[CONTRIBUTION FROM COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

The Complexing of Hydrazine with Calcium Ion as Determined by Distribution Measurements[1]

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Measurements of the distribution of hydrazine and ammonia between benzyl alcohol and aqueous calcium nitrate solutions have been made and interpreted in terms of the hypothesis of the formation of complexes of these non-electrolytes with calcium ion. The extent of complexing with ammonia, as calculated on this basis, appears in accord with the values obtained by J. Bjerrum from potentiometric measurements. The extent of complexing indicated for hydrazine is similar to but slightly greater than that for ammonia.

The insolubility of most hydrazine-containing complex salts has been a handicap to the determination of the extent to which ions in solution combine with hydrazine. Since precipitation does not occur with calcium salts, calcium nitrate was chosen for this study. It was expected that rather high concentrations of hydrazine would be required to ensure sufficient complexing to be measurable. It was thought that, under these conditions, distribution experiments might give the most reliable measurements. When this study was initiated no measurements of the complexing of hydrazine in solution had been reported. Recently, the complexing of nickel and zinc with hydrazine in fluoborate solutions has been determined by Schwarzenbach and Zobist[2] through potentiometric measurements, and of zinc in perchlorate solution, polarographically, by Rebertus, Laitinen and Bailar.[3]

The experimental operations consisted in equilibrating aqueous solutions containing calcium nitrate and hydrazine with a non-miscible liquid, followed by separation of the liquid layers and determination of the hydrazine concentration in each. The apparent concentration of uncombined hydrazine in the aqueous phase was obtained by multiplying the concentration in the non-aqueous phase by a previously determined distribution ratio. The difference between the total hydrazine concentration in the aqueous layer and the concentration of uncombined hydrazine gave the concentration of combined hydrazine.

The solubility of hydrazine in liquids which are non-miscible with water is slight in general. Only with alcohols was the concentration of hydrazine in the non-aqueous layer found to be large enough that a reasonably precise determination could be made. After trying *n*-amyl, cyclohexyl and benzyl alcohols, the latter was chosen as most satisfactory.

Distribution ratios were measured for hydrazine between aqueous potassium nitrate and benzene alcohol rather than between water and benzyl alcohol. The concentration of potassium nitrate was chosen to have the same aqueous vapor pressure as the calcium nitrate solution in order that the concentration of water in the alcohol layer should be constant. Since it was observed that potassium nitrate had very little effect on the distribution, its concentration is not an important factor.

The distribution ratio for hydrazine between aqueous potassium nitrate and benzyl alcohol, although little dependent on the potassium nitrate concentration, varied with hydrazine concentration. The ratio was determined at a number of hydrazine concentrations and a plot of the distribution ratio against the concentration of hydrazine in the alcohol phase used to obtain the distribution ratios needed in the calculations for the calcium nitrate solutions.

The concentration of calcium nitrate in the alcohol layer was determined by evaporating a sample to dryness, adding sulfuric acid, and heating to constant weight. A concentration of 0.003 mole per liter was found in benzyl alcohol shaken with 0.9 *M* calcium nitrate and 0.0025 mole per liter when shaken with a solution 0.8 *M* in calcium nitrate and 1.0 *M* in hydrazine. It was assumed that these concentrations were too small to be significant.

The distribution technique is a method of measuring the activity of hydrazine in the aqueous phase. The decrease in the activity of hydrazine which is observed in the presence of calcium nitrate may be due to any type of interaction between hydrazine and calcium nitrate. That it is due to a decrease in hydrazine concentration because of the formation of complex ions has been assumed in the calculations. The existence of complex ions of hydrazine and calcium in solution seems highly probable since such solids as $CaBr_2 \cdot 2N_2H_4$ have been prepared by precipitation from aqueous solution.

To check the validity of the method, the experiments were repeated using ammonia in place of hydrazine, since constants for the complexing of ammonia with calcium ion have been calculated by Bjerrum[4] from potentiometric measurements.

Experimental

Materials.—Eastman Kodak Co. benzyl alcohol and Fairmount 100% hydrazine hydrate were used without further treatment. The calcium nitrate solution was made by adding excess calcium carbonate to nitric acid of known concentration, filtering, and diluting to give a concentration of 0.90 mole per liter. The potassium nitrate solution contained 1.7 moles per liter.

Method.—Measured volumes of either potassium or calcium nitrate solution and benzyl alcohol were placed in a small separatory funnel in a constant temperature bath at 25 ± 0.1°. After a stream of nitrogen had been bubbled through the mixture for about 15 minutes, a measured volume of hydrazine hydrate was added and stirring maintained by the passage of nitrogen for an hour. After stand-

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[2] G. Schwarzenbach and A. Zobist, *Helv. Chim. Acta*, **35**, 1291 (1952).

[3] R. L. Rebertus, H. A. Laitinen and J. C. Bailar, Jr., THIS JOURNAL, **75**, 3051 (1953).

[4] J. Bjerrum, "Metal Ammine Formation in Aqueons Solution," P. Haase and Son, Copenhagen, 1941, p. 147.

ing two hours or more the separate layers were transferred to burets and titrated with 0.2 *N* hydrochloric acid, using brom cresol green indicator. The analytical results were checked in several cases using KIO_3 to determine hydrazine content. The procedure with the ammonia solutions differed only in that manual shaking replaced the nitrogen bubbling.

It is estimated that the distribution ratios are correct to ±2%. Probably the chief reason for failure to get better precision is the difficulty of obtaining absolutely clean phase separation.

Results

Data on the distribution of hydrazine and ammonia between benzyl alcohol and aqueous potassium nitrate are given in Table I. C_w and C_{alc} represent the concentrations of hydrazine, or ammonia, in the water and alcohol phases, respectively; the concentration of potassium nitrate (KNO_3) in the water phase also is given. All concentrations are in moles per liter of solution. In contrast to hydrazine, the distribution ratio, C_w/C_{alc}, for ammonia is altered significantly by potassium nitrate, being about 10% lower for the potassium nitrate solutions than for pure water. This was expected since it is known that such salts increase the vapor pressure of ammonia over aqueous solutions.

TABLE I

DISTRIBUTION OF HYDRAZINE AND AMMONIA BETWEEN BENZYL ALCOHOL AND AQUEOUS POTASSIUM NITRATE SOLUTIONS

(KNO_3)	C_w	C_{alc}	C_w/C_{alc}
	Hydrazine solutions		
1.66	0.189	0.0251	7.55
1.65	.360	.0503	7.17
1.63	.624	.0917	6.80
1.59	.991	.147	6.73
1.57	1.32	.201	6.55
1.53	1.66	.266	6.25
1.47	2.04	.343	5.95
	Ammonia solutions		
1.60	0.389	0.178	2.19
1.57	.522	.235	2.22
1.53	.708	.325	2.18
1.49	1.06	.462	2.29
1.44	1.31	.567	2.31
1.35	1.77	.762	2.34
1.30	2.00	.842	2.37

Data for the distribution of hydrazine and ammonia between benzyl alcohol and aqueous calcium nitrate solutions are summarized in Table II, ($Ca(NO_3)_2$), C_w and C_{alc} being formal concentrations of calcium nitrate, hydrazine (or ammonia) in the water phase and hydrazine (or ammonia) in the alcohol phase. (N_2H_4) and (NH_3) are concentrations of the uncombined species as calculated from the distribution ratio, whereas *n* represents the number of moles of combined hydrazine or ammonia per mole of total calcium.

In Fig. 1 the values of *n* of Table II are plotted against the concentrations of uncombined hydrazine and ammonia. Some of Bjerrum's values for *n* in ammonia solutions have been added. It appears that the effects measured by the potentiometric and distribution methods, when interpreted on the basis of complex formation, are in agreement. Values of *n* for the hydrazine solutions are close to but slightly greater than those for ammonia. Since the solid compound $CaBr_2 \cdot 3N_2H_4$ is known, it seems probable that at least three molecules of hydrazine can combine with one calcium ion. The line on the figure was obtained by assuming for three successive formation constants K_1, K_2 and K_3, the "empirical" values of 0.69, 0.23 and 0.077 and calculating *n* from

$$n = \frac{K_1(NH_4) + 2K_1K_2(N_2H_4)^2 + 3K_1K_2K_3(N_2H_4)^3}{1 + K_1(N_2H_4) + K_1K_2(N_2H_4)^2 + K_1K_2K_3(N_2H_4)^3}$$

In view of the arbitrary assumption of a maximum of three coördinated hydrazine molecules and the scattering of the points from the line, no great significance should be attached to the numerical values of the constants. In solutions as concentrated as those with which the experiments were made it is doubtful whether such constants have any thermo-

TABLE II

DISTRIBUTION OF HYDRAZINE AND AMMONIA BETWEEN BENZYL ALCOHOL AND AQUEOUS CALCIUM NITRATE SOLUTIONS

($Ca(NO_3)_2$)	C_w	C_{alc}	(N_2H_4)	*n*
		Hydrazine Solutions		
0.888	0.305	0.0262	0.196	0.123
.877	.489	.0452	.320	.185
.874	.576	.0485	.349	.260
.865	.746	.0661	.462	.328
.857	.940	.0905	.617	.377
.845	1.17	.111	.752	.496
.843	1.34	.135	.906	.518
.818	1.75	.189	1.23	.637
.800	2.10	.235	1.50	.750
.795	2.31	.263	1.63	.846
.783	2.48	.303	1.84	.823
		Ammonia Solutions		
($Ca(NO_3)_2$)	C_w	C_{alc}	(NH_3)	*n*
0.857	0.340	0.109	0.235	0.123
.840	.508	.164	.358	.178
.797	.960	.312	.696	.331
.750	1.44	.470	1.07	.495
.692	2.01	.667	1.57	.642

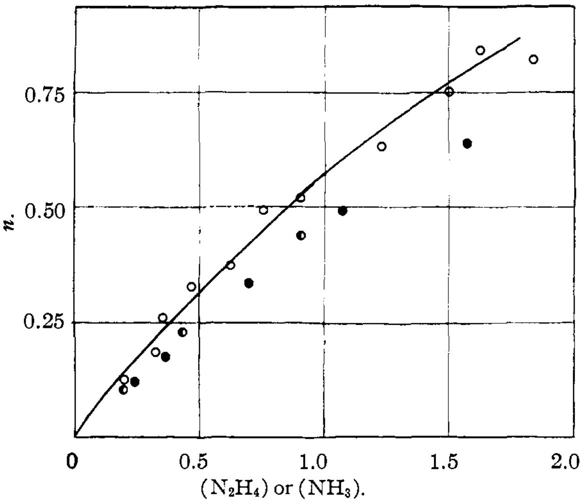

Fig. 1.—Moles combined hydrazine or ammonia per mole of calcium ion: ○, hydrazine; ●, ammonia; ◐, ammonia—Bjerrum.

dynamic significance, since the activity coefficients of water, hydrazine and the ions are unknown. The experiments, however, indicate that calcium ion forms complexes with hydrazine and ammonia of very nearly the same degree of stability. Schwarzenbach and Zobist have shown this to be true for nickel and zinc ion.

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The Conversion of Chlorosilanes to Siloxanes by Dimethylformamide

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Solutions of organochlorosilanes in dimethylformamide undergo reaction at their boiling points to replace all the silicon–chlorine bonds with silicon–oxygen bonds, the oxygen coming from the dimethylformamide. The tetrachlorides of silicon and titanium appear to be oxygenated in a similar way. The chlorine appears as dimethylamine hydrochloride, and carbon monoxide is produced at the same time. The reaction is slow at 153° but is complete in two to ten days if 1.6 to 2.0 molecules of dimethylformamide per atom of chlorine have been employed. It is shown that the reaction is not a hydrolysis of the chlorosilane in water produced by condensation of the aldehyde hydrogen with carbonyl groups, for such a "conventional" condensation is neither spontaneous nor brought about by small amounts of hydrochloric acid; even if it had occurred, it could furnish only half of the oxygen required. The molar ratios of products indicate that a condensation of N-methyl hydrogen and carbonyl oxygen takes place under the influence of the chlorosilane as a Lewis acid, followed immediately by oxygenation of the chlorosilane and absorption of the chlorine as dimethylamine hydrochloride.

Although silicon tetrahalides and some organochlorosilanes form solid addition compounds with dimethylformamide, $HCON(CH_3)_2$[2,3] (hereafter called DMF), many other organochlorosilanes undergo solvolytic dissociation in dimethylformamide to provide highly-conducting solutions.[4] In order to gain more information concerning the extent of such dissociation in 0.01 to 0.5 *M* solutions, measurements of the elevation of the boiling point of the solvent were undertaken. We were surprised to find that the boiling points of solutions of triphenylchlorosilane in DMF rose continuously, as though more ions were being produced hourly no matter how well the solutions were protected from the atmosphere. Furthermore, after extended periods of boiling such solutions, large crystals of hexaphenyldisiloxane precipitated upon cooling. Since the amounts of water originally present in the DMF would suffice to form only 0.06 to 0.08 g. of hexaphenyldisiloxane, whereas several grams separated, it became evident that the chlorosilane was being oxygenated by the carbonyl oxygen of the amide. This was the more unexpected because ketones are commonly used as solvents for the hydrolysis of chlorosilanes, yet no reaction of the carbonyl group previously had been observed. The new reaction raised the possibility of preparing silicone polymers without the hydrolytic procedure now universally employed, a matter of some interest because polymers prepared under radically different conditions might be expected to be different in their structure and properties.

This paper reports the reactions of ten organochlorosilanes and four Group IV tetrachlorides with DMF. All were refluxed with the DMF for extended periods, and all except tin tetrachloride reacted to exchange their chlorine for oxygen. Although the reactions occurred at different rates, in all instances where oxygenation occurred dimethylamine hydrochloride was identified as a product. The reaction mixtures also evolved carbon monoxide, and the loss of weight due to such evolution was determined. The course of the general reaction was followed by studying its stoichiometry, and the explanation which follows the Experimental section is based upon the observed molar ratios.

Experimental

DMF.—Specifications for the du Pont dimethylformamide indicated not over 0.15% water; titration with Karl Fischer reagent showed 0.05% in our sample. Drying with calcium hydride caused some decomposition, probably because of the alkalinity of the desiccant. The best method of drying was found to be distillation with reagent-grade benzene, yielding a benzene-free fraction containing (by titration) less than 0.003% water. This dried material was used in all the experiments.

Other Reagents.—Highest-purity mono-, di- and trimethylchlorosilanes were received from the General Electric Company, and all other organochlorosilanes were purchased in purified grades. The triphenylchlorosilane of that grade was found to contain 2% of silicon tetraphenyl, but a single distillation at 378° gave the chlorosilane in 99.5% purity. The other reagents were satisfactory as received.

Procedure.—Solutions of the organochlorosilanes in DMF were prepared at room temperature (at which there was no perceptible reaction) and then were refluxed for extended periods. The proportions and conditions are listed in Table I. Atmospheric moisture was excluded by drying tubes at the ends of the reflux condensers. The cobalt salt present in the indicating Drierite within these tubes was found to be a sensitive indicator of amines evolved through overheating of the solutions or from decomposition of a caked mass in the boiling flask, for the cobalt ion soon formed complexes of characteristic intense blue or green when such amines were present. Such decomposition could be avoided in most instances by using heating mantles operated at minimum temperature.

In several experiments the gas evolved from the reaction mixture was led into two traps, the first cooled to −80° and and the second to −196°. No material ever condensed in the first; the colorless liquid that condensed in the second was identified as carbon monoxide by its low boiling point and by its infrared absorption spectrum. Whenever the carbon monoxide was not condensed and collected, the loss of weight of the reaction flask was followed to determine how much carbon monoxide was evolved.

The reaction mixtures were acid at the start, and became alkaline only when all of the Si–Cl bonds were converted to Si–O– bonds. In some instances (see Table I) the precipi-

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(1) Procter and Gamble Fellow at Harvard University, 1952–1953.

(2) Kurt Gingold and Eugene G. Rochow, THIS JOURNAL, **76**, 288 (1954); T. S. Piper and Eugene G. Rochow, *ibid.*, **76**, 4318 (1954).

(3) Kurt Gingold, System of Chlorosilanes and Amides, Thesis, Harvard University, 1953, Chapter 3.

(4) Kurt Gingold, Eugene G. Rochow, Dietmar Seyferth, Albert C. Smith, Jr., and Robert West, THIS JOURNAL, **74**, 6306 (1952).