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Fig. 1

Figure 1: Fig. 1

Abstract

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STUDY OF PHOTOCHEMICAL REACTIONS IN COMPLEX OXALATES BY THE E.P.R. METHOD

(Presented by Academician A. A. Grinberg, 1 XII 1964)

The present work is part of our systematic study of the effect of ultraviolet and γ-radiation on complex compounds of transition metals. Most of the compounds to be discussed in this and the following communication have already been considered by us from the standpoint of photo- and radiation-chemical transformations at ordinary temperatures in aqueous solutions. Some results of these studies have been published (^{1}).

Of interest also is the detection, by means of the e.p.r. method, of free radicals formed under the action of radiation on frozen solutions of complex compounds, in particular atomic hydrogen (formed in the process of reduction of water). The question of the formation of hydrogen atoms in the course of the electron transfer

variable-valence metal —water

or

mononegative anion (for example, I^-) —water

under the action of ultraviolet radiation has been discussed in the literature more than once. In some cases (^{2}) the liberation of molecular hydrogen could be established; later (^{3}), under special conditions excluding recombination of atomic hydrogen, its presence in irradiated systems was proved from the characteristic e.p.r. spectrum.

Fig. 1. E.p.r. spectrum of a frozen solution of 0.1 mole/liter $K_3[Co(C_2O_4)_3]$ in 20% H_2SO_4 irradiated at 77°K with ultraviolet light; **a**—general view, **b**—central line of the spectrum recorded at a slower speed; the arrow indicates the position of the line from DPPH.

Fig. 2. Central part of the spectrum of Fig. 1a at higher gain

Figure 2: Fig. 2. Central part of the spectrum of Fig. 1a at higher gain

In the present communication we give the results of measurements of e.p.r. spectra in solutions irradiated with ultraviolet light at 77°K and containing complex oxalate ions: $[Co(C_2O_4)_3]^{3-}$, $[Cr(C_2O_4)_3]^{3-}$, $[Fe(C_2O_4)_3]^{3-}$, $[Mn(C_2O_4)_3]^{3-}$, as well as the simple oxalate ion $C_2O_4^{2-}$ in the case of $K_2C_2O_4$ and $[Co(NH_3)_6]_2(C_2O_4)_3$.

Dilute sulfuric acid and an aqueous-alcohol mixture were used as solvents. The concentration of sulfuric acid was varied from 0.5 to 20%, and the concentration of the salts from 0.025 to 0.1 M. The frozen solutions were irradiated in quartz tubes, in a Dewar vessel with liquid nitrogen, near a PRK-7 lamp. The e.p.r. spectrum was recorded at a temperature of 77°K on an RE-1301 radiospectrometer at a frequency of about 9335 MHz. The first or second derivative of the true absorption line could be recorded.

Figure 1a reproduces the e.p.r. spectrum (first derivative) of an irradiated solution of $K_3[Co(C_2O_4)_3]$ in 20% H_2SO_4. Attention is drawn to $\cdots$

first of all, a doublet with a splitting of ≈ 505 oersted, which is undoubtedly due to the presence of hydrogen atoms. A doublet with a similar splitting has been observed for free hydrogen atoms (4), and also repeatedly in experiments where stabilization of atomic hydrogen in a rigid matrix is possible (3, 5). In addition to the hydrogen doublet, in the central part of the spectrum near the g-factor, equal to 2.0036, there is a somewhat asymmetric line, which is shown in Fig. 1b at slow recording. A similar line shape is characteristic of paramagnetic centers with an anisotropic g-factor in glassy or powder specimens (6). From the line shape it may be concluded that the symmetry of the g-factor tensor is close to axial, while the magnitude of the anisotropy is small in comparison with the width of an individual line.

Fig. 2. Central part of the spectrum of Fig. 1a at higher gain

If the central part of the spectrum is recorded at increased amplification, then on both sides of the central line discussed above additional weaker lines are observed (Fig. 2). These two weak lines belong to one paramagnetic center, since they always appear together with unchanged relative intensity, and are lines of hyperfine structure (h.f.s.). Thus, in the irradiated specimens we have three types of paramagnetic centers: the first (A)—hydrogen atoms, giving a doublet with a splitting of 505 oersted; the second type (B) is characterized by a single line in the center of the spectrum; and the third type (C)—a doublet with a total splitting of about 130 oersted.*

The formation of three types of radicals in irradiated solution of $K_3[Co(C_2O_4)_3]$ was followed down to an H_2SO_4 concentration of 1%.

With decreasing H_2SO_4 concentration the relative intensity of the three groups of lines changes: the intensity of line B, for example, decreases in comparison with group of lines C.

An analogous spectrum with three groups of lines was also obtained for solutions in 20% H_2SO_4 of the following salts:

$$K_3[Fe(C_2O_4)_3],\ [Co(NH_3)_6]_2(C_2O_4)_3 \text{ and } K_2C_2O_4.$$

It was observed that the intensity of the hydrogen doublet decreases together with the intensity of line B in the series

$$Fe(C_2O_4)_3^{3-} > Co(C_2O_4)_3^{3-} > Cr(C_2O_4)_3^{3-},$$

so that for the last complex only lines A and B are observed; the lines of group C evidently disappear in the noise.

The oxalate complex of Mn^{3+}, $K_3[Mn(C_2O_4)_3]$, is unstable in sulfuric acid, and therefore its solution in a 1:1 water–alcohol mixture was taken. Already after five-minute UV irradiation at $77^{\circ}K$ the specimen becomes decolorized and gives the EPR spectrum shown in Fig. 3 (the second derivative is recorded). Again the hydrogen doublet (A) and the single line in the center (B) are visible; the lines of group C cannot be observed (if they are present) against the background of the spectrum of divalent Mn^{2+} ions appearing in the specimen after irradiation. Solutions of $K_3[Fe(C_2O_4)_3]$ and $K_3[Co(C_2O_4)_3]$, when irradiated in a water-alcohol mixture, also show in the EPR spectrum a doublet from hydrogen atoms. Thus, it may be said that hydrogen atoms can sta– be stabilized not only in aqueous solutions of acids (H_2SO_4, $HClO_4$, H_3PO_4, etc.), but also in an aqueous solution of ethyl alcohol.

On the basis of the results obtained upon irradiation of trioxalate complexes of Fe^{3+}, Co^{3+}, Cr^{3+}, Mn^{3+}, and also taking into account data on the irradiation of complexes of the hexammine type, we may say that the nature of the coordinated ligand strongly affects the appearance or absence of H atoms in the course of the action of UV radiation on frozen systems. Furthermore, irrespective of the nature of the complex-forming metal, in all the oxalates considered a hydrogen signal was observed in the EPR spectra. The intensity of the spectral lines indicates that the yield of hydrogen atoms is maximal in the case of the oxalate of Fe^{3+} and minimal in the case of Cr^{3+}.

It may be considered that the primary act in the action of UV-light quanta on the coordination compounds examined is excitation of an electronic transition ligand—central atom, which leads to the appearance of Me^{2+} : Fe^{2+}, Co^{2+}, etc.,

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* *Note added in proof.* It was established later that this doublet belongs to the formyl radical HCO.

Fig. 3. EPR spectrum (second derivative) of irradiated, at 77°K, with UV light, a 0.1 mole/liter solution of $K_3[Mn(C_2O_4)_3]$ in a water-alcohol mixture (1:1)

Figure 3: Fig. 3. EPR spectrum (second derivative) of irradiated, at 77°K, with UV light, a 0.1 mole/liter solution of $K_3[Mn(C_2O_4)_3]$ in a water-alcohol mixture (1:1)

and also $C_2O_4^-$, indications of the very active character of which may be found in Weiss (7). It is quite possible that the central line of the EPR spectrum in all irradiated oxalate complexes is due to the presence of the ion-radical $C_2O_4^-$.

Fig. 3. EPR spectrum (second derivative) of irradiated, at 77°K, with UV light, a 0.1 mole/liter solution of $K_3[Mn(C_2O_4)_3]$ in a water-alcohol mixture (1 : 1)

Thus, the question of the formation of hydrogen atoms is reduced to the reduction of water molecules present in the hydration shell of the complex, the "acidity" of which near triply negatively charged complex ions, by virtue of electrostatic considerations, may prove higher than that of water molecules in the bulk of the solution. Apparently, when the matter concerns the greatest yield of H atoms in the case of $K_3[Fe(C_2O_4)_3]$, it should be assumed that the concentration of Fe^{2+} is also considerably higher here. However, there is still another point of view regarding the mechanism of formation of hydrogen atoms. This is the primary photodissociation of the complex with liberation of oxalate ions, which can reduce water:

$$C_2O_4^{2-} + HOH \rightarrow C_2O_4^- + H + OH^-,$$

just as this apparently occurs in the case of irradiation under the same conditions of $K_2C_2O_4$ and $[Co(NH_3)_6]_2(C_2O_4)_3$.

It should be noted that processes associated with the reduction $Co^{3+} \rightarrow Co^{2+}$ were observed by us upon irradiation with UV and γ-rays of certain complexes of the cationic type of Co, and especially upon irradiation of an aqueous solution of $K_3[Co(C_2O_4)_3]$ at room temperature. There is no reason to deny that analogous processes also occur in the condensed phase.

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