Summary

The amount of hydrazine formed by pyrolysis of liquid ammonia with the aid of a tungsten filament heated to 3000° was found to vary inversely with the pressure, in accordance with the equation $x^{0.423}y = 5.2$.

The yields of hydrazine under the conditions of the experiments varied from 0.774 g. per k. w. h. at 80 mm. to 0.205 g. at 1870 mm.

The presence of solutes of various types was in no case found to augment the yield of hydrazine beyond the value to be expected from the equation.

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The Catalysis of Eder's Reaction by Cobalt Compounds[1]

BY G. H. CARTLEDGE AND T. G. DJANG

The photochemical reduction of mercuric chloride to calomel by oxalates, which is known as Eder's reaction, has been the object of many investigations.[2] No completely satisfactory theory of the reaction mechanism has yet been offered, although it is a chain reaction according to Roseveare and Olson[2] and Oberhauser and Schormüller.[2] The reaction may be induced in the dark by the manganioxalate ion, $Mn(C_2O_4)_3^{3-}$, and by the analogous cobaltic complex, whereas at room temperature the ferrioxalate ion is inactive. It has seemed to us that a comparison of the action of these complexes might well throw light upon the manner in which the inductor participates in the reaction mechanism.

Induction by Potassium Cobaltioxalate

Materials.—The mercuric chloride and potassium oxalate used were Baker C. P. chemicals, which were further recrystallized three times to reduce the iron content.

The potassium cobaltioxalate, $K_3Co(C_2O_4)_3 \cdot 3.5H_2O$, was prepared from cobaltous chloride and potassium oxalate using lead dioxide as the oxidant, following a modification of the method proposed by Jaeger and Thomas.[3] The complex salt can be recrystallized readily in the cold or by the use of alcohol, and is much more stable than the corresponding manganic salt. Crystals kept in the dark at laboratory temperature show no alteration after three years. Determinations of cobalt and oxalate on a sample washed with alcohol and ether and dried over calcium chloride agreed closely with the

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[1] The larger part of this paper is abstracted from a dissertation presented by T. G. Djang to the Faculty of Philosophy of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Eder, *Ber.*, **13**, 166 (1880); Wyckoff and Baker, *Am. J. Roentgenol. Radium Therapy*, **22**, 551 (1929); Jodlbauer and Tappeiner, *Ber.*, **38**, 2602 (1905); Jodlbauer, *Z. physik. Chem.*, **59**, 513 (1907); Roseveare and Olson, THIS JOURNAL, **51**, 1716 (1929); Roseveare, *ibid.*, **52**, 2617 (1930); Dhar, *J. Chem. Soc.*, **111**, 707 (1917); Kastle and Beatty, *Am. Chem. J.*, **24**, 182 (1900); Oberhauser and Schormüller, *Ann.*, **470**, 111 (1929); Dhar, *J. Chem. Soc.*, **111**, 690 (1917); Winther, *Z. wiss. Phot.*, **7**, 409 (1909), **8**, 197, 237 (1910).

[3] Jaeger and Thomas, *Proc. Acad. Sci. Amsterdam*, **21**, 693 (1919).

formula above, although the water content appears to be variable. The cobaltioxalate possesses a deep green color and at a dilution of 0.001 *M* its concentration can be readily measured colorimetrically. A Dubosc colorimeter was used for the measurements, and it was found that Beer's law is followed so closely that no corrections are required in the concentration range employed. The presence of excess potassium oxalate does not affect the color comparisons. The aqueous solutions are less stable than the crystals, and acids accelerate the decomposition to cobaltous oxalate and carbon dioxide. In a solution containing no free acid cobaltous oxalate precipitates after a long while, in the dark at room temperature, the change in color of a 0.01 *M* solution being detectable colorimetrically after three weeks. No change is observable after twenty-four hours in the dark at 25°. So far as possible, freshly prepared solutions were used in the experiments.

The decomposition of the cobaltioxalate solution is markedly retarded by oxygen. The experiments were made in Pyrex flasks, using in one case bright sunlight and in the other a small carbon arc. In some experiments the dissolved air was expelled before illumination by boiling the solution in a vacuum in the dark; in others, air or oxygen was bubbled through the solution during the illumination.

TABLE I

INHIBITING EFFECT OF OXYGEN IN THE PHOTOLYSIS OF POTASSIUM COBALTIOXALATE

Light source	Exposure, min.	Conditions	Colorimeter reading (mm.) (Initial = 15.0 mm.)	Percentage decom-position	Percentage decompn. per min.
Sun	10	Oxygen	37.7	60.2	..
Sun	10	Vacuum	52.7	71.5	..
Arc	5	Air	16.0	6.2	1.24
Arc	10	Air	17.4	13.8	1.38
Arc	15	Air	19.5	23.0	1.53
Arc	5	Vacuum	17.2	12.8	2.56
Arc	10	Vacuum	20.2	25.8	2.58
Arc	15	Vacuum	24.3	38.4	2.56

It is evident that in the early stages of the reaction air reduces the speed to about one-half the rate observed in a vacuum; this effect is not so great as it is in the case of Eder's reaction, in which oxygen may reduce the yield of calomel to one-eightieth the yield in the absence of oxygen. This difference in retardation corresponds to the difference in quantum efficiencies in the two reactions, Eder's reaction having long chains, whereas in the decomposition of the cobaltioxalate the quantum yield is approximately unity.[4,5] The table also indicates that under the conditions of the group of experiments with the arc the absorption was so strong as to give a reaction of zero order in the vacuum runs. The slight increase in rate in the air experiments may be ascribed to incomplete saturation with oxygen, or it may be a real acceleration due to the cobaltous salt produced.

Potassium cobaltioxalate induces the Eder reaction in the dark, at room temperature, at concentrations of 0.001 *M* or less, depending upon the oxygen pressure. Experiments were made to determine whether there is a

(4) Vranek, *Z. Elektrochem.*, **23**, 336 (1917).

(5) Allmand and Webb, *J. Chem. Soc.*, 1518, 1531 (1929).

finite induction factor in the reaction, the induction factor in this case being the number of moles of bichloride reduced per mole of cobaltioxalate decomposed. Solutions were made up containing, in a total volume of 60 cc., 10 cc. of 0.01004 *M* $K_3Co(C_2O_4)_3$, 40 cc. of 0.2 *M* $K_2C_2O_4$, and 10 cc. of 0.2 *M* $HgCl_2$. The solutions were prepared in bottles completely covered by tin foil, and were set aside at a temperature of approximately 20° for the specified time. The solutions were fully exposed to the air. The induction is so slow under these conditions that colorimetric readings can be made by artificial light in a dark room without interference from calomel formation. After a suitable time the calomel was filtered with suction in the dark room and determined, either by weighing after drying at 105°, or by the iodate method.[6] The filtrate was compared colorimetrically with the original cobaltioxalate standard containing no mercuric chloride. The colors were matched five times from different sides and the average reading taken; it was found that 0.5 mm. on the scale was about the limit of accuracy in the comparison. The results after fifteen hours and forty hours are given in Table II; the initial colorimeter reading was 30.0 mm.

TABLE II

INDUCTION BY 0.00167 *M* POTASSIUM COBALTIOXALATE

Time in hours	15	40
Mercurous chloride formed, grams	0.0694	0.1603
Percentage reduction of mercuric chloride	14.7	34.0
Colorimeter reading, mm.	30.2	30.2

The results show that while 34% of the mercuric chloride was being reduced, too little of the cobalt complex was decomposed to be certainly determined. The induction factor is, therefore, very large, if not infinite, at room temperature.

Experiments were made to ascertain whether the large induction factors indicated might be ascribed to atmospheric reoxidation of the cobaltous oxalate complex formed by decomposition of the cobaltioxalate. It is well known that the analogous oxidation of ferrous salts leads to extensive induction, and we have found the same to be true of manganous salts. The experiments were made in the absence of light and at room temperature, with exposure to the air, as in the preceding experiment. The results are given in Table III, the three series being done at slightly differing temperatures.

The results show that in contact with air cobaltous salts *alone* may produce only traces of calomel in twenty-four hours; the cobaltous salt accelerates the induction by cobaltioxalate ions, but to an appreciable degree only when the cobaltous salt concentration is considerably greater than 0.01 millimole in 50 cc. (0.0002 *M*). The yield of calomel in the

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(6) Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Co., New York.

TABLE III

EFFECT OF COBALTOUS SALTS ON THE INDUCED REACTION

Total volume 50 cc., 0.1 *M* in $HgCl_2$ and 0.1 *M* in $K_2C_2O_4$

No.	Milli-moles of $K_3Co(C_2O_4)_3$	Milli-moles of $CoSO_4$	Hg_2Cl_2 formed (g.) after		No.	Milli-moles of $K_3Co(C_2O_4)_3$	Milli-moles of $CoSO_4$	Hg_2Cl_2 formed (g.) after
			15 hours	24 hours				24 hours
A 1	0.2	0.00	0.0866	0.1287	B 1	0.2	0.00	0.1465
2	.2	.01	.0860	.1259	2	.2	.01	.1483
3	.2	.10	.0925	.1462	3	.2	.05	.1508
4	.0	.10	.0005	None	4	.2	.10	.1598
5	.0	.00	None	None	5	.2	.50	.3092
					C 1	.0	.01	.0012
					2	.0	.10	.0017

induction by potassium cobaltioxalate cannot therefore be ascribed either to the direct reduction of mercuric chloride by cobaltous salts or to the accelerating action of cobaltous salts, since the colorimeter readings show that no appreciable concentration of cobaltous compounds could have been formed during the 40-hour experiments.

The *small* amounts of calomel sometimes produced by cobaltous sulfate alone can be ascribed to atmospheric oxidation to cobaltioxalate. When faintly acidified potassium oxalate containing a small quantity of cobaltous sulfate is left exposed to the air at room temperature a slight green color is found to appear after some days. The same change occurs within an hour or so if a few drops of hydrogen peroxide is added, and at once if the peroxide mixture is warmed slightly. This oxidation of cobaltous oxalate by hydrogen peroxide produces a slight induction if carried out in Eder's solution. Five cc. each of mercuric chloride and potassium oxalate saturated with cobaltous oxalate were separately treated with a few drops of hydrogen peroxide to oxidize any traces of ferrous salts that might be present as impurities. After about five minutes, the solutions were mixed in the absence of actinic light. There was slight induction accompanied by the gradual formation of the cobaltioxalate ion. In similar experiments in which ferrous salts are oxidized by hydrogen peroxide in Eder's solution, copious and immediate precipitation of calomel occurs. The cobaltous salt oxidizes in air far too slowly to account for the high induction factor of the cobaltioxalate induced reaction.

Catalysis of the Light Reaction by Cobalt Compounds.—When the photolytic Eder's reaction is studied in a similar fashion it is found that cobaltous sulfate is essentially inactive at low concentrations. Solutions were illuminated for five minutes in Pyrex flasks, open to the air, using a carbon arc. The solutions were 0.1 *M* in $HgCl_2$ and 0.1 *M* in $K_2C_2O_4$, the total volume being 50 cc. Table IV shows the results.

Experiments were made to ascertain the relation between the catalytic effect of the cobaltioxalate and its concentration. Mixtures were prepared 0.1 *M* in $HgCl_2$ and 0.1 *M* in $K_2C_2O_4$, and containing varying amounts

TABLE IV

CATALYSIS OF THE LIGHT REACTION

Experiment number	1	2	3	4	5
Millimoles of $K_3Co(C_2O_4)_3$	0.002	0.002	0.002	0.000	0.000
Millimoles of $CoSO_4$	.000	.001	.010	.000	.010
Mercurous chloride formed, g.	.0575	.0568	.0563	.0032	.0040

of potassium cobaltioxalate in a total volume of 51 cc. The solutions were put in a round-bottomed 125-cc. flask with the neck ground to fit the connection to a Toepler pump. The flask was completely wrapped in tin foil, evacuated, and boiled under the vacuum for about fifteen minutes, having an ice-jacketed tube just above the flask to act as a reflux condenser. This treatment removed the dissolved air very effectively, and after a few pumpings the solution could be boiled only with great difficulty. No appreciable amount of calomel formed during the deaeration. The solution was then exposed to the carbon arc for five minutes, making the conditions of illumination as nearly uniform as possible. The results are shown in Table V, which includes also experiments done in exactly similar manner, except that the solutions were saturated with air just prior to illumination, which was extended to fifteen minutes on account of the retardation.

TABLE V

CATALYSIS OF THE LIGHT REACTION

A. Oxygen absent; exposure, 5 min. B. Saturated with air; exposure, 15 min.

Experiment number A	1	2	3	4	5	6
Millimoles of $K_3Co(C_2O_4)_3$	None	1×10^{-6}	1×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-2}
Hg_2Cl_2 formed, grams	0.0503	0.0832	0.1120	0.1658	0.4378	1.1736
Hg_2Cl_2 formed, millimoles	.106	.176	.237	.351	.928	2.486
Reduction of $HgCl_2$, %	4.25	7.05	9.48	14.0	37.1	99.5

Expt. number B	1	2	3	4	5	6	7
Millimoles of $K_3Co(C_2O_4)_3$	None	1×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-2}	2×10^{-2}	5×10^{-2}
Hg_2Cl_2 formed, grams	0.0133	0.0129	0.0137	0.0354	0.1233	0.1772	0.2669
Hg_2Cl_2 formed, millimoles	.0281	.0274	.0290	.0750	.261	.375	.565
Reduction of $HgCl_2$, %	1.12	1.10	1.16	3.00	10.4	15.0	22.6

Experiment A2 reveals the extreme sensitiveness of the reaction rate to minute amounts of cobaltioxalate. Under the conditions of the experiment, with oxygen effectively excluded, the presence of 10^{-9} mole of cobaltioxalate in 51 cc. increases the reaction rate by 66%. In the presence of air at least a hundred-fold more cobalt is required to produce definite acceleration.

The large yield of calomel in proportion to the quantity of cobaltioxalate present is also noteworthy. No attempt was made to estimate the extent to which the cobaltioxalate itself was decomposed in these experiments, but by reference to the results in Table I it is seen that such decomposition could not have been very extensive, certainly under 25%. But even if the cobaltioxalate were completely decomposed, and if we subtract the amount of calomel produced with no cobaltioxalate present, the induction factor in experiment A2 would still be 140,000 moles of mercuric chloride per mole of cobaltioxalate, and the actual value is undoubtedly much larger. With increasing concentration of the cobalt complex the relative yield of calomel diminishes rapidly. It is seen also that with the same concentrations of cobaltioxalate the relative yield is reduced to one-tenth or less when air is present (experiments A5, 6 and B4, 5).

These experiments, together with those in Table II, make it clear that both the induced dark reaction at room temperature and the photolysis of Eder's reaction in the presence of minute amounts of cobaltioxalate but without oxygen are essentially a catalysis without destruction of the catalyst.

It is also significant to observe the comparative inhibiting action of oxygen upon the photolysis of Eder's reaction alone, of the cobaltioxalate alone, and of Eder's reaction catalyzed by cobaltioxalate. In experiments A1 and B1 (Table V) the yield from the uncatalyzed Eder reaction in a vacuum is about 11.5 fold greater than that with air, if we assume the yield to vary directly with time in the B series. Table I shows that under nearly similar conditions the rate of the cobaltioxalate photolysis is roughly doubled by removing the air. In experiments with 10^{-4} and 10^{-3} millimole of cobaltioxalate catalyzing Eder's reaction the rate in a vacuum is roughly forty-fold faster (A4, 5 and B3, 4 Table V). If the net effect of the inhibitor is the shortening of the reaction chains, this comparison shows that the presence of small amounts of cobaltioxalate in Eder's solution greatly increases the length of the chains.

In their discussion of the reputed "active form" of oxalic acid Oberhauser and Hensinger[7] treated oxalic acid with a deficiency of potassium permanganate at 100° in the presence of mercuric chloride, and used the weight of calomel formed as a measure of the "active" oxalic acid. Inasmuch as our experiments indicated that it is the *presence* of the cobaltic complex rather than its *decomposition* that leads to the reduction of mercuric chloride, we predicted that if the cobalt complex were used in place of the less stable manganese complex in Oberhauser and Hensinger's experiments, the yield of calomel should be increased. Solutions were made containing 50 cc. of 0.1 M $H_2C_2O_4$, 1.25 g. of $HgCl_2$, and 2 cc. of 0.1 M inductor in a total volume of 150 cc. The solutions were heated in an actively boiling water-bath while carbon dioxide was bubbled through them to remove dissolved air. The inductors were potassium cobalti-

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[7] Oberhauser and Hensinger, *Ber.*, **61**, 521 (1928).

oxalate, potassium manganioxalate, and potassium permanganate. Precipitation of calomel and reduction of the inductor were complete after fifteen minutes. The yields of calomel are in accordance with the prediction, as shown in Table VI.

TABLE VI

COMPARATIVE INDUCTIONS AT 100°

Inductor, 0.2 mml.	$K_3Co(C_2O_4)_3$		$KMnO_4$		$K_3Mn(C_2O_4)_3$
Calomel formed g.	0.8148	0.8344	0.4404	0.4396	0.3174
Calomel formed mml.	1.72	1.76	.93	.93	.67
Reduction of $HgCl_2$, %	74.7	76.4	40.4	40.4	29.1
Moles of $HgCl_2$ reduced per mole of inductor	8.60	8.80	4.65	4.65	3.35

In these hot, acid solutions the tervalent manganese complex has a very transitory existence, experiments with the pure potassium manganioxalate having shown that the deep rose-colored solutions at room temperature become brown and decompose quite rapidly if the solution is made distinctly acid. The cobaltioxalate is less susceptible to changes in acidity. The increased yield from potassium permanganate as compared with the manganioxalate indicates that the effective life of the inducing complex is lengthened, presumably by the reaction between the manganous ion and the permanganate.

As further evidence that the presence of the tervalent ion complexes is significant for the increased oxidizability of oxalates, a few experiments were made on the oxidation of oxalic acid by very dilute potassium permanganate. It is well known that this reaction is markedly accelerated by manganous salts. Small quantities of permanganate were added to 25 cc. of 0.5 *M* oxalic acid, and to certain portions of the mixture potassium ferrioxalate or potassium cobaltioxalate was added (0.025–0.125 millimole). The time required for disappearance of the permanganate absorption bands was noted as closely as possible. In the absence of the catalysts the color faded very gradually, eight to ten minutes being required for the end-point. With the catalysts present the time was definitely reduced to about two minutes.

The most significant results of the present experiments may be briefly summarized as follows. 1. The effect of the cobaltioxalate complex ion upon Eder's reaction is essentially a pure catalysis in the light, and the induced dark reaction at room temperature also is characterized by a very large, if not infinite, induction factor.

2. Cobaltous salts alone, in the air, produce only traces of calomel, and vigorous oxidation of the cobalt, as by hydrogen peroxide, is much less effective in inducing Eder's reaction than is the analogous reaction with ferrous salts.

3. Cobaltous sulfate accelerates the induced dark reaction if present at

concentrations considerably over 0.0002 *M*. The catalyzed photolysis of Eder's reaction is not affected by the simultaneous presence of cobaltous salts at low concentrations.

4. The inhibiting effect of oxygen is greatest with the catalyzed photolysis of Eder's reaction, less with the uncatalyzed photolysis of Eder's reaction, and least with the photolysis of the cobaltioxalate alone.

5. At 100° in oxalic acid solution the induction factors decrease in the order: cobaltioxalate ion, potassium permanganate, and manganioxalate ion. The longer lived complex gives the largest yield of calomel. The induction factor is decreased by rise of temperature and by increase in acidity, both of which changes shorten the life of the inductor. The presence of the ferric and cobaltic oxalate complexes also accelerates the oxidation of oxalic acid by very dilute potassium permanganate.

These facts indicate that the presence of the cobaltioxalate or manganioxalate ion is significant for the enhanced oxidizing activity of the mercuric chloride. The discussion of the details of the mechanism of the reaction will be postponed until the experiments have been carried somewhat further.

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The Solubilities of Sparingly Soluble Salts Using Large Volumes of Solvents. I. The Solubility of Lead Sulfate[1]

BY R. B. PURDUM AND H. A. RUTHERFORD, JR.

A series of investigations has been begun in this Laboratory in an effort to obtain accurate data for the solubilities of sparingly soluble salts by the direct measurement of solution equilibrium using large volumes of solvents and samples prepared by different methods. This paper presents data on the solubility of lead sulfate in water and dilute sulfuric acid solutions at 20°. A number of recent investigations of the solubility of this salt have been reported.[2] These will be considered in connection with our own data.

Materials.—Four samples of lead sulfate were used. These were prepared as follows.

1. A slight excess of 5% sodium sulfate in 0.1 *N* sulfuric acid was slowly added with rapid stirring over a period of three hours to a 5% solution of lead nitrate. The precipitated lead sulfate was then washed repeatedly in two-week periods with 5-gallon portions of water for one year.

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(1) Presented before the division of Physical and Inorganic Chemistry at the Washington meeting of the American Chemical Society, March, 1933.

(2) (a) Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., New York, 1919, pp. 363–365, and Supplement to same, 1928, pp. 1266–1267; (b) Huybrechts and Ramelot, *Bull. soc. chim. Belg.*, **36**, 239 (1927); (c) Huybrechts and de Langeron, *ibid.*, **39**, 43 (1930).