radical Species. Magnesium and calcium ketyls of fluorenone, xanthone, and benzophenone all show well resolved solution epr spectra.[1] Examples of fluorenone ketyls are shown in Figure 1. The proton and carbonyl ^{13}C hyperfine splittings of the divalent metal ketyls are considerably different from those of alkali metal ketyls as shown in Table I. For example, the carbonyl ^{13}C splittings of the magnesium and calcium fluorenone ketyls in THF at 25° are 10.3 and 8.0 G, respectively, while that of sodium ketyl is 4.8 G. The perturbation of spin densities in divalent metal ketyls was treated in a way similar to that used in treating alkali metal ketyls.[13] As in the previous cases, perturbation was treated by changing the oxygen Coulomb parameter, $\alpha + \delta_0 \beta$, in the MO calculation. Using McClelland's treatment[14] of the

ion pair effect, change in δ_0 ($\Delta\delta_0$) due to ion pair formation is given approximately by

$$\Delta\delta_0 \simeq -Ze^2/\epsilon r_{OM} \qquad (1)$$

where ϵ is a screening factor due to solvation and r_{OM} is the distance between the carbonyl oxygen and the cation. Spin densities were calculated by using McLachlan's method.[15] The McConnell equation for proton splittings ($Q = -23.7$ G)[16] and the Fraenkel-Karplus equation[17] for ^{13}C splittings were used to convert the splittings into spin densities and vice versa. In Figure 2 calculated changes of the proton and the carbonyl ^{13}C splittings are plotted against δ_0 together with the observed values. The increase of δ_0 from the free ion values required to fit the experimental spin densities of the divalent metal ketyls is ~0.99 and ~0.65 for magnesium and calcium ketyls, respectively. These values are about twice as large as those for lithium (~0.45) and sodium (~0.32), respectively. Since the ionic radii of magnesium and calcium ions are similar to those of lithium and sodium, respectively, the observed spin distributions in the divalent metal ketyls are explained well by taking $Z = 2$ in eq 1 if ϵ is taken similar for both alkali and alkaline earth metal ketyls. This result indicates that in the ketyls of divalent cations,

(13) T. Takeshita and N. Hirota, *J. Amer. Chem. Soc.*, **93**, 6421 (1971).

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

(15) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(16) H. M. McConnell, *J. Chem. Phys.*, **24**, 762 (1956).

(17) G. K. Fraenkel and M. Karplus, *J. Chem. Phys.*, **35**, 1312 (1962).

anions are also directly attached to the cations forming contact structures as in the case of alkali metal ketyls. This conclusion excludes the previously suggested possibility that the ketyls of divalent cations may form solvent separated structures.[8,18] If the ketyls form solvent separated structures, much smaller values of δ_0 should be used to explain the observed values of spin densities. Another observation in favor of contact structures is the observation of ^{25}Mg splittings in several ketyls.[12] The existences of such splittings are difficult to explain on the basis of the solvent separated structures.

(B) Line Widths, Rotational Correlation Times, and the Approximate Sizes of the Ionic Species of Ketyls of Divalent Cations. Having decided that the ketyls are not simple biradical ($R^-M^{2+}R^-$), we have two possible structures for ketyls of divalent metals: (a) a monomer ion pair R^-M^{2+}; (b) a higher ion cluster $(R^-_2M^{2+})_n$.

The possibility of the first structure seems to be unlikely, since this species is positively charged. No free ions to balance the net charges were observed in the ethereal solutions. If the anions are parts of higher clusters, the rotational correlation times of the ketyls of divalent cations are expected to be much longer than those of monomer ketyls. We, therefore, investigated the line widths of the ^{13}C splittings of the sodium, magnesium, and calcium ketyls to estimate the rotational correlation times of the respective species. In the Freed–Fraenkel line width theory,[19] the width of the line corresponding to the magnetic quantum number m of a single nucleus

$$\frac{1}{T_{2m}} = J^D\left[I(I+1) + \frac{5}{3}m^2\right] + \frac{16}{3}J^{DG}B_0m + X \quad (2)$$

where J^D arises from the anisotropic part of the hyperfine interactions. Since the spin density on the carbonyl carbon atom is large, the main contribution to J^D comes from the unpaired electron density on the carbonyl carbon atom. Hence, to a good approximation J^D is given by

$$J^D = 9.76 \times 10^{16}(\rho_c{}^\pi)^2\tau_R \; \mathrm{sec}^{-1} \quad (3)$$

where τ_R is the rotational correlation time of the radical. Here we assumed an isotropic rotational correlation time. The second term in eq 2 is linear with respect to m and can be estimated from the differences of the widths of the lines corresponding to $m = \frac{1}{2}$ and $-\frac{1}{2}$. The line broadening of the ^{13}C lines due to the anisotropic part of the hyperfine interaction was estimated to be 0.10, 0.040, and 0.010 G for magnesium (THF), calcium (DME), and sodium (THF) ketyls, respectively, at room temperature. The corresponding correlation times were estimated to be 2.6 $\times$ 10^{-10}, 1.3 $\times$ 10^{-10}, and 3 $\times$ 10^{-11} sec, respectively. The correlation times of the divalent metal ketyls are clearly much longer than those of the monomer ketyls. Using Debye's formula for rotational correlation times[20]

$$\tau_R = (4r^3/3kT)\eta \quad (4)$$

r is estimated to be 8.1, 6.4, and 4.5 Å for magnesium,

(18) E. Warhurst and M. Wilde, *Trans. Faraday Soc.*, **66**, 2215 (1970).

(19) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

(20) P. Debye, "Polar Molecules," Chapter 5, Dover Publications, New York, N. Y., 1945.
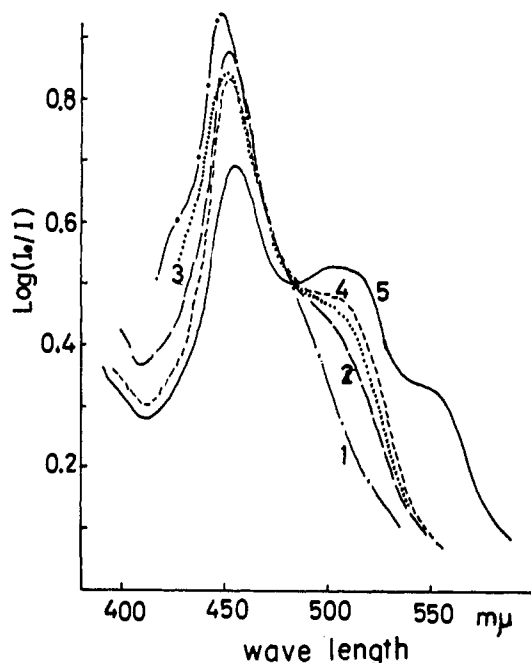
Figure 3. Visible absorption spectra of divalent metal fluorenone in the range of 400–600 mμ: (1) Mg in THF, $\sim$10^{-3} M (-·-); (2) Ca in MTHF, $\sim$10^{-3} M (- - -); (3) Sr in MTHF, $\sim$10^{-3} M (···); (4) Ca in 25% DMF and 75% MTHF, 10^{-3} M (- - -); (5) Ca in DMF, 10^{-3} M (—).

calcium, and sodium ketyls, respectively. Since the assumption of spherical radical and isotropic correlation time is very drastic, the obtained numerical values of r cannot be taken too seriously. Nevertheless, it is quite clear that the sizes of the divalent metal ketyls are much larger than those of the monomer alkali metal ketyls. This result supports the ion cluster structure (b) for the ketyls of divalent cations.

(C) Visible Spectra and Rigid Media Epr Spectra of Divalent Metal Ketyls. The visible spectra of the fluorenone ketyls of divalent cations are shown in Figure 3. The spectra strongly depend on the cation and the solvent. In the ethereal solvents, the major peak is at $\sim$460 mμ with a shoulder at $\sim$510 mμ. This shoulder becomes more distinct as the size of the metal ion increases. There is also a weak long wavelength absorption band at $\sim$650 mμ. Contrary to the cases of alkali metal ketyls the visible spectra of the divalent metal ketyls do not depend much on the type of ethereal solvent or concentration. However, striking changes of the absorption spectra were observed when DMF was added to the ethereal solutions. These are shown in Figure 3. The relative intensity of the shoulder at 510 mμ increases as the fraction of DMF is increased. The relative intensity of this peak also increases upon dilution in the solution of a given DMF/ether ratio.

These observations indicate that the divalent metal ketyls exist as different ionic species depending on solvent and concentration. The magnesium and calcium ketyls seem to form higher ion clusters in ethereal solution but to dissociate in more polar solvents.

The rigid media epr spectra of fluorenone ketyls of divalent cations are given in Figure 4. In the case of magnesium and calcium ketyls in the ethereal solvents, only narrow spectra (half-widths of $\sim$15 G) were obtained at $g \simeq 2.003$. The species responsible
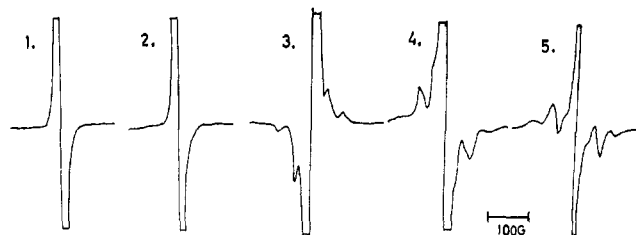
Figure 4. Rigid media epr spectra of divalent metal fluorenone ketyls: (1) Mg in MTHF, $\sim$2 $\times$ 10^{-3} M; (2) Ca in MTHF, $\sim$2 $\times$ 10^{-3} M; (3) Sr in MTHF, $\sim$$10^{-3}$ M; (4) Ca in 25% DMF and 75% MTHF, $\sim$2 $\times$ 10^{-3} M; (5) Ca in 25% DMF and 75% MTH, 5 $\times$ 10^{-5} M.
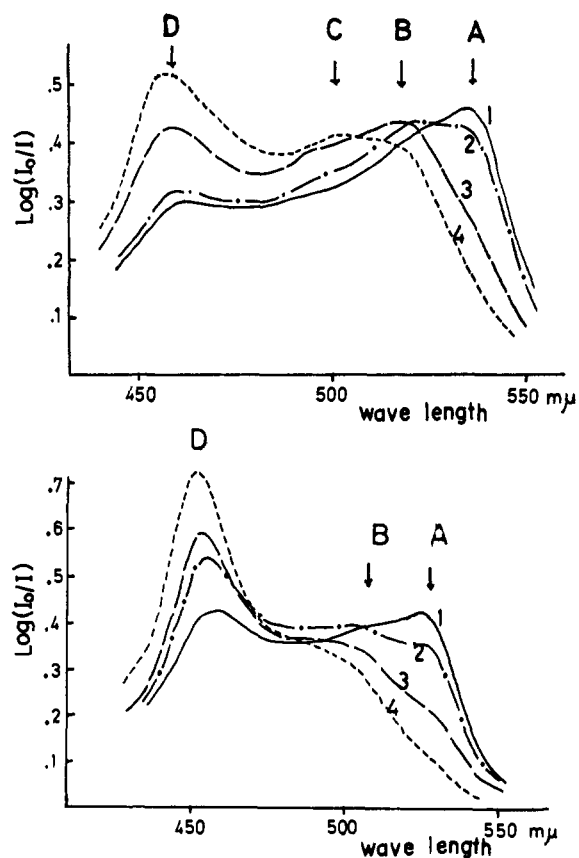

Figure 5. Concentration dependence of the visible absorption spectra (420–550 mμ) of potassium and sodium ketyls. Optical path lengths of the cell were changed so that log (I_0/I) is similar at different concentrations. Top figure, potassium fluorenone in THF at 25°: (1) $\sim$4 $\times$ 10^{-5} M, (2) $\sim$1 $\times$ 10^{-4} M, (3) $\sim$1 $\times$ 10^{-3} M, (4) $\sim$1 $\times$ 10^{-2} M. Bottom figure, sodium fluorenone in MTHF at 25°: (1) $\sim$2 $\times$ 10^{-5} M, (2) $\sim$2 $\times$ 10^{-4} M, (3) $\sim$1 $\times$ 10^{-3} M, (4) $\sim$1 $\times$ 10^{-2} M.

for these narrow spectra are identified as those giving well resolved solution epr spectra at higher temperatures. Rigid media epr spectra of strontium and barium ketyls show the satellites due to biradicals in MTHF as reported in the previous work.[4] In the case of calcium ketyl, the rigid media epr spectrum starts to show the characteristic biradical spectrum upon addition of DMF. With 25% of DMF and at 10^{-3} M a considerably larger fraction of biradical species exists in solution at $-150°$. The relative amount of the biradical species further increases upon dilution (Figure 4). The comparison between the visible spectra and the rigid media epr spectra shows that the biradical species
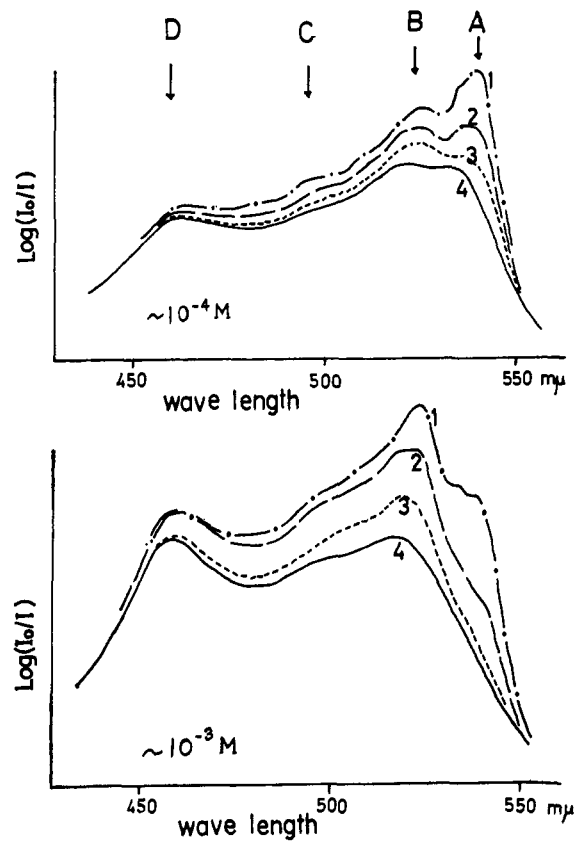

Figure 6. Temperature dependence of the visible absorption spectra of potassium fluorenone. Top figure, $\sim$$10^{-4}$ M in MTHF: (1) $-140°$, (2) $-110°$, (3) $-50°$, (4) 20°. Bottom figure, $\sim$$10^{-3}$ M in MTHF: (1) $-140°$, (2) $-110°$, (3) $-70°$, (4) 20°.

have the absorptions at $\sim$510 mμ. These results further indicate that the magnesium and calcium ketyls form higher ion clusters in ethereal solution and dissociate into biradical species in more polar solvents.

(II) Alkali Metal Ketyls. (A) Concentration, Cation, Solvent, and Temperature Dependence of the Visible Spectra. The visible spectra of fluorenone ketyls in the range of 400 to 600 mμ at room temperature normally consist of three or four broad peaks (Figure 5). The relative intensities of these peaks depend on the cation, the solvent, the concentration, and the temperature. At lower temperatures the spectra generally show four main peaks, though further fine structures are sometimes observable (Figure 6). The location of each peak only slightly depends on the cation, the solvent, and the temperature. In the case of sodium ketyls, four peaks are located at $\sim$530 mμ (A), $\sim$515 mμ (B), $\sim$495 mμ (C), and $\sim$460 mμ (D). These peaks cannot be due to the vibrational structures because the relative intensities of these four peaks vary tremendously depending on the concentration, the solvent, the cation, and the temperatures, as shown in Figures 5 and 6.

The solvent and cation dependence of the intensity of the peak in the A region is in the following order (Table II): solvent, DME > THF > MTHF > dioxane; cation, Cs > K > Na > Li. As the concentration of the ketyl increases, or the solvating power of the cation decreases, the relative intensities of the peaks in regions B, C, and D increase. When the concentration of the ketyl is high ($>10^{-2}$ M) in ethereal solvents, peak D

Table II. Absorption Peaks of Fluorenone Ketyls in the Range of 400–600 mμ

Metal	Peak	Solvent	Temp, deg	ν, mμ	Assignment
Na	A	MTHF	23	529	Ion pair and/or
		THF	23	532	triple ion
		DME	23	533	
	B	MTHF	−148	513	Paramagnetic
		THF	−141	516	ion quadruplet
		DME	23	517	
	C	MTHF	−148	490	Higher ion
		THF	−141	495	cluster
		DME	23	495	
	D	MTHF	−148	455	Diamagnetic ion
		THF	−141	460	cluster
		DME	23	465	
K	A	MTHF	23	535	Ion pair and
			−140	540	triple ion
	B	MTHF	23	520	Paramagnetic ion
			−140	525	quadruplet
	C	MTHF	23	500	Higher ion
			−140	∼500	cluster
	D	MTHF	23	458	Diamagnetic ion
			−140	466	cluster
Ca		DMF/MTHF	23	510	Paramagnetic triple ion
			23	455	Diamagnetic ion cluster
Sr		MTHF	23	∼510	Paramagnetic triple ion
			23	455	Diamagnetic ion cluster

Figure 7. Rigid media epr spectra of alkali metal fluorenone ketyls. Sodium fluorenone: (1) ∼10^{-2} M in MTHF, (2) ∼10^{-3} M in MTHF, (3) ∼5 × 10^{-5} M in MTHF, (4) ∼10^{-2} M in THF. Potassium fluorenone: (5) ∼10^{-2} M in MTHF, (6) ∼4 × 10^{-4} M in MTHF, (7) ∼8 × 10^{-5} M in MTHF.

becomes the main one in the cases of lithium, sodium, and potassium ketyls.

These observations indicate that there are at least four distinct ionic species of alkali metal fluorenone ketyls in ethereal solution and that their relative concentrations depend on the concentration, the cation, and the solvent. In addition to these absorptions, fluorenone ketyls show weak absorptions at 600–800 mμ.[11] The characteristics of these absorptions are summarized in the following.

(1) The transition energies (ΔE) of the long wavelength absorptions of different ketyls in different solvents are of the following order: $\Delta E_{Mg} > \Delta E_{Ca} > \Delta E_{Na} > \Delta E_{K} > \Delta E_{Cs}$ and $\Delta E_{MTHF} > \Delta E_{THF} > \Delta E_{DME} > \Delta E_{DMF}$.

(2) The relative intensities of the long wavelength absorptions are strongly dependent on the concentration and the solvent, particularly in alkali metal ketyls. They are very weak in the cesium and potassium ketyls in DME at 5 × 10^{-5} M but considerably stronger in the sodium and potassium ketyls in MTHF at 10^{-2} M. The alkaline earth metal ketyls in ethereal solutions, on the other hand, give relatively strong absorptions even at low concentrations.

(3) The intensities of these bands seem to correlate strongly with the intensities of the absorption at ∼460 mμ.

(B) Low-Temperature Epr Spectra. The low-temperature rigid media epr spectra of alkali metal fluorenone ketyls were investigated in the various solvents at different concentrations. The cases of sodium and potassium fluorenone ketyls are shown in Figure 7. In both systems epr spectra consist of central peaks and those characteristic of biradicals. In both systems biradical spectra with large fine structure splittings were obtained at high concentration, but upon dilution these

spectra were replaced by the other biradical spectra with smaller splittings. The spectra obtained at higher concentrations are the same as those reported by Hirota and Weissman, which were assigned to ion quadruplets.[4] The central peaks obtained in the low-concentration solutions are due to ion pairs, but those obtained in the high-concentration solutions cannot come from ion pairs. They are most likely due to higher aggregates. The fine structure splittings (defined as shown in Figure 7-1) determined from the low-temperature epr spectra are given in Table III. The following is a summary of the observations.

(1) In most ethereal solvents there are at least two biradical species at low temperatures. At low concentration the species with small splitting (∼40 G) is the dominant one, but at higher concentration, the species with large splittings (80–130 G) becomes the dominant one. The species with intermediate splittings (70 G) appeared in some systems, but usually these peaks are very minor. In the polycrystalline samples, the spectra with large splittings were often split into two or more components with slightly different splittings.

(2) There is considerable solvent dependence on the splittings as shown in Table III.

(3) The fine structure splittings of the species existing at high concentration decrease with the size of the cation as was noted in the previous work.[4,8]

(4) At the same concentration, relative concentrations of the species with small splittings are higher in the cases of the ketyls with large cations and in the solvents of stronger solvating power.

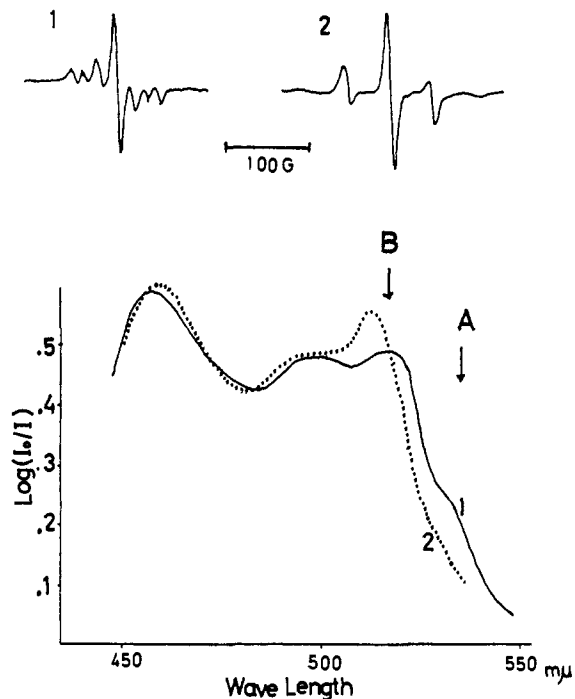(5) In the concentrated solutions (>10^{-2} M) the relative intensity of the central peak with respect to the

Figure 8. Effect of the addition of $Na^+BPh_4^-$ on the rigid media epr spectra and the visible absorption spectra of sodium fluorenone. Top figures, rigid media epr spectra of sodium fluorenone in MTHF at $\sim 5 \times 10^{-5}$ M: (1) before addition of $Na^+BPh_4^-$, (2) after addition of $\sim 10^{-3}$ M $Na^+BPh_4^-$. Bottom figure, optical spectra of the same solution as above: (1) before addition of $Na^+BPh_4^-$, (2) after addition of $Na^+BPh_4^-$.

Table III. Summary of the Fine Structure Splittings of the Rigid Media Epr Spectra of Fluorenone Ketyls

Metal	Solvent	State[a]	Fine structure splitting, G[b]	Comment
Li	Dioxane	P.C.	135.3	
			125.6	
	MTHF	G	126.1	No other peak observed
	THF	P.C.	128.7	Main
			86.5	Very weak
			39.7	Very weak
	DME	P.C.	141	
			127	
			118	
			90.5	
	DMF	P.C.	134.2	
Na	MTHF	G	103	Main at $>10^{-4}$ M
			75	
			42	Strong at $<10^{-5}$ M
	THF	P.C.	118	Main at $>10^{-3}$ M
			45	Main at $\sim 10^{-4}$ M
	DME	P.C.	110	
	DMF	P.C.	111.9	
			94	
K	MTHF	G	91.5	Main at $>10^{-3}$ M
			40.7	Main at $<10^{-5}$ M
	THF	P.C.	110.8	
			98.1	
			82.9	
			40	Main at $<10^{-4}$ M
	DME	P.C.	107.3	
			77.8	
	DMTHF	G	96.6	Main at 10^{-3} M
			77.8	
			47.8	
Ca	MTHF/DMF	G	100–80	
Sr	MTHF	G	45	

[a] G stands for glass; P.C. stands for polycrystals. [b] Fine structure splittings determined here are S ($1/2$ of the separations between two outside peaks) defined by 1 in Figure 7. This value is slightly larger than true value of D.

biradical peaks increases with concentration indicating that the species responsible for the central peaks in the concentrated solutions are higher aggregates.

Some more specific observations concerning the individual systems are given below.

Lithium Fluorenone. In MTHF only the species with large splitting was detected even at very low concentration (5 × 10⁻⁵ M). Generally, speaking, the spectra due to the species with small splittings are very weak.
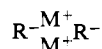
Sodium Fluorenone. In MTHF and THF concentration dependence of the rigid media epr spectra was observed very clearly as shown in Figure 7. The species with small splittings become dominant at only very low concentrations ($\sim 10^{-5}$ M).

Potassium Fluorenone. In both MTHF and THF, changes from the spectra with large splittings to those with small splittings were clearly observed upon dilution. In MTHF only the spectrum with small splittings was obtained at $\sim 5 \times 10^{-5}$ M.

We now consider the possible interpretations of the above observations.

(a) Species with different fine structure splittings correspond to the structurally different ion quadruplets, such as contact- and solvent-shared structures.

(b) The species with a small splitting is a triple ion, $R^-M^+R^-$, and the one with a large splitting is an ion quadruplet

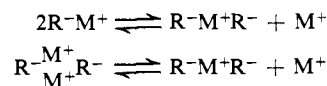$$R^-\overset{M^+}{\underset{M^+}{}}R^-$$

Since the relative concentrations of these two species are strongly concentration dependent, possibility "a"

seems to be unlikely. The triple ion can be formed by the following processes.

$$2R^-M^+ \rightleftarrows R^-M^+R^- + M^+$$

$$R^-\overset{M^+}{\underset{M^+}{}}R^- \rightleftarrows R^-M^+R^- + M^+$$

Hence, it is expected that the concentration of the triple ion with respect to that of the ion quadruplet strongly depends on the concentration of M^+, if the second possibility is correct. We have investigated the effect of the addition of $Na^+BPh_4^-$ on the epr and visible spectra of sodium fluorenone ketyl in MTHF. As shown in Figure 8, the biradical spectrum with a small splitting disappears upon the addition of a very small amount of $Na^+BPh_4^-$. This observation seems to be strongly in favor of the second possibility. Process (b) is the dissociation of a cation from an ion quadruplet. It is known that the dissociation of triple ions $R^-M^+_2$ into ion pairs and cations takes place at a low temperature.[21] Thus it does not seem unreasonable that the dissociation of the ion quadruplet into the triple ion takes place at low temperatures, and this process is more important in the solvents of stronger solvating power.

(C) Correspondence between the Optical and Epr Spectra. Assignment of the Optical Absorptions. The

(21) K. S. Chen and N. Hirota, *J. Amer. Chem. Soc.*, **94**, 5550 (1972).

ion pair, $R_2C-O^-M^+$ has an absorption band in the A region (530–540 mμ). The rigid media epr spectra of $\sim10^{-5}$ M of sodium fluorenone and $\sim10^{-4}$ M of potassium fluorenone in MTHF at 120°K indicate that the major species in solution is the triple ion rather than the ion pair. The absorption spectra under similar conditions show that the main absorption peaks are in the A region. Thus it is concluded that both the triple ion and ion pairs have absorption peaks in the same region. This is reasonable since an anion is associated with a cation in both cases. The absorption peak in the A region often shows further structures at low temperature as shown in Figure 6. This could be due to differences of the absorption peaks of the ion pair and the triple ion, although the structurally different ion pairs can give rise to slightly different absorptions.

As the concentration of the solution increases the relative intensity of the A peak decreases and the intensities of the peaks in the B and C region increase. The comparison between the optical and rigid media epr spectra indicates that the peak B is most likely due to the ion quadruplet with large fine structure splittings.

The addition of M^+ to the solution reduced the peak intensity in the A region and enhances the intensity in the B region as shown in Figure 8. The assignment that the triple ion has an absorption in the A region and the ion quadruplet has one in the B region is, therefore, consistent with this observation. It was shown that the biradicals with divalent metal ketyls have an absorption also in the B region (~510 mμ). Perturbations due to cations in ion quadruplets and ketyls with divalent cations are similar and both systems have absorptions in the same regions. The absorptions in the C and D regions are likely due to ion clusters higher than quadruplets. In the solutions of poor solvating solvents such as diethyl ether, the major absorption peak is in the D region. In such systems the total paramagnetism is much lower than expected from the radical concentration. Hence ion clusters having absorptions in the D region are assigned to be diamagnetic. These diamagnetic ion clusters are, however, entirely different from covalently bonded species such as pinacolates discussed in the previous work.[4]

The changes in the visible spectra on going from the paramagnetic clusters to the diamagnetic clusters are characterized by the shifts of the ~510-mμ peak by ~50 mμ and the enhanced absorptions at long wavelength, 600–800 mμ. The shifts of absorptions and the appearance of the long wavelength absorptions have been found in a number of cases associated with the formation of radical dimers.[22-26] The above described changes in the visible spectra of ketyls somewhat resemble the cases of the formation of radical dimers. It is thus tempting to ascribe the observed changes to the formation of radical anion dimers in which two unpaired electrons become paired to form the singlet state. However, the ~460-mμ absorption peaks of the diamagnetic clusters are only ~20 mμ away from those of the monomeric dinegative ions. Thus the possibility that the ~460-mμ peaks and the

(22) K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1959).
(23) R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965).
(24) M. Itoh and S. Nagakura, *J. Amer. Chem. Soc.*, **89**, 3959 (1967).
(25) M. Kimura, H. Yamada, and H. Tsubomura, *J. Chem. Phys.*, **48**, 440 (1968).
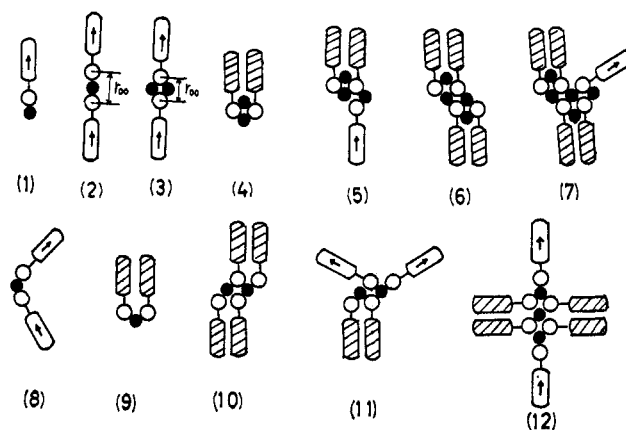(26) E. M. Kosower and M. Itoh, *J. Amer. Chem. Soc.*, **90**, 1843 (1968).

Figure 9. Possible structures of ionic species of ketyls: (1) ion pair, (2) triple ion, (3) paramagnetic ion quadruplet, (4) diamagnetic ion quadruplet (radical anion dimer), (5-7) are some of the possible structures of higher ion clusters of alkali metal ketyls, (8) triple ion, (9) diamagnetic triple ion radical anion dimer, (10-12) some of the possible structures of higher ion clusters of alkaline earth metal ketyls. (●) Indicates cation, (○) indicates an oxygen atom, (–○) indicates the ring part of the fluorenone anion, (○–⊖) represents the paramagnetic anion, (○–▨) represents the diamagnetic species.

absorptions at long wavelength are due to dinegative ions produced by disproportionation of mononegative ions in ion clusters cannot be excluded on the basis of the present data. Further studies are needed to clarify the exact natures of the diamagnetic clusters.

In the previous paper[4] thermodynamic quantities for the ion pair–ion quadruplet equilibria were estimated from the visible spectra. Because of the revisions made on the assignments of the absorption peaks, numerical values of the thermodynamic quantities given there are not correct. However, small dissociation constants ($\sim10^{-5}$ M) and large negative entropies for dissociation of the ion quadruplets are believed to be correct, and the qualitative discussions made on the thermodynamic quantities are considered to be still valid.

(III) Structures of Ionic Species of Ketyls. We now consider the structures of ionic species of ketyls which can explain all the observations described in sections I and II consistently. The possible ionic structures suggested are given in Figure 9.

(A) Basis of Analysis of Rigid Media Epr Spectra. The rigid media epr spectra of biradical species are characterized by a well known spin Hamiltonian.[4,12]

$$\mathcal{H} = \beta H \cdot gS + DS_z^2 + E(S_x^2 - S_y^2) \quad (5)$$

In the cases of biradicals formed from ion pairs, E is normally small and D is approximated as[8]

$$D \simeq -\frac{3}{4}g^2\beta^2\sum_i\sum_j \rho_{ai}\rho_{bj}\left\langle\frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5}\right\rangle_{ij} \quad (6)$$

where ρ_{ai} and ρ_{bj} are the spin densities in the $2p\pi$ orbitals of the i and j carbon atoms of the a and b molecules. r_{12} is the distance between two electrons and z_{12} is its z component.

(B) Solvent Effect and Solvation of the Ion Quadruplet. The contact structure of the ion quadruplet was suggested previously for the biradical species with large dipole interactions.[4] The data given in Table III show, however, that D for the same cation varies slightly de-

pending on the solvent. The structures of ion quadruplets are considered to be contact, but the cations are presumably solvated in the open space and the anion–anion distances are slightly dependent on solvation.

In order to confirm the existence of solvation in the ion quadruplet, we studied the epr spectra of lithium fluorenone in the mixtures of DMF and MTHF. It is known that DMF preferably solvates cations in the mixtures of DMF and ethereal solvents.[27] In MTHF, lithium fluorenone gives the spectrum with the splitting of 126 G. In pure DMF, lithium fluorenone gives the spectrum of 134-G splitting. When the mole percent of DMF in MTHF is less than 3%, we observed the superposition of the two spectra, one with the splitting of 126 G and the other with the 134-G separation. When DMF is more than 5%, the spectrum always gives the spectrum observed in pure DMF. At 0.6 and 1.2 mol % of DMF, the intensity ratios of the DMF type spectrum to the MTHF type are 2 and 3.3, respectively. At slightly higher temperatures, the two split peaks emerge into one at the averaged position. These observations clearly show that selective solvation of cations by DMF in ion quadruplets takes place at the low fraction of DMF as in the case of monomer ion pairs studied in our laboratory.[27]

(C) *D* Values and Structures of Biradicals. In the previous paper[8] we have estimated *D* of several ketyls based on the assumed structures. Since the spin distributions in ketyls are better known now, we made calculations of *D* of various biradical species. The calculations were made in the following way.

(1) Spin distributions in the triple ion, the ion quadruplet, and the divalent ketyls were estimated from those of ion pairs and divalent metal ketyls given in this paper and the previous one.[14] (2) For the spin densities in the phenyl ring point spin densities were assumed at the carbon atoms. (3) For the spin densities on the carbonyl group, one-half of the spin density is placed at 0.83 Å above and below the molecular plane according to the position of the maximum spin density of the $2p\pi$ Slater orbital. (4) C–O distance was taken as 1.2 Å and the radius of oxygen was assumed to be 1.4 Å. The radii of Ca^{2+} and Na^+ were assumed to be 0.99 and 0.95 Å, respectively.

(a) Triple Ion. (i) Alkali Metal Ketyls. The *D* value was calculated to be 40 G for sodium fluorenone. This value is in good agreement with the observed values for biradicals with small splittings. In general, the observed *D* for the triple ions seems to be reasonably well explained by the structure given in Figure 9.

(ii) Alkaline Earth Metal Ketyls. The *D* calculated is 35 and 55 G for $r_{OO} = 4.8$ and 4.0 Å, respectively. The observed value for strontium fluorenone in MTHF, is 40 G in agreement with the calculated one. However, the observed *D* of calcium fluorenone in the MTHF–DMF mixture is 80–95 G. This value seems to be too large to be explained by the simple triple ion structure. One possible explanation for the relatively large *D* is to assume a bent structure in which two anions are close to each other (8 in Figure 9). Biradicals of divalent metal ketyls may take bent structures because of solvation or the species having large *D* may be a higher aggregate such as shown by structure 11 in Figure 9.

(b) Ion Quadruplets. Since the distance between two oxygens can be different slightly, exact comparisons between the observed and the estimated ones cannot be made. We obtain $D = 80–100$ G by taking r_{OO} to be 3–4 Å. These values are in good agreement with the observed values. In general, *D* obtained for the ion quadruplets appears to be reasonable for structure 3 in Figure 9.

(IV) Structures of Diamagnetic Ion Clusters. The simplest form of diamagnetic clusters of alkali metal ketyls is the closed form ion quadruplet shown by 4 in Figure 9. The 460-mμ peak and the bands at 650 mμ are fairly strong in the sodium fluorenone ketyls even at 10^{-4} *M* in MTHF. At this low concentration it seems rather unlikely that the ion clusters higher than quadruplets exist to a very large extent. Thus, the closed form diamagnetic ion quadruplet (4 in Figure 9) may exist in equilibrium with the open form biradical quadruplet.

The possible structures of ionic species to account for the observations made for ketyls of divalent cations are schematically given in Figure 9. Structures 8 and 11 can give rise to the biradical epr spectra, while 9, 10, and 11 can contain diamagnetic ion clusters. The structure, such as 12, can give well resolved solution epr spectra with relatively long rotational correlation times.

Some possible structures of higher ion clusters of alkali metal ketyls are schematically given by the structures 5 to 7. The structures 5 and 7 can give well resolved hyperfine splittings in solution.

(V) Structures of the Other Related Ketyls. The structures and equilibrium schemes discussed here are considered to be generally applicable to other ketyls, possibly with slight modifications. We here reinterpret the epr spectra of some other ketyls based on the present model.

Aliphatic ketyls such as sodium hexamethylacetone and pentamethylacetone show alkali metal splittings due to two cations.[28] An ion quadruplet structure

$$R-\overset{M^+}{\underset{M^+}{}}R^-$$
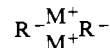
was originally suggested to account for this observation, but the narrow line widths of the solution spectra indicate that they cannot be contact ion quadruplets. Solvent-separated ion quadruplet structures were previously suggested for these species,[8] but in view of the results presented in this paper, it seems more likely that these ketyls exist as higher ion clusters such as structures 5 and 7 in Figure 9. Similarly, the splittings due to two alkali metal ions found in lithium benzophenone in THF[29] and sodium benzophenone in MTHF[30] are likely due to higher ion clusters, rather than triple ions or ion quadruplets suggested in the original papers.[31]

Well resolved solution epr spectra have been reported for other divalent metal ketyls such as phenanthrenequinone[32] and acenaphthenequinone.[18] We think that

(27) K. S. Chen, S. W. Mao, K. Nakamura, and N. Hirota, *J. Amer. Chem. Soc.*, 93, 6004 (1971).

(28) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, 82, 4424 (1960).
(29) A. H. Reddoch, *J. Chem. Phys.*, 43, 3411 (1965).
(30) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, 86, 2537 (1964).
(31) In these ketyls the exchange rates between the cations associated with the anions and those in solution are very slow. (The second-order rate constant is smaller than 10^5 M^{-1} sec^{-1}.) This observation is in contradiction with the triple ion structure, since cation exchange in the triple ion is considered to be fast.
(32) K. Maruyama, *Bull. Chem. Soc. Jap.*, 37, 553 (1964).

Table IV. Zero Field Splittings of Biradical Ion Clusters of Radical Ions Containing Heteroatoms

Anion	Cation	Solvent	Fine structure splitting, G
Quinoxaline	Li	MTHF	79.3
Terephthalonitrile	Li	MTHF	47.8
4-Chloronitrobenzene	Li	MTHF	111.9
Anthraquinone	Li	THF	20

the solution epr spectra of these species are due to higher ion clusters rather than solvent-separated triple ion biradicals.

(VI) Paramagnetic Ion Quadruplets in Other Systems. The various forms of paramagnetic and diamagnetic ion clusters such as discussed here are likely to exist commonly in the solutions of other radical ions containing heteroatoms. In order to establish the general existence of paramagnetic ion clusters in other types of systems, we have investigated the rigid media epr spectra of MTHF solutions of the radical anions of quinoxaline, terephthalonitrile, 4-chloronitrobenzene,[33] and anthraquinone. These systems gave relatively strong rigid media epr spectra at 10^{-3} in MTHF. Fine structure splittings of these systems are given in
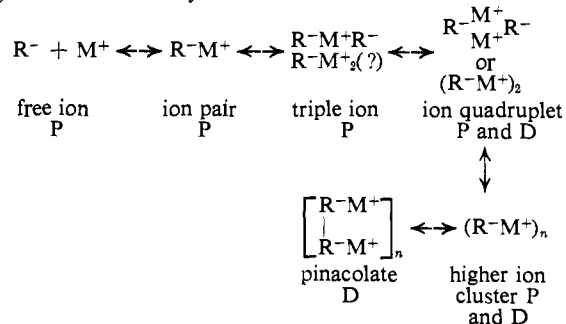
(33) A paramagnetic ion cluster of the nitrobenzene anion was reported by C. A. McDowell and F. Nakano, *J. Phys. Chem.*, 75, 1205 (1971).

Table IV. Various forms of ionic species such as discussed in this paper may exist in these solutions.
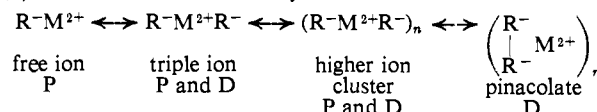
Conclusions and Summary

The equilibrium scheme for ketyls is summarized as follows.

(a) Alkali metal ketyls

(b) Alkaline earth metal ketyls

P and D stand for paramagnetic and diamagnetic species.

Studies of Membrane Processes. IV. Structure of the Acetate Ion and Degree of Orientation of the Ionic Head Groups in the Electrical Double Layer[1]

D. M. Chen,[2a] L. W. Reeves,*[2a,b] A. S. Tracey,[2c] and M. M. Tracey[2c]

Contribution from the Instituto de Química, Universidade de São Paulo, São Paulo, Brazil, and the Chemistry Department, University of Waterloo, Waterloo, Ontario, Canada. Received November 15, 1973

Abstract: A model membrane based on the cationic detergent decylammonium chloride has been prepared and studied. Nematic middle soap phases of this detergent have been used to homogeneously orient the acetate ion and simultaneously the lipophilic region of the model system. The structure of the acetate ion has been determined, apart from the oxygen positions, by studying nuclear magnetic resonance spectra of oriented 1-^{13}C and 2-^{13}C acetate. In other experiments the acetate and perdeuterioacetate ions have been oriented in the same phase, and by studying both the proton and deuterium magnetic resonance spectra the deuterium nuclear quadrupole coupling constant in the acetate ion has been determined. Similar nematic middle soap phases have been prepared from the 1,1,-1,2,2-pentadeuterated decylammonium detergent. The deuterium magnetic resonance spectra are composed of three doublets arising from first-order quadrupolar interactions at the terminal $-ND_3^+$, adjacent $-CD_2-$, and D_2O nuclei. The variation of the partially averaged quadrupole splitting in these ionic and methylene head groups of the membrane electrical double layer have been measured as a function of temperature. Very large temperature dependence of the local microdegree of orientation is indicated over small temperature ranges between 24.5 and 33.5°. A consideration of degrees of order of small ionic and molecular species, which reside mostly in the aqueous region of the phase, and those of the head groups in the electrical double layer has shown that movement of the head groups is considerably restricted. A clearer picture of this membrane model has emerged from studies of deuterium magnetic resonance spectra and these in turn have indicated that further studies of specifically deuterated lipophilic components in these phases are required.

The oriented superstructures of the middle soap nematic phases consist of cylindrical arrangements

of the ionic head groups of detergent ions. The in-