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Abstract

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ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF SOME AROMATIC AND ALIPHATIC METAL KETYLS IN SOLUTIONS

We have published studies of the electron paramagnetic resonance (EPR) spectra of some metal ketyls ([1], [2]). In the present work new results are presented on the EPR spectra of solutions of a series of aromatic and aliphatic metal ketyls. The study of EPR spectra in solutions is of interest in connection with the possibility of resolving the hyperfine structure (h.f.s.), from the character of which one may judge the distribution of the spin density of the unpaired electron in the radical. Of special interest are the aliphatic metal ketyls, which are almost the only representatives of long-lived aliphatic free radicals.

We investigated the EPR spectra of dilute solutions of phenanthrenequinone-K-ketyl, benzil-K-ketyl, hexamethylacetone-K-ketyl, diethylpinacolin-K-ketyl, and triethylpinacolin-K-ketyl in 1,2-dimethoxyethane.

Unfortunately, anthraquinone-K-ketyl and *p*-quinone-K-ketyl dissolve neither in 1,2-dimethoxyethane nor in tetrahydrofuran.

For a solution of phenanthrenequinone-K-ketyl, an h.f.s. consisting of five components was obtained (Fig. 1*a*) with a splitting of 1.1–1.2 gauss. The spectrum shows that not all 8 protons of phenanthrenequinone are equivalent, but that there are two different groups of protons, four in each, differing from one another. At first glance it seems that the spectrum does not correspond to the intensity ratio required for 4 equivalent protons, $1 : 4 : 6 : 4 : 1$. Poole and Anderson ([3]) theoretically obtained the form of spectra with h.f.s. for different numbers of equivalent protons and for different ratios of the splitting interval to the width of the hyperfine components. In the case where this ratio is less than or equal to unity, the form of the spectrum for 4 equivalent protons agrees well with that obtained by us. Because of the unresolved second-order h.f.s. from the remaining four protons, the hyperfine components for phenanthrenequinone-K-ketyl are broad, which leads to this form of the spectrum. The question arises why the experiment gives a quintet for the h.f.s. of phenanthrenequinone-K-ketyl. The explanation should apparently be sought in the energetic inequivalence of localization of the unpaired electron at all centers from 1 to 8.

One may imagine the presence of the unpaired electron at four centers according structural scheme 1

Figure 1: structural scheme 1

to schemes 1-4. Calculation shows that the resonance energy in the presence of the unpaired electron in positions 1 and 3

greater conjugation energy of the system in the presence of an electron at 5 and 7 by 0.5β, i.e., by 8.5 kcal. (for the usual value of the resonance integral).

[chemical structures 1-4]

Thus, counting from the other oxygen (since in the metal ketyl both oxygens are equivalent), the positions of the unpaired electron at 6 and 8 correspond to a greater conjugation energy than at 2 and 4 by the same amount, 0.5β. Thus, the four positions 1, 3, 6, and 8 are energetically more favorable, which leads to resolution of the quintet in the spectrum.

If the empirical McConnell equation is used for calculating spin densities ($a = Q\rho$, where a is the splitting constant, ρ is the spin density, and $Q = -22.5$), then an approximate calculation (since the spectrum cannot be completely resolved) shows that in the rings the total spin density is smaller than in the case of benzophenone-K-ketyl (^{2}).

The data obtained therefore indicate a significant localization of the unpaired electron on the carbonyl carbons.

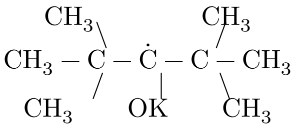
For dilute solutions of benzil-K-ketyl in 1,2-dimethoxyethane and

[benzil-K-ketyl structure]

Fig. 1. EPR spectra: a −phenanthrenequinone-K-ketyl, −benzil-K-ketyl, −hexamethylacetone-K-ketyl, −diethylpinacolin-K-ketyl in 1,2-dimethoxyethane

tetrahydrofuran a spectrum was obtained in which 7 components of the h.f.s. are only just discernible (Fig. 1). It was not possible to resolve the spectrum well, since the splitting is very small (the distance between component maxima is 0.6-0.7 gauss). However, the spectrum obtained also indicates that, as in benzophenone-K-ketyl (^{2}), the ortho and para positions in the benzene rings are equivalent, while the small splitting and the narrowness of the absorption line testify to an even more significant localization of the unpaired electron on the carbonyl carbons than in phenanthrenequinone-K-ketyl.

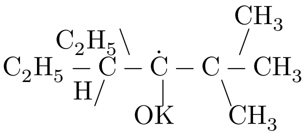
Hexamethylacetone K-ketyl in dimethoxyethane gave a very narrow singlet signal, 0.5-0.7 gauss wide, over a fairly wide range of concentrations (Fig. 1c).



$$\begin{array}{ccccccc} & CH_3 & & & & CH_3 & \\ CH_3 - & C & - & \dot{C} & - & C & - CH_3 \\ & CH_3 & & OK & & CH_3 & \end{array}$$

The narrowness of the line indicates a high degree of localization of the unpaired electron on the carbonyl carbon. The absence of hyperfine structure is explained by the fact that near the carbonyl carbon, on which the unpaired electron is localized, there are no nuclei with nonzero spin. The molecule contains protons, but they are bound only to the γ-carbons, and, as is known, γ-protons do not produce splitting (^{4}).

Diethylpinacolin K-ketyl in dilute solutions gave a completely resolved doublet (splitting 2.1 gauss) (Fig. 1d). Apparently, the splitting is caused by the single β-proton bound to the β-carbon.



$$C_2H_5-\underset{H}{\overset{C_2H_5}{C}}-\underset{OK}{\dot{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

For triethylpinacolin K-ketyl, a narrow singlet signal with two very weak side components was obtained. Analysis of the spectrum and comparison with the spectrum of diethylpinacolin K-ketyl showed that the weak side components are due to a very small admixture of diethylpinacolin K-ketyl. The point is that triethylpinacolin was synthesized by us by ethylation of diethylpinacolin, and in isolating triethylpinacolin we were unable to remove completely the impurities of diethylpinacolin.

In general, the data obtained for aromatic metal ketyls show that the distribution of spin density agrees well with the idea of additional stabilization of free radicals through delocalization of the unpaired electron into the ring. But, probably, this delocalization is not the chief factor determining the existence of metal ketyls, since to a considerable extent the unpaired electron is concentrated on the carbonyl carbon. The data on aliphatic metal ketyls confirm this assumption.

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