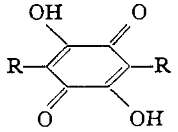
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

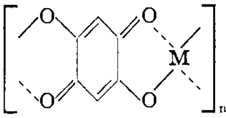
Metallic Complexes of 2,5-Dihydroxy-1,4-benzoquinones

BY ROBERT L. FRANK, GEORGE R. CLARK AND JAMES N. COKER

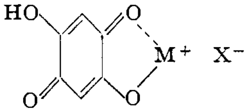
An interest in the properties of the fungus pigment polyporic acid (I)[1] has led us to this study of the metallic complexes of 2,5-dihydroxy-1,4-benzoquinones. Most of the work has been carried out with the readily available parent compound, 2,5-dihydroxy-1,4-benzoquinone (II).[2]



I, R = C_6H_5
II, R = H



III



IV

2,5-Dihydroxy-1,4-benzoquinones may be considered as stabilized enols of 1,2-diketones, and while 1,2-diketones as such do not generally coordinate with metallic ions,[3] the enolic structure enables one to predict the formation of five-membered chelate rings (III and IV). 2,5-Dihydroxy-1,4-benzoquinone, as its soluble ammonium salt, does in fact form insoluble colored precipitates with a variety of cations, as described in the Experimental Part.

The fact that there are two keto–enol pairs in the 2,5-dihydroxy-1,4-benzoquinone molecule suggests that the use of di- or polyvalent cations might lead to the formation of polymeric chelated structures (III). Investigation of this possibility has been rendered difficult by lack of solubility of the complexes and also by the fact that they are hydrated so that analyses are difficult to interpret. Consideration of the metal-to-carbon ratios, however, indicates simple combinations (such as IV, in which M is divalent and X is hydroxyl or some other anion) rather than polymeric structures. The complex with silver, and probably that with mercury, has two atoms of metal for one of quinone; those with magnesium, calcium, strontium, copper, cadmium, lead and ferric iron contain one atom of metal for one of quinone; that with barium analyzes for a three-to-two ratio of barium to quinone. Complexes with zinc and thorium have one atom of metal for two of quinone.

Evidence that the complexes are not polymeric has been obtained with the lead derivative of 2,5-dihydroxy-1,4-benzoquinone. Three samples, prepared using 2:1, 1:1 and 1:2 molar ratios of lead nitrate to quinone, had essentially identical compositions. If the samples had been polymeric, their compositions would have been expected to vary with the ratios of starting materials, due to differences in their end groups.

The behavior of 2,5-dihydroxy-1,4-benzoquinone with the alkaline earth cations varies with the individual ions and suggests a means of differentiating them based on the colors of the complexes, their rates of formation, and their solubilities in dilute hydrochloric acid. Further analytical possibilities are suggested by a comparison of the structures of 2,5-dihydroxy-1,4-benzoquinone and its complexes with those of the useful reagent rhodizonic acid.[4]

2,5-Dihydroxy-1,4-benzoquinone does not form precipitates when treated with solutions of salts of aluminum, chromium, arsenic, or stannic tin. Furthermore, these cations effectively prevent the formation of a number of complexes which are ordinarily insoluble, and one can therefore conclude that they form rather stable water-soluble complexes.

Polyporic acid (I) has also been found to form precipitates with a variety of cations. These were obtained almost without exception as gelatinous precipitates and were brown or black. Determinations of metal-to-carbon ratios indicated mixtures rather than definite compositions, although ferrous iron formed a black crystalline complex containing one iron atom for each polyporic acid unit.

The ability of polyporic acid to form highly insoluble complexes with most metallic ions may be of some importance in connection with its occurrence in nature. The free acid constitutes as much as 43% of the dried fruit body of the mushroom *Polyporus rutilans* (*P. nidulans*),[5] and may function to protect the spores against microörganisms and insects by precipitating and thereby removing essential minerals from such invaders. As a corollary to its polyporic acid content, it is no surprise that the fruit body is also unusual in having a comparatively low mineral content.[6]

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(1) Kögl, *Ann.*, **447**, 78 (1926); Kögl and Becker, *ibid.*, **465**, 219 (1928).

(2) Jones and Shonle, THIS JOURNAL, **67**, 1034 (1945).

(3) Diehl, *Chem. Revs.*, **21**, 39 (1937).

(4) Feigl and Suter, *Ind. Eng. Chem., Anal. Ed.*, **14**, 840 (1942).

(5) Stahlschmidt, *Ann.*, **187**, 177 (1877).

(6) Ignitions of air-dried *P. rutilans*, mixed with ammonium sulfate or sulfuric acid, showed a mean value of 0.72% ash (ten determinations, maximum deviation from mean ±0.26%) as metallic sulfates (*ca.* 0.39% calculated as metallic oxides). Mineral contents of most mushroom fungi are much higher; Rhodes (*Chem. News*, **109**, 28 (1914); *C. A.*, **8**, 1443 (1914)) has reported values in the range 5.9–12.2%; Freise (*Perfumery Essent. Oil Record*, **26**, 91 (1935)) has given 7.62–10.36% for a large variety of species. Of further interest is the fact that analysis of the ash from *P. rutilans*, kindly carried out by Mr. E. R. Nightingale using a Beckman flame spectrometer, showed the cation content to be mainly potassium (69.8%) and sodium (16.0%). Salts of these cations do not precipitate polyporic acid.

The mycelium of *P. rutilans*, on the other hand, when raised in culture, contains no polyporic acid.

Experimental

Diammonium Salt of 2,5-Dihydroxy-1,4-benzoquinone.—Stirring of the quinone[2] with 2.1 equivalents of 28% ammonium hydroxide resulted in the formation of a red precipitate. This was collected on a filter, washed with small portions of ether, and air-dried to give a nearly quantitative yield of the red diammonium salt, which decomposed without melting at temperatures above 130°. It can be recrystallized from hot water.

Anal.[7] Calcd. for $C_6H_{10}O_4N_2$: N, 16.09. Found: N, 15.18, 15.36.

An approximately 0.1 molar solution for use in forming the complexes was prepared by dissolving 1.6 g. of the salt in 92 ml. of water. This was stored in a refrigerator, or used immediately, as it was observed to turn from red to brown when allowed to stand at room temperature.

Complexes of 2,5-Dihydroxy-1,4-benzoquinone.—The complexes were formed by addition of excess of the cation (usually a saturated solution of a soluble salt) to the 0.1 molar diammonium salt of the quinone. The red color of the latter disappeared as the mixture took on the color of the precipitating complex. The precipitates were collected by centrifugation and washed, also by centrifugation, with water, ethanol and acetone. Individual complexes are described as follows:

Silver.—From silver nitrate; brown precipitate at *p*H 3, 7 and 11, orange powder when dry; insoluble in water, ethanol and ether, soluble in pyridine. *Anal.* C, 19.98; H, 0.93; Ag, 60.81. Atomic ratio: C:Ag::6.00:2.08.

Mercury.—From mercuric chloride; brown precipitate at *p*H 3 and 7, pink precipitate, partially soluble, at *p*H 11, brown powder when dry; insoluble in water, ethanol, ether and pyridine. *Anal.* C, 10.15; H, 0.99.

Magnesium.—From magnesium sulfate; excess quinone salt was required, and precipitate appeared after fifteen to thirty minutes; pink precipitate at *p*H 3, 7 and 11, and when dry; insoluble in ethanol, ether and pyridine, slightly soluble in water, not appreciably soluble in 0.001 *N* hydrochloric acid. *Anal.* C, 34.36, 34.30; H, 3.48, 3.51; Mg, 12.74, 13.25. Atomic ratio: C:Mg::6.00:1.08 or 1.14.

Calcium.—From calcium chloride; red precipitate forms readily at *p*H 7 and 11, brown powder when dry; insoluble in ethanol, ether and pyridine; slightly soluble in water and 0.001 *N* hydrochloric acid. *Anal.* C, 26.99; H, 4.02; Ca, 16.37. Atomic ratio: C:Ca::6.00:0.96.

Strontium.—From strontium nitrate; bright red crystalline precipitate forms readily at *p*H 7, brown precipitate at *p*H 11, red crystals when dry; insoluble in ethanol, ether and pyridine, slightly soluble in water, moderately soluble in 0.001 N hydrochloric acid. *Anal.* C, 27.00; H, 2.52; Sr, 32.53. Atomic ratio: C:Sr::6.00:0.99.

Barium.—From barium acetate; orange precipitate forms readily at *p*H 7 and 11, tan powder when dry; insoluble in ethanol, ether, pyridine and 0.001 *N* hydrochloric acid, slightly soluble in water. *Anal.* C, 20.45; H, 1.47; Ba, 61.23. Atomic ratio: C:Ba::6.00:1.55.

Copper.—From cupric chloride; black precipitate at *p*H 3, 7 and 11, dark green when dry; insoluble in ethanol, ether, pyridine and water. *Anal.* C, 31.80, 31.93; H, 1.79, 1.96; Cu, 26.40, 27.10. Atomic ratio: C:Cu::6.00:0.94 or 0.96.

Cadmium.—From cadmium chloride; brown precipitate at *p*H 3, purple precipitate at *p*H 7 and 11 and when dry; insoluble in ethanol, ether, pyridine and water. *Anal.* C, 27.40; H, 2.06; Cd, 36:23. Atomic ratio: C:Cd::6.00:0.85.

Lead.—From lead nitrate; brown precipitate at *p*H 3, 7 and 11 and when dry; insoluble in ethanol, ether, pyridine and water. The lead complex as made with 2:1, 1:1 and 1:2 molar ratios of quinone to lead nitrate. Analyses cited are those of the three samples, respectively. A qualitative test for nitrogen showed the absence of nitrate ions in the complex. *Anal.* C, 19.86, 19.82, 20.18; H, 1.31, 1.32, 1.37; Pb, 56.07, 56.12, 56.26. Atomic ratio: C:Pb::6.00:0.98, 0.99 or 0.97.

Ferric Iron.—From ferric nitrate; black precipitate at *p*H 3, 7 and 11 and when dry; insoluble in ethanol, ether and pyridine, slightly soluble in water. *Anal.* C, 32.54; H, 2.19; Fe, 20.53. Atomic ratio: C:Fe::6.00:0.81.

Zinc.—From zinc sulfate; purple precipitate at *p*H 3, 7 and 11 and when dry; insoluble in ethanol, ether and pyridine, slightly soluble in water. *Anal.* C, 28.08; H, 2.83; Zn, 12.87. Atomic ratio: C:Zn::12.00:1.01.

Thorium.—From thorium nitrate; purple precipitate at *p*H 3, 7 and 11 and when dry; insoluble in ethanol, ether and pyridine, soluble in water. *Anal.* C, 28.29, 28.85; H, 2.25, 2.27; Th, 41.18, 39.02. Atomic ratio: C:Th::12.00:0.90 or 0.84.

Other cations which formed precipitates, but the complexes of which were not analyzed, were mercurous (brown), stannous (brown), ferrous (brown), cobaltous (brown), manganous (purple), nickelous (brown), antimony (orange) bismuth (yellow), neodymium (pink), ceric (pink) and uranyl (brown).

Arsenic chloride solutions changed the red color of the diammonium salt of 2,5-dihydroxy-1,4-benzoquinone to yellow; no precipitate formed. When aqueous solutions of salts of calcium, strontium, iron (ferrous and ferric), zinc, copper, lead, nickel, uranium (UO_2^{++}), thallium, neodymium and thorium were subsequently added, there was still no precipitation, but stannous chloride gave a copious brown precipitate. Chromic ions changed the red color of the diammonium salt to brown, with no precipitation. Subsequent addition of the aforementioned ions failed to form precipitates. Aluminum and stannic ions gave colorless solutions with the diammonium salt; these also prevented the formation of complexes of the other ions.

Complexes of Polyporic Acid.—Ammonium polyporate was obtained only in solution, since the solid loses ammonia readily on drying. Polyporic acid[8] was dissolved in an excess of 28% ammonium hydroxide and the uncombined ammonia removed by gentle boiling of the solution. The solution (*ca.* 0.02*N*) was most stable when slightly alkaline (*p*H 7.4–7.7). Complexes were formed by addition of this to an aqueous solution of two to three equivalents of the cation. Precipitates were washed with distilled water, absolute ethanol, and absolute ether and dried *in vacuo* over phosphorus pentoxide.

Silver.—From silver nitrate; dark brown crystals; insoluble in pyridine. *Anal.* C, 43.71; H, 3.60; Ag, 31.6. Atomic ratios: C:Ag::18.00:1.44.

Ferrous Iron.—From ferrous nitrate; readily-formed black crystals; insoluble in water, ethanol, ether and pyridine. *Anal.* C, 53.21; H, 4.55; Fe, 13.6. Atomic ratios: C:Fe::18.00:0.99.

Thorium.—From thorium nitrate; readily-formed black crystals; insoluble in water, ethanol, ether and pyridine. *Anal.* C, 47.13; H, 4.03; Th, 30.36. Atomic ratios: C:Th::18.00:0.60.

The additional cations studied with 2,5-dihydroxy-1,4-benzoquinone were also tried with polyporic acid. All gave insoluble precipitates, uniformly dark brown or black.

Culture of *Polyporus rutilans* (*P. nidulans*).—A culture of *P. rutilans*, obtained from Mr. Ross Davidson, Division of Forest Pathology, Bureau of Plant Industry, U. S. Department of Agriculture, was propagated by Dr. Leland Shanor and Mr. Richard K. Benjamin, to whom we are indebted. The culture medium was a mixture of 30 g. of malt extract (Difco Laboratories, Inc.) and 15 g. of purified agar (Difco) per liter of water. The culture gave no red or purple color when treated with aqueous ammonium or potassium hydroxides, sensitive reagents for the detection of polyporic acid.

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(7) Microanalyses were carried out by Miss Emily Davis, Mrs. Jane Wood and the Clark Microanalytical Laboratories.

(8) For the preparation of polyporic acid see the preceding article.

Acknowledgment.—One of us (G. R. C.) wishes to thank the Sunbeam Corporation for financial assistance.

Summary

2,5-Dihydroxy-1,4-benzoquinone and its 3,6-diphenyl derivative, polyporic acid, form chelated complexes with a variety of cations. The structures and properties of these complexes are discussed.

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Equilibrium Studies on the Hydrindene–Indene–Hydrogen System

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Introduction

In connection with investigations being carried out in this laboratory, it became of interest to obtain some of the thermodynamic constants for the system hydrindene–indene–hydrogen. The equilibrium constants were determined by a catalytic flow method at temperatures ranging from 375 to 525°. From these data, it was possible to calculate the free energy, heat and entropy of the reaction, of which only the heat of reaction (by difference) had been previously reported.[1]

Experimental

Materials.—Commercial indene was fractionally recrystallized, after treating with 40% NaOH at reflux for four hours (to remove benzonitrile), and was then shaken for twenty-four hours with 6 *N* HCl (to remove tar bases). A final distillation at 100 mm. gave a product boiling at 114.5°, freezing at −1.80°, n^{20}D 1.5763. Literature values for indene are summarized by Breston and Gauger[2] and indicate freezing points ranging from −2.0 to −1.5°, refractive indices (n^{20}D) ranging from 1.5711 to 1.5768 and boiling points at 100 mm. of 114.5°, and at 760 mm. ranging from 179.5 to 183°.

Hydrindene was prepared by catalytic hydrogenation of purified indene, both in liquid phase with Adams platinum catalyst and in vapor phase over commercial chromia-alumina catalyst. The hydrindene was fractionally redistilled to give a product boiling at 177–178° (765 mm.), n^{20}D 1.5384. Literature values for hydrindene, found in standard references, give boiling points ranging from 176 to 177° and refractive indices (n^{20}D) ranging from 1.5381 to 1.5385. Hydrogen was used as furnished in commercial cylinders.

The chromia–alumina catalyst was a commercial product purchased from The Harshaw Chemical Company as Cr-181-5-13-47-A6937 in the form of $^1/_8$-inch pellets.

Apparatus.—The apparatus consisted of an electrically-heated, stainless steel and glass reactor, with preheater, and condensing system cooled by circulating ice-water.

Method of Operation.—Hydrogen at the rate of approximately 0.8 liter per minute was metered through the vaporizer and gas preheater, together with the reactants (indene, hydrindene or mixtures of the two). The reactants were pumped by displacement with water delivered by a precision gear-driven cylinder pump at a constant rate in the range of 0.3 to 10 ml./min. The preheater was kept within 5° of the main reactor temperature. Temperatures were recorded on a 12-point Brown "Electronik" strip-chart multiple record potentiometer, and the main reactor temperature was controlled by a Brown "Electronik" potentiometer controller. Temperatures were measured by iron–constantan pipe-type thermocouples in the thermo-wells placed at appropriate points. Temperatures in the catalyst bed (volume, 100 ml.) were measured by a multi-point pipe-type thermocouple constructed in this Laboratory. The iron–constantan junctions were made along the side of the iron pipe so that several points were present in each of the regions above, below, and within the catalyst bed. Several measurements were made at about 450° with a single-point iron–constantan pipe-type thermocouple calibrated at the boiling points of water (100°) and sulfur (444.6°). The organic product was collected in the condensing system, and the non-condensable gases were measured as hydrogen by a precision wet-test meter. Samples were collected at regular intervals and the values obtained after a steady state was reached were reported. The catalyst was activated before each run by heating at 500° for one hour in a current of air, flushing with nitrogen for several minutes, and then treating with hydrogen for one hour. No loss in activity was noted after many reactivation cycles.

Analytical Methods.—The indene content of the reaction products was determined by the bromine absorption method of Hammick,[3] by a refractive index method, and by a benzaldehyde condensation method, the latter two developed in this Laboratory. The bromine absorption method is claimed to yield results with a standard deviation of 5×10^{-5}. With precautions as to reduced illumination during bromination, we obtained a standard deviation of 7×10^{-5}. A study of mixtures of pure indene and hydrindene by means of a Bausch & Lomb Abbe-type refractometer with thermostat control yielded an equation for determining the mole fraction (N) of indene from the refractive index of the sample. The equation is

$$\mathrm{N} = -69.233 + 62.984\ (n^{25}\mathrm{D}) - 11.650\ (n^{25}\mathrm{D})^2$$

with a standard deviation of ±0.0045. The benzaldehyde condensation method (to be described elsewhere) was developed for high indene concentrations, and was not satisfactory for analyzing low indene-content reaction products. It provided useful correlating data at indene contents above about 50%, since the method distinguishes between indene and other unsaturates.

Experimental Results

The procedure outlined was chosen because it is insensitive to minor changes in most of the variables.[4] The estimated precision of the indene analyses was not less than ±3% while that of the temperature measurements was ±2°. We calculate that variations of such magnitude will affect the precision of ΔF by approximately 200 cal.[5] The summarized results are presented in Table I.

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(1) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, THIS JOURNAL, **59**, 831 (1937).

(2) N. J. Breston and A. W. Gauger, (Penn State College) Amer. Gas Assoc., Tech. Sect., Jt. Prodn. and Chem. Committee Conf., June 1946, mimeographed paper.

(3) D. L. E. Hammick and D. Langrish, *J. Chem. Soc.*, 797 (1937).

(4) A. H. Cubberley and M. B. Mueller, THIS JOURNAL, **68**, 1149 (1946).

(5) Whittaker and Robinson, "Calculus of Observations," Blackie & Sons, Ltd., London, 1929.