When $[Fe(NO)_2Br]_2$ is dissolved in carbon tetrachloride, a very weak seven-line trace is obtained whose isotropic g value is 2.060 and hyperfine splitting is 23.3 G. The origin of this signal is not clear. The septet presumably indicates either two equivalent bromine or chlorine atoms. The former could occur if the dimer were not sufficiently strongly exchange coupled and a small population of a low-lying triplet state occurs. To test this idea we examined the epr spectra of the solid dimer. This produced a single line at $g \approx 2$; however raising or lowering the temperature did not change the signal intensity so that a thermally populated triplet can be ruled out. The presence of a small amount of impurity is possible, but since the sample was purified by sublimation, it is difficult to envisage what this could be.

On adding a complexing agent such as acetone or dimethyl sulfoxide to the solution of the bromide dimer, the seven-line pattern disappeared and an intense single broad line was obtained. This signal is no doubt due to a complex of the form $Fe(NO)_2Br(CH_3COCH_3)$ in which the spin density on the bromine atom has been reduced.

The iodide dimer, however, behaves differently, on dissolving in carbon tetrachloride. In this case the epr spectrum, shown in Figure 4, consists of a six-line pattern with an isotropic g value of 2.063 and a hyperfine splitting of 18.2 G. This spectrum may be attributed to the species $Fe(NO)_2I(CCl_4)$ since its spectral parameters are quite similar to those of $Fe(NO)_2I(H_2O)$. Again the addition of a complexing agent leads to the formation of a single intense line. The behavior of both dimers in solution in the presence of coordinating ligands is at present being investigated.

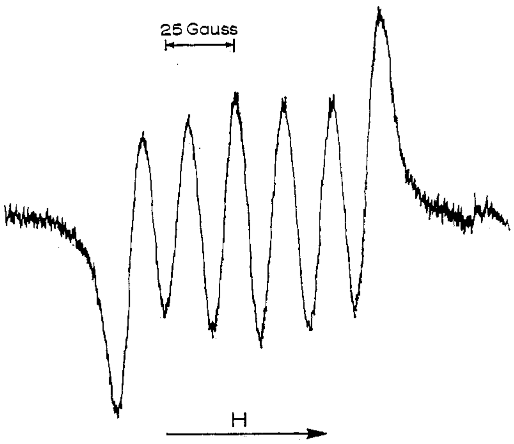

Figure 4.—The epr spectrum of $[Fe(NO)_2I]_2$ in CCl_4 solution at 20°. The species present is probably $Fe(NO)_2I(CCl_4)$.

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The Thermal Decomposition of Potassium Tris(oxalato)ferrate(III)

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The thermal decomposition of potassium tris(oxalato)ferrate(III) has been studied in the temperature range of 233–262°. The stoichiometry of the reaction may be represented by the equation $2K_3Fe(C_2O_4)_3 \rightarrow 2CO_2 + 2FeC_2O_4 + 3K_2C_2O_4$. This reaction follows a pattern that is characteristic of a number of solids. The rate of thermal decomposition at a given temperature is low, initially, then increases passing through a maximum, and finally decreases. During a major portion of the decomposition the rate follows the relationship $d\alpha/dt = k\alpha(1 - \alpha)$, where α is the fraction decomposed, t the time in seconds, and k the rate constant in reciprocal seconds. The addition of 1% iron(II) oxalate decreased the time required to attain 50% decomposition but it did not alter the rate constant. Data from two different samples and a sample containing iron(II) oxalate fell on a single Arrhenius plot from which an activation energy of 46 kcal mol^{-1} was estimated. A mechanism that is consistent with the kinetic data and the acceleratory effect of iron(II) oxalate has been suggested. A new apparatus and new techniques for the study of solids which decompose to form volatile products have been described.

Introduction

The thermal decompositions of solids and the rate laws which apply to these decompositions have been studied by many investigators.[1]

A new apparatus and new techniques have been applied to the study of the decomposition of potassium tris(oxalato)ferrate(III). The thermal and the photolytic decompositions of this compound have been extensively investigated.[2-7]

In the temperature range of 233–262° potassium tris(oxalato)ferrate(III) decomposes to form carbon dioxide and solid decomposition products. The reaction exhibits an induction period, an acceleratory period, and a decay period. Reactions which exhibit these characteristics have often been associated with models requiring the formation of growth nuclei on the surface which enlarge as the reaction proceeds.[1] A simpler

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model has been suggested for the decomposition of silver oxide,[8,9] but this model has not been favorably received.[10] The simple model requires that the kinetic behavior fit the relationship, $d\alpha/dt = k\alpha(1 - \alpha)$, where α is the fraction decomposed in time t and k is a rate constant in reciprocal seconds. It is based on the assumptions that one of the decomposition products makes possible additional reaction and that the reaction is first order in the decomposing substance. Both the chemical and kinetic data obtained in our study of the decomposition of potassium tris(oxalato)ferrate(III) are consistent with this simple model.

Experimental Section

Materials.—Potassium tris(oxalato)ferrate(III) was prepared as described in the literature.[11] As observed by others this compound lost 11% on drying at 150° and an additional 8.9% due to the evolution of carbon dioxide at 260°. Three standard samples of material were used in this work. Two of these samples were prepared by grinding a single preparation in a Wig-L-Bug (Crescent Dental Mfg. Co.) and adding to half of the ground material 1% iron(II) oxalate dihydrate. The doped sample (KD series) and the undoped sample (K series) were again ground in the Wig-L-Bug. Another preparation was ground to a fine powder in an agate mortar (T series). The three samples were stored in vials which were covered with aluminum foil.

Apparatus.—The twin-tube injector used in this work had been developed for a study of the volatile products formed during the thermal activation of an organosilica–alumina cracking catalyst and for the determination of the activity of the catalyst.[12,13]

It consisted of two parallel chambers in a brass cylindrical block 4 in. long and 1.25 in. in diameter. The block was enclosed in a furnace and contained a thermocouple well. The temperature of the block could be set at any value and maintained at that value by a stepless controller (West Gardsman, Model JS series). Each chamber was equipped with an injection port and a gas-entry line. The exit lines from each chamber were connected by means of a two-way valve (Loenco valve, L-204-4) to a single chromatographic column. The column used in most of this work was a 24-in. length of $^1/_8$-in. diameter stainless steel tubing that was packed with 50–80 mesh Poropak Q (Waters Associates, Inc.).

With this arrangement helium carrier gas could be routed to the column by way of either chamber while the other chamber was bypassed. Gaseous products were trapped in the bypassed chamber. By changing the valve, carrier gas was routed through the bypassed chamber and carried volatile products into the chromatographic column. When the valve was returned to its original position, the sample chamber was again bypassed and helium flowing through the other chamber continued the analysis of the volatile products in the column. Injection ports for each chamber were used to introduce standard samples so that quantitative relationships could be established between the observed peak areas and the quantity of each volatile product. The products exited from the column to a thermal conductivity cell (Gow-Mac microcell, Model JDC-133). Changes in thermal conductivity were recorded by a Sargent-Welch recorder, Model SRG, which contained an integrator.

Operating Techniques.—Samples to be studied were introduced into the sample chamber in a thin-wall glass tube 3.5 in. in length and $^1/_8$-in. in outside diameter. A similar glass tube packed only with Chromosorb (Johns-Manville) was introduced into the other tube. The sample (25 mg) was mixed with an amount of Chromosorb so that it was evenly dispersed over the central 1.25 in. of the sample tube. Chromosorb which was held in place by glass wool plugs filled the remaining spaces above and below the sample.

At the beginning of a run helium carrier gas was alternately routed through the two chambers to sweep out the air that was introduced with the sample. When no air peaks appeared on the recording on changing gas flow from one chamber to the other, the temperature of the sample was raised to the range of 150–180° while the sample was bypassed. Carrier gas was then switched to the sample chamber for 30 sec to sweep the volatile products into the column, then to the bypass position for 90 sec, and this schedule was repeated until no more water peaks were observed. Water was then injected to establish the relationship between peak area and the quantity of water. Since the observed water consistently represented the quantity expected, the sample was often merely weighed before and after flushing to be sure that the sample was properly dried.

The temperature of the brass block was then raised rapidly to the operating temperature. At this temperature carrier gas was routed through the sample chamber for 30 sec and to the bypass chamber for 90 sec on a regular schedule. There appeared a series of carbon dioxide peaks at 2-min intervals from the beginning to the end of a run. Near the end of a run the temperature was raised to 280° to drive out and to record the last traces of carbon dioxide. Peak areas could be quantitatively related to the amount of carbon dioxide by the injection of standard samples. In the present work this method of standardization was not necessary. The decomposition of 25.0 mg of potassium tris(oxalato)ferrate(III) trihydrate produced exactly 5.09 × 10^{-5} mol (2.24 mg) of carbon dioxide. The cumulative peak area divided by the total peak area gave the value of the fraction decomposed, and half of the peak area divided by the total area was a direct measure of the change of the fraction decomposed per minute.

A computer program using the observed times and peak areas was used to obtain print-outs of the various kinetic parameters.

Results

Figure 1 shows a tracing of the peaks obtained in a run at 259°. The first peak is to the right of Figure 1 and the run proceeds to the left with each peak representing gas production during a 2-min interval. Not shown are eleven following peaks which decrease in size and two small peaks representing residual carbon dioxide that was evolved on raising the temperature to about 280°. Assuming 1 mol of carbon dioxide/mol of compound decomposing, all peaks represent 5.09 × 10^{-5} mol (2.24 mg) of carbon dioxide. Because of the high rate of gas production at 259° the magnification used for this run was only $^1/_{256}$th of its maximum value. The first peak at the right of Figure 1 represents 0.02 mg of carbon dioxide and corresponds to less than 1% decomposition. At lower temperatures higher magnifications were used, the runs required a longer time for completion, and many more peaks were recorded. Peaks representing as little as 5 × 10^{-4} mg of carbon dioxide (about 0.02% decomposition) were easily observed.

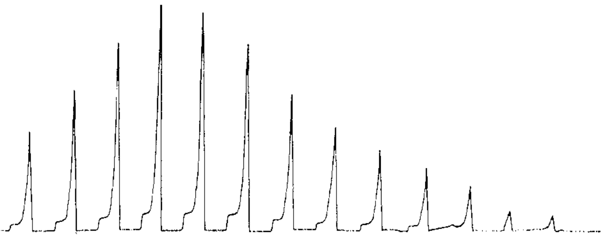

Figure 1.—Tracing of carbon dioxide peaks at 259°; 2-min samples, 30-sec duration, and 256× magnification.

Figure 2, in which the fraction decomposed, α, has been plotted against time in minutes, shows four representative curves for doped and undoped samples which were obtained from data such as those shown in Figure 1. Curve a representing a sample containing 1% iron(II) oxalate dihydrate reached 50% decomposition in about 40 min at 244° while the undoped sample at 245° (curve

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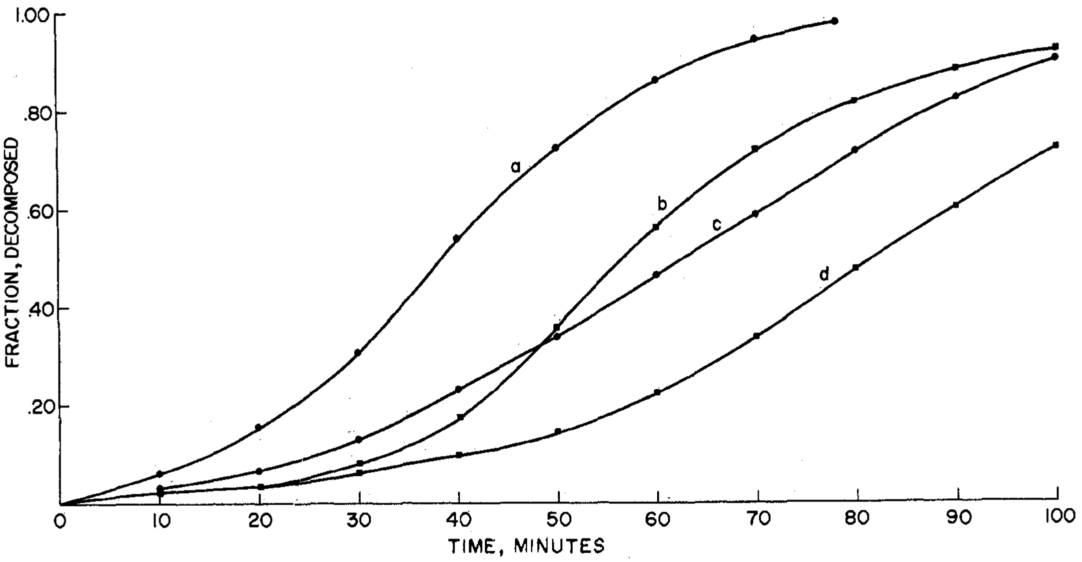

Figure 2.—Fraction decomposed *vs.* time curves: (a) $K_3Fe(C_2O_4)_3$ plus 1% FeC_2O_4 at 244°; (b) $K_3Fe(C_2O_4)_3$ at 245°; (c) $K_3Fe(C_2O_4)_3$ plus 1% FeC_2O_4 at 239°; (d) $K_3Fe(C_2O_4)_3$ at 240°.

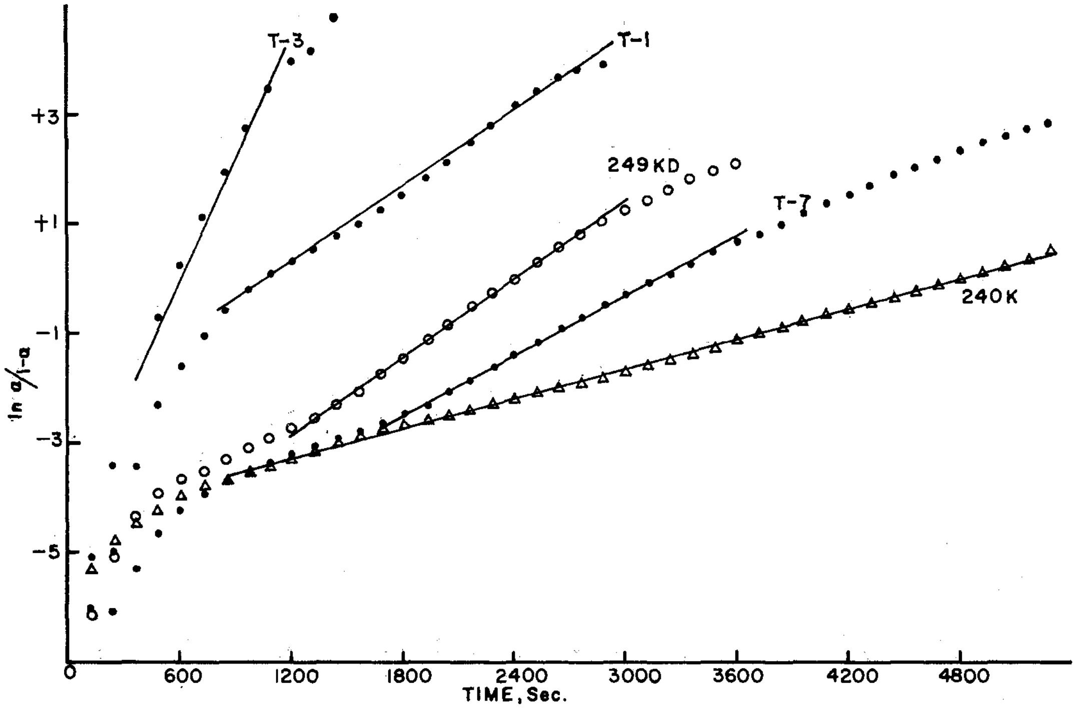

Figure 3.—Representative plots of ln $[\alpha/(1 - \alpha)]$ *vs.* time for designated runs from T series, K series, and KD series.

b) required over 55 min. A similar acceleratory effect of added iron(II) oxalate is shown by curves c and d of Figure 2.

Representative plots of ln $[\alpha/(1 - \alpha)]$ *vs.* t are shown in Figure 3. Plots for all runs were made on large graph paper and the slopes of the straight-line portions representing k in the equation $d\alpha/dt = k\alpha(1 - \alpha)$ were determined. These k values in reciprocal seconds, the temperatures in degrees centigrade, and the ranges of the fraction decomposed which gave satisfactory straight lines are reported in Table I. When a reaction exhibited a long induction period, the plots of ln $[\alpha/(1 - \alpha)]$ *vs.* t of Figure 3 have the appearance of deviating from the straight-line portion excessively. However, these straight-line portions as shown in Table I actually represent a major portion of each decomposition and include the region at 0.5α where the maximum rate was attained.

Figure 4 is an Arrhenius plot showing the natural logarithm of the rate constant *vs.* the reciprocal of the absolute temperature. Data from two different samples and one of these samples doped with 1% iron(II) oxalate are shown. From the slope of the line a single activation energy of 46 kcal/mol and a frequency factor of 4×10^{16} sec^{-1} were estimated.

Discussion

The thermal decomposition of potassium tris(oxalato)ferrate(III) in the temperature range from 233 to 262° may be represented by the same equation that has

TABLE I

SUMMARY OF k, TEMPERATURE, AND RANGE OF FRACTION FOR WHICH THE EQUATION $d\alpha/dt = k\alpha(1 - \alpha)$ HOLDS

Run no.	Temp, °C	10^3k, sec^{-1}	Range of fraction decomposed for which kinetic eq holds
233-KD[a]	233	0.71	0.20–0.73
236-KD	236	0.78	0.08–0.70
T-5[b]	238	0.90	0.05–0.65
239-KD	239	0.92	0.20–0.90
240-K[c]	240	0.83	0.08–0.80
244-KD	244	1.55	0.11–0.95
245-K	245	1.57	0.02–0.60
T-4	245.5	1.71	0.03–0.67
T-7	246	1.72	0.03–0.90
T-8[d]	247	1.73	0.30–0.95
T-9[e]	247	1.76	0.20–0.73
249-KD	249	2.36	0.07–0.73
T-1	249	2.32	0.25–0.95
T-6	251	3.13	0.03–0.80
T-2	254.5	2.82	0.30–0.96
255-K	255	3.03	0.02–0.60
259-K	259	3.89	0.05–0.76
T-3	262	7.31	0.20–0.94

[a] KD series was doped with 1% iron(II) oxalate. [b] T series was another preparation of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$. [c] K series was the sample of KD series without added iron(II) oxalate. [d] T-8 was decomposed briefly at 265°, cooled to 150°, and then raised to the run temperature. [e] T-9 was decomposed at 237°, cooled to 150°, and then raised to run temperature.

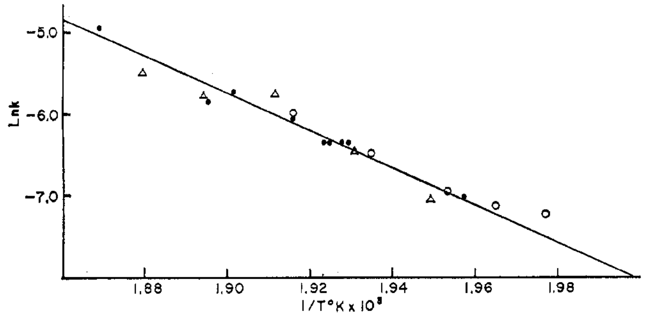

Figure 4.—Ln k *vs.* $1/T°K \times 10^3$: ●, T series; △, K series; ○, KD series.

been established for its photochemical decomposition:[5] $2K_3Fe(C_2O_4)_3 \rightarrow 2CO_2 + 2FeC_2O_4 + 3K_2C_2O_4$. Whether the iron(II) product is present as the simple oxalate, as a complex ion, $Fe(C_2O_4)_2^{2-}$,[2] or as a dinuclear species, $K_6Fe^{II}_2(C_2O_4)_5$,[7] is not important for this discussion. It is important to recognize that the iron(II) ion formed in the decomposition participates in and is essential for the subsequent decomposition of the tris(oxalato)ferrate(III) ion to carbon dioxide and solid decomposition products. An iron(II) ion formed in a matrix of tris(oxalato)ferrate(III) ions may be assumed to become an iron(III) ion by electron transfer through oxalate bridges to any other iron(III) in the matrix. Supporting this assumption are the observations that electron transfer through oxalate bridges is very fast in aqueous solutions[14] and that potassium tris(oxalato)ferrate(III) is photoconducting.[15]

The mobility of electrons within the matrix allows any iron(II) ion to become an iron(III) ion thereby creating an iron(III) ion bridged *via* oxalate to another iron(III) ion in the tris-oxalato complex. This is exactly the situation which Wendlandt and Simmons have considered to be essential for photochemical decomposition.[5] Furthermore, the mobility of electrons within the matrix *via* oxalate assumes that the solid product, iron(II) ion, can, in effect, participate in oxalate decomposition throughout the crystal.

The participation of solid product throughout the crystal is one of the conditions which is required for a decomposition reaction to exhibit first-order dependence upon solid product. Young has suggested that this condition is very unlikely because of the low mobility of the solid components.[10] Since mobility of electrons is required in the present model, Young's criticism does not seem especially pertinent.

If, in addition to being first order in the decomposition product, the reaction is first order in the decomposing component, the kinetic equation $d\alpha/dt = k\alpha(1 - \alpha)$ should represent the data in regions of decomposition where these kinetics obtain. In the integrated form this equation becomes $\ln [\alpha/(1 - \alpha)] = kt + c$, where α is the fraction decomposed in time t, k is a rate constant, and c is the constant of integration.

Plots of $\ln [\alpha/(1 - \alpha)]$ *vs.* t as shown in Figure 3 gave straight lines of slope k. As recorded in Table I, the straight-line portions where the kinetic equation held always included the 50% decomposition value where the rate was a maximum and held in every example for more than half of the decomposition. The appearance of the rate maximum at 0.5α as was observed within experimental error for all runs is consistent with the suggested kinetic equation. Thus, the change in rate with α, $dr/d\alpha$, where r is $d\alpha/dt$, may be set equal to zero to calculate a theoretical value of 0.5α at the maximum rate: $r = k\alpha(1 - \alpha)$, $dr/d\alpha = k - 2\alpha k = 0$, and $\alpha = 0.5$.

It is not unusual at the beginning of a decomposition and at the end of a decomposition that the kinetic equation does not hold.[1] The fact that the straight-line sections include appreciable portions of both the acceleratory and deceleratory periods is a desirable feature of the model.

Other model equations have assumed that growth nuclei form, grow, and terminate in a crystal. Decomposition occurs on these nuclei and their rate of formation and rate of growth may not depend in any simple way upon the rate of decomposition.

Runs T-8 and T-9 reported in Table I give evidence which seems to support the simple model rather than a model in which nuclei are formed somewhat independent of the decomposition. In run T-8 a standard sample was partially decomposed at 265°, cooled to 150° where all decomposition ceased, and then raised to 247° where the rate of isothermal decomposition as a function of time was observed. In T-9 a period of decomposition at 237° was followed by cooling to 150°; then the sample was raised to the decomposition temperature of 247°. The straight-line portion of the run T-8 was from 0.30 to 0.95 fraction decomposed and a rate constant of 1.73×10^{-3} sec^{-1} was calculated. For run T-9 the straight-line portion was from 0.20 to 0.73 fraction decomposed and the rate constant was 1.76×10^{-3} sec^{-1}. The rate constant for T-7, a normal isothermal run at 246°, fit the equation from 0.03 to 0.90 fraction decomposed and had a rate constant of 1.72×10^{-3} sec^{-1}. The very good agreement of rate constants for the different pretreatment appears to

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support the concept that the rate depends upon α and not upon some other process requiring the independent formation and growth of nuclei.

The addition of 1.0% iron(II) oxalate dihydrate as shown in Figure 2 reduced appreciably the time to reach 0.5 fraction decomposed, yet at this concentration iron(II) oxalate did not significantly alter the rate constant of the reaction. In the KD series of Table I the rate constants at 239 and 244° are 0.92×10^{-3} and 1.55×10^{-3} sec^{-1}, respectively, and are essentially the same as the rate constants of the undoped K series of 0.83×10^{-3} sec^{-1} at 240° and 1.57×10^{-3} sec^{-1} at 244°.

The Arrhenius plot of Figure 4 includes data from two different samples and a sample containing added iron(II) oxalate. Both samples and the doped sample have the same energy of activation, and, of course, the energy of activation does not change as iron(II) oxalate is produced during the decomposition.

Reactions which increase in rate as decomposition proceeds have been called "autocatalytic."[10] The addition of iron(II) oxalate or its formation *in situ* clearly increases the rate of the reaction but it does not do so by lowering the activation energy. Probably this type of reaction is not truly catalytic. A better name for the iron(II) oxalate might be an acceleratory agent. It functions in a manner that is opposite that of an inhibitor. An inhibitor in a simple sense may be considered to remove a reactive component so that the large number of events potentially possible from that active component does not take place. An acceleratory agent such as the iron(II) oxalate in the present study makes possible the reaction of the activated complex but it does not lower the activation energy as a catalyst would be expected to do.

The activation step in the photochemical decomposition of potassium tris(oxalato)ferrate(III) has been described as the promotion of an electron from an oxalate to the antibonding Eg orbitals of the iron(III) to which it is coordinated.[16] From a plot of quantum yield as a function of wavelength for solutions of potassium tris(oxalato)ferrate[17] a threshold value of approximately 50 kcal mol^{-1} can be estimated. This is sufficiently close to our value of 46 kcal mol^{-1} that it is tempting to suggest that the thermal activation step is the same as that of the photochemical. Whatever may be the activation step, the presence of iron(II) ion is considered to be essential for the reaction of activated complex to products.

Conclusions

A new apparatus and new techniques have been used to study the kinetics and the chemistry of the decomposition of potassium tris(oxalato)ferrate(III) in the temperature range 233–262°. Both the kinetic results and the chemical observations support a simple mechanism for the decomposition that may be represented by the equation $d\alpha/dt = k\alpha(1 - \alpha)$.

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CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INC., MURRAY HILL, NEW JERSEY 07974, AND THE
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Hydrogen-1 and Indium-115 Nuclear Magnetic Resonance Hydration and Complex Formation Study of Indium Halide Solutions in Water–Acetone Mixtures

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A hydration and complex formation study of indium halide solutions in water–acetone mixtures has been carried out by proton and indium-115 nuclear magnetic resonance techniques. At −100°, the proton- and ligand-exchange rates in these solutions are slow enough to permit the direct observation of pmr signals for bulk water and water molecules in the In^{3+} primary hydration shell. From the relative intensities of these signals, cation hydration numbers were calculated. These results were correlated with indium-115 nmr measurements which revealed signals attributed to $In(H_2O)_6^{3+}$ and InI_4^- in iodide solutions and $InCl_4^-$ and $InBr_4^-$ in the other halide systems. The data were interpreted in terms of indium hexahydrate and tetrahalide complexes, along with additional species at higher halide concentrations.

Introduction

In addition to electrochemical,[1,2] Raman,[3-5] and ion-exchange[6-10] methods, recent publications have demonstrated the utility of the direct proton magnetic resonance (pmr) technique as a complementary tool for

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