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A STUDY OF POTASSIUM 2-GERMAACETATE AND
AN ATTEMPT TO SYNTHESIZE POTASSIUM GERMYL MERCAPTIDE

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ABSTRACT

In dilute aqueous acid solutions ($0.05 - 0.5 \text{ M H}^+$), 2-germaacetic acid decomposes to form carbon monoxide, an orange-yellow solid of approximate composition $\text{GeH}_{0.6}$, and small amounts of germane. The rate law for the reaction is $-\text{d}[\text{GeH}_3\text{COOH}]/\text{dt} = k[\text{H}^+][\text{GeH}_3\text{COOH}]$. The value of k was determined to be $(5.59 \pm 0.14) \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ at 22.5° and at ionic strength of 1.0 M . The rate was studied in the range $0-39.5^\circ$ and the activation energy was determined to be 16.9 kcal/mol . When the reaction is carried out in strongly acidic solutions (e.g., $>6 \text{ M HCl}$, $>4 \text{ M H}_2\text{SO}_4$, or $>6 \text{ M HClO}_4$), carbon monoxide is evolved quantitatively, but no solid hydride or germane forms. The resulting solution contains the GeH_3^+ group, probably stabilized by coordination to water or to the

anion of the aqueous acid. The data implicate GeH_2 as an intermediate of the reaction in dilute acid solutions.

In neutral and alkaline solutions, the 2-germaacetate ion decomposes to give germane and bicarbonate (or carbonate): $\text{GeH}_3\text{CO}_2^- + \text{H}_2\text{O} \rightarrow \text{GeH}_4 + \text{HCO}_3^-$. The rate of this decarboxylation is pH independent and is first order in the germaacetate ion. The rate constant at 60° and ionic strength of 1.0 is $1.62 \times 10^{-5} \text{ sec}^{-1}$; the activation energy is 28.6 kcal/mol. In strongly alkaline solutions (especially at hydroxide concentrations above 1 M), a second decomposition reaction, producing hydrogen and the insoluble brown polymer $\text{H}_2\text{Ge}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, competes with the decarboxylation: $2\text{GeH}_3\text{CO}_2^- + 2\text{OH}^- + (3+x)\text{H}_2\text{O} \rightarrow 6\text{H}_2 + \text{H}_2\text{Ge}_2\text{O}_3 \cdot x\text{H}_2\text{O} + 2\text{CO}_3^{2-}$. The rate of the latter reaction is first order in germaacetate ion and is inversely proportional to the Hammett acidity function h_- (i.e., first order in hydroxide ion); $-\text{dln}(\text{GeH}_3\text{CO}_2^-)/\text{dt} = k_2/h_-$. At 60° in 1 M NaOH, $k_2 = 2.5 \times 10^{-19} \text{ M sec}^{-1}$; the activation energy is 20.8 kcal/mol. Probable mechanisms of the reactions are discussed.

The reaction of potassium germyl with sulfur was tried in an attempt to prepare potassium germyl mercaptide, GeH_3SK . Addition of iodomethane to the reaction mixture of potassium germyl and sulfur under different conditions was tried to prepare methyl germyl mercaptide, CH_3SGeH_3 . Germane evolution in the reaction of potassium germyl and sulfur suggests decomposition of GeH_3SK . Two possible mechanisms by which GeH_3SK decomposes are proposed.

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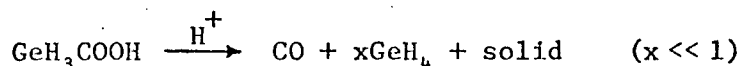
PART I. THE DECARBONYLATION OF 2-GERMAACETIC ACID
IN AQUEOUS SOLUTIONS

ABSTRACT

In dilute aqueous acid solutions ($0.05 - 0.5 \text{ M H}^+$), 2-germaacetic acid decomposes to form carbon monoxide, an orange-yellow solid of approximate composition $\text{GeH}_{0.6}$, and small amounts of germane. The rate law for the reaction is $-d[\text{GeH}_3\text{COOH}]/dt = k[\text{H}^+][\text{GeH}_3\text{COOH}]$. The value of k was determined to be $(5.59 \pm 0.14) \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ at 22.5° and at ionic strength of 1.0 M . The rate was studied in the range $0 - 39.5^\circ$, and the activation energy was determined to be 16.9 kcal/mol . When the reaction is carried out in strongly acidic solutions (e.g., $>6 \text{ M HCl}$, $>4 \text{ M H}_2\text{SO}_4$, or $>6 \text{ M HClO}_4$), carbon monoxide is evolved quantitatively, but no solid hydride or germane forms. The resulting solution contains the GeH_3^+ group, probably stabilized by coordination to water or to the anion of the aqueous acid. The data implicate GeH_2 as an intermediate of the reaction in dilute acid solutions.

INTRODUCTION

The decarbonylation of 2-germaacetic acid in aqueous acid has been studied by Kuznesof and Jolly.¹ They reported that the reaction produces a quantitative yield of carbon monoxide, variable amounts of germane, and an insoluble orange solid containing germanium and hydrogen:



The purpose of this study was to determine the immediate and ultimate products of the reaction and to investigate the mechanism of the reaction.

EXPERIMENTAL

General

All manipulations were carried out using a standard vacuum line or a nitrogen-filled glove bag. Commercial 1,2-dimethoxyethane was dried with potassium hydroxide, filtered, refluxed with sodium metal, and then distilled. Germane gas from the Matheson Co. (minimum purity, 99.8%) was used without further purification.

The identification of reaction products was aided by infrared spectrometry with Perkin-Elmer spectrometers (Models 337 and 283), by mass spectrometry with a Finnigan Instruments Corp. quadrupole mass spectrometer, and by Raman spectrometry with a Coherent Radiation Co. Raman spectrometer (Model 1401).

GeH₃COOK

Potassium germyl in 1,2-dimethoxyethane was prepared by a method similar to that previously described.² The solution of KGeH₃ was stirred and shaken at 0° under approximately one atmosphere pressure of carbon dioxide. When absorption of the CO₂ was complete, the precipitated product was collected by suction filtration on a frit.

A 1.228-mmol sample of GeH₃COOK was heated in a sealed tube at 510° for 24 hrs. The pyrolysis products were analyzed as described by Kuznesof and Jolly.¹ Sample purity was calculated on the basis of the reaction $2\text{GeH}_3\text{COOK} \xrightarrow{\Delta} 3\text{H}_2 + \text{CO} + 2\text{Ge} + \text{K}_2\text{CO}_3$. The purity was 97.0%, based on the amount of noncondensable gas formed (collected 2.382 mmol, theory 2.456 mmol), and 99%, based on the carbon dioxide liberated upon acidification of the residue (collected 0.608 mmol, theory 0.614 mmol).

A 1.016-mmol sample of GeH_3COOK was treated with 100 ml of 1 M NaOH in a Teflon-lined reaction vessel at 60° for 100 hrs. The volatile products were fractionated through two -78° traps and a -196° trap. Germane (0.368 mmol) collected in the -196° trap. Germanium in the reaction solution was determined by the mannitol method³ after treating the solution with acid peroxide to ensure that all the germanium was in the tetra valent oxidation state. The solution was found to contain 0.631 mmol of Ge. The total Ge found in the sample, 0.999 mmol, corresponds to a purity of 98.3%.

Chemical Analysis of Reaction Products

A round-bottom flask with a stopcock and a 24/40 male joint, containing 30 ml of 1 M HCl, was cooled to 0° , evacuated, and then cooled to -78° . A weighed sample of GeH_3COOK was added to the flask while flushing with nitrogen, and the flask was reevacuated and warmed to 0° . The reaction produced an initially white compound which became yellowish and later orange-yellow. After the reaction was complete, the volatile gases were fractionated through a -78° trap, a trap filled with an intimate mixture of glass helices and yellow HgO to remove HCl, a -78° trap and a -196° trap. The noncondensable gases were Toepler-pumped into a calibrated gas buret. The germane in the -196° trap and the carbon monoxide in the gas buret were measured. Then 50 ml of 0.1000 N dichromate solution and 35 ml of degassed 6 N H_2SO_4 were added to the reaction mixture under nitrogen, and the solution was stirred overnight. The excess dichromate was titrated by the iodometric method⁴ using standardized thiosulfate solution. From the data for two separate analyses, the total number of equivalents of

reducing power per mole of germanium in the products of the decarbonylation was calculated to be 6.01 and 5.93. These results closely correspond to an average oxidation state of -2 for the germanium in the products. In both analyses 99.0% of the theoretical CO was obtained.

Another sample of GeH_3COOK (0.918 mmol) was prepared in a 3 cm diameter, 20 cm long tube provided at one end with a 24/40 male joint, and was decomposed as described above. After 0.902 mmol of carbon monoxide and 0.383 mmol of germane had collected, the water in the reaction tube was completely removed by pumping. The remaining orange-yellow solid was heated at 300° for 10 hrs, forming hydrogen gas (0.160 mmol) and black germanium. From these data we calculate that the H/Ge ratio in the yellow solid was 0.6, and that the overall H/Ge ratio in the yellow solid and the germane was 2.02.

Reactions in Highly Acidic Solutions

Potassium germaacetate was added to an excess of stirred 8 M HCl at -78° in a closed evacuated system. Dissolution occurred slowly. No gas was evolved at -78° , but when the solution was warmed, CO began to be evolved around -50° and was quantitatively evolved at 0° . The resulting solution did not evolve any further gases at room temperature and only slowly evolved hydrogen at 80° . Four solutions prepared in this manner were separately analyzed by heating in closed tubes at $155 - 200^\circ$ for 7-15 days. The measured moles of H_2 evolved per mole of GeH_3COOK originally used were 1.98, 1.85, 1.95 and 1.88. The resulting solutions were analyzed both qualitatively and iodometrically and were shown to contain Ge(II).

Germyl chloride was prepared by the reaction of germane with tin tetrachloride.⁵ Solutions in aqueous hydrochloric acid were prepared on the vacuum line by distilling appropriate amounts into tubes containing the acid. Complete dissolution of the GeH_3Cl in these acids was slow, sometimes requiring several days.

When strongly acid solutions of " GeH_3^+ " (prepared either from GeH_3COOH or from GeH_3Cl) were diluted with water, pale yellow precipitates of germanium subhydride formed and small amounts of germane were evolved. The precipitates did not redissolve upon addition of concentrated acid to the mixture.

Nmr Experiments

Proton nmr measurements were made using a Varian NV-14 spectrometer operating at 60 MHz, equipped with a variable temperature probe. The signal of the solvent was used for locking. The chemical shifts were measured in ppm downfield from the proton resonance of external TMS contained in coaxial 2-mm capillaries centered in the 8-mm sample tubes. Solutions were prepared directly in the nmr tubes. The spectra of 0.3 M GeH_3COOH in 8 M HCl and of 0.5 M GeH_3COOH in 4 M H_2SO_4 , as a function of temperature and time, are shown in Figs. 1 and 2, respectively. Within $\pm 5\%$, the sum of the peak areas in each spectrum at a given temperature is constant, showing that the GeH_3 group of GeH_3COOH is converted to a species containing three equivalent hydrogen atoms.

Procedure for Kinetic Study

A fragile bulb containing ~ 1.0 mmol of GeH_3COOK was lowered into the reaction vessel, which contained 120 ml of aqueous hydrochloric acid.

While the acid was stirred at 0°, the vessel was connected to a vacuum pump until the air was completely removed. Then the vessel was placed in a thermostatted oil bath ($\pm 0.1^\circ$). When the system reached the thermostat temperature, the fragile bulb was broken and a timer was started. At measured times during the reaction, a stopcock between the reaction vessel and an evacuated 3-liter bulb was momentarily opened. This procedure allowed the gaseous reaction products ($\text{CO} + \text{GeH}_4$) which had collected in the 30-ml gas space of the reaction vessel to expand into the bulb, thus flushing more than 99% of the gaseous products from the reaction vessel. After each gas transfer of this type, the water vapor and germane in the bulb were fractionally condensed in traps at -78° and -196° , and the carbon monoxide was Toepler-pumped into a calibrated gas buret and measured.

RESULTS AND DISCUSSION

Study of the Solid Product

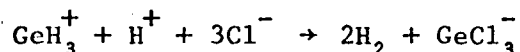
Two different methods of chemical analysis (one involving redox titrimetry and the other involving the measurement of hydrogen formed during pyrolysis) showed that the average oxidation state of the germanium in the reaction products is -2. When the decarbonylation was carried out in dilute acid solutions, the germanium ended up as germane and as a solid orange-yellow polymeric hydride of empirical composition $\text{GeH}_{0.6}$. Infrared spectrometry showed that the latter compound is a hydride, without any Ge-O-Ge or Ge-OH linkages. A Nujol mull spectrum of the solid showed an absorption at 2060 cm^{-1} , characteristic of Ge-H stretching,⁶ a broad band at 760 cm^{-1} due to Ge-H bending,^{6a} and an absorption at 315 cm^{-1} probably

due to Ge-Ge stretching.^{6c} A Raman spectrum of the orange-yellow solid showed an absorption at 285 cm^{-1} , probably due to Ge-Ge stretching,^{6c} and a band at 2055 cm^{-1} , undoubtedly due to Ge-H stretching.⁶

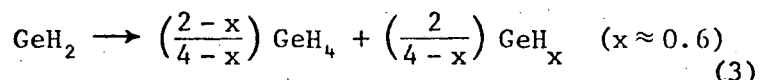
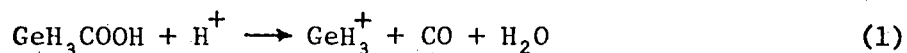
When the decarbonylation was carried out in strongly acidic solutions (e.g., $>6\text{ M HCl}$, $>4\text{ M H}_2\text{SO}_4$, or $>6\text{ M HClO}_4$), quantitative yields of carbon monoxide were obtained, but no solid hydride or germane formed. However, when the resulting solutions were diluted with water, the latter compounds did form. An nmr study of the decarbonylation reaction in cold 8 M HCl showed that the proton signal of the germaacetic acid was gradually replaced by a signal of equal intensity, 1.04 ppm toward lower field. Solutions of germyl chloride in 8 M HCl were found to have the same chemical properties, and essentially the same nmr chemical shift, as those prepared by the decarbonylation of germaacetic acid in 8 M HCl . The chemical shifts of such solutions were found to be a function of the concentration of HCl. For example, the shifts for GeH_3Cl dissolved in 8 M and 6 M HCl were -5.9 and -5.3 ppm from external TMS, respectively. The chemical shift for the species in $4\text{ M H}_2\text{SO}_4$ was -6.2 ppm.

The data indicate that, in strongly acidic solutions, the decarbonylation produces a relatively stable intermediate species containing the GeH_3^+ group, either as a cation (probably hydrated, as $\text{H}_3\text{GeOH}_2^+$) or associated with the anion of the acid (e.g. as GeH_3Cl or $\text{GeH}_3\text{OSO}_3\text{H}$). Equilibria between the cationic form and the associated forms probably exist in these solutions, and the exact characterization of these species will be the subject of future research. For simplicity in the following discussion, we shall represent this intermediate by the formula GeH_3^+ . The intermediate is remarkably stable in the strongly acidic solutions. In 8 M HCl , it

appears to be stable indefinitely at room temperature. After heating such solutions for a week at 200°, decomposition to hydrogen and germanium(II) (probably as GeCl_3^-) occurs.



Although we have no direct evidence for the formation of monomeric GeH_2 when strongly acidic solutions of GeH_3^+ are diluted, the fact that we obtained germane and an insoluble subhydride strongly suggests the intermediacy of GeH_2 . Previous workers have established that GeH_2 , however it is formed, readily decomposes at ordinary temperatures to these ultimate products.⁷⁻⁹ We may therefore represent the decarbonylation of germaacetic acid as a three-step process.



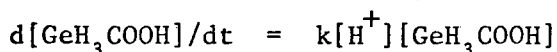
It is significant that, when potassium germaacetate is dissolved in 8 M HCl at -78°, no carbon monoxide is evolved until the solution is warmed to about -50°. This result shows that kinetically stable solutions of germaacetic acid can actually be prepared and suggests that the pure acid may be isolable under appropriate conditions.

Kinetic Study

The kinetic study was carried out in dilute acid solutions, where the second and third steps of the overall reaction are rapid compared to the first step. The rate of reaction was measured by determining the

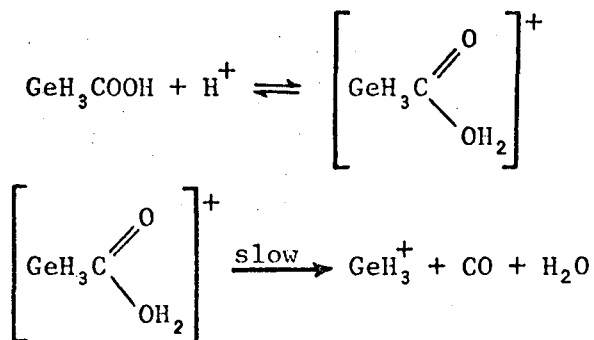
carbon monoxide evolved as a function of time. From plots of $\log(P_{\infty} - P)$ versus time, the hydrolysis was found to be first order in GeH_3COOH as shown in Fig. 3. The observed first-order rate constant was calculated from the slope. The rate constant was determined at various acid concentrations to find the rate dependence on H^+ ion concentration; the data are summarized in Table I.

The results shown in Table I indicate that the observed first-order rate constant is proportional to the acid concentration, i.e., $k_{\text{ob}} = k[\text{H}^+]$, where k has a value of $(5.59 \pm 0.14) \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ at 22.5° . The overall rate is therefore first order in both H^+ and GeH_3COOH :



The second-order rate constant, k , was measured at different temperatures to obtain the activation energy of the reaction. The results are summarized in Table II, and from a plot of $\log k$ versus $1/T$, shown in Fig. 4, the activation energy was calculated to be 16.9 kcal/mol. The yield of carbon monoxide in each kinetic run was in the range 97 - 99%.

The observed rate law for the decarbonylation of 2-germaacetic acid is analogous to the rate laws which have been reported for the decarbonylation of organic carboxylic acids.¹⁰ If we write a mechanism for the first step of the decarbonylation (i.e., reaction 1) similar to that proposed by Ropp^{10c} for organic acids, we obtain:



Of course, our data do not permit us to distinguish between this mechanism, involving a $\text{GeH}_3\text{COOH}_2^+$ *intermediate*, and a one-step process involving a $\text{GeH}_3\text{COOH}_2^+$ *activated complex*. In either case, the facile decomposition of GeH_3COOH relative to the difficult decomposition of most organic acids can be explained by the relative stabilities, in aqueous solutions, of GeH_3^+ and carbonium ions. It is well known that as one goes down the Group IV family, the ease of forming cationic species such as MR_3^+ increases.¹⁸

It seems reasonable to suppose that the intermediate which we formulate as GeH_3^+ is structurally analogous to the SnH_3^+ ion which has been proposed as the product of the reaction of SnH_4 with cold strong acid solutions.¹¹ However, the SnH_3^+ ion is an extremely unstable species, decomposing to hydrogen and tin(II) even below 0° . This instability of SnH_3^+ , compared to the stability of GeH_3^+ , is undoubtedly related to the fact that Sn-H bonds are much weaker than Ge-H bonds, and is not inconsistent with the fact that cationic tin species are less hydrolyzed and less associated with anions than the corresponding germanium species.

Triaryl and trialkyl analogs of 2-germaacetic acid are relatively stable compounds which undergo decarbonylation only when heated.¹²⁻¹⁷ Apparently no kinetic or detailed mechanistic studies of these reactions have been made. We have no explanation for the lower reactivity of the organo analogs.

TABLE I. Effect of acid concentration on the value ^{α} of the observed first-order rate constant, k_{ob} , and the first-order rate constant, k , at 22.5° and $\mu = 1.0$

$[H^+], \underline{M}$	$T_{1/2}, \text{min}$	$10^5 k_{ob}, \text{sec}^{-1}$	$k = k_{ob}/[H^+], \underline{M}^{-1} \text{sec}^{-1}$
0.10	220	5.25	5.25×10^{-4}
0.20	102	11.33	5.67×10^{-4}
0.30	68	16.99	5.66×10^{-4}
0.40	50	23.10	5.78×10^{-4}
0.50	41.3	27.97	5.59×10^{-4}
		Average	$5.59 \pm 0.14 \times 10^{-4}$

$$\alpha [\text{GeH}_3\text{COOH}] \approx 1.2 \times 10^{-2} \underline{M}$$

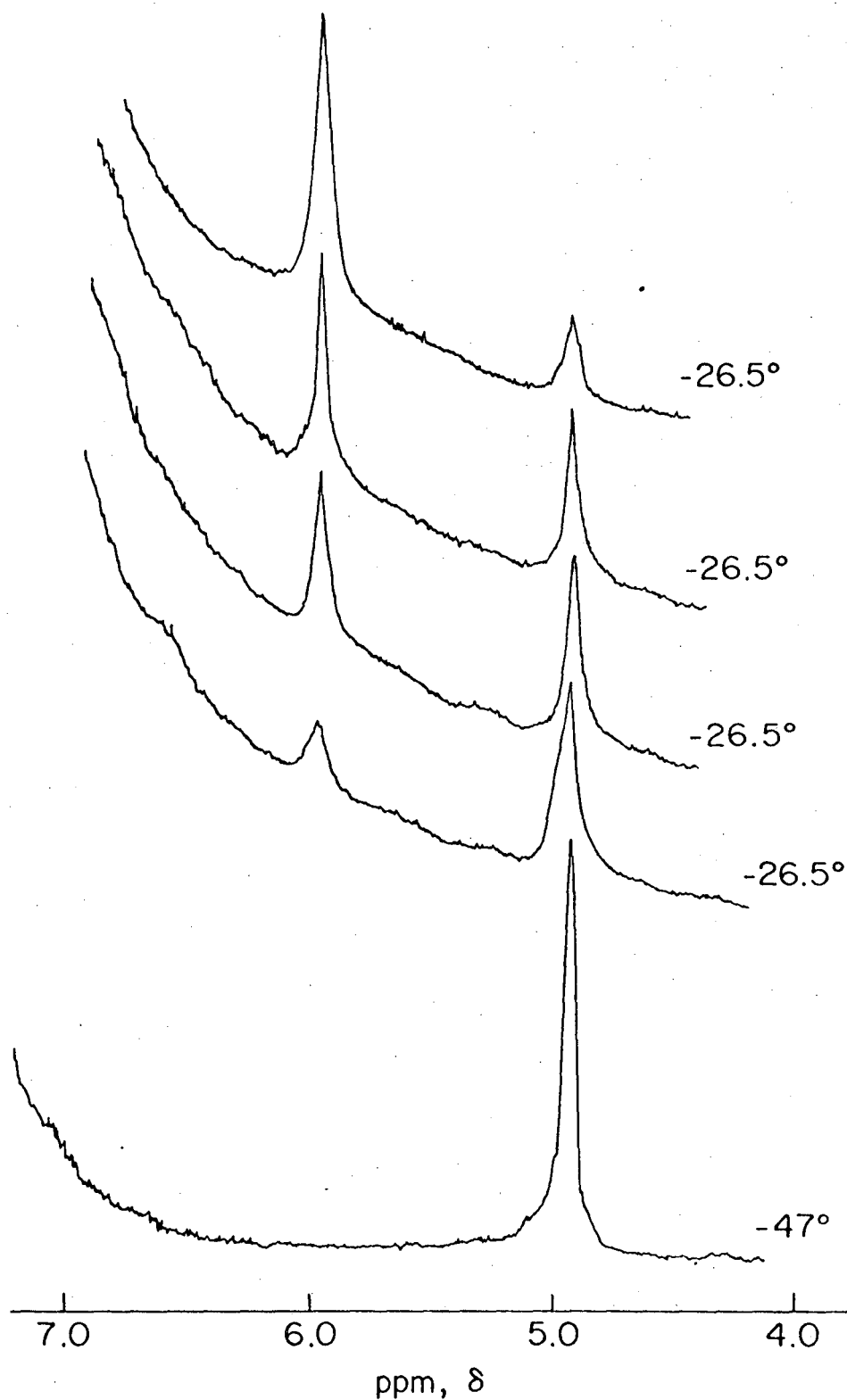
TABLE II. Temperature dependency of k^a at $\mu = 1.00$.

Temp, °C	[H ⁺]	T _{1/2} , min	10 ⁵ k, <u>M</u> ⁻¹ sec ⁻¹
0.0	0.10	2080	5.55
22.5	0.10	220	52.51
31.0	0.10	76	152.0
35.5	0.05	114	202.6
39.5	0.05	83	278.6

$$^a[\text{GeH}_3\text{COOH}] \approx (0.05 - 1.2) \times 10^{-2} \text{ M}$$

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XBL 776-9157

Fig. 1. Nmr spectra of a solution of GeH_3COOK in 8 M HCl at -47° and -26.5° . The -26.5° spectra were obtained at approximately 8 min intervals and show the gradual conversion of GeH_3COOH to GeH_3^+ .

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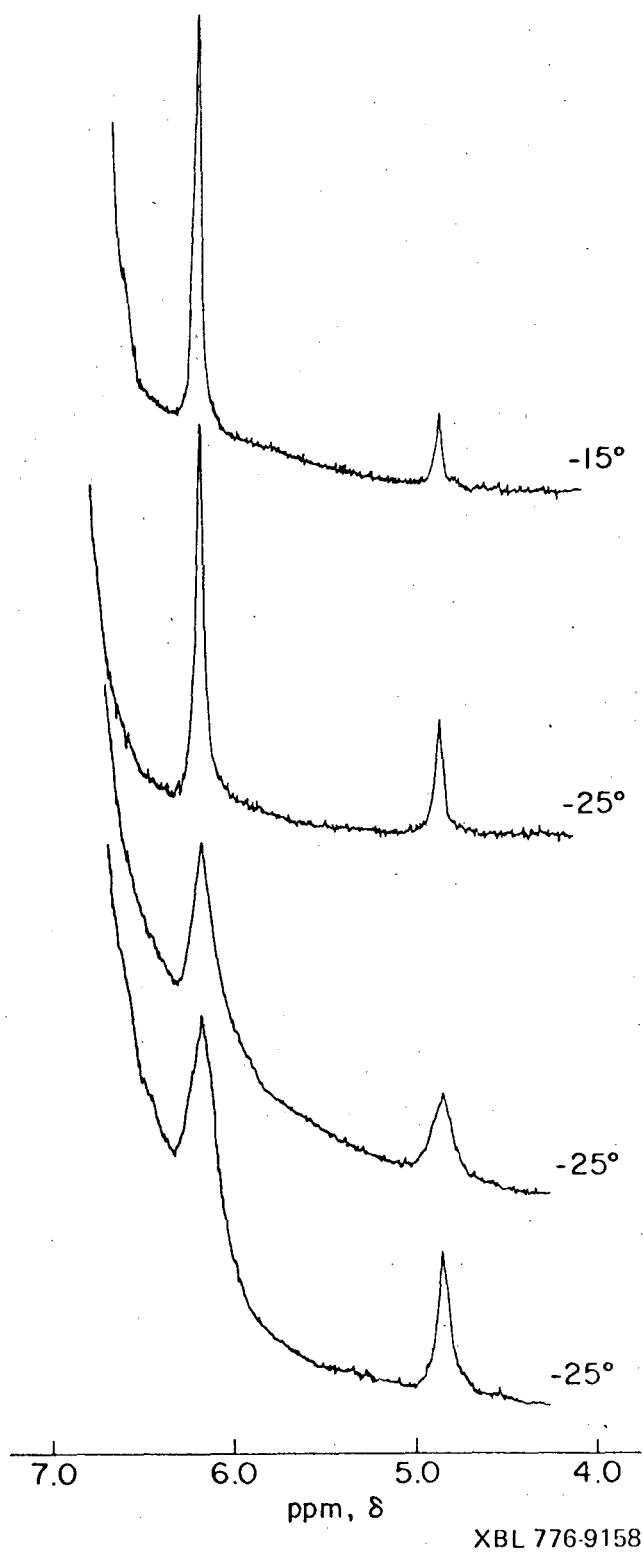
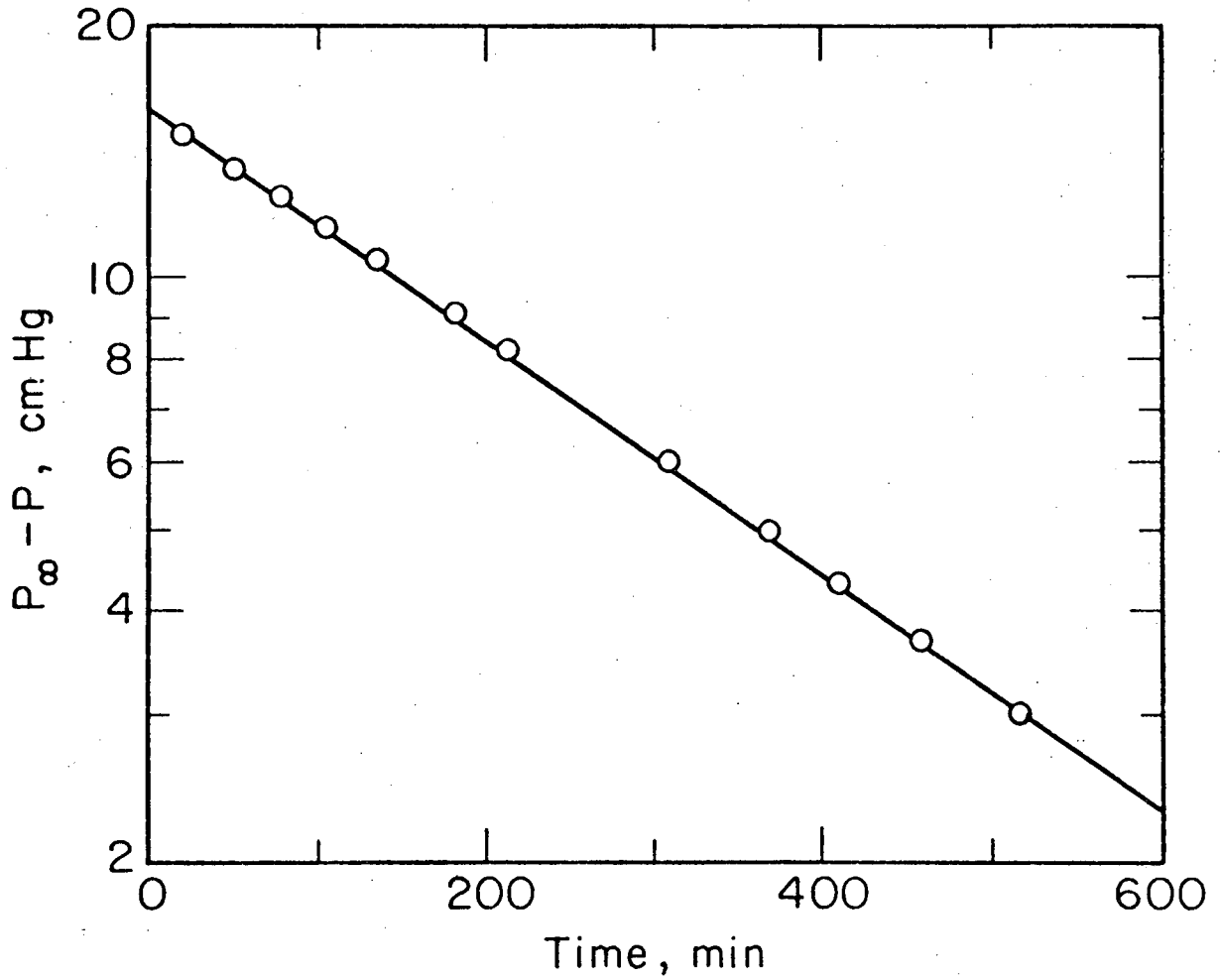
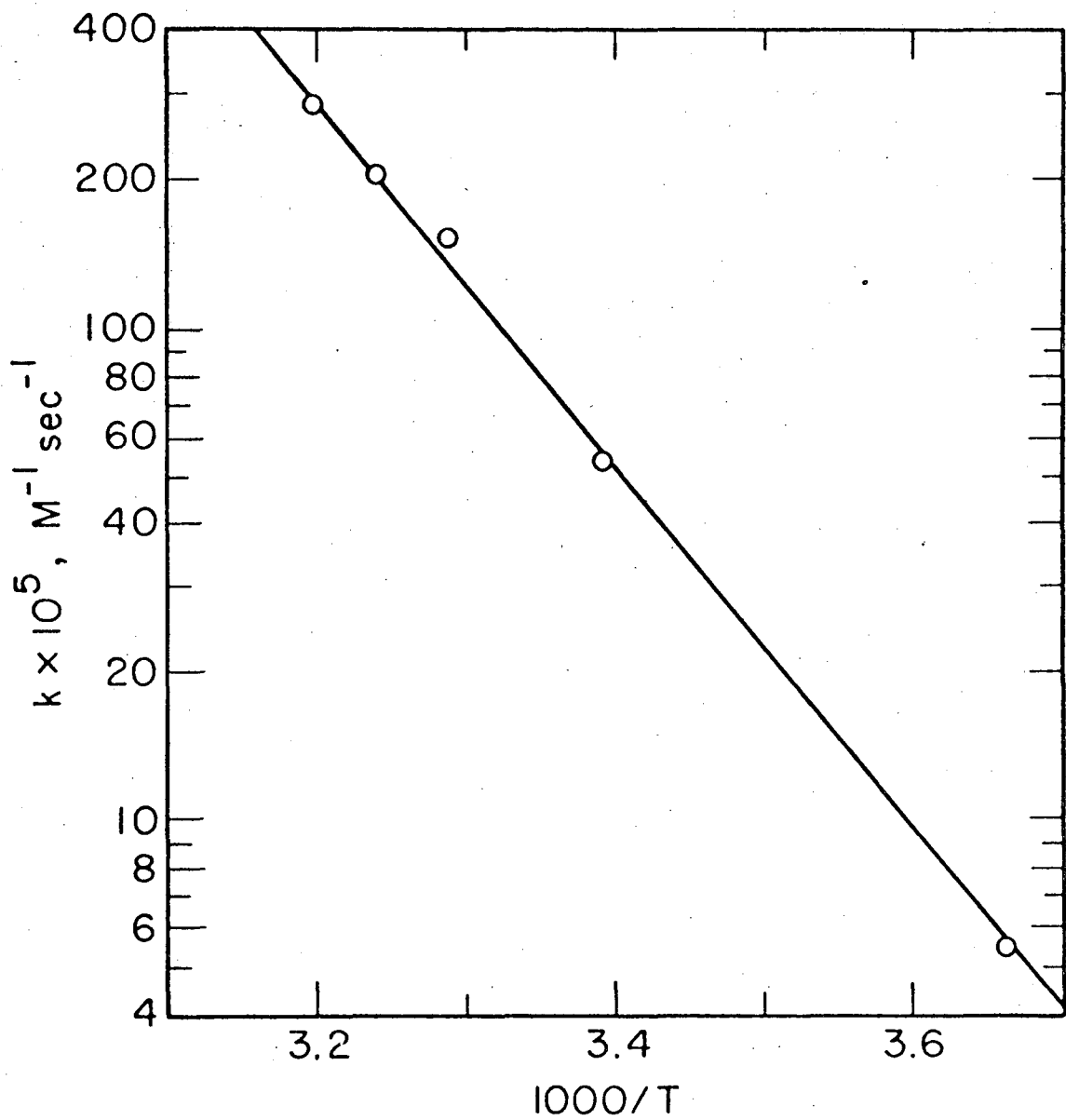


Fig. 2. Nmr spectra of a solution of GeH_3COOK in $4 \text{ M H}_2\text{SO}_4$ at -25° and -15° . The -25° spectra were obtained at approximately 15 min intervals; the -15° spectrum was obtained 25 min after the last -25° spectrum.



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Fig. 3. $\log(P_{\infty} - P)_{\text{CO}}$ versus time for the decarbonylation of GeH_3COOH at $[\text{H}^+] = 0.1 \text{ M}$ and 22.5° .



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Fig. 4. Arrhenius plot for the decarboxylation of GeH_3COOH .
Plot of $\log k$ versus $1000/T$.

PART II. A KINETIC STUDY OF THE HYDROLYSIS OF
2-GERMAACETATE IN NEUTRAL AND ALKALINE SOLUTIONS

ABSTRACT

In neutral and alkaline solutions, the 2-germaacetate ion decomposes to give germane and bicarbonate (or carbonate): $\text{GeH}_3\text{CO}_2^- + \text{H}_2\text{O} \rightarrow \text{GeH}_4 + \text{HCO}_3^-$. The rate of this decarboxylation is pH independent and is first order in the germaacetate ion. The rate constant at 60° and ionic strength of 1.0 is $1.62 \times 10^{-5} \text{ sec}^{-1}$; the activation energy is 28.6 kcal/mol. In strongly alkaline solutions (especially at hydroxide concentrations above 1 M), a second decomposition reaction, producing hydrogen and the insoluble brown polymer $\text{H}_2\text{Ge}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, competes with the decarboxylation: $2\text{GeH}_3\text{CO}_2^- + 2\text{OH}^- + (3+x)\text{H}_2\text{O} \rightarrow 6\text{H}_2 + \text{H}_2\text{Ge}_2\text{O}_3 \cdot x\text{H}_2\text{O} + 2\text{CO}_3^{2-}$. The rate of the latter reaction is first order in germaacetate ion and is inversely proportional to the Hammett acidity function h_- (i.e., first order in hydroxide ion); $-\text{dln}(\text{GeH}_3\text{CO}_2^-)/\text{dt} = k_2/h_-$. At 60° in 1 M NaOH, $k_2 = 2.5 \times 10^{-19} \text{ M sec}^{-1}$; the activation energy is 20.8 kcal/mol. Probable mechanisms of the reaction are discussed.

INTRODUCTION

It has previously been shown that hot aqueous solutions of potassium 2-germaacetate decompose to give germane and bicarbonate.¹ In this study we investigated the kinetics of the reaction from pH 6 to pH ~15 in the temperature interval 45-75° to obtain information regarding the mechanism

of the reaction and to allow comparison with similar data for the decarboxylation of organic carboxylates. We discovered that a second decomposition reaction (involving the formation of hydrogen and a brown precipitate) occurs concurrently in the strongly alkaline solutions. We identified the products, established the stoichiometry, and studied the kinetics of this reaction.

EXPERIMENTAL

Manipulations were carried out using a vacuum line or a nitrogen filled glove bag. Commercial 1,2-dimethoxyethane was dried with potassium hydroxide, filtered, refluxed with sodium metal, and then distilled. Germane gas from the Matheson Co. (minimum purity, 99.8%) was used without further purification. The identification of reaction products was aided by infrared spectrometry with a Perkin-Elmer Infracord spectrometer (Model 337) and by mass spectrometry with a Finnigan Instruments Corp. quadrupole mass spectrometer.

Preparation and Analysis of $\text{GeH}_3\text{CO}_2\text{K}$.

A solution of potassium gerymyl in 1,2-dimethoxyethane was prepared by a method similar to that of Dreyfuss and Jolly.² The solution of KGeH_3 was stirred and shaken under approximately one atmosphere pressure of carbon dioxide in an ice bath. After about two hours, when the pressure in the closed system had become constant, the precipitated product was collected by suction filtration on a frit.

A 1.228-mmol sample of $\text{GeH}_3\text{CO}_2\text{K}$ was heated in a sealed tube at 510° for 24 hrs. The pyrolysis products were analyzed as described by Kuznesof and Jolly.¹ Sample purity was calculated on the basis of the reaction

$2\text{GeH}_3\text{CO}_2\text{K} \rightarrow 3\text{H}_2 + \text{CO} + 2\text{Ge} + \text{K}_2\text{CO}_3$. The purity was 97.0% based on the total amount of noncondensable gas (collected 2.382 mmol, theory 2.456 mmol), and 99.0% based on the carbon dioxide liberated upon acidification of the residue (collected 0.608 mmol, theory 0.614 mmol).

A 1.016-mmol sample of $\text{GeH}_3\text{CO}_2\text{K}$ was treated with 100 ml of 1 M NaOH in a Teflon-lined reaction vessel at 60° for 100 hrs. Germane gas (0.368 mmol) was isolated from the volatile products. Germanium in the solution was analyzed by the mannitol method³ after treatment with acid and peroxide to ensure that all the germanium was in the +4 oxidation state. The solution was found to contain 0.631 mmol of Ge. The total Ge found, 0.999 mmol, corresponds to a purity of 98.3%.

Chemical Analysis of Dark Brown Compound

A dark brown precipitate was obtained by heating a solution of $\text{GeH}_3\text{CO}_2\text{K}$ in 7 M NaOH at 75° for 1 hr. The material was centrifuged and washed with degassed distilled water until the wash water was neutral. The sample was kept for several days at 0° in an evacuated system containing Drierite. The dehydrated sample was observed to be darker in color than the original wet sample. The reducing power per gram of sample was determined by treatment with a known excess of triiodide (under argon in the dark) followed by titration with standard thiosulfate solution, and the number of moles of germanium per gram of sample was measured by the mannitol method.³ The reducing power per gram of sample was found to be 20.77 and 20.70 meq/g; average 20.74 meq/g. The number of millimoles of germanium per gram of sample was found to be 10.54, 10.86, and 10.84 mmol/g; average 10.75 mmol/g.

Alkali-digested germanous hydroxide was prepared by digestion of fresh germanous hydroxide⁴ in 7 M NaOH at 75° for 1 hr, followed by the same purification as described for the dark brown compound. Nujol mull infrared spectra of the dried dark brown compound and of alkali-digested germanous hydroxide are shown in Fig. 1.

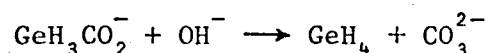
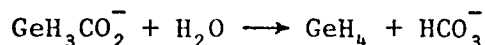
Procedure for Kinetic Study

A solution of $\text{GeH}_3\text{CO}_2\text{K}$ ($\sim 10^{-2}$ M in a buffer solution) was prepared at 0°. The ionic strength of the solutions in the pH range 6-14 was adjusted to $\mu = 1.0$ by appropriate addition of potassium chloride. The solution was placed in a flask with a magnetic stirring bar and connected to a vacuum line by means of a glass joint attached to a stopcock. The flask was evacuated while stirring the solution at 0°, and the solution was then warmed to the reaction temperature in a thermostatted ($\pm 0.1^\circ$) oil bath. At measured intervals the volatile reaction products which formed in the 20-ml space over the solution in the reaction vessel were allowed to expand into an evacuated 3-liter bulb by momentarily opening the stopcock. By this procedure, more than 99% of the gaseous products were transferred. The germane in each batch of gas was isolated and measured. When the gaseous reaction products consisted only of germane or of germane and carbon dioxide (pH < 13), the gases in the bulb were fractionated through two -78° traps, an Ascarite trap, another -78° trap, and a -196° trap. The germane collected in the -196° trap was transferred to a system of known volume and measured. When the volatile reaction products consisted only of germane and hydrogen (pH > 13), the gases were fractionated through two -78° traps and a -196° trap into a calibrated gas collection system by means of a Toepler pump. In these cases both the germane and hydrogen were measured as a function of time.

RESULTS

Kinetics in the pH Interval 6-13

It was confirmed that, in the pH interval 6-13, the principal reaction is decarboxylation with evolution of germane:



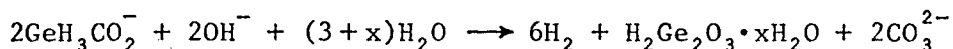
Although some carbon dioxide was evolved along with the germane in the solutions of low pH, the yield of carbon dioxide was never quantitative. Therefore the rate of reaction was followed by measuring the germane gas as a function of time. The plots of $\log(P_\infty - P)$ of germane versus time were straight lines (as shown by the typical plot in Fig. 2), indicating that the hydrolysis of $\text{GeH}_3\text{CO}_2^-$ is first order in $\text{GeH}_3\text{CO}_2^-$. The first order rate constant, k_1 , was calculated from the slopes of such plots. The values of k_1 measured in different pH buffer solutions are summarized in Table I. The results show that the rate is pH independent. Thus, the rate can be expressed by $-d(\text{GeH}_3\text{CO}_2^-)/dt = k_1(\text{GeH}_3\text{CO}_2^-)$ where $k = (1.62 \pm 0.03) \times 10^{-5} \text{ sec}^{-1}$ at 60° .

Products and Stoichiometry of the Hydrogen-Producing Reaction

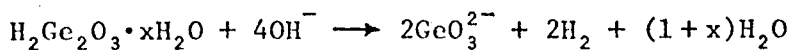
The decomposition of $\text{GeH}_3\text{CO}_2^-$ in solutions of pH greater than 13 involves the formation of hydrogen and a dark brown solid as well as germane and carbonate. A dried sample of the dark brown solid was found to contain 20.74 milli-equivalents of reducing agent per gram and 10.75 millimoles of germanium per gram. Thus 20.74/10.75 (or essentially two) equivalents of reducing agent are associated with each mole of germanium

in the compound. This result, together with the color and amorphous character of the compound, suggest that the compound is germanous hydroxide $\text{Ge}(\text{OH})_2$.⁵ However, the infrared spectra show that the compound is not ordinary germanous hydroxide, but rather the compound $\text{H}_2\text{Ge}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ which forms when germanous hydroxide is digested with hot alkaline solutions.⁶ This isomer of germanous hydroxide contains Ge-H bonds, as shown by the characteristic Ge-H stretching band at 2000 cm^{-1} and the Ge-H deformation band at 750 cm^{-1} . The measured equivalent weight of the dried sample, 48.2 g/eq, is very close to the theoretical value 48.8 g/eq, corresponding to the composition $\text{H}_2\text{Ge}_2\text{O}_3$.

If $\text{H}_2\text{Ge}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and hydrogen are the only additional products of the decomposition of $\text{GeH}_3\text{CO}_2^-$ in strongly alkaline solutions, these products must be formed in accord with the following equation.



That is, for each mole of $\text{GeH}_3\text{CO}_2^-$ which decomposes in this way instead of decomposing to give germane and carbonate, three moles of hydrogen should be formed. In some of the kinetic runs which were allowed to proceed to essentially 100% reaction, the total amounts of hydrogen and germane were measured. The data, presented in Table II, show that the moles of hydrogen divided by the moles of $\text{GeH}_3\text{CO}_2^-$ which did not decompose to germane was always close to the theoretical value of 3. Some of the values, particularly those for runs with hydroxide concentrations greater than 1 M, are significantly greater than 3. The extra hydrogen is probably due to the decomposition of a small amount of the $\text{H}_2\text{Ge}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ as follows.⁷



Kinetics in Strongly Alkaline Solutions

The overall decomposition of $\text{GeH}_3\text{CO}_2^-$ at pH values greater than 13 was found to follow first-order kinetics at any given hydroxide concentration. From plots of $\log(P_\infty - P)$ (for germane) versus time, the overall first-order rate constant, k_{ob} , was measured for various base concentrations. The overall first order rate constant is the sum of two first order rate constants, i.e., $k_{ob} = k_1 + k_2'$, where k_1 is the first order rate constant for the germane-producing reaction and k_2' is the pseudo first-order rate constant for the hydrogen-producing reaction. The constants, k_1 and k_2' , were calculated using the relation

$$\frac{k_1}{k_2'} = \frac{\% \text{ yield of GeH}_4}{100 - \% \text{ yield of GeH}_4}$$

The results are summarized in Table III. The values of k_1 are essentially constant, with an average value of $(2.5 \pm 0.5) \times 10^{-6} \text{ sec}^{-1}$, whereas the k_2' values increase with increasing basicity. It can be seen that the values of the product $k_2' h_-$ [where h_- is the effective hydrogen ion activity, or $\text{antilog}(-H_-)$]⁸ are almost constant, with the average value $(4.48 \pm 0.30) \times 10^{-20} \text{ M sec}^{-1}$. Hence we can define $k_2 = k_2' h_-$ and write, for the hydrogen-producing reaction,

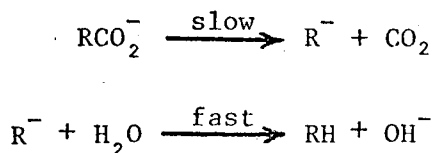
$$-d\ln(\text{GeH}_3\text{CO}_2^-)/dt = k_2/h_-$$

This result we interpret as evidence that the hydrogen-producing reaction is overall second order: first order in germaacetate, and first order in hydroxide. Because of the unavailability of H_- values in the temperature region of our studies, we used H_- values determined at 20° in our calculations. For this reason the calculated value of k_2 lacks rigorous theoret-

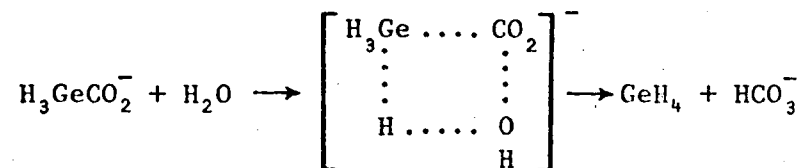
ical significance, and the product $K_w k_2$ is only an approximate value of the rate constant for the rate law involving hydroxide ion activity. The values of k_1 and k_2' for 1.0 M NaOH at various temperatures are summarized in Table IV. Plots of $\log k_1$ and $\log k_2'$ versus $1/T$ are shown in Fig. 3; the calculated activation energy for the germane-producing reaction is 28.6 kcal/mol and that for the hydrogen-producing reaction is 20.8 kcal/mol.

DISCUSSION OF MECHANISMS

The germane-producing reaction is analogous to the decarboxylation of an organic carboxylate ion, RCO_2^- . Such decarboxylation is facilitated when R contains electron-withdrawing groups, such as halogen atoms, which stabilize the carbanion R^- . It has been proposed that, in some decarboxylations of this type,^{9,10} the reaction mechanism involves the formation of an intermediate R^- ion:

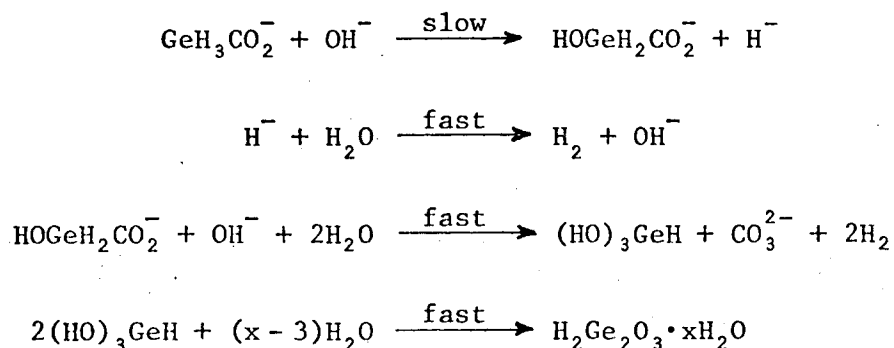


One would expect the rate of the slow step to be closely correlated with the protonic acidity of RH. In fact, such correlation can be seen in the fact that the 2-germaacetate and trichloroacetate ions undergo decarboxylation under comparable conditions.¹¹ The pK of germane (~25)¹² is close to that of chloroform (~24).¹³ Although the above mechanism is reasonable for the germane-producing decomposition of 2-germaacetate, it should be pointed out that our data are also consistent with a four-center mechanism involving initial attack of a water molecule:



In fact, the kinetic data for some decarboxylations of organic carboxylates are also consistent with this type of mechanism.⁹⁻¹¹

The base-catalyzed hydrogen-producing reaction is somewhat analogous to the well-known base-catalyzed hydrolyses of silicon hydride derivatives.¹⁴⁻¹⁷ The latter reactions involve the attack of hydroxide ion on the silicon atom, with displacement of hydride ion. These reactions may be S_N2 processes, or they may involve fleeting pentacoordinate intermediates. It seems reasonable to assume the same sort of process in the case of the 2-germaacetate ion, corresponding to the following mechanism.



Complete hydrolysis to germanate(IV) does not immediately occur because of precipitation of the insoluble polymer H₂Ge₂O₃·xH₂O after the evolution of three moles of hydrogen per germanium atom and the hydrolytic cleavage of the Ge-C bond.

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TABLE I. First-order rate constant, k_1 , at 60° and ionic strength of 1.0 [GeH_3COO^-] $\approx 10^{-2}$ M.

pH	$k_1 \times 10^5, \text{sec}^{-1}$
6.0	1.63
7.3	1.60
8.3	1.67
9.9	1.58
11.4	1.60
13.0	1.61

TABLE II. Gaseous products of the decomposition in strongly alkaline solutions.

NaOH, M	t, °C	GeH ₃ CO ₂ K, mmol	GeH ₄ , mmol	H ₂ , mmol	H ₂
					GeH ₃ CO ₂ K - GeH ₄
0.1	70	1.169	1.080	0.268	3.01
1.0	46	1.184	0.406	2.356	3.03
1.0	60	1.260	0.543	2.197	3.06
1.0	60	1.506	0.687	2.614	3.19
2.0	46	1.236	0.222	3.321	3.28
2.0	75	1.256	0.434	2.649	3.22
3.0	46	1.171	0.128	3.341	3.20

TABLE III. Rate constants at various base concentrations at 45.8°.

NaOH conc., M	H ₋ ^a	GeH ₄ , % yield	Rate Constants			
			Sec ⁻¹ , × 10 ⁶			M sec ⁻¹ , × 10 ²⁰
			k _{ob}	k ₁	k ₂ ¹	k ₂ = k ₂ ¹ h ₋
1.0	13.9	34	5.5	1.9	3.6	4.53
2.0	14.4	18	12.6	2.3	10.3	4.10
3.0	14.7	11	23.6	2.6	21.0	4.19
4.0	14.9	8	42.0	3.4	38.6	4.86
5.0	15.2	3	77.0	2.3	74.7	4.71

^aFrom ref. 8.

TABLE IV. Temperature dependence of rate constants in 1.0 M NaOH.

Temp, °C	% Yield of GeH ₄	$10^{-5} \times \text{sec}^{-1}$		
		k_{ob}	k_1	k_2
45.8	34	0.55	0.19	0.36
54.4	42	1.76	0.74	1.02
60.0	45 ^a	3.60	1.62 ^b	1.98
65.0	52	5.25	2.73	2.52
70.1	55	8.43	4.64	3.79
74.4	59	14.44	8.57	5.87

^aAverage of three values; (45 ± 1.1)%

^bThis value is close to the average value in Table I

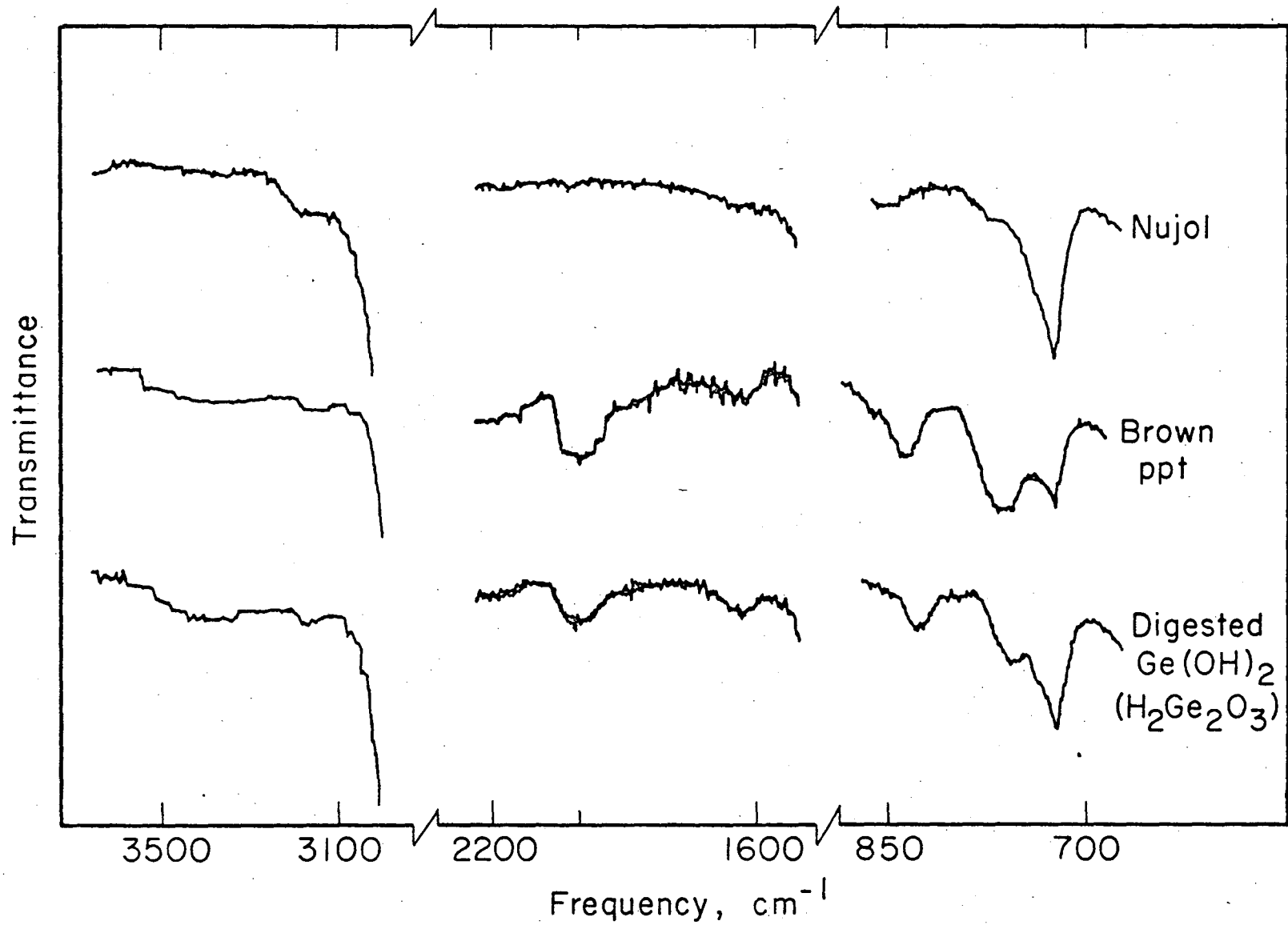
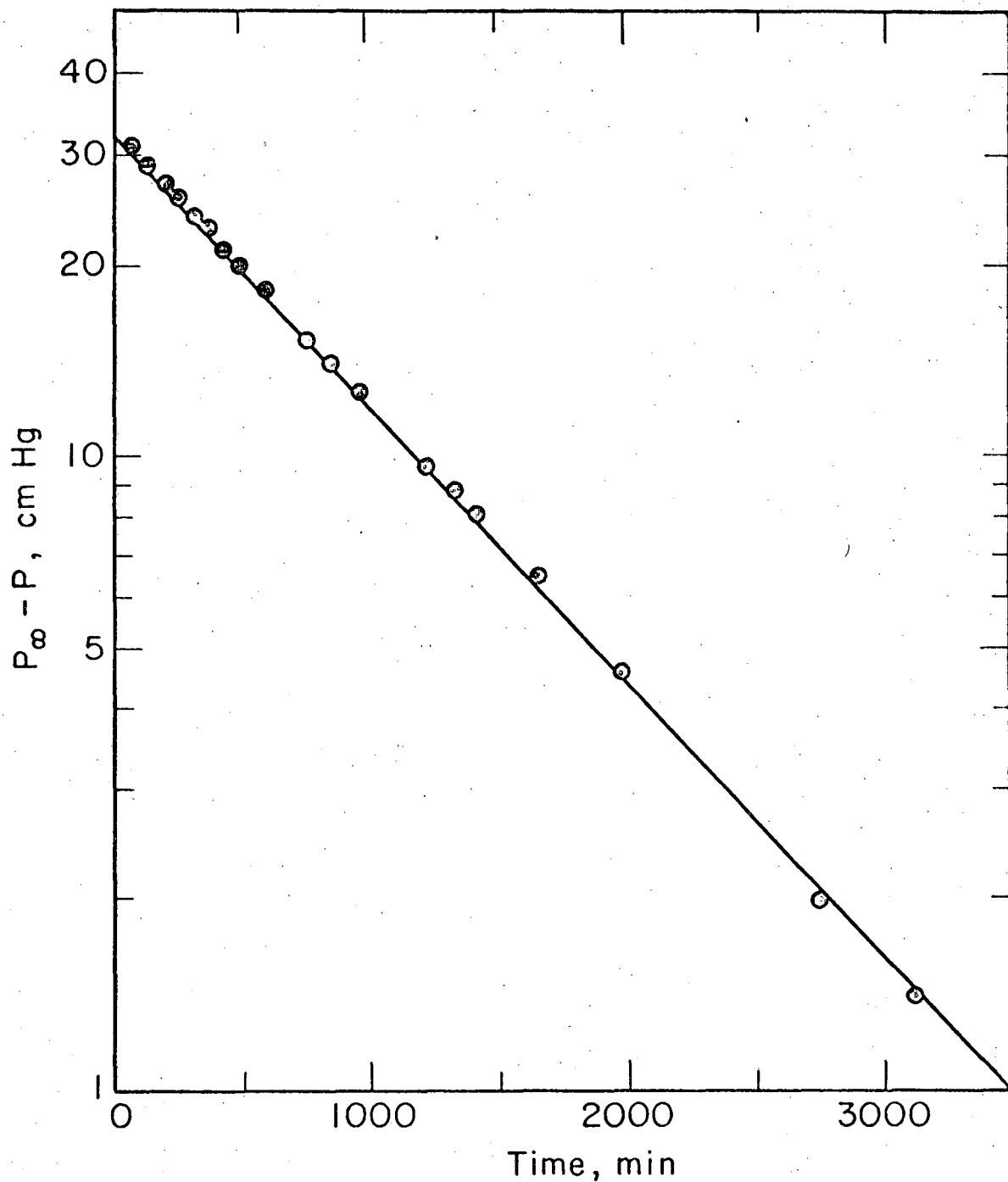


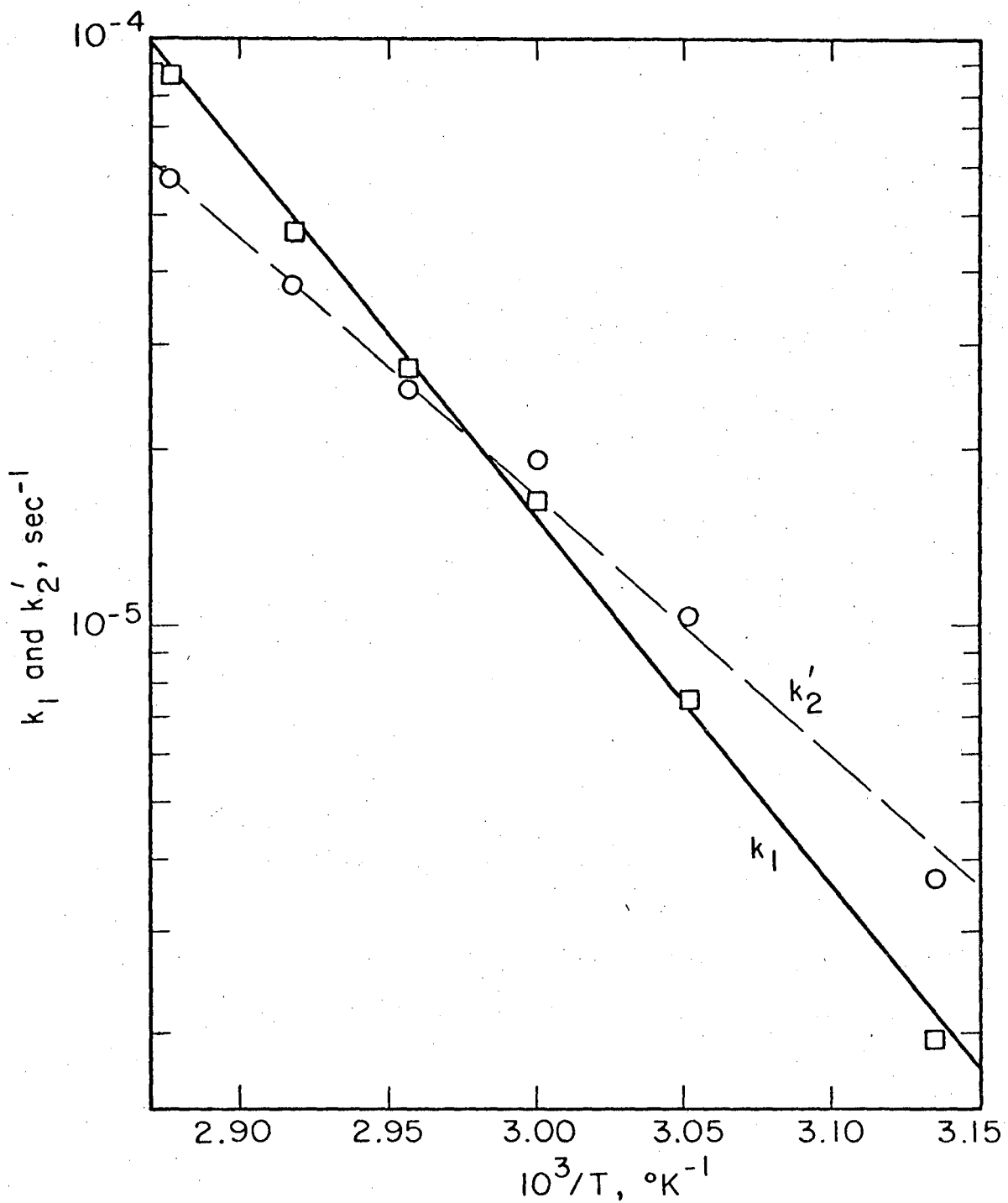
Fig. 1. Comparison of the Nujol mull infrared spectra of the dark brown insoluble product of the hydrogen-producing reaction and alkali-digested germanous hydroxide (H₂Ge₂O₃).

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Fig. 2. $\log(P_{\infty} - P)_{\text{GeH}_4}$ versus time for the hydrolysis of GeH_3COO^- at pH 9.9 at 60° ($\mu = 1.0$).



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Fig. 3. Semilogarithmic plot of k_1 and k_2' versus $1/T$. Squares correspond to k_1 ; circles correspond to k_2' .

PART III. AN ATTEMPT TO PREPARE POTASSIUM
GERMYL MERCAPTIDE AND METHYL GERMYL MERCAPTIDE

ABSTRACT

The reaction of potassium germyl with sulfur was tried in an attempt to prepare potassium germyl mercaptide, GeH_3SK . Addition of iodomethane to the reaction mixture of potassium germyl and sulfur under different conditions was tried to prepare methyl germyl mercaptide, CH_3SGeH_3 . Germane evolution in the reaction of potassium germyl and sulfur suggests decomposition of GeH_3SK . Two possible mechanisms by which GeH_3SK decomposes are proposed.

INTRODUCTION

Potassium germyl is known to react with Lewis acids such as diborane and carbon dioxide to form the stable adducts KGeH_3BH_3 ¹ and KGeH_3CO_2 ² respectively. Reaction of lithium triphenyl germyl with sulfur has been used to synthesize various compounds containing Ge-S-CO and Ge-S-C linkages.³ Likewise potassium germyl mercaptide, GeH_3SK , may also prove to be useful for the synthesis of a series of new compounds. We have attempted to prepare methyl germyl mercaptide, CH_3SGeH_3 , by the reaction of iodomethane with the reaction mixture of sulfur and germyl solutions in monoglyme, diglyme and tetrahydrofuran under different reaction conditions. We found that due to the instability of GeH_3SK , the preparation of CH_3SGeH_3 was not possible.

EXPERIMENTAL

Materials and General Procedures

Germane was obtained from Matheson Co. and used without further purification. Monoglyme was purified by distillation from sodium metal after drying with potassium hydroxide. Diglyme was purified by distillation from sodium metal followed by distillation from calcium hydride. Tetrahydrofuran was prepared by distillation from lithium aluminum hydride. Iodomethane was purified by distillation. Reagent grade sulfur was obtained from Baker and Adamson. Potassium germyl solutions in monoglyme, diglyme and tetrahydrofuran were prepared by the method of Dreyfuss and Jolly.⁴ Infrared spectrometry, mass spectrometry and vapor pressure measurements were used to identify volatile products.

Reaction of Sulfur with $KGeH_3$ in Monoglyme

To 44.8-mmol of $KGeH_3$ in monoglyme at 0° under N_2 was added 44.9-mmol sulfur (calculated as "S"). A brown slurry formed immediately after the addition of sulfur and turned to a white precipitate after stirring for three hours at 0° . The precipitate was dried under vacuum at 0° overnight. The color changed white to yellow. Onto the excess amount of the yellow compound at -196° , iodomethane was condensed in a closed system. For complete reaction the mixture was brought to room temperature and then cooled to -196° several times. The volatile products were fractionated through -46° , -64° , and -196° traps. Methanethiol, CH_3SH , collected in the -64° trap and was identified by its mass spectrum. The presence of sulfide ion in the yellow compound was confirmed by the sulfide test. The sulfide ion was also found in the precipitates prepared by the reaction of sulfur with $KGeH_3$ in diglyme and tetrahydrofuran.

Reaction of Sulfur with KGeH_3 in Diglyme at 0°

To 37.0-mmol of KGeH_3 in diglyme at 0° was added 36.4-mmol sulfur while volatile reaction products were continuously being pumped through -78° and -196° traps on a vacuum line. The mixture was stirred for two hours at 0° and it formed a white precipitate. Even after the formation of the precipitate, GeH_4 was still collected in the -196° trap, which amounted to 15.1-mmol. Iodomethane (16.2 mmol) was then condensed into the reaction vessel at -78° , stirred for two hours at 0° and fractionated through -45° , -63° , -78° , -130° , and -196° traps. The -130° trap contained CH_3SH and CH_3GeH_3 (total of 12.2 mmol). In the -196° trap a total of 16.5-mmol GeH_4 was collected.

Reaction of Sulfur with Excess of KGeH_3 in Monoglyme at -78°

To 13.07-mmol of KGeH_3 in monoglyme at -78° was gradually added 6.56-mmol sulfur in a closed system. Upon addition, it produced a yellow solution and a small amount of GeH_4 (0.13 mmol). When the solution was warmed to -48° at a rate of 10° per hour it slowly formed a white precipitate. After keeping the solution overnight at 0° with constant stirring, a total of 0.58-mmol GeH_4 was collected.

Reaction of Sulfur with KGeH_3 in Diglyme at Low Temperature

To 25.0-mmol KGeH_3 in diglyme at -196° was added 26.0-mmol sulfur in a closed system. Upon vigorous shaking the mixture melted to a yellowish brown solution which was continuously shaken for an hour and a half with occasional cooling to -78° . It was then fractionated at -78° through -78° and -196° traps. The -196° trap contained 3.06-mmol GeH_4 . Iodomethane (16.5 mmol) was condensed into the system at -196° and the mixture was

vigorously shaken for two hours at room temperature with occasional cooling to -78° . It was then fractionated at 0° through -45° , -78° , -130° , and -196° traps. The -196° trap contained 3.70-mmol GeH_4 and -130° trap contained a mixture of CH_3GeH_3 and CH_3SH (14.0 mmol).

To 17.7 mmol KGeH_3 in diglyme at -196° was added 18.7-mmol sulfur. When the mixture was stirred for five hours at -44° it formed a yellow precipitate. When the precipitate was repeatedly warmed to -20° and cooled back to -44° for an additional five hours the color turned from pale green to white. The volatile reaction products were fractionated through -78° and -196° traps. The -196° trap contained 2.0-mmol GeH_4 . After 14.0-mmol iodomethane was condensed into the reaction vessel at -78° and the mixture was slowly warmed to 0° it was fractionated through -45° , -78° , -130° , and -196° traps. The -196° trap contained a total of 7.26 mmol GeH_4 and -130° trap contained a mixture of CH_3GeH_3 and CH_3SH (7.04 mmol).

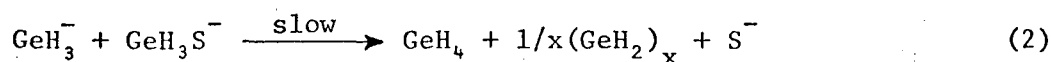
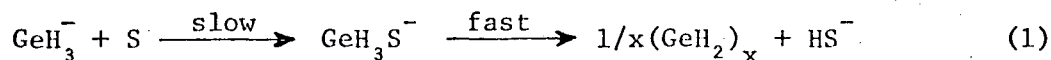
Reaction of Excess Sulfur with KGeH_3 in Monoglyme at -78°

To 13.1-mmol KGeH_3 in monoglyme at -78° was gradually added 25.4-mmol sulfur in a closed system. Upon addition it formed a brown solution and produced GeH_4 . The solution was then slowly warmed to 0° and stirred for eight hours. The solution formed a white precipitate and a total of 2.02-mmol GeH_4 was collected.

RESULTS AND DISCUSSION

Our failure to synthesize CH_3SGeH_3 is most likely due to the instability of GeH_3SK in the solvent systems used. Continuous evolution of germane was observed upon addition of sulfur to potassium germyl

solution and also after the formation of a white precipitate in the reaction mixture. The presence of sulfide in the precipitate was confirmed by qualitative sulfide ion test and by the formation of CH_3SH in the iodomethane reaction with the precipitate. The yellow color of the dried precipitate indicates the formation of germanium hydride. GeH_2 species is known to decompose to GeH_4 and yellow solid germanium hydride, GeH_x ($x < 2$).⁴⁻⁶ Thus these results support our view that GeH_3SK is unstable. We propose the following decomposition reactions:



Reaction (1) can be preceded by nucleophilic attack substitution⁴ of a germyl anion on sulfur, which produces unstable GeH_2 and HS^- . Reaction (2) is a Lewis acid-base reaction. In both reactions GeH_2 is formed which can easily decompose to germane and solid germanium hydride. However, reaction (1) provides a more favorable mechanism because the yield of GeH_4 was minimized in the reaction of sulfur with excess of GeH_3K . Furthermore, CH_3SH was found in the reaction of iodomethane with the precipitate.

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