

this way in [FeS]. A more likely possibility is that we have here a parallel of the behavior of Fe(III) in ferriheme hydroxide. In this compound Fe(III) appears, on the basis of magnetic measurements, to be square bonded.

Pauling and Coryell⁷ have suggested that in ferriheme hydroxide Fe(III) is linked by four bonds which resonate among six positions. A similar resonance in [FeS] would explain the observed moment. It is interesting to note that, as judged by the magnetic criterion, the modes of attachment of Co(II) and Fe(II) to the sexadentate are quite different.

The moment of [CuS] lies within the range of values found for other complexes of Cu(II). Its value reveals little or nothing about the constitution of the substance. On the basis of the known structures of Cu(II) complexes as revealed by X-ray crystal analysis⁸ it is suggested that Cu in [CuS] is attached to the sexadentate molecule by four strong square (dsp^2) bonds and two longer, weaker bonds in the 1,6-octahedral positions.

(7) L. Pauling and C. D. Coryell, *THIS JOURNAL*, **59**, 633 (1937).

(8) A. F. Wells, *Acta Crystallographica*, **2**, 175 (1949); see also "The Nature of the Chemical Bond," L. Pauling, Cornell University Press, Ithaca, N. Y., 1940, p. 105.

The moment of 3.00 Bohr magnetons found for the compound [NiS] is consistent with the view that the chelating molecule is bound by six covalent bonds. Other structural possibilities are however not excluded since the same magnetic moment may occur with tetrahedrally bound Ni(II).

Summary

The susceptibility of the Co(III) complex of 3,6-dithia-1,8-bis-(salicylideneamino)-octane and the corresponding β -hydroxy- α -naphthylidene complex confirms the fact, established earlier by a resolution into optical antipodes, that these chelate molecules function as sexadentates. Magnetic susceptibilities of the Co(II), Ni(II) and Fe(II) complexes of 3,6-dithia-1,8-bis-(salicylideneamino)-octane are also reported. The Fe(II) complex is unique in having two unpaired electrons which is interpreted as meaning that Fe(II) is bound to the sexadentate in the same manner as Fe(III) in ferriheme hydroxide—by four bonds resonating among six positions.

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The Osmium Tetroxide Catalyzed Oxidation of Fumaric and Maleic Acids¹

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The oxidation of fumaric and maleic acids to racemic and mesotartaric acids by aqueous osmium tetroxide-potassium chlorate solution was first studied by Hoffmann² who suggested that the reaction mechanism involves a complex of the osmium tetroxide and potassium chlorate. In a more extended study Milas³ checked the stoichiometry of the reaction, showed that potassium chloride was the principal reduction product of the chlorate, there being only traces of chlorite and hypochlorite, and suggested as a mechanism alternate reduction of the tetroxide by the maleic acid and oxidation by the chlorate. Criegee⁴ in a general study of the influence of osmium tetroxide on the conversion of various olefins to their corresponding glycols observed the formation of a precipitate on the addition of the tetroxide to the olefin in an anhydrous medium. Analysis of the precipitate showed it to contain one atom of osmium for each molecule of olefin. As a mechanism of the over-all reaction he suggested the formation of this compound as a first step succeeded by its hydrolysis to the

glycol and a partially reduced oxide of osmium which is subsequently reoxidized. The present work was undertaken to check this mechanism by a rate study and thus to determine the rate-controlling step.

Experimental

Reagents.—Maleic and fumaric acids were recrystallized from hot water several times until the melting points checked the literature values of 130.5° and 287°. The potassium chlorate was C. P. grade, free of chloride and the purity was checked by the procedure used in the analysis. Lithium chlorate was prepared from equimolar amounts of lithium sulfate and barium chlorate solutions, the barium sulfate precipitate was filtered and the remaining solution evaporated slowly to dryness and finally under vacuum. The composition was checked by analysis. The osmium tetroxide, C. P. grade, was found to melt between 39 and 39.5°, the latter being the reported melting point. Dioxane was purified from a commercial sample by refluxing with metallic sodium for one week followed by distillation. A fraction boiling between 101.2 and 101.8° was used.

Procedure.—For a run the desired amounts of standard fumaric or maleic acid and standard potassium chlorate were mixed in a glass-stoppered bottle and placed in a thermostat at $25 \pm 0.05^\circ$ for about an hour. During this time no detectable reaction occurred. In fact no reaction occurred under these conditions in two weeks. Zero time for a run was noted at the instant of addition of the osmium tetroxide solution. At the higher temperatures the three solutions were preheated separately and then rapidly mixed. Aliquot samples were removed and analyzed for chlorate at various time intervals.

(1) Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, February, 1950.

(2) Hoffmann, *Ber.*, **46**, 1657 (1913).

(3) Milas, *Text Journal*, **47**, 1413 (1925).

(4) Criegee, *Ann.*, **522**, 75 (1936).

A series of runs to study the influence of hydrogen ion concentration on the rate was made by adding hydrochloric acid or sodium hydroxide to the reaction system before the osmium tetroxide catalyst was added. The hydrogen ion concentration was measured using a Beckmann pH meter and a calomel electrode.

In the chlorate analysis of the aliquots, 3 ml. of concd. HCl was added to 25 ml. of solution. To remove air, three 200-mg. portions of NaHCO₃ were added in succession and the solution immediately treated with 1 g. of solid potassium iodate and 22 ml. of concd. HCl. After standing stoppered for five minutes, the solution was titrated with 0.1 *N* sodium thiosulfate. The analysis is accurate to $\pm 0.5\%$. Fumaric and maleic acids as also small amounts of osmium tetroxide such as were used were shown to be without effect on the analysis.

To determine the influence of water on the rate of reaction several runs were made in dioxane containing known amounts of water. Dioxane was found to interfere with the chlorate analysis and had to be removed first. The aliquot of the reaction mixture was distributed between chloroform and water, the chloroform removing the dioxane and osmium tetroxide. Three successive extractions and separations were found satisfactory. The precision of this modified procedure for chlorate analysis was found to be $\pm 1\%$. Since potassium chlorate is insoluble in dioxane, lithium chlorate was used. That the lithium salt did not affect the reaction rate in aqueous solution was demonstrated by its use in place of potassium chlorate under these conditions.

Results

Experiment showed that osmium tetroxide does not appreciably increase the rate of decomposition of chlorate in acid solution except at very high chlorate concentration. The production of tartaric acid from fumaric acid is known to be approximately 100%. It follows therefore from the stoichiometry of the reaction that in the runs here reported where the reaction is carried only to about 50% completion, the concentration of fumaric or maleic acid at any instant is equal to the initial concentration minus three times the amount of chlorate decomposed. Rate constants were calculated in the usual way using the first order equation $k = 1/t \cdot \ln(a/(a-x))$ where a is the acid concentration. This experimental constant k divided by the concentration of osmium tetroxide, the catalyst, gives k_r reported in the tables. In many cases the slopes of graphs of $\log(1/(a-x))$ against time were used to determine the constant k . Data for a typical run are presented in Table I.

TABLE I

RATE OF OXIDATION OF FUMARIC ACID, TEMP. 25°, OsO₄, 0.000849 MOLE/L.

Time, hr.	KClO ₃	Fumaric acid	$k_r \cdot 1$ mol. ⁻¹ hr. ⁻¹
0	0.0314	0.0509	...
1.07	.0291	.0440	162
2.30	.0267	.0368	170
3.38	.0250	.0317	169
5.33	.0221	.0230	176
6.55	.0208	.0191	181
		Mean	172
		By graph	171

Table II summarizes all the data obtained for fumaric acid at 25° and shows the effects of vary-

ing the concentrations in turn of acid, chlorate, catalyst, hydrogen ion and water, the latter in dioxane solution. It should be noted that the analytical precision for the dioxane solutions is much less than for the aqueous solutions. The

TABLE II

RATE CONSTANTS FOR OXIDATION OF FUMARIC ACID AT 25°

Fumaric acid	Moles per liter		k_r	
	KClO ₃	OsO ₄		
0.0509	0.0314	0.000213	176	
.0509	.0314	426	172	
.0509	.0314	604	167	
.0509	.0314	849	172	
.0513	.0318	515	} 171	
.0513	.0211	515		
.0513	.0172	515		
.0513	.0084	515		
.0513	.0422	515		
.0513	.0636	515	a	
.0563	.0191	0.000982	169	
.0236	.0074	394	172	
.0314	.0202	519	176	
.0478	.0296	786	165	
.0471	.0148	786	165	
			pH	
.0508	.0315	.000511	1.0 (HCl added)	120
.0508	.0315	511	1.4 (HCl added)	132
.0508	.0315	511	2.2 (No HCl)	176
.0508	.0315	511	3.15 (NaOH added)	307
.0508	.0315	511	3.5 (NaOH added)	318
			KCl	
0.0519	319	0.000174	0.194	176
			H ₂ O in dioxane	
0.0788	0.00406	0.000196	0.0694	} ~ 126
.0788	.00406	196	.104	
.0788	.00406	196	.139	
.0788	.00406	196	.208	
.0508	.0276	417	Aq.	
		849	Aq.	173

a At high chlorate concentration the solutions became yellow probably due to chlorine dioxide and showed an abnormal rate of disappearance of chlorate.

TABLE III

RATE CONSTANTS FOR OXIDATION OF MALEIC ACID AT 25°

Maleic acid	Moles per liter		k_r	
	KClO ₃	OsO ₄		
0.0510	0.0313	0.00213	28.0	
.0510	.0313	426	28.0	
.0510	.0313	604	26.4	
.0510	.0313	851	29.1	
.0514	.0212	516	} 26.8	
.0514	.0421	516		
.0514	.0171	516		
.0514	.0127	516		
			pH	
.0505	.0315	843	1.45	21.4
.0505	.0315	843	2.06	34.2
			KCl	
.0515	.0316	851	0.151	29.1
			H ₂ O in dioxane	
.0771	0.00368	951	0.0681	} ~ 16
.0771	.00368	951	.102	
.0771	.00368	951	.136	
.0771	.00368	951	.204	

slope of the graph of $\log(1/(a-x))$ against time for the runs at varied water concentrations averaged 126 for k_r , with possible extreme values being 115 and 138.

Table III summarizes similarly the data for maleic acid at 25°.

The effect of temperature was studied over the range 9–95° for both fumaric and maleic acid. The data are presented in Tables IV and V. The rate constant at each temperature is the average from two runs. The energies of activa-

TABLE IV

EFFECT OF TEMPERATURE ON FUMARIC ACID OXIDATION	
Fumaric Acid 0.0260; KClO ₃ 0.0161; OsO ₄ 0.000175	
Temp., °C.	k_r
9.0	47.6
25.0	167
35.3	324
45.0	676
55.3	1120
65.1	1930
74.1	3380
85.2	4760
95.2	6250

TABLE V

EFFECT OF TEMPERATURE ON MALEIC ACID OXIDATION	
Maleic acid 0.0255; KClO ₃ 0.0156; OsO ₄ 0.000840	
Temp., °C.	k_r
9.0	8.30
25.0	29.7
35.3	55.6
45.0	108
55.3	224
65.1	414
74.1	662
85.2	1240
95.1	2070

tion calculated by the Arrhenius equation for each successive ten-degree interval and then averaged are for fumaric acid 13.1 ± 0.7 kcal. and for maleic acid 13.3 ± 0.4 kcal. The values are the same within the limits of the precision.

Discussion

The constancy of k_r in the above tables as well as the observed linearity of graphs of the logarithms of the unreacted acid plotted against time for all runs necessitates that the over-all reaction is kinetically of second order, first with respect to the acid and first with respect to the catalyst, osmium tetroxide. The absence of effect of variation, first, in the concentration of the chlorate at constant acid and catalyst concentration and second in the water concentration in the dioxane runs shows these to be of zero order.

These observations are satisfactorily accounted for, if the results of Criegee showing the addition of osmium tetroxide to a double bond is taken as the rate controlling step. The resulting fumaric or maleic acid complex with the catalyst, must be

rapidly transformed in the presence of chlorate, to tartaric acid to account for the absence of effect of water and any reduced oxide of osmium resulting, must be rapidly reoxidized by the chlorate. This conclusion was borne out qualitatively by an experiment in dioxane. When osmium tetroxide in dry dioxane was added to a dry dioxane solution of maleic acid, a gradual formation of a black precipitate was observed, the precipitate becoming perceptibly more intense with time. Addition of a dry dioxane solution of lithium chlorate caused no apparent change in the precipitate but addition subsequently of a small amount of water brought about an instantaneous solution of the precipitate. Addition of aqueous lithium chlorate to the system with the black precipitate gives the same result. There can be no doubt that a reaction of the acid and osmium tetroxide is slow and that the transformation of the complex in the presence of chlorate is a rapid reaction.

Addition of potassium chloride to the aqueous reaction system is seen also to be without effect on the rate. Absence of neutral salt effect is to be expected on the basis of the Brönsted theory of ionic reactions when at least one of the reactants forming the reaction complex is a neutral molecule. Osmium tetroxide is such an extremely weak electrolyte that it probably enters into the reaction in its molecular form. Both fumaric and maleic acids are comparatively weak acids and will exist in aqueous solution as un-ionized molecules as well as ions. Addition of hydrochloric acid will increase the former; of base, the latter. The results at different pH show that the over-all rate is decreased at low pH and increased at high pH values. At the extreme values of pH 1.0 and 3.5 studied in the case of fumaric acid the k_r values are 120 and 318, respectively. The actual over-all rates corresponding to these specific rates may be considered as the sum of the rate due to the un-ionized molecule and the rate due to the ion. Taking the ionization constants of fumaric acid as 1×10^{-3} and 3×10^{-5} , at pH 1 and an acid concentration 0.05 mole per liter the fumarate ion concentration is negligible. At pH 3.5, the ion concentration is 0.035, the molecule concentration 0.015. Hence from the simultaneous equations

$$0.05 \times 120 = 0.05k_a$$

$$0.05 \times 318 = 0.015k_a + 0.035k_i$$

where k_a is the specific reaction rate for the un-ionized molecule and k_i , that for the ion, it follows that $k_i/k_a = 3.35$ and $k_a = 121$ and $k_i = 408$. Similar calculations for the maleic acid at pH's 1.45 and 2.06 show $k_i/k_a = 5.0$ with $k_a = 9.8$ and $k_i = 49.0$, the ionization constants being taken as 1.5×10^{-2} and 2.6×10^{-7} .

Since in a reaction showing no salt effect a dielectric effect is not to be expected, the above results serve to account for the reduced values of k_r in the moist dioxane runs which are some

20% lower than in aqueous solution. The concentrations of fumarate and maleate ions in the moist dioxane must be considerably less than in water.

The approximately six-fold higher value of k_r for fumaric acid than for maleic acid may be analyzed further as an eight-fold higher value for the fumarate ion over the maleate ion and a twelve-fold higher value for the un-ionized fumaric acid. This discrepancy is probably due to steric factors. In maleic acid the carboxyl groups on the same side of the double bond are able to block the approach of an osmium tetroxide molecule much more than would the carboxyls which are on opposite sides in the fumaric acid molecule. It is not unexpected also that this hindrance could be less for the ions than for the acid molecule as observed. The discrepancy lends further evidence in favor of the rate-controlling step postulated, since the addition reaction of the acid and catalyst is the most likely step to be affected by steric considerations; ease of transformation of the complex is probably the same for both the maleic and fumaric complexes.

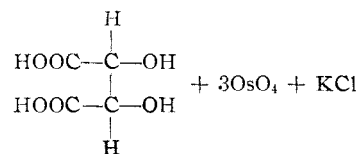
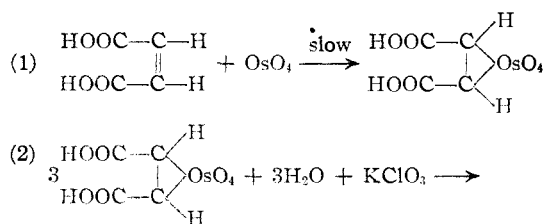
It is significant further in this connection that the energy of activation of the reactions of the two acids is the same. The difference in the rates is then to be attributed to the frequency factor in the Arrhenius equation, that is, on the basis of collision theory where $k_r = PZe^{-E/RT}$ to a difference in the product PZ . At 25° taking 13 kcal. as the energy of activation the values 1.8×10^8 and 3.1×10^7 sec.⁻¹ are found for PZ for fumaric and maleic acid, respectively.

On the basis of the absolute reaction rate theory the product PZ may be related to the entropy of activation by the equation $PZ = ekT/h \cdot e^{\Delta S^\ddagger/R}$ where e is the base of natural logs, k is the Boltzmann gas constant, h is Planck's constant and ΔS^\ddagger is the entropy of activation. At 298° K., ΔS^\ddagger is found to be -22 and -20 entropy units for maleic and fumaric acids, respectively.

The interpretation of these entropy decreases must depend on the structure of the acid-osmium tetroxide addition compound. If one assumes that the formation of this compound involves the opening of the ethylenic double bond of the acid to yield two single bonds which then attach directly to the osmium atom in osmium tetroxide, the restriction of the osmium-oxygen vibrations might account for the entropy decrease. The older view historically, that the addition of the single carbon bonds is to two oxygens of the osmium tetroxide molecule seems unlikely in view of the specificity of osmium tetroxide over many other oxides which are not at all catalytic and also in view of the recognition of the prev-

alence of carbon-metal bonds in numerous molecules. Accepting the former view it should be noted that the assumption is necessary that the activated complex of the rate-controlling step closely resembles the addition compound.

It is impossible from any of the work here reported to identify the reduced state of the osmium tetroxide during or after transformation of the addition compound nor does it appear necessary to speculate concerning it. Possibly of significance in this respect is the suggestion made by Hoffman² in the original work, of a complex of osmium tetroxide and potassium chlorate. As evidence for this he reports that the solubility of potassium chlorate in water is increased by the addition of osmium tetroxide and that the oxidation potential of a solution containing both chlorate and tetroxide is higher than that of either constituent alone. Neither of these results was tested in this work. It is conceivable however that the reduced state of the tetroxide need not necessarily be identified with one of the well-known lower oxides of osmium but in presence of chlorate could be a transitory lower oxide such as OsO₃. The over-all reaction could then be written as



Summary

The rates of oxidation of fumaric and maleic acids by aqueous osmium tetroxide-potassium chlorate solutions have been studied as functions of substrate, catalyst and oxidant concentrations at temperatures from 9° to 95°. The rate-controlling step is identified as the formation of a complex of acid and catalyst, subsequent glycol production being rapid. Study of the effect of pH shows that the specific rate for the ions is from three to five times greater than that of the un-ionized acid molecule. The energy of activation is 13 kcal. in both cases while the entropies of activation are -20 and -22 entropy units for fumaric and maleic acids, respectively.

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