Preparation of *n*-Butyl-2,2,3-trimethylbutanoate.—The *n*-butyl ester of 2,2,3-trimethylbutanoic acid was prepared by refluxing a solution of 229 g. of 2,2,3-trimethylbutanoic acid, 3 ml. of concentrated sulfuric acid and 400 g. of *n*-butyl alcohol for twenty-four hours with intermittent removal of the water of reaction. The product was washed successively with 10% sodium carbonate and water, and fractionated to obtain 316 g. of *n*-butyl ester, b. p. 90–91° (16 mm.), $n^{20}D$, 1.4220.

Hydrogenolysis of *n*-Butyl 2,2,3-Trimethylbutanoate to 2,2,3-Trimethyl-1-butanol.—A stainless-steel shaker tube was charged with 220 g. of *n*-butyl 2,2,3-trimethylbutanoate and 20 g. of copper chromite catalyst. After closing, the vessel was cold-pressured to 210 atm. with hydrogen and the temperature was raised and held at 269–281° over a period of six and one-half hours, during which time the pressure was maintained in the neighborhood of 1000 atm. by intermittent pressuring with hydrogen. There was a total pressure drop of 310 atm. The vessel was then cooled, bled of excess hydrogen, opened and discharged. After filtering off the catalyst, the product was distilled to give 108 g. of 2,2,3-trimethyl-1-butanol, b. p. 157–158°, $n^{20}D$ 1.4320.

Hydrogenolysis of 2,2,3-Trimethyl-1-butanol to Triptane.—A stainless-steel shaker tube was charged with 100 g. of 2,2,3-trimethyl-1-butanol and 20 g. of cobalt-on-alumina catalyst, closed, and pressured with hydrogen to 225 atm. The temperature was then raised to 300° and held in the range of 298–308° for eighteen hours, during which time the pressure dropped from a maximum of 965 atm. to 740 atm. The vessel was cooled, bled of hydrogen, discharged, and the product was filtered and dried. Distillation yielded the fractions

Fraction	Boiling point, °C.	Weight, g.	Composition
I	67–81	5.6	Foreshot
II	81–82	27.0	Triptane
III	82–157	8.0	Triptane and alcohol
IV	157–157.5	28.0	Recovered alcohol
Holdup	....	4.0	Recovered alcohol

Acknowledgments.—The Grignard synthesis of the triptane used as a reference compound in this work was carried out by Dr. J. C. Thomas, and the infrared characterization of triptane by Dr. J. R. Downing.

Summary

A method for the conversion of 2,2,3-trimethyl-1-butanol, a neopentyl-type alcohol, to the hydrocarbon trimethylbutane (triptane) has been worked out. This method involves hydrogenolysis over a cobalt catalyst at 1000 atmospheres pressure.

WILMINGTON, DELAWARE RECEIVED APRIL 5, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Urea–Formaldehyde Kinetic Studies

BY GEORGE A. CROWE, JR.,[1] AND CECIL C. LYNCH

During polarographic studies of the reaction of various substances with formaldehyde in dilute basic solutions, it was observed that the reaction of urea and formaldehyde to form monomethylolurea did not go to completion. Also, when alkali was added to a dilute solution of monomethylolurea, polarographic measurements indicated that free formaldehyde was liberated.

Smythe,[2] on the basis of kinetic studies, found that in neutral solutions the reaction of urea and formaldehyde to form monomethylolurea proceeded to more than 95% completion. The reaction was essentially bimolecular.

The kinetic study described in this paper has shown that the reaction is reversible

$$NH_2CONH_2 + HCHO \rightleftarrows NH_2CONHCH_2OH$$

In dilute basic solutions, the forward reaction was found to be bimolecular and the reverse reaction monomolecular.

Experimental

The polarographic measurements were made with an E. H. Sargent and Company Model XII Polarograph. The dropping mercury electrode was of the original Heyrovsky type.[3,4] The mercury mass, *m*, was 1.495 mg. sec.$^{-1}$, and the drop time, *t*, was 5.01 sec. in 0.05 *N* lithium hydroxide containing dissolved air, and with an open electrical circuit. The $m^{2/3}t^{1/6}$ value was 1.71.

The polarographic method for formaldehyde analysis was similar to that of Jahoda,[4,5] although 0.05 *N* lithium hydroxide was used as the supporting electrolyte instead of 0.03 *N* sodium hydroxide. The diffusion current, i_d, due to formaldehyde was proportional to the formaldehyde concentration over the range used. The half-wave potential of formaldehyde in 0.05 *N* lithium hydroxide was −1.56 volts *vs.* the mercury pool electrode, and −1.67 volts *vs.* the saturated calomel electrode.

The diffusion current constant,[6] *I*, for formaldehyde in 0.05 *N* lithium hydroxide containing dissolved air (oxygen not removed) at 25.0°, using maximum galvanometer swing values was

$$I = i_d/Cm^{2/3}t^{1/6} = 1.26$$

(where i_d is diffusion current in microamperes and *C* is concentration in millimolar solution.

The urea was J. T. Baker Analyzed, C.P. and was dried for two and one-half hours at 105°; combined moisture and volatile matter was 0.2%.

The formaldehyde was Merck and Co. neutral reagent grade. The formaldehyde content was 36.7% by the hydroxylamine hydrochloride method.[2] The solution was diluted to 0.00346 *M* for polarographic measurements.

Lithium hydroxide (Merck, lithium hydrate) was made up to 0.100 *N* by standardization against a primary sulfuric acid standard solution. Titration with the sulfuric acid solution was made to phenolphthalein and methyl orange end-points, to correct for a small amount of carbonate (less than 0.001 *M*).

Monomethylolurea was prepared by the method of Ein-

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(1) Present address, Hercules Powder Company, Experiment Station, Wilmington, Delaware

(2) Smythe, *J. Phys. Colloid Chem.*, **51**, 369 (1947).

(3) Polarographic kinetic studies for several other organic reactions are reviewed in Heyrovksy, "Polarographie," Springer Verlag, Vienna, 1941.

(4) Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N Y., 1941.

(5) Jahoda, *Coll. Czechoslov. Chem. Commun.*, **7**, 415 (1935).

(6) Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

horn and Hamburger.[7,8,9] Its melting point was 111°. Monomethylolurea was analyzed for free formaldehyde and combined formaldehyde by a modified hydroxylamine hydrochloride method as follows: 0.1800 g. of monomethylolurea (0.002 mole) was diluted to 25 ml. with distilled water; 3 drops of brom phenol blue indicator (0.4% in ethanol) and 0.30 g. of hydroxylamine hydrochloride (Eastman Kodak Co.) were added. A color standard was prepared, consisting of all reagents except monomethylolurea. The sample was titrated with standardized 0.1 N sodium hydroxide immediately to find the amount of free formaldehyde, and also from time to time to find when the reaction was complete. This reaction appeared to take place at a rate of about 3×10^{-5} sec.$^{-1}$ at 25.0°, and continued until the monomethylolurea was completely consumed. In the prepared monomethylolurea, the free formaldehyde was nil, and the combined formaldehyde was 0.00194 mole (per 0.00200 mole of monomethylolurea), indicating that the monomethylolurea contained 97% of its theoretical amount of formaldehyde.

Polarographic measurements were made by adding 2 ml. of formaldehyde solution and 1 ml. of urea solution to 3 ml. of 0.1 N lithium hydroxide, or 3 ml. of monomethylolurea solution to the lithium hydroxide solution, all solutions being kept at 25.0° by a constant-temperature bath. Timing was started from the middle of the addition of the final reagent which caused the reaction (urea or monomethylolurea). Frequent formaldehyde measurements were taken until repeated constant values were obtained, demonstrating that equilibrium was established.

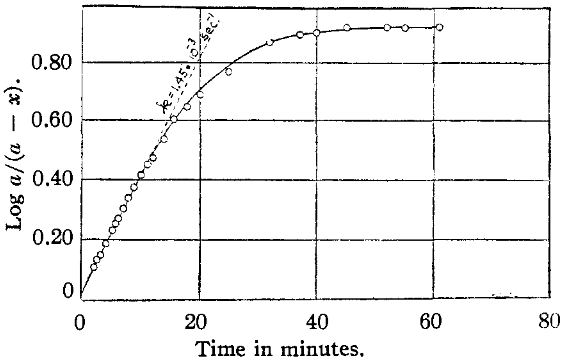

Fig. 1.—Decomposition of 0.00344 M monomethylolurea in 0.05 N lithium hydroxide solution, as measured by increase in free formaldehyde content of solution, where a is the original monomethylolurea concentration, and x is the amount of monomethylolurea decomposed at time t.

The reaction of 0.00344 M monomethylolurea to urea and formaldehyde proceeded rapidly in 0.05 N lithium hydroxide at 25°. Equilibrium was established in about forty-five minutes, with about 90% of the formaldehyde liberated. The pH was 12.7; the reaction was monomolecular as would be expected (see Fig. 1). The reaction rate was 1.45×10^{-3} sec.$^{-1}$. The equilibrium constant, as calculated from reaction rates and equilibrium values, is given in Table I. These values agreed within the limits of polarographic error (±3% of the value determined). It was assumed that the equilibrium does not undergo a shift at the surface of the dropping electrode as the formaldehyde is removed by reduction. This assumption appears justified when one considers the drop time and the measured velocity constants.

The reaction of urea with formaldehyde was studied using various amounts of urea. With molecular equivalents of urea and formaldehyde in 0.05 N lithium hydroxide, only about 10% of the formaldehyde reacted. In order to obtain a sufficient decrease in the concentration of the formaldehyde to permit accurate measurements with the polarograph, it was necessary to increase the urea concentration tenfold (Fig. 2). The second-order reaction rate (0.0297 sec.$^{-1}$) and the resulting equilibrium constant (k_F/k_R) of this reaction were in agreement with equilibrium constants calculated from equilibrium values of formaldehyde reacted with various amounts of urea (Table I). In view of these findings, it appears unlikely that much dimethylolurea was formed.

TABLE I

EQUILIBRIUM CONSTANT FOR THE REACTION $NH_2CONH_2 + HCHO \rightleftarrows NH_2CONHCH_2OH$

In 0.05 N lithium hydroxide solution at 25.0°, where K = (Monomethylolurea)/(Urea)(Formaldehyde), and K = k_F/k_R = (velocity constant for forward reaction/velocity constant for reverse reaction)

Starting substances	K
0.00356 M urea, 0.00346 M formaldehyde	26.8
.00712 M urea, .00346 M formaldehyde	24.3
.0178 M urea, .00346 M formaldehyde	28.3
.0356 M urea, .00346 M formaldehyde	27.4
.00344 M monomethylolurea	25.7
k_F/k_R = 0.0297/0.00145 =	20.5

where k_F = 0.0297 sec.$^{-1}$ and $k_R = 1.45 \times 10^{-3}$ sec.$^{-1}$

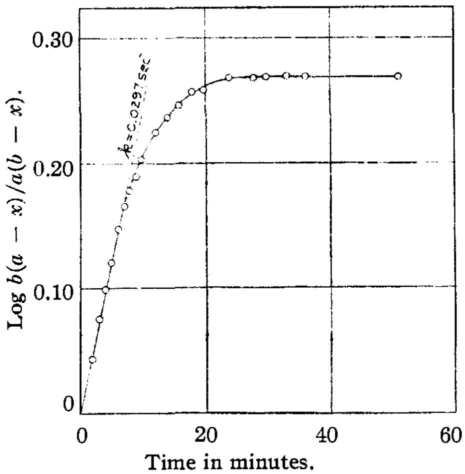

Fig. 2.—Reaction of 0.00346 M formaldehyde and 0.0356 M urea in 0.05 N lithium hydroxide solution as measured by formaldehyde content of solution, where a is the initial urea concentration, b is original formaldehyde concentration, and x is formaldehyde combining in time t. k = 0.0297 sec.$^{-1}$.

Summary

It was found that an equilibrium exists between monomethylolurea and urea and formaldehyde. Polarographic measurements indicated that in 0.05 N lithium hydroxide, about 90% of a dilute (0.004 M) monomethylolurea solution decomposed into urea and formaldehyde, the reaction being monomolecular. Reaction rates are given for the reaction in both directions, and the equilibrium constant was calculated from reaction rates and equilibrium data.

In acid solution, the monomethylolurea equi-

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[7] Einhorn, *Ann.*, **361**, 113 (1908).

[8] Einhorn and Hamburger, *Ber.*, **41**, 24 (1908).

[9] Walker, "Formaldehyde," A. C. S. Monograph 98, Reinhold Publishing Corp., New York, N. Y., 1944.

librium was shifted by removing formaldehyde with hydroxylamine hydrochloride; eventually all of the monomethylolurea was consumed, and a molecular equivalent of hydrochloric acid was liberated. This method was used to determine the amount of combined formaldehyde in monomethylolurea.

NEWARK, DELAWARE RECEIVED APRIL 28, 1948

[CONTRIBUTION FROM COATES LABORATORIES, LOUISIANA STATE UNIVERSITY]

Kinetics of the Thermal Decomposition of Isopropyl Chlorocarbonate

BY ARTHUR R. CHOPPIN AND EDGAR L. COMPERE

Earlier investigations by the senior author[1,2] have shown that the gas phase thermal decomposition of ethyl chlorocarbonate, which was studied at 150–200°, is homogeneous and unimolecular. It follows the equation

$$C_2H_5OCOCl \longrightarrow C_2H_5Cl + CO_2$$

The decomposition has been shown to occur without side reactions and a mechanism of internal rearrangement was proposed. The rate constant is given by the equation

$$k = 5.5 \times 10^{10}e^{-29410/RT}$$

This reaction appears to be one of the few uncomplicated gas reactions known, and as such furnishes valuable data for testing theory. From this viewpoint the investigation of the behavior of homologous compounds would be of interest.

Ramsperger and Waddington[3] observed that trichloromethyl chlorocarbonate decomposed into two molecules of phosgene. The reaction was found to be first order, and only a slight degree of heterogeneity was noted. The first order rate constant is given by the equation

$$k = 1.4 \times 10^{13}e^{-41500/RT}$$

The only other investigation of the kinetics of chlorocarbonate decomposition is that of Lessig,[4] who reports two rate determinations in a constant volume apparatus on isobutyl chlorocarbonate. At 267° he observed a half life of 160 min. and a $^3/_4$ life of 380 min. At 302° a half life of 16 min. and a $^3/_4$ life of 35 min. was reported. The final pressure was more than twice the initial, indicating decomposition into more than two particles. A graph, in which time was plotted against the logarithm of the difference between final and observed pressures, gave a straight line, indicating a first order reaction. From these data an approximate equation for the first order rate constant may be developed

$$k = 1 \times 10^{13}e^{-40000/RT}$$

Other chlorocarbonates decompose to yield a variety of products. Merck[5] has reported that tertiary amyl chlorocarbonate decomposed at room temperature with evolution of gas. Choppin and Rogers[6] found that liquid α-phenylethyl chlorocarbonate decomposed, when held at 100° for a short time, yielding α-phenylethyl chloride, carbon dioxide, styrene and hydrogen chloride. Aromatic chlorocarbonates decompose into phosgene and the aromatic carbonate, according to Bowden.[7]

It is planned to investigate the decomposition kinetics of various chlorocarbonates. Methyl, ethyl, isopropyl and tertiary butyl chlorocarbonate are of particular interest since they permit a study of the effect of increased methylation of the alpha carbon atom. This paper reports a study of the kinetics of the thermal decomposition of isopropyl chlorocarbonate.

Experimental

Eastman Kodak Co. isopropyl chlorocarbonate was purified by fractionating at 200 mm. pressure through a 40-inch adiabatic glass column packed with $^5/_{32}$ inch glass helices. A fraction taken between 66–67° was treated several hours with phosphorus pentoxide. This treatment, which is believed to remove alcoholic impurities, was necessary in order to obtain a high final purity in the chlorocarbonate. The treated cut was redistilled, and the middle portion of a fraction boiling at 66.3° (200 mm.) was used in this investigation. Analysis of this material for chlorine indicated a purity of 99.4% or better. Isopropyl carbonate, b. p. 147°,[8] found as an impurity in the original sample boiled at 102.6° at 200 mm. pressure.

The decomposition was first studied in the static apparatus described elsewhere[1,9] in which the decomposition is followed by observing pressure changes in an all-glass system. Decomposition was observed at 220–232°. Graphs of time *versus* the logarithm of the difference between final pressure and observed pressure, gave good straight lines, which indicated a first order reaction. A curvature of the plot during the early part of the run possibly indicated a more rapid initial rate, but it was difficult to separate this effect from that due to temperature rise occurring as the reaction vessel was immersed in the thermostat to initiate the reaction.

The results of the various static runs are summarized in Table I. An examination of the data indicates that the ratio of initial to final pressures is always greater than two, but is relatively constant between 2.45 and 2.52. This would indicate that more than two reaction products were present and that probably two or more reaction mechanisms were also involved in the decomposition. The last two runs which were made in cells packed with glass wool show a materially increased rate constant indicating a cata-

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(1) A. R. Choppin, H. A. Frediani and G. F. Kirby, THIS JOURNAL, **61**, 3176 (1939).

(2) A. R. Choppin and G. F. Kirby, *ibid.*, **62**, 1592 (1940).

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(5) E. Merck, German Patent 254,471 (1913).

(6) J. W. Rogers, Master's Thesis, Louisiana State University, 1942.

(7) S. T. Bowden, *J. Chem. Soc.*, 310 (1939).

(8) P. N. Kogerman and J. Kranig, *Chem. Abst.*, **21**, 1729 (1927).

(9) F. Daniels, "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1939.