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The Photochemistry of Potassium Trisoxalatoferrate(III) Trihydrate in the Solid State*

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The gaseous and solid state products of decomposition on uv exposure of polycrystalline $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ have been investigated by mass-spectrometry, ir- and Mössbauer spectroscopy, and chemical and X-ray phase analysis. CO_2 and CO are obtained as photoproducts. The volume ratio, $CO:CO_2$, generated depends on the exposure conditions and approximately equals 1:3 on photodecomposition in air and 1:2 on decomposition in vacuum. Comparison of the experimental and literature data leads to the following conclusions. The Fe(II)-containing final products of photolysis, radiolysis, and low-temperature (250–260°) thermal decomposition are identical; FeC_2O_4 is missing among the principal final solid state products. Arguments are presented in favor of the view that the Fe(II)-containing final products of photodecomposition is a polymer of composition $(K_2[Fe(C_2O_4)_2])_n$. On the basis of the experimental and literature data, the flow sheet and stoichiometry of the photodecomposition has been determined. A comparison is made of the spectral dependences of photoconductivity and of photolysis in air. The type of charge carrier is established. Questions related to the mechanisms of photodecomposition are discussed.

Introduction

Potassium ferrioxalate attracts the attention of investigators as a model compound for the study of the various factors bearing on the mechanism of solid state photolysis (*1*), and it is also of applied significance as an essential component in silverless photosensitive systems (*2*). In spite of this, the photodecomposition of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ has been investigated rather incompletely. In particular, there is missing convincing experimental data on the composition of the final products. Analysis of the literature leads to the conclusion that existing ideas about the final products of the photodecomposition are largely based on incorrect extrapolation to photolysis of crystalline salts from ideas on products of photolysis in aqueous solutions (FVR).

Upon uv exposure of aqueous solutions of chelate complexes of the type

$$[Me(III)(C_2O_4)_3]^{3-}, \quad Me(III) = Co, Fe, Mn \tag{1}$$

oxidation–reduction decomposition occurs. The final products of the FVR are $[Me(C_2O_4)_2]^{2-}$, Me(II), $C_2O_4^{2-}$, and CO_2 (*3*). In the case of FVR of potassium ferrioxalate, the formation of free Fe^{2+} and $C_2O_4^{2-}$ leads to precipitation of slightly soluble FeC_2O_4. In photolysis of polycrystalline potassium ferrioxalate (*4*) (by uv exposure in air at room temperature), CO_2 and FeC_2O_4 are assumed as products

$$2K_3[Fe(C_2O_4)_3]\cdot 3H_2O = 2FeC_2O_4 + 3K_2C_2O_4 + 2CO_2 + 6H_2O. \tag{2}$$

The conclusion in Ref. (*4*) about the practicability of the scheme described in Eq. (2) is based fundamentally on a comparison of the

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diffuse reflectance spectra of photolyzed samples and FeC_2O_4, which, given the slight characteristicness of these spectra, is very unconvincing.

Only in Ref. (*1*) is a more detailed experimental investigation of the photoproducts undertaken. Upon mass spectrometric analysis, besides CO_2, formation of CO is found. The investigation was carried out on single crystals, polycrystalline powders, and layers of microcrystals deposited on a support (subsequently, we shall refer to these samples as films). Evolution of CO_2 occurs for samples of all three types. However, upon irradiation of the single crystals and of the powders, CO is not detected, or is found only in small amounts. It was stated that attempts to identify the Fe(II) produced through X-ray photographs of the photoproducts were unsuccessful, allowing only the conclusion that it was not FeC_2O_4, and that $K_2C_2O_4$ was among the products.

It is known that photolysis, radiolysis, and thermal decomposition frequently lead to identical final products (*3*). Consequently, it was expedient to collect information on the radiolysis and NTTR (low-temperature thermal decomposition) for comparison with data on the photodecomposition.

The authors of Ref. (*4*) used NTTR and photolysis of polycrystalline salts of potassium with complexes of the type (1) and came to the conclusion that their decomposition on NTTR and uv irradiation is identical and goes by the scheme

$$2K_3[Me(C_2O_4)_3]\cdot 3H_2O = 2K_2[Me(C_2O_4)_2] + K_2C_2O_4 + 2CO_2 + 6H_2O. \quad (3)$$

Only the photolysis of potassium ferrioxalate, according to the data of Wendlandt and Simmons (*4*, *5*) is specific and goes to other final products. Data for the NTTR of potassium ferrioxalate in air corresponding to the decomposition scheme described by Eq. (3) are contained in Ref. (*6*). We note that, above all, the authors (*6*) proceeded with the assumption that CO_2 is the only gaseous product.

For the radiolysis of polycrystalline salts of potassium with complexes of the type (1) under the influence of ^{60}Co γ-irradiation, the following scheme of decomposition was proposed (*7*)

$$2K_3[Me(C_2O_4)_3]\cdot 3H_2O = K_2[Me(C_2O_4)_2] + K_4[Me(C_2O_4)_3] + 2CO_2 + 6H_2O. \quad (4)$$

For this the authors carried over to radiolysis of polycrystals the mechanism accepted in the literature for interpreting FVR. In the FVR investigation it is supposed that there are formed not only the complexes $[Me(C_2O_4)_2]^{2-}$, but also complexes that are considerably less stable in solution, $[Me(C_2O_4)_3]^{4-}$. In (*7*) it is assumed that the latter are more stable in the solid phase, so that on radiolysis equal amounts of the two complexes are formed.

With the help of Mössbauer and ir spectra, there was established in Refs. (*8*–*10*) presence of two principal radiolysis products containing divalent iron. Both products appeared to be compounds of high-spin, octahedrally coordinated Fe(II). One of these was stable (we call it "phase I"); the other compound was metastable ("phase II"). In Ref. (*10*), phases I and II were identified as *trans*- and *cis*-$K_2[Fe(C_2O_4)_2(H_2O)_2]$, respectively. In Ref. (*9*), phase I was identified as $K_6[Fe_2(C_2O_4)_5]$, i.e., the authors put forth a suggestion of formation of tetradentate oxalate bridges

$$[(C_2O_4)_2FeO_2C_2O_2Fe(C_2O_4)_2]^{6-}. \quad (5)$$

Phase II in Ref. (*9*) is identified as $K_2[Fe(C_2O_4)_2(H_2O)_2]$.

In Ref. (*11*) a Mössbauer investigation of NTTR of polycrystalline potassium ferrioxalate was carried out, and it was shown that the final Fe(II)-containing product was identical to the phase I that is formed on radiolysis.

In the present work, a detailed analysis is carried out of the final gas-phase and solid solid state products of the photolysis of polycrystalline potassium ferrioxalate with the aim of determining to what extent the actual crystalline texture of the compound and size effects control the difference of decomposition products from the products of FVR. In the process, we use experimental data on the Mössbauer investigation of the photolysis of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ from Ref. (*12*). These studies were expanded; Mössbauer spectra of NTTR and supplementary spectra of photolyzed specimens were obtained [the conditions and operations were as described in (*12*)] ir spectra and X-ray photographs of photolyzed specimens and of assumed photo products were taken.

Experimental Details

The original salt was synthesized by a standard procedure (*13*). Three kinds of samples were employed: polycrystalline powders or single crystals from aqueous solutions and films deposited on quartz supports [deposition out of aqueous solutions was achieved by use of ethanol with conditions and methods as described in (*14*)]. The entire operation of synthesis and preparation of the specimens was carried out under inactive illumination. Ultra violet irradiation was performed with PRK-7, PRK-2M, and DRSH-250 lamps. Control by Mössbauer and ir spectra showed that exposure with or without light filters led to identical results. Some heating which takes place on irradiation without the light filters favors conversion of intermediate products to final end-products of photolysis. An assembly of mercury and interference filters was used for the monochromatic radiation. The polycrystalline powders and, in some cases, single crystals were crushed in an agate mortar. Films that allowed consecutive alternate-side irradiation were used to favor maximum extent of photoconversion. Depending on the type of specimens, irradiation was carried out from 10 to 30 hr.

The composition of gaseous photoproducts was determined by means of a mass spectrometer of the omegatron type IPDO-1. The instrument allowed recording of the gas spectra and tracing of an uninterrupted record of the ion current for selected mass numbers. The cell with the sample had a quartz window and was pumped out to a residual pressure of the order of 10^{-7}–10^{-8} mm Hg. Up to the beginning of measurements by determination of the composition of the photoproducts, the specimens were conditioned in vacuum for about 48 hr. The spectra of the residual gases in the vacuum system were recorded before irradiation. To eliminate possible error arising from coincidence of m/e for N_2 and CO and also from possible predissociation of CO_2 into CO at the cathode, a nitrogen trap was placed between the cell with the sample and the omegatron lamp.

Infrared spectra were taken with IKS-14, IKS-22B, and Perkin–Elmer 457 spectrophotometers. The region from 250 to 1800 cm^{-1} was investigated, using pressed pellets in KBr and CsI matrices. X-ray investigations were carried out with a URS-50 IM diffractometer as well as by a photographic method with RKD-57 camera using iron and chromium anodes.

The composition of the gaseous products for specimens photolyzed in air was determined by chemical analysis. The chemical analysis was based on reaction of CO with a solution of palladium chloride and of CO_2 with barium hydroxide solution. Qualitative experiments for determination of CO and CO_2 were carried out on specimens of various types. An approximate quantitative evaluation of the CO/CO_2 ratio was made for the specimens in the form of films. The experiment was carried out in the following manner.

The film which was deposited on the wall and bottom of a quartz flask was exposed through the bottom of the flask. The gas–air mix containing the photoproducts was admitted under hermetically sealed conditions through glass tubes into two flasks, one of which contained a solution of $PdCl_2$ while the other had $Ba(OH)_2$. Change in the concentration of $Ba(OH)_2$ was determined conductimetrically, and the formation of metallic palladium was established quantitatively by a standard colorimetric method (*15*). Consideration was taken of the fact that the absorption reactions of CO and CO_2 proceed at different rates, during which, on absorption of CO by $PdCl_2$ solution, CO_2 is formed. With full account taken of the correction arising from these factors, a CO and CO_2 mixture led into the system in a ratio of 1 : 1 is measured after 24 hr to have a CO/CO_2 ratio of 0.8. The electrical conductivity of the barium hydroxide solution and the colorimetric analysis were carried out 24 hr after irradiation of the salt, at which time the standard correction was taken into account.

Experimental Data and their Discussion

Mass spectrometric analysis of the gas generated on monochromatic uv irradiation of potassium ferrioxalate showed that for both CO_2 and CO the threshold of sensitivity is located around 500 nm. Rate curves for the yield of CO and CO_2 had an initial straight-line portion with subsequent change to saturation. Saturation corresponds to equality of rates of pumping out and gas evolution. Since the form of the rate curves is partly determined by the rate of evacuation of the gas during the time of measurement, the less affected beginning portions of the curves were used for determination of the value of the ratio CO/CO_2. Over the entire spectral range investigated that is higher than the threshold of sensitivity, the CO/CO_2 ratio was constant and did not depend on the intensity of illumination. The ratio was larger for measurements on preirradiated samples [the same kind of change was found for film specimens in Ref. (*1*)].

Numerous measurements performed on films and single crystals obtained by various means all led to an identical value of 1/2 for the CO/CO_2 ratio. Thus the dependence of CO/CO_2 ratio on the type of photolyzed specimens, as obtained in Ref. (*11*) was not confirmed in our experiments. The evolution of CO is undoubtedly dependent on the photolysis of the potassium ferrioxalate itself and not on some interaction of the photoproducts with organic solvents trapped by the crystals, as was suggested by the authors of Ref. (*1*). Indeed, considerable quantities of CO leading to the indicated higher value of CO/CO_2 are evolved even on photolysis of single crystals made from aqueous solutions without participation of organic solvents.

One might think that a change in composition of the gaseous photoproducts as compared to FVR could be dependent on specific photolysis under the high vacuum conditions. In connection with this, it was interesting to compare photolysis in a vacuum with photodecomposition in air. Qualitative experiments through chemical analysis of the composition of the gaseous photoproducts showed presence of both CO_2 and CO in case of specimens of several types—polycrystalline salts synthesized from aqueous solutions, single crystals grown from aqueous solutions, powders obtained by pulverizing single crystals and polycrystals, and films formed after vaporization of ethanol from alcohol–water suspension. For specimens of the last type, quantitative evaluation of the CO/CO_2 ratio was made. According to the chemical analysis, the ratio CO/CO_2 for photolysis in air was equal to 1/3. Evidently, the ratio CO/CO_2 depends somewhat on the conditions of the experiment but the corresponding change is not great.

Thus, FVR and photolysis of crystalline salts lead to different gaseous products. There are two possible reasons for this difference—change in the primary step of photolysis and differing secondary reactions. Because the absorption spectra of crystalline potassium ferrioxalate and its aqueous solution are very close to each other in the region of interest to us (*16*), it can be assumed that the different photoproducts are formed by different secondary reactions. Formation of CO indicates that on photolysis of the crystals there takes place a more complicated transformation of the oxalate groups than with FVR. Apparently it is in this way that the great role of the "cage effect" appears in the case of crystals.

Let us go over to consideration of the solid phase products. It was shown in Ref. (*12*) that on variation of the conditions of uv irradiation identical Mössbauer spectra result. Besides retention of the broad Fe(III) line, there appears a clear doublet of narrow lines. This doublet has a quadrupole splitting ε and an isomer shift characteristic of high-spin divalent, octahedrally coordinated iron. The lines of the doublet agree well in their parameters with those of the final stable products of radiolysis (phase I). The Mössbauer spectra thus indicate identity of the final stable products of photolysis and radiolysis.

The extremely large value of ε (of the order of 4 mm/sec) excludes the possibility of identifying the Fe(II)-containing final product of photolysis as FeC_2O_4, if one is to have it as an oxalate in the form of a separate phase.

Indeed, according to Ref. (*17*), the ε obtained for $FeC_2O_4 \cdot 2H_2O$ is 1.76 mm/sec at room temperature and 2.14 mm/sec at liquid nitrogen temperature; in FeC_2O_4, the corresponding values of ε are 2.45 and 2.83 mm/sec. If one were to proceed from the Mössbauer data alone for the photolyzed specimens, then in principle one would have to assume that there arises not a separate phase but a complex in the matrix of original material having composition corresponding to FeC_2O_4. However, this possibility is excluded by the direct data of the experiment.

Actually, according to (*11*), NTTR leads to a decomposition product identical with phase I. We also carried out Mössbauer investigations of the NTTR of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$. Mössbauer spectra corresponding to 30, 50, and more than 90% conversion, as monitored by weight loss, showed phase I without any qualitative transformation of the lines of the characteristic doublet beyond the ordinary thermal variation of spectrum parameters. An analogous result occurred also on heating uv-irradiated specimens. (In this case, samples were brought in a furnace in the course of 1 hr to a temperature of the order of 100–150°C, thermostatted, and Mössbauer measurements carried out in the process of warming.) The fact that the Mössbauer spectra of the samples exposed to deep thermal decomposition (up to nearly complete) give doublet parameters of phase I identical to those for photolysis and radiolysis, whereas initial heating of the specimens gives rise to no essential changes in the spectra of phase I, indicates first that there is identity of final stable Fe(II)-containing products in all the three cases of decomposition and second that it is a separate phase. The specimens subjected to deep thermal decomposition showed X-ray photograph lines corresponding to presence of crystalline structure. Formation of crystalline structure in the photoproducts is also indicated by X-ray photographs of specimens with deep photoconversion.

Besides the lines characteristic of phases I and II, the authors of Refs. (*8–10*) found in the Mössbauer spectra additional series of lines of weak intensity associated with various intermediate products of decomposition. For the photolyzed specimens these lines as well as the lines that may correspond to phase II could be identified only with great difficulty and were extremely unreliable. In addition to the Mössbauer investigations, ir measurements were carried out for better comparison with the data of Refs. (*9–11*) and for getting complementary information on the solid photoproducts. Infrared spectra were obtained for specimens with various degrees of photodecomposition, specimens exposed to air and annealed at 110°C, potassium ferrioxalate that was subjected to deep thermal decomposition, and anhydrous potassium ferrioxalate exposed directly in the KBr matrix (in any case, almost complete dehydration resulted from preliminary initial heating).

The ir spectra obtained are very close to those obtained in experiments on radiolysis and NTTR (*9–11*) and agree well with literature data on the original salt (*18–20*). Some typical spectra are presented in Fig. 1. Figure 1a is the spectrum of a film subjected to prolonged irradiation in air; it is very close to the ir spectrum corresponding to deep

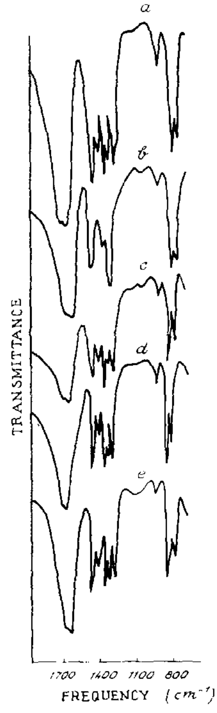

FIG. 1. Infrared spectra.

thermal decomposition, Fig. 1d (the sample was heated to a temperature of 260°C in the course of 1 hr and annealed at this temperature for 40 min). The ir spectra 1a and 1d are compared with the ir spectra corresponding to prolonged radiolysis without limitation of air access (*9*, *10*) and NTTR (*11*). In Refs. (*9–11*) corresponding ir spectra were correlated with decomposition products containing phase I in their makeup. Thus, the ir spectra serve as definite evidence that not only does phase I appear as a final product of photolysis, radiolysis, and NTTR but also that the general composition of the final solid state products is identical in the case of all three types of decomposition.

Figure 1b shows the ir spectrum of potassium ferrioxalate that has been heated for 1 hr in a KBr matrix at 110°C and then irradiated directly in the matrix. Comparison with ir spectra from Refs. (*9* and *10*) leads to the conclusion that on photolysis that is carried out in a matrix in the absence of air access, the photoproducts are identical with the products of radiolysis in the absence of air or in its restricted access. Under these conditions, radiolysis products are formed which contain the main intermediate, metastable phase II. As shown in (*9*, *10*) by Mössbauer and ir spectra, annealing can result in conversion of phase II into phase I. An analogous situation occurs in the case of photolysis. This is illustrated in Fig. 1c which shows the ir spectrum of anhydrous potassium ferrioxalate that has been irradiated in a KBr matrix (spectrum 1b) and then annealed for 1 hr at 110°C.

It seems to us that the authors of Ref. (*10*) are not correct in their interpretation of phase I; several facts indicate that this Fe(II) compound does not contain coordinated water. Gravimetric measurements and DTA data (*21*, *22*) indicate this, as does the fact that phase I appears as the final product of NTTR. The absence of coordinated water is supported also by ir spectra (*9*). [We are inclined to attribute our observation of a band in the 3400–3500 cm^{-1} region to uptake of adsorbed water (*23*).] Near coordination to the Fe(II) must thus be provided by the oxygen atoms of the oxalate groups only. The main final product of the decomposition cannot be the complex $[Fe(C_2O_4)_3]^{4-}$. It contradicts the stoichiometry of the reaction; in particular, the scheme represented in Eq. (4) is clearly inapplicable. In this situation the supposition of authors (*9*) about the formation of oxalate bridges seems natural and logically explains the conservation of octahedral coordination of the iron despite a "deficit" of ligands arising from removal of a part of the oxalate groups.

In our opinion, the principal indication of bridge structure in the ir spectra appears to be the shift to lower frequencies of the broad intense structured band (the band in the region 1650–1715 cm^{-1}) by about 40 cm^{-1} in going from starting salt to phase I. According to Ref. (*19*), frequencies ν_1 (1677 and 1648 cm^{-1}) and ν_7 (1713 cm^{-1}) of potassium ferrioxalate correspond to vibration of the C═O bond. On formation of bridges, the bonds between C and O in the oxalate must be leveled out and the bond order of C═O lowered. As another indication of formation of bridge structure, one can consider the strong change of the ir spectrum in the low-frequency region (Fig. 2). It deserves attention

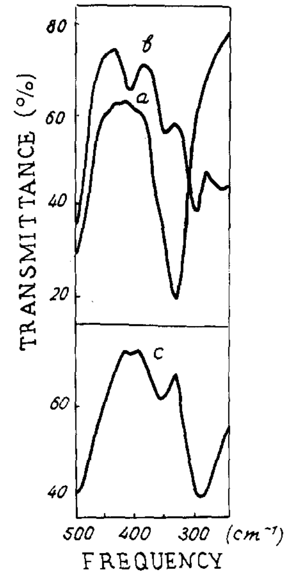

FIG. 2. Infrared spectra, low-frequency region. (a) $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$; (b) potassium ferrioxalate after NTTR; (c) $FeC_2O_4\cdot 2H_2O$.

that in the region from 250 to 400 cm^{-1} the ir spectra of the products of NTTR of potassium ferrioxalate are very close to the spectrum of $FeC_2O_4 \cdot 2H_2O$, for which the presence of oxalate bridges is well established (*24*).

According to the data of Refs. (*9* and *10*), on going over from phase II to phase I the quadrupole splitting of the characteristic doublet in the Mössbauer spectrum is increased approximately 1.4 mm/sec and reaches a value that is one of the largest for compounds of iron (*25*). We think that the hypothesis about the presence of oxalate bridges in the structure of phase I allows one to account for the experimental fact of an extremely large electrical field gradient (EFG) at the iron nucleus, which leads to an observed large ε. In other words, the exceedingly large value of ε can be taken as experimental manifestation of a bridge structure. The proposed idea is supported by quantum chemical considerations (*26*).

Although we support the hypothesis of authors (*9*) about the presence of oxalate bridges (Fig. 3) in the structure of phase I, we cannot agree with their identification of this compound. The same authors (*9*) noted a discrepancy in the chemical analysis results for the ratio between Fe^{2+} and $C_2O_4^{2-}$ corresponding to complexes indicated by (5). We carried out the synthesis by the method described in (*10*). The freshly prepared salt so obtained of composition $K_2[Fe(C_2O_4)_2]$ gave a Mössbauer spectrum coinciding with the spectrum of phase I. X-ray photographs (see Table I) also attest to identity of the

TABLE I

X-Ray Analysis Data

$K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ Exposure	$K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ Exposure and initial heating	$K_2[Fe(C_2O_4)_2]$ Synthesized salt	$K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ NTTR (heated 40 min in air at $t = 260°C$)	$K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ Literature data (*34*)
	6.80 VS	6.86 S	6.99 S	6.9 VS
	5.76 S	5.78 S	5.74 S	6.6 W
4.28 S	4.28 VS	4.27 VS	4.28 VS	4.96 VS
3.54 VS	3.55 VS	3.55 VS	3.54 VS	4.68 W
3.51 VS	3.51 VS	3.50 VS	3.49 VS	4.43 M
3.24 M	3.26 S	3.22 M	3.24 M	4.09 M
3.07 M	3.13 VS			3.61 VS
2.96 W	2.94 M	2.95 S		3.48 W
2.88 W	2.89 M	2.79 W	2.90 S	3.34 M
2.68 VS	2.68 VS	2.67 VS	2.68 VS	3.16 S
2.44 S	2.44 M	2.46 W		3.03 S
2.31 W	2.31 S	2.31 W	2.32 VS	2.85 W
2.21 M	2.21 M	2.19 S		2.67 VS
2.15 W	2.14 M	2.14 S	2.13 W	2.58 M
2.00 W	1.94 S	1.85 W	1.96 W	2.46 W
1.87 S				2.36 W
1.60 W	1.54 W	1.56 W		2.31 W
				2.18 VS
				2.12 W
				2.03 W
				1.96 W
				1.90 W
				1.85 W
				1.81 W
				1.75 W
				1.71 W
				1.67 W

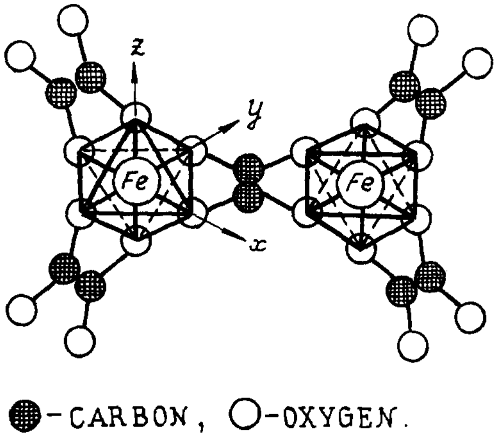

FIG. 3. $[(C_2O_4)_2FeO_2C_2O_2Fe(C_2O_4)_2]^{6-}$.

synthesized Fe(II)-containing salt with the final product of photolysis and NTTR. Identity of the final products of photolysis, radiolysis, and NTTR of potassium ferrioxalate had been noted above. From the literature data on all three kinds of decomposition, one can conclude that the most likely composition of phase I is $K:Fe:C_2O_4 = 2:1:2$, not 6:2:5 as assumed in (*9*). At the same time, the physical measurement data described above allow us to fix the structure of the compound of the indicated composition.

The presence of oxalate bridges in the composition $K:Fe:C_2O_4 = 2:1:2$ can be understood if, in contrast to FVR, we assume that on disintegration of the crystalline salt the nascent complexes form trimers or eventually (phase I) a three-dimensional polymeric structure $(K_2[Fe(C_2O_4)_2])_n$. Taking account of the well-known fact that oxalates easily take on a stable nonplanar configuration (*27*), we can conjecture that the ligands form bridge bonds so that the spatial configuration of each Fe(II) with the triplet of oxalate ligands directly bound to it has symmetry close to D_3. In the light of the suppositions made, the following complementary considerations might be expressed. It is known that polymeric structures are generally characteristic of carboxylic acids (*30*). Analysis of the structure of potassium ferrioxalate (*28*, *29*) as well as of the isomorphous structure $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ (*31*) permits one to conclude that this structure is extremely favorable for formation of a three-dimensional polymer after elimination of a fraction of the ligands. References (*35* and *36*) bear witness to the fact that, for fixed oxidation state and fixed six-coordination of iron, transfer from terminal to bridge ligands as well as structural changes associated with the polymerization process manifest themselves in large changes of EFG.

In the opinion of the authors of Ref. (*4*), the specificity of the photolysis of potassium ferrioxalate depends on the fact that the photodecomposition proceeds by a scheme corresponding to Eq. (3), but, in the long run, it goes to products different from this scheme because $K_2[Fe(C_2O_4)_2]$ in air at room temperature is unstable. The synthesis mentioned above in fact goes to an unstable salt, and there follows gradual oxidation of Fe(II) to Fe(III). In this, a compound is formed which supposedly (according to Mössbauer data) can be identified as $Fe_2(C_2O_4)_3\cdot nH_2O$. The stability strongly depends on the carefulness of the synthesis, and our data in this respect completely agree with the data of Ref. (*10*). The characteristic doublet corresponding to partial back-oxidation is observed in photolysis as well as in radiolysis (*8–10*), but this oxidation is extremely retarded relative to oxidation of the synthesized salt. Phase I, resulting from solid state decomposition is considerably more stable than the synthesized salt of identical composition.

It is standard to consider that on decomposition of potassium salts of complexes such as indicated in (1), there is formed a mixture of solid products. In a series of experiments on the basis of ir spectra [for example, Ref. (*6*)] and X-ray photographs, one is led to the conclusion that $K_2C_2O_4$ is present among the products. Only in Ref. (*9*) is there supposed to be presence of a single solid final product; $K_2C_2O_4$ formed at the beginning is considered to interact with phase II to form phase I.

It seems to us that on decomposition of potassium ferrioxalate, solid products other than $(K_2[Fe(C_2O_4)_2])_n$ are formed also. This conclusion is already dictated by the fact that CO is among the gaseous products. Since, according to Mössbauer-spectroscopy data, oxides and the carbonate of iron are missing from the principal products of the decomposition, the presence of CO must be matched by presence of potassium carbonate among the products. Indeed, for formation of CO there could be a sequence of transformations of the oxalate groups such as the following: $C_2O_4^{2-} \rightarrow 2CO_2^-$; $2CO_2^- \rightarrow CO_3^{2-} + CO$; $C_2O_4^- \rightarrow CO_2 + CO_2^-$; $C_2O_4^- + CO_2^- \rightarrow CO_3^{2-} + CO_2 + CO$; $CO_2^- \rightarrow CO + O^-$; $CO_2^- + O^- \rightarrow CO_3^{2-}$. The presence of carbonate among the decomposition products is verified by qualitative chemical analysis for carbonate ion. Analysis of ir spectra and X-ray photographs of photolyzed specimens leads to the conclusion that these data can be accounted for by assuming presence of potassium oxalate and carbonate among the solid state products of the photolysis. True well-defined identification is difficult; a series of lines in the ir spectra for $K_2C_2O_4$ and K_2CO_3 (*32*) is overlapped by intense lines of phase I. Identification of $K_2C_2O_4$ by X-ray photographs is complicated by the existence in this salt of several crystallographic modifications (*33*). We note that the polymorphism of potassium oxalate indicates "mobility" of its structure. This is conducive to formation of $K_2C_2O_4$ in the matrix of a decomposing substance, particularly if one takes into consideration the possible deformation of the structure of the salt in the matrix.

By combining the published and the stated experimental facts, one can formulate the following decomposition scheme.

$$6nK_3[Fe(C_2O_4)_3]\cdot 3H_2O = 6(K_2[Fe(C_2O_4)_2])_n + nK_2C_2O_4 + 2nK_2CO_3 + 6nCO_2 + 2nCO + 18nH_2O. \qquad (6)$$

The stoichiometry reflects, in particular, the experimental fact that potassium carbonate and oxalate are included in considerably lesser quantity than is phase I. In Fig. 1e there is depicted the ir spectrum of a mixture of synthesized salt, potassium oxalate, and potassium carbonate, taken in the ratio corresponding to the stoichiometry of the reaction as written in Eq. (6).

The discussion above concerned final photoproducts. Having these data, however, still does not allow a well-defined opinion on the mechanism and intermediate stages of the decomposition. In particular, the question of the precise mechanism for the effect of moisture on the decomposition process requires further study. Our observations on the photolysis support the data of Refs. (*1*, *8*–*10*) that this effect is significant. For the present, there is the feeling that the role of moisture is rather that of a catalytic influence on the processes that occur, including possibly polymerization, than direct participation of H_2O in the chemical transformations.

In order to compare the mechanisms of photodecomposition and photoconductivity, some electrophysical measurements were carried out: the spectral distribution of photoconductivity (curve "B" in Fig. 4) was determined and the sign of the photocurrent charge carriers was established by the method of condensor photo-emf. Electron ("*n*-type") character of the conductivity was ascertained. Figure 4 (curve "A") presents the spectral distribution of the quantum yield Φ for photolysis in air. It is evident that the maxima in the conductivity and Φ do not correspond. From this it follows that either the photoconductivity in the main peak and the photodecomposition are dependent on different electronic excitations (which seems rather probable) or identical excitation is responsible for both processes but there is an important influence of secondary reactions on the value of Φ. It should be noted that even in the case of reaction being analyzed that is certainly initiated by electronic phototransport, the influence of free electrons on photo-

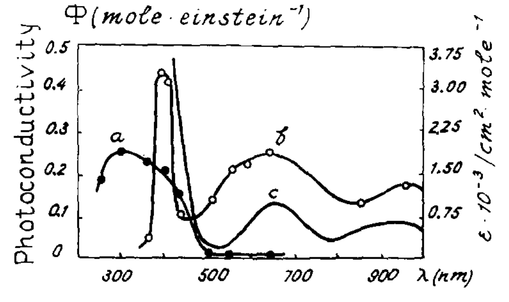

FIG. 4. Spectral distribution (a) of Φ and (b) of photoconductivity for $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$. (c) Absorption spectrum (*16*).

decomposition, as follows from experiment, is more complicated than generally assumed.

Mössbauer data on radiolysis (*8–10*) attest to the formation of $[Fe(C_2O_4)_2]^{2-}$ and $[Fe(C_2O_4)_3]^{4-}$ as intermediate products, and one can imagine that these complexes play the role of fragments for building up the conjectured trimers or polymers. Bridges between complexes of two- or three-valent iron can evidently be formed as intermediates. We note that the idea about formation of oxalate bridges and the process of polymerization allows one to give an explanation for observations noted in a series of studies on the implication in reaction of adjacent complexes (one of the most important pieces of evidence for this is the large quantum yield for potassium ferrioxalate).

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