

the "method of approximations," which had been developed previously for handling addition compounds of low volatility,¹³ was utilized.

The results of a typical determination are given in Table IV and represented graphically in Fig. 6-B.

TABLE IV
DISSOCIATION DATA FOR QUINUCLIDINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obsd.	mm. Calcd. ^a	Degree of dissocn., α	Dissocn. constant, K (atm.)
135.2	35.08	18.454	0.9009	0.1988
140.5	35.96	18.694	.9236	.2745
145.0	36.64	18.816	.9390	.3592
150.1	37.34	19.127	.9522	.4775
155.1	37.97	19.353	.9620	.6197
160.3	38.60	19.588	.9706	.8263
165.1	39.14	19.805	.9763	1.049
170.2	39.71	20.036	.9819	1.403
175.2	40.23	20.262	.9855	1.784

^a The pressure of quinuclidine-trimethylboron in the dissociation tensimeter was approximated to be 12.345 mm. (calculated to 0° as a perfect gas).

(13) M. Gerstein, "The Dissociation of the Addition Compounds of Trimethylboron with Cyclic Imines," Ph.D. Dissertation, University of Chicago, 1945. In the method of matched samples the size of the sample of addition compound in the dissociation tensimeter is determined by combining carefully matched samples of each of the two components, measured as a gas. In the method of approximations the size of the sample of the addition compound in the tensimeter is not known. Instead, a small quantity of the carefully purified addition compound is introduced into the tensimeter and the pressures exhibited by the completely volatilized sample over a wide range of temperature are observed. The size of the sample is determined by utilizing the fact that for the relatively short temperature intervals under consideration, the heat of dissociation, ΔH , is constant. Thus, only the correct value of the sample size yields a linear relationship between $\log K$ and $1/T$ as required by the van't Hoff equation

$$\frac{d \ln K}{d 1/T} = \frac{-\Delta H}{R}$$

A full description of the procedure will be published shortly.

The values of the dissociation constants are reproduced by the equation

$$\log K_P = -(4360/T) + 9.975$$

The heat of dissociation is calculated to be 19.94 ± 1.0 kcal. and the value of the dissociation constant at 100° is 0.0196. At 100° the free energy of dissociation constant at 100° is 0.0196. At 100° the free energy of dissociation is 2.916 ± 0.05 kcal., and the entropy of dissociation is 45.6 ± 1.0 e. u. Several determinations yielded results which varied within the limits indicated.

The data clearly establish the high stability of the quinuclidine derivative relative to the triethylamine product.

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Summary

1. Quinuclidine-trimethylboron has been prepared and characterized. The dissociation of the addition compound in the vapor phase has been studied, and the values of ΔH , ΔF_{100}° and ΔS for the dissociation have been determined.

2. The addition compound is far more stable than the corresponding derivative formed by triethylamine. It is concluded that the results support the proposed steric configuration for triethylamine. Moreover, the results indicate that triethylamine should be considered a relatively hindered base with large steric requirements, while quinuclidine should be considered a relatively unhindered base with smaller steric requirements.

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Vapor Pressure Studies in the System, Aluminum Bromide-Hydrogen Bromide-Paraffin Hydrocarbon¹

BY C. M. FONTANA AND R. J. HEROLD

In the recent literature pertaining to aluminum halide catalysis the hypothesis has frequently been put forward that the activity of these catalysts is due to the formation of the active complex "HAIX₄." Thomas² postulated the formation of the intermediate complex HAlCl₄, which was assumed to be highly reactive by virtue of its easily ionizable proton. Leighton and Heldman³ and

(1) This work was part of a program of fundamental studies into the mechanism of Friedel-Crafts catalyzed reactions.

(2) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, Chapter 4.

(3) P. A. Leighton and J. D. Heldman, THIS JOURNAL, **65**, 2276 (1943).

Heldman⁴ have assumed the reaction of hydrogen bromide with aluminum bromide to form HAlBr₄ to be essentially complete in order to account for the kinetics of isomerization of normal butane in the presence of that catalyst system.

By analogy with the stability of such well known substances as the alkali metal halide-aluminum halide addition compounds⁵ it might be expected that the corresponding acid, sometimes called "aluminic acid," should also be stable.

(4) J. D. Heldman, *ibid.*, **66**, 1786, 1789 (1944).

(5) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. V, Longmans, Green and Co., Ltd., New York, N. Y., 1929.

However, the acid has never been isolated and some doubt has persisted as to its existence. Ipatieff and Grosse⁶ investigated the action of hydrogen chloride under pressure and did not observe any absorption on aluminum chloride. Ipatieff, Pines and Schmerling⁷ assumed that HAlCl_4 reacts with an olefin to form an ester, RAlCl_4 , in an explanation of the mechanism of alkylation. Pines and Wackher⁸ have shown that hydrogen bromide-promoted aluminum bromide under mild conditions has no effect on paraffin hydrocarbons in the total absence of olefins.

The present experimental work was carried out to test directly the hypothesis for the formation of " HAlBr_4 " by comparison of the solubility of hydrogen bromide in aluminum bromide-hydrocarbon solutions with that in the hydrocarbon alone, in the temperature range from about 0 to 30°. Any complex formation should result in a corresponding increase in the solubility of hydrogen bromide at a given partial pressure, in the solution containing the aluminum bromide. In connection with this work some new solubility data have also been obtained.

Experimental

The apparatus used is shown schematically in Fig. 1. It consisted essentially of a small stainless steel solubility bomb (217.5 cc. capacity) held by a mechanical shaker, and submerged in a constant temperature bath. The bomb was fitted with charging and pressure measuring apparatus. Hydrogen bromide was supplied from a stainless steel cylinder also immersed in the constant temperature bath. The bath was always maintained below room temperature to prevent condensation in the copper lines outside the bath.

The volumes of various parts of the system were carefully calibrated in order to correct for the amount of mate-

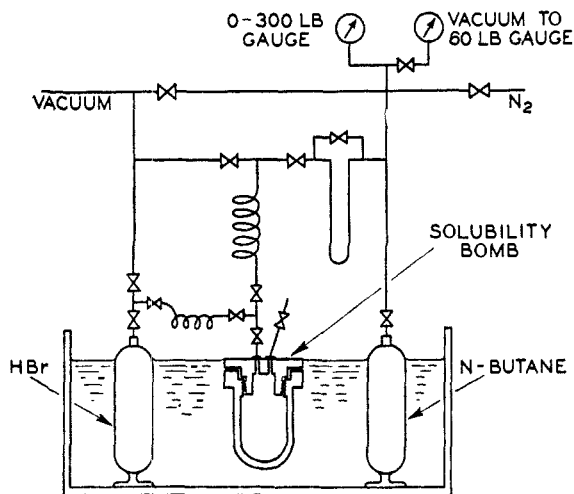


Fig. 1.—Diagram of the solubility measuring apparatus.

(6) V. N. Ipatieff, "Catalytic Reactions at High Pressures and High Temperatures," The Macmillan Company, New York, N. Y., 1936, p. 564.

(7) V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 255-263 (1940).

(8) H. Pines and R. C. Wackher, *THIS JOURNAL*, **68**, 595 (1946).

rial in the gas phase and the volume of the lines was kept as small as practicable. The change in volume of the manometer arm was also taken into account in the corrections.

The general procedure was to first weigh the solvent or solution into the solubility bomb and measure its vapor pressure at the temperature to be used. Hydrogen bromide was then introduced from its own previously weighed container directly into the solubility bomb and after equilibrium was established (five to ten minutes) the pressure was again measured. The amount entered was determined by removing the hydrogen bromide container and reweighing it, taking into account the small amount of loss upon opening the joint for each weighing. The procedure was repeated from five to ten times during each run to obtain measurements at higher pressures. At the end of the run an over-all weight balance for hydrogen bromide transfer to the solubility bomb was generally checked to about ± 0.1 g. for perhaps 30 g. of hydrogen bromide transferred. The bath temperature during the run was maintained constant to ± 0.05 .

In the low pressure range, pressure readings were taken from a mercury-filled differential manometer backed by the vapor pressure of the pure solvent supplied from another vessel in the same bath. In the higher pressure ranges, Bourdon tube gages, calibrated against a dead weight piston gage to $\pm 1\%$, were used to measure the reference pressure backing the differential manometer.

Materials.—The normal butane was obtained from large scale fractionators and had a purity of 99+%. It was thoroughly dried and degassed before use. Measurement of its vapor pressure in the apparatus described checked well with the literature.

The hexane used was commercial *n*-hexane purified by extended treatment with fuming sulfuric acid followed by careful fractionation to remove methylcyclopentane and other impurities. The refractive index of the purified product was n_D^{25} 1.3721; literature n_D^{25} 1.3722.

The hydrogen bromide was obtained from the Dow Chemical Company. It was stored in the small stainless steel cylinder and thoroughly degassed before using.

The aluminum bromide was doubly distilled over aluminum chips at low pressures and was sealed into glass ampoules under vacuum for storage until used. The final material was a clean, white crystalline solid. Solutions of aluminum bromide were made up in the solubility bomb by breaking the ampoule with shaking after the hydrocarbon had been introduced.

Results and Discussion

The measurements were generally extended to 30 to 35 lb. absolute partial pressure of hydrogen bromide and were found to follow Henry's law quite well within this pressure range. The Henry's law constants were determined over the

TABLE I

THE SOLUBILITY OF HYDROGEN BROMIDE IN HYDROCARBONS AND IN ALUMINUM BROMIDE-HYDROCARBON SOLUTIONS

Solvent	Temp., °C.	Mole % Al_2Br_6 ^a	Henry's law constant ^b
<i>n</i> -Butane	25.0	0.0	443
<i>n</i> -Butane	25.0	2.80	479
<i>n</i> -Butane	5.0	0.0	326
<i>n</i> -Butane	5.0	1.30	346
<i>n</i> -Hexane	20.0	0.0	348
<i>n</i> -Hexane	20.0	2.65	385
<i>n</i> -Hexane	5.0	0.0	265
<i>n</i> -Hexane	5.0	1.05	293

^a The mole per cent. aluminum bromide in the solution, before adding hydrogen bromide, is calculated on the dimer, Al_2Br_6 . ^b The units of Henry's law constants are: lb./sq. inch mole fraction (HBr).

total pressure range using the method of least squares and are given in Table I. A sample of the data is illustrated in Fig. 2. The figure also shows the theoretical line assuming complete association of the hydrogen bromide and aluminum bromide.

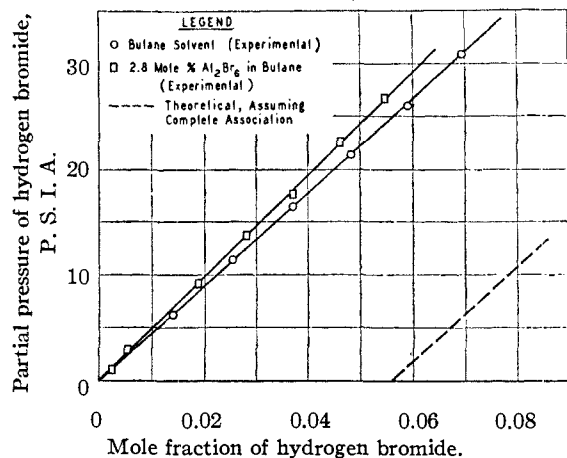


Fig. 2.—Solubility of hydrogen bromide in *n*-butane and in a *n*-butane-aluminum bromide solution at 25°. Dotted line shows the expected result for complete association to form HAlBr_4 .

Figure 3 shows a comparison of the solubility of hydrogen bromide in butane, the solubility in hexane and the ideal solubility calculated from Raoult's law. As would be expected the solutions become more nearly ideal as the temperature is increased. The heats of solution of hydrogen bromide in *n*-butane and *n*-hexane are determined from these data to be about 2,510 and 3,050 calories per mole, respectively.

It is readily seen that there is no evidence of any association of hydrogen bromide with the aluminum bromide. As a matter of fact there appears to be a small decrease in the solubility of hydrogen bromide which is probably a medium effect of the aluminum bromide. The same result is true over the given temperature range for both solvents

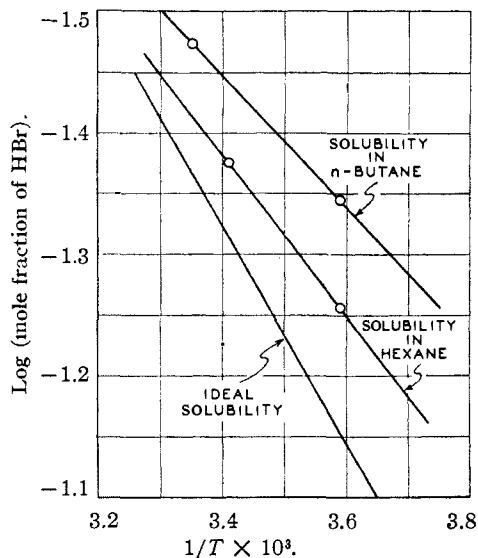


Fig. 3.—Comparison of the solubility of hydrogen bromide at atmospheric pressure in *n*-butane and *n*-hexane with the ideal solubility. Log (mole fraction HBr) versus the reciprocal of absolute temperature.

used. It must therefore be concluded that the evidence for the existence of the compound, HAlBr_4 , under these conditions is negative.

Summary

The solubilities of hydrogen bromide in *n*-butane and *n*-hexane and selected solutions of aluminum bromide in the same hydrocarbons have been determined. The solutions have been found to obey Henry's law over the pressure range 0–30 lb. absolute partial pressure of hydrogen bromide and in the temperature range 0–30°. Henry's law constants and approximate values for the heats of solution have been determined.

The evidence for the existence of the compound " HAlBr_4 " has been found to be negative over the pressure and temperature ranges indicated.

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