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FREE RADICAL SPIN RESONANCE SPECTRA OF OX-INDIGO

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Abstract—The ESR spectra of ox-indigo radicals obtained under various conditions are discussed. It is proposed that ox-indigo differs from other indigoid molecules in that its semi-reduced form contains a chelate ring. Evidence for this is the observation that the molecule may form a metallic complex with potassium. The ESR spectrum of this complex is shown and analyzed.

1. INTRODUCTION

AT THE time of the first synthesis of ox-indigo by Fries and Fink[1] it became apparent that the newly made molecule differs in a peculiar way from the other members of the large indigoid family. Thio-indigo and seleno-indigo are vat dyes of great stability and fastness, of about the same dull red colour and having very similar ESR spectra.[2] Ox-indigo is bright lemon yellow, does not easily form a vat and is not very stable. In a water-alcoholic alkaline solution it rapidly disintegrates into a red substance, by opening of the cumarone rings. Because of this instability ox-indigo cannot be synthesized in a way analogous to the production of other indigoids by oxidation of cumarone, nor can it by the usual alkaline reduction be applied as a vat dye.

Ox-indigo hardly dissolves in any of the common organic solvents except xylene. In contrast with thio-indigo it dissolves well in glacial acetic acid. If zinc dust is added to such a solution a soluble leuco compound is formed which is colourless.

2. EXPERIMENTAL TECHNIQUE

We used a standard ESR spectrometer of Varian Associates. The microwave power was kept exceptionally low. Its frequency of 9·5 kmc/s was stabilized to a rectangular sample cavity of the reflection type resonating in the TE_{102} mode. The magnetic field modulation was set to very small amplitude and was at 100 kc/s, producing side bands at about ±35 mG. In our experiments this may have been one of the limiting factors for the smallest observable width of the spectral lines. The magnet has flat pole faces of 30 cm diameter and 6·3 cm separation and was run at about 3400 G. The motor driven field sweep was usually set to about 40 mG per second and, in case of high resolution, to 5 mG per second. The recorder had a response time of 1 second for full scale.

The fine structure lines of the ox-indigo radicals may be very narrow. Without difficulty in a standard run we recorded lines of 60 mG width (between points of maximum slope). With special care the linewidth could be reduced to 20 mG, lines of 15 mG apart being clearly separated.

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[1] K. Fries and G. Fink, *Ber. Dtsch. Ges.* **41**, 4271 (1908); *Ibid.* **44**, 124 (1911); see also K. Fries, A. Hasselback and L. Schroeder, *Ibid.* **405**, 346 (1914).

[2] F. Bruin, F. W. Heineken, and M. Bruin, *J. Org. Chem.* (1963). In press.

The sample cavity contained a small quartz dewar in which the sample tube was placed. Cooled nitrogen gas could be passed through it and the temperature of this gas controlled with a thermostat.

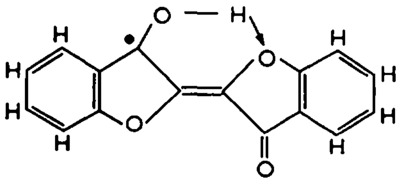
The magnetic field scale was calibrated by running a standard sample. For this purpose usually a tube containing a red thio-indigo radical[3] in acetone was used, the ESR spectrum of which was calibrated against tetracene in sulphuric acid.[4] In this way in all experiments an inaccuracy in the splitting constants of less than 3% was easily secured. This procedure was further checked against proton resonance with a standard NMR field meter which was compared directly to a frequency standard.

The samples were prepared in quartz tubes of 4 mm O.D. When applying the alkali mirror technique, oxygen gas was first removed from the solvent by successively freezing and thawing it several times *in vacuo*. The alkali mirror was produced *in vacuo* by evaporation after heating the metal in a special arm of a conventional pyrex structure and the solution poured into the tube after having made sufficient contact with the mirror.

3. RESULTS AND DISCUSSION

A. *Ox-indigo semiquinone.* As it is to be expected that ox-indigo in glacial acetic acid forms a redox-system with its leuco, we tried to observe the ESR spectrum of the corresponding semiquinone. Such a spectrum was reproduced in an earlier publication.[2] Comparison with previously obtained data[3] revealed that the spectrum of ox-indigo consists of two partly overlapping spectra, each of which is similar in structure to the one of thio-indigo. This led to an interpretation involving a relatively large doublet splitting, due to a single bonded proton, and four different triplet splittings, due to four different pairs of equivalent aromatic ring protons.

For other indigoid dyes[2] (thio-indigo, seleno-indigo, dehydro-indigo) the odd-electron density in the outer aromatic rings was found to be approximately proportional to the electronegativity of the hetero-atoms. For ox-indigo, however, the hetero-atoms (oxygen) have large electronegativity and the splittings, although large, are still somewhat smaller than what one would expect on the basis of the above proportionality. The new data reported on below indicate that the extra proton in the ox-indigo semiquinone may have formed a hydrogen bridge in a chelate-ring structure like:



The ring formation stabilizes the *trans*-configuration in a way similar to that in which hydrogen bridges stabilize the *trans*-form in the indigo molecule.

The radical in glacial acetic acid is greenish and the spectrum shows a doublet splitting of 1·64 G due to the bonded proton. The other splittings may be seen in the first line of Table 1.

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[3] M. Bruin, F. Bruin and F. W. Heineken, *J. Chem. Phys.* **37**, 135 (1962).

[4] H. W. Brown and J. S. Hyde, *J. Chem. Phys.* **37**, 368 (1962).

B. *Radicals with lithium and sodium mirrors.* On the basis of the assumption of a chelate ring one would expect the formation of metal chelates when ox-indigo is brought into contact with mono- or di-valent metal ions. We therefore obtained ESR spectra of ox-indigo dissolved in oxygen-free dioxane with, respectively, lithium, sodium, potassium and cesium mirrors. Rubidium was excluded because it has two natural isotopes with different nuclear spins which would complicate the analysis.

The spectra of radicals prepared at room temperature by lithium and sodium mirrors turned out to be the same (see Fig. 1). From this it follows that the radicals concerned cannot be complexes with different metals. In both cases either the same radical or the same mixture of radicals is formed. A lithium mirror can only be made at relatively high temperature and experiments were carried out so as to make sure that the solvent reacted with the lithium metal only and not with sodium impurities.

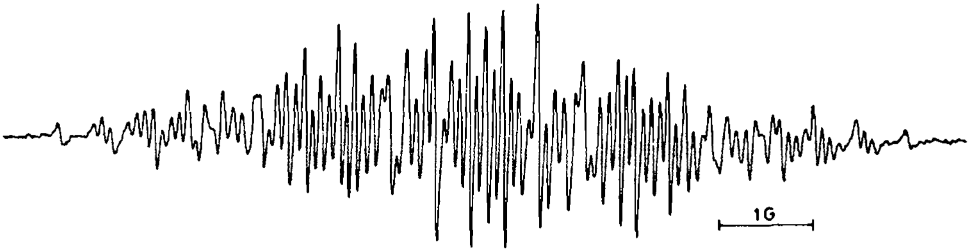


FIG. 1. ESR spectrum of an ox-indigo radical dissolved in dioxane at room temperature and prepared with a Na-mirror under vacuum.

If the dioxane solution is cooled to near the freezing point the spectra produced by lithium or sodium are almost the same as the one obtained with glacial acetic acid. Surprisingly, however, for the organic solvent all splitting constants are reduced by a factor of roughly 1·3 as compared to the acid solution. The splitting constants, as obtained from our analysis, are given in Table 1. The first line in this Table refers to the radical in glacial acetic acid, the others to the radicals in dioxane, all at room temperature.

TABLE 1. TOTAL WIDTH AND SPLITTING CONSTANTS IN GAUSS FOR THE ESR SPECTRA OF SEMIQUINONES AND METAL COMPLEXES OF OX-INDIGO

Ion	I	Total width	Doublet, quartet or octet	Triplets			
				4,4′	5,5′	6,6′	7,7′
H	1/2	11·6	1·64 (d)	1·78	0·59	2·04	0·68
Li, Na	3/2	8·8	1·22 (d)	1·37	0·42	1·57	0·52
K	3/2	8·0	0·086 (q)	1·36	0·37	1·54	0·51
Cs	7/2	22	1·08 (o)	—	—	—	—

When the temperature of the samples prepared in dioxane is decreased from about +30° to near the freezing point of the solvent (+12°) one observes remarkable changes in the recorded ESR spectra. For example the intense central lines of the spectrum shown in Fig. 1 disappear almost completely. This phenomenon can be explained as follows. In glacial acetic acid only the *trans*-form of the radical with the chelate ring is observed. In dioxane at room temperature, in addition to the *trans*-form, also the *cis*-form with a single non-chelating hydrogen occurs. When the solvent is cooled and the viscosity increases, gradually all molecules convert to the more stable *trans*-form and form a chelate ring. The spectrum of Fig. 1 must then be considered to be due to a mixture of about equal amounts of radicals in *cis*- and *trans*-form. As follows from the spectra the doublet splitting due to the single proton of the *cis*-form would be 0·4 G, whereas for the chelate ring the corresponding splitting would be 1·22 G.

No such mixture of spectra is observed for the potassium complex (see below) so that apparently in this case the *cis*-form does not exist in an appreciable amount. We observed a similar effect for indigo in ethanol. Upon cooling the sample containing the indigo radical, new narrow fine structure lines appeared and became quite intense at the cost of other lines. No such effect was found for the radicals of thio-indigo in ethanol or acetone. The *cis*- and *trans*-forms of the red thio-indigo dyestuff are well known and have been separated. Contrary to the dye itself (and contrary also to the radicals discussed above) the thio-indigo radicals have a central bond which is predominantly single, and the *cis*- and *trans*-forms can not be separated physically. Perhaps the variation in linewidth, as observed for a number of thio-indigo derivatives[3] must be ascribed to an averaged out *cis-trans* effect, as a result of rapid rotation around the central bond. The investigation of these interesting phenomena requires further investigation before definite conclusions can be drawn.

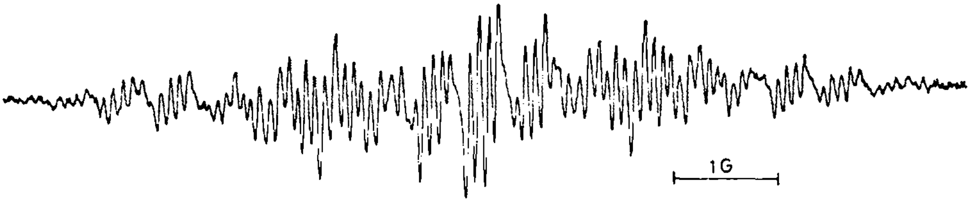
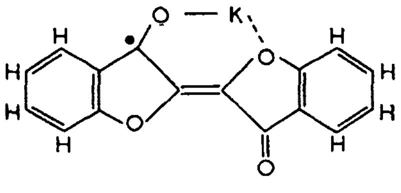


FIG. 2. ESR spectrum of the K-ox-indigo metal complex in dioxane at room temperature

C. *Potassium mirror*. The spectrum of the ox-indigo radical as obtained in dioxane at room temperature with a potassium mirror is shown in Fig. 2. It is completely different from the previous ones, which is an indication that in this case a metallic chelate is formed. Narrow quartets of equal intensity are easily recognized and, contrary to the former spectra, the spacings and intensities remain the same even under extreme resolution. The quartets must therefore be attributed to the nuclear spin of 3/2 of potassium. The structure of the complex would be of the form:



The quartet splitting constant is only 86 mG. The coupling of the potassium ion with the ox-indigo molecule is about 8 times smaller than the coupling of the sodium atom with 2,2′-dipyridyl,[5] where the corresponding splitting constant is 3·80 G. The splittings due to the aromatic ring protons are the same as for lithium and sodium,

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[5] A. Zahlan, F. W. Heineken, M. Bruin, and F. Bruin, *J. Chem. Phys.* **36**, 2783 (1962).

within the observational error. Temperature dependence could not be investigated because of the instability of the radical.

D. *Cesium mirror*. For a cesium chelate each fine structure line would split into 8 components ($I = 7/2$). We observed a spectrum of 21 regularly spaced broad lines at 1·08 G mutual separation, in agreement with what would be expected for a metallic complex. The abundance of fine structure lines apparently diffused the spectrum, so that in this case the aromatic splitting constants could not be determined.

If one compares the chelate splittings of Table 1 with the corresponding values μ/I, one may find the amount of bonding between the ox-indigo structure and the complexing metal ion. One thus observes about the same bonding for H and K and an increase of bonding in the series H, K, Cs. Apparently the gap in which the ions are trapped is relatively large, giving a best fit for cesium.

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