concentrations, the bases are the least compressible, the acids the most, and the salts occupy the intermediate position. The order of increasing compressibility of the alkali bases and chlorides is not, however, in the order of increasing atomic weights, as is the case with the solid chlorides.

A study of the existing compressibility data has been made by Gucker[5] in which it has been shown that the apparent molal compressibility is a linear function of the square root of the concentration, over a wide range of concentration, temperature, and pressure. Results based on the data given in this paper were included in this study, and were found to be in agreement with this relationship, as is shown in Fig. 3.

Fuller discussion of these results is taken up in a later paper by Gucker.[6] He states here that Scott,[7] who has made a more complete study of the compressibility of the alkali halides, has independently reached similar conclusions.

Summary

The compressibility coefficients of aqueous solutions of LiCl, NaCl, KCl, LiOH, NaOH, KOH, HCl, HAc, and KAc have been determined, each one at three concentrations; one mole of solute to twenty-five moles of water, one to fifty, and one to one hundred. The compressibility of glacial acetic acid was also determined. All measurements were made at 25°, and between 100 and 300 megabars.

The linear relationship between the apparent molal compressibility and the square root of the concentration which was pointed out by Gucker,[5] has been confirmed by these data.

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[5] Gucker, THIS JOURNAL, **55**, 2709 (1933).

[6] Gucker, *Chem. Rev.*, **8**, 117 (1933).

[7] Scott, to be submitted to *J. Phys. Chem.*

BRYN MAWR, PA. RECEIVED NOVEMBER 8, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OREGON STATE COLLEGE]

Studies on Hydrazine: The Dissociation Pressures of Hydrazinium Dichloride and Dibromide

BY B. E. CHRISTENSEN AND E. C. GILBERT

It has been shown by Hantzsch, Brönsted, Hall and others[1] that the strength of an acid in a given solvent depends upon three factors, the nature of the solvent, its dielectric constant, and the intrinsic affinity of the anion for the proton. In the case of acids such as hydrobromic and hydrochloric in the solvent water, the affinity of the solvent for the proton is so much greater than that of the anion that the reaction

$$HX + H_2O \longrightarrow X^- + H_3O^+$$

goes practically to completion and there is no marked difference in the strength of the two acids. In a solvent which did not have as great affinity for the proton, differences in the third factor, *i. e.*, the intrinsic affinity of the anion, should be more apparent. Measurements in other solvents[1a,1b,2] have indeed shown that under such conditions hydrobromic acid is stronger than hydrochloric, *i. e.*, the bromide ion shows less affinity for the proton than does the chloride ion.

The thermal dissociation of the phosphonium and ammonium halides[3] offers an interesting verification of this same viewpoint. Since this reaction involves the formation of gaseous molecules from the halide ion and a proton in a "solvent" (air or the vapor phase) which has no proton affinity, it might be expected that the halide ion having lesser affinity for a proton would form fewer molecules and its salt would show a lower dissociation pressure This is found to be true, the bromide exhibiting a lower dissociation pressure than the chloride.

The hydrazinium dihalides might be expected to furnish further verification. When heated slightly above 100° the solid salts dissociate.[4]

$$N_2H_4{\cdot}2HX \rightleftharpoons N_2H_4{\cdot}HX + HX$$

The dissociation is reversible and the extent depends upon the temperature. The dissociation pressures, however, have never been determined. The difluoride is volatile and sublimes undecomposed, while the iodide decomposes upon heating.[4] Curtius and Schultz, however, pre-

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[1] (a) Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923); (b) Brönsted, *Ber.*, **61**, 2048 (1928); (c) Hall, *J. Chem. Ed.*, **7**, 782 (1930).

[2] Schreiner, *Z. physik. Chem.*, **111**, 419 (1929).

[3] Landolt-Börnstein-Roth, "Tabellen," Fourth edition, 1912, p. 400.

[4] Curtius and Schultz, *J. prakt. Chem.*, [2] **42**, 521 (1890).

pared the monohydrochloride of hydrazine by heating the dihydrochloride to 140–160° but made no mention concerning the corresponding bromides. The present work represents a determination of the dissociation pressure of the dihydrochloride and dihydrobromide over a range of temperatures.

Experimental Part

Materials.—Hydrazine dihydrochloride (Kahlbaum) was recrystallized twice from water and dried in a vacuum. The hydrobromide was prepared by neutralization of hydrazine hydrate with hydrobromic acid (Merck) and purified by repeated recrystallization. It was dried in a vacuum over potassium hydroxide. Analysis for hydrazine content showed it to be 100.0% pure.[5]

Procedure.—The dissociation pressures were determined by the dynamic isoteniscope method of Smith and Menzies.[6] The isoteniscope was maintained at a constant temperature by means of a well insulated vapor-stat,[7] employing various liquid mixtures.[8] Temperatures were taken (within 0.1°) by means of a mercury thermometer which had been compared with a standard thermometer calibrated by the Physikalisch-technische Reichsanstalt. Pressures were measured on a closed arm manometer to 0.1 mm. with a cathetometer. Paraffin was used as the confining liquid and corrections for hydrostatic head and capillarity made as directed by Smith and Menzies. Several samples were used and the values were reproducible. Some difficulty was experienced with the bromide since at the higher temperatures permanent decomposition was found, with discoloration of the sample. Readings had to be restricted to the lower temperatures and were taken more rapidly than with the chloride to avoid possible decomposition. They do not represent the same degree of accuracy as those for the chloride. Nevertheless, they lie upon a smooth curve, are reproducible and agree with some preliminary determinations made several years ago by the static method.

Results

The results are shown in Tables I and II. Inspection shows that the dissociation pressures of the bromide are practically the same as for the chloride, instead of showing the marked difference expected, and actually observed in the dissociation of the ammonium halides. The curve of log P against T over the temperature range investigated is a straight line for both substances. The equation for the chloride data is

$$\text{Log } P_{\text{mm.}} = -(4989.96/T) + 13.4779$$

In the third column of Table I is given the temperature calculated from the equation, and in the last column the difference between the calculated and observed temperatures. A variation of ±0.1° corresponds to a difference of ±0.02 mm. at the lowest temperature and ±0.8 mm. at the highest temperature of this work. The agreement of calculated and observed values is considered quite satisfactory. Working with ammonium chloride in a similar apparatus, Smith and Menzies estimated their accuracy as ±5 mm. at somewhat higher temperatures.

TABLE I

DISSOCIATION PRESSURES OF HYDRAZINE DIHYDROCHLORIDE

P, mm.	T°, K. (obs.)	T,°K. (calcd.)	ΔT
1.25	372.8	372.9	+0.1
6.2	393.3	393.3	± .0
7.8	396.5	396.5	± .0
8.2	397.3	397.2	− .1
9.6	399.2	399.3	+ .1
9.7	399.5	399.5	± .0
16.3	406.5	406.8	+ .3
16.7	407.4	407.2	− .2
17.1	407.7	407.5	− .2
17.7	408.1	408.0	− .1
17.8	408.2	408.1	− .1
18.2	408.1	408.4	+ .3
20.7	410.4	410.3	− .1
66.0	427.7	428.0	+ .3
68.8	428.5	428.6	+ .1
72.4	429.8	429.5	− .3
84.9	431.8	432.1	+ .3
72.6	429.9	429.6	− .3

TABLE II

DISSOCIATION PRESSURES OF HYDRAZINE DIHYDROBROMIDE

P, mm.	1.4	3.0	4.8	7.9	17.8
T, °K. (obs.)	373.1	383.8	389.9	397.1	407.9

From the equation the calculated temperature of complete dissociation of the hydrochloride is 197.8°, which agrees within the limit of error with the recorded melting point of the substance, 198°. It also indicates the feasibility of preparing the monohydrochloride of hydrazine by heating the dihydrochloride. The rapid decomposition of the dihydrobromide instead of reversible dissociation at higher temperatures precludes the analogous procedure for preparing the monohydrobromide.

From the slope of the curve ΔH for the dissociation of the dihydrochloride may be estimated to be 22,828 calories per mole.

Summary

1. Dissociation pressures for the dihydrochloride and dihydrobromide of hydrazine have

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[5] The dihydrobromide upon crystallization from water forms a dihydrate. This fact has not previously been reported in the literature. Details will be given in a later communication. Upon drying in a vacuum the crystals lose water and form the anhydrous salt which was used in this work.

[6] Smith and Menzies, THIS JOURNAL, **32**, 1448 (1910).

[7] Noyes and Coolidge, *Carnegie Inst. Wash. Pub.*, **63**, 13 (1907).

[8] "International Critical Tables," Vol. 1, 1929, p. 66.

been determined by the dynamic isoteniscope method.

2. Dissociation of the dihydrochloride is complete at 197.8° under one atmosphere pressure.

3. The dihydrobromide undergoes decomposition at temperatures below its melting point and satisfactory dissociation pressures are obtainable only at lower temperatures.

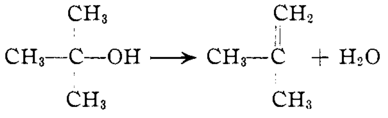
CORVALLIS, OREGON RECEIVED NOVEMBER 27, 1933

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Thermal Decomposition of Tertiary Butyl and Tertiary Amyl Alcohols. Homogeneous Unimolecular Reactions

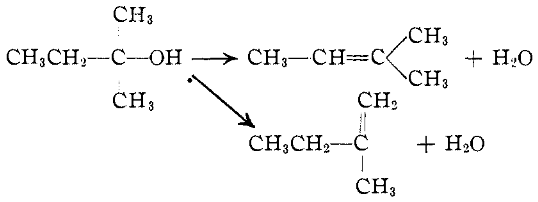
BY RAYMOND F. SCHULTZ AND G. B. KISTIAKOWSKY

The work described below, on the decomposition of tertiary butyl and tertiary amyl alcohols, was undertaken in an attempt to find more homogeneous unimolecular reactions which do not involve a complete rupture of the molecule; here instead merely the breaking of two bonds (one a C—H the other a C—O) with the formation of water is involved. The main reactions occurring can be written schematically as follows.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \longrightarrow CH_3-\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}} + H_2O$$

and



$$CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH \longrightarrow CH_3-CH=C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} + H_2O$$

$$\searrow CH_3CH_2-\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}} + H_2O$$

The only previous work on these has been done with catalysts like Al_2O_3 and various metals. The decomposition of tertiary butyl alcohol into water and isobutylene has been reported in the presence of graphite at 480–500°,[1] copper at 280–400°,[2] $AlPO_4$ at 200°,[3] and bauxite at about 100°.[4] The formation of the theoretical quantity of water has been observed when the alcohol is heated in a steel bomb for two hours at about 400–500°.[5] The work of Dohse[4] on the catalytic dehydration over bauxite is a detailed kinetic study from which he calculated an activation energy of 20,000 cal. for a first order reaction. He used a flow method with continuous removal of water by barium oxide to prevent saturation of the catalyst.

The decomposition of tertiary amyl alcohol into trimethylethylene, methylethylethylene or a mixture of both and water has also been observed under a variety of conditions. This reaction has been studied by passing the alcohol vapor through an iron tube at 660–700° and 750–800°,[6] over Al_2O_3 at 380°,[7] over $AlPO_4$ at 300–350°,[3] by flow method over iron or static in iron bomb at 600–610°,[8] at 260, 400 and 540° over Al_2O_3[9] at 300° over copper and at 220–230° over nickel,[2] and at 45–75° over Al_2O_3.[10] The last work was a thorough kinetic study which yielded an activation energy of 17,500 cal. Those reactions taking place at 500° and higher were undoubtedly to some extent homogeneous, since, as will be shown below, the homogeneous reaction is quite fast in this temperature range.

For our investigation a static method was used and the temperature range covered was 487–555°.

Experimental Procedure

Purification of Compounds.—The starting point was a commercial "absolute" tertiary butyl alcohol known to have originated from cracked petroleum hydrocarbons. Thus it was certain to be contaminated with other adjacent secondary and tertiary alcohols. Fractional distillation was used to remove all the alcohols except isopropyl, which boils within 0.5° of tertiary butyl alcohol. Isopropyl alcohol was removed by fractional crystallization since tertiary butyl freezes at 25° and isopropyl at −85°. When the freezing point of the mixture became constant it was again fractionally distilled to remove most of the water picked up in the freezing out process. This was followed by distillation over 2% of its weight of metallic sodium to remove the last traces of water. The material

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(1) Ipatiew, *Ber.*, **35**, 1064 (1902).

(2) Sabatier and Senderens, *Compt. rend.*, **136**, 986 (1903).

(3) Senderens, *ibid.*, **144**, 1110.

(4) Dohse, *Z. physik. Chem.*, **B6**, 343 (1929).

(5) Herndon and Reid, THIS JOURNAL, **50**, 3066 (1928).

(6) Ipatiew, *Ber.*, **34**, 600 (1901).

(7) Ipatiew, *ibid.*, **36**, 2002 (1903).

(8) Ipatiew, *ibid.*, **37**, 2980 (1904).

(9) Ipatiew, *ibid.*, **37**, 3001 (1904).

(10) Dohse, *Z. physik. Chem.*, Bodenstein Festband 533 (1931).