Kinetics of the Reaction Between Urea and Formaldehyde in the Presence of Sulfuric Acid

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Synopsis

The kinetics of the reaction between urea and formaldehyde were studied in the presence of various amounts of sulfuric acid (5–45% by weight) at different temperatures (5°, 15°, and 25°C). The reaction was shown to follow first-order kinetics. The activation energy for the reaction varies from 12.51 kcal/mole to 14.59 kcal/mole in the range of sulfuric acid concentration studied.

INTRODUCTION

The chemical reactions of urea and formaldehyde have been extensively studied owing to their commercial importance in textile resin finishing operations. The formation of mono- and dimethylol ureas has been studied in detail by Crowe and Lynch,[1,2] Smythe,[3,4,5] Dejong and Dejonge,[6] Landquist,[7] and Ito.[8]

Smythe[3] found that in neutral solutions, the reaction between urea and formaldehyde to form monomethylol urea proceeded to more than 95% completion and that the reaction was essentially bimolecular. Crowe and Lynch[1] found that the reaction involves urea anion (NH_2CO—NH^- or
$$NH_2\text{—}\underset{\underset{O^-}{|}}{C}\text{=}NH)$$
and unhydrated formaldehyde. Subsequently, they[2] showed by studying the effect of varying the pH and temperature on the reversible reaction,

$$NH_2 \cdot CO \cdot NH_2 + HCHO \rightleftharpoons NH_2 \cdot CO \cdot NH \cdot CH_2OH$$
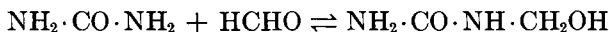
that the rate of the forward reaction is dependent on the rate of dehydration of formaldehyde and on the rate of anion formation of urea.

Landquist[7] has shown that the activation energy of the primary formation of methylol urea is 15.4 kcal/mole and that of the hydrolysis of this compound (hydrolysis reaction) is 20.4 kcal/mole. These studies made on the reaction between urea and formaldehyde were base catalyzed. Under acidic conditions, methyleneureas such as methylenediurea, dimethylenetriurea, trimethylenetetraurea, etc., are formed. Under mildly acidic conditions, these condensation products eventually lead to the formation of

complex transparent resins, but in the presence of a strong acid, insoluble condensation products are precipitated directly from the reaction mixture.[9-13] Kadowaki[14] prepared methylenebisurea, $CH_2(NHCONH_2)_2$, by the controlled reaction of formaldehyde with excess of urea under mildly acidic conditions.

From a survey of literature, it appears that the kinetics data of acid-catalyzed reaction between urea and formaldehyde are not available. The present communication deals with the kinetics of the reaction between urea and formaldehyde (molar ratio 10:1) in the presence of different amounts of sulfuric acid at three temperatures.

EXPERIMENTAL

Chemicals. Paraformaldehyde (Veb Laborchemie, Apolda, Germany) was used as the source of formaldehyde. When analyzed iodometrically, it gave a purity of 97 ± 1%. Urea of BP grade with a purity of 95 ± 2% and sulfuric acid of Analar grade were used.

Estimation of Formaldehyde. The iodometric method of Romijin[15] was used for the estimation of formaldehyde in the solution. This method depends on the oxidation of formaldehyde by hypoiodite formed when sodium hydroxide is added to a solution of formaldehyde to which a known excess of standard iodine solution has been added. The excess iodine is back-titrated after acidification.

Kinetics of Reaction Between Urea and Formaldehyde. Two grams paraformaldehyde was dissolved in 100 ml sulfuric acid of required concentration, and 50 ml of this stock solution was diluted to 1 liter with sulfuric acid of the same concentration. To 100 ml of the diluted solution, 2 g urea was added at the required temperature, and the formaldehyde content of the reaction mixture was periodically estimated by the above method.

RESULTS AND DISCUSSION

The kinetics data obtained for the reaction between urea and formaldehyde in the presence of various amounts of sulfuric acid (5-45%) at different temperatures (5°, 15°, and 25°C) for varying periods of time (0–18 min) were analyzed according to first-order reaction kinetics. The results obtained for the reaction in the presence of 45% sulfuric acid are shown in Figure 1, in which log $(a - x)$ is plotted against t for all the three temperatures studied, where a is the initial concentration of formaldehyde and x is its concentration at time t. The rate constant k for the reaction was calculated from the slope of the straight lines obtained, and the period of half-life was also calculated. The results are given in Table I. It is seen that when the rate constant or the period of half-life is taken as a criterion of the ease with which urea reacts with formaldehyde, increasing concentration of sulfuric acid retards the reaction. An increase from 5% to 45% sulfuric acid results in slowing down of the reaction rate to one-fourth at

TABLE I

Rate Constant and Period of Half-life for the Reaction Between Urea and
Formaldehyde in the Presence of Different Amounts of Sulfuric Acid

| Concentration of sulfuric acid, wt-%	Rate constant, k, min^{-1}			Half-life, $t_{1/2}$, min		
	5°C	15°C	25°C	5°C	15°C	25°C
5	0.1118	0.2771	0.5134	6.201	2.501	1.351
10	0.0867	0.2467	0.4710	7.997	2.810	1.472
15	0.0778	0.1965	0.4662	8.910	3.528	1.487
20	0.0676	0.1732	0.3436	10.260	4.003	2.018
25	0.0525	0.1548	0.2698	13.200	4.478	2.569
30	0.0469	0.1464	0.2436	14.780	4.735	2.845
35	0.0414	0.1262	0.2314	16.740	5.493	2.996
40	0.0338	0.0836	0.1865	20.510	8.292	3.718
45	0.0287	0.0819	0.1429	24.150	8.475	4.851
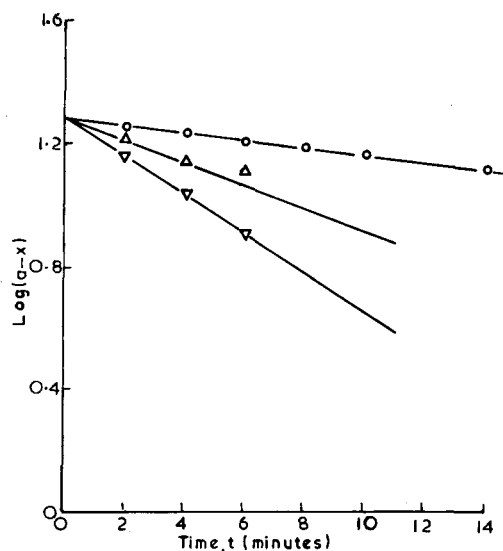
Fig. 1. First-order kinetics plots for the reaction between urea and formaldehyde in the presence of 45% sulfuric acid at different temperatures: (O) 5°C; (Δ) 15°C; (∇) 25°C.

5°C. This effect is slightly less pronounced at other temperatures. As with most of the reactions, an increase in the temperature increases the rate of reaction of urea with formaldehyde at all the concentrations of sulfuric acid taken. With an increase of 20°C in the temperature (from 5° to 25°C) the reaction takes place about five times faster at all the concentrations of sulfuric acid.

The activation energy, E, for the acid-catalyzed reactions between urea and formaldehyde was calculated from the slopes of straight lines obtained by plotting $\log k$ against $1/T$. Using this value of E, the Boltzmann factor and the frequency factor were also calculated. The results

TABLE II

Activation Energy and Other Parameters for the Reaction Between Urea and
Formaldehyde in the Presence of Different Amounts of Sulfuric Acid

Concentration of sulfuric acid, wt-%	Activation energy E, kcal/mole	Boltzmann factor $e^{-E/RT} \times 10^{10}$			Frequency factor $A = \dfrac{k}{e^{-E/RT}} \times 10^{-9}$		
		5°C	15°C	25°C	5°C	15°C	25°C
5	12.51	1.663	3.639	7.551	0.672	0.762	0.680
10	12.75	1.159	2.443	5.129	0.749	1.009	0.918
15	13.05	0.631	1.439	3.069	1.233	1.366	1.519
20	13.36	0.372	0.851	1.837	1.820	2.034	1.871
25	13.51	0.282	0.646	1.416	1.863	2.343	1.905
30	13.82	0.159	0.501	0.851	2.959	2.921	2.863
35	14.05	0.107	0.257	0.576	3.864	3.900	4.021
40	14.29	0.071	0.174	0.389	4.774	4.810	4.793
45	14.59	0.039	0.100	0.234	7.550	8.191	6.096

are given in Table II.   It is seen that the activation energy increases from
12.51 kcal/mole for 5% sulfuric acid to 14.59 kcal/mole for 45% sulfuric
acid.   In contrast to these figures, the base catalyzed reaction of urea and
formaldehyde, leading to the formation of methylol urea, has an activation
energy of 15.4 kcal/mole, as reported by Landquist.[7]

References

1. G. A. Crowe and C. C. Lynch, *J. Amer. Chem. Soc.*, **70**, 3795 (1948).
2. G. A. Crowe, and C. C. Lynch, *J. Amer. Chem. Soc.*, **71**, 3731 (1949).
3. L. E. Smythe, *J. Phys. Colloid Chem.*, **51**, 369 (1947).
4. L. E. Smythe, *J. Amer. Chem. Soc.*, **73**, 2735 (1951).
5. L. E. Smythe, *J. Amer. Chem. Soc.*, **74**, 2713 (1952).
6. J. Dejong, and J. Dejonge, *Rec. Trav. Chim.*, **71**, 643, 661 (1952); *Chem. Abstr.*, **47**, 5775d (1953).
7. N. Landquist, *Acta. Chem. Scand.*, **10**, 244 (1956); *Chem. Abstr.*, **50**, 16314 d(1956).
8. Y. Ito, *J. Chem. Soc. Japan.* **64**, 382 (1961); *Chem. Abstr.* **57**, 3287g (1962).
9. C. Goldschmidt, *Ber.*, **29**, 2439 (1896); *Chem. Ztg.*, **21**, 460, 586 (1897).
10. E. Ludy, *J. Chem. Soc.*, **56**, 1059 (1889).
11. F. M. Litterscheid, *Ann.*, **316**, 180 (1901).
12. A. E. Dixon, *J. Chem. Soc.*, **113**, 238 (1918).
13. M. H. Van Laer, *Bull. Soc. Chim. Belg.*, **28**, 381 (1919); *Chem. Abstr.*, **16**, 2113 (1922).
14. H. Kadowaki, *Bull. Chem. Soc. Japan*, **11**, 248 (1936); *Chem. Abstr.*, **30**, 5944 (1936).
15. G. Z. Romijn, *Anal. Chem.*, **36**, 36 (1897); J. F. Walker, *Formaldehyde*, Chapman and Hall, London, 1964, p. 489.