THE STRUCTURE OF METAL KETYLS DERIVED FROM

XANTHONE ANALOGUES II

On the Electronic Interaction in Ketyl Radicals

By Kazuhiro Maruyama, Masaharu Yoshida and Jiro Osugi

In the preceding paper we have reported on the structure of monomer ketyls derived from xanthone analogues. In this paper we discussed the structure of paramagnetic dimer which exists in the solution. The ESR spectra of these ketyls in rigid media are also examined and the spin-spin separation was estimated. Their possible structures in solution were discussed.
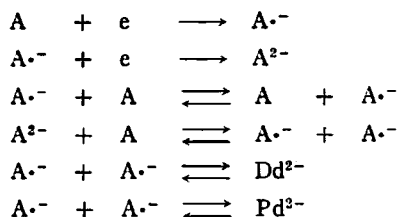
Introduction

In the previous paper[1] we have reported on the monomer ketyls derived from xanthone analogues and referred to the existence of the different kind of paramagnetic species from the monomer ketyls in solution according to the change of the experimental conditions.

Originally, the existence of the other paramagnetic species in addition to the monomer ketyl has been 'pointed out by Hirota and Weissman[2], who have investigated the ketyls derived from fluorenone, benzophenone and xanthone by the optical method and by the ESR spectroscopy in rigid media.

As we have observed the different kinds of paramagnetic species (radical II) from the monomer ketyl (radical I) in solution at room temperature as well as in a rigid medium at low temperature by the ESR spectroscopy, we shall deal with the behavior and possible structures of the paramagnetic species in this paper.

In the solution there may be an equilibrium among the several kinds of reduction products resulting from the reaction of a ketone with a metal;

$$A + e \longrightarrow A\cdot^-$$
$$A\cdot^- + e \longrightarrow A^{2-}$$
$$A\cdot^- + A \rightleftharpoons A + A\cdot^-$$
$$A^{2-} + A \rightleftharpoons A\cdot^- + A\cdot^-$$
$$A\cdot^- + A\cdot^- \rightleftharpoons Dd^{2-}$$
$$A\cdot^- + A\cdot^- \rightleftharpoons Pd^{2-}$$

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1) K. Maruyama, M. Yoshida, I. Tanimoto and J. Osugi, This Journal, 39, 117 (1969).

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

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A : neutral ketone

A·⁻ : monomer ketyl radical (radical I)

A^{2-} : dianion

Dd : diamagnetic dimer

Pd : paramagnetic dimer (radical II)

Such an equilibrium in solution has been investigated by several other investigators[3]~[7].

Experimental

Preparation of ketyls and synthesis of the correponding ketones were described in the preceding paper. Observation of ESR spectra in rigid medium was carried out at the temperature of liquid nitrogen in a dewar equipped with qualtz cell. Coupling constant (13.0 gauss) due to nitrogen atom of Fremy's salt and coupling constant (70.0 gauss) due to manganese atom of manganese oxide were used as a standard.

Results and Discussion

Spectra observed in solution

We have observed two different kinds of spectra corresponding to the radical I and radical II for each of the sodium ketyls derived from xanthone, thioxatnhone and selenoxanthone. The experimental conditions to observe the each of the two radicals are the same in solvent, the same at the temperature but different in the concentration of neutral ketone. That is, the concentration of the
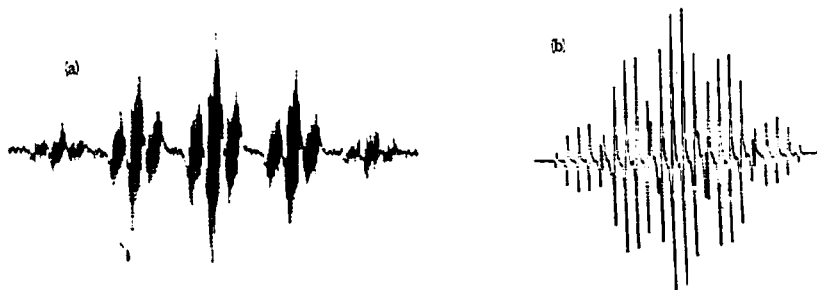

Fig. 1   ESR spectra of sodium ketyl of xanthone in solution

(a)   type I spectrum

(b)   type II spectrum

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

4) P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, **1963**, 5412

5) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2537 (1964)

6) N. Hirota, *ibid.*, **89**, 31 (1967)

7) N. Hirota, *J. Phys. Chem.*, **71**, 127 (1967)

ketone in which to observe the spectra of the type of radical I (type I spectra) is about 10^{-5} mole/l, whereas those to observe the spectra of the type of radical II (type II spectra) is about 10^{-3} mole/l. On the other hand, the condition in which to observe each of the two types of spectra depends on the species of solvents. In the more polar solvents we can observe preferentially the type I spectra in the dilute solution explained above, but in the less polar solvents the type II spectra even if in the dilute solution. Moreover, when we observe the changes of spectra depending on temperature, the coupling constants due to sodium of the type II spectra change in greater degree than those of the type I spectra. The changes in the spectral aspect and in the coupling constant due to sodium are shown in Figs. 2 and 3. The typicals of two types of spectra are shown in Fig. 1.

Comparing with the two types of spectra, the coupling constants due to sodium are quite large for the type II spectra. The coupling constants analyzed from both types of spectra are shown in Table 1.

Table 1   Coupling constants obtained from analyses of two types of spectra
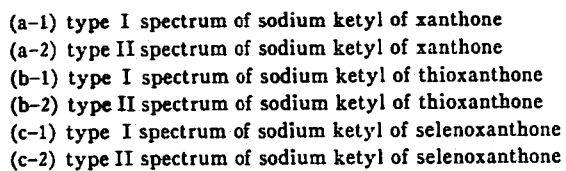at room temperature

Position	Coupling constant, G					
	Type I spectrum			Type II spectrum		
X	O	S	Se	O	S	Se
$H_{1,8}$	3.72	3.41	3.31	3.93	3.49	3.51
$H_{2,7}$	0.10	0.11	—	—	0.32	0.57
$H_{3,6}$	3.72	3.72	3.70	3.93	3.86	4.03
$H_{4,5}$	1.00	0.99	1.00	0.95	1.12	1.05
Na	0.20	0.22	0.24	0.95	1.12	1.03
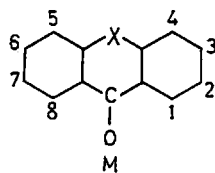
From the results shown above, it is reasonable to deduce that radical I and radical II correspond to the two kinds of ion pairs, and we will discuss the structure of the ion pair, which shows the type II spectrum, especially from the larger coupling constant due to sodium and from its larger temperature dependency. In an ion pair solution it has been shown that the coupling constant due to counter cation depends on temperature[8]–[11]. Coupling constants in ketyls, in general, increase as temperature goes up. For this phenomenon the following two possible mechanisms have been proposed:

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

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

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Fig . 2 Temperature dependency of ESR spectra in solution

(a-1) type I spectrum of sodium ketyl of xanthone
(a-2) type II spectrum of sodium ketyl of xanthone
(b-1) type I spectrum of sodium ketyl of thioxanthone
(b-2) type II spectrum of sodium ketyl of thioxanthone
(c-1) type I spectrum of sodium ketyl of selenoxanthone
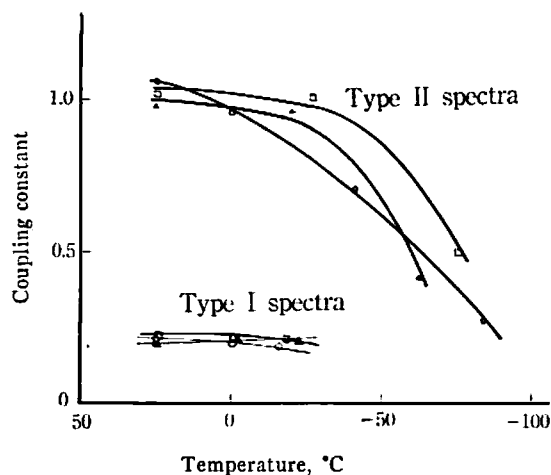(c-2) type II spectrum of sodium ketyl of selenoxanthone

Fig. 3 Temperature dependency of coupling constants due to sodium.

▲ : Xanthone, ○ : S-xanthone, □ : Se-xanthone

i) In monomer metal ketyls metal ion may sit next to oxygen and lie on the nodal plane of its $2p\pi$-orbital[10]. At the position the coupling constant due to metal is to be smallest because of minimum overlap integral with $2p\pi$-orbital. Any deviation from this position at a higher temperature must produce a larger coupling constant due to metal (Fig. 4).
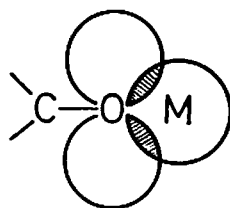

Fig. 4 Overlap of s- and $2p\pi$-obitals M: counter cation

ii) A rapid equilibrium among different ion pairs, which contain structuraly solvent molecules gotten between metal ion and the organic rest of radical ion, changes with temperature. Therefore, the "tight" ion pair at a higher temperature changes into the "loose" ion pair with more solvation at a lower temperature[11].

Referring to both the mechanisms proposed so far and to the results obtained in this study, the following will be presented as possible structures for the two kinds of ion pair. An ion pair which shows the type I spectra is to be the monomer ketyl radical of structure I. This contains one radical ion and one metal ion in one solvent cage. An ion pair which shows the type II spectrum may correspond to the dimer of structure II. This consisted of two pairs of radical ions and sodium ions in one solvent cage (Fig. 5).

10) B. J. McClelland, *Trans. Faraday Soc.*, **57**, 183, 1458, 2073 (1961)

11) N. Hirota, *J. Am. Chem. Soc.*, **89**, 31 (1967)

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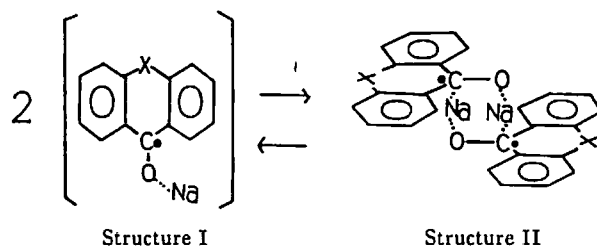

Structure I   Structure II

Fig. 5   Structures of monomer (Structure I) and dimer (Structure II)

In structure II, sodium cations taking place between the two organic rests in sandwitch form sit near to the carbonyl carbon on which the highest spin density is found. For this reason the overlap integral between sodium s-orbital and carbon $2p\pi$-orbital is to be larger than that in the structure I. Structure II will get further support from the experiments in rigid media which will be referred to the next section. Although we could observe the two types of ion pair for sodium metal ketyls, we could not observe the same kinds of metal ketyls for those produced by the reduction with other metals. This may be ascribed to the smaller magnetic momenta of another metal. However, we could observe such a dimer for these metal ketyls in glassy medium at the temperature of liquid nitrogen.

Spectra observed in glassy rigid media

Structure II has two spins in a cluster and if it is true, the spectrum corresponding to the triplet state must be observed owing to the spin-spin dipolar interaction. Rigid media ESR spectra of aromatic and aliphatic ketyls were studied first by Hirota and Weissman[12]. Analysis of the shape of
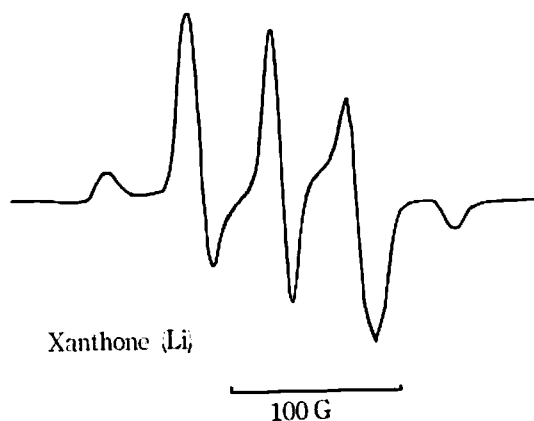

Fig. 6   ESR spectrum of lithium xanthone ketyl in rigid medium

Xanthone (Li)

100 G

12)   N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2538 (1964); N. Hirota and S. I. Weissman, *Mol. Phys.*, **5**, 537 (1962); N. Hirota, *J. Am. Chem. Soc.*, **89**, 32 (1968)

ESR spectra has been made by Wasserman, Snyder and Yager[13] and by Kottis and Lefevbre[14].

ESR measurement was carried out at 77°K in α-methyltetrahydrofuran as a solvent. The ketyls which were investigated in this study were those derived from xanthone, thioxanthone and seleno-xanthone by the reaction with metallic lithium, sodium, potassium, calcium and barium. The spectra observed consisted of five broad lines (Fig. 6). The central line originated from either the monomer ketyl or the dimer with the small dipolar interaction. After eliminating the central line the four broad lines which are typical for the biradical system of ketyls remain. The spin Hamiltonian of the biradical system may be written as

$$H = g\beta HS + DS_z^2 + E(S_x^2 + S_y^2) + I \cdot A \cdot S,$$

where D and E are zero field splitting parameters[15].

From the examination of the spectra observed we can conclude as $E \cong 0$. The quantity of D is directly related to the separation between two unpaired electrons. By a suitable assumption[12] we can write the average separation of two unpaired electrons $\bar{r}_{12}$ as follows ;

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

The quantities of D and $\bar{r}_{12}$ obtained from the analyses of spectra are summarized in Table 2.

Table 2   Zero field splitting parameter (D) and separation (r_{12}) between two spins

Counter cation	Xanthone		Thioxanthone		Selenoxanthone		Atomic[*] radius
	D	r_{12}	D	r_{12}	D	r_{12}	
Li	104.8 G	6.5 Å	109.0 G	6.4 Å	113.4 G	6.3 Å	0.70 Å
Na	98.4	6.6	103.3	6.5	106.0	6.4	1.00
K	92.0	6.8	94.2	6.7	98.8	6.6	1.33
Ca	47.9	8.4	54.8	8.0	56.1	7.9	1.05
Ba	~0		~0		~0		1.38

[*] Atomic radius of the metal which was used for the reduction of xanthone analogues.

For the ketyls derived from the reaction with a metal the separation between two spins de-creases, in general, in the order of xanthone-, thioxanthone- and selenoxanthone-ketyls. On the other hand, concerning the ketyls derived from the reaction with equivalent metals the separation between two spins increases with the radius of metal atom. However, we can recognize a notable difference in the separation of two spins among the ketyls derived from the reaction with monovalent metals and divalent metals.

This does not depend on the radius of metal, but may be the reflection of different structural

13)   E. Wasserman, L. C. Snyder and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964)
14)   R. Kottis and R. Lefevbre, *ibid.*, **41**, 379 (1964)
15)   K. W. H. Stevens, *Proc. Roy. Soc. (London)*, A214, 237 (1952); A. D. Mclachlan, *Mol. Phys.*, **6**, 441 (1963)

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arrangement of the dimers. As the most probable structural models, we shall propose structure II for the ketyl dimers derived from the reaction with alkali metals as described above and structure III for that derived from the reaction with alkali earth metals. Apparently, structure III has the larger separation between two spins than structure II (Fig. 7).
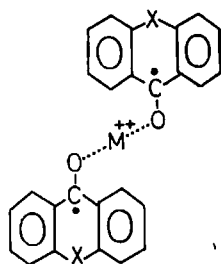
Structure III

Fig. 7   Structure of dimer which was produced by the reaction of xanthone analogues with divalent metals

The quantity of D does not only depend on the separation between two spins but also the spin density. Deviation from the coplanarity in a molecule results in the decrease of the delocalization of spin. Thus, deviation from coplanar arrangement in an aromatic ketyl results in the larger localization of spin around the carbonyl group. Differences of D in xanthone-, thioxanthone- and seleno-xanthone-ketyl, therefore, may be ascribed to the decrease in the coplanarity produced by the change of the atomic radius of VIa atoms.

Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan