Magnetic Susceptibility.—The method of Gouy[12] was used, and the nickel formyl camphor proved to be definitely paramagnetic. The details of the method and the quantitative value of the molecular magnetic susceptibility (approximately 2500×10^{-6}) will be given in a forthcoming paper on the magnetic susceptibilities of several nickel salts.

[12] Gouy, *Compt. rend.*, **109**, 935 (1889).

Summary

New data are presented on the ultraviolet absorption spectrum and ultraviolet rotatory dispersion of nickel formyl camphor. The conclusion is drawn that the configuration of the nickel complex is tetrahedral and not square coplanar. The conclusion is confirmed by the evidence that the compound is paramagnetic.

WELLESLEY, MASS. RECEIVED SEPTEMBER 17, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

A Study of the Catalytic Properties of Beryllium Chromite

BY R. K. LADISCH[1] AND J. C. W. FRAZER

In work previously reported[2] from this Laboratory, beryllium chromite was found to be a catalyst for the oxidation of carbon monoxide. An effort was made to measure the adsorption of oxygen by beryllium chromite but the amount of oxygen adsorbed increased with each succeeding run. It was thought that the alternate oxidation and reduction involved in the adsorption of the oxygen and the subsequent preparation of the catalyst for a succeeding run activated it.

The present work was undertaken to find the limit to which beryllium chromite could be activated by alternate oxidation and reduction. It was found that the increasing adsorption of oxygen took place only on catalysts that were washed with distilled water after decomposition of the original compound and not on unwashed catalysts. The unwashed catalyst was found to have a definite composition and was reproducible; so it was studied in greater detail. (A study of the washed catalyst is now in progress.)

By decomposition of double beryllium ammonium chromate, beryllium dichromate was formed quantitatively. This was quantitatively reduced to chromite by hydrogen. This observation is of importance because it shows that the readily available beryllium dichromate can be used as a catalyst after reduction instead of a chromite made by thermal decomposition of double beryllium ammonium chromate.

Experimental

Beryllium chromite catalyst was made by thermal decomposition of the double beryllium ammonium chromate, $Be(NH_4)_2(CrO_4)_2$, and subsequent reduction. The double salt was heated in a balloon flask, raising the temperature to 175° at the rate of a few degrees per hour. Slow decomposition began at 175° and was complete at 250°. A vacuum was maintained in the flask by means of a mechanical oil pump.

The product of the thermal decomposition of the double salt was completely soluble in 2% hydrochloric acid except for a few white, flocculent particles. Three samples of the product were analyzed according to the method of Moser and Singer.[3] Samples 1 and 2 contained some residual water from the decomposition. Sample 3 was heated to 1000° for one hour. These samples gave values very close to the correct analysis for beryllium dichromate.

Anal. Calcd. for $BeCr_2O_7$: BeO, 11.1; Cr_2O_3, 67.6. Found: Sample 1, BeO, 10.8; Cr_2O_3, 65.7; Sample 2, BeO, 10.8; Cr_2O_3, 62.8; Sample 3, BeO, 11.5; Cr_2O_3, 67.7.

X-Ray diffraction spacings were obtained from powder photographs which were taken using unfiltered molybdenum radiation. No lines were obtained from the sample of catalyst heated in air to 250° for one hour. Samples of catalyst heated to 300° for forty hours, to 500° for five

TABLE I

No. of line	Intensity	Spacing in Å.
1	Strong	4.01
2	Strong	3.26
3	Weak	2.60
4	Weak	2.41
5	Weak	2.28
6	Weak	2.12
7	Weak	2.02
8	Weak	1.69
9	Strong	1.64
10	Weak	1.39

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[1] Condensed from a dissertation presented to the faculty of The Johns Hopkins University in partial fulfillment of the requirement for the M.A. degree in Chemistry. Original manuscript received October 23, 1939.

[2] Heard and Frazer, *J. Phys. Chem.*, **42**, 855 (1936).

[3] Moser and Singer, *Monatsh.*, **48**, 673 (1927).

hours and 1000° for one hour gave crystal spectra. Spacings were determined from the last powder picture. The data obtained are given in Table I.

The surface of a sample of the unwashed beryllium chromite was measured by the adsorption of nitrogen at its boiling point, using the method of Emmett, *et al.*[4] The results obtained are given in Table II.

TABLE II

Heat treatment, hr.	1 at 250°	40 at 300°	1 at 1000°
Surface, sq. m./g.	142	98.5	2.2

The adsorption of oxygen was studied by the method described by Heard and Frazer[2] with a slight modification. Helium was used instead of nitrogen for measuring the dead space. The stepwise reduction was replaced by a continuous one. Hydrogen was used as reducing agent instead of carbon monoxide since the latter was strongly adsorbed by the catalyst and was not removable up to 300° under a vacuum of 10^{-6} cm.

The catalyst was prepared for adsorption measurements by passing hydrogen over it at 300° for forty minutes. The apparatus was then evacuated to a pressure of 10^{-6} cm. for forty minutes at 300°. This treatment did not affect the catalyst appreciably, since sintering took place only at a rate of 0.76% per hour, as calculated from the surface measurements. The catalyst bulb was cooled down to the desired temperature and oxygen admitted from the gas buret at a constant pressure of 150 mm.

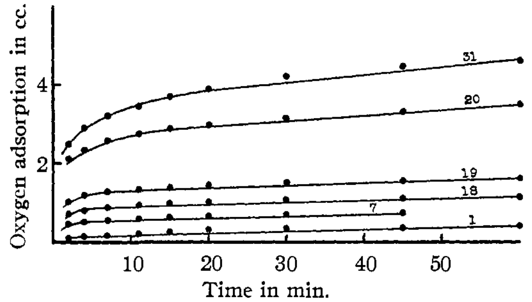

Fig. 1.—Rate of oxygen adsorption on 1 g. of washed beryllium chromite: oxygen pressure, 30 mm.; numbers refer to consecutive sorptions; runs 1 and 7 at 175°, 18 and 19 at 150°, 20 at 275° and 31 at 300°.

Figure 1 shows a series of isotherms for oxygen on one sample of a washed catalyst at 150°. The numerals show the number of consecutive runs made on this sample. From the graph it is seen that this sample adsorbed more oxygen after each succeeding run. Figure 2 shows isotherms at several temperatures on an unwashed sample of catalyst. These latter isotherms showed a high degree of reproducibility, in contrast to those runs on a washed catalyst.

Adsorption of Carbon Monoxide.—Prior to making the measurements, the unwashed catalyst was reduced as previously described. The adsorption of carbon monoxide was determined for the reduced catalyst only. Figure 3 shows the isotherms that were obtained. The lowest curve is an isotherm at 250° and 15 mm. The other isotherms were run at 150 mm.

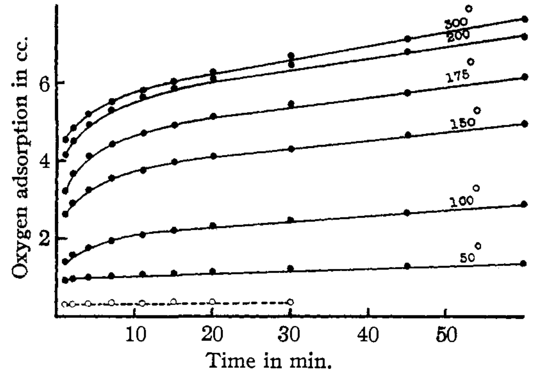

Fig. 2.—Rate of oxygen adsorption on 1 g. of unwashed beryllium chromite: oxygen pressure 150 mm.; full lines, partially crystallized catalyst with 98.5 sq. m./g. surface; broken line, crystalline catalyst (2.2 sq. m./g. surface) at 200 and 300°.

The desorption of carbon monoxide was measured in the following way. The catalyst surface was saturated with carbon monoxide at 300° and the catalyst bulb was then heated to 350 and 400°, respectively. The amount of gas given off by the catalyst at each of these temperatures was noted after attaining equilibrium. In a subsequent cooling to 250° this desorbed gas and an additional amount of carbon monoxide were again taken up by the catalyst. Figure 4 shows the sorption under 150 mm. pressure as well as under 15 mm.

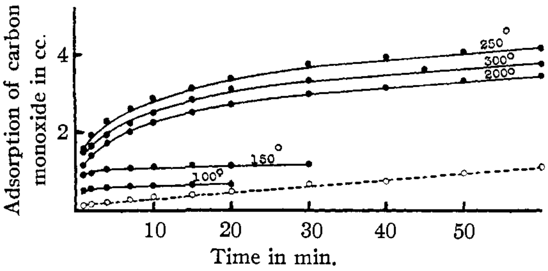

Fig. 3.—Rate of carbon monoxide adsorption on 1 g. of unwashed beryllium chromite: CO pressure, 150 mm.; broken line, at 250° and 15 mm.

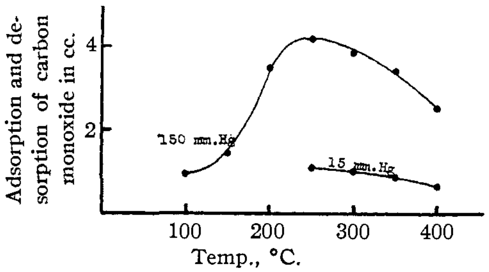

Fig. 4.—Adsorption and desorption of carbon monoxide on 1 g. of unwashed beryllium chromite.

The efficiency of the catalyst was determined by passing a mixture of 98% air and 2% carbon monoxide over it. The carbon dioxide developed was caught in a measured

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[4] Emmett, Brunauer and Teller, THIS JOURNAL, **60**, 309 (1938).

amount of 0.1 *N* barium hydroxide solution and the excess of alkali titrated back with 0.1 *N* oxalic acid. The flow velocity of the gas mixture was 25 cc./min. per gram of catalyst. The catalytic efficiency was found to be greatly influenced by the degree of oxidation and the crystalline state of the catalyst. Therefore, only samples of unwashed catalyst well defined with respect to these properties were employed. Sample 1 was amorphous and was reduced at 300° with hydrogen; sample 2 was amorphous and was oxidized at 200°. Samples 2a, 3 and 4 were, respectively, 8.4, 76 and 98% crystalline; all three were oxidized at 200° before testing. All five samples were dried under vacuum. The gas was dried with phosphorus pentoxide before passing it over the catalyst since it was found that water vapor acted as a poison, as shown by the following data. At 247° the conversion was 58.5% when the gases were dried; while a conversion of only 17.2% was obtained with the same sample at the same temperature when the gas mixture was bubbled through cold water prior to passing it over the catalyst.

The data obtained in these experiments are shown in Fig. 5 in which percentage conversion is plotted against temperature.

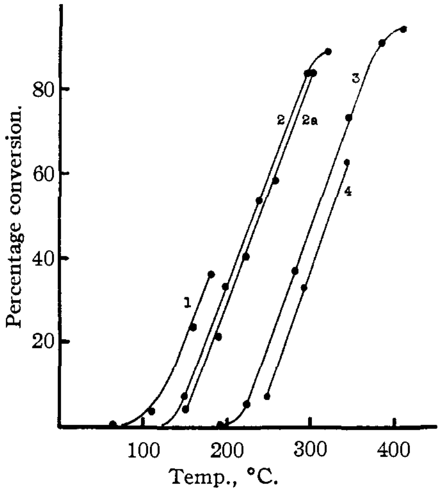

Fig. 5.—Conversion ranges in the oxidation of carbon monoxide by beryllium chromite. Numbers refer to properties of catalyst: 1, amorphous, reduced; 2, amorphous, oxidized; 2a, 8.4% crystallized, oxidized; 3, 76% crystallized, oxidized; 4, 98.5% crystallized, oxidized.

Discussion

Since the beryllium chromite was made by low temperature reduction of the dichromate by hydrogen, it might be expected that the chromite could be oxidized back to dichromate when oxygen was admitted to the system. Complete reoxidation was not attempted since our interest centered on the surface which is more directly connected with catalytic action. The adsorption of oxygen on the surface occurred practically instantaneously (the very steep part of the isotherm), followed by a slow penetration of the adsorbed oxygen into the interior of the catalyst. The following experiment confirms this theory.

A sample of catalyst was reduced with hydrogen and thoroughly dried in a high vacuum. Oxygen was admitted at a pressure of 150 mm., when the catalyst was at a temperature of 150°. The adsorption was stopped at the end of five minutes by immersing the catalyst in ice water. The data obtained are represented by curve I, Fig. 6. The system was then evacuated to 10^{-6} cm. while the catalyst was maintained at 0°. A determination of the extent of the surface was then made by the adsorption of nitrogen. The result is shown by curve A, Fig. 7.

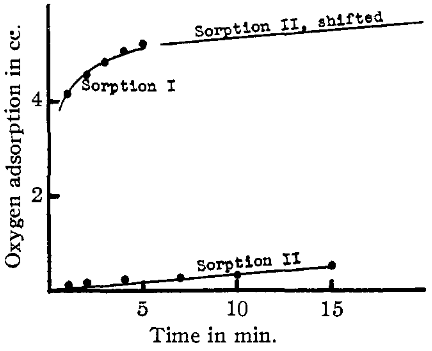

Fig. 6.—Oxygen adsorption by 1 g. of unwashed beryllium chromite at 150° and 150 mm.: sorption I, discontinued after 5 min.; sorption II, adsorption continued after heating under nitrogen at 150° for 3.5 hours. Sorption curve II falls along an extrapolation of sorption curve I when its origin is shifted to the discontinuation point of sorption I.

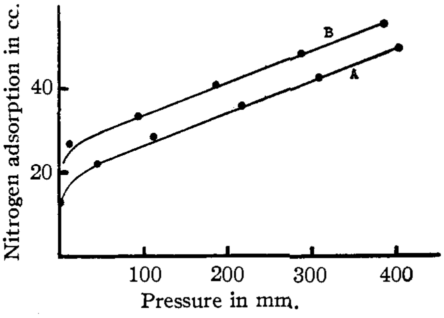

Fig. 7.—Nitrogen adsorption by 1 g. of unwashed beryllium chromite at −180°. A, catalyst oxidized at 150° and 150 mm. for five minutes; B, sample heated under nitrogen at 150° for 3.5 hours.

Next, the catalyst was heated to 150° in the presence of nitrogen at a pressure of 150 mm. It was kept under these conditions for three and one-half hours. The bulb was cooled and evacuated as before and another surface determination was made, curve B, Fig. 7. The system then was evacuated to 10^{-6} cm., and heated to 150° at this pressure. A second oxygen adsorption measurement was made at 150° and 150 mm. The result is represented by curve II, Fig. 6.

In Fig. 6, the first five minutes adsorption of oxygen is labelled sorption I and the second longer adsorption, sorption II, is plotted from the same origin. Curve II can be shifted to the end-point of sorption I. It falls then along an extrapolation of curve I.

Curve A, Fig. 7, shows that the apparent surface of the catalyst, loaded with oxygen, is less prior to the heat treatment (curve B). The extent of the surface indicated by curve B agrees very closely with that for the reduced catalyst. The lower nitrogen uptake, curve A, Fig. 7, is an indication that the oxygen is primarily loosely adsorbed on the surface in such a manner that it blocks the adsorption of nitrogen. Thereafter, the oxygen goes into solid solution by the action of heat, and the surface area becomes almost the same as that of the original catalyst. This solid solution process is followed by chemical combination of oxygen with surface of the chromite at higher temperature. The states of solution and chemical combination have not yet been strictly separated. The conversion studies, Fig. 5, indicate, however, that the chemical reaction to form chromate is limited to the crystalline catalyst, as will be discussed later.

Curve II of Fig. 6 is believed to represent oxidation of chromite to chromate. This appears to be a slow and straightforward process. The well-defined slope of the curve probably characterizes either the diffusion or reaction velocity of the oxygen.

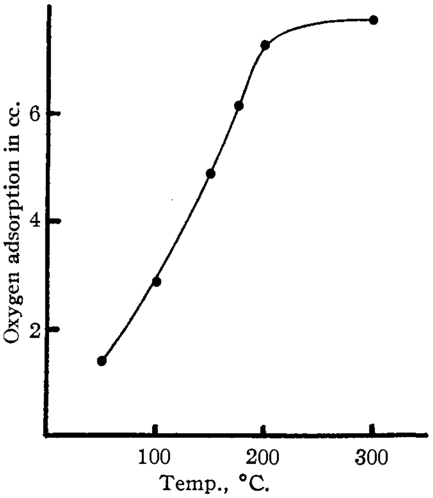

Fig. 8.—Oxygen adsorption by 1 g. of unwashed beryllium chromite.

On the basis of this theory, each adsorption isotherm for oxygen may be roughly divided, therefore, into three parts. This is shown schematically in Fig. 9. The first rapid, true adsorption, portion (1) of the curve is followed by a solid solution process or chemical reaction, portion (2). Part (3) of the curve represents diffusion as indicated by the steady further adsorption.

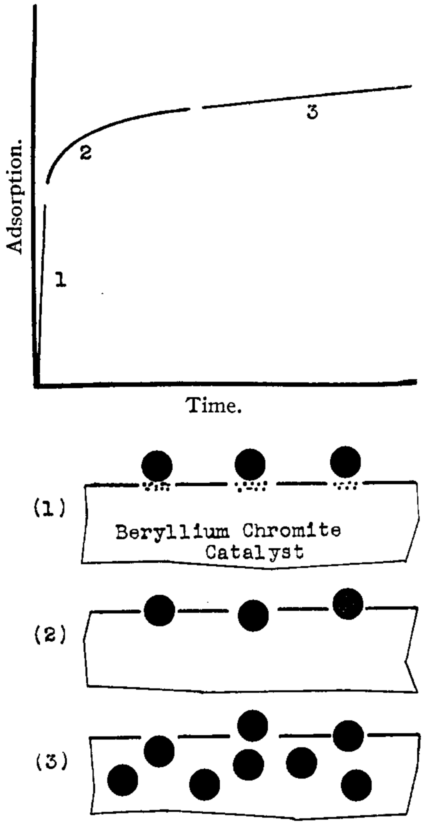

Fig. 9.—Adsorption isotherm schematically, numbers refer to type of process: no. 1, adsorption; no. 2, solution; no. 3, diffusion. Circles refer to gas molecules.

Activation energies were calculated for the first rapid adsorption, curve I, Fig. 9. They lie between 3 and 6 kcal./mole. Figure 8 shows the volume of oxygen adsorbed at different temperatures at the end of one hour. The volume adsorbed increased rapidly from 50 to 200°.

The amount of adsorption of oxygen on the steep parts of the curves, designated before as adsorption, was compared with the available surface. Table III shows the percentage of the surface covered by oxygen for several temperatures and catalysts.

TABLE III

Catalyst surface in sq. m./g.	142	98.5	2.2
Temp., °C.	Surface covered by oxygen in percentage		
50	..	4.9	..
100	..	5.7	..
150	12.3	12.8	..
175	..	16.4	..
200	..	21.2	23
300	..	22.0	23

The data in this table suggest that the absolute oxygen uptake is independent of the amount of crystallization of the catalyst.

The adsorption of carbon monoxide is probably analogous to that of oxygen. Activation energies were found to be between 5 and 11 kcal./mole. Figure 4 is a plot of the volume of carbon monoxide adsorbed *versus* the temperature. The volume of carbon monoxide adsorbed increased rapidly in almost the same temperature region in which oxygen also was rapidly adsorbed. The desorption of carbon monoxide above 250° has been mentioned before.

Evidence also was found for a strong binding of the carbon monoxide after heat treatment, just as in the case of oxygen, as surface measurements by means of nitrogen adsorption showed that the extent of the surface was essentially that of the untreated chromite catalyst. This great binding strength or even compound formation makes carbon monoxide undesirable for use as a reducing agent in preparing the catalyst.

The results obtained suggest the following mechanism for the oxidation of carbon monoxide by beryllium chromite. Starting with an amorphous, reduced catalyst, the reaction gas mixture of 98% air and 2% carbon monoxide is passed over it first at low temperatures. Up to about 150° both carbon monoxide and oxygen are adsorbed loosely with activation energies of around 5 kcal./mole. Because of the blocking effect of the adsorbed gases, as shown by the results of the low temperature adsorption of nitrogen, this state of adsorption should be referred to as "gas phase."

The conversion of carbon monoxide to carbon dioxide amounted initially to about 25% at 150°. It decreased rapidly, however, at this temperature, because in time oxygen and carbon monoxide cease to exhibit the loose kind of adsorption and become adsorbed on the surface so strongly after that that the whole surface can again adsorb nitrogen at a low temperature. This latter, stronger adsorption requires higher energies of activation, as shown by the higher temperatures required for conversion. The term "solution phase" has been suggested by the writers, because this state of decreased reaction must be considered as lying between van der Waals adsorption and a still further reduced reactivity of the catalyst which will be described immediately.

In order to make the catalytic oxidation continuous, it was found that the temperature of the system must be raised steadily. This behavior is explained by the progressive crystallization of the catalyst which is shown in Table III and which becomes significant from about 300° up. In the higher temperature region, in a state of a definite molecular arrangement of the catalyst, the oxygen is without doubt bound chemically on the surface. This state therefore should be called "phase of chemical binding."

A more practical reason justifies the distinction between "solution phase" and "phase of chemical binding." The conversion efficiency of the crystalline samples compared to the amorphous catalyst was much less than could be accounted for by the shrinkage of surface during the crystallization. An amorphous sample for instance showed considerable conversion at 180°; while no carbon monoxide was converted at this temperature by a sample which still had 24% of its original surface. A sample with 1.5% of the original surface did not convert any carbon monoxide even up to 220°.

In the last state of chemical combination catalysis is made possible only by supplying the high energy of activation by working at higher temperatures. The more rapid exchange of carbon monoxide between the catalyst surface and the gas phase above the surface at the higher temperatures facilitates the conversion. In the "phase of solution" and the "gas phase" the catalysis must be attributed to the lowered activation energies of the adsorbed oxygen and carbon monoxide.

Thanks are due to the Hynson, Westcott and Dunning Foundation and to the Oberlaender Trust for additional financial help.

Summary

1. A beryllium chromite catalyst has been prepared which is stable and reproducible with respect to the oxygen and carbon monoxide uptake. The catalyst has been analyzed.

2. Samples of this catalyst have been subjected to different temperature treatments and surface determinations, and X-ray investigations have been made.

3. The adsorption of oxygen on the catalyst has been determined at constant pressure.

4. The adsorption and desorption of carbon monoxide has been studied at pressures of 150 mm. and 15 mm., respectively.

5. The catalytic efficiency for high temperature oxidation of carbon monoxide has been determined for amorphous, crystallized, reduced and oxidized samples of the catalyst.

6. It has been suggested that adsorption on the catalyst occurs in the following three steps: nearly instantaneous adsorption with activation energies of 3–6 kcal./mole; solid solution of the adsorbed gas; penetration of the dissolved gas into the interior of the catalyst.

7. It has been suggested further that catalysis takes place in three states. These follow each other with rising temperature in the order: "gas phase," "solution phase," "phase of chemical binding."

This work will be continued on other chromites.

BALTIMORE, MD. RECEIVED JULY 19, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CREIGHTON UNIVERSITY]

The Partial Pressure of Hydrogen Bromide from its Solutions in Some Aprotic Solvents at 25°

BY S. JAMES O'BRIEN AND EDWARD G. BOBALEK[1]

Measurements of the partial pressure of hydrogen chloride from its solutions in various solvents have given evidence of an acid–base reaction in many solvents that are generally considered as aprotic, and in some cases have intimated the chelation and association of the solvent molecules.[2] It seemed of interest to determine how closely the conclusions derived for hydrogen chloride solutions parallel those for hydrogen bromide solutions.

In hydrogen chloride solutions where a reaction between solute and solvent seemed likely, the data were interpreted in terms of a reaction of the type[2a]

$$\mathrm{HX + S = SHX} \qquad \text{(I)}$$

or of the type

$$\mathrm{HX + S = SH^+ + X^-} \qquad \text{(II)}$$

in which S represents the solvent; SHX, an unionized acid–solvent complex; and $\mathrm{SH^+}$, a solvated proton. In either case the extent of the reaction is dependent, at least, on the strengths of the acid and the solvent base.[3] These factors are, then, included in the equilibrium constant for the reaction, and a comparison of the constants for two different acids in various solvents should show to what degree the reactions depend upon acidity and basicity alone. A method of deriving equilibrium constants for reactions such as (I) and (II) from vapor pressure data was outlined in the first paper of this series.[1a] In order to evaluate constants for hydrogen bromide to compare with those obtained for hydrogen chloride, measurements have been made of the partial pressure of hydrogen bromide from its solutions in benzene, toluene, and the ortho and meta isomers of nitrotoluene. These data and, in addition, measurements of the partial pressure of hydrogen chloride from toluene solutions, are reported in this paper.

Experimental

The apparatus and method were again the same as those employed in the previous work.[2c,4]

The benzene and toluene were of good quality. They had been stored over sodium and were distilled in an all-Pyrex apparatus before using. The nitrotoluenes were redistilled after standing over calcium oxide. Some physical constants of the liquids so treated are as follows: benzene, m. p. 5.48°; toluene, $n^{20}\mathrm{D}$ 1.4959; *o*-nitrotoluene, $n^{20}\mathrm{D}$ 1.5453; *m*-nitrotoluene, m. p. 15.35°, $n^{20}\mathrm{D}$ 1.5460.

Hydrogen bromide was prepared by the action of bromine on tetralin in an all-Pyrex apparatus. It was led through two long tubes, one containing red phosphorus and the other phosphorus pentoxide, before being introduced into the liquids.

Results

The results of the experiments are given in Table I. The first column of each section gives the molality of the hydrogen halide; the second its vapor pressure in mm. of mercury; and the third the Henry law constant, $k = p/m$, in atm.

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(1) Present address: Chemistry Department, University of Indiana, Bloomington, Indiana.

(2) (a) S. J. O'Brien, C. L. Kenny and R. A. Zuercher, THIS JOURNAL, **61**, 2504 (1939); (b) S. J. O'Brien and C. L. Kenny, *ibid.*, **62**, 1189 (1940); (c) S. J. O'Brien and J. B. Byrne, *ibid.*, **62**, 2063 (1940).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, especially pp. 251–262.

(4) J. Saylor, THIS JOURNAL, **59**, 1712 (1937).