Studies of the Metal Ketyls of Phenanthraquinone and Its Derivatives

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The electron-spin resonance (ESR) spectra of the potassium ketyl of phenanthraquinone and of the zinc ketyl of phenanthraquinone have been studied by Kazakoba et al.1) and Adams et al.2) respectively. They obtained rather broad ESR signals. Recently a more precise study of the ketyl, produced electrolytically in an *N, N*-dimethylformamide solution with tetra-*n*-butylammonium perchlorate as a supporting electrolyte, has been reported by Dehl and Fraenkel.3) The present author has been interested in how the free spin distribution varies with the introduction of a substituent into the aromatic nucleus. It is well known that the introduction of a substituent such as a chlorine atom and a nitro group into the aromatic nucleus of triphenylmethyl does not change its free spin distribution essentially.4) However, the electron-spin resonance spectra of monosubstituted benzene mononegative anions are very sensitive to the nature of the substituent; small changes in the substituent can lead to drastic changes in the appearance of the spectrum.5) Therefore,

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1) V. M. Kazakoba et al., *Zhur. Strukt. Khim.*, **3**, 536 (1962).

2) M. Adams, M. S. Blois, Jr., and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958).

3) D. Dehl and G. K. Fraenkel, ibid., **39**, 1793 (1963).

4) M. T. Johns, ibid., **35**, 1146 (1961). K. Maruyama, unpublished work.

5) J. A. Bedford, J. R. Bolton, A. Carrington and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963).

lithium-, sodium-, potassium-, cesium-, magnesium-, calcium and barium-ketyl of phenanthraquinone and the potassium-ketyls of 2-nitro-, 2, 7-dinitro-, 2, 7-dibromo- and 2, 7-diamino-phenanthraquinone are examined in the present study. Furthermore, the influence of metal species as a reducing agent upon the splitting constant and dimerization reaction of these ketyls is examined for the metal ketyls of phenanthraquinone in tetrahydrofuran.

Results and Discussion

Materials. — *Phenanthraquinone.*—Commercial phenanthraquinone was recrystallized from acetic acid; m. p. 207°C.

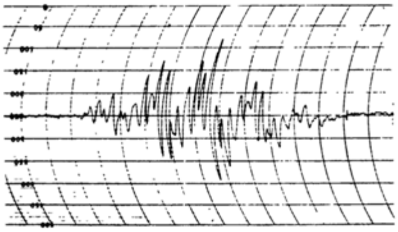

Fig. 1-1. Free ion radical, produced by reduction with potassium metal (liq. NH_3), overall width 7.8 gauss.

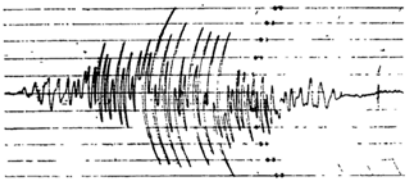

Fig. 1-2. Li-ketyl (THF), overall width 8.9 gauss.

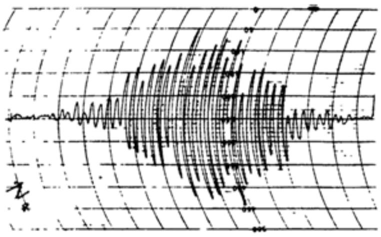

Fig. 1-3. Na-ketyl (THF), overall width 9.4 gauss.

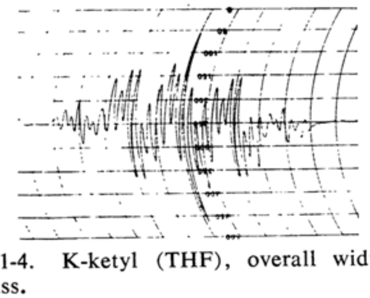

Fig. 1-4. K-ketyl (THF), overall width 8.0 gauss.

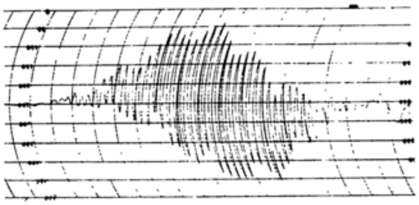

Fig. 1-5. Cs-ketyl (THF), overall width 9.85 gauss.

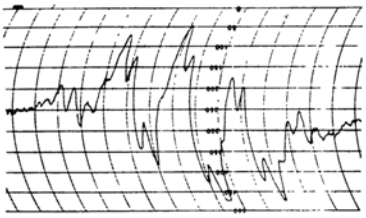

Fig. 1-6. Mg-ketyl (THF), overall width 9.6 gauss.

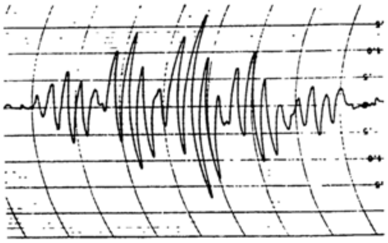

Fig. 1-7. Ca-ketyl (THF), overall width 9.6 gauss.

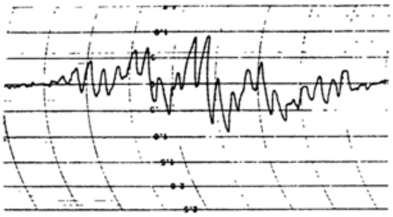

Fig. 1-8. Sr-ketyl (THF), overall width 9.1 gauss.

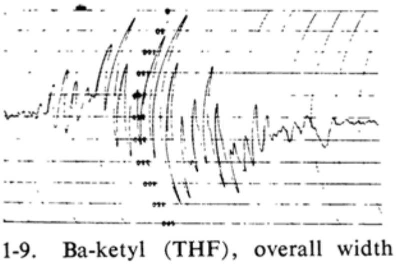

Fig. 1-9. Ba-ketyl (THF), overall width 9.5 gauss.

Fig. 1. ESR spectra of metal ketyls of phenanthraquinone.

TABLE I. SPLITTING CONSTANTS OF THE FREE ION RADICAL OF PHENANTHRAQUINONE IN LIQUID AMMONIA

		1st splitting	2nd splitting	3rd splitting
Equiv. hydrogen atoms		4H	2H	2H
Intensity ratio		1 : 4 : 6 : 4 : 1	1 : 2 : 1	1 : 2 : 1
Splitting constant (gauss)		1.56	0.44	0.36
Calculated free spin density	I[9]	0.0429 0.0399	0.0109	0.0077
	II[3]	0.068 0.056	−0.018	−0.006

Equiv. : equivalent

2-Nitrophenanthraquinone. — Commercial phenanthraquinone was treated with nitric acid (sp. gr. 1.4). The crude crystals were recrystallized from acetic acid ; m. p. 257°C.

2, 7 - Dinitrophenanthraquinone. — Commercial phenanthraquinone was treated with a mixture of nitric acid (sp. gr. 1.5) and conc. sulfuric acid. The crude crystal was recrystallized from acetic acid ; m. p. 302∼303°C.

2, 7-Dibromophenanthraquinone. — Commercial phenanthraquinone was treated with bromine in a sealed tube at 160°C. The crude crystal mass was recrystallized from acetic acid several times ; m. p. 323°C.

2, 7-Diaminophenanthraquinone. — 2, 7-Dinitrophenanthraquinone was reduced by tin and hydrochloric acid. Recrystallization was performed from alcohol. The crystals were deep violet needles and did not melt even above 300°C.

Measurement. — *Metal Ketyl of Phenanthraquinone.*—The electron-spin resonance measurement was performed by using a spectrometer with an X-band, and 100 kc. modulation. The low temperature runs were made by allowing cool nitrogen gas evaporated from liquid nitrogen to flow through.

The electron-spin resonance spectra of metal ketyls of phenanthraquinone produced by reduction with different metals are shown in Fig. 1. It is well known that mononegative anions produced by reduction with an alkali or an alkali earth metal form ion pairs.[6,7] Therefore, the observed additional hyperfine structure from the metal cation attached to the radical may be taken to indicate the ion pair formation. The term " ion pair " is used to represent the associated counter ions which weakly perturb each other. As the metal ketyls form ion pairs in a usual solvent, such as tetrahydrofuran and dimethoxyethane, the details of each spectra are different because of the different nuclear-spin quantum numbers of the metals used as reducing agents. However, the largest splitting consists of the five lines (intensity ratio; 1 : 4 : 6 : 4 : 1) due to four equivalent hydrogen atoms on the phenanthraquinone ring. On the other hand, it has been reported that benzophenone and other ketyls do not show any metal splittings in liquid ammonia ;[8] these ketyls do not form ion pairs in liquid ammonia but exist as completely dissociated mononegative anions. A mononegative anion in this state is designated by the term " free ion radical " in this article. From the examination of the spectrum of the free ion radical produced by the reduction of phenanthraquinone by potassium metal in liquid ammonia, it was found that the spectrum can be analysed into the following splitting pattern (Fig. 1-1, Table I).

Although the ESR spectra of metal ketyls of phenanthraquinone are more complicated than that of a free ion radical as the result of ion pair formation, their ESR spectra can be analyzed by means of a comparison of the spectrum with that of a free ion radical. Thus, the splitting constants of the first splitting due to the four equivalent hydrogen atoms of metal ketyls, which were in the ion-pair state in tetrahydrofuran, could be determined. These results are shown in Table II. It is interesting that the value of the splitting constant of the first splitting due to the four equivalent hydrogen atoms is affected by the species of metal. The cause of these changes in the splitting constants with the difference of metal is not clear. The same phenomena are found also in the case of the anion radical of nitrobenzophenone and others.[10]

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[6] N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **88**, 1330 (1961).

[7] R. L. Ward, *J. Chem. Phys.*, **32**, 410 (1960) ; *J. Am. Chem. Soc.*, **83**, 1296 (1961).

[8] N. Hirota, Thesis, Washington University, St. Louis 30, Mo., U. S. A. (1963).

[9] A. Streitwiesser, Jr., " Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York (1961), p. 156.

[10] Reported at the 2nd ESR symposium, Kyoto (1963).

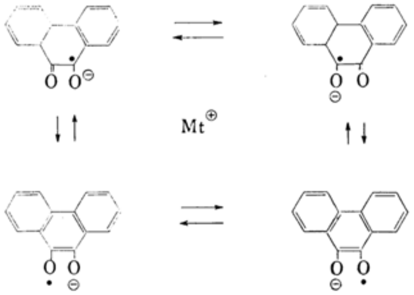
TABLE II. VARIATION OF SPLITTING CONSTANT BY CHANGING THE METAL IN THF

Metal	Overall width of spectrum (gauss)	Color of soln.	Splitting const. of the four equiv. hydrogen atoms (gauss)
Li	10.8	green[*2]	2.2
Na	9.4	green-red[*2]	1.7
K	8.0	red	1.5
Cs	9.8	red	—
Mg	9.6	green	1.7
Ca	9.6	green	1.7
Sr	9.1	green	1.6
Ba	9.5	green	1.6

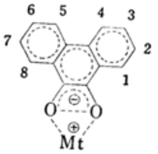
THF: tetrahydrofuran

The ESR spectra of metal ketyls of phenanthraquinone have a narrower overall width (the largest splitting constant due to the four equivalent hydrogen atoms is 1.56 gauss) than the metal ketyl of benzophenone (the largest splitting constant due to para hydrogen atoms is 3.4 gauss.[8]) This means that most of the free spin is accummulated around two carbonyl groups.

The structure of ketyl of phenanthraquinone may be represented by the next resonance formula (structure I), or it may be expressed more conveniently by structure II. The results shown in Table I can be satisfactorily explained by considering the structure proposed and the results of calculations.[3,9] That is, H_1, H_3, H_6 and H_8 are responsible for the first splitting, and H_4 and H_5 are responsible for the second splitting for a reason which will be described later; therefore, H_2 and H_7 are responsible for the third splitting.



Structure I Mt: metal



Structure II Mt: metal

The Metal Ketyl of Phenanthraquinone Derivatives. — The spectra obtained are shown in Fig. 2. From a comparision of the spectra of 2, 7-dibromophenanthraquinone potassium ketyl (Fig. 2-3) and of the free ion radical phenanthraquinone (Fig. 1-1), it can be concluded that the second splitting is caused by the two equivalent hydrogen atoms H_4 and H_5, because

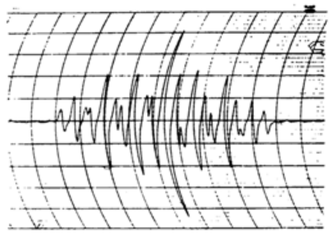


Fig. 2-1. K-ketyl of 2-nitrophenanthraquinone (THF), overall width 7.3 gauss.

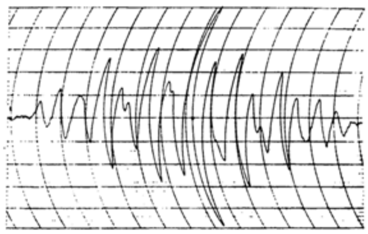


Fig. 2-2. K-ketyl of 2,7-dinitrophenanthraquinone (THF), overall width 7.1 gauss.

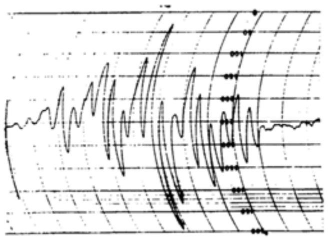


Fig. 2-3. K-ketyl of 2,7-dibromophenanthraquinone (THF), overall width 7.5 gauss.

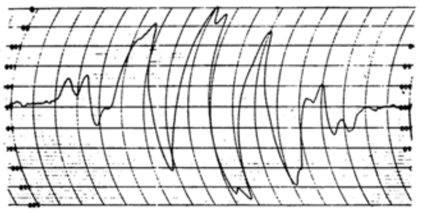


Fig. 2-4. K-ketyl of 2,7-diaminophenanthraquinone (THF), overall width 8.0 gauss.

Fig. 2. Metal ketyls of phenanthraquinone derivatives.

[*2] The red substance is paramagnetic. The green substance is diamagnetic and this becomes a red substance in an extremely dilute state. The red substance becomes yellow if it is in contact with a metallic surface; furthermore, this yellow substance is diamagnetic, This yellow substance becomes a red paramagnetic solution when it is mixed with a solution in which unreduced phenanthraquinone remains. Therefore, the yellow substance is a dinegative anion.

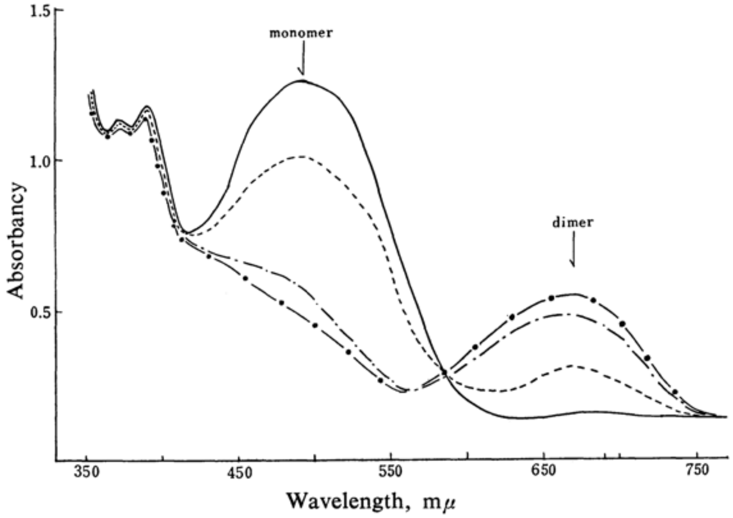


Fig. 3. Absorption spectra of Na-ketyl of phenanthraquinone at different temperatures.
—— 23°C ------ −30°C —·—· −70°C —•—• −85°C

the bromine atom, in general, does not show ESR splitting. This experimental result coincides with calculations based on the molecular orbital theory.[3,9),*3] With regard to the effect of the introduction of substituents into the aromatic nucleus upon free spin distribution, it seems reasonable to deduce that the introduction of bromine and amino groups does not change the intensity ratio (1:4:6:4:1) of the five line groups due to the four equivalent hydrogen atoms, but that the introduction of a nitro group does change the appearance of the spectrum. That is, i) in the K-ketyl of 2-nitrophenanthraquinone, the number of apparent line groups in the spectrum is seven and the intensity ratio is nearly 1:3:3:6:3:3:1, and ii) in the K-ketyl of 2,7-dinitrophenanthraquinone, the number of the apparent line groups is seven and the intensity ratio is nearly 1:2.5:3.5:6:3.5:2.5:1. However, the obtained spectra were too broad to obtain a quantitative estimation of the effect.

Equilibrium between Paramagnetic Monomers and Diamagnetic Dimers. — The existence of an equilibrium between the metal ketyl monomer and the dimer was examined by means of a study of absorption spectra in the visible region and by an absolute free spin determination by an overmodulated ESR technique.[11)] The results of the examination of the absorption of metal ketyls of phenanthraquinone in the visible region at different temperatures and with different reducing alkali metals are shown in Table III and Fig. 3.

TABLE III. ABSORPTION SPECTRA OF METAL KETYLS OF PHENANTHRAQUINONE AT DIFFERENT TEMPERATURES

Metal	Temp. °C	Paramagnetic monomer mμ	Diamagnetic dimer mμ
Li	23	484 v.s.	646 w.
	−50	484 w.	646 s.
	−70	—	646 v.s.
Na	23	494 v.s.	670 v.w.
	−30	494 s.	670 w.
	−85		670 v.s.
K	23	507 v.s.	
	−60	507 v.w.	641 s.
	−85	507 v.w.	641 v.s.
Mg	23	508 w.	646 w.
	−80	—	646 s.
Ca	23	—	670 v.s.
	−80	—	670 v.s.
Sr	23	—	670 v.s.
Ba	23	—	687 v.s.

Solvent: THF

v.w. : very weak
v.s. : very strong
w. : weak
s. : strong

It is interresting to note that the diamagnetic dimer shows an absorption band at longer wavelength region than does the paramagnetic monomer.

[*3] The splitting constant changes with the solvent and with the metal species used as a reducing agent. This coincidence with the results of molecular orbital calculations is, therefore, only a rough estimate.

11) a) K. Halbach, *Phys. Rev.*, **119**, 1230 (1960); b) J. E. Hyde and H. W. Brown, *J. Chem. Phys.*, **37**, 368 (1962).

On the other hand, the decrease of paramagnetic species with a decrease in temperature, was examined with the aid of an overmodulated ESR technique. This results are shown in Fig. 4. This process was found to be completely reversible by a temperature change. The tendency to dimerization is especially strong when a divalent metal such as magnesium, calcium, strontium or barium was used as the reducing agent. Almost all the metal ketyls produced from these reducing agents (in tetrahydrofuran and dimethoxyethane) dimerize in an equilibrium state at room temperature (color: green) except when they were extremely dilute (color: red). Even if the metal ketyl solutions were made by the reduction of phenanthraquinone with lithium, sodium and potassium, they became green when at a high concentration. Only the metal ketyl solution produced by reduction with cesium was strongly red even if it was at a high concentration at room temperature. These results accord with absorption spectrum examinations and with ESR measurements.

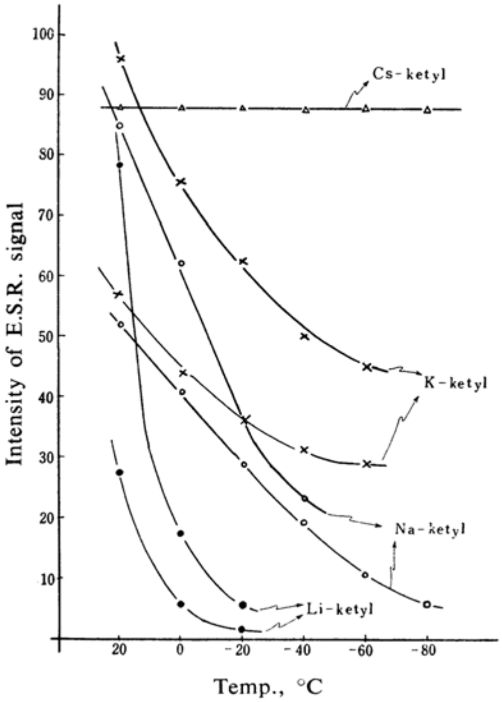


Fig. 4. Change of paramagnetic species with temperature.

To summarize the facts mentioned above:

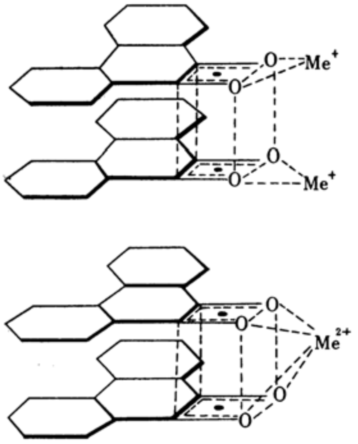
i) The dimer shows absorption at a longer wavelength region (~650 mμ) than the paramagnetic monomer (~500 mμ);

ii) The dimerization reaction is completely reversible with temperature and with concentration, and the dimer is diamagnetic;

iii) The tendency to form dimers is more remarkable in the metal ketyls produced by reduction with metals of smaller atomic size than in the metal ketyls produced by reduction with monovalent metals of larger atomic size. The metal ketyl produced by reduction with cesium metal does not appreciably dimerize even at −80°C.

iv) Metal ketyls produced by reduction with divalent metals show a strong tendency to dimerize.

Considering these results, the following structure, III, seems to be the most favorable for the diamagnetic dimer:



Structure III

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