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Benzophenone K-ketyl; Benzil K-ketyl; Fluorenone K-ketyl

Figure 1: Benzophenone K-ketyl; Benzil K-ketyl; Fluorenone K-ketyl

Abstract

Full Text

Chemistry

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Distribution of Spin Density in Some Metal Ketyls

(Presented by Academician B. A. Arbuzov, 21 V 1962)

Recently G. Vincow and G. K. Fraenkel (^{1}) calculated spin densities in a series of semiquinone ions by the molecular-orbital method. Their calculations agree well with experimental results obtained from the hyperfine structure of EPR spectra in these radicals. Ya. K. Syrkin and V. M. Kazakova (^{2}-^{4}) investigated the EPR spectra of free radicals of another type containing oxygen atoms—metal ketyls—and found the distribution of spin density from the experimental hyperfine-splitting constants by the well-known McConnell equation (^{5}).

The present work is an attempt at a theoretical calculation of spin densities in benzophenone K-ketyl, benzil K-ketyl, and fluorenone K-ketyl.

In doing so, it was assumed that ketyl formation occurs through transfer of an electron from the metal atom to the lowest vacant level of the ketone. The calculations were carried out using the simple MO LCAO method in the usual approximations of this method. To find the spin density, the squares of the coefficients at the atomic orbitals in the molecular orbitals corresponding to the lowest vacant levels of benzophenone, benzil, and fluorenone were determined. To take heteroatoms into account, the assumption was introduced that the Coulomb integral of the oxygen atom is equal to $\alpha + \delta\beta$, and the resonance integral of the C=O bond is $\gamma\beta$, where α and β are, respectively, the Coulomb integral of the carbon atom and the resonance integral of the CC bond.

Table 1

$\delta = 0,\ \gamma = 1.732$

Atom position	Spin densities	Spin densities
	exp.	theor.
1	–	0.22
2	–	0.04

Atom position	Spin densities	Spin densities
3	–	0.10
4,8 (ortho)	0.09	0.06
5,7 (meta)	0.03	0.02
6 (para)	0.09	0.11

In the calculation, in each case more than 40 values of the parameters δ and γ were used; moreover, the values of δ were chosen in all cases from 0 to 3, and the values of γ from 1 to 2 for benzil K-ketyl and fluorenone K-ketyl, and from 1 to 3 for benzophenone K-ketyl. These quantities include the limits for oxygen parameters usually used in the literature ([1], [6]).

Table 1 compares the spin densities in benzophenone K-ketyl,

found experimentally (2) and calculated by the LCAO MO method for values of the parameters δ and γ corresponding to the best agreement with experiment.

The calculation showed that in benzophenone-K-ketyl, for $\gamma < 2,\ 0 < \delta < 1$, changes in δ have almost no effect on the spin-density distribution. At $\gamma = 2.6$ and $\delta = 1$, the spin density on the carbon atoms bonded to protons changes hardly at all in comparison with the spin density given in Table 1. A noticeable difference is observed only in the spin density on the oxygen atom, the carbon atom of the carbonyl group, and in position 3. Although usually the limits of γ do not exceed 2, in the present case the value $\gamma = 2.6$ is probably associated with the large bond energy of $C = O$ in the ketone.

Table 2

$$\delta = 1, \quad \gamma = 1.414$$

Atom position	Spin densities	Spin densities
	exp.	theor.
1	–	0.194
2	–	0.164
3	–	0.008
4,8 (ortho)	0.035	0.045
5,7 (meta)	0.01	0.003
6 (para)	0.035	0.038

Calculation of the spin densities in benzil-K-ketyl also confirms the experimental picture of the splittings of the EPR spectra in this radical (3,4). The narrowness of the entire absorption line indicates a considerable localization of the unpaired electron on the carbon atoms of the carbonyl groups. The calculations (Table 2) show that almost 1/3 of the total spin density is located on atoms 2 and

2′. The spin densities in the ortho and para positions are almost equal, and the splittings caused by the presence of unpaired-electron density in the meta positions must be very small.

In benzil-K-ketyl, with increasing δ, the spin densities in the ortho and para positions and on the carbon atoms of the carbonyl groups increase somewhat, while, within a single value of δ, an increase in γ is reflected in a decrease of the spin density on the carbon atoms of the carbonyl groups and in the ortho positions and an increase in the para positions. Thus, in the present case both δ and γ affect the change in the spin-density distribution to an equal extent.

Table 3

$\delta = 1, \quad \gamma = 1$

Atom position	Spin densities exp.	Spin densities theor.
1	–	0.193
2	–	0.246
3	–	0.036
4	0.04	0.060
5	0.018	0.025
6	0.04	0.069
7	0	0.014
8	–	0.076

In fluorenone-K-ketyl, calculation of the spin densities explains the EPR spectrum, whose hyperfine structure consists of five triplets with spacings of 0.9 G between the components of the quintet and 0.4 G between the components of each triplet (4). At $\delta = 1$, $\gamma = 1$, it turns out that the spin density on atoms 7 and 7′ is extremely small (Table 3), and proton splittings at these atoms are practically not observed. The spin densities in positions 4 and 6, 4′ and 6′, are almost equal, and the presence of four atoms with similar unpaired-electron density gives a quintet, the components of which are then split into triplets. This splitting is caused by the interaction of the unpaired electron with protons in positions 5 and 5′.

The present calculations, like the data of Vinkau and Frenkel, show that, with an appropriate choice of the parameters δ and γ, application of the simple molecular-orbital method gives good agreement with experiment also for radicals containing heteroatoms, although the first application of the theory to the calculation of spin densities related to purely hydrocarbon radicals.

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Note: Figure translations are in progress. See original paper for figures.