increases with the number of fluorines on the molecule. (4) J_{HF} for a Sn–CH_2F group is greater than J_{HF} for a Sn–CHF_2 group. (5) $J_{^{117/119}Sn-F}$ values are much greater than $J_{^{117/119}Sn-H}$ values and appear to be dependent on the number of fluorines on the molecule. (6) Increased number of CF_3 groups causes a trend which lowers ^{19}F chemical shifts.

Besides the characteristic doublet and triplet patterns as a result of proton–fluorine coupling, the chemical shifts (in ppm) lead to ready identification of the groups. For protons: CH_3 (~0), CH_2F (~4.8), CHF_2 (~6.0). For fluorine: CF_3 (~–30), CHF_2 (~48), CH_2F (~190). Integration of the partially fluorinated species gives the number of CH_3 groups on tin.

The observation[10] that chlorine cleaves a methyl group rather than trifluoromethyl group from $Sn(CH_3)_3(CF_3)$ is intriguing for this reaction. If fluorine behaves in a similar manner, then once the groups CH_2F, CHF_2, and CF_3 form, they remain on the tin and a methyl group is cleaved. Schematically, the following is possible:

$$Sn(CH_3)_4 + F_2/He \rightarrow$$

$$Sn(CH_3)_3(CH_2F) + F_2/He \rightarrow Sn(CH_3)_2(CH_2F)F$$

$$Sn(CH_3)_2(CH_2F)_2 + F_2/He \rightarrow Sn(CH_3)(CH_2F)_2F$$

$$Sn(CH_3)_3(CHF_2) + F_2/He \rightarrow Sn(CH_3)_2(CHF_2)F$$

$$Sn(CH_3)_3(CF_3) + F_2/He \rightarrow Sn(CH_3)_2(CF_3)F$$

$$Sn(CH_3)_2(CF_3)_2 + F_2/He \rightarrow Sn(CH_3)(CF_3)_2F$$

It is possible that direct fluorination can be used for the two-step synthesis of fluorine-containing tetramethyltins. Previous to this report two fluoromethyltin compounds were reported: $Sn(CH_3)_3(CH_2F)$[8] and $Sn(CH_3)_3(CHF_2)$.[9] Quite vigorous conditions were required for the synthesis of the two compounds.

We are confident that with improvements in our fluorine technology, it may still be possible to synthesize $Sn(CF_3)_4$ by direct fluorination techniques. We have demonstrated that direct fluorination is indeed a useful method for the synthesis of trifluoromethyl compounds.[3–5] We are presently exploring other metal–alkyl systems.

Acknowledgment. Fluorine chemistry at the University of Texas is supported by the Air Force Office of Scientific Research (AFOSR-76-3031A).

Registry No. $Sn(CH_3)_4$, 594-27-4; $Sn(CH_2F)(CH_3)_3$, 4554-91-0; $Sn(CH_2F)_2(CH_3)_2$, 65059-35-0; $Sn(CHF_2)(CH_3)_3$, 29723-38-4; $Sn(CF_3)(CH_3)_3$, 754-25-6; $Sn(CF_3)_2(CH_3)_2$, 65059-36-1; $Sn(CH_3)_2F_2$, 3582-17-0; $Cd(CH_3)_2$, 506-82-1; F_2, 7782-41-4.

References and Notes

(1) J. G. A. Luyten and G. J. M. Van der Kerk, "The Bond to Carbon", Vol. I, Part II, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y. 1968, Chapter 4, p 91.
(2) D. Seyferth and E. G. Rochow, *J. Am. Chem. Soc.*, **77**, 1303 (1955).
(3) E. Liu and R. J. Lagow, *J. Am. Chem. Soc.*, **98**, 8270 (1976).
(4) E. Liu and R. J. Lagow, *J. Organomet. Chem.*, in press.
(5) E. Liu and R. J. Lagow, *J. Chem. Soc., Chem. Commun.*, 450 (1977).
(6) N. J. Maraschin and R. J. Lagow, *Inorg. Chem.*, **12**, 1458 (1973).
(7) N. J. Maraschin, Ph.D. Thesis, Massachusetts Institute of Technology, 1974.
(8) V. V. Khrapov, U. I. Gol'danskii, A. K. Prokof'ev, and R. G. Kostyanovskii, *Zh. Obshch. Khim.*, **37**, 3 (1967).
(9) W. R. Cullen, J. R. Sams, and M. C. Waldman, *Inorg. Chem.*, **9**, 1682 (1970).
(10) R. D. Chambers, H. C. Clark, and W. J. Willis, *J. Chem. Phys.*, **39**, 131 (1961).
(11) (a) R. A. Jacob and R. J. Lagow, *J. Chem. Soc., Chem. Commun.*, 104 (1973); (b) R. J. Lagow, L. L. Gerchman, R. A. Jacob, and J. A. Morrison, *J. Am. Chem. Soc.*, **97**, 518 (1975).
(12) R. G. Kostyanovskii and A. K. Prokof'ev, *Dokl. Akad. Nauk SSSR*, **164**, 1054 (1965).
(13) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", Vol. I, 3rd ed, Methuen, London, 1967, p 413.
(14) R. Eujen, mass spectral observations.

Contribution from the Department of Chemistry, University of California,
and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Decarbonylation of 2-Germaacetic Acid in Aqueous Solutions

DUCK J. YANG and WILLIAM L. JOLLY*

Received August 18, 1977

In dilute aqueous acid solutions (0.05–0.5 M H^+), 2-germaacetic acid decomposes to form carbon monoxide, an orange-yellow solid of approximate composition $GeH_{0.6}$, and small amounts of germane. The rate law for the reaction is $-d[GeH_3COOH]/dt = k[H^+][GeH_3COOH]$; $k = (5.59 \pm 0.14) \times 10^{-4}$ M^{-1} s^{-1} at 22.5 °C and ionic strength 1.0 M. From rate measurements in the temperature interval 0–39.5 °C, the activation energy was determined to be 16.9 kcal/mol. When the reaction is carried out in strongly acidic solutions (e.g., >6 M HCl, >4 M H_2SO_4, or >6 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 in the form of the germyloxonium ion, $GeH_3OH_2^+$. 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 was first studied by Kuznesof and Jolly.[1] They reported that the reaction produces 1 mol of carbon monoxide/mol of acid decomposed, variable small amounts of germane, and an insoluble orange solid containing germanium and hydrogen:

$$GeH_3COOH \xrightarrow{H^+} CO + xGeH_4 + \text{solid } (x << 1)$$

The purpose of this study was to determine more precisely the stoichiometry of the reaction and to investigate the mechanism of the reaction by the identification of intermediates and by a kinetic study.

Experimental Section

General Procedure. All manipulations were carried out using a standard vacuum line or a nitrogen-filled glovebag. 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.

0020-1669/78/1317-0621$01.00/0 © 1978 American Chemical Society

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).

GeH_3COOK. Potassium germyl in 1,2-dimethoxyethane was prepared by a method similar to that previously described.[2] The solution of $KGeH_3$ was stirred and shaken at 0 °C under approximately 1 atm pressure of carbon dioxide. When absorption of the CO_2 was complete, the precipitated product was collected by suction filtration on a frit.

A 1.228-mmol sample of GeH_3COOK was heated in a sealed tube at 510 °C for 24 h. The pyrolysis products were analyzed as described by Kuznesof and Jolly.[1] Sample purity was calculated on the basis of the reaction

$$2GeH_3COOK \xrightarrow{\Delta} 3H_2 + CO + 2Ge + K_2CO_3$$

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 °C for 100 h. The volatile products were fractionated through two −78 °C traps and a −196 °C trap. Germane (0.368 mmol) collected in the −196 °C trap. Germanium in the remaining solution was determined by the mannitol method[3] after treatment with acid peroxide to ensure complete oxidation of the germanium to the +4 state. The solution contained 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-bottomed flask with a stopcock and a 24/40 male joint, containing 30 mL of 1 M HCl, was cooled to 0 °C, evacuated, and then cooled to −78 °C. A weighed sample of GeH_3COOK was added to the flask while flushing with nitrogen, and the flask was reevacuated and warmed to 0 °C. 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 °C trap, a trap filled with an intimate mixture of glass helices and yellow HgO to remove HCl, a −78 °C trap, and a −196 °C trap to collect GeH_4. The noncondensable gas (CO) was Toepler pumped into a calibrated gas buret. The germane and carbon monoxide 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 method[4] 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 placed in a 3-cm diameter, 20-cm length 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 °C for 10 h, 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 °C in a closed evacuated system. Dissolution occurred slowly. No gas was evolved at −78 °C, but when the solution was warmed, CO began to be evolved around −50 °C and was quantitatively evolved at 0 °C. The resulting solution did not further evolve any gases at room temperature and only slowly evolved hydrogen at 80 °C. Four solutions prepared in this manner were separately analyzed by heating in closed tubes at 155–200 °C 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 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.

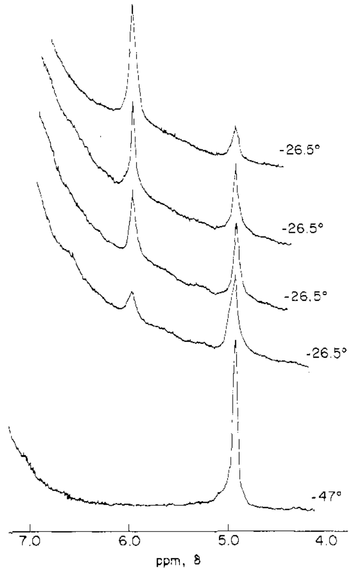


Figure 1. NMR spectra of a solution of GeH_3COOK in 8 M HCl at −47 and −26.5 °C. The −26.5 °C spectra were obtained at approximately 8-min intervals and show the gradual conversion of GeH_3COOH to GeH_3^+.

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 in concentrated acid.

NMR Experiments. Proton NMR spectra were obtained with 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 parts per million downfield from the proton resonance of external Me_4Si 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 as a function of temperature and time are shown in Figure 1. Within ±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 ca. 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 °C, the vessel was connected to a vacuum pump until the air was completely removed. Then the vessel was placed in a thermostated oil bath (±0.1). 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-L bulb was momentarily opened. This procedure allowed the gaseous reaction products ($CO + GeH_4$) 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 °C, 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 $GeH_{0.6}$. 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}, due to Ge–H stretching.[6]

Studies in Strongly Acidic Solutions. When the decarbonylation was carried out in strongly acidic solutions (e.g., >6 M HCl, >4 M H_2SO_4, or >6 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. (δ = 5.8–5.9 ppm to low field of Me_4Si.) The NMR spectra are shown in Figure 1. Solutions of germyl chloride in 6 and 8 M HCl, 6 and 8 M $HClO_4$, and 4, 6, and 8 M H_2SO_4 were found to have the same chemical properties and similar NMR chemical shifts, as those prepared by the decarbonylation of germaacetic acid in the same acid solutions.

The data indicate that, in strongly acidic solutions, the decarbonylation produces a relatively stable intermediate species containing the GeH_3^+ group, probably in the form of the hydrate, i.e., the germyl oxonium ion $GeH_3OH_2^+$. It is tempting to draw an analogy between this species and the species present in the analogous carbon system. Methyl chloride reacts with water to form methyl alcohol and hydrogen chloride. In aqueous hydrochloric acid an equilibrium can be achieved in which all the species in the following reactions are present in significant concentrations.[7,8]

$$CH_3Cl + H_2O \rightleftharpoons CH_3OH_2^+ + Cl^-$$

$$CH_3OH_2^+ + H_2O \rightleftharpoons CH_3OH + H_3O^+$$

Our data for the intermediate germanium species in the aqueous acids HX are consistent with equilibria involving the species GeH_3X, $GeH_3OH_2^+$, and GeH_3OH; however, the exact characterization of the system will require further research. For simplicity in the following discussion, we shall represent the intermediate in the strongly acidic solutions by the formula GeH_3^+. The intermediate is remarkably stable. In 8 M HCl, it appears to be stable indefinitely at room temperature. After such solutions are heated for a week at 200 °C, decomposition to hydrogen and germanium(II) (probably as $GeCl_3^-$) occurs.

$$GeH_3^+ + H^+ + 3Cl^- \rightarrow 2H_2 + GeCl_3^-$$

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.[9-11] We may therefore represent the decarbonylation of germaacetic acid as a three-step process.

$$GeH_3COOH + H^+ \rightarrow GeH_3^+ + CO + H_2O \qquad (1)$$

$$GeH_3^+ \rightleftharpoons H^+ + GeH_2 \qquad (2)$$

$$GeH_2 \rightarrow \left(\frac{2-4}{4-x}\right)GeH_4 + \left(\frac{2}{4-x}\right)GeH_x \quad (x \approx 0.6) \qquad (3)$$

It is significant that, when potassium germaacetate is dissolved in 8 M HCl at −78 °C, no carbon monoxide is evolved until the solution is warmed to about −50 °C. 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.

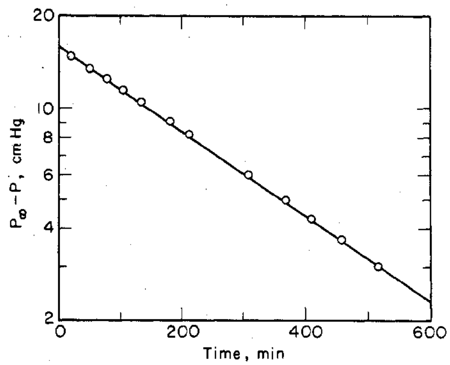


Figure 2. log $(P_\infty - P)_{CO}$ vs. time for the decarbonylation of GeH_3COOH at $[H^+]$ = 0.1 M and 22.5 °C.

Table I. Effect of Acid Concentration on the Value[a] of the Observed First-Order Rate Constant, k_{obsd}, and the First-Order Rate Constant, k, at 22.5 °C and $\mu = 1.0$

$[H^+]$, M	$T_{1/2}$, min	$10^5 k_{obsd}$, s^{-1}	$k = k_{obsd}/[H^+]$, $M^{-1}\ s^{-1}$
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}
		Av	$(5.59 \pm 0.14) \times 10^{-4}$

[a] $[GeH_3COOH] \simeq 1.2 \times 10^{-2}$ M.

Table II. Temperature Dependency of k[a] at $\mu = 1.00$

Temp, °C	$[H^+]$, M	$T_{1/2}$, min	$10^5 k$, $M^{-1}\ s^{-1}$
0.0	0.10	2080	5.55
22.5	0.10	220	52.5
31.0	0.10	76	152.0
35.5	0.05	114	202.6
39.5	0.05	83	278.6

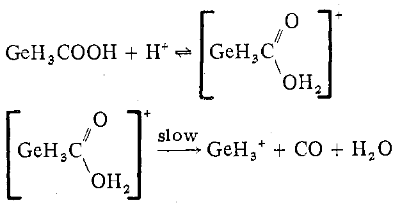
[a] $[GeH_3COOH] = (0.05\text{–}1.2) \times 10^{-2}$ M.

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 $(P_\infty - P)$ vs. time, the hydrolysis was found to be first order in GeH_3COOH as shown in Figure 2. 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; 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., $k_{obsd} = k[H^+]$, where k has a value of $(5.59 \pm 0.14) \times 10^{-4}\ M^{-1}\ s^{-1}$ at 22.5 °C. The overall rate is therefore first order in both H^+ and GeH_3COOH:

$$-d[GeH_3COOH]/dt = k[H^+][GeH_3COOH]$$

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 vs. $1/T$, 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.[12] If we write a mechanism for the first step of the decarbonylation (i.e., reaction 1) similar to that proposed by Ropp[12c] for organic acids, we obtain:



$$GeH_3COOH + H^+ \rightleftharpoons [GeH_3C(=O)OH_2]^+$$

$$[GeH_3C(=O)OH_2]^+ \xrightarrow{slow} GeH_3^+ + CO + H_2O$$

Of course, our data do not permit us to distinguish between this mechanism, involving a $GeH_3COOH_2^+$ *intermediate*, and a one-step process involving a $GeH_3COOH_2^+$ *activated complex*.[13,14] 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 4 family the ease of forming cationic species such as MR_3^+ increases.[15]

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.[16] However, the SnH_3^+ ion is an extremely unstable species, decomposing to hydrogen and tin(II) even below 0 °C. This fact at first seems inconsistent with the general trend of increased cation stability on going down the group 4 family, mentioned above. However, the instability of SnH_3^+, compared to the stability of GeH_3^+, is probably 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.

Our observed activation energy for the decomposition of GeH_3COOH, 16.9 kcal/mol, is consistent with the suggested mechanism and with the reported activation energies for analogous decompositions of organic acids. Most organic acids undergo decarbonylation only in very concentrated acid solutions, such as 98–100% sulfuric acid, with activation energies of 18–25 kcal/mol. For example, formic acid[17] decomposes in 97.6% sulfuric acid with an activation energy of 18.5 kcal/mol, and citric acid[18] decomposes in 99.3% sulfuric acid with an activation energy of 23.0 kcal/mol. However triphenylacetic acid,[19] which can form the relatively stable triphenylcarbonium ion, readily decomposes in 100% sulfuric acid with an activation energy of 15.1 kcal/mol.

Triaryl and trialkyl analogues of 2-germaacetic acid are relatively stable compounds which undergo decarbonylation only when heated.[20-25] Apparently no kinetic or detailed mechanistic studies of these reactions have been made. We have no explanation for the lower reactivity of the organo analogues.

Acknowledgment. This work was supported by the U.S. Energy Research and Development Administration. We wish to thank Dr. J. Scheer for help in obtaining the Raman spectrum, Miss C. Gin for preparing GeH_3Cl, and Messrs. K. Klotter and D. Lee for help in obtaining the NMR spectra.

Registry No. GeH_3COOK, 22054-96-2.

References and Notes

(1) P. M. Kuznesof and W. L. Jolly, *Inorg. Chem.*, **7**, 2574 (1968).
(2) R. M. Dreyfuss and W. L. Jolly, *Inorg. Chem.*, **10**, 2567 (1971).
(3) R. Belcher and C. L. Wilson, "New Methods in Analytical Chemistry", Reinhold, New York, N.Y., 1955, p 234.
(4) W. C. Pierce, D. T. Sawyer, and E. L. Haenisch, "Quantitative Analysis", 4th ed, Wiley, New York, N.Y., 1963, p 300.
(5) S. Cradock, *Inorg. Synth.*, **15**, 161 (1974).
(6) (a) R. J. Cross and F. Glockling, *J. Organomet. Chem.*, **3**, 146, 152 (1965); (b) F. Glockling, "The Chemistry of Germanium", Academic Press, London, 1969, p 15; (c) V. Crawford, K. Rhee, and M. Wilson, *J. Chem. Phys.*, **37**, 2377 (1962).
(7) D. W. F. Hardie in "Kirk-Othmer Encyclopedia of Chemical Technology", Vol. 5, 2nd ed, Interscience, New York, N.Y., 1964, pp 100–111.
(8) L. S. Levitt and B. W. Levitt, *Tetrahedron*, **27**, 3777 (1971).
(9) S. N. Glarum and C. A. Kraus, *J. Am. Chem. Soc.*, **72**, 5398 (1962).
(10) R. M. Dreyfuss and W. L. Jolly, *Inorg. Chem.*, **7**, 2645 (1968).
(11) R. M. Dreyfuss and W. L. Jolly, *Inorg. Chem.*, **10**, 2567 (1971).
(12) (a) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968, p 315; (b) L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 1940, p 283; (c) G. A. Ropp, *J. Am. Chem. Soc.*, **82**, 842 (1960).
(13) The stable form of $RCOOH_2^+$ has one proton on each of the oxygen atoms.[14] However, the *activated complex* which yields R^+, CO, and H_2O, would be expected to have both protons on one oxygen atom. There is no reason to expect an activated complex to have exactly the same structure as a known stable species.
(14) R. J. Gillespie, *Acc. Chem. Res.*, **1**, 202 (1968).
(15) R. S. Tobias, *Organomet. Chem. Rev.*, **1**, 93 (1966).
(16) J. R. Webster and W. L. Jolly, *Inorg. Chem.*, **10**, 877 (1971).
(17) E. R. Schierz, *J. Am. Chem. Soc.*, **45**, 447 (1923).
(18) E. O. Wiig, *J. Am. Chem. Soc.*, **52**, 4729 (1930).
(19) H. R. Dittmar, *J. Phys. Chem.*, **33**, 533 (1929).
(20) A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **76**, 77 (1954).
(21) A. G. Brook, *J. Am. Chem. Soc.*, **77**, 4827 (1955).
(22) F. Glockling and K. A. Hooton, *J. Chem. Soc.*, 3509 (1962).
(23) R. J. Cross and F. Glockling, *J. Chem. Soc.*, 4125 (1964).
(24) E. J. Bulten and J. G. Noltes, *Tetrahedron Lett.*, 1443 (1967).
(25) E. J. Bulten and J. G. Noltes, *J. Organomet. Chem.*, **29**, 409 (1971).