Molecular Addition Compounds of Dinitrogen Tetroxide. V.[1] The Ternary System 1,4-Dioxane–Tetrahydropyran–Dinitrogen Tetroxide

By Betty J. Gibbins,[2] Gunther L. Eichhorn[3] and Harry H. Sisler

The ternary system 1,4-dioxane–tetrahydropyran–dinitrogen tetroxide has been studied and it has been shown that no ternary compounds are formed. This finding supports the belief previously expressed in the fourth paper of this series that the binary compound $N_2O_4 \cdot 1,4$-dioxane has a bicyclic structure.

Introduction

In the first paper in this series,[1] one of the authors and his co-workers reported the formation of the molecular addition compounds $N_2O_4 \cdot 1,4\text{-}C_4H_8O_2$ (m.p. 45.2°) and $N_2O_4 \cdot 2C_5H_{10}O$ (m.p. −56.8°). In an effort to explain the relatively high melting point of the complex $N_2O_4 \cdot 1,4\text{-}C_4H_8O_2$, two alternative structures were proposed: (a) indefinitely extended chains composed of alternate dioxane and dinitrogen tetroxide molecules and (b) a bicyclic configuration formed by the coördination of each of the oxygen atoms of one dioxane molecule to a different nitrogen atom of one dinitrogen tetroxide molecule.

A study of the ternary system 1,4-dioxane–tetrahydropyran–dinitrogen tetroxide was undertaken to compare the stabilities of the binary compounds $N_2O_4 \cdot 1,4\text{-}O(CH_2CH_2)_2O$ and $N_2O_4 \cdot 2C_5H_{10}O$ over a large concentration range, to investigate the possibility of the formation of a ternary compound, and thereby to obtain information which might help to determine which, if either, of the proposed structures for the binary 1,4-dioxane compound is correct. The assistance of the Ordnance Corps, U. S. Army, through a contract with The Ohio State University Research Foundation, is gratefully acknowledged.

Experimental

Preparation of Materials.—The 1,4-dioxane, tetrahydropyran and dinitrogen tetroxide were purified by methods described in a previous publication of this series.[1] Mixtures containing fixed mole ratios of the ethers were prepared by combining the calculated weights and were treated in the same way as the pure ethers previously described.

Procedure.—The procedure followed was to study sections of the ternary system represented by vertical planes from one corner and intersecting the opposite face at regular intervals. Since mixtures with a fixed tetrahydropyran/dioxane mole ratio are easily prepared and stored, it was convenient to study systems containing fixed ratios of tetrahydropyran to dioxane and varying amounts of dinitrogen tetroxide. Sections corresponding to tetrahydropyran to dioxane ratios of 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 88/12, 90/10, 92/8 and 96/4 were studied. In addition it was found desirable to investigate portions of systems containing fixed tetrahydropyran to dinitrogen tetroxide mole ratios and variable amounts of dioxane. Systems studied in this group included those in which the tetrahydropyran–dinitrogen tetroxide ratio was 94.1/5.9, 91.8/8.2, 86.6/13.4, 77.2/22.8, 65.1/34.9 and 54.2/45.8.

(1) The first four papers in this series, are, respectively, B. Rubin, H. Sisler and H. Shechter, This Journal, **74**, 877 (1952); D. Davenport, H. Burkhardt and H. Sisler, *ibid.*, **75**, 4175 (1953); F. Whanger and H. Sisler, *ibid.*, **75**, 5188 (1953); H. Ling and H. Sisler, *ibid.*, **75**, 5191 (1953).

(2) Taken in part from the dissertation submitted by B. J. G. in partial fulfillment of the requirements for the Ph.D. degree at The Ohio State University.

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Freezing point–composition phase diagrams for the systems listed above were constructed by methods described in a previous publication of this series.[1] Briefly, the freezing points of various mixtures were determined by cooling curves measured by a Micromax self-recording potentiometer with a copper–constantan thermocouple, using a completely enclosed cell equipped for continuous magnetic stirring. Although mixtures containing more than 80 mole per cent. tetrahydropyran were slowly oxidized by dinitrogen tetroxide, the effects of the reaction were minimized by not warming the mixtures any higher than necessary and by frequently taking fresh samples. It is believed that the ternary phase diagram has not been appreciably affected by this factor.

Results

Complete freezing point–composition phase diagrams were constructed for the systems listed in Table I. Pertinent portions of the diagrams were constructed for the additional systems listed in Table II. Each complete curve contains two minima and the one maximum listed in Table I.

Table I

MAXIMA OF TEMPERATURE–COMPOSITION CURVES

System	N_2O_4, mole %	Max. temp., °C.
10/90 $C_5H_{10}O/C_4H_8O_2$	50.0	43.5
20/80 $C_5H_{10}O/C_4H_8O_2$	50.0	40.0
30/70 $C_5H_{10}O/C_4H_8O_2$	50.0	37.0
40/60 $C_5H_{10}O/C_4H_8O_2$	50.0	31.75
50/50 $C_5H_{10}O/C_4H_8O_2$	50.0	28.5
60/40 $C_5H_{10}O/C_4H_8O_2$	46	22.75
70/30 $C_5H_{10}O/C_4H_8O_2$	45	16.5
80/20 $C_5H_{10}O/C_4H_8O_2$	44	8.25
88/12 $C_5H_{10}O/C_4H_8O_2$	42.5	− 2.75
90/10 $C_5H_{10}O/C_4H_8O_2$	42.0	− 6.25
92/8 $C_5H_{10}O/C_4H_8O_2$	41.0	−13.0
96/4 $C_5H_{10}O/C_4H_8O_2$	41.0	−29.25

The freezing points and compositions of the binary eutectic mixtures were determined from the minima and are listed in Table II.

Figure 1 was constructed by plotting the compositions of these binary eutectic mixtures on an equilateral triangle whose corners represent the three components of the system. The resulting diagram is a projection of the ternary phase diagram on its triangular base.

The compositions of the ternary eutectic mixtures were determined from the intersections in Fig. 1, and are listed in Table III. Their freezing points were obtained from plateaus in the experimental cooling curves.

A three-dimensional model of the ternary phase diagram was constructed by combining phase diagrams for the systems listed in Table II with previously reported[1] diagrams for the binary systems 1,4-dioxane–dinitrogen tetroxide and tetrahydro-

Table II

Binary Eutectic Mixtures

System	N_2O_4, mole %	F.p., °C.
10/90 $C_5H_{10}O/C_4H_8O_2$	11.0	− 0.5
10/90 $C_5H_{10}O/C_4H_8O_2$	89.0	−17.5
20/80 $C_5H_{10}O/C_4H_8O_2$	10.5	− 4.25
20/80 $C_5H_{10}O/C_4H_8O_2$	88.0	−18.25
30/70 $C_5H_{10}O/C_4H_8O_2$	11.0	− 9.0
30/70 $C_5H_{10}O/C_4H_8O_2$	86.0	−19.0
40/60 $C_5H_{10}O/C_4H_8O_2$	10.5	−14.0
40/60 $C_5H_{10}O/C_4H_8O_2$	85.0	−18.75
50/50 $C_5H_{10}O/C_4H_8O_2$	12.5	−20.0
50/50 $C_5H_{10}O/C_4H_8O_2$	84.0	−20.0
60/40 $C_5H_{10}O/C_4H_8O_2$	10.5	−24.5
60/40 $C_5H_{10}O/C_4H_8O_2$	81.5	−22.0
70/30 $C_5H_{10}O/C_4H_8O_2$	11.0	−32.0
70/30 $C_5H_{10}O/C_4H_8O_2$	79.0	−24.25
80/20 $C_5H_{10}O/C_4H_8O_2$	11.0	−48.75
80/20 $C_5H_{10}O/C_4H_8O_2$	73.0	−28.75
88/12 $C_5H_{10}O/C_4H_8O_2$	10.5	−66.0 to −67.0
88/12 $C_5H_{10}O/C_4H_8O_2$	68.5	−31.0
90/10 $C_5H_{10}O/C_4H_8O_2$	9.5	−86.0 to −90.0
90/10 $C_5H_{10}O/C_4H_8O_2$	66.5	−33.0
92/8 $C_5H_{10}O/C_4H_8O_2$	10.0	−86.5 to −90.0
92/8 $C_5H_{10}O/C_4H_8O_2$	66.5	−35.0
96/4 $C_5H_{10}O/C_4H_8O_2$	10.0	−88.0 to −90.0
96/4 $C_5H_{10}O/C_4H_8O_2$	59.5	−44.0

System	Mole %. dioxane	F.p.. °C.
94.1/ 5.9 $C_5H_{10}O/N_2O_4$	8.8	−67.5
91.8/ 8.2 $C_5H_{10}O/N_2O_4$	7.0	−74.5
86.6/13.4 $C_5H_{10}O/N_2O_4$	2.8	−84.0
77.2/22.8 $C_5H_{10}O/N_2O_4$	1.9	−67.5
65.1/34.9 $C_5H_{10}O/N_2O_4$	1.2	−57.0
54.2/45.8 $C_5H_{10}O/N_2O_4$	0.7	−64.5

Table III

Ternary Eutectic Mixtures

Dioxane, mole %	Tetra-hydropyran, mole %	Dinitrogen tetroxide, mole %	F.p.. °C.
5.0	85.0	10.0	−87.5 to −90.0
3.0	87.0	10.0	−87.5 to −90.0
0.25	47.75	52.0	−65.0 to −67.0

pyran–dinitrogen tetroxide and with the diagram for the system dioxane–tetrahydropyran. The eutectic in the binary dioxane–tetrahydrofuran system was found to be −51° at approximately 13.1 mole % of dioxane. A sketch of the ternary diagram is shown in Fig. 2. The model is a right triangular prism with an equilateral triangle as the base. The concentrations of the three components, in mole percentages, are plotted on the base, and the freezing points, in degrees centigrade, are plotted perpendicularly to the base.

Discussion

In the sketch of the ternary phase diagram (Fig. 2) ABCET, DFBA, FIGCB, INHG and CGHE represent the surfaces of primary crystallization for tetrahydropyran, 1,4-dioxane, dinitrogen tetroxide-dioxane, dinitrogen tetroxide and dinitrogen tetroxide-2 tetrahydropyran, respectively. The curves AB, FB, BC, CE, CG, HG and GI represent the curves of binary eutectic crystallization for mixtures
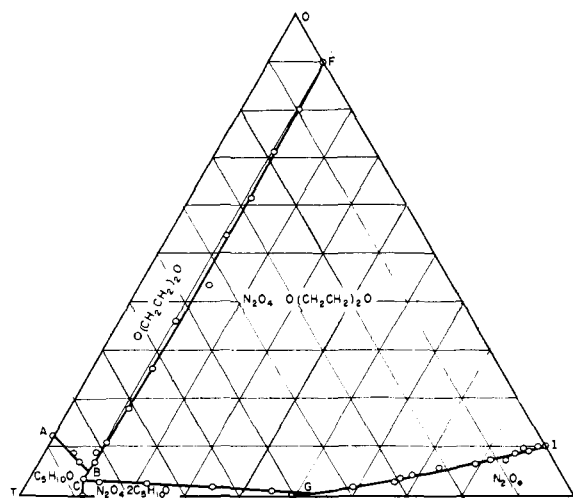
Fig. 1.—The system N_2O_4–$C_5H_{10}O$–$O(CH_2CH_2)_2O$.

of $C_5H_{10}O$ and $C_4H_8O_2$, $C_4H_8O_2$ and $N_2O_4 \cdot C_4H_8O_2$, $C_5H_{10}O$ and $N_2O_4 \cdot C_4H_8O_2$, $C_5H_{10}O$ and $N_2O_4 \cdot 2C_5H_{10}O$, $N_2O_4 \cdot C_4H_8O_2$ and $N_2O_4 \cdot 2C_5H_{10}O$, $N_2O_4 \cdot 2C_5H_{10}O$ and N_2O_4, and N_2O_4 and $N_2O_4 \cdot C_4H_8O_2$, respectively. Points B, C and G represent ternary eutectic mixtures of $C_4H_8O_2$, $C_5H_{10}O$ and $N_2O_4 \cdot C_4H_8O_2$; of $C_5H_{10}O$, $N_2O_4 \cdot C_4H_8O_2$ and $N_2O_4 \cdot 2C_5H_{10}O$; and of N_2O_4, $N_2O_4 \cdot C_4H_8O_2$ and $N_2O_4 \cdot 2C_5H_{10}O_2$, respectively.

Figures 1 and 2 indicate that there is no ternary compound formation under the conditions of this experiment. The existence of a ternary compound would have been indicated by a peak or slope change on the surface of primary crystallization. So many points on the surface were determined that it is extremely unlikely that such a slope change and a complete curve of binary eutectic crystallization could have been missed.

Figure 1 also indicates that the field of primary crystallization for the compound $N_2O_4 \cdot 1,4$-O(CH$_2$-CH$_2$)$_2$O is by far the largest on the diagram, whereas that of $N_2O_4 \cdot 2C_5H_{10}O$ is extremely small. Considering the similarity of the molecular structures of 1,4-dioxane and tetrahydropyran, one would not expect the ethers to differ much in their tendency to form addition compounds with dinitrogen tetroxide, unless the structures of the two compounds differ greatly. Thus it is believed that the structures of the two compounds are considerably different, that of the dioxane compound yielding a higher stability.

The curves on the faces of the prism (Fig. 2) indicate that under the conditions of this experiment the only binary compounds formed are those with the empirical formulas $N_2O_4 \cdot 2C_5H_{10}O$ and $N_2O_4 \cdot O(CH_2CH_2)_2O$. Furthermore, viscosity and molecular weight determinations[1] have shown that the dioxane compound exists as a monomer at temperatures just above its melting point.

It is believed that each of the oxygen atoms in the 1,4-dioxane molecule, a Lewis base, shares one of its unshared pairs of electrons with one of the nitrogen atoms of the dinitrogen tetroxide molecule, a Lewis acid. In the "boat" form of the 1,4-dioxane molecule, the "effective" oxygen to oxygen dis-
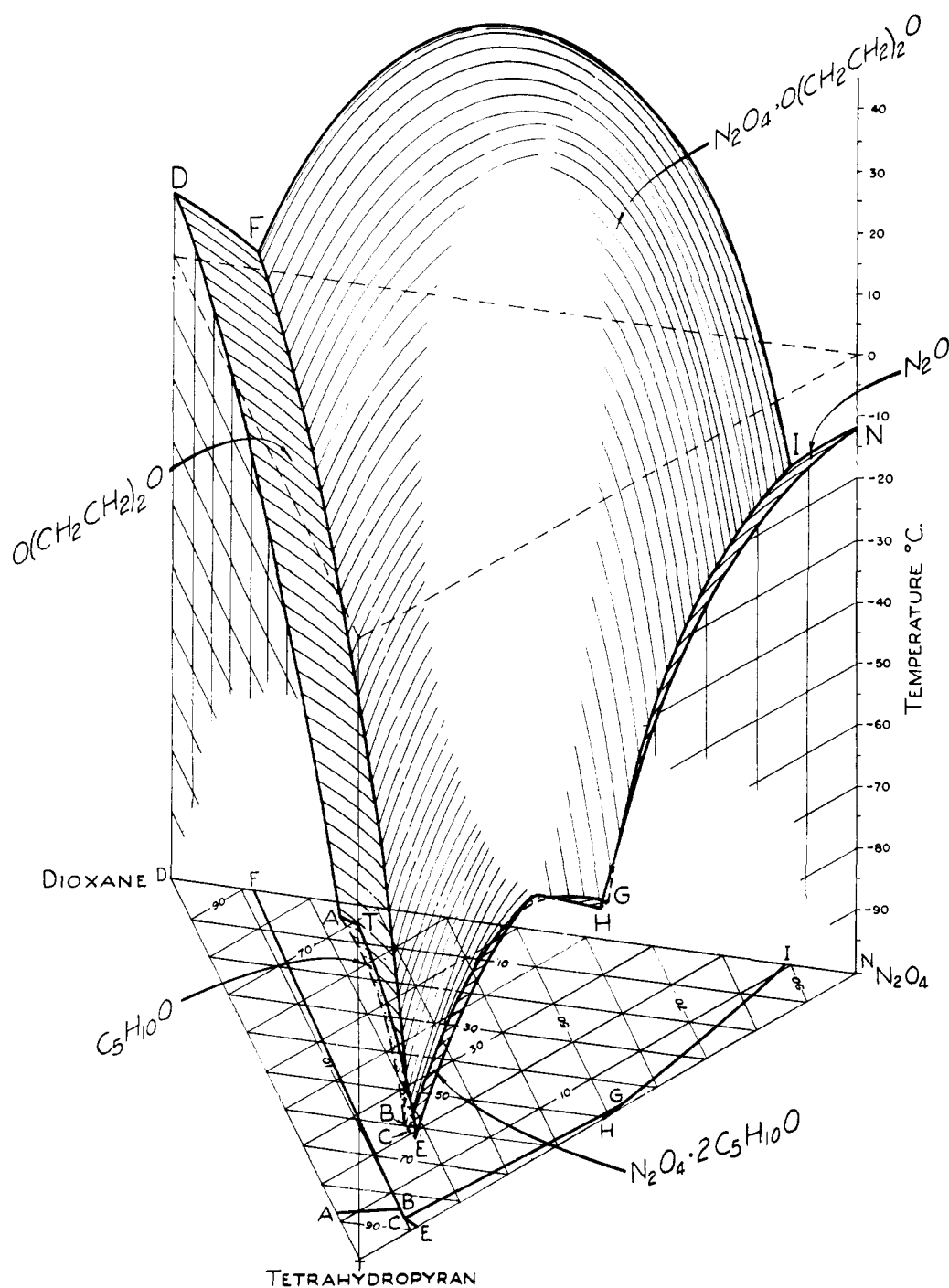
Fig. 2.—The system N_2O_4–doixane–tetrahydropyran.

tance and the orientation of the orbitals occupied by an unshared pair of electrons on each of the ether oxygen atoms is such that it appears reasonable that these orbitals can form bonds with two "pi" orbitals of the nitrogen atoms in the dinitrogen tetroxide molecule. If some rehybridization occurs at the nitrogen atoms, the "effective" interatomic distances and orientations of the bonding orbitals are even more favorable for the formation of such a bicyclic structure. It is, however, difficult to see how the "chair" form of the 1,4-dioxane molecule

could form such a structure with dinitrogen tetroxide. Although electron diffraction data[4] indicate that free 1,4-dioxane exists in the "chair" form, it seems probable that the activation energy for the conversion is of about the same magnitude for 1,4-dioxane as for cyclohexane, and if this is true, the "chair" form of the 1,4-dioxane molecule could readily be converted to the "boat" form during compound formation. The fact that tetrahydropyran does not form a stable addition compound

(4) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

with a mole ratio of one to one may be because the tetrahydropyran molecule cannot act as a bidentate group and form such a bicyclic structure with dinitrogen tetroxide. The fact that neither a stable dinitrogen tetroxide·2(1,4-dioxane) nor a stable ternary compound is formed may be due to the high stability of such a bicyclic structure for the compound N_2O_4·1,4-dioxane. In such a structure there are no bonding orbitals on the nitrogen atoms available for coördinating a second ether molecule.

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Equilibrium Constants for the Formation of Complexes between Metal Ions and Amines Containing Sulfur[1,2]

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The complexes of copper, nickel, cobalt(II) and zinc with methyl 2-aminoethyl sulfide, bis-(2-aminoethyl) sulfide, 1,8-diamino-3,6-dithiaoctane and bis-(2-aminoethyl) disulfide have been studied. Formation constants were calculated for the complexes of nickel and copper with methyl 2-aminoethyl sulfide, those of nickel and cobalt(II) with bis-(2-aminoethyl) sulfide, and those of nickel, copper and cobalt(II) with 1,8-diamino-3,6-dithiaoctane at 30°. Formation constants were also obtained at 0 and 50° for complexes of nickel with each of the ligands for which constants were obtained at 30° and for the complex of cobalt(II) with bis-(2-aminoethyl) sulfide. From the data at different temperatures ΔH and ΔS values were calculated for the reactions involved. In all cases the sulfur-containing amines give less stable complexes than the analogous polyamines containing no sulfur.

Bjerrum[4] has shown that the formation of complexes between metal cations and ammonia or amines is a stepwise process. Further, he has shown how measurements of the hydrogen ion concentrations of solutions containing amines and salts of complex-forming metals may be used to determine the successive formation constants and the composition of the coördinatively saturated complex ion.[5] There are presently available data on ammonia,[4] monoamines,[6] ethylenediamine,[4,5] propylenediamine,[5] diethylenetriamine,[7–9] triethylenetetramine,[8,10] 1,2,3-propanetriamine,[11] tris-(2-aminoethyl)-amine,[12] and N-alkylethylenediamines.[13,14]

This paper reports the results of a study of the formation constants of complexes of copper, nickel, cobalt and zinc ions with methyl 2-aminoethyl sulfide, bis-(2-aminoethyl) sulfide and 1,8-diamino-3,6-dithiaoctane.

(1) This investigation was carried out under contract N6-onr 26913 between The Pennsylvania State University and The Office of Naval Research.

(2) A portion of a thesis presented by Ely Gonick in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1951.

(3) University of Pittsburgh, Pittsburgh 13, Pennsylvania.

(4) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(5) For definition of terms and method for the calculation of constants see G. A. Carlson, J. P. McReynolds and F. H. Verhoek, THIS JOURNAL, 67, 1334 (1945).

(6) R. V. Bruehlman and F. H. Verhoek, ibid., 70, 1401 (1948).

(7) H. B. Jonassen, R. B. LeBlanc and R. M. Rogan, ibid., 72, 4968 (1950).

(8) H. B. Jonassen, G. G. Hurst, R. B. LeBlanc and A. W. Meibohm, J. Phys. Chem., 56, 16 (1952).

(9) J. E. Prue and G. Schwarzenbach, Helv. Chim. Acta, 33, 985 (1950).

(10) G. Schwarzenbach, ibid., 33, 974 (1950).

(11) J. E. Prue and G. Schwarzenbach, ibid., 33, 995 (1950).

(12) J. E. Prue and G. Schwarzenbach, ibid., 33, 963 (1950).

(13) F. Basolo and R. K. Murmann, THIS JOURNAL, 74, 5243 (1952).

(14) H. Irving, Report No. BRL/146, May, 1951. Presented at Discussions on Coördination Chemistry held by Imperial Chemical Industries Limited at Welwyn, Herts, September, 1951.

Experimental

Bis-(2-aminoethyl) sulfide, bis-(2-aminoethyl) disulfide,[15] methyl 2-aminoethyl sulfide and 1,8-diamino-3,6-dithiaoctane[16] were prepared according to published methods and carefully purified.

The general procedure involved the titration of 100 ml. of solution, 1 M in neutral electrolyte (either KCl or KNO_3) and containing known concentrations of metal salt and mineral acid. The titrant was either pure amine or a standardized aqueous solution of amine. In the case where the amine was in the form of the acid salt, a weighed amount of the salt was placed in the solution to be titrated and a standardized solution of sodium hydroxide was the titrant.

The pH measurements were made with the Beckman Model G pH meter using a glass electrode with a saturated calomel electrode as the reference electrode. A nitrogen atmosphere was maintained over all the solutions titrated and the titrant was protected from atmospheric carbon dioxide by means of a soda lime tube. Measurements were made at 0 ± 0.1°, 30 ± 0.1° and 50 ± 0.1°. The 30 and 50° baths were regulated by means of thermoregulators controlled by mercury switches. The 0° bath was obtained by means of a stirred water–ice mixture.

Aqueous solutions of the acids and metal salts used were prepared and analyzed by means of generally accepted methods. The pH meter was standardized both before and after the titrations against buffer solutions prepared from National Bureau of Standards buffer salts. In the titrations it was found that equilibrium was obtained in most cases as rapidly as the solution could be stirred and the heat of reaction dissipated to the bath. From twenty to forty pH readings were taken in each titration.

The acid dissociation constants of the amines were determined in similar titrations substituting barium ion, a noncoördinating ion, for the coördinating metal ions.

Data and Results

Dissociation Constants of the Amines.—The results are given in Table I.

Complexes of Sulfur-containing Amines.—The measurements of pH and calculation of $\bar{n}$ and A yield the results which are recorded as formation curves in Figs. 1–3. From these curves the formation constants given in Table II were calculated.

(15) E. J. Mills, Jr., and M. T. Bogert, THIS JOURNAL, 62, 1173 (1940).

(16) E. Gonick and W. C. Fernelius, submitted for publication.