

potassium hydroxide in 50% aqueous ethyl alcohol. This extends the observations of Barnett and his co-workers to more drastic conditions.

Two interpretations of this and similar facts are considered, that a Walden inversion must attend such a replacement reaction, or that a carbonium ion must be formed in which the central carbon atom and the three atoms directly combined with it lie in a common plane. The latter concept, advocated previously by Bartlett and Knox by analogy to boron compounds, is here correlated with the resonance normally present in an arylated carbonium ion. This interpre-

tation is favored but not conclusively proved.

The bromine can be replaced by hydrogen by means of reduction with sodium and alcohol.

Maleic anhydride has been added to ethyl *N*-9-anthrylcarbamate to yield a bridged-ring urethan (VII) which is readily hydrolyzed to the amino-dibasic acid related to II. Nitrous acid converts this into a compound which is probably the dibasic acid with hydroxyl on the bridge-head. As expected by Barnett, this compound is very unstable to alkali. Its decomposition is interpreted as ketol cleavage.

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

## The Partial Pressure of Hydrogen Chloride from its Solutions in *o*-Nitrotoluene, *m*-Nitrotoluene and *n*-Hexane at 25°

BY S. JAMES O'BRIEN AND CHRISTOPHER L. KENNY

In an earlier paper<sup>1</sup> the partial pressure of hydrogen chloride from its solutions in various solvents was interpreted in terms of an acid-solvent reaction. The results so obtained may be taken as a measure of the relative basicities of the solvents used. It also has been pointed out<sup>2,3,4</sup> that the problem of solvent basicity can be attacked by means of infrared absorption studies. In work of this type the position of a certain absorption band, which is attributed to the formation of a hydrogen bond and which shifts to longer wave lengths in the more basic solvents, is considered a measure of the basicity of the solvent. It seemed of interest to determine to what extent the conclusions concerning the basicities of solvents obtained from such infrared absorption data parallel those obtained from partial pressure experiments. It was decided, then, to measure the partial pressure of hydrogen chloride from its solutions at 25° in the ortho and meta isomers of nitrotoluene in order to compare these and other similar available data with those obtained from infrared absorption investigations.<sup>5</sup>

(1) S. J. O'Brien, C. L. Kenny and R. A. Zuercher, *THIS JOURNAL*, **61**, 2504 (1939).

(2) W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939).

(3) W. Gordy, *ibid.*, **7**, 93 (1939).

(4) W. H. Rodebush and A. M. Buswell, *J. Phys. Chem.*, **43**, 219 (1939).

(5) Since this paper was written, an article by W. Gordy and S. C. Stanford, *J. Chem. Physics*, **8**, 170 (1940), has appeared in which a study of this kind has been made. Gordy and Stanford relate the basicities of solvents as derived from shifts of the OD vibrational band of CH<sub>3</sub>OD in these solvents, to those derived from

Also, a few measurements of the partial pressure of hydrogen chloride from *n*-hexane solutions at the same temperature were made in order to determine whether the deviation of hydrogen chloride from the law of Raoult in this solvent is positive, as might be anticipated from the results obtained with haloforms in hydrocarbon solutions,<sup>6</sup> and from the fact that the rate of addition of hydrogen chloride to ethylenes is so very much greater in aliphatic than in aromatic hydrocarbons.<sup>7</sup>

### Experimental

**Apparatus and Method.**—The apparatus and method were in general the same as those employed in the previous work.<sup>1,8</sup> The time allowed for the establishment of the solution-vapor equilibria ranged from two to five days. In the analysis of the solutions of the nitrotoluenes it was found to be advantageous to add a drop or two of capryl alcohol to the solutions before titration with sodium hydroxide. The constant temperature bath was regulated at 25.00 ± 0.02°.

**Materials.**—The liquids used were Eastman Kodak Company products. The *m*-nitrotoluene and *n*-hexane were not further purified. Since the *o*-nitrotoluene had a slightly pink color which turned to a deep purple on the

measurements of the solubilities of monofluorodichloromethane. This comparison seems to be in accord with the opinion, stated later in this paper, concerning the discrepancies between the basicities of solvents as intimated by infrared absorption and solubility studies.

(6) G. F. Zellhoefer, M. J. Copley and C. S. Marvel, *THIS JOURNAL*, **60**, 1337 (1938).

(7) S. F. O'Connor, L. H. Baldinger, R. R. Vogt and G. F. Hennion, *ibid.*, **61**, 1454 (1939).

(8) J. Saylor, *ibid.*, **59**, 1712 (1937).

addition of hydrogen chloride, it was purified by allowing it to stand over calcium oxide and distilling it from phosphorus pentoxide. The liquid obtained was yellow in color and maintained this color when hydrogen chloride was added. Results obtained using the unpurified *o*-nitrotoluene were, however, not significantly different from those obtained using the purified material as is shown in Table I. The physical constants of the liquids, taken as an index of purity, are as follows: *n*-hexane,  $n_D^{20}$  1.3741; *o*-nitrotoluene,  $n_D^{20}$  1.5476; *m*-nitrotoluene,  $n_D^{20}$  1.5479; m. p. 15.35°.

The hydrogen chloride was generated and introduced into the liquids as in the previous work.<sup>1</sup>

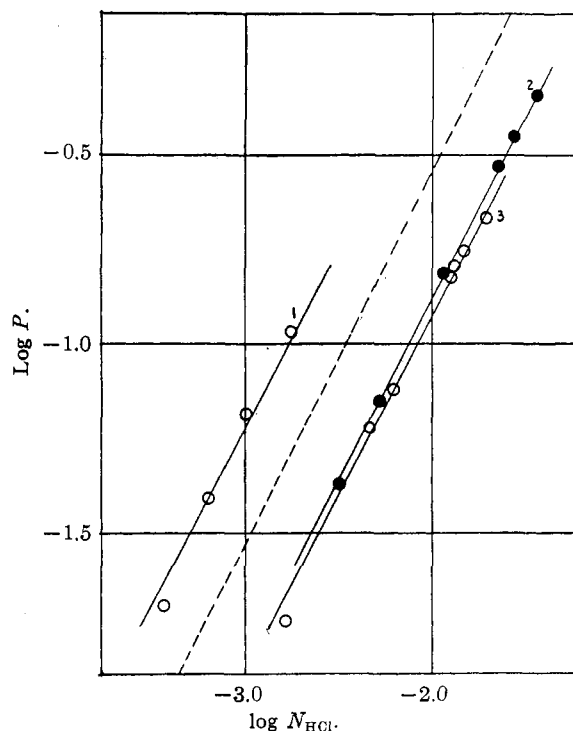


Fig. 1.—The partial pressure of hydrogen chloride from solutions in (1) *n*-hexane, (2) *o*-nitrotoluene and (3) *m*-nitrotoluene. The broken line represents Raoult's law.

### Results

The results obtained are given in Tables I, II and III, in which the first column gives the

TABLE I

THE PARTIAL PRESSURE OF HYDROGEN CHLORIDE FROM ITS SOLUTIONS IN *o*-NITROTOLUENE AT 25°

| <i>m</i> | <i>p</i> , mm. | <i>k</i>          |
|----------|----------------|-------------------|
| 0.259    | 340            | 1.72 <sup>a</sup> |
| .202     | 269            | 1.75              |
| .164     | 224            | 1.79              |
| .0839    | 113            | 1.78              |
| .0821    | 112            | 1.79              |
| .0382    | 53.1           | 1.82              |
| .0233    | 31.9           | 1.80              |
|          |                | Mean 1.77 ± 0.03  |

<sup>a</sup> Unpurified solvent was used.

TABLE II

THE PARTIAL PRESSURE OF HYDROGEN CHLORIDE FROM ITS SOLUTIONS IN *m*-NITROTOLUENE AT 25°

| <i>m</i> | <i>p</i> , mm. | <i>k</i> |
|----------|----------------|----------|
| 0.1385   | 167            | 1.54     |
| .1037    | 132            | 1.68     |
| .0939    | 122            | 1.71     |
| .0918    | 116            | 1.67     |
| .0438    | 56.7           | 1.70     |
| .0343    | 44.3           | 1.69     |
| .0116    | 13.9           | 1.58     |

Mean 1.65 ± 0.05

TABLE III

THE PARTIAL PRESSURE OF HYDROGEN CHLORIDE FROM ITS SOLUTIONS IN *n*-HEXANE AT 25°

| <i>m</i> | <i>p</i> , mm. | <i>k</i> |
|----------|----------------|----------|
| 0.020    | 81.5           | 5.4      |
| .0111    | 49.2           | 5.8      |
| .0073    | 28.3           | 5.1      |
| .0042    | 15.7           | 4.9      |

Mean 5.3 ± 0.3

molal concentration of hydrogen chloride in the solutions, the second gives the partial pressure of hydrogen chloride from the solutions in mm. of mercury, and the third column gives the Henry law constant,  $k = p/m$ , in atmospheres per mole per 100 g. of solvent.

The mean value of the Henry law constant was taken as the slope of the best straight line, intersecting the origin, that could be drawn through a plot of pressure against molality. The deviation indicated is the average deviation from this mean.

The data listed in the tables are also shown graphically in Fig. 1, where the logarithm of the pressure is plotted against the logarithm of the mole fraction of the solutions. The theoretical curve was obtained using the value of 30.3 atm., calculated in the previous paper<sup>1</sup> for the fugacity of hydrogen chloride from the pure liquid at 25°.

### Discussion

In Table IV, the reciprocals of the Henry law constants (molal solubility at 1 atm.) for hydrogen chloride in benzene, nitrobenzene, the nitrotoluenes, ethyl acetate and diethyl ether are compared with the positions in these solutions of the hydrogen chloride infrared absorption band which occurs at 3.46  $\mu$  in the pure hydrogen chloride. From this it will be seen that with the exception of the two nitrotoluenes the order of basicities as suggested by the two types of measurement is, in general, the same. The greater solubility of hydrogen chloride in the meta compound is, however, in accord with the assumption of a greater tend-

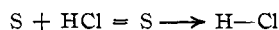
TABLE IV

| Solvent                | Position of band (microns) | $1/k$              |
|------------------------|----------------------------|--------------------|
| Benzene                | 3.48 <sup>a,b</sup>        | 0.491 <sup>d</sup> |
| Nitrobenzene           | 3.69 <sup>a,c</sup>        | .505 <sup>d</sup>  |
| <i>m</i> -Nitrotoluene | 3.75 <sup>a</sup>          | .607               |
| <i>o</i> -Nitrotoluene | 3.78 <sup>c</sup>          | .565               |
| Ethyl acetate          | 3.88 <sup>c</sup>          | 5.7 <sup>e</sup>   |
| Diethyl ether          | 4.08 <sup>c</sup>          | 6.0 <sup>e</sup>   |

<sup>a</sup> D. Williams, *Phys. Rev.*, **50**, 719 (1939). <sup>b</sup> E. K. Plyler and D. Williams, *ibid.*, **49**, 215 (1939). <sup>c</sup> Ref. 2. <sup>d</sup> Ref. 1. <sup>e</sup> These are simply molal solubilities calculated from the data of D. R. Chesterman, *J. Chem. Soc.*, 906 (1935).

ency for chelation in the ortho compound,<sup>9</sup> since chelation has been shown to result in a reduction of solubility if that property depends on the formation of a hydrogen bond.<sup>10</sup> That a chelate bond of this type should be stable in the presence of hydrogen chloride seems, however, contrary to the interpretation of the results obtained in the preceding paper<sup>1</sup> (p. 2507).<sup>11</sup> There, the high solubility of hydrogen chloride in ethylene glycol in comparison with that of monofluorodichloromethane in this solvent was explained in terms of a reduction of the association of the glycol molecules by the presence of hydrogen chloride.<sup>12</sup> This point is being further investigated, by similar partial pressure studies in progress in this Laboratory. If the solubility of hydrogen chloride can be taken as an index of the basic character of the solvent, it seems that the intensity, as well as the position of the absorption band must be taken into consideration when this property is to be interpreted not only in terms of the occurrence but also the extent of the solvent-solute reaction.<sup>13</sup>

Since hydrogen chloride solutions in the nitrotoluenes correspond with the law of Henry, and since the deviations from the law of Raoult are negative, the data may be interpreted in terms of the reaction between the solute and solvent represented by the equation



(9) N. V. Sidgwick and R. K. Callow, *J. Chem. Soc.*, **125**, 527 (1924).

(10) M. J. Copley, G. F. Zellhoefer and C. S. Marvel, *THIS JOURNAL*, **60**, 2672 (1938).

(11) It should be pointed out that J. J. Fox and A. E. Martin, *Proc. Roy. Soc. (London)*, **A162**, 437 (1937), suggested a similar interpretation of the infrared absorption of phenol in chloroform solutions as compared with its absorption in carbon tetrachloride solutions. The high "concentration" of the solvent, chloroform, would favor a phenol-chloroform reaction in such solutions, although this is a reaction which may not occur when the haloform is the solute, as intimated by solubility measurements<sup>9</sup> (pp. 2667-2668).

(12) See, however, J. Errera and H. Sack, *Trans. Faraday Soc.*, **34**, 740-741 (1938).

(13) Fox and Martin, *loc. cit.*; J. Errera, R. Gaspart and H. Sack, *J. Chem. Physics*, **8**, 63 (1940).

where S represents the solvent and  $S \longrightarrow \text{H}-\text{Cl}$  a compound formed by means of a hydrogen bond, some atom in the solvent acting as the electron donor. The equilibrium constant for this reaction is given by the equation<sup>1</sup>

$$K_a = f_0 - km_s/km_s \quad (1)$$

where  $f_0$  is the fugacity of liquid hydrogen chloride (30.3 atm. at 25°),  $k$  the Henry law constant and  $m_s$  the number of moles of solvent in 1000 g. Values of  $K_a$  calculated from the above data are 1.35 and 1.53 for ortho- and meta-nitrotoluene, respectively. As a measure of the basicity of the solvent,  $K_a$  should be more suitable than the molal solubility used in Table IV. This equilibrium constant was not used in the table, however, due to the inclusion of ethyl acetate and ether solutions, for which the existing data are not sufficient to show whether equation (1) is applicable.

While the value being used for the fugacity of liquid hydrogen chloride is far from satisfactory, there can be little doubt that the data obtained for the *n*-hexane solutions demonstrate a positive deviation from the law of Raoult, since the vapor pressure of hydrogen chloride from the solutions is greater than that required by the law even if the fugacity of liquid hydrogen chloride were equal to its vapor pressure (46.8 atm. at 25°). Treatment of these results in terms of association of the solvent seems to be out of the question for a liquid like hexane. Solutions which show a positive deviation from the law of Raoult can, no doubt, be better interpreted through a consideration of the internal pressures of the liquids involved.<sup>14</sup> However, it seems best to postpone further discussion along these lines until additional data can be presented.

### Summary

1. Measurements are reported of the partial pressure of hydrogen chloride at 25° from its solutions in *o*-nitrotoluene, *m*-nitrotoluene and *n*-hexane over the concentration ranges 0.023-0.259, 0.012-0.139 and 0.004-0.02 molal, respectively.

2. The conclusions concerning the basicity of liquids derived from these measurements are compared with those obtained from the infrared absorption spectra of hydrogen chloride in various solvents. The comparison seems to show that

(14) J. H. Hildebrand, "Solubility of Non-electrolytes," second edition, Reinhold Publishing Co., Inc., New York, N. Y., 1936, especially pp. 107-122.

intensities as well as position of infrared absorption bands are required for an accurate estimate of the basicity of solvents.

3. In the nitrotoluene solutions, hydrogen chloride corresponds with the law of Henry and shows negative deviations from the law of Raoult.

The data in these solutions are interpreted in terms of a reaction between solute and solvent. In the hexane solutions hydrogen chloride also corresponds with the law of Henry, but the deviation from the law of Raoult is positive.

OMAHA, NEBRASKA

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## Preparation of Cobalt Carbonyl, Cobalt Nitrosyl Carbonyl and Cobalt Carbonyl Hydride by the Cyanide Method

BY ARTHUR A. BLANCHARD AND PAUL GILMONT

Brockway and Anderson<sup>1</sup> have prepared cobalt nitrosyl carbonyl for the purpose of electron diffraction studies by the method of Blanchard, Rafter and Adams,<sup>2</sup> saturating an alkaline suspension of cobaltous cyanide with carbon monoxide, but they state that on passing nitric oxide into the still alkaline solution no nitrosyl carbonyl is formed. They obtain this product only after acidification. This is contrary to the findings of Blanchard, Rafter and Adams, who found that cobalt nitrosyl carbonyl vapor could be swept from the still alkaline solution. The present studies confirm the latter statement. Furthermore, the product obtained by treating the alkaline solution with nitric oxide is undoubtedly purer than that obtained from the acidified solution.

Ewens and Lister<sup>3</sup> prepared cobalt carbonyl hydride, also for electron diffraction studies, by a modification of the method of Coleman and Blanchard<sup>4</sup> by saturating an alkaline suspension of cobaltous cyanide with carbon monoxide, then acidifying and sweeping the volatile hydride from the solution. The fact that the volatile hydride  $\text{HCo}(\text{CO})_4$  is obtained when cyanide is used as a carrier makes it seem probable that the fundamental reaction of oxidation and reduction is the same as when cysteine is the carrier, namely:  $2\text{CoCl}_2 + 11\text{CO} + 12\text{KOH} \rightarrow 3\text{K}_2\text{CO}_3 + 2\text{KCo}(\text{CO})_4 + 4\text{KCl}$ . In absence of the carrier, no absorption of carbon monoxide takes place. The carrier, whether cysteine or cyanide, forms an intermediate complex containing carbon mon-

oxide and cobalt; the latter reacts further to yield the salt of  $\text{HCo}(\text{CO})_4$  and the carrier is regenerated. Schubert<sup>5</sup> has very beautifully identified the intermediate complexes in the case of cysteine. Acidification liberates the volatile acid  $\text{HCo}(\text{CO})_4$  from its salt. Treatment with NO produces the volatile nitrosyl carbonyl, probably according to the reaction:  $\text{KCo}(\text{CO})_4 + \text{NO} + \text{H}_2\text{O} \rightarrow \text{Co}(\text{CO})_3\text{NO} + \text{CO} + \text{KOH} + \frac{1}{2}\text{H}_2$ .

### Experimental

A large number of runs with varying proportions of cyanide and alkali were carried out and the proportions given in the following statements were found to produce the best results in the shortest time.

A shaking apparatus capable of keeping the liquid in the condition of a fine spray and yet allowing the passage of gases during the shaking is provided. It is swept out with carbon monoxide and approximately 50 ml. of a solution about 0.5 formal in cobalt nitrate, 0.5 formal in potassium cyanide and 4.0 formal in potassium hydroxide is introduced as follows: 7.3 g. of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 15 ml. of water is allowed to enter through a side arm, then 5 cc. of water to wash the arm, then 11.2 g. of potassium hydroxide in 11 ml. of water, then 5 cc. of water, then 1.6 g. of potassium cyanide in 3 ml. of water and lastly, 5 cc. of water.

The exit stopcock is closed and the solution shaken. A total absorption of 2200 to 2600 cc. of carbon monoxide takes place in about seven hours, 2 liters in the first two to three hours, the rate falling during the next three to five hours. During this absorption the solution changes from a blue suspension, through a pink suspension, to a yellow solution almost free of suspended matter.

**Cobalt Nitrosyl Carbonyl.**—The yellow liquid is a solution of the potassium salt of cobalt carbonyl hydride. The carbon monoxide is displaced from the shaker by nitric oxide and the shaker is started. Soon the solution turns red and after a while a deep yellow gas begins to show in

(1) Brockway and Anderson, *Trans. Faraday Soc.*, **33**, 1233 (1937).

(2) Blanchard, Rafter and Adams, *THIS JOURNAL*, **56**, 16 (1934).

(3) Ewens and Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).

(4) Coleman and Blanchard, *THIS JOURNAL*, **58**, 2160 (1936).

(5) Schubert, *ibid.*, **55**, 1877 (1933).