[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF VERMONT]

THE EQUILIBRIUM BETWEEN THIO-UREA AND AMMONIUM THIOCYANATE

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As a preliminary step to a study of certain other reactions of thio-urea, an extension seemed needed of previous determinations of its equilibrium with ammonium thiocyanate. The purpose of the present paper is to record the results of this further examination. For earlier work on the subject, reference should be made to the papers of Volhard,[1] of Waddell,[2] of Reynolds and Werner,[3] of Findlay,[4] and of Atkins and Werner.[5]

In the present instance, measurements have been made of the equilibrium, at several temperatures, attained in the presence of each of two solvents, namely, anhydrous *n*-propyl alcohol and anhydrous *n*-butyl alcohol, as well as when the isomers were heated together without additional solvent.

Experimental Part

Before use in the following experiments, thio-urea and ammonium thiocyanate of good grade were each twice crystallized from alcohol. The resulting thiocyanate, after drying, was faintly yellow. Titration with silver nitrate solution indicated about 0.25% of impurity. As closely as titration with iodine solution could detect, the thio-urea was quite pure.

The propyl and butyl alcohols were dried over lime and finally over sodium. The dried samples distilled within a temperature range of about 1° in case of the butyl alcohol, and less than this in the case of the propyl alcohol.

The solutions and melted mixtures to be brought to equilibrium were sealed in Pyrex glass tubes, of about 5 cc. and 1 to 2 cc. capacities, respectively. These tubes were placed in vapor baths maintaining the desired temperatures.

In case of the solutions, the tube content was so adjusted as to leave, when at the temperature of the bath, but little free gas space.

The alcoholic solutions used were all of the same total molar concentration, namely 0.76 g. (0.01 mole) of thio-urea or of ammonium thiocyanate, or of a mixture of these, in 25 g. of solution. Since thio-urea at room temperature does not dissolve to this concentration in either of the alcohols, it was usually in part replaced by ammonium thiocyanate, yet kept in percentage above that corresponding to equilibrium.

When equilibrium was thought attained, the tubes were quickly withdrawn from the constant-temperature bath, immediately immersed in cold water, opened, and the contents subjected to analysis. Under each set of conditions, the equilibrium was approached from both sides.

[1] Volhard, *Ber.*, **7**, 92 (1874).

[2] Waddell, *J. Phys. Chem.*, **2**, 525 (1898).

[3] Reynolds and Werner, *J. Chem. Soc.*, **83**, 1 (1903).

[4] Findlay, *ibid.*, **85**, 403 (1904).

[5] Atkins and Werner, *ibid.*, **101**, 1167 (1912).

After heating, the alcoholic solutions were light yellow; the mixtures heated without solvent became bright yellow. Marked gaseous pressure of hydrogen sulfide and ammonia was developed, especially in the tubes without solvent. This pressure appeared greatest in the tubes longest heated, though these were the ones held at the lower temperatures. Preliminary qualitative experiments showed that these gases are evolved at an appreciable rate even at temperatures below 130°, and when moisture is carefully excluded.

The occurrence of such side reactions renders desirable the direct determination of each of the two main constituents of the equilibrium mixture. This was not done by Reynolds and Werner who, while recognizing the presence of side products, determined the thio-urea only, or by others who have studied the system. In most of these earlier studies, however, the temperatures employed were such as to lead rapidly to equilibrium, reducing to a minimum the effect of the more gradual side reactions. In the present experiments, the sum of the weights of thio-urea and ammonium thiocyanate found to be formed at 132° equalled about 92%, and at 156°, about 82% of the weights initially taken.

Thio-urea was determined iodimetrically, using the procedure developed by Reynolds and Werner, with this modification, that, before titration, air was bubbled for 30 minutes through the slightly acidified solution of the sample, at room temperature. This displaced the hydrogen sulfide, present as such, or as ammonium sulfide, in the equilibrium mixture.

As pointed out by Waddell, ammonium thiocyanate cannot be titrated successfully with silver nitrate and ferric alum as indicator, in the presence of any considerable concentration of thio-urea, presumably because of formation of a complex ion. Thiocyanate can, however, be determined in this way in a sample in which the thio-urea has first been titrated with iodine solution, the value in terms of standard silver nitrate solution of the iodide present in the reduced iodine solution being subtracted from the total volume of silver nitrate used. And this was the method employed. In the first titration, it is well to take care not to introduce an unnecessarily large amount of starch as indicator, for the presence of large amounts of starch holds in colloidal suspension the silver iodide formed in the second titration, and this masks somewhat the final end-point.

As applied to synthetic mixtures of thio-urea and ammonium thiocyanate, the method of analysis was found to be adequate, both when hydrogen sulfide and small amounts of cyanamide were present, and in the absence of these substances.

In the experiments that were carried out in propyl and butyl alcohol solutions, these solvents were evaporated at about 40° and under reduced pressure, before proceeding with the analysis, transformation products of the alcohols interfering with this, though the pure alcohols themselves do not so interfere. The residues were dissolved in water and made up to a definite volume.

The results obtained are summarized in Table I. Great accuracy is not claimed for them, since small amounts of material were used (this in part to facilitate rapid cooling) and since the influence on the analyses of certain of the possible side products is unknown. They are, however, believed to be essentially reliable.

TABLE I

RESULTS

Tube	Temp. of bath °C.	Hours heated	Solvent	Side from which approached	Equilibrium composition (% of NH_4SCN in total NH_4SCN + $CS(NH_2)_2$ found)
19	132	65	Propyl alc.	T (thio-urea)	80.5
22	132	65	Propyl alc.	A (cyanate)	80.9
20	156	17	Propyl alc.	T	76.3
24	156	19	Propyl alc.	A	76.7
28	132	89	Butyl alc.	T	76.1
25	132	89	Butyl alc.	A	75.9
29	156	22	Butyl alc.	T	71.6
26	156	22	Butyl alc.	A	71.5
17	132	57	No solvent	A	66.4[a]
37	132	54	No solvent	T	66.4[b]
38	132	54	No solvent	A	66.8[b]
32	156	19	No solvent	A	73.9[a]
33	156	19	No solvent	T	73.3[a]
35	156	17	No solvent	T	73.1[b]
36	156	17	No solvent	A	72.7[b]
41	182	2	No solvent	T	76.0[b,c]
42	182	2	No solvent	A	76.0[b,c]
43	182	6	No solvent	T	77.6[b]
44	182	6	No solvent	A	78.0[b]

[a] Reaction tube about $^1/_4$ full of melt.

[b] Reaction tube about $^3/_4$ full of melt.

[c] Tubes 41 and 42 were chilled simultaneously but, it is thought, not rapidly enough.

In instances in which comparison is possible, the results recorded in the table differ considerably from those of earlier observers. Reynolds and Werner find approximately 75% of thiocyanate at 182° (76.5%, if the average is taken of experiments in which the melt was maintained at 182° for 30 minutes or longer), as against 77.6–78.0% here given, and there is evidence that this may be somewhat below the true value. Two sources of error seem to be present in the analytical procedure of Reynolds and Werner, namely, that their determination of ammonium thiocyanate is by difference and that the iodine titration value of any sulfide present in the reaction mixture was apparently calculated as thio-urea. Further, and more significant, since for each analysis they withdrew 12 to 14 g. of the equilibrium mixture, it is probable that the chilling to which the samples were subjected in order to check the reaction did not take place rapidly enough to accomplish this purpose. The present work shows that a shift so caused would lower the percentage of thiocyanate.

Waddell, on the other hand, finds higher percentages of thiocyanate in the melt even at considerably lower temperatures, namely 78.8% at 152–153°, and 79.1% at 160–161°. As he recognized, his method of analysis was faulty and his results are undoubtedly somewhat in error.

From examination of earlier determinations, most of which were at closely neighboring temperatures, Findlay concludes that the heat of transformation of one of the isomers into the other is practically zero. The magnitudes of the temperature coefficients show that this is not the case, and, in case of the melted mixtures, fix the heat of transformation, between 132° and 156°, of one mole of ammonium thiocyanate into one mole of thio-urea at approximately 4600 cal.

So, employing the van't Hoff isochore and assuming the above heat of reaction constant over the temperature range involved, from the equilibrium values without solvent at 132° and 156°, the percentage of ammonium thiocyanate that should be present at 182° is calculated to be 79.6. That the values found by experiment are lower than this may be due to a shifting of the equilibrium during chilling of the tubes, as the reaction velocity is high in the neighborhood of this higher temperature. But also, the assumptions on which the calculated value is based are not wholly justified.

It will be noted that the equilibrium compositions found vary according to whether a solvent is or is not present, and with the nature of the solvent. Also, while the temperature coefficients of each of the two solvents are nearly the same, these are opposite in sign to that found in the experiments in which no solvent was present. The method of analysis, however, simply determines total ammonium cyanate and total thio-urea in the equilibrium mixture, and even these only after the mixture is chilled. Were methods available for determining at a particular bath temperature each of the molecular species present in the equilibrium mixture, such as may result from association or dissociation or other processes, we may assume that the state of equilibrium at a given temperature between these individual molecular species would be found independent of the presence or of the nature of the solvent and that, therefore, the temperature coefficient would be the same with or without solvent.

The author wishes to express his appreciation of the hospitality shown him at the Sterling Chemistry Laboratory, of Yale University, where it was his privilege to be a guest and where the experiments were made.

Summary

New determinations have been made of the equilibrium at several temperatures between the dynamic isomers ammonium thiocyanate and thiourea, when these are melted together.

Determinations have also been made of the equilibrium between these substances when dissolved in *n*-propyl alcohol and in *n*-butyl alcohol.

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STUDIES IN ALCOHOLYSIS. VELOCITY CONSTANTS IN THE ALCOHOLYSIS OF ESTERS OF ALPHA-BETA-UNSATURATED ACIDS AND OF THEIR CORRESPONDING SATURATED ANALOGS

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Introduction

In a previous communication[1] results were given for the alcoholysis of the ethyl and methyl esters of crotonic and cinnamic acids having double linkage of carbon atoms in the α,β-position referred to the carboxyl, and also of their corresponding saturated analogs, with a large excess of nearly absolute methyl or ethyl alcohol, respectively. These reactions were carried out at 30° in the presence of dry hydrogen chloride dissolved in the reacting alcohol as catalyst. In all cases the velocity constants were proportional to the strength of the catalyst in the reacting mixture, and these constants were tabulated for strength of catalyst of 0.02 *N*. As was expected from analogous reactions, hydrolysis and esterification of these esters, the double linkage of the α,β-carbons exerted a strong retarding influence on the alcoholysis. While in esterification the constant sank to 1/42, and in hydrolysis to 1/29.5, in alcoholysis it was only 1/16.5 of the value for the corresponding saturated analog.[2] The substitution of the β-methyl group by phenyl slightly decreased the velocity constant. The ratio of the constants for the direct and the reverse reaction was the same for butyrate, crotonate, hydrocinnamate and cinnamate, as was also found by Kolhatkar[3] for acetates, propionates and butyrates, although the ratios differ to some extent.

The study of the alcoholysis in the presence of an excess of alcohol has now been extended to the following series of reactions with optically-active esters, in the presence of dry hydrogen chloride as catalyst, and at 30°: (1) menthyl butyrate + methyl alcohol $\longrightarrow$ methyl butyrate + menthol;

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[1] B. Dasannacharya and J. J. Sudborough, *J. Indian Inst. of Sci.*, 4, 181 (1921).

[2] Ref. 1, p. 202.

[3] Kolhatkar, *J. Indian Inst. Sci.*, **1**, 130 (1915).