

lytic effect of small amounts of water on the rate of exchange, points to an effect of ion pair dissociation.

In the acid region we pick up a reaction path involving acid catalysis, but we see that the presence of an acid is no prerequisite for the  $\text{ROCl}-\text{Cl}^-$  chlorine exchange, as it is in the case of the  $\text{HOCl}-\text{Cl}^-$  exchange. The acid path becomes appreciable only at acid concentrations above  $10^{-7}$ -molar where we may assume  $t\text{-BuOCl}^+$  as intermediate. Estimating the dissociation constant of  $t\text{-BuOHC}^+$  at  $10^2$  we derive a specific rate constant for this reaction  $k = 4 \times 10^7 \text{ l. mole}^{-1} \text{ min.}^{-1}$  at  $27^\circ$ .

In the basic region we are surprised by the well established catalytic effect of  $t\text{-BuO}^-$  concentration on the rate of exchange. We suggest three ways to explain this effect: one is to assume that a butoxide ion forms a complex with  $t\text{-BuOCl}$  which facilitates the interaction with  $\text{Cl}^-$ . It is hard however to see, why should  $(t\text{-BuO})_2\text{Cl}^-$  be more liable to a nucleophilic attack than  $t\text{-BuOCl}$ ; if such a complex would be formed, it might probably suppress the rate of exchange. An alternative explanation may be by the reaction  $t\text{-BuOCl} + t\text{-BuOLi} \rightleftharpoons t\text{-BuOCl}^{\text{Li}} + t\text{BuO}^-$  whereafter  $t\text{-BuOCl}^{\text{Li}}$  is attacked by  $\text{Cl}^-$ ;  $t\text{-BuOCl}^{\text{Li}} + \text{Cl}^- \rightleftharpoons t\text{-BuOLi} + \text{Cl}_2$ . This assumption would require a second-order effect of  $\text{LiCl}$  concentration, which has not been observed. The third explanation may be the effect of  $\text{BuO}^-$  on the availability of

free  $\text{Cl}^-$  ions in our system. If we assume that the  $\text{LiCl}$  exists in solution in an undissociated form, then by the reaction  $\text{LiCl} + \text{BuOLi} \rightleftharpoons \text{BuOLi}_2^+ + \text{Cl}^-$  more chloride ions are available for exchange. Still there is no evidence available for the existence of complexes of the type  $t\text{-BuOLi}_2^+$ . We conclude that it is hard to offer an explanation for the  $t\text{-BuO}^-$  effect.

The effect of acetate ions on the rate of chlorine exchange is not clear. It is hard to assume acetyl hypochlorite as intermediate because its rate of formation is slower<sup>8</sup> than the catalytic effect of acetate ions on the chlorine exchange. The  $p\text{H}$  dependence here is not well established, whereas the dependence on the chloride ion concentration points to competing reactions between  $\text{AcO}^-$  and  $\text{Cl}^-$  ions. We may conclude that the effect of acetate ions on the chlorine exchange requires further investigation.

### Conclusion

Our results give more evidence that the  $\text{HOCl}$  system differs basically from the  $\text{HOBr}$  system. Having a much stronger  $\text{HO}-\text{X}$  bond,  $\text{HOCl}$  follows different mechanisms of interaction with nucleophilic reagents the  $\text{HOCl}$  molecule requires occasionally an additional proton to make its chlorine accessible. Next it has been shown that the trihalide like ions  $\text{HOX}_2^-$  or  $\text{HOXY}^-$  may occasionally occur as intermediates in  $\text{HOX}$  reactions.

REHOVOTH, ISRAEL

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS]

## The System $\text{NaF}-\text{HF}-\text{H}_2\text{O}$ at 0 and $-15^\circ$ <sup>1</sup>

BY JAMES S. MORRISON AND ALBERT W. JACHE

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The system  $\text{NaF}-\text{HF}-\text{H}_2\text{O}$  has been studied at 0 and  $-15^\circ$ . The solid phases include  $\text{NaF}\cdot\text{HF}$ ,  $\text{NaF}\cdot 2\text{HF}$ ,  $\text{NaF}\cdot 3\text{HF}$  and  $\text{NaF}\cdot 4\text{HF}$  at both temperatures.  $\text{NaF}$  exists in the  $0^\circ$  case and presumably at  $-15^\circ$ .

### Introduction

Ternary systems involving an inorganic fluoride, hydrogen fluoride and water have been studied by relatively few workers. Tananaev has investigated systems involving hydrogen fluoride, water and lithium fluoride,<sup>2</sup> potassium fluoride,<sup>3</sup> zirconium(IV) fluoride<sup>4</sup> and iron(III) fluoride.<sup>5</sup> Clark<sup>6</sup> has listed some data on the solubility of sodium fluoride in various concentrations of aqueous hydrogen fluoride.

Our interest in the ternary system sodium fluoride-hydrogen fluoride-water ( $\text{NaF}-\text{HF}-\text{H}_2\text{O}$ ) was stimulated by the lack of complete data for this system and the disagreement in the literature con-

cerning the fluorides in this system. Simons<sup>7</sup> states that, with aqueous or anhydrous  $\text{HF}$ , the acid salt  $\text{NaF}\cdot\text{HF}$  results and is the only acid fluoride of sodium known. According to Jache and Cady,<sup>8</sup> the analysis of the solid phase in equilibrium with  $\text{HF}$  saturated with  $\text{NaF}$  indicated the presence of 1 mole of  $\text{NaF}$  to 4.10 of  $\text{HF}$  at  $-24.3^\circ$ . Tananaev<sup>9</sup> has also studied part of this system but his results seem not to have been noted by later workers.

We have studied this system at 0 and  $-15^\circ$  using the Schreinemakers wet residue method.<sup>10</sup>

### Experimental

Samples were made up from reagent grade  $\text{NaF}$  and aqueous  $\text{HF}$ . When  $\text{HF}$  of concentration greater than 48% was needed it was made up from mixtures of anhydrous  $\text{HF}$

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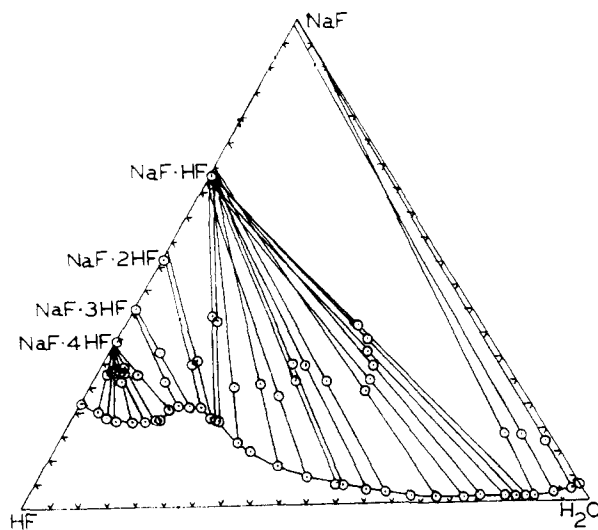
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TABLE I

ANALYSIS OF THE SOLUTIONS AND WET RESIDUES AT 0°

Solutions, wt. %		Wet residues, wt. %		Composition of solid phase
HF	NaF	HF	NaF	
0	3.42	...	...	NaF
1.90	2.57	1.45	12.36	NaF
5.23	1.79	5.03	13.87	NaF
9.30	0.927	7.81	14.00	NaF
10.66	1.01	21.86	37.06	NaF·HF
12.36	1.01	21.73	34.09	NaF·HF
14.28	1.01	23.09	31.31	NaF·HF
18.73	1.58	23.51	28.69	NaF·HF
26.46	1.47	27.50	23.22	NaF·HF
34.87	2.28	33.18	25.25	NaF·HF
37.74	2.92	35.01	28.88	NaF·HF
41.74	4.03	37.06	29.33	NaF·HF
42.09	4.39	38.74	25.54	NaF·HF
46.73	5.37	43.37	22.28	NaF·HF
50.05	8.01	45.02	25.00	NaF·HF
55.19	12.90	49.64	24.45	NaF·HF
56.01	17.88	46.01	38.15	NaF·HF
56.70	17.77	45.29	38.47	NaF·HF
56.89	18.70	46.45	39.50	NaF·HF
57.26	18.04	53.51	30.50	NaF·2HF
58.44	20.50	54.88	29.34	NaF·2HF
59.91	20.76	59.02	32.08	NaF·3HF
61.39	21.03	61.23	26.06	NaF·3HF
63.56	20.21	65.38	27.68	NaF·4HF
67.24	18.33	67.31	28.94	NaF·4HF
69.01	17.69	68.10	27.23	NaF·4HF
71.43	17.85	69.35	26.01	NaF·4HF
74.49	17.79	69.82	28.04	NaF·4HF
75.64	18.29	69.52	28.42	NaF·4HF
76.54	19.65	70.99	27.48	NaF·4HF
Liquid HF	21.79 <sup>8</sup>	...	...	

and aqueous HF. The anhydrous HF used was the middle fractions obtained from a commercial cylinder. This was distilled from the cylinder into a polyethylene collection bottle and redistilled through an all polyethylene system. The first and last fractions of each distillation were discarded. The liquid HF could be saturated with NaF to reduce its vapor pressure and stored until needed.

Fig. 1.—The system NaF-HF-H<sub>2</sub>O at 0°.

Various mixtures of HF, H<sub>2</sub>O and NaF were placed in 250 cc., wide mouth polyethylene bottles. These were placed in an ethylene glycol-water bath whose temperature was

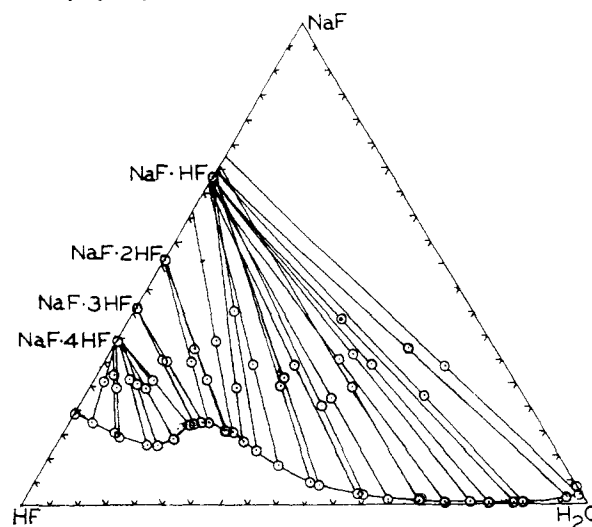
TABLE II

ANALYSIS OF THE SOLUTIONS AND WET RESIDUES AT -15°

Solutions, wt. %		Wet residues, wt. %		Composition of solid phase
HF	NaF	HF	NaF	
0	3.80	...	...	NaF
0.365	2.02	10.78	28.97	NaF·HF
2.62	1.98	15.03	32.91	NaF·HF
11.18	0.602	17.11	23.21	NaF·HF
12.74	.587	24.09	39.03	NaF·HF
17.04	.567	23.22	29.24	NaF·HF
20.08	.650	25.57	31.84	NaF·HF
24.88	.754	28.59	30.40	NaF·HF
29.15	1.09	29.36	24.45	NaF·HF
34.48	1.68	34.09	22.77	NaF·HF
38.45	2.37	36.34	21.04	NaF·HF
38.95	2.47	37.03	29.67	NaF·HF
45.03	4.59	40.10	26.85	NaF·HF
46.10	5.30	41.82	24.77	NaF·HF
46.46	5.18	41.03	27.53	NaF·HF
50.25	8.37	44.29	29.55	NaF·HF
52.87	11.37	41.75	40.54	NaF·HF
54.23	13.11	49.46	24.45	NaF·HF
54.86	15.74	48.22	34.41	NaF·2HF and NaF·HF
55.68	15.75	52.77	32.89	NaF·2HF
56.13	15.90	53.83	26.46	NaF·2HF
58.58	17.30	54.95	30.08	NaF·2HF
59.27	17.34	59.09	30.73	NaF·3HF
59.97	17.42	63.02	27.65	NaF·3HF
61.49	17.01	59.74	30.35	NaF·3HF
61.96	17.06	63.20	26.26	NaF·4HF
65.77	14.16	65.57	24.63	NaF·4HF
69.26	12.29	67.13	25.52	NaF·4HF
71.13	12.70	67.60	26.47	NaF·4HF
75.10	15.12	69.96	27.45	NaF·4HF
75.23	14.35	70.38	24.77	NaF·4HF
78.21	17.32	72.32	26.01	NaF·4HF
81.02	19.01 <sup>8</sup>	...	...	

regulated to  $\pm 0.06^\circ$ . These bottles were agitated in the bath. If no solid phase remained, more NaF was added.

Liquid samples were removed by means of a sampler using a 18 hypodermic needle fitted through a Teflon adapter to small polyethylene bottle.

Fig. 2.—The system NaF-HF-H<sub>2</sub>O at -15°.

The liquid samples and wet residues were analyzed for HF by a simple titration with sodium hydroxide solution.

The NaF was determined by careful evaporation in platinum crucibles over a heat lamp followed by ignition at  $750^\circ$ . The weighing form was NaF.

### Discussion and Results

The results of the analyses of the solution and wet residues are given in Tables I and II and have been plotted in Fig. 1 and 2. At  $-15^\circ$  at HF concentrations of less than 11%, all phases appear to be solids.

The solid phases existing in equilibrium with solution at both temperatures include NaF·HF, NaF·2HF, NaF·3HF and NaF·4HF. NaF exists

in the  $0^\circ$  case and presumably at  $-15^\circ$ . No solid phases containing water exist. The HF (wt. %) concentration limits for the solid phases at  $0^\circ$  are: NaF, 0 to 9.5%; NaF·HF, 10 to 57%; NaF·2HF, 55 to 58.5%; NaF·3HF, 58.5 to 62%; and NaF·4HF, 62 to 100%. In general, the solid phases containing HF are more stable at lower HF concentrations at  $-15^\circ$  than they are at  $0^\circ$ . The solubility of NaF is in general somewhat lower at the lower temperature.

COLLEGE STATION, TEXAS

[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION]

## Change in the Ratio of Hydroxyl Groups Attached to Silicon and Aluminum Atoms in Silica-Alumina Catalysts upon Activation

By H. G. WEISS, J. A. KNIGHT AND I. SHAPIRO

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A method for measuring the number of hydroxyl groups attached to silicon relative to those attached to aluminum atoms in silica-alumina catalysts is described. Essentially, the method consists of two steps: (a) exposing diborane to the catalyst in order to replace the proton of the hydroxyl group with boron atoms and (b) measuring the number of these boron atoms that can participate in boron exchange with labeled diborane. By this technique, it is found that initially hydroxyl groups are attached to both silicon and aluminum atoms; however, upon aging of the catalyst at temperatures below  $400^\circ$  hydroxyl groups, lost as water, must come predominantly from the silicon rather than the aluminum atoms. At temperatures above *ca.*  $400^\circ$  the ratio of hydroxyl groups attached to aluminum and silicon atoms goes through a maximum value.

The relation of bound water to the surface structure of silica gel, silica-alumina and aluminum oxide catalysts has been the subject of several investigations.<sup>1-3</sup> The influence of small amounts of water on the catalytic activity of alumina and silica-alumina also has been reported.<sup>4-6</sup> In this connection various methods<sup>7,8</sup> have been devised for measuring bound water content of catalysts; however, such methods (ignition,  $\text{D}_2\text{O}$  or  $\text{D}_2$  exchange, etc.) are satisfactory for bulk determinations but do not lend themselves readily to determination of the location of the bound water.

The nature of bound water (hydroxyl groups) in silica gel has previously been elucidated by a study of its reaction with diborane.<sup>9</sup> From the relative amount of diborane consumed to hydrogen generated, it was determined that the hydroxyl groups in silica gel lie principally on the surface of the solid, with the surface composition consisting of Si-O-BH<sub>2</sub> units. Similar results were indicated for reaction of diborane with silica-alumina.

The diborane-treated silica-alumina catalyst<sup>10</sup> exhibited a pronounced activity toward cyclization of acetylene to benzene, and from a detailed study of the cyclization reaction<sup>11</sup> there were indications that alumina provided the active sites in silica-

alumina catalysts. That the borane counterpart is not the principal active site was indicated by the inactivity of diborane-treated silica gel; treated alumina gave only an initial reaction with acetylene. Further experiments with diborane now point to a way of distinguishing between hydroxyl groups located on silica and those on alumina sites.

In the exposure of silica gel and silica-alumina to diborane, hydrogen is liberated in the initial reaction. In experiments in which these two catalysts were activated at low temperatures (*ca.*  $250^\circ$ ), the hydrogen-diborane ratio indicated no apparent differences in the nature of the borane-surface compound formed. However, with alumina and silica-alumina activated at higher temperatures ( $>400^\circ$ ) there was a decrease in the hydrogen-diborane ratio, thus precluding the possibility of only M-OBH<sub>2</sub> units forming. Boron-10 exchange experiments between gaseous diborane and the boron-surface compounds showed differences in the amount of exchangeable boron on the surface. Total boron exchange (100%) occurred in the borane-silica compound formed from diborane and silica gel. With alumina, however, only one-half (50%) of the attached boron atoms were capable of exchange. When exchange experiments were carried out in the silica-alumina-borane compound, the amount of boron participation varied between these limits. From the equilibrium exchange values, the ratio of hydroxyl groups on alumina to those on silica has been calculated. The results indicate that the hydroxyl groups in silica-alumina are on both aluminum and silicon atoms and that those attached to silica are more easily removed on heating.

Details of the exchange reactions between the diborane surface complexes and gaseous diborane are given.

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