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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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[CONTRIBUTION FROM THE RESEARCH LABORATORY, THE BARRETT DIVISION, ALLIED CHEMICAL & DYE CORPORATION]

Equilibrium Studies on the Hydrindene–Indene–Hydrogen System

BY EDWARD S. NAIDUS AND MAX B. MUELLER

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°, $n^{20}\mathrm{D}$ 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 ($n^{20}\mathrm{D}$) 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.), $n^{20}\mathrm{D}$ 1.5384. Literature values for hydrindene, found in standard references, give boiling points ranging from 176 to 177° and refractive indices ($n^{20}\mathrm{D}$) 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.

TABLE I

Temp., °C.	Approach	K equil.
373	B	0.0338
375	B	.0346
378	A	.0349
400	B	.0786
431	B	.139
432	A	.137
446	B	.183
448	B	.178
448	B	.176
450	A	.176
450	A	.225
452	A	.184
455	B	.266
498	B	.604
504	A	.603
504	B	.662
523	A	1.031

The column headed "approach" signifies that equilibrium was approached from the hydrindene side (A) or the indene side (B). A graphical presentation of the data is found in Fig. 1.

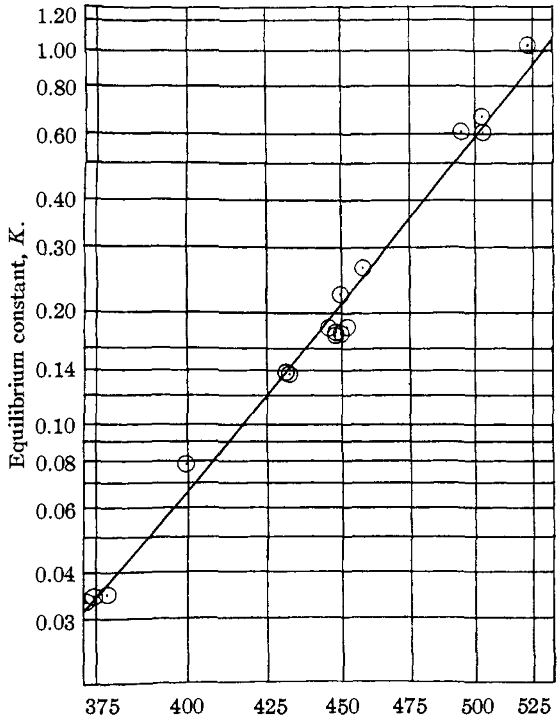

Fig. 1.

Discussion

The heat capacity equations for indene and hydrindene were estimated by the method described by Stull and Mayfield.[6] ΔC_p equation for the reaction

$$C_9H_8(g) + H_2(g) \longrightarrow C_9H_{10}(g)$$

is given by

$$\Delta C_p = 5.71 - 0.0067T$$

The experimental values of T and K_{EQ} listed in Table I were used to calculate the mean values of ΔH_0 and I in the equation

$$\Delta H_0 T + I = \Sigma = -4.575 \log K + 13.15 \log T - 0.00335T$$

By the method of least squares, we obtain

$$\Delta H_0 = 20{,}221 \text{ cal.}$$
$$I = 10.32 \text{ cal./deg.}$$

Values of ΔH_T and $\Delta F_T{}^0$ are given by

$$\Delta H_T = 20{,}221 + 5.71T - 0.00335T^2$$
$$\Delta F_T{}^0 = 20{,}221 + 13.15T \log T + 0.00335T^2 + 10.32T$$

and

$$\Delta F^0_{298} = 13{,}788$$
$$\Delta H_{298} = 21{,}626^7$$
$$\Delta S_{298} = 26.30$$

The standard deviations of the mean values of the quantities calculated above are

$$s_{\overline{\Delta H}} = s_{\overline{\Delta H}_T} = 140 \text{ cal.}$$
$$s_I = s_{\overline{\Delta S}} = 0.21 \text{ e.u.}$$
$$s_{\overline{\Delta F}_{298}} = 16 \text{ cal.}$$

The validity of the thermodynamic constants obtained in this work depends, chiefly, on the closeness with which the indene–hydrindene ratios at various temperatures correspond to the equilibrium values. The following criteria were applied to the experimental work to support the conclusion that equilibrium conditions were achieved: (1) The given mixture of indene and hydrindene was recycled over the catalyst until no change in refractive index and bromine addition analyses occurred. (2) Mixtures of indene and hydrindene were brought to an analytically stable composition at a given temperature from both the indene and hydrindene sides of the equilibrium value. (3) Runs were made using different batches of catalyst and different batches of reactants with corresponding results at a given temperature. (4) The catalyst was never found to be inactive, after the standard reactivation procedure, in either the hydrogenation or dehydrogenation reaction. (5) No analytically significant side reactions were observed, as indicated by the interrelationships between the methods of analysis; *i. e.*, the bromine absorption method determines total unsaturates while the benzaldehyde condensation method determines total active methylene group compounds; of the possible compounds present in the reaction product only indene would permit agreement between the results of the two analytical procedures; further, the presence of compounds other than indene or hydrindene, in significant amounts, would be indicated by a lack of agreement between the results of the two methods and the refractive index method. (6) It is probable that the side-reaction involving hydrogenation of the benzene ring is sub-

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(6) D. R. Stull and F. D. Mayfield, *Ind. Eng. Chem.*, **35**, 639 (1943).

(7) $\Delta H_{355} = 23{,}952$ [calculated from Kistiakowsky's data in (1)].

stantially non-existent at temperatures above 350°. This conclusion is supported by thermodynamic data and calculations in references 8 and 9. (7) The material balances were found to be satisfactory (about 1% losses).

Summary

1. The equilibrium constants for the system hydrindene–indene–hydrogen at temperatures between 375 and 525° have been determined.

2. The free energy equation for the reaction has been calculated.

3. A refractive index–composition equation for indene–hydrindene mixtures is given.

EDGEWATER, NEW JERSEY RECEIVED JUNE 9, 1949

(8) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chem. Catalog Co., Reinhold Publ. Corp., New York, N. Y., 1932.

(9) G. H. Burrows and C. Lucarini, THIS JOURNAL, **49**, 1157 (1927).

NOTES

2,4- and 4,6-Dinitro- and Diamino-*m*-xylenes

BY ROGER ADAMS AND A. S. NAGARKATTI

There is no convenient method yet described for preparing pure 2,4- and 4,6-dinitro- or 2,4- and 4,6-diamino-*m*-xylenes. Because of the need for 2,4-diamino-*m*-xylene, a study of the separation of the mixed dinitro- and diamino-*m*-xylenes was undertaken.

When *m*-xylene is nitrated by means of nitric and sulfuric acids, a mixture of 2,4- and 4,6-dinitro-*m*-xylenes always results.[1,2,3] It has been reported that the two products may be separated by fractional crystallization from ethanol but this is difficult and unsatisfactory. The 4,6-dinitro-*m*-xylene is usually present in larger amounts. It is the less-soluble of the two and fractions can be obtained which consist mostly of this constituent. It is entirely impossible to obtain by this procedure the 2,4- isomer in any reasonable degree of purity. The pure 2,4-dinitro-*m*-xylene has previously been synthesized by nitration of 2-nitro-*m*-xylene.[4] The product from the nitration of *m*-xylene when crystallized from ethanol gives a crystalline material, usually with a melting point of 57–62°, which is not changed by further recrystallization.[2] It has now been found that by crystallization of this mixture from chloroform in which it is very soluble, a product results which, after two recrystallizations from the same solvent, melts sharply at 84°. About 10–15% of this product was obtained from the original mixture. This was characterized as pure 2,4-dinitro-*m*-xylene by reduction first with ammonium sulfide to 2-nitro-4-amino-*m*-xylene (m. p. 81°) and second by hydrogenation in presence of Raney nickel to 2,4-diamino-*m*-xylene (m. p. 65–66°). The diamine separated as an oil which by scratching was readily induced to crystallize. Upon one recrystallization from petroleum ether it was pure. This proved to be one satisfactory method for obtaining 2,4-diamino-*m*-xylene.

The 2,4- and 4,6-diamino-*m*-xylenes have been prepared previously by reduction (1) of the difficultly obtained dinitro compounds, (2) of the 2-nitro-4-amino-*m*-xylene[4] and 6-nitro-4-amino-*m*-xylene,[1] and (3) of 2,4-dinitro-3,5-dimethylbenzoic acid and of 2,6-dinitro-3,5-dimethylbenzoic acid, by means of tin and hydrochloric acid, with simultaneous loss of carbon dioxide.[5] Morgan[2] attempted the separation of the mixed diamines resulting from reduction of the mixture of dinitro-*m*-xylenes. Acetylation followed by crystallization then hydrolysis, crystallization of the diamine hydrochlorides, and finally fractional distillation of the free amines obtained from the salts gave a certain amount of 4,6-diamine in pure form but none of the pure 2,4-diamine.

A more simple separation of the mixed diamines has now been achieved. Catalytic reduction of the mixed dinitro compounds gave an oil which could not be induced to solidify. It was converted into the dihydrochlorides by addition of the required amount of concentrated hydrochloric acid. The solid dihydrochlorides have distinct differences in solubility in water and were separated by removal of successive amounts of solvent from the solution. The less-soluble material which crystallized first consisted of 2,4-diamino-*m*-xylene dihydrochloride; that obtained later proved to be 4,6-diamino-*m*-xylene dihydrochloride. Since the dihydrochlorides have high and unsharp melting points, fractions were made alkaline, the bases extracted with ether, dried and the melting points of the bases determined in order to follow the fractionation. About 10% of the mixture proved to be the 2,4-isomer which is in agreement with the amount found by separation of the two dinitro compounds by means of chloroform. To obtain the pure 2,4-dihydrochloride, one treatment more than for the 4,6-dihydrochloride was required ow-

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(1) Grevingk, *Ber.*, **17**, 2422 (1884).

(2) Morgan, *J. Chem. Soc.*, **81**, 86 (1902).

(3) Ruggli, Zimmermann and Thouvay, *Helv. Chim. Acta*, **14**, 1250 (1931).

(4) Noelting, Braun and Thesmar, *Ber.*, **34**, 2242 (1901).

(5) Bamberger and Demuth, *ibid.*, **34**, 27 (1901).