[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Oxygen-carrying Synthetic Chelate Compounds. II. The Rates of Oxygenation of the Solid Compounds[1]

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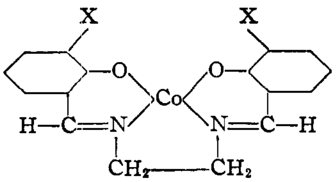
The rate of reaction of oxygen with three cobalt chelates has been studied in an attempt to determine the process by which the oxygenation takes place. The compounds were: cobalt salicylaldehyde ethylenediimine, I; its 3-fluoro derivative, II; and its 3-ethoxy derivative, III.



I, X = H
II, X = F
III, X = OC_2H_5

Apparatus.—The apparatus is diagrammed in Fig. 1. It consisted of a thermostatted reaction vessel, two mercury-filled gas burets, a mercury manometer, an oil manometer, and an oxygen reservoir. Measurements were made by admitting oxygen, at the desired pressure, into the outgassed sample, and measuring the gas volume at regular time intervals at constant temperature and pressure.

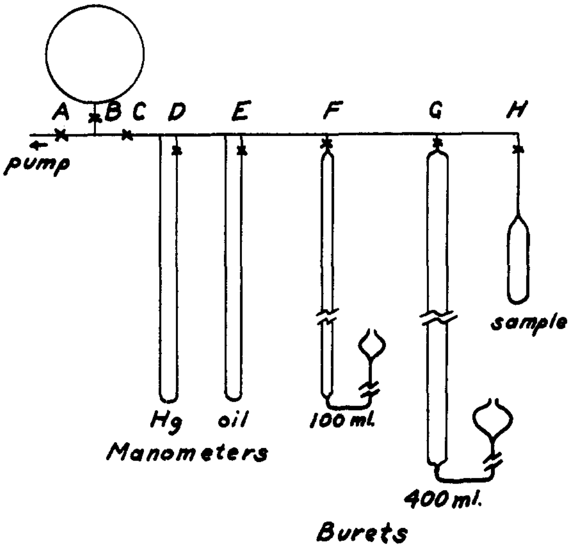


Fig. 1.—Diagram of the rate measuring apparatus.

For efficient temperature control, a copper sample tube, Fig. 2, was used. The bath liquid was circulated through the central tube; the radial fins insured good thermal contact. Use of this type of vessel was indicated because of the exothermic nature of the reaction. It was, however, demonstrated that heat transfer was not a likely factor in the rate measured in the copper tube, by comparing the uptake rate in the copper tube with that in an insulated vessel, Fig. 2. At room temperature, there was no observable difference in uptake rate of the 3-fluoro compound, but at temperatures below 0°, the rates in the glass were quite appreciably faster than those in copper. A rapid temperature rise was observed in the glass tube. The copper runs could be fitted to known rate laws; the glass runs could not. Since the rate increases with rising temperature in the region below 0°, the observations prove that heat conductivity does not limit the rate of reaction in the copper vessel. Small deviations from the rate laws during the initial half of the reaction were attributed to local heating.

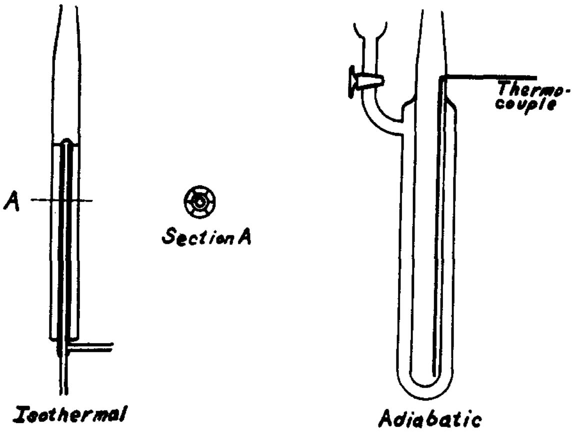


Fig. 2.—Sample vessels; the isothermal vessel is constructed entirely of copper, the adiabatic one entirely of glass.

The Rate Laws for the Reaction.—Typical uptake curves for the compounds are shown in Fig. 3, with the conditions as indicated on the figure. The rate laws were determined by the usual method of plotting logarithmic and reciprocal functions and testing for linearity. Thus, if the rate were proportional to the first power of the unreacted chelate available, A

$$d(O_2)/dt = k_1' P_{O_2}[A]$$

where (O_2) represents the oxygen absorbed and P_{O_2} represents the constant pressure of oxygen in the system. Since the pressure is constant, we may write

$$d(O_2)/dt = k_1[A]$$

The remaining unreacted chelate is given by the difference between the starting chelate, (A_0),

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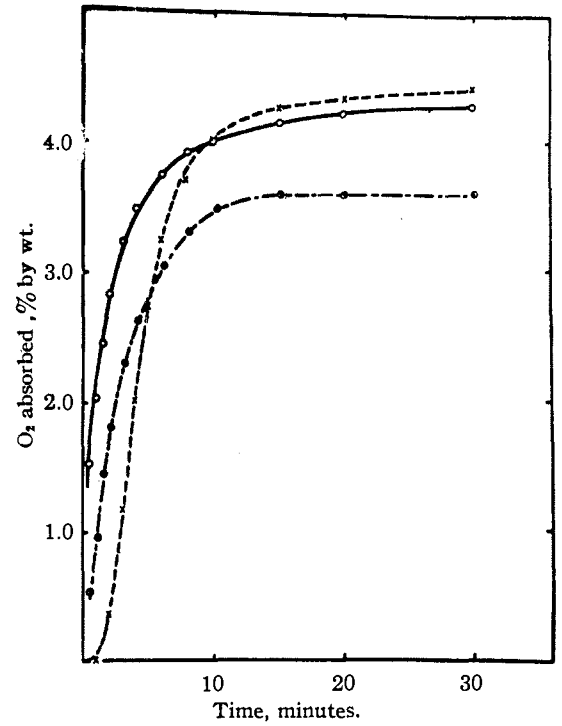

Fig. 3.—x---x, CoSalEn at 25° and 76.0 cm. O_2; ⊙--⊙, Co-3EtoSalEn from pyridinate at 25° and 15.1 cm. O_2; O—O, Co-3FSalEn at 25° and 15.1 cm. O_2.

and the amount of oxygen absorbed, (O_2), so that

$$d(O_2)/dt = k_1[(A_0) - (O_2)]$$

which upon integration becomes

$$-\ln [(A_0) - (O_2)] = k_1t + \text{constant}$$

Since at $t = 0$, $(O_2) = 0$, we have

$$-\ln [(A_0) - (O_2)] = k_1t - \ln(A_0)$$

$$-\ln \frac{(A_0) - (O_2)}{(A_0)} = k_1t$$

$$-\ln \left(1 - \frac{(O_2)}{(A_0)}\right) = k_1t$$

Expressing both the (O_2) and (A_0) in terms of the per cent. by weight of oxygen absorbed, the useful relation is

$$-\ln \left(1 - \frac{\%\text{ absorbed}}{\text{total capacity }(\%)}\right) = k_1t$$

In a similar fashion, if the rate were proportional to the second power of the unreacted chelate

$$d(O_2)/dt = k_2[A]^2$$

which upon integration gives

$$\frac{1}{1 - \dfrac{\%\text{ adsorbed}}{\text{total capacity }(\%)}} = k_2t$$

As shown in Figs. 4, 5 and 6, the oxygenation of the parent and its 3-ethoxy derivative are first order with respect to chelate concentration, while that of the 3-fluoro derivative is second order.

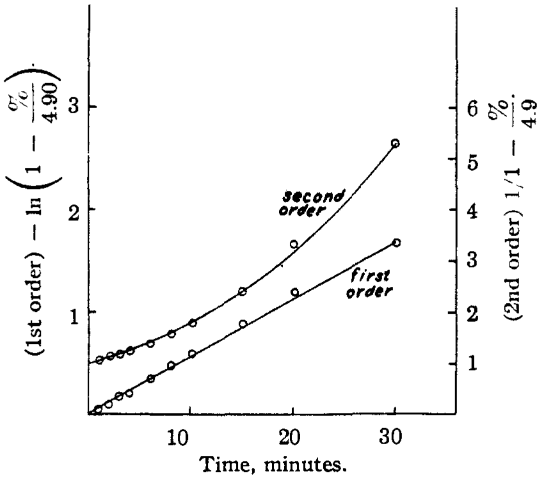

Fig. 4.—CoSalEn, −30°, 76.0 cm. O_2.

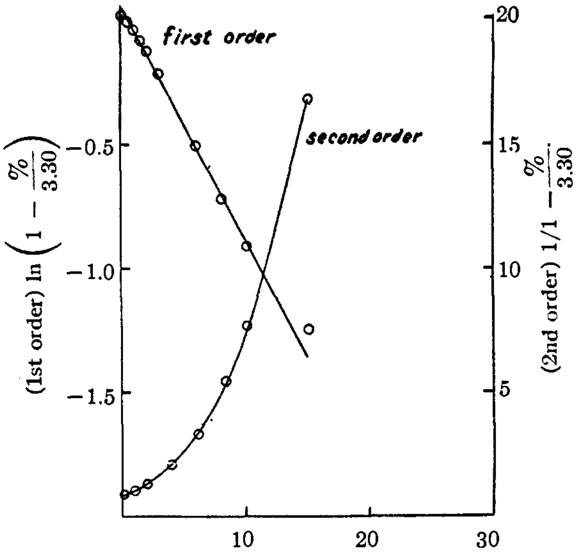

Fig. 5.—3EtO, 25°, 15.1 cm. O_2.

Temperature Dependence of Rate; Activation Energy.—The activation energies of the reactions were determined in the usual way; the rate constants, at constant pressure, were determined at a series of temperatures, and the natural logarithm of k, the rate constant, was plotted against reciprocal temperature, giving a straight line whose slope was equal to $-\Delta E/R$. Figure 7 shows these plots, giving the following activation energies: I, 7,000 cal.; II, 5,000 cal.; III, 10,000 cal.

The reaction rates show an unusual temperature dependence, due to the fact that we were studying reactions near equilibrium condition. At low temperature, −80 to 0°, the reactions were well-behaved, but at higher temperatures, the rates fall off from the values determined by the activation energies, reaching a maximum, then decreasing rapidly above this optimum temperature. Induction periods are apparent in the higher temperature curves. Two typical families of curves are shown in Figs. 8 and 9, show-

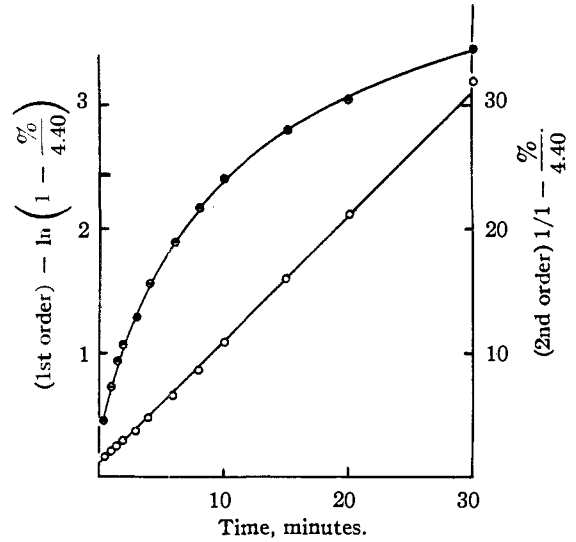

Fig. 6.—Co3FSalEn, 25°, 15.1 cm. O_2: ⊖ first order; O, second order.

ing the behavior of II and III. The optimum temperatures were estimated to be +35 and +25°, respectively. Similarly, the parent compound was shown to have an optimum temperature of +10° at 1 atmosphere oxygen pressure.

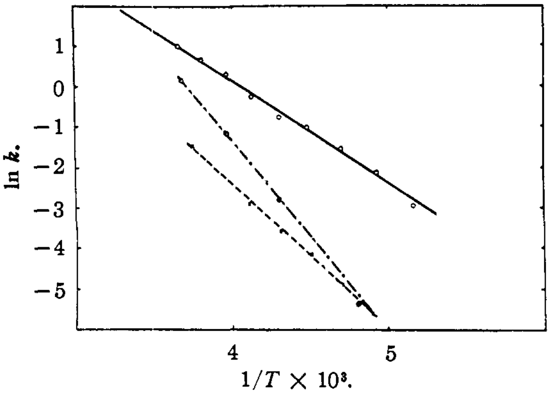

Fig. 7.—O—O, Co3FSalEn; ⊙—⊙, Co3EtOSalEn; x---x, CoSalEn.

The Effect of Pressure.—To determine the reaction order with respect to oxygen pressure, we determined the rate constants at a series of pressures of oxygen for two of the compounds. Figures 10 and 11 show plots of k, as defined previously, against pressure, for II and III under the conditions indicated. Both are clearly first order with respect to oxygen.

The effect of pressure on the rate of uptake of II was studied at temperatures well above the optimum. Figure 12 shows three typical uptake curves. Since it was impossible to determine rate constants by the usual method, due to the induction period, the slope of the uptake curve at 50% oxygenation was arbitrarily set equal to the rate constant and plotted against pressure. Figure 13 shows three such plots, at temperatures indicated. It can be shown thermodynamically that the reaction rate should be dependent upon the excess of oxygen pressure over the equilibrium value provided the absorption rate far from equilibrium is first order with respect to oxygen pressure; thus, these plots enable us to estimate vapor pressures. The values are: 35°, 2.0 cm.; 60°, 13.0 cm.; 65°, 17.5 cm. Substitution in the Clausius–Clapeyron equation yields a value of ΔH of −15.3 kcal./mole, contrasted with the calorimetrically-determined value of −20 kcal./mole.

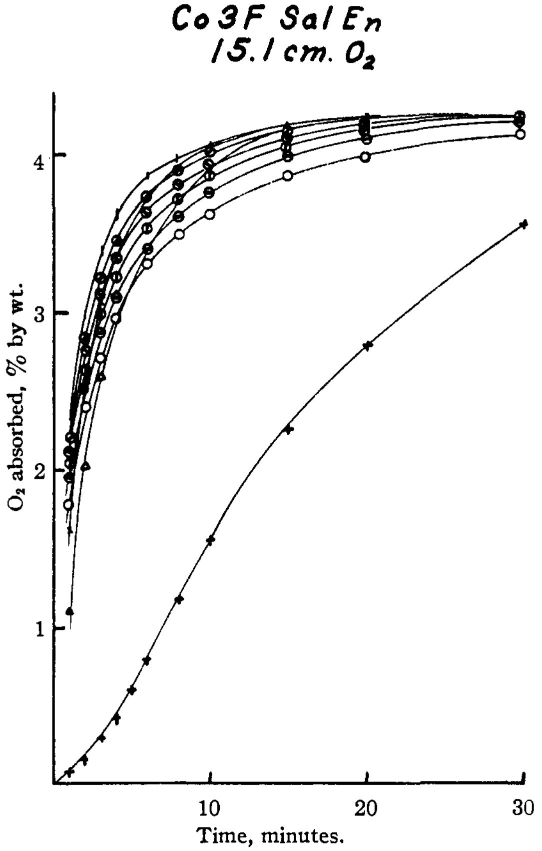

Fig. 8.—Effect of temperature, °C., on absorption by the 3F compound: O, 0; ⊖, 5; ⦶, 10; ⊘, 15; ⌀, 20; |, 25–40; X, 45; △, 50; +, 60.

The Optimum Temperature.—If we define r as (dO_2/dt) which is equal to $k(P_{O_2} - P^0_{O_2})f(A)$ where k is the rate constant, P_{O_2} is the pressure, $P^0_{O_2}$ is the equilibrium pressure, and $f(A)$ is [A] or $[A]^2$, depending on the reaction order with respect to chelate, and since

$$k \equiv C_1e^{-\Delta E/RT} \text{ and } P^0_{O_2} \equiv e^{-\Delta F/RT}$$

where ΔE is the activation energy and ΔF is the free energy of the reaction, we have

$$r = C_1e^{-\Delta E/RT}[P_{O_2} - e^{-\Delta F/RT}]f(A)$$

and

$$\left(\frac{\partial r}{\partial T}\right) P_{O_2}[A] = C_1 f(A) \left[\frac{\Delta E}{RT^2} e^{-\Delta E/RT}\{P_{O_2} - e^{-\Delta F/RT}\} + e^{-\Delta E/RT}\left\{\frac{\Delta H}{RT^2} e^{-\Delta F/RT}\right\}\right]$$

at the optimum temperature, T_{opt}, $\partial r/\partial t = 0$

$$C_1 f(A) e^{-\frac{\Delta E}{RT_{opt}}} \left[\frac{\Delta E}{RT^2_{opt}} P_{O_2} - e^{-\frac{\Delta F}{RT_{opt}}}\left\{\frac{\Delta H}{RT^2_{opt}} + \frac{\Delta E}{RT^2_{opt}}\right\}\right] = 0$$

or

$$\Delta E P_{O_2} - e^{-\Delta F/RT_{opt}}\{\Delta H + \Delta E\} = 0$$

solving for T_{opt} gives

$$T_{opt} = \frac{-\Delta H}{R \ln \frac{\Delta E \cdot P_{O_2}}{\Delta H + \Delta E} + \Delta S}$$

Substituting known values of ΔE, ΔH and ΔS,[2] leads to the following values for T_{opt}:

	T_{opt} (calcd.)	T_{opt} (meas.)
I	+ 5°	+10°
II	+40°	+35°
III	+30°	+25°

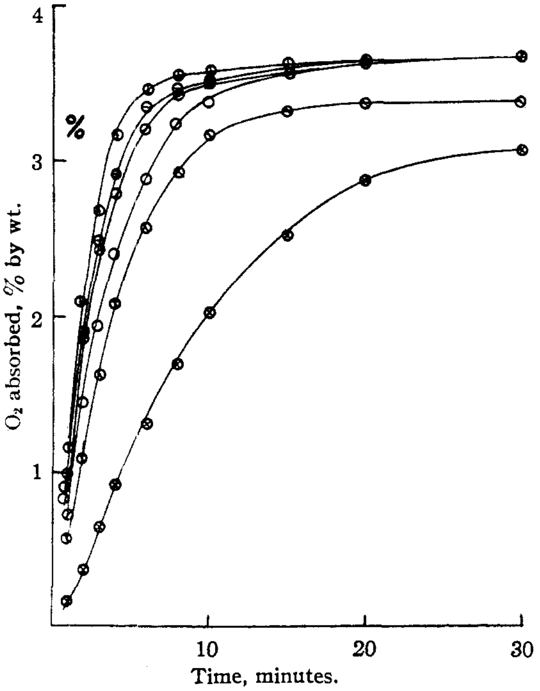

Fig. 9.—Effect of temperature, °C., on absorption by the 3EtO compound, 15.1 cm. O_2: O, 0; ⊖, 5; ⦶, 10–30; ⊘, 40; ⦸, 50; ⊗, 60.

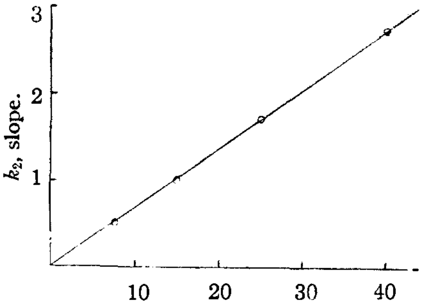

Fig. 10.—Effect of oxygen pressure on the 2nd order rate constant for the 3F compound, Co3FSalEn, at −40°

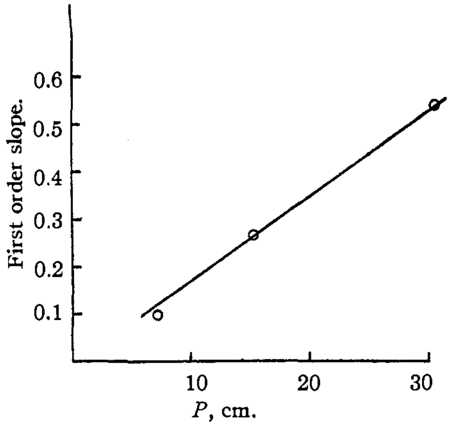

Fig. 11.—Effect of oxygen pressure on the 1st order rate constant for the 3EtO compound at 0°.

The Mechanism of Oxygenation.—Before devising a mechanism consistent with the above observations, it will be necessary to consider a few physical characteristics of the active chelate compounds.

First, there is the particle size of the material. The method of formation of the active material, forced desolvation of crystalline solvates, indicates that the crystals must be very small, since it is not likely that relatively large pyridine or piperidine molecules could be removed from a lattice without tearing it asunder. Clear, neither blurred nor spotty, X-ray powder patterns could be obtained without grinding with both active and completely oxygenated samples of all compounds, as well as all intermediate stages of oxygenation, indicating a crystal size of between 10^{-3} and 10^{-5} cm. Microscopic examination of an active sample showed it to be a mass of randomly oriented crystallites of minute size. It appears from the the above-mentioned X-ray data that peroxide particles of this size are formed early in the oxygenation process.

There are two types of gas diffusion to be considered in the reaction: that through the gas phase, in the pores and cracks of the crystals, and that through the "holes" in the crystal lattice. These "holes" are passages through the lattice shown by X-ray analysis to be present in all active compounds and absent in at least the inactive form of the parent compound. If

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[2] The values of ΔH and ΔS were obtained from the calorimetric measurement of the heat of reaction by Taylor, Miller and Calvin (forthcoming) and the equilibrium pressure measurement of Hughes, Wilmarth and Calvin, This Journal, **68**, 2273 (1946).

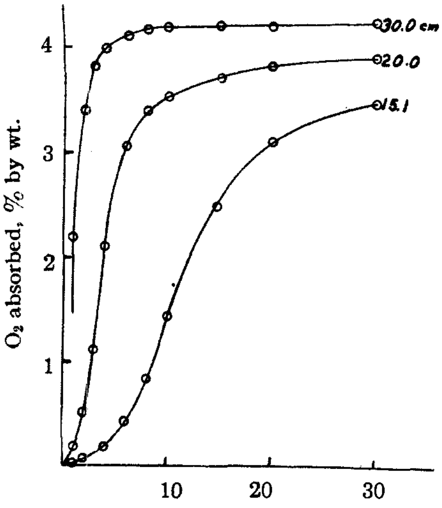

Fig. 12.—Effect of oxygen pressure on the oxygen absorption by the 3F compound at 60°.

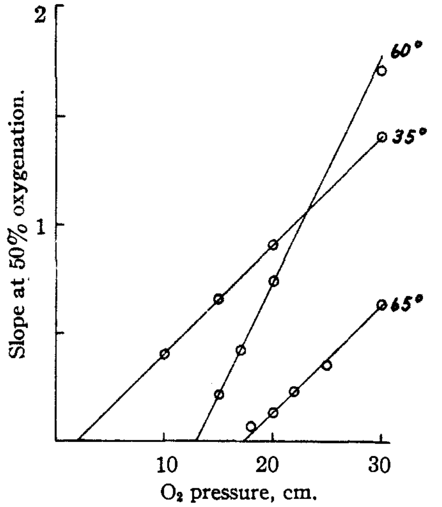

Fig. 13.—Determination of the equilibrium pressure at 50% oxygenation over the 3F compound from rate measurements.

either type of diffusion were to determine the rate, physical considerations lead us to the conclusion that the latter type would be the slower. A reaction whose rate-determining step is this type of diffusion would consist of surface formation of peroxide centers on the crystallites, with the peroxide phase slowly progressing toward the center. Mampel[3] has considered the mathematics of such a reaction, and has shown that for particles that are small compared with the distances travelled by gas molecules in unit time, the reaction is first order with respect to solid. This diffusion limited reaction fails to account for the second order reaction of the 3-fluoro compound, or for the fact that relatively large peroxide centers are formed early in the process. Consideration of this latter point shows that diffusion must be rapid, with some other process determining the rate of uptake.

Since we cannot have free diffusion of chelate molecules through the lattice, we are forced to postulate a multi-step reaction to explain the second order behavior of the 3-fluoro compound. A rapid equilibrium followed by a rate determining step is consistent with the second order reaction. Retaining the same two reactions but making the second one a rapid follow reaction after the initial rate determining step would give a first order rate. Thus we can write the following sequence of events:

1. Formation of activated oxygen molecules in proportion to the number of unoccupied chelate molecules in the crystal mass

$$[A] + O_2 \underset{k''}{\overset{k_1'}{\rightleftarrows}} O_2^*;\ \text{at equilibrium } O_2^* = K_{1\text{eq}}[A]P_{O_2}$$

The equilibrium for this reaction will always be relatively far to the left. The nature of the activated oxygen molecules is of great interest. They must be such as to have available to them the entire crystal mass; they must be capable of passing from crystallite to crystallite (at their contact points presumably) as well as through each crystallite. In other words, it behaves as though it were in solid solution in the entire crystal mass. An identical behavior would obtain if one assumes that the surface–volume ratio is the same for all preparations of a given compound and that this first reaction is a surface reaction. One suggestion is that this oxygen is bonded to only one chelate molecule and is free to migrate from cobalt atom to cobalt atom throughout the solid sample

$$A + O_2 \underset{k_1''}{\overset{k_1'}{\rightleftarrows}} AO_2;\ \text{at equilibrium } [AO_2] = K_{1\text{ eq.}}[A]P_{O_2}$$

with no change in the position of the chelate molecules, *i.e.*, no phase change.

2. The next step is the formation of the complete oxygenated pair of chelates in some crystallite brought about by a suitable collision of one of these activated oxygens with another chelate molecule

$$AO_2 + A \xrightarrow{k_2'} A_2O_2$$

At this point the rearrangement of the chelate molecules commences. Once the rearrangement has begun in any given crystallite, the complete oxygenation of that crystallite follows very rapidly, probably not only through the agency of the activated oxygen but directly by oxygen from the gas phase as well.

In the case of the second order reaction, the first step will be a rapid reversible equilibrium and the rate of oxygen absorption will be proportional to the rate of formation of the complete oxygenated pairs involving the movement of

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[3] Mampel, Z. physik. Chem., 187, 43, 235 (1940).

chelate molecules into their new positions. This is given by

$$d(O_2)/dt = k_2'[AO_2][A]$$

or

$$d(O_2)/dt = k_2'K_{1\ \text{eq.}}P_{O_2}[A]^2$$

Since the reactions are done at constant oxygen pressure

$$d(O_2)/dt = k_2[A]^2$$

For the first order reaction the first step will be the slower with the rate given by

$$d(O_2)/dt = k_1[A]P_{O_2}$$

or at constant P_{O_2}

$$d(O_2)/dt = k_1[A]$$

The Induction Period.—The behavior of the reaction at temperatures above the optimum is of interest in that induction periods are observed with all compounds This autocatalysis is consistent with the mechanism proposed above if we assume the rates of the two main steps, k_1 and k_2, to have temperature coefficients such that they become comparable at higher temperatures. It is well known that consecutive reactions of nearly equal rates lead to an induction period in the formation of the final product, since the rate of formation of the latter is proportional to the concentration of an intermediate, which is also increasing with time.

These results can be achieved somewhat more formally from a steady state analysis of the reaction. If the steady state concentration of $[AO_2]$ and its rate of change with time remain small, the rate of O_2 uptake is given by

$$\frac{k_2'k_1'(A)^2(O_2)}{k_1'' + k_2'(A)}$$

A first order reaction will be observed if $k_2'(A)$ is large with respect to k_1'' and k_1'; that is, if the first step is the slower; a second order reaction will be observed if $k_1'' \cong k_1' \gg k_2'\ (A)$; that is, under conditions of a rapid reversible first step. An induction period will be observed if $k_1'' \cong k_2'$, since it can be shown that the rate of oxygen uptake reaches a maximum at an intermediate value of (A) under these conditions.

The phenomenon of the optimum temperature is observed since we are studying a reaction near equilibrium; similarly, a negative temperature coefficient of the rate of the first step in the process outlined above could be expected above its optimum. Thus the induction period in the second order reaction is caused by a slowing of the rate of oxygen activation, and in the first order, it is caused by a slowing of the second or main reaction, both of which are properties of systems near equilibrium.

It is known that different preparations of the same material can have different rates. For example, the 3-ethoxy compound can be prepared from a yellow hydrate, in addition to that prepared from the red hydrate. The active powders were identical in every respect except rate, that from the red being considerably faster. This is interpreted as exposure of different lattice faces in the crystallite caused by different activation processes.

The molal paramagnetic susceptibility of a sample of the parent compound, I, was determined at a series of oxygenations, and found to decrease linearly from a value of $+2{,}490 \times 10^{-6}$ at 0% oxygen to $+160 \times 10^{-6}$ at saturation. This indicates a single unpaired spin in the active material, which in the peroxide is paired with one of the oxygen electrons.

Summary

It has been shown from kinetic considerations that the oxygenation of cobalt chelates probably takes place in several steps, that it involves an activated oxygen, and that diffusion is rapid. The induction period is believed to result from the same effects which lead to the phenomenon of the optimum temperature; namely, the behavior of a reaction near equilibrium conditions and the existence of successive reactions of comparable rates.

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