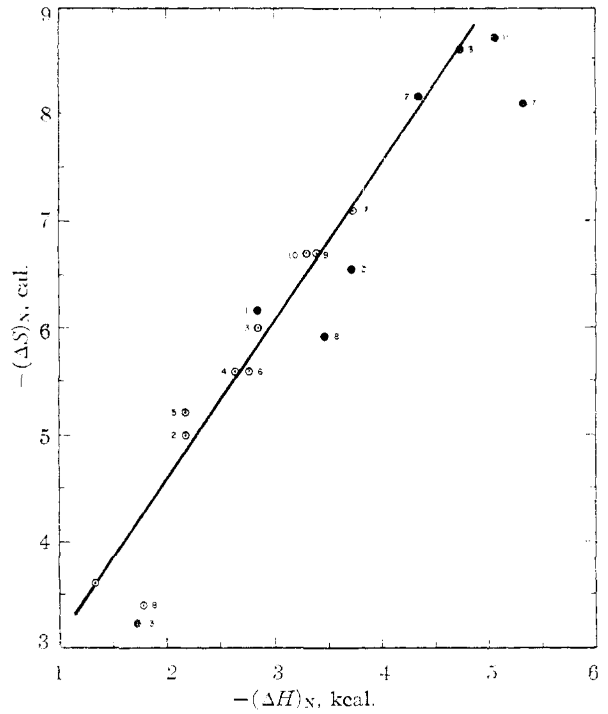

Fig. 3.—Variations in $\Delta S_{25°}$ with $\Delta H_{25°}$ for the iodine and iodine monochloride complexes. The significance of symbols and numbers is the same as in Fig. 2.

of Fig. 3) are similar. Since, however, relatively small errors in ΔF and ΔH have an appreciable effect on the magnitude of ΔS, no unqualified interpretation of these similarities seems justified.

It is apparent from the studies[4] on iodine complexes that the treatment of Figs. 2 and 3 is applicable to at least a few donors other than the alkylbenzenes. It is not surprising (in view of the results on iodine complexes) that the thermodynamic data for aromatic–iodine monochloride complexes conform to linear plots, but it is remarkable that a single graph suffices reasonably well to correlate data for the two halogens. It is possible that such a correlation would not be observed were the acceptor structures more different in chemical properties and in physical dimensions.

For all of the complexes which owe their low stabilities to alkyl group steric effects (those of 1,3,5-*t*-butyl-, pentaethyl- and hexaethylbenzene[3]), the wave lengths of maximum complex absorption are close to those of complexes of the corresponding polymethylbenzenes. In other words the position of maximum absorption is approximately characteristic of the number of alkyl substituents in the benzene nucleus[15] and is not obviously related to the thermodynamic constants.

Acknowledgment.—The authors are indebted to Research Corporation for a grant in support of this research.

[15] It has previously been suggested that the complex absorption frequency is a function of the ionization potential of the donor molecule; *cf.* H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953); S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, THIS JOURNAL, **75**, 2901 (1953).

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The Catalytic Effect of Water upon the Addition of Hydrogen Chloride Gas to Solid Sodium Sulfate[1]

BY SIDNEY W. BENSON AND RYDEN L. RICHARDSON

RECEIVED MARCH 22, 1955

HCl gas reacts rapidly and completely with a mixture of the solid Na_2SO_4 + $Na_2SO_4 \cdot 10H_2O$ to give NaCl + $NaHSO_4$ + $H_2O(g)$ at partial pressures of HCl which are less than 0.1 mm. A second mole of HCl can be added to the system at higher pressures to give what must be a solid solution of H_2SO_4 + NaCl. This last stage is reversible at 25° but the first stage is not. This is concordant with free energy data for the system. Anhydrous Na_2SO_4, however, will not add HCl gas at low pressures and only to a slight extent and very slowly at pressures up to 40 atmospheres. Thus water vapor acts as a true catalyst in this system.

I. Introduction

In the course of some work on the use of thermostated $Na_2SO_4 \cdot 10H_2O$ as a source of constant vapor pressure H_2O it was discovered that the salt undergoes spontaneous reaction with HCl gas. We then set about measuring the sorption isotherm of the salt with HCl. In a further effort to clarify the nature of this isotherm it was decided to study the simpler anhydrous system: $Na_2SO_4(s)$ + HCl(g). To our surprise there was no detectable reaction of the gas with the anhydrous material even after several days contact time. It thus appeared that (a) either water vapor was a true catalyst for the reaction or (b) the reaction of HCl with Na_2SO_4 required the presence of hydrated salt as an intermediate. To elucidate further the behavior of the anhydrous system we studied the reaction at sufficiently high partial pressures of HCl to permit comparison of HCl and H_2O as adsorbates. Under these conditions there is a very slow reaction between HCl and dry Na_2SO_4 which we have not followed to completion.

II. Experimental

For the low pressure, sorption isotherms, measurements were made using a modified McBain sorption balance.[2] This consisted of a Pyrex, sample boat supported by a quartz helix having a sensitivity of 47.09 mg./cm., mounted in a Pyrex cylinder. Extensions of the helix were measured with a Gaertner Cathetometer, the probable error in read-

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[1] (a) This work was supported by a grant (G-3541) from the Public Health Service, National Institutes of Health; (b) presented as part of the doctorate thesis of Ryden L. Richardson to the Graduate School, University of Southern California (July, 1954).

[2] J. W. McBain and A. M. Bakr, THIS JOURNAL, **48**, 690 (1926).

ings being ±0.007 cm. ≅ ± 0.3 mg. The cathetometer was also used to measure pressures recorded by a mercury manometer which together with the jacketed balance was submerged in a large water-bath. The bath temperature was set at 25.0° by a calibrated thermometer and kept regulated to ±0.005°. Samples were evacuated to $<10^{-3}$ mm. and pumped on for several hours prior to a run.

J. T. Baker Analyzed reagent grade sodium sulfate (anhydrous powder) was used as a source of salt. It contains less than 0.002% Cl. It was further ground in a mortar to provide a finely divided reactant. The H_2O samples used were deionized, boiled and degassed and isothermally distilled into the vacuum system. The HCl was obtained from a commercial cylinder (Matheson Co., Inc.), dried and purified by several isothermal distillations in the vacuum system.

III. The System $Na_2SO_4 + H_2O + HCl$

A 145-mg. sample of anhydrous Na_2SO_4 (*i.e.*, 1.0 mmoles) was placed on the balance and the system evacuated at 25° to below 10^{-3} mm. Water vapor was then admitted to the system and a sorption plateau was observed (Fig. 1) at a vapor pressure of 19.4 mm.[3] The sorption was followed until the mole ratio of $H_2O/Na_2SO_4 = 0.80$. This corresponds to the formation of 8 mole % of the decahydrate in the sample. At this point HCl gas was admitted to the system and a further sorption was observed at a constant total pressure equal to the initial water vapor pressure. This sorption continued until the total increase in weight (over that due to H_2O) was 36.5 mg. If it is assumed that no water is lost in this HCl sorption[4] this would represent a 1:1 addition of HCl to Na_2SO_4 corresponding to the reaction

$$Na_2SO_4(s) + HCl(g) \longrightarrow NaHSO_4(s) + NaCl(s) \quad (1)$$

It is, of course, impossible to tell from the present data whether or not the HCl is being added at constant pressure. All we can say is that its partial pressure in the system is less than 0.1 mm. Thus it is also impossible to tell whether or not there are two separate solid phases present or if the NaCl and $NaHSO_4$ form a solid solution.

As the amount of sorption increases past what appears to be a mole ratio $HCl/Na_2SO_4 \sim 1.0$, the pressure begins to rise, slowly at first and then more rapidly until at an apparent mole ratio $HCl/Na_2SO_4 \sim 1.6$, sorption seems to cease. This behavior is shown in Fig. 1. This second stage appears to correspond to a further reaction

$$NaHSO_4(s) + HCl(g) \rightleftarrows NaCl\cdot H_2SO_4(ss) \quad (2)$$

in which there is a solid solution of NaCl and H_2SO_4 which probably includes the original water of hydration.

The desorption curve is shown in Fig. 1 also. It appears to be parallel to the sorption curve and has been deliberately displaced from it by an amount equal in weight to the originally bound H_2O. The reason for doing this was the expectation that this H_2O would remain bound during the sorption process but be removed, on desorption. This is of course open to question.

Of particular interest, however, is the fact that the HCl desorption cannot be driven below mole ratio 1 even after 33 hours continuous pumping at 10^{-5} mm. so that the original reaction (eq. 1) of $HCl(g) + Na_2SO_4(s)$ is completely irreversible under our experimental conditions. This is in agreement with what thermodynamic data are available. For the reaction

$$Na_2SO_4\cdot 10H_2O(s) + HCl(g) \rightleftarrows NaHSO_4(\text{Hyp. } 1\ M) + NaCl(s) + 10H_2O(g) \quad (3)$$

one can calculate $\Delta F° = +12.9$ kcal.[5] If one makes the quite reasonable assumption that the reaction

$$NaHSO_4(\text{Hyp. } 1\ M) \rightleftarrows NaHSO_4(s) \quad (4)$$

has a $\Delta F°$ of the order of +1 kcal. then for the reaction[6]

$$Na_2SO_4\cdot 10H_2O(s) + HCl(g) \rightleftarrows NaHSO_4(s) + NaCl(s) + 10H_2O(g) \quad (5)$$

$\Delta F° = +13.9$ kcal. and

$$K_p(25°) = 1 \times 10^{-10} = p^{10}_{H_2O}/p_{HCl} \quad (6)$$

At 25° the equilibrium vapor pressure of water above the decahydrate is 19.2 mm. and the maximum vapor pressure of water at this temperature is the vapor pressure of pure water = 23.8 mm. = 0.0314 atm. If we substitute this last value in equation 6 and solve for p_{HCl} we find 1.3×10^{-5} atm. = 0.097 mm. which would not have been measurable under the conditions of the initial sorption (Fig. 1). This is probably an upper limit since any tendency to form solid solutions or hydrates will result in a smaller $\Delta F°$ and consequently a lower equilibrium pressure of HCl.

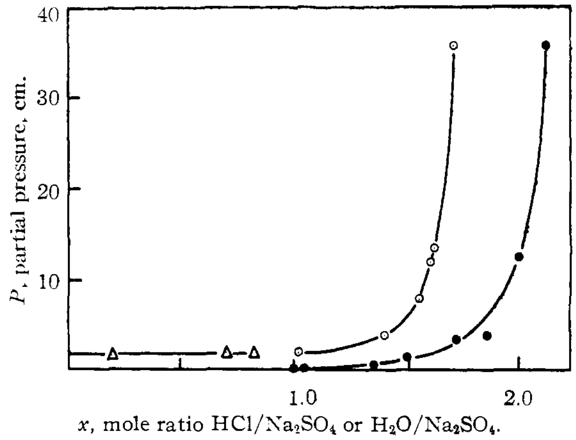

Fig. 1.—Sorption isotherm at 25.0° for $Na_2SO_4(s)$–$H_2O(g)$ and $Na_2SO_4\cdot 10H_2O(s)$–$Na_2SO_4(s)$–$HCl(g)$: △, sorption of H_2O; ○, sorption of HCl; ●, desorption of HCl. (Note, the desorption curve has been shifted toward the right as explained in text.)

From the calculated $\Delta F°$ for reaction 5 one can calculate a $\Delta F°$ for reaction 1 and we find $\Delta F°$ (eq. 1) = −7.8 kcal., so that $K_p°$ (eq. 1) = 5×10^5 atm.$^{-1}$. This latter value gives an equilibrium vapor pressure of HCl in equilibrium with $Na_2SO_4(s)$ of 1.5×10^{-3} mm. at 25° which is again consistent with the results observed in desorption.[7]

IV. The System $Na_2SO_4(s) + HCl(g)$

Since a complete analysis of the ternary systems seemed to involve a too extensive labor, an attempt was made to study the binary system, omitting H_2O. A weighing tube technique was used. A 0.9-g. sample of anhydrous Na_2SO_4 was placed in a Pyrex weighing tube closed by a stopcock and attached to the vacuum line through a ground joint and pumped for several days at 10^{-5} mm. HCl gas at 15 mm. pressure was then admitted to the tube at 25°. After 4 days exposure there was no gain in weight, the sensitivity of weighing being ±0.2 mg. This failure of HCl to add to Na_2SO_4 in the absence of H_2O is suggestive of Feigl's observation[8] that SO_2 added to $KMnO_4$ only in the presence of water and similarly for $KI(s) + SO_2(g)$.

This catalytic effect of water may be ascribed to any of the following: (a) HCl reacts only with the hydrated salt; (b) H_2O being at a higher relative pressure in the system than HCl (and also at a lower reduced temperature) is more strongly sorbed on the crystal surfaces and acts thus as a catalyst for the sorption of HCl; (c) H_2O is a true catalyst for the heterogeneous transition.

The first possibility can be examined by working at either sufficiently low partial pressures of H_2O or sufficiently high

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[3] This compares very well with the vapor pressure of $Na_2SO_4\cdot 10H_2O$ reported in the "International Critical Tables" (Vol. VII, p. 304) of 19.2 mm. at 298.1°K.

[4] This can certainly be true up to a mole ratio HCl/Na_2SO_4 = 0.92. Past this point one might expect that the further sorption of HCl could be accompanied by loss of H_2O and a resulting increase of the partial pressure of H_2O in the system. This is, however, complicated by possible formation of H_2SO_4 and its hydrate in the sorption past mole ratio = 1.

[5] Data from the National Bureau of Standards, Circular No. 500 (1952), Govt. Printing Office, Washington, D. C.

[6] The probable error in this is not greater than ±1 kcal.

[7] For reaction 1, ΔH^0 is known, −14.4 kcal. so that at 25° ΔS^0 = −22 cal./mole °K. with an error of not more than ±2 cal./mole/°K. This yields a value for the standard entropy of solid $NaHSO_4$ of 41 ± 2 cal./mole °K.

[8] F. Feigl, *J. Chem. Ed.*, **22**, 558 (1945).

temperatures. Unfortunately this possibility was not tested by us in detail. However, some preliminary experiments at 40° (above the temperature of stability of the decahydrate) made by Mr. Robert L. Altman of these laboratories indicate that HCl will add to Na_2SO_4 in the presence of H_2O vapor at about 0.8 relative humidity.

The second possibility, namely, that water acts merely to enhance the surface concentration of sorbed HCl was tested by studying the interaction of HCl at high pressures and thus high relative partial pressures where we might expect to saturate the surface layers of the solid. The tubes used for these experiments were made of 2 mm. i.d. Pyrex capillary tubing bent into the shape of an S and mounted vertically. One end of the S was sealed off, the other open. Very fine (90 mesh) powders of anhydrous Na_2SO_4 were poured into the open end and "tapped" down into the sealed end. Sample sizes were about 150 mg. The capillaries were then sealed at the open, vertical end to a vacuum line and pumped for several hours at 150° in a block oven to less than 10^{-5} mm. pressure to ensure outgassing of sorbed water. The tube was then allowed to cool, some HCl gas was condensed in liquid N_2 in the U-shaped bend of the vertical S and the capillary slowly sealed off while pumping. The tubes were then permitted to warm to 20° where they were kept for several hours. The HCl was then recondensed into the U-bend and this section was sealed off from the dead end containing the Na_2SO_4 powder. Finally this latter section was opened and the powder analyzed for Cl and SO_4. The results of these experiments are shown in Table I.

TABLE I

REACTION OF HCl GAS + ANHYDROUS Na_2SO_4 AT 20°

Pressure of HCl (atm.)	Duration of run (hr.)	Cl, %	SO_4, %	Mole ratio Cl/SO_4
2–25	24	2.30	62.4	0.10
33–42	16	3.89	62.53	.17

As can be seen, there is an extremely slow reaction of HCl, the rate of which appears to increase with increasing partial pressure. It is not, of course, possible to say that there are no traces of water in these systems so that trace catalysis by H_2O is not excluded. However, these rates are at least 10^5 times slower than the rates with the decahydrate so that if there is a direct reaction of HCl gas with the anhydrous salt its rate must be very much slower than the rate of reaction with the decahydrate and the effect cannot be ascribed to low sorption concentration of HCl.[9]

We therefore conclude that the HCl either reacts directly with the decahydrate or else that sorbed H_2O is a true catalyst in the system. These two possibilities should be easily distinguishable experimentally and it appears that this system might then be a very useful one in which to explore quantitatively the heterogeneous catalysis by water.

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[9] At the partial pressures used, one would estimate almost complete coverage of the surface.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Kinetics of the Thermal Decomposition of Nitric Acid Vapor. III. Low Pressure Results

BY HAROLD S. JOHNSTON, LOUISE FOERING AND JAMES R. WHITE

RECEIVED FEBRUARY 14, 1955

The decomposition of nitric acid vapor has been studied at low pressures (0.5 to 20 mm.) in two Vycor bulbs at temperatures between 375 and 425° without and with the addition of argon, carbon dioxide, oxygen, water, nitrogen dioxide or nitric oxide. The broad important features of the mechanism are the same as found before $HNO_3 \underset{b}{\overset{a}{\rightleftarrows}} HO + NO_2$, $HO + HNO_3 \xrightarrow{c} H_2O + NO_3$, ($NO_2 + NO_3 = 2NO_2 + {}^1/_2O_2$ as with N_2O_5). However, an attempt to separate out the unimolecular decomposition, step a, at low pressures revealed the presence of a side reaction (or side reactions) involving water, nitrogen dioxide and nitric oxide. From known kinetic and thermodynamic data it is concluded that these effects might be due to nitrous acid acting as a reactive intermediate. However, the reaction is so complex under these conditions that the secondary processes could not be clearly separated, nor is the reaction a suitable one for unimolecular reaction rate studies.

Introduction

A preliminary study of the reaction

$$2HNO_3 = 2NO_2 + H_2O + {}^1/_2O_2 \qquad (1)$$

in the presence of nitrogen at one atm. total pressure gave first-order kinetics and indicated that an important step in the mechanism is[1]

$$HNO_3 \xrightarrow{a} HO + NO_2$$

Working at low pressures of reactants in the absence of foreign gases, Frejacques found reaction (1) to be second order.[2] An additional study, still at one atm. total pressure, showed inhibition of the first-order rate by nitrogen dioxide and results followed the further mechanism[3]

$$HO + NO_2 \xrightarrow{b} HNO_3$$

$$HO + HNO_3 \xrightarrow{c} H_2O + NO_3$$

$$(NO_3 + NO_2 \longrightarrow 2NO_2 + {}^1/_2O_2 \text{ as with } N_2O_5) \qquad (2)$$

$$(NO_3 + NO \longrightarrow 2NO_2, \text{ as with added NO}) \qquad (3)$$

Over a wide range of temperature, additives such as carbon monoxide, hydrogen, methane and benzene were oxidized at about the same rate as the rate of decomposition of nitric acid alone, which gave support to this mechanism since hydroxyl radicals would attack these molecules. This mechanism reconciled most of the disagreement between ref. 1 and ref. 2 upon the assumption that Frejacques was working close to the second-order region of the unimolecular decomposition a. However, the values of activation energy and the effects of nitric oxide were not completely reconciled.[4]

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(1) H. S. Johnston, L. Foering, Y. S. Tao and G. H. Messerly, THIS JOURNAL, **73**, 2319 (1951).

(2) C. Frejacques, *Compt. rend.*, **232**, 2206 (1951).

(3) H. S. Johnston, L. Foering and R. J. Thompson, *J. Phys. Chem.*, **57**, 390 (1953).

(4) C. Frejacques, Thesis, University of Paris, 1953.