pentamethylbenzene all show a substantial (positive) MCD while the very closely related, but more symmetrical benzene, *sym*-mesitylene and hexaethylbenzene have a very much smaller MCD. A possible partial explanation of this finding comes from an examination of the C_{2v}, D_{2h}, D_{3h}, and D_{6h} point groups. In the first two groups, to which the compounds showing MCD belong, the electric dipole transition moments to the B_{1u} and B_{2u} states are not symmetry forbidden and their vector cross products are parallel to the symmetry-permitted magnetic dipole transition moment between these states. Thus, the theoretical requirements for the existence of a "B term" MCD[6] are not symmetry forbidden. On the other hand, in the D_{6h} and D_{3h} groups the electric dipole transitions are all symmetry forbidden, and therefore the MCD should be symmetry forbidden. While this argument is suggestive, it is quite clear that the difference in the MCD of these two groups of compounds is more than just the result of their having either symmetry-permitted or symmetry-forbidden MCD's since the molar absorptivities of both the symmetry-permitted and -forbidden transitions are similar in magnitude. Furthermore, there is at least one exception known: hexachlorobenzene (negative MCD). This molecule is in point group D_{3d}[9] and, therefore, has one permitted magnetic and one permitted electric transition moment perpendicular to the ring; *i.e.*, the MCD is symmetry forbidden.

[9] O. Schepp and R. Kopelman, *J. Chem. Phys.*, 30, 868 (1959).

Electron Paramagnetic Resonance Studies of Ion Pairs. Metal Ketyls[1]

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Abstract: The temperature dependence of the alkali metal and C^{13} hyperfine splittings of the epr spectra of fluorenone monomer ketyls is reported. The mechanism to produce such temperature dependence is discussed in terms of rapid ion-pair equilibria among structurally different ion pairs. Rigid media and low-temperature epr spectra of various aliphatic and aromatic ketyls are presented. The observed spectra are explained by the presence of contact and solvent-shared ion quadruplets. The zero-field parameters in aliphatic ketyls are estimated from the contact ion quadruplet structures and compared with the observed values. The equilibrium processes involving ketyl radicals are modified including the possibility of the presence of contact and solvent-shared structures. The factors which affect such equilibria are also discussed.

In the previous epr and optical studies,[2] the presence of the monomer–dimer[3] equilibrium in the ion pairs of ketyls was demonstrated. The detailed natures of the structures of these ion pairs, however, remained to be investigated more thoroughly. In the present paper we report the epr evidences for the presence of structurally different ion pairs[4] in monomer and dimer ketyls, respectively, and discuss their structures.

Temperature dependence of the alkali metal splittings in ketyls is now well known.[5] The mechanism of the temperature dependence, however, is not fully established. We have investigated temperature dependence of both C^{13} and metal splittings in monomer ketyls in the hope of clarifying the mechanism of the temperature dependence. A decrease in the magnitude of both C^{13} and metal splittings at lower temperatures seems to indicate that the average separation between positive and negative ions increase at lower temperatures. This is explained in terms of rapid equilibrium among different ion pairs.

Rigid media epr spectra of many ketyl ion quadruplets were previously found[2] to be characterized by a spin Hamiltonian.

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

The magnitude of D, however, varies very much from one system to another (D/hc varies from 0.01 cm^{-1} to less than 0.001 cm^{-1}). Such a large difference seems to indicate that they may have quite different structures. Although the ion quadruplets with large dipole interaction can only show broad solution spectra, some ion quadruplets showed very narrow solution spectra at room temperature. Such narrow spectra are compatible only with the species of small dipole interaction. From these observations it is speculated that in many ion quadruplets two negative ions may be separated from each other by solvent molecules giving small magnitude of dipole interaction.

Accordingly, we have investigated epr spectra of various ketyls from 77 to 300°K in order to answer the question of the structures of ion quadruplets. Our results show the presence of both contact and solvent-shared species and the equilibria among them in most systems.

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[1] This research is partially supported by a grant from the National Science Foundation (GP-5040).

[2] N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2538 (1964).

[3] Throughout the present paper the word "ion quadruplet" is used to describe the paramagnetic species which was designated as paramagnetic dimer in the previous paper. This species should be clearly distinguished from the diamagnetic dimer, such as pinacolate.

[4] Evidences for the presence of structurally different ion pairs in hydrocarbon negative ions by optical spectra and conductivity measurements were given recently by T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307, 318 (1966).

[5] (a) N. Hirota and S. I. Weissman, *ibid.*, **86**, 2537 (1964); (b) P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, 5412 (1963).

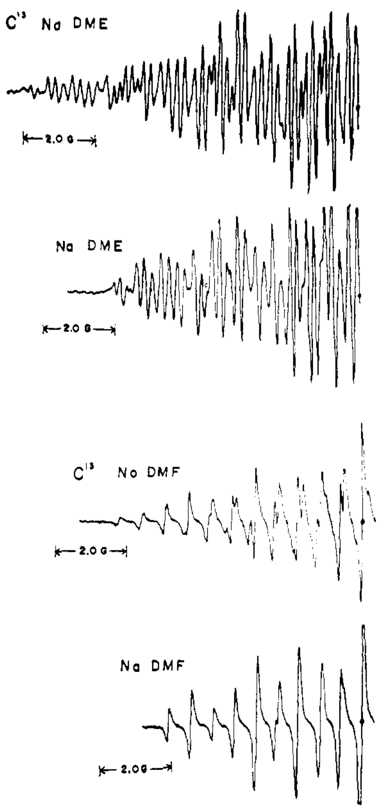

Figure 1. Epr spectra of sodium fluorenone ketyls (from top to bottom): 57% C^{13} fluorenone sodium in DME at 25°; sodium fluorenone in DME at 25°; 57% C^{13} fluorenone in DMF at 25°; sodium fluorenone in DMF at 25°.

Experimental Section

Various ketyls were prepared by the reduction of ketones with alkali and alkaline earth metals following the standard procedures already described elsewhere[2] except divalent metal aliphatic ketyls such as magnesium hexamethylacetone. These ketyls were prepared by the exchange reactions, such as

$$(R_2\dot{C}O)_2(Na^+)_2 + MgCl_2 \rightleftharpoons (R_2\dot{C}O)_2Mg^{2+} + 2NaCl$$

All reactions were carried out in a sealed-off glass apparatus which included a cell for epr measurement. All epr measurements were made with a Varian 4502 spectrometer with a "field dial" using 100-kc field modulation. Low-temperature experiments were made using a Varian variable-temperature control unit. The temperature reading was found to be accurate within ±3°. At 77°K sample tubes were placed in the tip of a quartz dewar which was inserted into a resonant cavity.

C^{13} hyperfine frequencies were determined by taking both C^{13} and C^{12} fluorenone spectra at the same temperature and measuring the difference between two spectra. At least two consistent runs were made for both C^{13} and C^{12} samples at each temperature (Figure 1). The averages of more than two measurements were given in the figures.

All hyperfine frequencies were calibrated using a Harvey-Wells proton gaussmeter and a Hewlett-Packard frequency counter. All chemicals except C^{13} fluorenone were obtained commercially. Approximately 57% enriched C^{13} fluorenone was given to the author by the courtesy of Professor S. I. Weissman of Washington University. Solvents used in the present research are 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), diethyl ether (DEE), and N,N-dimethylformamide (DMF).

Results and Discussions

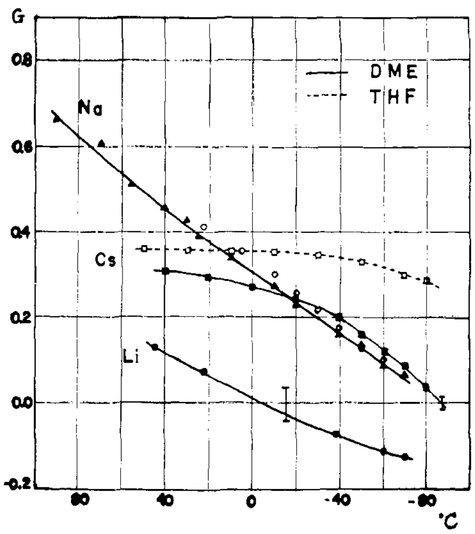

Figure 2. Temperature dependence of the alkali metal splittings: ●, lithium in THF; ▲, sodium in DME; ○, sodium in THF; ■, cesium in DME; □, cesium in THF. Uncertainties in the measurements of the splitting in the each point is not greater than 0.1 gauss.

A. Monomer Ketyls. 1. Temperature Dependence.

The temperature dependence of the metal splittings in many monomer ketyls is well known from the previous studies.[2,5] Except in some α-diketone ketyls,[6] metal splittings in ketyls generally decrease as temperature goes down. The temperature dependence of the alkali metal splittings in fluorenone ketyls are given in Figure 2. As discussed originally by Atherton and Weissman,[7] the observed metal splitting, a, at one temperature is given by the average over the splittings at different states in the limit of rapid average among different states.

$$a = \sum_i P_i a_i$$

Here a_i is the splitting in the ith state and P_i is the probability of finding the ith states. Although the exact mechanism to produce spin density at the positive ion is not fully established, two possible mechanisms have been proposed for the temperature dependence of alkali metal splittings.

(1) One is to assume that the positive ion vibrates around the most stable position. Since the magnitude of the alkali metal splitting depends on the relative position of the positive ion with respect to the negative ion, vibration of the positive ion would give rise to a temperature-dependent alkali metal splitting. Such an explanation was given to several cases.[7–9] In ketyls the positive ion probably sits next to the oxygen and lies on the nodal plane of its 2pπ orbital in the most stable structure.[10] At such a position we would expect a small metal splitting because of the minimum overlap integral between the ketyl 2pπ orbitals and the s orbitals of the metal ion. Any deviation from this

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(6) N. Hirota, unpublished observation.

(7) N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961).

(8) H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi, and H. Takaki, *Mol. Phys.*, **9**, 153 (1965).

(9) J. Santos-Veiga, *ibid.*, **9**, 395 (1965).

(10) McClelland calculated the most stable position for the positive ion in ketyls and found it somewhere between the oxygen and the carbon atoms of the carbonyl group. However, in his calculation the effects of solvation of solvent molecules to positive ion is neglected. We feel that the position mentioned in the text is more stable, if we take into account the effect of solvation, because this position allows the maximum solvation: B. J. McCelland, *Trans. Faraday Soc.*, **57**, 183, 1458, 2073 (1961).

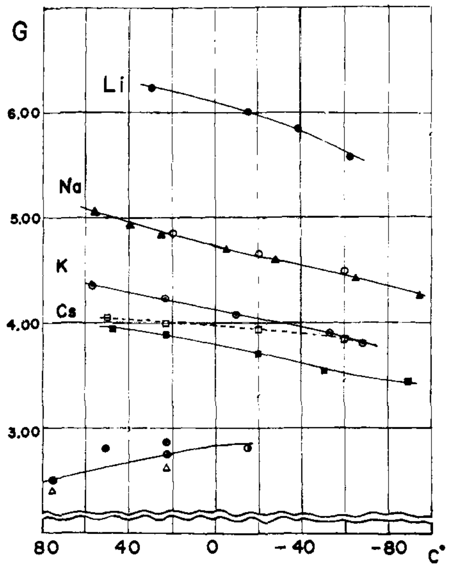

Figure 3. Temperature dependence of the C^{13} splitting of ketyls: ●, lithium fluorenone in DME; ▲, sodium fluorenone in DME; ○, sodium fluorenone in THF; ⊙, potassium fluorenone in DME; ■, cesium fluorenone in DME; □, cesium fluorenone in THF; △, ◑, ⊕, sodium fluorenone in DMF. Uncertainties in the measurements of the splitting are not greater than 0.03 gauss.

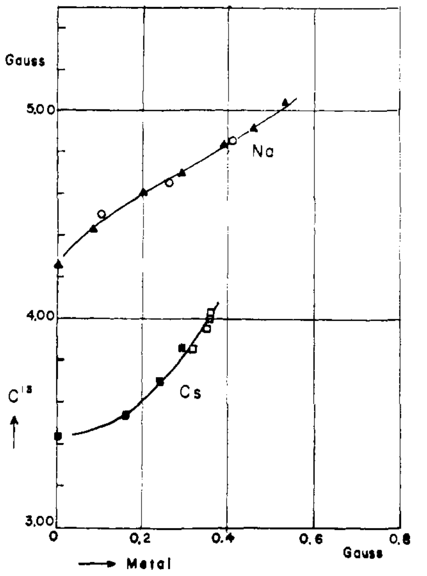

Figure 4. Correlation diagram between C^{13} splitting and alkali metal splitting in fluorenone ketyls: ▲, sodium in DME; ○, sodium in THF; ■, cesium in DME.

position at higher temperature would produce a larger splitting.

(2) The alternative explanation is to consider a rapid equilibrium among structurally different ion pairs. A decrease of the metal splittings at lower temperatures is explained by assuming the larger average separation of the positive and the negative ions at lower temperatures. This explanation was found to be very satisfactory in interpreting the line-width variations of epr spectra of many hydrocarbon negative ions.[11] In many hydrocarbon negative ion systems, the ion pair changes its structure from a tight ion pair with less solvation to a looser ion pair with more solvation at lower temperatures. It should be noted that recent investigations on the conductivities and the visible spectra of ether solutions of hydrocarbon negative ions support the latter explanation.[4]

Since both mechanisms can be responsible for the temperature dependence of the metal splittings, we investigated the temperature dependence of the C^{13} splittings of fluorenone ketyls as well as the metal splittings in order to decide which of the above two mechanisms is the main mechanism. Previous studies[12] of the dependence of the C^{13} splittings on the nature of the metal ions involved gave an empirical correlation between the magnitude of the C^{13} splitting and the electrostatic interaction between the positive and the negative ions. The correlation is at least qualitatively explained in terms of a valence-bond picture or an MO treatment taking into account the effect of the electrostatic interactions between ions.[13] A stronger electrostatic interaction between the positive and the negative ions places more charge and less spin density on the oxygen atom. From Karplus and Fraenkel's formula for C^{13} splitting[12,14]

$$a^{C^{13}} = (S^{C} + 2Q_{CC'}{}^{C} + Q_{CO}{}^{C})\rho_{C}{}^{\pi} + 2Q_{C'C}{}^{C}\rho_{C'}{}^{\pi} + Q_{OC}{}^{C}\rho_{O}{}^{\pi}$$

we can explain the empirical correlation between the C^{13} splittings and the electrostatic interaction. Therefore, if the ion pair changes the structure from a less solvated structure to a more solvated structure and if the average separation between the positive and the negative ion actually increases at lower temperature, the C^{13} splittings in ketyls are expected to decrease considerably at lower temperatures. On the other hand, if mechanism 1 is the main one, no large temperature dependence of the C^{13} splitting is expected. The temperature dependence of the C^{13} splittings in fluorenone ketyls is given in Figure 3.[15] The correlation between the C^{13} splittings and the alkali metal splittings is given in the Figure 4.

The temperature dependence of the cesium and the C^{13} splitting in DME and THF is specially noteworthy. In DME both cesium and C^{13} splittings markedly decrease at lower temperatures, but both splittings decrease very slightly in THF. If mechanism 1 is the main mechanism, it is difficult to understand such a large difference in two solvents, because the vibration of the cesium ion with respect to the ketyl ion is expected not to change drastically in these two solvents. On the other hand, the solvation power of THF and DME toward cesium ion is known[16,17] to be different, and it is quite conceivable that the structures of the ion pairs in these two solvents are considerably different, particularly at low temperatures. Based on these observations we think that mechanism 2 is the major one for the temperature dependence of the alkali metal splitting.

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(11) N. Hirota and R. Kreilick, *J. Am. Chem. Soc.*, **88**, 614 (1966).

(12) N. Hirota, *J. Chem. Phys.*, **37**, 1881 (1962).

(13) N. Hirota, Thesis, Washington University, 1963.

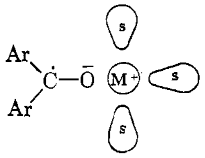
(14) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1962).

(15) Small temperature dependence of hyperfine splittings in free radicals was reported by Das and Fraenkel. However, the magnitude of the dependence reported here is much larger than those reported by them: M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 793 (1965).

(16) N. Hirota, paper presented at the American Chemical Society Summer Esr Symposium, East Lansing, Mich., Aug 1966, to be published.

(17) C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965).

Although the exact structure of the ion pair is still a matter for speculation, we suggest a model which could explain the increased average separation between ions at lower temperatures. We consider a model of the possible ion-pair structures based on our epr observations on ketyls and hydrocarbon negative ions. In this model the ketyl ion is considered to be another molecule in the solvation sphere and competing with solvent molecules in solvating to the positive ion. Some of the possible structures are **1**–**4**. Structure **1** is a contact ion pair and **4** is a solvent-separated ion pair. **2** and **3** may be considered to be intermediates between contact and solvent-separated ion pairs. It is known that the more dissociation of the ion pair or the change from the less solvated ion pair to the more solvated ion pair takes place at lower temperatures in many systems. Generally negative, $\Delta H°$ and $\Delta S°$ are known for such processes.[4,7] The evidence for the presence of the rapid equilibria among structurally different ion pairs has been shown in several systems.[16] We may expect that such equilibria are taking place in the present ketyl systems. Obviously the degree of solvation increases in going from the ion pair **1** to **2** or **3**. In the limit of rapid equilibrium among structurally different ion pairs, the observed metal and C^{13} splittings are given by the average over all possible structures. The line widths of four sodium hyperfine lines in sodium anthracene were found to depend on the magnetic quantum number of sodium.[11] Interconversion rates between two distinct ion pairs were found to be 10^8 sec^{-1} at $-55°$ in MTHF. In all ketyls so far studied, four sodium hyperfine lines were found to have the same line width over the temperature range from 50 to $-90°$. Therefore, if such equilibria among different ion pairs are taking place, the interconversion rates must be greater than $\sim 10^8$ sec^{-1} from the known formula for the exchange narrowing. The change from ion pair **1** to ion pair **2** and **3** requires only slight displacement of the ketyl ion from the first solvation sphere. Such a change does not require a large rearrangement of the solvation sphere, and the rates of interconversion among such different ion pairs may be very fast.



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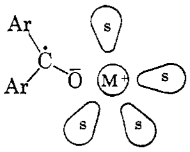

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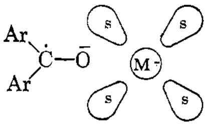

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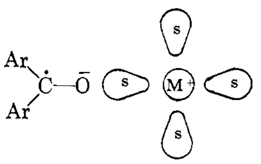

4

Although the model presented here seems to explain the observation, this is only a suggestion and further studies will be made in order to test the validity of the model.

Closer inspections of Figures 2 and 3 reveal several interesting features. Some of them are described here.

(1) At room temperature metal dependence of the C^{13} splitting is very large. This probably indicates that the ion pair is close to a contact ion pair at higher temperatures, because C^{13} splittings are expected not to depend so much on the nature of the metal ion in the solvent-separated ion pair.

(2) Although the metal splittings (Na, K, Cs in DME and Na, K in THF) disappear at about $-80°$, the C^{13} splittings clearly indicate the presence of considerably large perturbation due to the positive ions. At the lowest obtainable temperature in these solutions, ketyls exist as ion pairs, not as dissociated ions. At $-80°$ the metal ion dependence of the C^{13} splitting is still large. In the ion pairs of small ions the average separation between counterions at low temperature seems to be still shorter than expected from the solvent-separated ion pair, such as **4**.

(3) Lithium splitting seems to change the sign from positive to negative. Sodium splittings in DME and THF and cesium splittings in DME may also go negative, but it was not possible to go to further lower temperatures to confirm this. The significance of this observation is discussed in the following section.

(4) DME and THF behave in the same way for Na but quite differently for Cs as mentioned earlier. The solvation power of THF toward larger positive ions is known to be weaker than that of DME.[16,17]

(5) In DMF the C^{13} splittings increased slightly at lower temperatures. No metal splittings were observed in these solutions. The C^{13} splittings, however, were found to vary slightly depending on the temperature and the length of time after preparation. These observations seem to indicate that there exists still some weak interaction between positive and negative ions in DMF solution.

2. Origin of the Alkali Metal Splittings. Although we do not intend to discuss the origin of the alkali metal splittings in detail, some remarks concerning this problem can be made based on our observation.

Several different mechanisms to describe the origin of the spin density at the metal nucleus have been proposed by several authors.[7,18,19] The mechanism to produce positive spin density at the metal ion was discussed in terms of nonorthogonality of the molecular orbital or charge-transfer mechanism.

In the former mechanism the overlap integral, $\langle ns|m + 1\rangle$[7,18] between singly occupied molecular orbital of the negative ion and s orbitals of the metal ion determines the magnitude of the splitting. In the latter mechanism the magnitude also depends on the electron affinity of the organic molecule and the ionization potential of the alkali metal as well as $\langle ns|m + 1\rangle$. In ketyls and in several hydrocarbon negative ions, the spin density at the metal nucleus was generally found to be much larger for Na than for Cs despite the fact that cesium ion pair can form a contact ion pair more easily. These observations seem to suggest that the determining factor is not simply the overlap integral, but more systematic investigations are necessary to answer this question definitely.

Recently de Boer suggested that there are two different mechanisms to produce metal splittings:[19] one mechanism leads to positive spin density at the metal nucleus and the other leads to negative spin density. He discussed the mechanism to produce negative spin density at the metal nucleus in terms of configuration

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(18) S. Aono and K. Oohashi, *Progr. Theoret. Phys.* (Kyoto), 30, 1330 (1963).

(19) E. de Boer, *Rec. Trav. Chim.*, 84, 609 (1965).

interaction involving an excitation of the $(n - 1)$s orbital of the metal ion to the ns orbital. He pointed out that lithium splitting through this mechanism should be negative. The temperature dependence of the lithium splitting in fluorenone, in fact, seems to support de Boer's suggestion that there are two different contributions to produce metal splitting. Lithium splitting in fluorenone ketyl seems to change the sign from positive to negative (or *vice versa*). Further studies concerning the alkali metal splittings are in progress.

B. Ion Quadruplets Ketyls. General Features of Two Spin Systems ($S = 1$). The analysis of the rigid media epr spectra of the randomly oriented triplet state is now well established following the work by Wasserman, Snyder, Yager, and others.[20,21] Here we briefly summarize the results which are used in the later discussion.

The spin Hamiltonian is written after an appropriate transformation as

$$\mathcal{H} = g\,\beta\vec{H}\cdot\vec{S} + DS_z^2 + E(S_x^2 - S_y^2) \tag{1}$$

with

$$D = \frac{3}{4}g^2\beta^2\left\langle \Phi(1.2)\left|\frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5}\right|\Phi(1.2)\right\rangle$$

$$E = \frac{3}{4}g^2\beta^2\left\langle \Phi(1.2)\left|\frac{y_{12}^2 - x_{12}^2}{r_{12}^5}\right|\Phi(1.2)\right\rangle$$

where $\Phi(1.2)$ is the antisymmetrized spatial portion of the wave function for two unpaired electrons and r_{12} is the distance between two unpaired electrons. The analysis of the shape of epr spectra under various conditions has been discussed in detail in the above-mentioned references.

In the present ion-quadruplet systems, $\Phi(1.2)$ is given by

$$\Phi(1,2) = \frac{1}{\sqrt{2}}\{\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)\} \tag{2}$$

where ψ_a and ψ_b are the molecular obitals of each molecule, a and b, in the quadruplet and can be written in terms of atomic orbitals

$$\psi_a = \sum_i C_{ai}\varphi_{ai},\ \psi_b = \sum_i C_{bj}\varphi_{bj}$$

Here φ_{ai} and φ_{bj} are the atomic orbitals of molecules a and b. D in 1 is now expanded in terms of atomic orbitals and is given by the sum of Coulomb and exchange integrals.[22] Since r_{12} is relatively large in the present biradical systems, exchange and multicenter integrals may be neglected to a good approximation.

In this approximation D is given by

$$D \cong \frac{3}{4}\,g^2\beta^2\sum_{ij}C_{ai}^2C_{bj}^2\left\langle \varphi_{ai}(1)^2\left|\frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5}\right|\varphi_{bj}(2)^2\right\rangle \tag{3}$$

$$= \frac{3}{4}g^2\beta^2\sum_{ij}\rho_{ai}\rho_{bj}\left\langle\frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5}\right\rangle_{ij} \tag{4}$$

where the angular brackets $\langle\ \rangle_{ij}$ designate the Coulomb integral between the i and j atomic orbitals, ρ_{ai} and ρ_{bj} are the spin densities on the i and j atoms. In many biradical systems we may assume $r_{12} \cong z_{12}$, if two unpaired electrons are well separated. In this case D is approximately given by

$$D = -\frac{3}{2}g^2\beta^2\left\langle\frac{1}{r_{12}^3}\right\rangle$$

Then we can write

$$\bar{r}_{12} = \left(\frac{2D}{3g^2\beta^2}\right)^{1/3} \tag{5}$$

as the average separation between two unpaired electrons.

The complete analysis of the epr spectra of two spin systems in solution over the whole temperature region is complicated, but in the limit of exchange narrowing the contribution to the line width from the zero field splitting is given by

$$\frac{1}{T_2} = \frac{1}{60}\left(\frac{2D^2 + E^2}{3}\right)\left(18\tau + \frac{30\tau}{1 + 4\pi\nu^2\tau} + \frac{12\tau}{1 + 16\pi^2\nu^2\tau^2}\right) \tag{6}$$

as given by Carrington and Luckhurst.[23] Here τ is the correlation time for the tumbling of the molecule.

C. Aliphatic Ketyls. 1. Epr Spectra of Aliphatic Ketyls at Low Temperatures. Rigid media epr spectra of alkali and alkaline earth metal ketyls of hexamethylacetone and alkali metal ketyls of pentamethylacetone were obtained in MTHF and the mixture of MTHF (65%) and toluene (35%) at 77°K. Some of the representative epr spectra are given in Figures 5 and 6. The 77°K spectra of all alkali metal ketyls clearly consist of the spectra of two different species. One of these can be approximately described by the Hamiltonian (1). The values of D and E for various ketyls are tabulated in the third and the fourth columns of the Table I. Another species which gives the central narrow peak must have small zero field parameters.

The species with large D seems to be well accounted for by the contact ion quadruplets, and its structure is discussed in detail in section C2. The nature of the central peak can be understood from the temperature dependence of the spectra. A representative example of the temperature dependence is shown in Figure 6. As we raise the temperature, the peaks with large D decrease their intensity and come close together. At around 150°K the central peak of sodium hexamethylacetone spectrum starts to show seven hyperfine splittings due to two sodium ions. At the same time the weak broad peaks with large D are still seen at this temperature. The central peak most likely originates from an ion quadruplet with small dipole interaction ($D/hc \leq 0.001$ cm^{-1}) and not from a dissociated monomer.

The quadruplet structure of this species is supported by the following observations.

(1) Each negative ion is associated with two sodium ions and no free ion spectra are observed.

(2) Rates of electron transfer between ketone and ketyl and sodium ion exchange between sodium iodide and sodium ion associated with ketyl are too slow to be

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[20] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

[21] P. Kottis and R. Lefebvre, *ibid.*, **41**, 379 (1964).

[22] M. Godfrey, C. W. Kern, and M. Karplus, *ibid.*, **44**, 4459 (1966).

[23] A. Carrington and G. R. Luckhurst, *Mol. Phys.*, **8**, 125 (1964).

Table I. Zero Field Parameters in Contact Ion Pairs

System	Doublet peak separation,[a] gauss	D/hc, cm^{-1}	E/hc, cm^{-1}	$\bar{r}_{12}$,[b] A
Hexamethylacetone				
Li	225	0.0210	~0.0000	5.0
Na	167	0.0155	~0.0000	5.6
K	179	0.0167	~0.0000	5.4
Rb	...	0.0149	0.0008	...
Cs	No well-defined peak	...	...	...
Pentamethylacetone				
Na	161	0.0150	~0.0000	5.6
K	150	0.0140	~0.0000	5.7
Rb	...	0.0142	0.0006	...
Cs	No well-defined peak	...	...	...
Benzophenone				
Li	137	0.0127	~0.0000	5.9
Na	103	0.0096	~0.0000	6.5
Fluorenone				
Li	120	0.0111	~0.0000	6.2
Na[c]	99	0.0092	~0.0000	6.6
K[c]	78	0.0072	~0.0000	7.1

[a] Uncertainties in the measurements are about ±2 gauss. [b] Computed from eq 5. [c] Taken from ref 2.

measured by epr. The rate constants for these bimolecular reactions were found to be $\sim 10^8$–10^9 mole^{-1} l. sec^{-1} for monomer ketyls and less than 10^7 mole^{-1} l. sec^{-1} for ion-quadruplet ketyls at 25°.[5a]

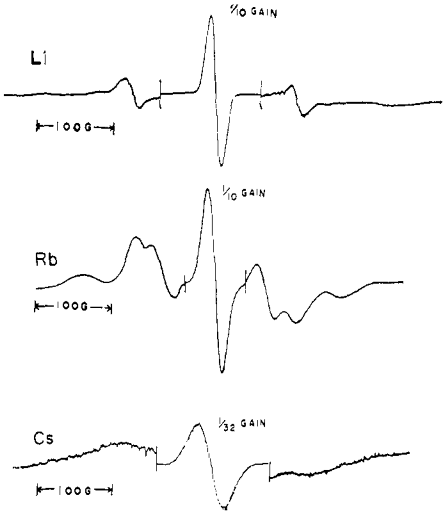
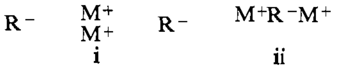


Figure 5. Rigid media epr spectra of hexamethylacetone ketyls in MTHF at 77°K (from the top to bottom): lithium hexamethylacetone, rubidium hexamethylacetone, cesium hexamethylacetone. The central portions of the spectra were taken with smaller amplifier gain compared with the rest of the spectra. The relative gains are specified in the figure.

The possibility that the species is the dissociated ion R^- or R^-M^+ is immediately ruled out. The possibility that the species is the triple ion ($R^-M_2^+$) cannot be ruled out entirely, but this possibility seems to be very remote by the following reasoning.

The sodium ion exchange reaction, $M^+R^- + M^+ \rightleftarrows M^+ + R^-M^+$, proceeds with the rate constant $\sim 10^8$ mole^{-1} l. sec^{-1}. Therefore, the similar ion-exchange reaction for triple ion is expected to proceed with the similar rate. In the present systems, however, the sodium ion exchange was found to be very slow ($k <$ 10^7 mole^{-1} l. sec^{-1}), and it seems to be more reasonable to assume an ion quadruplet (i) rather than a triple ion (ii).[24]



$$\underset{\text{i}}{R^- \; \begin{matrix} M^+ \\ M^+ \end{matrix} \; R^-} \qquad \underset{\text{ii}}{M^+R^-M^+}$$

Since the magnitude of D/hc must be less than 0.001 cm^{-1}, the average separation between two unpaired electrons ($\bar{r}_{12}$) must be larger than about 12 A. Such a small value of D and large $\bar{r}_{12}$ would only be compatible with the solvent-shared ion pair. Recently Luckhurst reported the temperature dependence of the epr spectra of hexamethylacetone in THF, MTHF, and the mixed solvent of THF and MTHF, and concluded that the

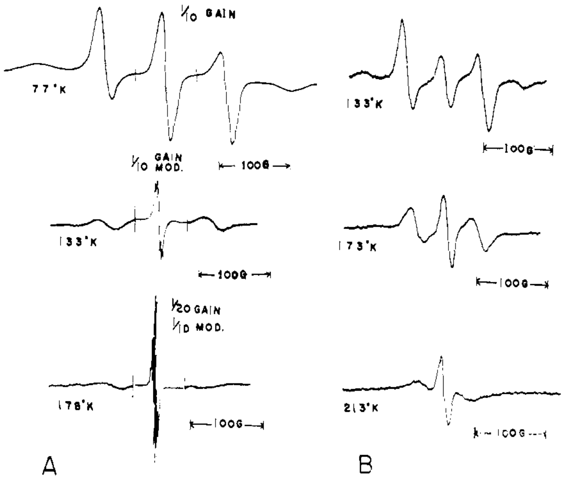


Figure 6. Temperature dependence of the spectra of ketyls. (A) Sodium hexamethylacetone in MTHF. Central portions of the spectra were taken with reduced modulation amplitude and amplifier gain as specified in the figure. (B) Sodium benzophenone in the mixture of MTHF (65%) and toluene (35%).

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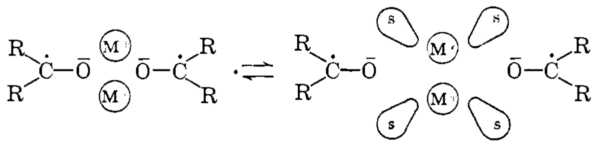
[24] This view was also given by Professor M. C. R. Symons, paper presented at the American Chemical Society Summer Esr Symposium, East Lansing, Mich., Aug 1966.

ketyl ion quadruplet is solvent shared.[25] Our present observations are in agreement with his conclusion.

The observations are summarized in the equilibrium

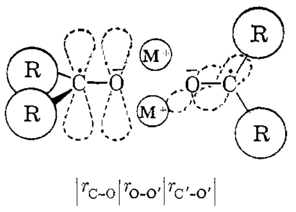


The line width of the solution spectra of the solvent-shared ion pair of hexamethylacetone is approximately 0.05 gauss at room temperature. From the eq 5, $1/T_2 \propto D^2$. Going from a contact ion pair to a solvent-shared ion pair, D would decrease at least by a factor of 15. From the simple Debye model, τ is expected to increase by a factor of 4 or so corresponding to the difference in the size of the ion pair for the same change.

If we assume that $1/T_2$ of the contact ion pair is in the order of a few gauss corresponding to the $\tau = 10^{-10}$ sec for the contact ion pair at room temperature, $1/T_2$ for the solvent-shared ion pair would be around 0.05 gauss, which is consistent with the observed line width.

Rigid media epr spectra of all divalent aliphatic ketyls showed only central narrow peaks whose line widths are around 15 gauss. Therefore, these ketyls must be solvent-shared triple ions ($R^-M^{2+}R^-$).

2. Structure of Contact Ion Pairs. The observed rigid media epr spectra for the species with large dipole interaction show $E \cong 0$ for all contact ion pair ketyls except for Rb and Cs ketyls. Symmetry requirement for $E = 0$ is satisfied by the structure in which $>\dot{C}-\bar{O}$ planes of each negative ion are mutually perpendicular as shown below. In order to check if this contact ion-pair structure is consistent with the observed magnitudes of D, estimates of D values are made according to the following procedures, using the eq 4. (1) We assume that spins are localized on the carbonyl groups. (2) Spin densities on the carbon and oxygen 2p orbitals were estimated from the Hückel MO calculation using the following parameters:[26] $\alpha_O = \alpha_C + 1.5\beta_{CC}$, $\beta_{CO} = 1.6\beta_{CC}$. The effect of the electrostatic interactions are taken into account in the same way as it was done previously.[10,27,28] (3) The following interatomic distance and the radius of oxygen atom were assumed. The C–O distance (r_{C-O}) is 1.30 A and the radius of oxygen atom is 1.40 A. O–O′ ($r_{O-O'}$) distances for various ketyls were estimated so that the entire system had the lowest electrostatic energy. (4) In the calculation of Coulomb integrals, one-half of the assigned spin density on each carbon and oxygen atom was placed at 0.83 A from the center of the carbon and the oxygen atom corresponding to the position of the maximum electron density of the Slater 2p orbital. D was then calculated from eq 4.



The computed D values (cm^{-1}) are 0.0217 for Li, 0.0160 for Na, and 0.0140 for K. These numbers should be compared with the observed D values listed in the Table I. Considering the crudeness of the model and the assumptions made above, the agreement is considered to be good. The observed value of D generally decreases with the size of the positive ion. However, potassium hexamethylacetone was found to be an exception. Although the structures of these ion pairs are contact ion pairs, solvation to the positive ion is expected for the open space and this may affect the separation between the positive and the negative ions slightly.

The upper limit for E obtained from the spectra of lithium and sodium ketyls is approximately 0.0002 cm^{-1}. The calculated values of E for a coplanar arrangement of the two carbonyl groups are 0.0008 cm^{-1} for lithium and 0.0007 cm^{-1} for sodium ketyls. Therefore, these ketyls seem to have perpendicular structures described earlier. In the case of rubidium ketyls E was found to be nonzero. In the case of cesium only broad spectra were obtained. These are shown in Figure 5. These observations probably indicate that more freedom is allowed for the structure of the contact ion pair of large cation. In cesium ketyls different structures with different D and E values may be present to give only broad structureless spectra.

The reason why the mutually perpendicular structure is the preferred one for the contact ion quadruplet with small cations is not obvious, but factors, such as the solvation of the solvent molecules and the steric hindrance between the negative ion and the solvated solvent molecules, would have to be considered. In the ion quadruplets with larger cations, weaker solvation and the larger size of the cation would give more freedom to the system.

3. Solvent-Shared Ion Quadruplets. The sodium splittings of the solvent-shared ion pairs of hexamethylacetone and pentamethylacetone ketyls were found to be rather temperature insensitive in DME and THF, but a marked temperature dependence was observed in diethyl ether and MTHF solution. In diethyl ether the sodium splitting decreases gradually from about 1 gauss at room temperature to almost zero at −15°. The spectrum does not change at temperatures lower than −15°. In MTHF the sodium splitting decreases with a rise of temperature as reported by Luckhurst. Our data of the temperature dependence of the sodium splitting in MTHF are in reasonably good agreement with Luckhurst's.[25] Luckhurst suggested that temperature dependence is due to solvent contraction. We feel that this change reflects the change in the ion-pair structure. We consider the two forms of ion pair, A and B, are in rapid equilibrium each other. We assume that ion pair, A and B, has different sodium splittings, a_A and a_B. Using the similar analysis as given in the previous paper, we estimated the equilibrium constants, K, at various temperatures from the observed sodium splitting, $\bar{a}$. $\bar{a}$ and K are related to each other by the equation $\bar{a} = (a_A + Ka_B)/(1 + K)$ with $a_A = 0.50$ and $a_B = 1.80$ gauss. a_A and a_B are the extrapolated values of the sodium splittings at high- and low-temperature limit. Since the radical is very

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[25] R. G. Luckhurst, *Mol. Phys.*, **9**, 179 (1965).

[26] The choice of these parameters was made according to P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1963).

[27] N. S. Hush and J. R. Rowlands, *Mol. Phys.*, **6**, 201 (1963).

[28] A. H. Reddoch, *J. Chem. Phys.*, **43**, 225 (1965).

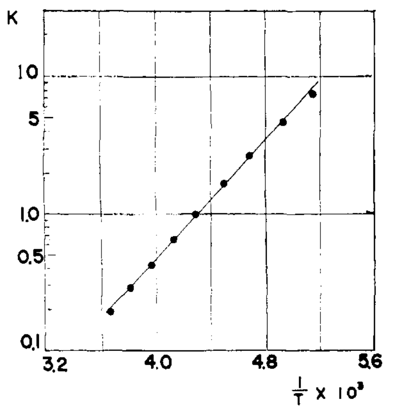


Figure 7. Log K *vs.* $1/T$ for sodium hexamethylacetone in MTHF.

unstable and the sodium splittings overlap considerably, an accurate measurement of the extrapolated value at high temperature was not feasible, but it is clear that the temperature dependence at the high (>20°) and low (<−90°) temperature region is small. K *vs.* $1/T$, determined using the above parameter, gave a fairly straight line over a wide range of temperature as is shown in Figure 7. $\Delta H° = -2.5$ kcal and $\Delta S° = -10$ eu were obtained for this equilibrium process.

4. Equilibria between Contact and Solvent-Shared Ion Quadruplets. From the rigid media epr spectra of various hexamethylacetone ketyls, we can obtain the relative concentration of the contact and solvent-shared ion quadruplets. The ratio of the concentration between the contact and the solvent-shared ion quadruplets in rigid MTHF at 77 °K was found to be approximately 0.4 for Li, 0.9 for Na, and 1.8 for Rb hexamethylacetone. The temperature dependence of the epr spectra and the visible ultraviolet spectra showed that the relative concentration of the contact ion quadruplet rapidly decreases and at around −80° the predominant species is the solvent-shared ion quadruplet.

D. Aromatic Ketyls. The epr spectra of benzophenone, fluorenone, and xanthone were studied in MTHF and in the mixed solvent of MTHF and toluene from low temperature to room temperature. The mixed solvent of MTHF and toluene was used to reduce the fraction of monomer. In the mixture of MTHF and toluene, intensities of the well-resolved hyperfine spectra are much weaker than in THF and DME. The well-resolved spectra of dilute solution of sodium xanthone and fluorenone in MTHF–toluene at room temperature were identified as monomer spectra. The spectra of sodium and lithium benzophenone are asymmetric and cannot allow any simple interpretation with one species. In the solution of 0.1 M excess parent ketone or saturated solution of NaI, hyperfine spectra of xanthone and fluorenone disappeared to leave only very weak broad spectra. Under this condition hyperfine splittings of the monomer spectra should be completely broadened by the exchange process.[5a] The spectrum of sodium benzophenone in the 0.1 M of excess benzophenone is more simplified and symmetric and can be interpreted by assuming the existence of sodium splittings due to two sodium ions ($a_{\mathrm{Na}} \cong 0.3$ gauss). As we have pointed out previously, this spectrum should belong to the ion quadruplet.[5a]

In Figure 6b an example of the temperature dependence of the spectra are shown for sodium benzophenone.

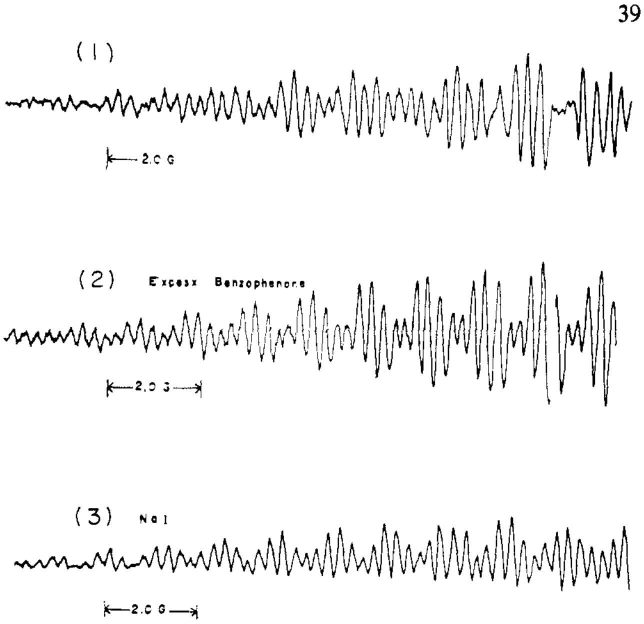


Figure 8. Sodium benzophenone in MTHF under different conditions: (1) sodium benzophenone in MTHF; (2) sodium benzophenone in MTHF with 10^{-1} M excess benzophenone; (3) sodium benzophenone in MTHF saturated with NaI.

At lower temperatures the spectra were taken with larger modulation amplitude. All aromatic ketyls studied showed absorption lines due to the species with large dipole interaction plus narrow central lines as in aliphatic ketyls.

We estimate the magnitude of D for the aromatic contact ion quadruplet in a way similar to that for the aliphatic ketyls, assuming that the species with large dipole interaction is a contact ion quadruplet. Spin distributions in aromatic ketyls are not exactly known but from the hyperfine splittings in Mg benzophenone we estimate that approximately 0.6 spin density on the rings and 0.4 spin density on the carbonyl group. Based on this information we put 0.1 spin on the oxygen, 0.3 on the carbonyl carbon, and 0.3 on each ring. Using the known bond distances as we used in the previous calculation, the value of D/hc for lithium benzophenone was estimated to be 0.010 cm^{-1}. The observed value for lithium benzophenone was 0.013 cm^{-1}. The structure of the contact ion quadruplet is considered to be perpendicular as in the case of aliphatic ketyls.

In the previous studies[2] of divalent metal ketyls it was found that most of ketyls show well-resolved hyperfine splittings in the room-temperature solution spectra. The magnitude of D in the solvent-shared ion pair must be equal to or less than 0.001 cm^{-1}. The contribution to $1/T_2$ from the zero field splitting is expected to be small from the similar arguments as described in section C.

We summarize our observations in MTHF and in the mixed solvent of MTHF and toluene as follows.

(1) At least three different types of ion pairs (contact ion quadruplet, solvent-shared ion quadruplet, and monomer ion pair) exist. (More strictly speaking, a monomer ion pair perhaps exists as a rapid equilibrium mixture among structurally different ion pairs.)

(2) In the MTHF and MTHF–toluene solutions of aromatic ketyls whose concentration is higher than 10^{-3} M, the predominant species is a contact ion quadruplet.

(3) The amount of solvent-shared ion quadruplet in sodium xanthone and fluorenone is very small. In sodium and lithium benzophenone, there is appreciable concentration of solvent-shared ion quadruplet, though a contact ion quadruplet is still the predominant species.

(4) In the divalent metal ketyls of benzophenone, xanthone, and fluorenone in MTHF, THF, and DME, the predominant (or almost exclusive) species is the solvent-shared triple ion ($R^-M^{2+}R^-$) except for some ketyls with Ba and Sr.

In the other ether solvents, such as THF and DME, the essential feature is perhaps the same, but the relative concentration of each species depends on the nature of the solvent.

Based on our observations a few remarks can be made on the related work which have appeared in the literature recently. Reddoch[29] found that the main species in lithium benzophenone is an ion quadruplet, but he failed to observe any species with large dipole interaction. From the preceding arguments it is considered that the species which he observed is the solvent-shared ion quadruplet. Since DME is a better solvating solvent than MTHF and lithium is a small ion, the equilibrium probably shifts toward solvent-shared ion quadruplet from contact ion quadruplet. Garst and his co-workers[30] reported the spectral shift in sodium benzophenone in different solvents. Their observations can be well interpreted on the basis of our model. Epr observations clearly show that the predominant species in the solution of sodium benzophenone in MTHF, DEE, and dioxane is a contact ion quadruplet with some mixture of monomer and solvent-shared ion quadruplet. At room temperature the structure of monomer is probably close to contact ion pair but depends on the nature of the solvent used.

In DME and THF the relative concentration of the monomer and ion quadruplet, of course, varies very much with concentration, but more monomer exists in DME than in THB. The magnitudes of the sodium and C^{13} splittings of sodium benzophenone in THF and DME are very similar. This indicates that the average structure of the monomer ion pair in both solvents is very similar. Therefore, large differences in the optical spectra between sodium benzophenone in THF and in DME cannot be due to the structural changes in the monomer ion pair, but must mainly come from monomer–dimer equilibrium. However, it is true that we have to consider several different types of ion pair as discussed in this paper in order to account for the optical spectra correctly, as mentioned by Garst, *et al.*, in footnote 15 of ref 30a.

E. **Equilibria among Different Ion Pairs.** Based on the observations described in the previous section, we summarize the equilibrium constants and the sign of $\Delta H°$ and $\Delta S°$ for the process, ion pair A $\leftrightarrows$ ion pair B, in the systems studied here (Table II). Ion quadruplet A is a contact ion quadruplet and B is a solvent-shared ion quadruplet. This distinction is not clear in monomers, but A is a contact ion pair and B is an ion pair with more solvation.

Table II

	K (+25°)	$\Delta H°$	$\Delta S°$
Ion pair: aromatic	?	–	–
Ion quadruplet: aliphatic	>1	+	+
Ion quadruplet: aromatic	<1	Very small	Very small

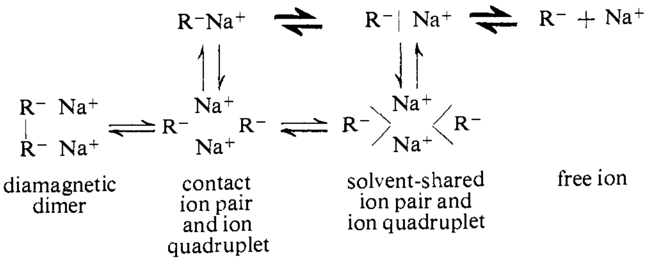
The analysis of the equilibrium processes in terms of a simple ion pair model, assuming continuous dielectric medium, seems to be hopeless in these systems. Enthalpy changes in these systems are given by $\Delta H° = \Delta H°(\text{ion–ion}) + \Delta H°(\text{ion–solvent}) + \Delta H°(\text{solvent–solvent})$. Here $\Delta H°$(ion–ion) is positive. The negative $\Delta H°$ values in monomer aromatic ketyls are caused mainly by the increased solvation in solvent-shared ion pair and the large negative $\Delta H°$(ion–solvent). The small positive $\Delta H°$ values in aliphatic ion quadruplet ketyls are probably due to the large positive $\Delta H°$(ion–ion) values which exceed the negative $\Delta H°$(ion–solvent) values. This is presumably due to the stronger electrostatic interaction between ions in aliphatic ion quadruplets. It should be noted that the negative charge is localized in the carbonyl group in aliphatic ketyls. These quadruplets were also studied in MTHF and mixtures of MTHF and toluene. Since the solvation power of these solvents is poorer than those of THF and DME, $\Delta H°$(ion–solvent) is expected to be smaller in absolute magnitude.

The negative entropy changes in the monomer ketyls are explained in the same way as discussed in the several similar systems.[4,7] More ordering of the solvent molecules in the solvent shared ion pair seems to be primarily responsible for these changes. $-\Delta S°$ values in monomer ketyls are estimated to be smaller than those obtained for several hydrocarbon ion pairs. $-\Delta S°$ values in ketyls are probably about 10 eu or smaller. The positive entropy changes in aliphatic ion quadruplets are probably due to the loss of the degree of freedom of the system in the contact ion quadruplet. As discussed in the previous section contact dimer ion pairs were found to have fixed structures. In the solvent-shared ion quadruplet two ketyls ions are more loosely bounded and more degrees of freedom of motion may be allowed.

Concluding Remarks

The equilibria in alkali metal ketyls described in the previous paper are now refined, including the several

Scheme I



⇌ Fast process: Unimolecular rate constant is faster than 10^8 sec^{-1}. Bimolecular rate constant is $\sim 10^8\ M^{-1}$ sec^{-1}.

⇌ Slow process: Rate constants are too slow to be measured by epr. Rate constants are slower than $10^5\ M^{-1}$ sec^{-1} (or sec^{-1}).

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[29] A. H. Reddoch, *J. Chem. Phys.*, **43**, 3411 (1965), reported the hyperfine splittings from two lithium ions in benzophenone.

[30] (a) J. F. Garst, R. A. Klein, D. Walmsley, and E. R. Zabolotny, *J. Am. Chem. Soc.*, **87**, 4080 (1965); (b) J. F. Garst, C. Hewitt, W. R. Richards, and E. R. Zabolotny, *ibid.*, **86**, 412 (1964).

possible ion-pair structures. A simplified scheme[31] is that shown in Scheme I. The position of the equilibrium strongly depends on the nature of positive ion, negative ion, and solvent. The similar equilibrium scheme involving monomer ion, cluster ion, and diamagnetic dimer or polymer may be quite common to many ion-pair systems. Similarities between some of the processes described here and the other systems should be noted.[32,33]

Acknowledgment. I am very grateful to Professor S. I. Weissman of Washington University for his gift of C^{13}-labeled fluorenone. By his courtesy, studies of temperature dependence of C^{13} splittings were made possible. Financial support from the National Science Foundation (GP-5040) is greatly appreciated.

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(31) The existence of many structurally different monomer ion pairs is neglected in this scheme in order to simplify the illustration.

(32) I. M. Brown, S. I. Weissman, and L. C. Snyder, *J. Chem. Phys.*, **42**, 1105 (1965).

(33) H. Van Willigen, Thesis, Amsterdam, 1965. I thank Dr. H. Van Willigen for sending me a copy of his thesis.

Valence-Shell Expansion in Electronically Excited States of Aromatic Sulfur Compounds[1]

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Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana. *Received July 28, 1966*

Abstract: The extent of valence-shell expansion in photoexcited states of aromatic sulfur compounds has been investigated. Acid dissociation constants of phenols with sulfur-containing substituents have been determined in the ground, lowest triplet, and first excited singlet states, by fluorescence, phosphorescence, and ultraviolet absorption spectroscopy. Substituent groups included sulfone, sulfoxide, sulfide, and sulfonium functions. A linear-free-energy treatment of phenols containing sulfone, sulfonium, and sulfoxide groups shows that the extent of electron-attracting conjugation by the substituents is greatly enhanced in photoexcited states, compared with the ground state. In contrast, σ constants for electronically excited sulfides are not appreciably different from those in the ground state unless alkyl groups are situated *ortho* to the sulfide function, in which case a large increase in σ occurs upon excitation. This result suggests that the sulfide group participates in both electron-releasing and -attracting conjugation in the ground state and that the extent of both forms of conjugation increases in a roughly equivalent fashion upon excitation, unless electron-releasing p_π conjugation is sterically inhibited. Steric factors exert very much less influence upon the excited-state acidities of sulfones, sulfoxides, and sulfonium salts, indicating that p_π orbitals in these compounds do not engage in significant conjugation, either electron releasing or withdrawing, in photoexcited states.

There has been continuing interest in the nature of the carbon–sulfur bond in aromatic sulfur compounds, especially with respect to participation of sulfur d_π orbitals in electron-withdrawing conjugation ("valence-shell expansion").[2] It seems generally accepted that such conjugation is significant in the ground electronic states of aryl sulfones, sulfoxides, and sulfonium salts. However, the extent of sulfur electron-accepting conjugation in aryl sulfides remains in some doubt. Recent spectral "substituent interference experiments" reported by Goodman and Taft[3] indicate significant population of sulfur 3d orbitals in the ground states of thiophenols and thioanisoles. Earlier spectral evidence, however, had been interpreted as demonstrating the absence of significant valence-shell expansion in compounds of divalent sulfur.[4] The influence of sulfide groups on the acidities of benzoic acid and phenol also has implied that recognizable expansion of the sulfur valence shell does not occur unless an extremely potent electron donor is present; chemically, the principal conjugative effect of a sulfide substituent frequently appears to be electron *donation*.[5]

While the influence of valence-shell expansion upon the chemical properties of ground-state aromatic sulfur compounds has received considerable attention, surprisingly little has been done to elucidate the extent of the effect in electronically excited states. Beginning with the work of Fehnel and Carmack[6] and Koch,[7] several attempts have been made to relate the nature of conjugative perturbations introduced by sulfur-containing substituents to the direction and magnitude of shifts in the ultraviolet absorption maxima of aromatic compounds. In that manner, it has been concluded that, in aryl sulfides, electron-*donor* conjugation may be appreciably more important in photoexcited states than in the ground state,[7–9] but there is no clear spectral

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(1) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 11–16, 1966.

(2) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press, New York, N. Y., 1962; H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1963; C. Y. Meyers, *Gazz. Chim. Ital.*, **93**, 1206 (1963).

(3) L. Goodman and R. W. Taft, *J. Am. Chem. Soc.*, **87**, 4385 (1965).

(4) See, for example, G. L. Bendazzoli and C. Zauli, *J. Chem. Soc.*, 6827 (1965), and A. Mangini, *Pure Appl. Chem.*, **7**, 103 (1963).

(5) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **78**, 854 (1956).

(6) E. A. Fehnel and M. Carmack, *ibid.*, 71, 84, 231, 2889 (1949); **72**, 1292 (1950).

(7) H. P. Koch, *J. Chem. Soc.*, 387, 408 (1949); 2892 (1950).

(8) A. Mangini and C. Zauli, *ibid.*, 4960 (1956).

(9) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **79**, 717 (1957).