The equilibrium in the second step should lie far to the right in aqueous solutions since HNCS unlike HNCO is a strong acid.[26] Such an equilibrium can be used to explain the very low yields of thiourea from ammonium thiocyanate obtained in water solutions (Table III).

Formation of the activated complex in Step I is assumed to involve the partial intramolecular transfer of a hydrogen ion from one nitrogen atom to the next. This step can be rationalized by assuming an attraction of the embryonic proton on N by the unshared electron pair on N′. Examination of models also reveals that a hydrogen atom on N is close enough to the unshared pair on N′ to experience relatively easy transfer. Since the mechanism assumes an intramolecular hydrogen transfer, the reaction rate should not be influenced by *p*H.

The observed frequency factor in water is slightly larger than ekT/h indicating a positive entropy of activation[27] of about 3.9 e.u. Reactions in the gas phase involving a cyclic activated complex, however, proceed with a negative entropy of activation. In view of the high dipole moment of thiourea it is possible that the activated complex is less polar than the reactant. Formation of a less polar activated complex from the solvated dipolar reactant could, consequently, lead to the release of bound solvent molecules to begin a more random existence in solution. Such an increase in entropy could more than balance the orderliness conferred by the formation of a cyclic activated complex. A detailed analysis of this point must await the collection of more comprehensive data on the reaction in different solvents.

It is interesting to note that, aside from the slightly positive entropy of activation, the reaction studied in this work has many features in common with so-called "four-center reactions."[28] The mutually similar features include: involvement of four key atoms, little effect of solvent, no requisite acid or base catalysis, etc.[28]

The products obtained by the thermal decomposition of substituted thioureas now under investigation in this Laboratory can be predicted by assuming an intramolecular hydrogen transfer from nitrogen to nitrogen. This finding, if completely confirmed, can also be used to rationalize the postulated mechanism or establish a more satisfactory one.

Acknowledgment.—The authors gratefully acknowledge the generous grant from Research Corporation of New York that made this study possible.

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[26] H. E. Williams, "Cyanogen Compounds," Edward Arnold and Co., London. 2nd Edition. 1948, p. 309.

[27] S. Glasstone. K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 417.

[28] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York. N. Y., 1956, pp. 453–465.

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Interaction between Methyl Borate and Amines as Evidenced from Vapor Pressure Studies

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Mixtures of methyl borate and a number of aliphatic and heterocyclic amines have partial vapor pressures of methyl borate substantially less than would be calculated for ideality. The partial vapor pressures of methyl borate over a number of such mixtures have been measured and the departures from ideality, which should reflect the degree of amine–borate interaction, have been tabulated. Studies have been extended to systems containing the third component, methanol. Interaction is greatest for the difunctional amines, piperazine and ethylenediamine and for triethanolamine. It is least for trimethylamine, di-*i*-propylamine and pyridine. The role of methanol, which markedly increases the apparent amine–borate interaction in some cases, but not in others, is still not clear.

Interaction between methyl borate and amines varies markedly with the structure of the amine. At one extreme are methylamine,[1] ethylenediamine[2] and triethanolamine, which rapidly form solid and readily isolable addition compounds. At the other extreme are pyridine, triethylamine and diisopropylamine, none of which appear to interact with methyl borate at room temperature, even on long standing. In intermediate cases, the partial pressures of methyl borate over mixtures of amine and borate have been found to be substantially lower than would be predicted from Raoult's law. Since this departure from ideality is, in a sense, a measure of amine–borate interaction, we here compare the partial vapor pressures of methyl borate over a number of such mixtures to those partial pressures expected for ideal solutions. Dissociation constants of the addition compounds in the vapor state could not be obtained by gas density measurements since association appeared to be measurable only at temperatures slightly above the condensation points where departure from the ideal gas law is appreciable. The dissociation pressures of the solids themselves cannot be readily converted to thermodynamic dissociation constants since the vapor in equilibrium with the solid addition compounds does not necessarily have the same composition as the solid (*i.e.*, the addition compounds may exist as solids over a *range* of compositions at temperatures where both components are liquid when alone).

Because the interaction between methyl borate and some amines was found to be affected by added methanol,[2] vapor pressure studies were extended

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[1] J. Goubeau and R. Link, *Z. anorg. Chem.*, **267**, 27 (1952).

[2] S. V. Urs and E. S. Gould, THIS JOURNAL, **74**, 2948 (1952).

also to ternary mixtures of methyl borate, methanol and amine.

Experimental

Methyl Borate.—The methyl borate–methanol azeotrope was prepared from boric acid and methanol, and pure methyl borate was recovered from the azeotrope using lithium chloride. The procedures are those of Schlesinger.[3]

Liquid and solid amines were Eastman Kodak Co., white label grade. The liquids were redistilled before use, discarding the first and last 10% of the distillate. Gaseous amines were obtained from the Matheson Company.

Analyses.—Mixtures containing both amine and borate were analyzed as follows. The sample was added to a known excess of dilute HCl, the excess acid titrated with base to the methyl orange end-point, and the equivalents of amine calculated by difference. An excess of base was added, the solution boiled vigorously to expel the amine, and the borate determined by the method of van Liempt.[4]

Methylamine–Methyl Borate Adduct.—Although addition compounds having a boron/nitrogen atom ratio ranging from 0.83 to 1.10 were encountered, a solid having a composition very close to that corresponding to a 1:1 adduct could be prepared as follows. To 10 cc. of liquid methylamine collected at −80°, was added 1.0 cc. of methyl borate. The excess methylamine was allowed to evaporate, leaving a white solid. This was pulverized in a "dry box," then slowly sublimed at 40° in a closed system; yield 750 mg. (59%).

Anal. Calcd. for $C_4H_{16}NO_3B$: N, 10.38; B, 8.02. Found: N, 10.14; B, 7.85; N/B ratio, 1.00.

Vapor pressure *vs.* temperature studies, carried out on this addition compound yielded the function

$$\log P = \frac{-2.30 \times 10^3}{T} + 10.16$$

where P is in mm. This function is in poor agreement with that determined by Goubeau and Link,[1] presumably for the same compound

$$\log P = \frac{-3.0396 \times 10^3}{T} + 12.465$$

However, the vapor pressure of the material is found to depend markedly on the method of isolation. The vapor pressures of unsublimed material are much higher than those of the sublimed material (a reflection of the high amine content), whereas if the sublimation is carried out *in vacuo*, the vapor pressures becomes still lower (a reflection of the low amine content).

Association of the Methylamine–Methyl Borate Adduct in the Vapor Phase.—A 138.8-mg. sample of the addition compound was weighed into a bulb having a volume of 208.2 ml. The sample was vaporized quickly by water at 80°, then cooled slowly while the pressure of the gas was measured at various temperatures. From these pressures, apparent molecular weights were calculated from the ideal gas law (complete dissociation corresponds to an apparent molecular weight of 66.5). The following values were obtained

T, °C.	Mol. wt. (apparent)	T, °C.	Mol. wt. (apparent)
79.0	62.0	40.8	74.5
72.4	61.6	36.5	84.3 (condensation)
67.8	62.8	31.4	118.8
59.4	62.5	28.4	136.8
52.4	62.6	26.2	149.5
45.6	62.7	22.7	164

Vapor Pressure Studies.—Carefully weighed quantities of amine and methyl borate (or the methanol–methyl borate azeotrope) were mixed at −80°. About 1.87 g. (18 mmoles) of methyl borate or 2.63 g. of the azeotrope was generally used, together with slightly more than an equivalent quantity of amine. The mixture was allowed to warm to room temperature while its vapor filled a 565-ml. evacuated bulb. When equilibrium had been attained, the liquid was closed off, the vapor was condensed at −80°, the condensate diluted with cold water, made basic and boiled to drive off the amine. The borate in solution was titrated in the usual manner. The borate–amine mixture taken was large enough so that its composition was not appreciably changed by loss of 565 cc. of its vapor, and two successive runs with the same mixture generally gave results agreeing to within 3%. A second experiment, run at the same temperature with pure methyl borate and no amine, determined the vapor pressure of the borate alone.

To compare amine–borate interactions in the various mixtures we have calculated for each mixture an "interaction ratio," I, where

$$I = \frac{\text{partial vapor pressure of }(\text{MeO})_3\text{B over the mixture}}{\text{p.v.p. calcd. for ideality (Raoult's law)}}$$

Experiments were run at temperatures ranging from 21 to 25°. The mole fraction of amine ranged from 0.51 to 0.55 for the binary mixtures and from 0.35 to 0.39 for the ternary mixtures. Although the partial vapor pressures change with both composition and temperature, the observed I values were, within experimental error, independent of both variables when each was held within the range specified.

As an example, 565 ml. of the vapor over a typical mixture (1.720 g. of piperidine and 1.50 g. of methyl borate) contained 0.405 milliequivalent of boron at 25°, corresponding to a partial vapor pressure of methyl borate of 13.4 mm. Similarly, pure methyl borate at this temperature was found to have a vapor pressure of 92.7 mm. The partial vapor pressure of methyl borate is therefore 0.310 as great as that calculated for an ideal solution, *i.e.*, I for piperidine in the above mixture is 0.31. Similar calculations for each of the other binary and ternary mixtures yielded the ratios summarized in Table I.

TABLE I

VALUES OF I, THE RATIO OF THE OBSERVED PARTIAL VAPOR PRESSURE OF METHYL BORATE OVER A MIXTURE TO THE VALUE CALCULATED FOR IDEALITY. MIXTURES OF METHYL BORATE AND AMINES, WITH AND WITHOUT METHANOL, ARE INCLUDED

Amine	I values Methanol absent	I values Methanol present
Primary		
Methylamine	1.11	0.10
Ethylamine	0.27	.21
n-Propylamine	0.73	.58
i-Propylamine	0.87	.53
Allylamine	0.55	.71
n-Butylamine	1.26	.69
t-Butylamine	1.44	.77
Ethylenediamine	0.03	.04
Secondary		
Dimethylamine	0.71	0.21
Diethylamine	.75	.21
Di-*n*-propylamine	.72	.69
Di-*n*-butylamine	.72	.93
Di-*n*-amylamine	.65	.81
Di-*i*-propylamine	1.00	1.13
Diethanolamine	2.16	0.11
Tertiary		
Trimethylamine	1.18	0.94
Triethylamine	0.86	.95
Tri-*n*-butylamine	.67	.73
Triethanolamine	.07	.05
Heterocyclic		
Pyrrolidine	0.70	0.17
Piperidine	0.31	.21
Pyridine	1.07	.87
Piperazine	0.26	.16
Morpholine	0.74	.17

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[3] H. I. Schlesinger, H. C. Brown, D. L. Mayfield and J. R. Gilbreath, THIS JOURNAL, **75**, 213 (1953).

[4] J. A. M. van Liempt, *Rec. trav. chim.*, **39**, 358 (1920).