der this assumption, comparison of reduction of cations in differing solvents can be made by noting the difference, $\Delta E_{1/2}$, between the potassium half-wave potential and the half-wave potential of the particular metal. This is at least a reasonable approach to absolute comparison of half-wave potentials. Tabulation of these data for acetonitrile and aqueous solutions (non-complexing supporting electrolyte) shows several interesting points. Of the ions studied (outside of the alkali metals) the $\Delta E_{1/2}$ values are most similar for thallium, 1.70 v. in acetonitrile and 1.66 v. in water. This is reasonable when one considers that thallous ion does not form complex ions and presumably is not highly solvated, or at least the degree of solvation is the same in water as in acetonitrile.

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IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF ARKANSAS]

The Neutral and Acid Hydrolysis of Ethyl Dibromoacetate in Acetone–Water Solvents[1]

BY FREDERICK N. HORNYAK AND EDWARD S. AMIS

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The neutral and acid hydrolysis of ethyl dibromoacetate was carried out at three temperatures and in water–acetone solvents containing various percentages of acetone. In the neutral hydrolysis the acid formed produced a departure from the first-order law at greater than 8% reaction. The acid-catalyzed runs followed the pseudo first-order law strictly for at least 85% of completion of reaction. The parameters of the Arrhenius equation are presented and discussed. The dependence of the rates on the dielectric constant of the media is compared with that of the acid hydrolysis of ethyl dichloroacetate in acetone–water solvent.

Introduction

As part of the general problem of the effect of solvent and molecular substituent changes upon reaction rate in solution, a study of the neutral and acid-catalyzed hydrolysis of ethyl dibromoacetate was carried out.

Experimental

Materials.—All water was twice distilled; the last distillation employed alkaline potassium permanganate. The water was then boiled to ensure carbon dioxide removal and was stored and delivered from vessels protected with ascarite tubes.

A. C. S. reagent grade acetone was purified according to the procedure of Åkerlöf.[2]

Ethyl dibromoacetate (product of Sapon Laboratories, Inc.) was washed briefly with concentrated sodium bicarbonate and then with calcium chloride solution. After drying over drierite, distillation at 14.5 mm. gave the ester with b.p. 81–82.5° (reported[3] 66–70° at 7 mm.); d^{22} 1.9081; $n^{22}\text{D}$ 1.4973; $n^{12.5}\text{D}$ 1.5018 (reported[4] d^{20}_{20} 1.9025; $n^{12.5}\text{D}$ 1.50167). Observed molar refraction and neutralization equivalent were 37.72 and 244 ± 2, respectively (calculated 37.86 and 246).

Barium hydroxide solutions, 0.002500 and 0.02500 *N*, were made up periodically from concentrated stock solution and were checked frequently against aliquots of standard potassium acid phthalate solutions. The hydrochloric acid solution was 0.3700 *N*. C.P. chemicals were used and all normalities were determined to four significant figures.

Methods and Apparatus.—Reaction temperatures were kept constant to ±0.03° and were determined with a NBS thermometer.

All pipets and burets were calibrated.

Hydrolysis were carried out in glass-stoppered 100-ml. volumetric flasks. By lightly greasing the stoppers (Fisher Rubber Compound Stopcock Lubricant) and fastening them down with rubber bands evaporation of solvent was made negligible. The grease was insoluble and had no apparent effect.

The reaction solution for a kinetic study was prepared as follows. Appropriate amounts of acetone, water and hydrochloric acid (if any) were weighed into a tared volumetric flask. The flask was then stoppered and placed in the constant temperature bath for several hours to reach thermal equilibrium. Weighings were made to 0.02 g. and the weight of hydrogen chloride (if any) was taken into account when calculating the weight of water present. The reaction was started by adding 10.00 ml. of a standard acetone–ester solution and adjusting to the mark with water at the temperature of the experiment. The flask was then shaken and the time noted. At convenient intervals 10.00-ml. samples were withdrawn, run into 25 ml. of ice-cold water and titrated with standard base. Sufficient accuracy in the times of starting and of sample withdrawal was easily attained because of the slowness of the reaction. The actual sample volume delivered by the pipetting procedure was checked by weight and also by titration and allowance was made in subsequent calculations.

The concentration of ester in all runs was 0.0500 molar and the concentration of hydrochloric acid in the acid runs was 0.0500 molar. The acetone percentages employed are shown in the tables of results.

In this work it was found that the standard base, during the titration of an ice-cold reaction sample, reacted in part with unhydrolyzed ester giving an acid value that was too high. It was found that identical samples of reaction mixture gave widely different acid values depending on the strength of the base used; the stronger base gave the highest value. In the titration of standard acid with standard base the addition of pure ester and acetone vitiated the results even under ice-cold conditions. An ester solution alone, without the presence of acid showed a zero acid value on titration with standard base (immediate end-point).

Because of these facts it was necessary to standardize the titration procedure and determine the errors involved. The titrating base solution was run in always at approximately the same rate and the reaction sample was stirred constantly in an ice-bath.

A series of mixtures of standard acid phthalate, acetone, water and ester were made up to correspond to compositions which would be obtained for titration at various stages of reaction. These mixtures were freshly made up and titrated ice-cold in the same manner as the actual run samples. The errors obtained were reproducible and found for acid hydrolyses to be a linear function of the amount of unhydrolyzed ester present. These corrections were applied to the actual run titrations to determine the true amount of acid present.

The acid runs employed the stronger 0.02500 *N* base and the titration error was about 5% in the early stages of reaction where the amount of unhydrolyzed ester is large.

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(1) The authors wish to thank the National Science Foundation for a grant which made this research possible.

(2) G. Åkerlöf, THIS JOURNAL, **54**, 4132 (1932).

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TABLE I

NEUTRAL HYDROLYSIS, K_H IN LITERS MOLE^{-1} AND k_m IN HOUR^{-1}

Temp., °C.	Wt. % acetone	D	$k_m \times 10^6$	$k_H \times 10^6$
34.61	31.1	57.5	747	20.9
	38.7	52.8	332	10.6
	48.0	47.2	149	5.76
	77.8	29.4	6.09	0.592
35.04	58.3	40.8	53.5	2.63
44.83	31.1	54.8	1230	34.6
	38.6	50.5	563	18.1
	4.84	44.7	262	10.3
	58.1	39.0	124	6.09
	78.3	27.8	12.4	1.25
51.29	30.8	53.3	1540	43.3
	38.4	49.0	782	25.1
	47.9	43.6	372	14.5
	57.6	38.2	157	7.70
	77.2	27.4	18.9	1.83

TABLE II

ACID HYDROLYSIS, k^1 IN HOUR^{-1} AND k_a IN LITERS MOLE^{-1} HOUR^{-1}

Temp., °C.	Wt. % acetone	D	$k^1 \times 10^4$	$k_a \times 10^2$
35.04	31.1	57.4	44.2	7.34
	38.7	52.8	31.9	5.72
	47.6	47.4	23.5	4.40
	58.3	40.8	15.6	3.01
	78.6	28.8	9.45	1.88
44.83	31.0	54.8	99.1	17.4
	38.5	50.5	69.7	12.8
	47.9	45.0	49.4	9.35
	58.1	39.0	34.8	6.72
	77.6	28.2	24.9	4.95
51.29	31.0	54.2	170	31.0
	38.6	49.0	112	20.8
	48.05	43.5	84.0	16.1
	57.9	38.1	62.3	21.1
	77.6	27.2	45.2	9.00

The neutral runs employed the 0.00250 N base and the titration error was found to be less than 1%.

The pseudo first-order rate constants k_m and k^1 for neutral and acid-catalyzed runs, respectively, were obtained from plots of log $(M_\infty - M)$ against t where M and M_∞ are the corrected milliliters of standard base required for neutralization of formed acid at time t and time infinity, respectively. M_∞ was calculated.

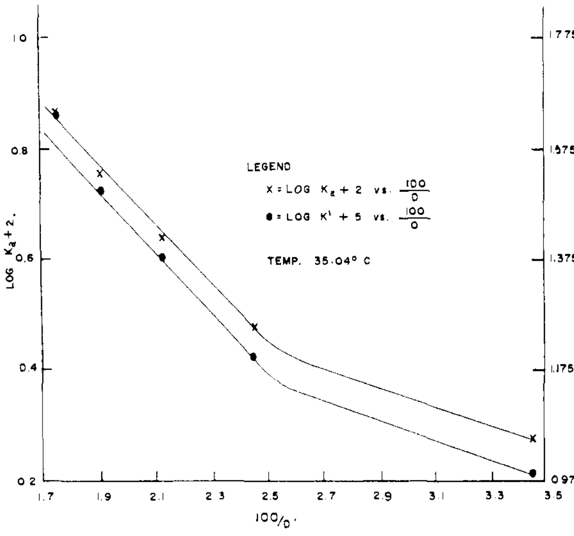

Fig. 1.

The second-order rate constants k_H and k_a for the neutral and acid hydrolysis, respectively, were calculated employing the relationship

$$k^1 = k_a(0.0500) + k_H(H_2O)$$

activation parameters were obtained from plots of log k_H and log k_a *versus* $1/T$.

Discussion

The neutral hydrolyses proceeded very slowly so that 0.00250 N base was used to measure the production of small amounts of acid. The normality of this base could not be as accurately determined as that of the stronger base and the sensitivity of the indicator was decreased but these disadvantages were outweighed by the greatly increased accuracy of buret readings. Readings could be made to 0.1 ml. easily and end-points were easy to observe.

In the neutral hydrolyses the dibromo acid formed produced a departure from the first-order law at greater than 8% of reaction. The weak base enabled the reaction to be followed with accuracy to this small extent so that fairly good first-order constants were obtained. Acid catalysis by the dibromo acid is to be expected because the electronegative substituents make the acid very much stronger than acetic acid. The rate constants obtained varied with solvent composition and temperature in a reasonable way. Duplicate and triplicate rate constants checked to within ±5–12% generally.

TABLE III

ACTIVATION PARAMETERS[a]

Wt. % acetone	Neutral hydrolysis		Acid hydrolysis	
	$\log_{10} Z$	ΔE, kcal.	$\log_{10} Z$	ΔE, kcal.
31	7.2	8.25	13.4	17.6
39	8.3	10.3	12.0	15.8
48	8.6	11.0	11.8	15.8
58	8.6	11.5	12.6	17.1
78	9.1	13.1	13.8	19.1

[a] Based on the second-order rate constants k_H and k_a.

The acid-catalyzed runs followed the pseudo first-order law very strictly for at least 85% of completion of reaction. Apparently the ionization of the produced dibromo acid is insignificant in the presence of the very strong hydrochloric acid. Pseudo first-order rate constants were very reproducible and duplicate runs checked within 2–5%. Also ln k_a *versus* $1/T$ plots were very accurately linear.

The activation energies for the neutral runs showed an increase with increasing acetone percentage. The statistical errors for these activation energies range from 0.9 to 2.1 kcal. per mole.

The activation energies for the acid-catalyzed runs show a minimum at about 45% acetone. This observed minimum might not be real since the statistical errors in these activation energies were from 0.3 to 0.9 kcal. per mole.

The activation energies increased as log Z increased.

In Fig. 1, log k_a and log k^1 are plotted *versus* 100/D for 35.04°. In this region of higher dielectric constants, these plots are straight lines of negative slope as was found by Nair and Amis[5] for the acid

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(5) P. M. Nair and E. S. Amis, THIS JOURNAL, **77**, 3452 (1955).

hydrolysis of ethyl dichloroacetate in acetone–water mixtures. The present curves have a less negative slope in regions of lower dielectric constant instead of changing to a positive slope as was found by Nair and Amis.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Pyrolysis of Lead Oxalate; Isotope Effects and Product Composition

BY PETER E. YANKWICH AND JAMES L. COPELAND

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The composition and isotopic constitution of the gaseous products of the pyrolysis of lead oxalate have been studied for reaction between 350 and 625°. Variations with temperature of the ratio of carbon dioxide to carbon monoxide in the product gases and of carbon isotope distribution are considered in terms of simple models in which: (a) it is assumed that the primary products are modified by a secondary reaction among themselves which competes with escape of the gaseous products from the decomposing mass, or (b) oxygen abstraction and C–C bond rupturing processes are presumed to compete. Models in group (a) are shown to correspond to temperature dependences of the molar yield ratio of gaseous products which are not in accord with observation. Consideration of models in group (b) is based primarily on the Bigeleisen–Wolfsberg treatment of three center reactions; satisfactory agreement with experiment is obtained for a model of the activated complex which includes a lead atom.

Introduction

Several investigations have been made of the products obtained when crystalline lead oxalate is decomposed thermally. At temperatures of pyrolysis above about 250° all of the carbon can be obtained as carbon dioxide or monoxide, but there is little unanimity concerning the molar ratio, Y, of these gases in the products. Maumene[1] finds $Y = 2$ and records the stoichiometry $3PbC_2O_4 = 2PbO + Pb + 4CO_2 + 2CO$, while mentioning that previous workers observed Y to be 3. Maumene reported that at higher temperatures some reduction of lead oxide to metal may occur; Sveda[2] studied the pyrolysis in an initially evacuated vessel and found that the extent of this reduction was proportional to the time of contact between solid and gaseous products of the primary reaction.

Denham[3] found that there was no reaction between the solid product (which he and Pascal and Minne[4] believed to be a lead suboxide) and the carbon monoxide produced if the total pressure was below 5 cm. at 270°; he reported $Y = 3$.

Bircumshaw and Harris[5] studied the products of the decomposition at temperatures in the range 310–470°. They found a dioxide/monoxide ratio of 2, established by X-ray and electrical conductivity measurements that the solid was a mixture of metallic lead and red tetragonal lead oxide, and observed that removal of the gaseous products by continuous pumping had only a slight effect on their composition. In a second paper[6] the kinetics of the pyrolysis was studied at temperatures between 309 and 350°. The rate data conformed to predictions based on a model in which decomposition starts at nuclei and spreads through branching chains along paths of lateral strain; the strain is relieved by the formation of Smekal cracks along which the decomposition is favored.

In the present paper we report a study of the composition and isotopic constitution of the gaseous products over the temperature range 350–625°. The study was carried out to elucidate the character of the molecular mechanism of the process, and no kinetics measurements were made.

Experimental

Lead Oxalate.—A slight excess of aqueous reagent oxalic acid was added slowly with constant stirring to a 1 *M* aqueous solution of reagent grade lead nitrate; after standing in contact with the supernatant for one hour at room temperature, the lead oxalate was removed by filtration, washed with distilled water, then dried in air for 3 hours at 110°.

Apparatus and Procedure.—The pyrolyses were carried out in a stream of dry, oxygen-free helium. The train employed was made up as follows. Sample decomposition took place in a 2 cm. i.d. Vycor tube, the second half of which passed through an electric furnace which maintained a predetermined temperature constant to 2°; the gaseous products passed first through a trap cooled in liquid nitrogen, thence to a combustion tube at 750° filled with copper oxide wire, and finally through another trap cooled in liquid nitrogen. Preliminary tests showed that carbon monoxide and carbon dioxide were separated quantitatively in the first trap at the helium flow rate employed (50 cc. per min.). In a typical experiment 0.45–0.50 g. of lead oxalate was weighed into a shallow platinum boat which was placed in the unheated end of the pyrolysis tube. The train was assembled and the helium flow maintained for one hour to remove traces of oxygen. At the start of most of the runs the pyrolysis tube was tipped, causing the boat to slide into the heated zone. Since the reaction becomes very rapid at the higher temperatures employed, a few runs in that region were made in which the contents of the boat were dumped by an externally operated tipper onto a thick platinum foil in the heated zone to ensure the most rapid possible heating to the run temperature. At 350° the decomposition is complete in 40 minutes[6]; so that no time variable would be introduced, the helium sweep was maintained for 60 minutes in all runs. The two gaseous samples were measured manometrically, then reserved for mass spectrometric analysis.

Isotope Analyses.—The procedures and calculation methods used for the carbon isotope ratio determinations have been detailed in previous publications from this Laboratory.[7,8] The final oxygen isotope ratios were obtained by applying to the observed values of the ratio $(m/q\ 46)/m/q\ 44 + 45)$ corrections for the magnitude of $(m/q\ 45)/(m/q\ 44)$, and for daily variations in the response of the mass spectrometer; analysis showed that corrections to these ratios for incomplete resolution and the contribution to the peak at m/q 46 of the species $C^{13}O^{16}O^{17}$ (assumed

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