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Potassium 2-Germaacetate, an Analog of Potassium Acetate

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Potassium germyl reacts with carbon dioxide to give a salt, $KGeH_3CO_2$. The infrared and ultraviolet spectra and the products of hydrolysis suggest a structure for the anion analogous to that of the acetate ion. Aqueous solutions of $KGeH_3CO_2$ undergo very slow hydrolysis at room temperature; at 85° hydrolysis is essentially complete in 2 days: $GeH_3CO_2^- + H_2O \rightarrow GeH_4 + HCO_3^-$. Acidification of aqueous $KGeH_3CO_2$ yields a solution of 2-germaacetic acid ($pK = 3.5$) which undergoes decomposition to give a quantitative yield of carbon monoxide and nonstoichiometric amounts of germane and an orange solid containing germanium and hydrogen. The effects of the vacant $4d_\pi$ orbital of germanium on the physical and chemical properties of 2-germaacetate are discussed.

Introduction

It has previously been shown[1] that potassium germyl reacts with diborane to form the adduct $K^+H_3GeBH_3^-$. In this investigation we have found that potassium germyl reacts with carbon dioxide to form the adduct $K^+H_3GeCO_2^-$, which we believe to be structurally analogous to potassium acetate. By comparing the physical and chemical properties of the $H_3GeCO_2^-$ ion with those of the acetate ion, it is possible to learn the effect of replacing a carbon atom adjacent to a π-bonded system with a germanium atom. In previous comparisons of this type (involving organo-α-germyl and -α-silyl ketones[2,3] and carboxylic acids[4]) the interpretations have been complicated by the presence of organic groups attached to the germanium atom.

It appears likely that a wide variety of germyl derivatives can be conveniently prepared by the reaction of potassium germyl with Lewis acids and with compounds containing displaceable electronegative groups (such as alkyl halides[5]). Potassium germyl can be prepared by the reaction of germane with potassium metal in liquid ammonia[6,7] (where considerable side reaction to form $Ge(NH_2)_2$ occurs), in dimethoxyethane[1,8] (where the reaction is slow because of the low solubility of the potassium), or in hexamethylphosphoryltriamide[9] (where, because of the low volatility of the solvent, soluble nonvolatile products from subsequent reactions are difficult to isolate). We have found that potassium germyl is most conveniently prepared by the reaction of germane with a slurry of potassium hydroxide in a nonhydroxylic solvent, although the reaction with potassium in dimethoxyethane is preferred when it is desired to isolate quantitatively a given quantity of potassium germyl.

Results and Discussion

Spectral Studies.—Potassium germyl in 1,2-dimethoxyethane reacts quantitatively with carbon dioxide to produce a white solid, $KGeH_3CO_2$: $KGeH_3 + CO_2 \rightarrow KGeH_3CO_2$. At present, our best evidence that the $GeH_3CO_2^-$ ion has a structure like that of the acetate ion is the infrared spectrum shown in Figure 1. The absorptions at 1540 and 1325 cm^{-1} are characteristic of the carboxylate group;[10] for sodium acetate, CO_2^- vibrations appear at 1560 and 1410 cm^{-1}. The band at 2060 cm^{-1} is characteristic of Ge–H stretching in germyl compounds.[11–13] Absorptions at 873, 825, and 800 cm^{-1} are probably GeH_3 deformation modes.[14] The 678-cm^{-1} band may reasonably be assigned to a GeH_3 rocking vibration on the basis of assignments for the 670- and 664-cm^{-1} absorptions in digermoxane[15] and fluorogermane,[16] respectively. The last band at 557 cm^{-1} occurs in the region (600–520 cm^{-1}) assigned to asymmetric Ge–C stretching vibrations.[17]

The bathochromic shift of the infrared CO_2^- vibrations on going from $CH_3CO_2^-$ to $GeH_3CO_2^-$ may be explained in terms of p_π–d_π back-bonding from the carboxyl group into the vacant d orbitals of germanium. Such back-bonding would be expected to reduce the double-bond character of the CO_2^- group, resulting in a frequency shift to lower energy. In this manner, Brook, *et al.*,[18] have interpreted the relative carbonyl stretching frequencies for a series of organo-substituted α-germyl, α-silyl, and α-methyl ketones. However, it should be pointed out that such interpretations have been criticized. Thus, Yates and Agolini[19] have discussed the data of Brook, *et al.*, in terms of an inductive effect in order to obtain a correlation

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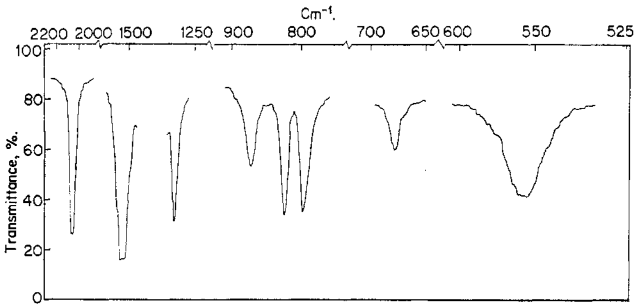

Figure 1.—The infrared spectrum of a Nujol mull of $KGeH_3CO_2$. Nujol absorptions have been deleted.

with their ketone basicity measurements. And from a recent X-ray determination of the structure of triphenylgermyl methyl ketone[2] it has been inferred that the extent of back-π-bonding in the solid is insignificant.

The electronic spectrum of the 2-germaacetate ion consists of a band at 239 mμ (ϵ <500 M^{-1} cm^{-1}) as a shoulder on an intense end absorption. This transition (presumably n $\rightarrow$ π^*) is bathochromically shifted from that for the acetate ion (<210 mμ).[20] As for the α-silyl and α-germyl ketones, the shift may be interpreted[21,22] in terms of interaction of the vacant d_π orbital of germanium with the vacant antibonding π^* orbital of the CO_2^- group. This causes an energy lowering of the n $\rightarrow$ π^* excited state while leaving the ground state virtually unaffected.

The proton nmr spectrum of $KGeH_3CO_2$ in aqueous solution is, as expected, a single line, indicating only one type of proton.

Aqueous Chemistry.—The hydrolysis products of $GeH_3CO_2^-$ provide further support for the 2-germaacetate configuration. Aqueous solutions of the salt are fairly stable at room temperature, but upon heating at 85° for 2 days, essentially quantitative evolution of germane occurs: $GeH_3CO_2^- + H_2O \rightarrow GeH_4 + HCO_3^-$. This reaction is analogous to the decarboxylation of organic carboxylates, but it occurs much more readily than most organic decarboxylations. In general, ready decarboxylation of RCO_2^- occurs when the group R is capable of stabilizing a negative charge.[23] The much greater stability of the GeH_3^- group as compared with most aliphatic carbanions can be seen by comparing the acidity of germane (pK = *ca.* 25)[24] with that of alkanes (pK's = 40–58).[25] Thus it is not unreasonable that the 2-germaacetate ion undergoes decarboxylation more readily than most organic carboxylates.

In acidified solutions of 2-germaacetate, the conjugate acid which forms (see below) rapidly undergoes decomposition (half-life *ca.* 30 min at pH 2) to give a quantitative yield of carbon monoxide and nonreproducible amounts of germane and an insoluble orange solid containing both germanium and hydrogen

$$GeH_3CO_2H \xrightarrow{H^+} CO + xGeH_4 + \text{solid}$$

The value of x ranges from 0.1 to 0.6. It seems reasonable to compare this reaction with acid-catalyzed decarbonylations of organic carboxylic acids. Possibly a mechanism of the following type is involved.

$$GeH_3CO_2H + H^+ \longrightarrow [GeH_3CO_2H_2{}^+]$$

$$[GeH_3CO_2H_2{}^+] \longrightarrow [GeH_3{}^+] + CO + H_2O$$

$$[GeH_3{}^+] + H_2O \longrightarrow xGeH_4 + \text{solid}$$

The more facile decarbonylation of 2-germaacetic acid as compared with that of organic carboxylic acids may be understood in terms of the above mechanism by recognizing that decarbonylation is favored whenever the group attached to the CO_2H group can form a relatively stable cation.[26] Now it is well known that the tendency for the formation of cations of the type $MR_3{}^+$ in the group IV elements increases on going down the family.[27] Thus $SnR_3{}^+$ ions are stable in aqueous solution, whereas most carbonium ions are very high-energy species. Consequently it is plausible that the postulated $GeH_3CO_2H_2{}^+$ intermediate undergo ready decomposition to $GeH_3{}^+$, CO, and H_2O. The suggested mechanism is reasonable in view of the products of decarbonylations of organo-α-germyl- and -α-silyl carboxylic acids[28–30] under similar reaction conditions. Decarbonylation of these acids is accompanied by formation of the corresponding organometallic alcohol, ether, or a mixture of the two. This suggests $(GeH_3)_2O$ and/or the unknown GeH_3OH as possible intermediates[31] in the acid hydrolysis of 2-germaacetic acid. The variability of x (the GeH_4:CO ratio) may be a consequence of variable decomposition paths for these unstable intermediates.

When an aqueous solution of potassium 2-germaacetate is acidified, the weak acid GeH_3CO_2H is formed. By carrying out rapid titrations with a pH meter, the pK_a value 3.5 has been determined. Thus 2-germaacetic acid is a stronger acid than acetic acid (pK_a = 4.75). This acidity order parallels the relative acidities of some organo-α-germyl-, -α-silyl-, and -α-methylcarboxylic acids.[4] The data may be rationalized in terms of p_π–d_π back-bonding from the carboxyl group into the vacant d orbital of silicon or germanium, thus permitting greater delocalization of negative charge in the anions containing these elements.

Experimental Section

General Information.—All manipulations were carried out in a preparative vacuum line or a nitrogen-filled glove bag.

Commercial 1,2-dimethoxyethane was distilled from lithium

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[28] R. A. Benkeser and R. G. Severson, *J. Am. Chem. Soc.*, **73**, 1424 (1951).

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[30] E. J. Bulten and J. G. Noltes, *Tetrahedron Letters*, 1443 (1967).

[31] However, we note the following statement of Goldfarb and Sujishi:[15] "The nature of the decomposition [of $(GeH_3)_2O$], which may be catalyzed by the presence of water, is not clear, but it is established that germane was not formed."

tetrahydroaluminate into a storage flask containing calcium hydride. Germane was prepared by the method of Jolly and Drake.[32] Carbon dioxide (Dry Ice) was passed through a −112° cold trap prior to use. Potassium was distilled *in vacuo* directly into the reactor. For quantitative work, potassium germyl was prepared by allowing excess germane to react overnight with potassium in 1,2-dimethoxyethane at *ca.* −70°[1,8] (the warm portion of a Dry Ice–acetone slush). For nonquantitative work, potassium germyl was prepared from germane and potassium hydroxide in 1,2-dimethoxyethane.[5]

The identity and purity of volatile substances were determined by infrared spectrometry[33–35] with Perkin-Elmer Infracord spectrophotometers (Models 137 and 137B), by mass spectrometry with a Consolidated Engineering Corp. mass spectrometer (Model 21-620), and by vapor pressure measurements.[36,37]

The basic reaction vessel with filter assembly has been described by Rustad and Jolly.[1] When necessary, provisions were made for easy disassembly using ground joints; the inner joints were standard-taper drip tips.

Reaction of $KGeH_3$ with CO_2.—Potassium germyl was prepared from potassium and germane in *ca.* 5 ml of 1,2-dimethoxyethane. Hydrogen (0.513 mmol) corresponding to 1.026 mmol of the germane reacted was evolved, whereas the measured unreacted germane indicated that 1.002 mmol had reacted. The $KGeH_3$ solution was filtered; the walls of the reactor were washed down by refluxing the solvent, and the filter assembly was sealed off with a flame from the tube containing the $KGeH_3$. An excess of CO_2 (1.180 mmol) was condensed into the reaction vessel at −196°. The tube was allowed to warm, and, when the solvent melted, an instantaneous reaction yielding a white precipitate was observed. The tube was warmed to room temperature with shaking to ensure that all of the $KGeH_3$ had reacted. All volatiles were fractionated through a −112° trap into a −196° trap. The material trapped at −196° (0.214 mmol) was identified as a mixture of carbon dioxide and germane and was passed through a U trap containing Ascarite (to remove CO_2) and then through a −112° trap (to remove water) into a −196° trap. The amount of germane (0.020 mmol) trapped at −196° indicated that $1.002 - 0.020 = 0.982$ mmol of potassium germyl had reacted with $1.180 - 0.214 + 0.020 = 0.986$ mmol of carbon dioxide. The stoichiometry corresponds to the formation of the compound $KGeH_3CO_2$. The compound hydrolyzes slowly in moist air and should be stored in a desiccator.

Analysis and Characterization of $KGeH_3CO_2$.—A sample of $KGeH_3CO_2$ (1.045 mmol) was placed in a sealed tube fitted with a break-seal and pyrolyzed at 480° in a muffle furnace for 3 hr. After cooling, the noncondensable volatile products were collected and measured (1.96 mmol) and then recycled with the Toepler pump through a U trap containing degassed Linde 4A Molecular Sieve at −196°. The molecular sieve quantitatively trapped carbon monoxide (identified in a preliminary run) while permitting passage of H_2 (1.47 mmol; theory is 1.57 mmol). By difference, 0.49 mmol of CO was formed. About 3 ml of 6 *M* HCl was distilled into the pyrolysis tube (which contained a Ge mirror and a solid gray residue). Reaction was permitted to occur, and the volatile products were fractionated through a −112° trap and a trap filled with an intimate mixture of glass helices and yellow HgO (to remove HCl) into a −196° trap. Carbon dioxide (0.475 mmol) collected in the last trap. Germanium remaining in the pyrolysis tube was oxidized and determined by alkalimetric titration of the germanic acid–mannitol complex:[38] found, 1.08 mmol; theory, 1.05 mmol. The pyrolysis may be represented by the equation

$$2KGeH_3CO_2 \xrightarrow{\Delta} 3H_2 + CO + 2Ge + K_2CO_3$$

The Nujol mull infrared spectrum of $KGeH_3CO_2$, shown in Figure 1, was obtained with a Perkin-Elmer Infracord spectrometer. The proton nmr spectrum of $GeH_3CO_2^-$ in D_2O is a single sharp resonance at −4.30 ppm relative to tetramethylsilane as external standard. A Varian A-60 spectrometer was used. The ultraviolet absorption spectrum of $GeH_3CO_2^-$ in water was obtained with a Cary 14 spectrophotometer.

An X-ray powder pattern of $KGeH_3CO_2$ was obtained using copper Kα radiation with a nickel filter.[39] The following *d* values (Å) were measured: 11.5 (s), 5.85 (w), 5.40 (vw), 4.45 (vs), 4.22 (w), 3.70 (vs), 3.55 (vw), 3.40 (vs), 3.34 (vs), 3.20 (w), 3.05 (vw), 2.92 (s), 2.83 (vw), 2.71 (w), 2.57 (vw), 2.40 (m), 2.34 (vw), 2.30 (w), 2.21 (m), 2.10 (s), 2.00 (m), 1.95 (vw), 1.92 (w), 1.86 (w, br), 1.80 (w), 1.68 (w), 1.58 (w), 1.50 (vw). An infrared spectrum of the X-ray sample, recrystallized from an ethanol–ether solution, showed two new weak absorptions at 1660 and 1315 cm^{-1}. The sample was loaded into a capillary in a glove bag and kept at or below −10° until the data were obtained. After collection of the data, the X-ray capillary was crushed and an infrared spectrum of the solid was obtained which agreed with that of the sample prior to loading of the capillary. The pattern could not be indexed properly for either a cubic or a tetragonal lattice system.

The pK_a of the conjugate acid of $KGeH_3CO_2$ was determined as 3.47 ± 0.15 at *ca.* 25° by measuring the pH at the midpoint of acid–base titrations. Titrations, using a Beckman Zeromatic pH meter, were performed first with 0.1000 *M* HCl and then with 0.1000 *M* NaOH. The back-and-forth titration was repeated as rapidly as possible three times to ensure reproducibility of the titration curve and to check on possible decomposition of the GeH_3CO_2H (see below). A typical pK_a measurement was completed in less than 10 min.

The rate of hydrolysis of a solution of $KGeH_3CO_2$ in 1 *M* $KHSO_4$ (*ca.* pH 2) in D_2O was roughly measured using proton nmr. The half-life of the species was roughly 30 min, based on the decrease in peak height of the −4.30-ppm resonance.

Aqueous Hydrolysis of $KGeH_3CO_2$.—After holding a solution of 0.639 mmol of $KGeH_3CO_2$ in 3 ml of water at room temperature for 18 hr, the volatile products were fractionated through a −112° trap into a −196° trap. Germane (0.0105 mmol) collected in the −196° trap. Material trapped at −112° was redistilled into the hydrolysis vessel which was then placed in an oil bath at *ca.* 50° for 10.5 hr. During this time 0.0242 mmol of germane was evolved. After 12 hr more at 50°, hydrolysis produced 0.0222 mmol of germane and a trace amount of digermane. After *ca.* 26 hr at *ca.* 85°, 0.583 mmol of germane and 0.118 mmol of carbon dioxide were evolved. About 1.5 ml of 9 *M* sulfuric acid was added to the hydrolysis vessel; reaction was permitted to occur, and 0.00742 mmol of carbon monoxide and 0.528 mmol of carbon dioxide were collected. From 0.639 mmol of $KGeH_3CO_2$, 0.640 mmol of germane and 0.650 mmol of carbon (as the monoxide and dioxide) were produced.

Acid Hydrolysis of $KGeH_3CO_2$.—In a typical run, approximately 3 ml of 2 *M* HCl was delivered, without admitting air, through the stopcock of a vessel containing 1.061 mmol of $KGeH_3CO_2$ at −196°. Upon warming to room temperature, reaction commenced immediately and was allowed to proceed overnight. A mixture of a white solid and an orange-yellow solid remained in the clear supernatant. The vessel was attached to the vacuum line, and all volatiles were removed and fractionated by Toepler pumping through traps at −112 and −196°.

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The noncondensable gas was determined to be 1.036 mmol of carbon monoxide. Condensable materials which were not stopped at $-112°$ were passed through Ascarite and then a trap filled with magnesium perchlorate cooled to 0°. The remaining material was germane (0.618 mmol). Nitric acid (1 ml, 8 *M*) was distilled into the hydrolysis vessel containing the solid substance. The tube was partially immersed in an oil bath at 75° for 0.75 hr in order to oxidize all Ge-containing species to Ge(IV) for determination as the mannitol complex; 0.323 mmol of Ge was found. The total Ge recovered was 0.941 mmol or 89% of theory. In another experiment, 0.986 mmol of $KGeH_3CO_2$ was hydrolyzed overnight with *ca.* 3 ml of 4 *M* HCl. A whitish solid was deposited in the reaction tube. A quantitative yield of carbon monoxide (0.986 mmol) was obtained in addition to 0.236 mmol of germane.

In general, quantitative yields of carbon monoxide were produced. However, the GeH_4:CO ratio varied widely from *ca.* 0.1 to 0.6, with the usual ratio in the neighborhood of 0.55. Unfortunately no more than 90% of the total germanium was ever accounted for in any of the runs.

Kolbe Electrolysis[40-42] of $KGeH_3CO_2$.—Attempts were made to couple electrolytically generated GeH_3 radicals to form digermane. An electrolysis cell with 1-cm^2 platinum foil electrodes *ca.* 3 mm apart was constructed to permit electrolysis on the vacuum line. Electrolyses of *ca.* 0.3 *M* $KGeH_3CO_2$ solutions (10-ml quantities were used) were carried out at 0° at current densities around 1 A/cm^2. The pressure was maintained between 100 and 300 mm by periodically opening a stopcock leading through a train of $-196°$ cold traps to the vacuum pump. The electrolyte was magnetically stirred. One electrolysis was performed in water; the voltage was varied randomly between 10 and 30 V during a 1-hr period. After 3 min of electrolysis, an orange-yellow solid had formed, indicating decomposition of the $KGeH_3CO_2$. Fractionation of the condensable gases showed only trace amounts of digermane; germane and carbon dioxide also were identified. A second 1-hr electrolysis at 25 V in *ca.* 80% methanol yielded a white precipitate; no digermane was produced. A third 1-hr electrolysis was carried out at 10 V in aqueous 1 *M* $KHSO_4$. A greenish white solid slowly formed on the walls of the cell. The solid eventually developed a yellow cast. Fractionation of the volatiles indicated *ca.* 5% yield of digermane based on the $KGeH_3CO_2$ used.

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A Neutron Diffraction Study of the Reaction Product of Acetonitrile and Hydrogen Chloride: Chloroacetiminium Chloride, $[CH_3C(Cl){=}NH_2^+]Cl^-$ [1]

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The crystal structure of $CH_3CN\cdot 2HCl$ has been determined by three-dimensional neutron diffraction analysis at $-5°$ and refined to a final weighted R factor of 8.5% for all 511 reflections observed. Crystals of the compound are orthorhombic, of space group Pnma, with $a = 8.72 \pm 0.01$, $b = 6.93 \pm 0.01$, and $c = 8.63 \pm 0.01$ Å and with four formula units per unit cell ($d_{\text{obsd}} = 1.43$, $d_{\text{calcd}} = 1.45$ g/cm^3). The compound does not contain the bichloride ion as was previously postulated; the chemical structure is that of an imine hydrohalide, $[CH_3C(Cl){=}NH_2]^+Cl^-$, not that of a nitrilium salt, $[CH_3CNH]^+[HCl_2]^-$. All atoms except two methyl hydrogens lie in mirror planes. The Cl^- ion is involved as an acceptor in two hydrogen bonds, 3.07 and 3.08 Å in length, which lie in the molecular plane and which serve to link the planar chloroacetiminium ions into infinite chains. The values 1.265 ± 0.007, 1.471 ± 0.010, and 1.694 ± 0.010 Å were found for the C–N, C–C, and C–Cl bond lengths, respectively.

Introduction

The hydrogen halides form numerous addition compounds with various aliphatic and aromatic nitriles. The freezing point diagram of the system CH_3CN–HCl indicates the existence of four intermediate compounds, $CH_3CN\cdot HCl$, $2CH_3CN\cdot 3HCl$, $CH_3CN\cdot 5HCl$, and $CH_3CN\cdot 7HCl$, all with melting points well below room temperature.[4] Another addition compound, $CH_3CN\cdot 2HCl$, first postulated by Gautier[5] in 1869, was not found in the above-mentioned cryoscopic study.

Hantzsch[6] prepared $CH_3CN\cdot 2HCl$, as well as $CH_3CN\cdot 2HBr$ and $CH_3CN\cdot 2HI$, in solid form and found that, although the latter two compounds can be made at room temperature, the dihydrochloride forms only below about $-16°$. Several studies have been carried out on crystalline dihydrohalides in the attempt to determine their molecular structures.[7,8] The three main structural proposals may be given as **1**—**3**.

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