

"prtr," were oxygenated in stages and the magnetic susceptibility at each stage measured. The oxygenations were carried out by suspending the weighed, filled tubes in a bomb and exposing to oxygen for various intervals of time. The extent of oxygenation was determined by weight.

The sample of the parent diamine showed the following behavior when exposed to 1 atmosphere of oxygen.

Time, min.	% O ₂	$\chi_m \times 10^6$
0	0.0	2490
2	0.21	2440
3	0.62	2290
15	1.44	1862
20	1.85	1550
30	3.11	990
50	4.34	476
	4.90 (complete)	160

The data are plotted in Fig. 14. The line is straight, showing simple additivity of susceptibilities, as would be expected for a two-phase solid system.

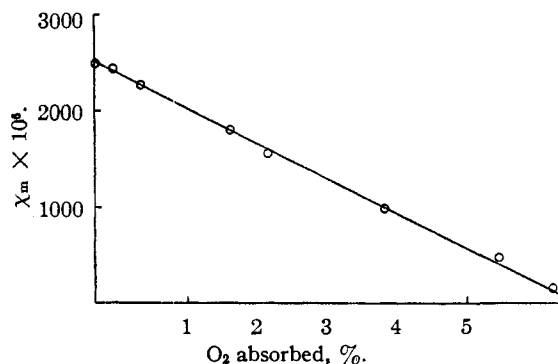


Fig. 14.—CoSaEn.

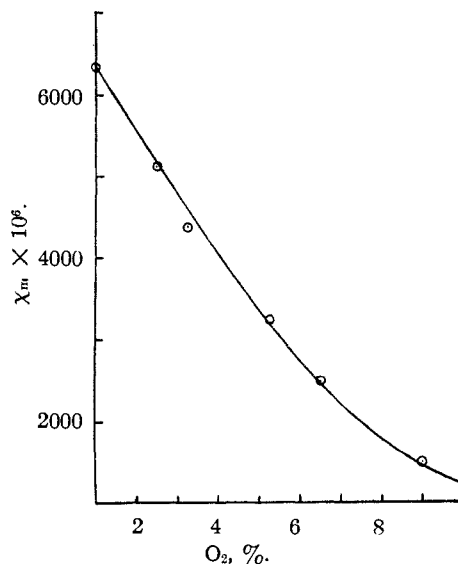


Fig. 15.—CoSaPrtr.

A similar plot of the parent triamine is shown in Fig. 15. The curvature of the line may be due to non-additivity of the components. It is also consistent with the possibility that irreversible oxidation is taking place as saturation is approached. Cobaltic compounds would be expected to have 2 or 4 unpaired spins, in any case more than the one for the peroxide.

Summary

Room temperature susceptibilities of a number of transition element chelates have been measured.

The variation of susceptibility with temperature has been studied, and characteristic anomalies discussed with respect to crystal symmetry.

Susceptibility as a function of oxygenation has been studied for two oxygen carriers.

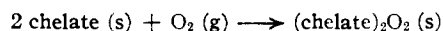
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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA, AND THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY¹]

The Oxygen-carrying Synthetic Chelate Compounds. V. Equilibrium with the Solid Compounds^{1a}

BY E. W. HUGHES,² W. K. WILMARTH³ AND M. CALVIN

The present work is concerned with the measurement of the equilibrium represented by the general reaction



where the chelates are of type I⁴ and bearing

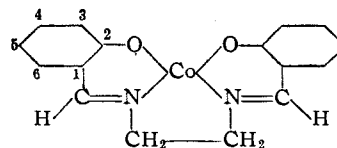
(1) No. 1065.

(1a) The work herein reported was done under a Contract (OEMsr-279) between the National Defense Research Committee and the University of California.

(2) Present address: California Institute of Technology, Pasadena.

(3) Present address: University of Southern California, Los Angeles.

(4) Calvin, Bailes and Wilmarth, *THIS JOURNAL*, **68**, 2254 (1946).



various substituents in the benzene ring.⁵

Both the oxygen equilibrium pressure and the X-ray powder diagrams of the solid phase were taken as a function of the oxygen content of the solid phase.

(5) We will use the abbreviation CoSaEn for this type, inserting the substituents as required.

The preliminary study showed that the equilibrium oxygen pressure was a function of the oxygen composition. The data indicate that the reaction is not simply the addition of oxygen to form the peroxide stoichiometrically with an accompanying phase change. However, the X-ray powder patterns of a chelate and its peroxide are distinctly different and, therefore, a phase change may be involved at some stage of the oxygenation. Powder patterns were then made of the chelate CoSaEn at various percentages of oxygenation. These data enable us to demonstrate a phase change and to fix the composition of the two phases existing during the process of phase change for this particular chelate.

Experimental

The sample of CoSaEn was prepared by pelleting the pyridinate,⁶ and activating by vacuum heating at 165° for one hour. The pelleted active sample originally absorbed the theoretical 4.92% by weight of oxygen. It was stored as the peroxide for one year before use and during this period the capacity dropped to 4.4%.

The 3-ethoxy-CoSaEn was also prepared and pelleted as a pyridinate.⁶ It was activated by vacuum heating for one and one-half hours at 170°. The pelleted active sample absorbed reversibly the 3.86% by weight of oxygen.

The 3-nitro-CoSaEn⁷ absorbed reversibly the calculated 3.85% when exposed to oxygen at 150 lb./sq. in. pressure. The sample was pelleted in its active form.

The 3-methoxy-CoSaEn sample was prepared by pelleting the hydrate.⁶ It was analyzed as a monohydrate; the results were C, 53.6, 53.3; H, 4.87, 4.96; Co, 14.51, 14.45; calculated for the monohydrate: C, 53.5; H, 4.96; Co, 14.63. The sample used reversibly absorbed the calculated 4.16% by weight of oxygen after activation.

A sample of approximately 10 g. was used in each measurement. It was prepared, in each case, by pressing either the pure active sample or a solvate of it with a hydraulic press to form a cake. The cake was then broken and forced through a wire screen. Granules of several millimeters in diameter were selected for the final sample.

These were activated by vacuum heating at the appropriate temperature and the capacity measured either gravimetrically or gasimetrically before the measurements were carried out. This oxygenation was carried out with oxygen at 1 atm. of pressure in all cases except the 3-NO₂-CoSaEn, as this chelate requires somewhat higher pressures of oxygen to form the peroxide stoichiometrically. The pelleted samples were used to prevent the fine powder from blowing through the apparatus during evacuation.

Apparatus.—The apparatus used in the early measurements consists only of a gas buret and mercury manometer connected by capillary tubing and the sample tube, which was immersed during the measurements in a 25° thermostat. The sample tube, holding approximately 7.5 g. of the chelate, was made of 10-mm. o. d. glass tubing. A stopcock was so arranged that the sample could be isolated from the gas buret and manometer when necessary. The free volume in the sample tube when filled with the chelate was measured volumetrically up to this stopcock with dry nitrogen.

The measurements were carried out by evacuation of the apparatus and, if necessary, deoxygenation or activation of the sample by vacuum heating. The sample was isolated from the rest of the apparatus by closing the stopcock and then pure dry oxygen was admitted to the oxygen buret and manometer. A known volume of oxygen was then admitted to the sample by opening the stopcock and the absorption at constant volume was followed on the mercury

manometer. The initial absorption was quite rapid but final equilibrium, especially at the higher per cents. of oxygenation, was reached rather slowly. The system usually reached equilibrium in one day but sometimes as much as three days was required. When it appeared that equilibrium was reached, a fresh volume of oxygen was delivered to the sample and the system again allowed to reach equilibrium. These equilibrium values were approached from larger pressures of oxygen than the equilibrium values.

The above apparatus was not entirely satisfactory because it was not convenient to approach the equilibrium from pressures both higher and lower than the equilibrium pressures. The following modification was added. The apparatus was equipped with a Toepler pump so the pressure of oxygen over the sample could be varied at will. Also, a very small differential oil manometer containing dibutyl phthalate was attached with capillary tubes so that it could be connected to the sample when the sample was isolated from the rest of the system. The method of studying then consisted not of waiting for the sample to reach an equilibrium pressure by absorption or desorption of oxygen, but rather to adjust the oxygen pressure to a value such that the sensitive oil manometer registered neither an absorption nor a desorption of oxygen. One could readily measure absorption or desorption of 1/200 cc. of oxygen at S. T. P. This corresponds to approximately 0.002% of the total oxygenation of these samples. This modified apparatus was used only in the study of the chelate CoSaEn.

Experimental Results

The data for the initial experimental studies, in which equilibrium was attained from higher pressures, are plotted in Figs. 1 and 2. The unit of pressure is cm. of mercury and the per cent. of total oxygenation is calculated from the experimental desorption of each sample.

The equilibrium oxygen pressure of the 3-NO₂-CoSaEn appears to be approximately constant, except for a short region of very low oxygenation, up to approximately 35% of the total oxygenation. The equilibrium pressure then appears to rise rapidly above this region and it will be noted that only ~75% of the total oxygen is absorbed at 1 atm. of pressure. It was correspondingly noted that equilibrium is also attained very slowly in this region.

It is seen that the shape of the curve for the 3-methoxy compound differs considerably in appearance from the others. The initial pressure increase is more pronounced and the region of constant equilibrium oxygen pressure appears to have completely disappeared. These equilibria were obtained somewhat more slowly than with the 3-nitro derivative and 1 to 3 days were spent in reaching equilibrium. The speed at which the oxygenation proceeds in both cases becomes markedly slower when one is working in the region of oxygenation in which the curve appears to be rising rapidly. It is possible that the 3-methoxy compound did not reach true equilibrium in the region of 40–65% oxygenation and the equilibrium curve may be horizontal in this interval. The point for the 3-methoxy at 79% oxygenation is open to question because of experimental difficulties, but its position seems quite reasonable.

(6) Bailes and Calvin, to appear.

(7) This particular sample was prepared and sent to us by Professor H. C. Diehl at the Iowa State College.

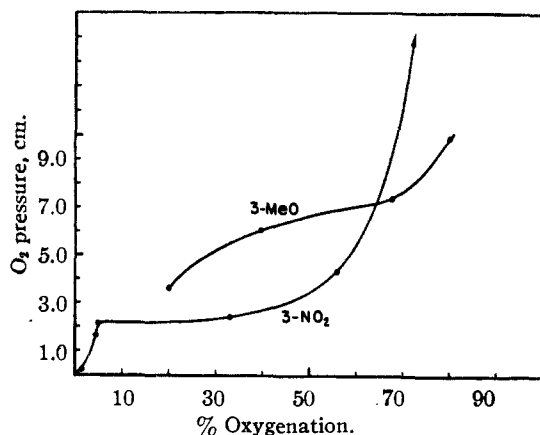


Fig. 1.—Oxygen equilibrium pressures over the 3-MeO- and 3-NO₂- compounds at 25°.

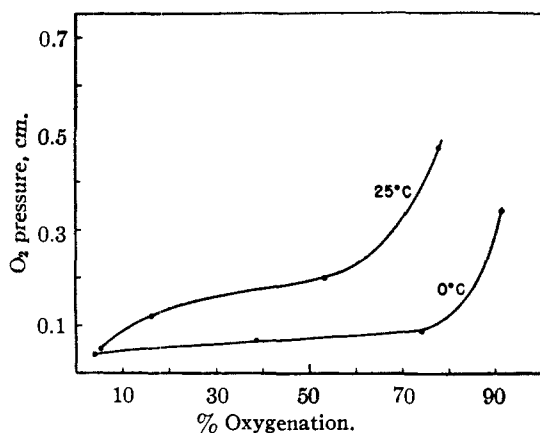


Fig. 2.—Oxygen equilibrium pressures over the 3-EtO- compound.

The data for the 3-ethoxy-CoSaEn plotted in Fig. 2 are subject to the largest percentage error because the apparatus used in the measurement was not designed to measure the rather small equilibrium pressures. The oxygen pressure may well be constant over the intermediate range of oxygenation.

An attempt was also made to study the equilibrium at 50° but it was abandoned because of the importance of other work. However, a single value of 2.23 cm. of pressure at 56% of total oxygenation was obtained.

The equilibrium data for the chelate CoSaEn (Fig. 3 and Table I) were acquired with the modified apparatus and are believed to be somewhat more accurate than those previously presented in this paper. However, even here the data should be considered as preliminary for several reasons. The most serious experimental difficulty was a noticeable hysteresis which must be investigated more carefully before a complete understanding of the system is reached.

A single value at a higher temperature was again obtained. The equilibrium pressure at 40° was found to be 23.5 cm. at 58% oxygenation.

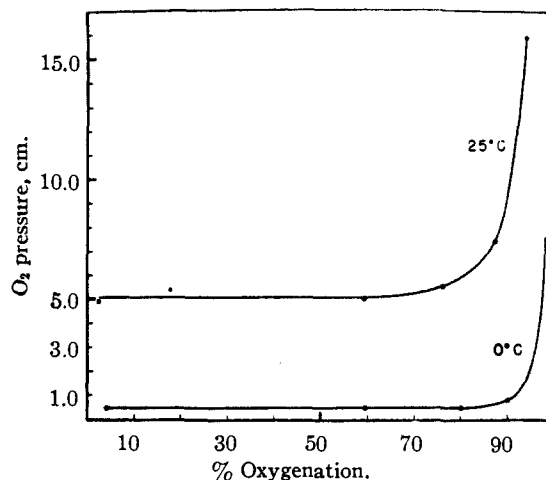


Fig. 3.—Oxygen equilibrium pressures over the parent compound CoSaEn.

TABLE I

Press., cm.	% Total oxygenation	Press., cm.	% Total oxygenation
3-NO ₂ -CoSaEn, 25°		3-EtO-CoSaEn, 25°	
0.2	1.45	0.05	5.23
1.6	4.7	.12	16.1
2.1	4.9	.20	53.2
2.4	33	.47	77.8
4.3	56	1.15	93.0
76	~75	CoSaEn, 0°	
3-MeO-CoSaEn, 25°		0.45	3.97
3.6	20.1	.48	54.6
5.5	39.3	.47	77.9
7.35	67.6	.77	90.2
9.9	79.6	.75	98.5
3-EtO-CoSaEn, 0°		CoSaEn, 25°	
0.037	3.57	4.9	2.38
.037	38.4	5.4	17.8
.088	74.0	5.0	59.3
.34	91.0	5.5	76.3
		7.4	87.4
		15.8	94.6

X-Ray Investigation. Experimental.—The X-ray powder photographs were prepared in a cylindrical gas-tight camera with 3-cm. radius. The camera was connected directly to a mercury manometer and through stopcocks either to a mechanical vacuum pump or to bubbling tubes, admitting oxygen, nitrogen, or air as desired. The pressure could be maintained anywhere between zero and one atmosphere.

The X-rays were from a copper target X-ray tube and were filtered through nickel foil to remove most of the white radiation and CuK β rays. A pinhole type collimator was used.

The samples were extruded from stainless steel tubing by a stainless steel wire and were approximately 0.35 mm. in diameter and 1 to 2 mm. long. They adhered to the extrusion wire and were mounted in the camera by means of it.

The X-ray beam was slightly wider than the sample diameter. Although no binder was used, these samples had sufficient strength to withstand repeated cycling of the camera pressure from zero to atmospheric and back without disintegrating.

The X-ray patterns of the parent compound and its oxide were prepared repeatedly using various preparations and techniques. Tentative indexings of the patterns have been given and a structure proposed for the parent chelate. The details of this work will be published separately.

From this extensive work, it appears that all preparations of the chelate contain a few per cent. of an impurity, which is probably an alternative active crystalline modification of the same substance. Upon oxygenation, two lines appear which do not fit the indexing of the oxide pattern and whose intensities do not bear a constant ratio to the intensities of the oxide pattern lines. The presence of this impurity of course introduces some uncertainty into the X-ray results described below. If the impurity always took up oxygen in the same ratio as the main sample, no error would result. This is certainly not true, but, on the other hand, the error is certainly not so large as would obtain if the same amount of an inactive impurity were present. The uncertainty from this source can hardly exceed $\approx 2.5\%$ of total theoretical oxygen uptake.

The material used was from the same sample as was used in the oxygen pressure work. The pellets were pulverized and passed through a 100-mesh sieve. A sample was extruded and photographed under 18 cm. of oxygen. Several grams were then deoxygenated in vacuum at 100° for two hours. Samples of about one to one and one-half grams each were weighed out rapidly in glass-stoppered weighing bottles and stored in vacuum. An X-ray sample was extruded and photographed in vacuum. The reaction with oxygen is slow enough so that no appreciable oxygen is absorbed in the few minutes required to extrude a sample and mount it in the camera.

One of the weighed samples was exposed to oxygen, the bottle being closed from time to time and shaken to ensure uniformity of the sample's oxygen uptake. After attaining about 50% oxidation, it was stored in a vacuum desiccator containing oxygen at the equilibrium pressure indicated by the pressure-oxidation curve. After two days the weight of the sample had changed only 0.3 mg. corresponding to about 0.3% oxidation. This is the order of magnitude of the weighing error. A sample was quickly extruded and photographed in the same pressure of oxygen. Essentially the same method was used to get samples of about 65% oxidation and 10% oxidation. In the latter case, however, the weighing bottle, which was smaller than usual, was placed in the X-ray camera during the X-ray exposure to check the constancy of composition.

The change in weight observed during exposure was again about 0.3 mg. Samples of about 5% and 20% oxidation were obtained by pumping oxygen off the 50% sample. The procedure was otherwise the same.

Some trouble was experienced with these last two samples of low oxygen content in holding the weight constant. When stored at the pressure indicated by the curve they gained weight and a reduced pressure had to be used to maintain constant weight. This is in contrast to the intermediate sample at about 10% oxidation obtained by adding oxygen. There is thus some evidence of hysteresis and the samples may not have been in complete equilibrium with respect to distribution of oxygen internally even though there was no change of weight in several days.

The exact compositions photographed were 0.0, 5.8, 13.5, 22.0, 47.4, 66.4 and 92.5% oxidation, assuming that the oxygen-free sample can take up 4.92% of its weight in oxygen. The uncertainty in these compositions is perhaps $\approx 1\%$ oxidation, not including the uncertainty discussed above which arises from the presence of active impurity.

All except the first and last show both patterns characteristic of the extreme samples. The two strongest lines are so nearly alike in spacing and intensity for both the chelate and its oxide that they cannot be used in identification. The strongest unique line of the oxygen-free pattern can be seen on the 66.4% picture and is quite weak. It is unfortunate that this strong oxygen-free line falls almost exactly on a very weak line of the oxygenated pattern and a correction must be made for the latter. This renders less reliable the estimation of the point at which the strong line disappears. But it seems more than likely that the oxygen-free form is eliminated somewhere about 75 to 80% oxidation. At the other end of the series the situation is more favorable. The strongest unique oxide line falls in an otherwise clear part of both patterns. It is easily visible on the 5.8% picture and is indeed 0.12 density unit above the background. A line 0.02 density unit above the background is usually detectable visually. Since in general several per cent. of a form must be present for its lines to be detected, we see that very little if any oxygen could be present as solid solution in the oxygen-free phase.

The important lines have been densitometered using an Eastman Model B Densitometer with a 0.012-in. spot. It has been shown in film tests recently made in these Laboratories that film and processing of the kind used yield optical densities which, when the chemical fog level is subtracted, are proportional to X-ray intensities when the densities are less than about 2.0. The heights of the lines above background were taken as approximations to the relative intensities of the lines on a given film. Since no absolute inten-

sities are known one can only consider the ratios of lines on a film and note how the ratios vary from sample to sample.

The two extraneous oxide lines mentioned above as being indicative of an active impurity are quite prominent for this material. The ratios of these lines to oxide lines are not constant. On pumping off oxygen, these lines fade out more slowly than the oxide lines. This other form of the material seems to give up its oxygen more slowly and perhaps has a lower equilibrium pressure.

The ratios of the strongest unique oxygen-free line to the strongest unique oxide line, after allowing for the weak oxygenated line which interferes with the latter, and the inverse of these ratios, are plotted on an arbitrary scale against per cent. oxidation in Fig. 4. The digressions of the points from smooth curves are no greater than expected in view of the approximations made and the experimental difficulties. For small values of the ordinates, each curve is expected to become linear. This facilitates extrapolation to zero ordinate for determination of the composition at which the various phases first appear. From Fig. 4 it is clear that to within the experimental error the oxide phase appears with the first oxygen added. There is no evidence for any solid solution of oxygen in chelate. On the other hand, the last of the oxygen-free phase vanishes when only about 75 to 80% of the stoichiometric load of oxygen has been absorbed. In view of the constancy of the oxygen equilibrium pressure up to this point, it seems reasonable to suppose that the first oxide phase formed is of this same concentration and that this oxygen ratio is not exceeded anywhere in the sample until the whole sample has achieved this ratio.

Discussion

The four chelates included in this study appear to have oxygen equilibrium curves which are rather similar in shape although differing in absolute magnitude. This shape is characterized by an initial rapid rise, a considerable interval of approximately constant pressure, and another final rise occurring before the oxygenation is complete.

The initial rise, shown most clearly in the curve for 3-NO₂-CoSaEn, may be due to a limited region of solid solution existing at low per cent. oxygenation. However, this interpretation is rendered doubtful because the X-ray study of the parent compound revealed the presence of a few per cent. of an oxygen-carrying impurity. This impurity appears to be another crystal form of the same compound with a somewhat lower oxygen pressure than that of the bulk of the crystals. The X-ray studies have been completed only in the case of the parent compound and we, therefore, cannot be certain that small amounts of similar impurities do not exist in the other chelates. This contamination, if it existed, would

also account for the shape of the curve in this region.

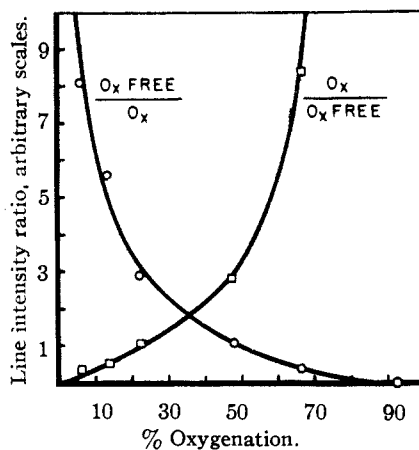


Fig. 4.

The intermediate interval of approximately constant pressure has been shown, in the case of the CoSaEn, to coincide with the crystalline phase change. The other chelates also appear to undergo oxygenation to a product which has not yet acquired the stoichiometrical amount of oxygen. This appears to be most marked in the case of the 3-NO₂-CoSaEn, where final rise must begin well below fifty per cent. of the total oxygenation.

The curves are finally characterized by a region in which the oxygen pressure rises very rapidly. Most of the chelates of this class absorb the stoichiometrical amount of oxygen when exposed to oxygen at one atmosphere pressure but the 3-NO₂-CoSaEn reaches only ~75% of the value under these conditions. The X-ray study shows that this interval of higher oxygen pressure, in the case of the CoSaEn, is definitely a region of solid solution and it is expected that similar X-ray results will be found for the other compounds. The data are not sufficiently extensive or accurate in this interval to justify calculation of the repulsive forces which must come into play between bound oxygen molecules. This problem can be discussed qualitatively more easily in a later paper dealing with the crystal structure of these compounds and it will be handled in more detail there.

TABLE II^a

	CoSaEn	3-NO ₂ -CoSaEn	3-MeO-CoSaEn	3-EtO-CoSaEn
ΔH , cal.	19,100		19,100	18,900
ΔF^0 , cal.	1,600	2000	1,450	3,500
$(\Delta H - \Delta F^0)/T$, e. u.	59		59	52

^a All values are per mole of oxygen.

The thermodynamic quantities for the oxygenation process are collected in Table II. The heats of oxygenation are average values for the oxygenation at 0° and are essentially equal to the ΔH for the reaction. The approximate calculation for ΔF^0 has been made by simply substituting the

(8) Taylor, Miller and Calvin, forthcoming.

equilibrium oxygen pressure in atmospheres into the formula $\Delta F^0 = +RT \ln P_{O_2}$. The value of the pressure in each case was chosen to fall on the linear portion of the equilibrium curve. The value of $\Delta H - \Delta F^0/T$ listed in line four is then approximately equal to the ΔS of the oxygenation.

The ΔH values, calculated from the oxygen pressures at 0 and 25° are 15,000 cal. for CoSaEn and 7,200 cal. for 3-EtO-CoSaEn. The agreement is not too bad for the CoSaEn and the large deviation, in the case of the 3-EtO-CoSaEn, is not expected since these data are less accurate than any of the other measurements. The discrepancy in both cases is believed to be due largely to a lack of attainment of equilibrium in the 0° measurements. This is confirmed by a calculation of the ΔH values from the 25° and the single point at 40° for CoSaEn and at 50° for the 3-EtO-CoSaEn. ΔH values of 19,200 cal. and 19,300 cal., respectively, are obtained in good agreement with the measured heats.

These are, of course, crude calculations but they are sufficient to illustrate the general nature

of the oxygenation process. It is apparent that the small change in free energy and appreciable oxygen pressures are a result of the rather large heat and entropy effects cancelling each other. The entropy loss of 50–60 entropy units is somewhat more than the translational entropy of oxygen gas and is even greater than the total molal entropy of oxygen at 25° (40.3 e.u.). However, this loss of translational entropy is probably the most important factor in the large entropy change.

Summary

The oxygen equilibrium pressures over four crystalline oxygen-carrying chelates have been measured as a function of the degree of oxygenation. The X-ray powder diagrams of one of these compounds have been followed through the range of composition from 0 to 92% oxygenation. It has been demonstrated by both methods on at least one compound that this is not a simple three phase system (gas and two solid phases) but also involves at least one region of solid solution.

BERKELEY, CALIFORNIA

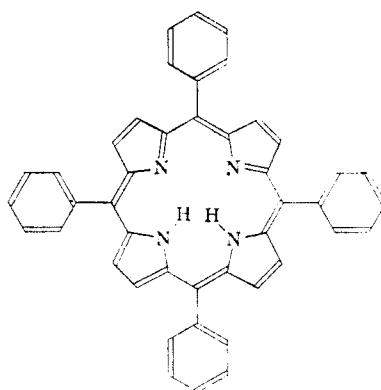
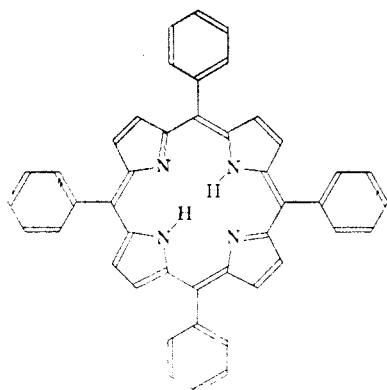
RECEIVED APRIL 30, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

A Further Study of the Porphine-like Products of the Reaction of Benzaldehyde and Pyrrole

BY RUSSELL H. BALL,¹ G. D. DOROUGH AND M. CALVIN

It has been observed² that the rather general reaction of aldehydes with pyrrole to give methine carbon substituted porphines many times yields two porphine-like products which are separable by acid fractionation or chromatography. Rothmund has proposed² that these two products are examples of isomers of the type



Only in the case of porphine itself, however, were the two forms isolated and analyzed; in all other

cases, the isomerism was inferred from differences in absorption spectra and basicity. The suggestion that these differences are due to an isomerism of the above type meets with several strenuous objections, the most important of which is the fact that the two compounds upon complexing with a metal such as copper yield different rather than identical porphine salts.

It is the purpose of this paper to demonstrate conclusively that in one case at least, that of the reaction of benzaldehyde with pyrrole, the two main porphine-like products formed are not isomeric. As in previous papers^{3,4} we shall refer to these products by the letters A and B. Occurring in the largest amount is

material A, which has a spectrum characteristic of etioporphyrins (see Fig. 1), and an HCl number of 13.5. In lesser amounts is material B, which has a spectrum unlike any known por-

(1) Abstracted in part from the thesis presented by Russell H. Ball to the University of California, 1945, for the M.S. degree.

(2) Rothmund, *THIS JOURNAL*, **61**, 2912 (1939); **63**, 267 (1941).

(3) Aronoff and Calvin, *J. Org. Chem.*, **8**, 205 (1943).

(4) Calvin, Ball and Aronoff, *THIS JOURNAL*, **65**, 2259 (1943).