Summary

1. Two diastereoisomeric forms of carbonato di-*l*-propylenediamine cobaltic carbonate have been prepared by a Walden inversion method. The inverted form is unstable in hot water, being converted to the more stable non-inverted form.

2. Rotatory dispersion curves have been made for *cis*-dichloro-di-*l*-propylenediamine cobaltic chloride and for the two diastereoisomeric forms of carbonato di-*l*-propylenediamine cobaltic carbonate. By comparison of these curves with those for analogous compounds in the diethylenediamine series, it has been possible to determine which of the two carbonato forms is obtained by an inversion about the central cobalt atom in the latter case.

3. A mechanism for the production of the two forms of the carbonato complex has been advanced. The non-inverted form is produced through the preliminary displacement of the chloride ions in the *cis*-dichloro-di-*l*-propylenediamine cobaltic chloride by water molecules, followed by the displacement of the water molecules by carbonato groups. The inverted form is produced by direct substitution of the carbonato group for the chloride ions within the complex. It was found possible by varying the reaction conditions on the basis of this mechanism to produce either form with either silver carbonate alone or potassium carbonate alone. Further it was found possible to produce the inverted form of carbonato diethylenediamine cobaltic carbonate with potassium carbonate for the first time.

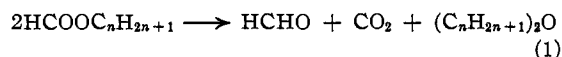## Kinetics of the Thermal Decomposition of Ethyl Formate

BY R. F. MAKENS[1] AND W. G. EVERSOLE

The vapor phase decomposition of ethyl formate in the absence of catalysts, other than the glass used as containers, has not been investigated extensively. Sabatier and Mailhe[2] found no appreciable decomposition when ethyl formate was passed through a glass tube at 400°. At 300° in a sealed flask the decomposition of this ester was reported by Engler and Grimm.[3] Hurd[4] states, "The esters with the general formula RCOOCH₂CH₂R should decompose into free acid and olefin." If this explanation is correct, ethyl formate should yield formic acid or its decomposition products and ethylene. The gases found by Engler and Grimm[3] were in accord with this theory; however, the amounts of the various constituents which they found varied greatly from those required by the reaction. Sabatier and Mailhe,[2] Pearce and Wing[5] and others have shown that this reaction does not predominate in the presence of any one of several different catalysts. Sabatier and Mailhe[2] found that the vapors of formic esters may decompose in two ways

$$2HCOOC_nH_{2n+1} \longrightarrow HCHO + CO_2 + (C_nH_{2n+1})_2O \quad (1)$$

$$HCOOC_nH_{2n+1} \longrightarrow CO + C_nH_{2n+1}OH \quad (2)$$

This paper reports quantitative data on the thermal decomposition of ethyl formate. The data permit the calculation of the order of the principal primary reaction and its energy of activation. Evidence of the other associated reactions including those given above also is presented.

Experimental

Materials.—Ethyl formate (Eastman Kodak Co.) was dried and distilled in a packed column, and the resultant product was redistilled. It was found that the middle portion, which was the part used in the investigation, boiled at 54.20–54.26° (corr.). The density was d^{25}_4 0.9055 and the refractive index $n^{25}D$ 1.3582.

Apparatus and Procedure.—The apparatus, a modification of that used by Thompson and Frewing,[6] was of the static type. The reaction vessel consisted of a 220-cc. Pyrex flask. For the rapid removal of gaseous decomposition products a large Toepler pump was provided. Liquid products were condensed by passing through a carbon dioxide–acetone trap and subsequently allowing the temperature to reach −10°. The resulting vapor was added to the main gas sample, while the remainder of the liquid was analyzed by micro-methods. A mercury vapor pump backed by a Hyvac oil pump comprised the evacuation equipment. Pressures in the system were reduced

(1) Present address: The Michigan College of Mining and Technology, Houghton, Michigan.

(2) Sabatier and Mailhe, *Compt. rend.*, **154**, 49–52 (1912).

(3) Engler and Grimm, *Ber.*, **30**, 2922 (1897).

(4) Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Company, New York, N. Y., 1929, p. 525.

(5) Pearce and Wing, *J. Phys. Chem.*, **36**, 709 (1932).

(6) Thompson and Frewing, *J. Chem. Soc.*, 1444 (1935).

to 0.2 micron or less before each run. During a run the pressures were read on an ordinary manometer connected through a heated capillary manometer to the reaction flask.

The furnace was controlled to ±0.3° by a circuit described by Zabel and Hancox.[7] A modified Orsat apparatus equipped with a flushing manifold was used for the gas analysis.

Cleaning of the reaction flask was effected by hot concentrated nitric acid and water followed by drying and evacuation at 450°.

Results

The decomposition of ethyl formate was very slow at 300°. Two runs were made; one at an initial pressure of 39.05 cm. and one at 39.86 cm. In the first run the pressure increase in thirty hours was 2.83 cm. and the volume of gaseous products was 5.85 ml.; in the second run the pressure increase was 2.92 cm., and the volume of gaseous products was 5.70 ml. The same gaseous decomposition products were present at all temperatures. The liquid product gave a very weak aldehyde test with Schiff reagent. Fractional distillation of the liquid product according to Emich and Schneider[8] permitted the identification of ethyl formate and water.

At 375° the decomposition rate was satisfactory, but at 350° it was much too slow. Table I shows the data for two duplicate series of decompositions made without disturbing the reaction flask.

TABLE I

GASEOUS PRODUCTS FROM ETHYL FORMATE
DECOMPOSITIONS AT 375°

Time, hours	2	4	6	8	10	30
Ml. of CO_2	1.5	2.6	3.7	4.0	4.1	11.0
Ml. of higher unsatd.	0.2	0.3	0.5	0.7	0.6	1.6
Ml. of C_2H_4	14.8	23.5	27.8	31.4	33.3	34.2
Ml. of H_2	0.8	1.7	2.3	3.2	3.7	10.2
Ml. of CO	3.6	10.6	16.2	21.8	25.3	32.1
Ml. of CH_4	0.3	0.6	0.4	0.4	0.5	0.5
Ml. of C_2H_6	0.1	0.2	0.2	0.2	0.1	0.5
Ml. of total gas	21.3	39.4	51.3	61.7	67.6	90.1
Initial pressure	38.8	38.0	37.8	38.8	38.5	37.9
Final pressure	51.3	61.0	68.9	75.5	78.2	86.3
Ml. of C_2H_4 formed[a]	15.0	24.3	29.2	32.4	34.3	37.7
$(a - x)$[b]	22.7	13.4	8.5	5.3	3.4	0.0

[a] Corrected for an average initial pressure of 38.3 cm.
[b] Maximum volume of ethylene formed minus the volume formed in the time interval given.

The polymerization of ethylene to butylene, noted by Storch,[9] no doubt accounts for the

(7) Zabel and Hancox, Rev. Sci. Instruments, 5, 28 (1934).
(8) Emich and Schneider, "Microchemical Laboratory Manual," John Wiley and Sons, Inc., New York, N. Y., 1932, pp. 34-38.
(9) Storch, THIS JOURNAL, 57, 2601 (1935).

presence of the higher unsaturates. Thus the total ethylene originally formed would equal the volume found plus twice the volume of higher unsaturates.

The production of ethylene conforms to a first order reaction as shown by plotting the logarithms of the values of $(a - x)$ in Table I against time. The liquid products contained ethyl formate, water, formic acid, and a small amount of some aldehyde. After distilling off and discarding the more volatile portion, the formic acid was identified in the residue by forming the cerous derivative and observing these crystals under crossed nicols.[10] The presence of an aldehyde was established by the use of Schiff reagent, which produced a weak reaction.

In like manner, without disturbing the reaction flask, two duplicate series of runs were made at 425°. The data reported in Table II are the average of these duplicate runs.

The production of ethylene at 425° conforms to a first order reaction as was shown in the previous instance. At 425° and at 375° the liquid decomposition products were also qualitatively identical. The specific velocity constants calculated from the data in Tables I and II are $K_{375°} = 0.824 \times 10^{-4}$ and $K_{425°} = 7.61 \times 10^{-4}$. The energy of activation calculated by substitution of these constants in the Arrhenius equation is 40,010 cal. The value of K from four duplicate runs made at 400° is 2.441×10^{-4}. Log K plotted against the reciprocal of the absolute temperature produces a straight line.

Preliminary work proved that the method of cleaning the reaction flask had a very decided effect on the rate of formation of carbon monoxide, carbon dioxide and hydrogen, but had no effect on the rate of formation of ethylene. This observation is in agreement with Hinshelwood, Hartley and Topley[11] who noted that the decomposition of formic acid varied with the nature of the glass surface. To avoid the difficulty the data were all obtained without disturbing the reaction flask.

Discussion

The principal primary reaction in the decomposition of ethyl formate produces ethylene by a reaction which is represented by the first order

(10) Emich and Schneider, "Microchemical Laboratory Manual," John Wiley and Sons, Inc., New York, N. Y., 1932, p. 121.
(11) Hinshelwood, Hartley and Topley, Proc. Roy. Soc. (London), A100, 575-577 (1922).

TABLE II

GASEOUS PRODUCTS FROM ETHYL FORMATE DECOMPOSITION AT 425°

Time, hours	0.25	0.50	0.75	1	1.333	2	4	8
Ml. of CO_2	1.8	2.3	5.0	4.4	4.6	8.6	9.0	13.7
Ml. of higher unsatd.	0.4	0.6	0.6	1.0	1.1	1.1	1.4	2.0
Ml. of C_2H_4	18.4	30.2	34.0	35.6	36.7	38.4	37.8	36.9
Ml. of H_2	0.8	1.5	3.5	2.7	3.3	6.4	6.6	11.7
Ml. of CO	2.3	8.0	10.6	14.7	17.2	21.0	28.3	29.5
Ml. of CH_4	0.4	0.6	0.4	0.7	0.7	0.8	0.7	0.9
Ml. of C_2H_6	.1	.1	.2	.3	.3	.3	.7	1.0
Total	24.2	36.1	54.3	59.4	63.9	76.6	84.5	95.7
Initial pressure	38.3	39.8	39.3	38.0	38.6	39.2	38.9	39.6
Final pressure	55.9	66.4	72.1	75.9	78.8	84.6	89.7	94.6
Ml. of C_2H_4 formed[a]	19.5	30.7	34.8	38.4	39.2	40.3	40.6	40.4
$(a - x)$[b]	20.9	9.7	5.6	2.0	1.2	0.0	0.0	0.0

[a] Corrected to an average initial pressure of 38.9 cm.   [b] Maximum volume of ethylene formed minus the volume formed in the time interval given.

equation. The greater part of the carbon monoxide and carbon dioxide must be produced by secondary reactions, as can be seen by an inspection of Fig. 1. (A similar curve is obtained by plotting the corresponding data from Table II.) Since the curves do not pass through the zero point, as shown by plotting according to the method of least squares, and since the final ratio of carbon monoxide and carbon dioxide to ethylene is greater than one, one or more minor primary reactions simultaneous with the principal primary reaction are present. The fact that the ratio of carbon dioxide to carbon monoxide was greater at the earlier stages of the decomposition suggests that at least one of these minor reactions produces carbon dioxide.

The reaction suggested by Hurd[4] in which the ethyl formate decomposes to form ethylene and formic acid is confirmed. Formic acid was identified in the liquid products; the production of carbon monoxide, carbon dioxide and hydrogen paralleled the decomposition of formic acid as observed by Hinshelwood, Hartley and Topley,[11] and by Nelson and Engelder.[12]

The minor primary reactions are probably those designated (1), (2) in this paper. Sabatier and Mailhe,[2] Senderens[13] and Pearce and Wing[5] have shown that these products are formed when ethyl formate is passed over various heated catalysts. These reactions and their secondary decomposition products account for the excess of carbon monoxide plus carbon dioxide over ethylene in the final runs, for part of the pressure change, for the small amounts of methane formed, and for the higher ratio of carbon dioxide to car-

(12) Nelson and Engelder, *J. Phys. Chem.*, **30**, 470 (1926).
(13) Senderens, *Compt. rend.*, **196**, 979 (1933).

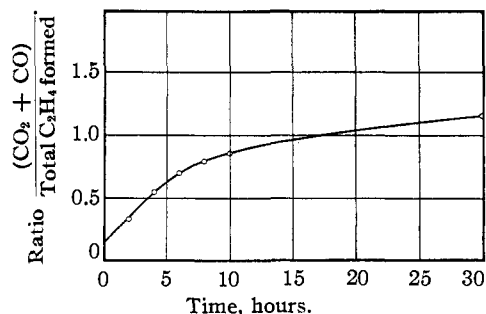bon monoxide in the shorter than in the longer runs.

Fig. 1.—The ratio of carbon monoxide plus carbon dioxide to the total ethylene formed at 375°.

If the principal reactions continued to completion and if no other reactions were present, the pressure theoretically would be tripled and the ratio of carbon monoxide plus carbon dioxide to ethylene formed would be one. Several factors contributed to a pressure ratio lower than would be predicted by these assumptions. The dead space in the apparatus used was about 2.3%. This would alter the theoretical pressure ratio from 3.0 to less than 2.9 when calculated on the basis of the equation developed by Allen.[14] The minor primary reactions postulated would produce less than three moles of product per mole of ethyl formate. Figure 1 indicates that the decomposition of the formic acid may not have been complete; the acid reaction of the final liquid decomposition products supports this assumption.

Summary

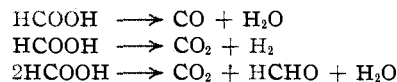1. The decomposition of ethyl formate has been shown to be very slow at 300°. At 375,

(14) Allen, THIS JOURNAL, **56**, 2053 (1934).

400, and at 425° the reaction rates were determined for the principal primary reaction. Evidence is presented concerning the other reactions involved.

2. The principal primary reaction is shown to be

$$HCOOC_2H_5 \longrightarrow C_2H_4 + HCOOH$$

This is followed by the decomposition of formic acid

$$HCOOH \longrightarrow CO + H_2O$$
$$HCOOH \longrightarrow CO_2 + H_2$$
$$2HCOOH \longrightarrow CO_2 + HCHO + H_2O$$

3. Evidence is presented that minor primary reactions occur, and the nature of these reactions is suggested.

4. Calculated from the present data, the energy of activation of the reaction producing ethylene is 40,010 cal.

HOUGHTON, MICHIGAN   RECEIVED AUGUST 10, 1939

Vapor-Liquid Equilibrium. IV. Carbon Tetrachloride-Cyclohexane Mixtures[1]

BY GEORGE SCATCHARD, S. E. WOOD AND J. M. MOCHEL

In the third paper of this series,[2] we showed that benzene–cyclohexane mixtures have an entropy increase on mixing which is larger than that of an ideal solution even at constant total volume, and which we attributed tentatively to some lack of randomness in at least one of the pure liquids. Since earlier calculations[3] had given no indication of such an effect for benzene–carbon tetrachloride mixtures, and since cyclohexane has an unusually small entropy of fusion, we have next studied carbon tetrachloride–cyclohexane mixtures. Although there is a slight excess entropy of mixing at constant total volume, it is less than a tenth of that for benzene–cyclohexane mixtures. Mixtures of cyclohexane with carbon tetrachloride agree with simple theory in every respect more closely than do those with benzene.

The cyclohexane was purified as in III. Merck c. p. carbon tetrachloride was refluxed for eleven hours with an aqueous solution 10% in potassium permanganate and 10% in sodium hydroxide. The carbon tetrachloride was distilled off, dried with calcium chloride and rectified in the column described in Paper III. The boiling points of the products and of the rejected portions were measured in a small Cottrell apparatus with a five-junction thermocouple. The normal boiling points, which should be used for relative values only, are:

	CCl₄	Product	76.69
Tops	75.93	76.54 76.67	76.69
Bottoms	76.72	76.69 76.68	
	C₆H₁₂	Product	80.73
Tops	79.29	80.41 80.69	80.68
Bottoms	82.64	80.99 80.74	

The gas heater for the equilibrium still was replaced by an electrical heater with a Variac control which greatly increased the accuracy of the regulation of the boiling. To prevent direct radiation to the thermometer, the bottom of the glass still is painted with black stovepipe enamel which is renewed when necessary. A hood of aluminum foil is placed over the top of the still, and for temperatures of 60° or higher a shield of aluminum foil is placed around the still. This protection prevents the increase of material in the inner boiler during the runs at high temperatures, but does not affect the decrease during the low temperature runs.

The thermocouple was recalibrated from 60 to 100° as before by measuring the vapor pressure of water and determining the temperature from this pressure by the equation of Smith, Keyes and Gerry,[4] and the low temperature calibration was checked by a determination of the transition point of sodium sulfate decahydrate. Measurements of the vapor pressure of cyclohexane agreed with those with the gas heated still except at 30 and 35°. Apparently there had been radiation from the flame to the thermometer which cancelled out at those temperatures at which the calibration had also been carried out in the still. So the measurements for benzene at 30, 35 and 40° were repeated, and new equations were derived for cyclohexane and benzene. The equations are

$$CCl_4: \quad \log p_1 = 6.68148 - 1045.022/T - 99,577/T^2$$
$$C_6H_{12}: \quad \log p_2 = 6.65859 - 1040.641/T - 104,865/T^2$$
$$C_6H_6: \quad \log p_3 = 6.66457 - 1007.742/T - 116,197/T^2$$

($T = t + 273.16$.) The standard (root mean square) deviations are 0.5, 1.3 and 1.5 × 10⁻⁴, respectively. The normal boiling point of carbon tetrachloride is 76.68₇°. Timmermans and Martin[5] give 76.75. The new boiling points of cyclohexane and benzene are 80.73₉ and 80.10₅°, which are 0.004 lower and 0.005° higher than our former values. The values of the vapor pressures of these three substances at rounded temperatures are given in Table II.

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, September 14, 1939.

(2) I and II are published in THIS JOURNAL, 60, 1275, 1278 (1938), and III in J. Phys. Chem., 43, 119 (1939).

(3) George Scatchard, Trans. Faraday Soc., 33, 160 (1937).

(4) L. B. Smith, F. G. Keyes and H. T. Gerry, Proc. Am. Acad. Arts and Sci., 69, 137 (1934).

(5) J. Timmermans and F. Martin, J. chim. phys., 23, 747 (1926).