against running distilled water until the dialysate was free of ammonia when tested with Nessler reagent. The solution was brought to *p*H 4.5 with hydrochloric acid. The precipitate was centrifuged and washed as in the previously described method. These products were air-dried, and ground to pass a 60-mesh screen.

The products were analyzed for total nitrogen by the Kjeldahl method, and for amino nitrogen by the Doherty and Ogg[7] modification of the Van Slyke method. Arginine was determined by the Sakaguchi method on a total hydrolysate of the protein; the reagents and conditions developed by MacPherson[8] were used. The presence of the other amino acids in the hydrolysate results in high arginine values by this procedure but the values obtained on a more extended series are sufficient to show that we get a proportionate increase in guanidine groups as the free amino groups are substituted. These analyses for the control and samples 1 and 2, respectively, are: total nitrogen, 14.97, 15.66 and 16.38; amino nitrogen, 0.91, 0.37 and 0.06; and apparent arginine, 5.53, —, 18.97.

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(7) D. G. Doherty and C. L. Ogg, *Ind. Eng. Chem., Anal. Ed.*, **15**, 751 (1943).

(8) H. T. MacPherson, *Biochem. J.*, **40**, 470 (1946).

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Kinetics of the Decomposition of Solid Mercurous Formate

BY GEORGE A. MILLER AND GEORGE W. MURPHY

The decomposition of solid mercurous formate into mercury, formic acid and carbon dioxide has been known for more than a century,[1] although no rate studies have been reported to date. In a kinetics study of this reaction, the present authors have found some interesting features.

Experimental

Preparation of Sample.—Mercurous formate was prepared by precipitation from a mixture of solutions of mercurous nitrate and sodium formate. In order to obtain a product of optimum purity, a fairly detailed technique was developed, which involved precipitation at −10° with a saturated solution of mercurous nitrate, slightly acidified with nitric acid, and an aqueous solution of sodium formate. Sufficient ethanol was added to prevent freezing. Previous experience had shown that precipitates obtained at room temperature had a grayish tint, which indicated that some decomposition had occurred. No evidence of decomposition appeared when the precipitation was carried out at low temperatures.

The precipitates were dried in a vacuum desiccator over calcium chloride or anhydrous sodium sulfate at room temperature. It is likely that the dehydration achieved by this method was never quite complete; drying at elevated temperatures, however, was obviously out of the question.

Analyses.—Analyses were performed on both the reactant and products, in order to verify the equation of decomposition. The mercury in a sample of mercurous formate was determined gravimetrically as mercurous chloride. A substantial sample of reaction products was obtained by decomposing a 3.5-g. sample of mercurous formate. The gaseous product was analyzed for carbon monoxide and carbon dioxide by standard methods, using the Francis Auto-bubbler type pipet. The water-soluble residue was titrated with sodium hydroxide, and the residual mercury was weighed.

The results are in agreement with a molecular formula for the formate of $HCOOHg \cdot H_2O$, contrary to reports of earlier workers, who write the formula $HCOOHg$. Furthermore, it will be seen that the kinetic data support the water of crystallization formula. The analyses show that the overall reaction is probably exclusively

$$2HCOOHg \cdot H_2O = HCOOH + CO_2 + 2Hg + 2H_2O$$

The gaseous product was found to be entirely CO_2, and in the correct amount indicated by the stoichiometry. Keller and Körösy[2] found that both silver formate and cuprous formate decompose with the evolution of equal parts of hydrogen and carbon dioxide. These authors also noted that the salts were somewhat volatile. In mercurous formate we have found no evidence of either hydrogen evolution or volatility, although our method was not sensitive to the latter phenomenon.

Kinetics.—The progress of the reaction was followed by measuring the volume of gas evolved as a function of the time. A Pyrex sample tube of 2-ml. capacity was connected through ground-glass joints and capillary tubing to an ice-trap and thence through rubber tubing to a 10-ml. buret with attached leveling bulb. Mercury was used as the confining liquid. The sample was held at a constant temperature ±0.15° in a small mineral oil-bath equipped with a motor stirrer and a Fenwal "Thermoswitch" control. Early experiments above 100° resulted in minor explosions of the sample. Thereafter, the highest temperature tried was 94°, where the reaction proceeded smoothly. Most runs were made at 80°. Samples were normally about 0.15 g., so selected as to yield a total of about 10 ml. of gas for measurement.

Results of Kinetics Studies

A definite though short induction period was observed in all runs on the pure solid material. As soon as the induction period was over, the reaction followed first order kinetics (Fig. 1). Additions of small amounts of mercury and of formic acid to the starting material had little effect on either the induction period or the rate of decomposition. Strong irradiation of samples by an AH-4 mercury vapor lamp had no observable effect on the reaction. On the other hand, the addition of one drop of water completely removed the induction period, changed the order from first to zero, and greatly accelerated the decomposition.

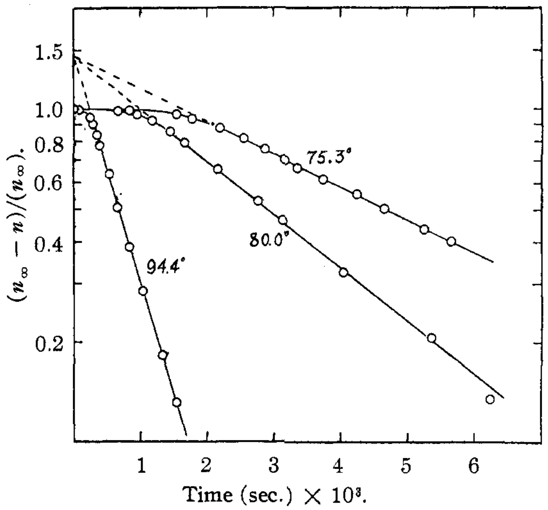

Fig. 1.—Rate data for decomposition of pure solid at three temperatures on semi-log plot.

We conclude tentatively from these results that water is the autocatalyst responsible for the induction period in the decomposition of the pure solid. The zero order kinetics observed with water is probably due to the limited solubility of mercurous formate. Apparently the chemically bound water in solid mercurous formate is not active in promoting decomposition. The reaction probably occurs at the interface between solid mercurous

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(1) Liebig, *Ann.*, **3**, 207 (1832).

(2) A. Keller and F. Körösy, *Nature*, **162**, 580 (1948).

formate and unbound water in the liquid or gaseous state

$$2HCOOHg \cdot H_2O + H_2O = HCOOH + CO_2 + 2Hg + 3H_2O$$

A trace of water on the crystal or in the vapor is sufficient to start the reaction, and the extra water released makes the decomposition of additional molecules of formate possible.

In order to interpret the rate data on the pure solid, we set up the following tentative mechanism: The reaction occurs heterogeneously between the crystal and water either in the vapor or the liquid phase. The amount of reaction which has occurred during the induction period is so small that we can consider the activity of the formate unchanged, and the rate controlled entirely by the changing partial pressure of water. After the induction period, the partial pressure of water is constant and equal to the saturation value, and the rate will be controlled only by the activity of the formate.

A mathematical analysis based on this mechanism leads to the equations

$$\log \frac{n}{n_\infty} = \frac{kp^0 n_\infty t}{2.303\ n_\tau} - \frac{kp^0 n_\infty}{2.303\ n_\tau} + \log \frac{n_\tau}{n_\infty} \quad t \leq \tau \quad (1)$$

and

$$\log \frac{n_\infty - n}{n_\infty} = -\frac{kp^0 t}{2.303} + \frac{kp^0 \tau}{2.303} + \log \frac{n_\infty - n_\tau}{n_\infty} \quad t \geq \tau \quad (2)$$

where

n = moles of CO_2 produced at any time, t
n_τ = moles of CO_2 produced at time τ, the end of the induction period
n_∞ = moles of CO_2 produced at end of reaction
p^0 = saturation vapor pressure of water

Equation 2 expresses mathematically the required first order rate law, where the apparent rate constant is seen to be equal to kp^0. These apparent rate constants vary much more sharply with temperature than required by the Arrhenius equation. Vapor pressures for the three temperatures studied can, however, be estimated from the data of Takagi,(3) and values of k can thus be determined. Sufficient data are not available for an exact treatment, but the composition of the vapor is close enough to that of the constant boiling mixture so that we may approximate the actual vapor pressure by the latter. The results, given in Table I, show that in all three cases the saturation pressure is below the partial pressure indicated by the stoichiometry, and condensation will therefore occur. Values of k thus derived obey the Arrhenius equation. This in itself constitutes some verification of our proposed mechanism. The activation energy is 16.6 ± 1 kcal.

TABLE I

SUMMARY OF RATE DATA

t, °C.	p^0, atm.	k (atm.$^{-1}$ sec.$^{-1}$) × 10^3
75.3	0.30	0.76
80.0	.36	1.00
94.4	.62	2.54

Other points to be noted on examination of the data in the light of Equations 1 and 2 are the following: (1) During the induction period, experimental values of $\log n/n_\infty$ are a linear function of t, as required by Equation 1. (2) Values of τ and n_τ/n_∞ derived from slopes and intercepts of both equations are self consistent at all temperatures. (3) Derived values of τ are strictly proportional to the product kp^0. (4) Within the limits of error, n_τ/n_∞ is the same for all temperatures. Its value is 0.11. In other words, the induction period is over when 11% decomposition has occurred, regardless of temperature. (5) The fact that consistent values of k (or more accurately kp^0) are obtained through both Equations 1 and 2 is evidence that precisely the same reaction is occurring before and after the induction period, as required by the proposed mechanism.

Thus the proposed mechanism seems amply verified not only by the observed effect of water on the reaction, but also by the excellent fit of the data to equations derived on the basis of the mechanism, the consistency of constants obtained from the equations, and the agreement of the actual rather than the apparent rate constants with the Arrhenius equation. On the other hand, we have not attempted to consider in detail the disintegrating crystal lattice during the induction period, and the mechanism cannot therefore be established at this time as unique.

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(3) Takagi, *Bull. Chem. Soc. Japan*, **14**, 508 (1939).

Bis-(substituted phenoxy)-methanes[1]

BY SIMON MIRON[2] AND ALEXANDER LOWY[3]

Varying yields, generally below 45%, have been reported in the literature for the Williamson-type synthesis between alkali-metal phenolates and methylene halides to produce bis-(substituted phenoxy)-methanes. The following procedure was employed to give consistently good yields of these compounds:

A methanolic solution of sodium hydroxide of normality approximately 1 was used to convert the phenols to their sodium salts. This solution was standardized prior to each synthesis by titration against standard acid. A weighed quantity of the pure phenolic compound was neutralized with the theoretical quantity of alkali in a round-bottom reaction flask. After removal of the methanol by distillation under reduced pressure, the equivalent amount, or slightly less, of pure methylene iodide was added to the flask, together with enough 3-methylbutanol to keep the reactants in solution at reflux temperature, and the mixture was refluxed for two to twelve hours. Following the reflux period, solvent was removed under reduced pressure and the crude residue was partially purified by repeated treatment with boiling aqueous potassium hydroxide solution (0.5–1.0%), until the alkaline extracts gave no phenolic precipitate upon acidification. The product was then washed free of alkali, dried and crystallized from a suitable solvent.

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(1) Taken from Part I of the dissertation presented by Simon Miron in August, 1941, in partial fulfillment of the requirements for the Ph.D. degree.

(2) Pan American Refining Corporation, Texas City, Texas.

(3) Deceased December 25, 1941.