tion at 140° is 32,000 cal., and the rate constant at 140° is 0.00024 sec.⁻¹. Studies in this Laboratory are in good agreement with Hinshelwood's results.⁴

It is thus seen that at 140° malonic acid decomposes in triethyl phosphate twenty-two times as fast as it does alone. We see that triethyl phosphate brings about a decrease in the entropy of activation, decreasing the probability of the formation of the activated state.⁶ However, this effect is compensated for by the lowering of the enthalpy of activation, so that less energy is required to bring about activation. The over-all effect is the lowering of the free energy of activation at 140° from 32,000 to 28,600 cal., resulting in an increase in the rate of reaction.

(6) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 24.

POLAROGRAPHIC THIOUREA-FORMALDEHYDE KINETIC STUDIES

BY MARTIN G. CHASANOV AND CECIL C. LYNCH

Department of Chemistry, University of Delaware, Newark, Del. Received February 29, 1956

The initial condensation of thiourea and formaldehyde in alkaline media was followed by polarographic analysis for formaldehyde. The reaction was found to be second order with respect to formaldehyde and thiourea. Values of the rate constant for the reaction were determined at 5, 15 and 25°. The value for the activation energy for this reaction, determined from these rate constants, is 23.4 kcal./mole.

Experimental

The polarographic determinations were made with an E. H. Sargent and Company Model XII Polarograph. Electrodes of the original Heyrovsky-Shikata type¹ were employed. For the determination of the half-wave potential of formaldehyde versus the saturated calomel electrode (SCE) the H-cell of Lingane and Laitinen² was used.

The formaldehyde employed was Merck and Company neutral reagent grade; analysis by the hydroxylamine method^s showed the formaldehyde content to be 36.5%; the solution was diluted to prepare a stock solution of molarity 0.01246 for use in the polarographic measurements. The half-wave potential of the formaldehyde versus the mercury pool was -1.56 v.; versus the SCE, -1.66 v. The limiting current, i_{s} , due to the formaldehyde was proportional to the formaldehyde concentration over the range studied.

The thiourea was Eastman Kodak White Label. The thiourea crystals were dried at 120° for two hours; volatile material was less than 1/2 of 1%. The dried crystals were dissolved in water to make up a stock solution of molarity 0.02588. The supporting electrolyte was 0.05 M sodium hydroxide (Baker C.P.). The drop mass for the capillary was 1.48 mg./sec.; the drop time was 4.74 sec.; the mercury head was 34.6 cm.

For kinetic determinations solutions were prepared and thermostated prior to use. Formaldehyde and the supporting electrolyte were mixed first; the thiourea was then added. When half of the thiourea had been added the timer was started; the reaction mixture was agitated for 30 seconds, and then it was placed in the polarographic cell. The limiting current was measured as the difference between the upper and lower plateaus of the formaldehyde wave.

(1) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, New York, N. Y., 1941.

(2) J. J. Lingane and H. A. Laitinen, Ind. Eng. Chem., Anal. Ed., 11, 504 (1939).

(3) L. E. Smythe, THIS JOURNAL, 51, 369 (1947).

The results of the kinetic determinations are shown in Table I. The data fitted a second-order rate plot for thiourea and formaldehyde. The values shown are the averages of three determinations for each concentration. The activation energy may be estimated from the Arrhenius relation

$$\frac{\mathrm{d}\,\ln\,k}{\mathrm{d}(1/T)} = = \frac{\Delta E_{\mathrm{A}}}{R}$$
TABLE I

RATE CONSTANT FOR THE REACTION OF FORMALDEHYDE WITH THIOUREA IN STRONGLY ALKALINE MEDIA AT 5, 15 AND 25°

°C.	Initial CH_2O concn., M	Initial thiourea concn., M	k(mole ⁻¹ sec. ⁻¹)
25	$415 imes10^{-5}$	431×10^{-5}	2.03
25	208 .	132	2.00
15	312	205	0.44
15	208	273	0.42
5	415	547	0.119
5	375	656	0.124

Discussion

Good yields of mono- and dimethylolthiourea have been produced by the reaction of thiourea and formaldehyde at temperatures less than 50°.⁴ Studies have shown that isomeric forms of the above exists. Pollak⁴ postulated the isomers of monomethylolthiourea as

H₂N--C--NH--CH₂OH (acidic media)

$$\parallel$$

S
A
HN=-C-S--CH₂OH (alkaline media)
NH₂
B

In alkaline media thiourea reacts to produce mercaptans, sulfur, and often H_2S . The reaction to form B may be postulated as

$$\begin{array}{c} S & SH \\ \downarrow \\ H_2N - C - NH_2 \longleftrightarrow HN = C - NH_2 \end{array}$$
(1)

$$H_{2}N \xrightarrow{\downarrow} C - NH_{2} + H \xrightarrow{\downarrow} C - H \xrightarrow{k_{1}} H_{2}N \xrightarrow{} C = NH$$
(2)

$$HN = C - NH_2 + OH^- \underbrace{\longleftrightarrow}_{H_2N} H_2 N - C - NH_2 + HS^- \quad (3)$$

$$H_{2}N - C - NH_{2} + HC - H \xrightarrow{k_{2}} H_{2}N - C - NH \qquad (4)$$

$$-\frac{\mathrm{d}C_{\rm F}}{\mathrm{d}t} = k_1 C_{\rm F} C_{\rm T} + k_2 C_{\rm F} C_{\rm U} - k_{-2} C_{\rm P} \qquad (a)$$

where

S

 $C_{\mathbf{F}}$ is the formaldehyde concn.

 $C_{\rm T}$ is the thiourea concn.

 $C_{\rm U}$ is the urea concn.

 $C_{\rm P}$ is the concn. of monomethylolurea

Crowe and Lynch⁵ have found at 25° that k_2 is 2.97 \times 10⁻² mole⁻¹ sec.⁻¹ and k_{-2} is 1.45 \times 10⁻³

(4) F. Pollak, Modern Plastics, 16, No. 10, 45 (1939).

(5) G. Crowe and C. C. Lynch, J. Am. Chem. Soc., 70, 3795 (1948).

sec.⁻¹. For $C_{\rm U} \ll C_{\rm T}$ and $k_1 \gg k_2$ equation a becomes

$$-\frac{\mathrm{d}C_{\mathrm{F}}}{\mathrm{d}t} = k_{\mathrm{I}}C_{\mathrm{F}}C_{\mathrm{T}} \qquad (b)$$

The experimental data fit (b) quite well. The activation energy, $\Delta E_{\rm A}$, was found to be 23.4 kcal./ mole.

CRYSTALLOGRAPHIC EVIDENCE FOR THE TRIHYDRATE OF ALUMINUM FLUORIDE¹

BY ROBERT D. FREEMAN²

Technical Division, Goodyear Atomic Corporation, Portsmouth, Ohio Received April 9, 1956

The existence of a hydrate of aluminum fluoride which contains either 3.0 or 3.5 moles of H₂O per mole of AlF₃ has been well established. Whether there are two distinct hydrates has been open to question. Ehret and Frere³ have pointed out the discrepancies in the literature regarding these hydrates and have reported evidence for the existence of two forms (α and β) of AlF₃·3H₂O. They also have listed X-ray diffraction data (dvalues and relative intensities) for their stable (β) form of AlF₃·3H₂O. It has been of interest to correlate similar data with a unit cell for possible crystallographic confirmation of their chemical evidence for AlF₈·3H₂O.

X-Ray powder diffraction patterns of "Reagent" grade hydrated aluminum fluoride (exptl.: 19.61%, Al, 39.7% loss on heating at 500° *in vacuo*; theoretical for AlF₃·3H₂O: 19.54% Al, 39.14% H₂O) were obtained with a Norelco diffractometer using nickel-filtered copper radiation (λ of Cu K $\alpha_1 = 1.5405$ Å.). Samples were passed through a 400mesh sieve and prepared for the diffractometer as suggested by Klug and Alexander.⁴

Interplanar distances, d, and relative intensities obtained for these samples are in good agreement with the data given for β -AlF₂·3H₂O by Ehret and Frere.³ The following table shows the planar indices, observed and calculated values of $\sin^2 \theta$ (using a tetragonal unit cell with a = 7.734 Å. and c = 7.330 Å.), and relative intensities. The agreement between the observed and the calculated values of $\sin^2 \theta$ listed in the table and the agreement between the observed and the calculated values of $\sin^2 \theta$ above 0.3 (which are not listed) is also good. From the pycnometric density, the volume, and

(1) This work performed under Contract-AT-(33-2)-1, United States Atomic Energy Commission.

(2) Dept. of Chemistry, Oklahoma A and M College, Stillwater, Okla.

(3) W. F. Ehret and F. J. Frere, J. Am. Chem. Soc., 67, 64 (1945).
(4) H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 300.

Crystallographic Data				
	Sin² θ	× 104		
hkl	Obsd.	Calcd.	I/I.	
110	200	199	100	
200	397	398	62	
002	445	444	5	
102	535	544	17	
112	644	643	14	
220	794	796	30	
202	842	842	9	
212	942	941	12	
310	993	995	56	
222	1239	1240	5	
302	1337	1339	2	
312	1440	1439	12	
400	1590	1592	13	
322	1736	1738	8	
004)	1796	1776\	7	
330∫	1780	1791∫	1	
104	1877	1876	8	
420	1991	1990	42	
412	2132	2135	5	
332	2233	2235	2	
2 14	2273	2273	2	
422	2433	2434	2	
510	2579	2587	5	

the tetragonal symmetry of the unit cell, it is readily deduced that, whether the correct formula is $AlF_3 \cdot 3H_2O$ or $AlF_3 \cdot 3.5H_2O$, there must be four formula units per unit cell. Using water as the pycnometric liquid and making no correction for solubility (0.41% by weight³), the density of the samples was found to be 2.03 g./cc. Calculated density, assuming $AlF_3 \cdot 3H_2O$, is 2.09 g./cc.; assuming $AlF_3 \cdot 3.5H_2O$, it is 2.23 g./cc. Obviously, the value for $AlF_3 \cdot 3H_2O$ is in better agreement with the observed value.

Examination of the indices for systematic absences reveals that the special reflections hk0 are present only when h + k = 2n; 0kl, only when l = 2n; and hhl, only when 2h + l = 2n. The only tetragonal space group which requires these particular conditions for possible reflections is P4/ncc $- D_{4b}^{4}$. In this space group, equivalent positions may occur only in sets of 4, 8 and/or 16. This restriction on the number of equivalent positions presents no problem if there are assumed to be 4 units of AlF₃·3H₂O per unit cell; both O and F atoms may be arranged in 3 sets of 4 equivalent positions each, or in two sets, one with 4, and one with 8, equivalent positions. However, the restriction is incompatible with the assignment of 4 units of AlF₃·3.5H₂O per unit cell; the fourteen O atoms cannot be divided into sets of equivalent positions each.