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# THE SYNTHESIS AND CHARACTERIZATION OF METHYL 2-GERMAACETATE AND ETHYL 2-GERMAACETATE

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## Summary

The methyl and ethyl esters of 2-germaacetic acid ($GeH_3CO_2H$) have been prepared, and their thermal decompositions and acid- and base-catalyzed hydrolyses have been studied.

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## Introduction

The chemical properties of an ester of a carboxylic acid are markedly changed by replacing the $\alpha$ carbon atom of the acid by a silicon or germanium atom [1—6]. Although esters of the type $R_3GeCO_2R'$ and $R_3SiCO_2R'$ have been studied, no studies of the corresponding unsubstituted esters, in which $R = H$, have been carried out. To further our understanding of these compounds and their reactions, we have prepared the methyl and ethyl esters of 2-germaacetic acid, $GeH_3CO_2H$, by reaction of the appropriate trialkyloxonium fluoroborates with potassium 2-germaacetate. We have investigated their thermal decomposition reactions and their acid- and base-catalyzed hydrolyses.

## Experimental

Triethyloxonium fluoroborate (m.p. 88 - 91°, lit. [7] 91 - 92°), was prepared by the reaction of epichlorohydrin (Matheson, Coleman and Bell; b.p. 115 - 117°) with boron trifluoride etherate (Matheson, Coleman and Bell; 98%). Trimethyloxonium fluoroborate (m.p. 138 - 140°, lit. [8] 141 - 143°) was prepared by the reaction of $[(C_2H_5)_3O]BF_4$ with dimethyl ether (Matheson; 99%). Potassium 2-germaacetate was prepared by the reaction of carbon dioxide with potassium germyl in either the dimethyl ether of ethylene glycol (monoglyme) or the dimethyl ether of triethylene glycol (triglyme) [9]. The monoglyme was removed from the salt under vacuum, whereas the potassium 2-germaacetate prepared as a suspension in triglyme was not isolated, but was allowed to react in suspension with the appropriate alkylating agent.

The identity and purity of substances were checked using spectra from the following instruments: Granville-Phillips Spectra-Scan Model 400 mass spectrometer, Perkin-Elmer Model 137 infrared spectrophotometer, and Varian Model T-60 NMR spectrometer. NMR spectra were referenced to tetramethylsilane (TMS) by tube interchange.

Standard vacuum line techniques were used to purify and to manipulate volatile compounds except in the case of esters prepared in triglyme. The alkylating agents reacted with triglyme even at 0° to produce dioxane, which could not be separated from the esters by ordinary fractional condensation techniques. Therefore, to separate the esters from dioxane, a gas chromatograph employing a thermistor (3000 ohms at 25°) was built into the vacuum line. The column consisted of a coil of 4′ of 7 mm glass tubing packed with 15% silicone S.E. 30 (methyl form; Varian Aerograph) on firebrick [10]. The column and detector were maintained at room temperature. Two traps at —196° separated by a three-way stopcock were used to condense the desired fractions. The flow rate of the helium carrier gas was adjusted to obtain retention times of 10 - 15 minutes and separations of 3 - 4 minutes.

### *Preparation of the esters*

To a magnetically stirred slurry of potassium 2-germaacetate (3.2 g; 20 mmol) at 0° in dry diethyl ether or triglyme, 50 mmol of alkylating agent was added from a side-arm of the reaction vessel. Reaction was allowed to proceed for 15 min, whereupon the reaction vessel was opened to two U-traps at —78° and one trap at —196°. When diethyl ether was the solvent, all volatile materials were pumped into the traps. When triglyme was the solvent, materials more volatile than triglyme were removed by pumping on the solution. In either case, the contents of the —78° traps were combined and subsequently purified by fractional condensation. Traps at —45, —63, —95, and —196° were used for the ethyl ester (collected at —63°), and traps at —63, —112 and —196° were used for the methyl ester (collected at —112°). The resulting crude esters were purified by repeated fractional condensation. When triglyme had been used as the solvent, purification by gas chromatography was necessary to remove dioxane.

Some physical properties and spectral data for the esters follow.
$GeH_3CO_2CH_3$: Vapor pressure (mm): 79.5 at 22°; 31.0 at 0°. IR ($cm^{-1}$): 2950 m, 2115 s, 1720 s, 1430 w, 1180 s, 1140 vs, 945 m, 810 vs, 675 w, 565 m. Mass spectrum (only the strongest peak of each cluster is given): 15($CH_3$); 31($OCH_3$); 75($GeH_x$); 91; 105($H_xGeCO$); 119($H_xGeCO_2$); 136($H_xGeCO_2CH_3$). NMR spectrum (neat): singlet, $\delta$ 4.0 ppm ($GeH_3$); singlet, $\delta$ 3.57 ($CH_3$). Integrated intensities: 1/1.
$GeH_3CO_2C_2H_5$: Vapor pressure (mm): 41.5 at 22°; 22.0 at 0°. IR ($cm^{-1}$): 3010m, 2110s, 1720s, 1415w, 1370w, 1145vs, 1030m, 810vs, 675w, 570m, Mass spectrum (only the strongest peak of each cluster is given): 15($CH_3$); 29($C_2H_5$); 43($C_2H_3O$); 75($GeH_x$); 91; 105($H_xGeCO$); 119($H_xGeCO_2$); 150 ($H_xGeCO_2C_2H_5$). NMR spectrum (neat): singlet, $\delta$ 3.82 ppm ($GeH_3$); quartet, $\delta$ 3.84 ppm, $J$ 7.0 Hz ($CH_2$); triplet, $\delta$ 0.92 ppm, $J$ 7.0 Hz ($CH_3$). Integrated intens-

ities: 3/2/3, respectively. The purity of both samples is attested by the fact that head and tail distillation fractions had the same vapor pressures.

*Reaction of the esters with basic and acidic aqueous solutions*

The ester was distilled into a reaction vessel containing a degassed acidic or basic aqueous solution (2 ml conc. $H_2SO_4$ plus 3 ml $H_2O$, or 1.5 g KOH in 5 ml $H_2O$), and the mixture was allowed to react with occasional agitation at 0° for 30 minutes. The condensable volatile products were separated by trap-to-trap fractional condensation in traps at −45, −63, −112, and −196°, and the noncondensable gas was collected with a Toepler pump. The mass spectra and infrared spectra of the contents of the traps were examined; no unreacted starting material was found. A considerable amount of relatively non-volatile germanium-containing residue remained in the reaction vessel. The reaction vessel was then held at 80° overnight, and the separation and analysis of volatile products was repeated. One of the basic solutions was acidified at this time by distilling 7 ml of glacial acetic acid into the vessel; carbon dioxide (0.033 mmol) was the only volatile product identified. The results are summarized in Table 1.

In one experiment, 9 ml of a triglyme solution of potassium germyl (0.153 *M*) was added to 0.70 mmol of $GeH_3CO_2C_2H_5$. The volatile products (carbon monoxide (0.17 mmol) and germane (0.46)) were separated and identified as above. The solution was then acidified with 10 ml of 4*N* $H_2SO_4$, and volatile products (0.717 mmol of germane and 0.32 mmol of digermane) were again separated and identified. Holding the solution at 80° overnight produced germane (0.102 mmol), digermane (0.06 mmol) and hydrogen (0.03 mmol).

*Thermal decomposition studies*

The esters were sealed in glass tubes fitted with fragile tips [11] and the tubes were heated in a tube furnace equipped with a Chromel-Alumel thermocouple. Germanium mirrors formed in each case. After various times, the fragile tips were broken, the condensable volatile products were collected in U-traps at −45, −63, −112, and −196°, and noncondensable gases were collected with a Toepler pump. The results are shown in Table 2.

TABLE 1

HYDROLYSIS OF METHYL 2-GERMAACETATE AND ETHYL 2-GERMAACETATE

| Reactant (mmol) | Time (h) | Temp (°C) | Products (mmol) | | | |
|---|---|---|---|---|---|---|
| | | | CO | $GeH_4$ | $CH_3OH^a$ | $C_2H_5OH^a$ |
| *Base Catalyzed* | | | | | | |
| $GeH_3CO_2CH_3$ | 0.5 | 0 | 0.099 | 0.099 | 0.4 | |
| (0.912)[b] | 12 | 80 | none | 0.045 | 0.05 | |
| $GeH_3CO_2CH_3$ (0.327) | 1 | 22 | 0.033 | 0.061 | 0.03 | |
| $GeH_3CO_2C_2H_5$ | 2.5 | 0 | 0.040 | 0.170 | | 0.1 |
| (0.812) | 12 | 80 | 0.005 | 0.06 | | 0.05 |
| *Acid Catalyzed* | | | | | | |
| $GeH_3CO_2CH_3$ | 2 | 0 | 0.68 | 0.009 | 0.1 | |
| (0.896) | 72 | 22 | none | 0.346 | 0.05 | |
| $GeH_3CO_2C_2H_5$ | 1 | 0 | 0.482 | 0.0133 | | none |
| (0.519) | 1 | 80 | none | 0.263 | | none |

[a] Accuracy of alcohol determinations ± 0.05 mmol. [b] 1.5 gm KOH in 2.5 ml $H_2O$, 2.5 ml dioxane

TABLE 2

THERMAL DECOMPOSITION OF METHYL 2-GERMAACETATE AND ETHYL 2-GERMAACETATE

| Reactant (mmol) | Time (h) | Temp. (°C) | Products (mmol) | | | | |
|---|---|---|---|---|---|---|---|
| | | | CO | $GeH_4$ | $CH_3OH$ | $C_2H_5OH$ | Other |
| $GeH_3CO_2CH_3$ (0.846) | 1 | 260 | 0.800 | 0.195 | 0.82 | | |
| $GeH_3CO_2C_2H_5$ (0.906) | 8 | 160 | 0.174 | 0.023 | | 0.14 | 0.720 ($GeH_3CO_2C_2H_5$) |
| $GeH_3CO_2C_2H_5$ (0.460) | 0.5 | >300 | | | | | 2.036 (CO, $H_2$, $CH_4$),<br>0.1 ($C_2H_4$) |

### *Reaction of the esters with $D_2O$*

Approximately 0.3 mmol portions of the esters were distilled into NMR tubes containing degassed $D_2O$ (International Nuclear and Chemical Corp. 98.8%), and the NMR spectra of the solutions were recorded. Reaction with $D_2O$ was negligible at room temperature; therefore the tubes were heated to 80°, and spectra were recorded periodically for several days thereafter.

As yellow solid decomposition products appeared in the tube, the two peaks assigned to methyl 2-germaacetate (singlet, $\delta$ 4.08 ppm; singlet, $\delta$ 3.60 ppm) decreased in intensity, until after three days they disappeared completely. A small peak at 4.1 ppm appeared and persisted for three days at 80°. It is assigned to $GeH_3CO_2D$ (Cf., $\delta$ 4.3 ppm for potassium 2-germaacetate in $D_2O$) [9]. Another peak appeared in the spectrum at $\delta$ 3.36 ppm, and it is assigned to $CH_3OD$, based on a comparison with a known sample of $CH_3OH$ in $D_2O$. The spectrum of the ethyl ester in $D_2O$ was at first quite poor because of the low solubility of the ester and the overlap of the peaks arising from the ethyl groups of the ester and $C_2H_5OD$. After 36 h at 80°, however, the spectrum became a triplet ($\delta$ 1.13 ppm; $J$ 7.5 Hz), a quartet ($\delta$ 3.62 ppm; $J$ 7.5 Hz) and a singlet ($\delta$ 4.15 ppm). The triplet and quartet are assigned to $C_2H_5OD$ by comparison with a known sample of $C_2H_5OH$ in $D_2O$. The intensity of the singlet decreased with time and disappeared entirely after four days at 80°. Since a similar peak also appeared and disappeared in the spectrum of the methyl ester, it is ascribed to $GeH_3CO_2D$. The NMR tube which had contained the ethyl ester was opened, and carbon monoxide (0.220 mmol), germane (0.071 mmol), carbon dioxide (trace), and ethanol (0.15 mmol) were found.

## Discussion

The methyl and ethyl esters of 2-germaacetic acid are volatile, thermally stable compounds with the sweet odor of organic esters. They are conveniently prepared in diethyl ether from potassium 2-germaacetate and the appropriate trialkyloxonium fluoroborates. Their NMR spectra are essentially as expected, but the infrared and mass spectra have interesting features. The strong bands near 1140 $cm^{-1}$ in the infrared spectra, assigned to the C—O (single bond) stretching, are shifted 100 $cm^{-1}$ below the corresponding strong bands in the infrared spectra of methyl and ethyl acetates [12]. The shift suggests a rather large bulk electronic effect arising from substitution of a germanium atom for a carbon atom.

The 50 $cm^{-1}$ shift of the C=O stretching frequency below that of the corresponding acetates [13], is comparable to that observed between $R_3GeCO_2H$ and $R_3CCO_2H$ [14].

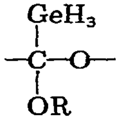
The mass spectrum of each ester has a cluster of peaks centered at 91 mass units, suggesting either (a) decarbonylation followed by the process $H_xGeOR^+ \rightarrow H_xGeO^+ + R$, or (b) the occurrence of the metastable process $H_xGeCO_2^+ \rightarrow H_xGeCO^+ + O$, which would be expected to give a metastable cluster centered at 91.1 mass units.

*Hydrolysis of the esters*

In contrast to the high yields (90%) of carbon monoxide obtained from the base-catalyzed decomposition of $(C_6H_5)_3SiCO_2R$ [6], where R = H, $CH_3$, or $C_2H_5$, the yields of carbon monoxide from the corresponding reactions of $GeH_3CO_2CH_3$ and $GeH_3CO_2C_2H_5$ are approximately 10% (Table 1). The side reaction suggested for the hydrolysis of $(C_6H_5)_3SiCO_2R$,

$$(C_6H_5)_3SiCO_2R + {}^-OR' \rightarrow (C_6H_5)_3SiOR' + {}^-OCOR$$

probably does not occur here because neither $HCO_2CH_3$ nor $HCO_2C_2H_5$ was found. The presence of high molecular weight substances (mol. wt. up to 285) (indicated by mass spectrscopy) in the contents of the —45° traps suggest that, instead of a side reaction to produce formates, a base-catalyzed polymerization reaction occurred to form species containing the repeating unit shown below.



$$-\overset{GeH_3}{\underset{OR}{C}}-O-$$

The high molecular weight substances show a strong infrared band at 1100 $cm^{-1}$, typical of ethers [12].

Acid-catalyzed decomposition of the esters produced carbon monoxide in yields up to 93%. The elimination of CO from esters in conc. $H_2SO_4$ is a well-known reaction that occurs most easily for esters which can readily produce an acylium ion, $RCO^+$ [13]. A germyl group is expected to stabilize such a cation [14]; therefore, the high yields of CO are not unexpected. The evolution of hydrogen after prolonged heating of the solution probably arises from the hydrolysis or decomposition of the polymeric germanium hydride.

Digermane obtained from the acidification of the potassium germyl—$GeH_3CO_2C_2H_5$ solution results from the following reaction.

$$GeH_3^- + GeH_3CO_2C_2H_5 \rightarrow Ge_2H_6 + CO + C_2H_5O^-$$

Digermane and germane accounted for 2.04 mmol of the 2.08 mmol of germanium used. The mechanism of the reaction probably involves either attack of the germyl ion on the germanium atom of the ester, as in the reaction of $(C_6H_5)_3SiCO_2R$ with base [6], or attack at the carbonyl group, to produce $GeH_3COGeH_3$ and $C_2H_5O^-$, followed by decomposition of the former to CO and $Ge_2H_6$.

### *Thermal decomposition of the esters*

Thermal decomposition of the esters produces carbon monoxide in nearly quantitative yield and the corresponding alcohol. No hydrogen is evolved if the temperature is kept below 300°. The ethyl ester produced a significant amount (10% yield) of ethylene, as expected for the pyrolysis of an ethyl ester [15].

### *NMR experiments*

The methyl and ethyl esters decompose in $D_2O$ after 24 - 48 h at 80°. Inasmuch as the acid, $GeH_3CO_2D$, does not appear in significant amounts in the NMR spectra, hydrolysis of the ester must proceed more slowly than the subsequent decomposition of the acid to carbon monoxide and $(GeH_2)_x$ polymer.

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