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

Germynyl Sesquioxide, an Isomer of Hydrous Germanium(II) Oxide

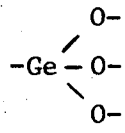
Duck J. Yang, William L. Jolly,* and Anthony O'Keefe

Germanium(II) hydroxide (hydrous germanium(II) oxide) is a white, yellow or brown noncrystalline material, only slightly soluble in water and alkaline solutions, having no definite stoichiometry, and generally represented by the formula $Ge(OH)_2$ or $GeO \cdot xH_2O$.[1-4] We have found that digestion of a suspension of either yellow or brown germanium(II) hydroxide in aqueous sodium hydroxide solutions yields a dark brown insoluble compound which has properties distinctly different from those of the starting hydroxide. The compound, after being thoroughly washed and dried in vacuo at room temperature, is a dark-brown pyrophoric powder with a composition close to $(HGe)_2O_3$. The empirical formula and properties of the compound suggest that it is a polymer consisting of Ge-H groups linked by oxygen atoms, i.e., "germynyl sesquioxide."[5-7]

Vibrational Spectra. Infrared spectra indicate that $(HGe)_2O_3$ is structurally different from various forms of germanium(II) hydroxide which have not been treated with hydroxide solutions. Figure 1 shows the pertinent regions of Nujol and halocarbon mull spectra of germanium(II) hydroxide samples that were subjected to the various treatments outlined in Table I. The bands near 3300 and 1650 cm^{-1} which appear in some spectra (especially those of samples B and C) are undoubtedly due to water.[8] These bands were very prominent in the spectrum (not shown) of a sample which had been purposely dried less thoroughly than the other samples. Samples B and C (which had not been treated with hydroxide) showed broad absorptions in the regions of 800 and 540 cm^{-1}, in agreement with a spectrum earlier reported for $Ge(OH)_2$.[3]

The bands near 2000, 835, and 760 cm^{-1}, which appear in the spectra

of the samples treated with hydroxide (D, E, and F), are characteristic of Ge-H stretching,[9] vibrations of a germanium-oxygen network of the type[7]



and Ge-H deformation,[9] respectively. It is significant that sample E (which was briefly washed with acid after the hydroxide treatment) had an infrared spectrum essentially the same as those of samples D and E. This result shows that $(HGe)_2O_3$ is not rapidly reconverted to $Ge(OH)_2$ by treatment with acid. Samples B and C, which were not treated with hydroxide, were brown and yet showed none of the distinctive absorptions characteristic of $(HGe)_2O_3$. This result shows that a change in the color of germanium(II) hydroxide from yellow to brown is insufficient evidence for conversion to germynyl sesquioxide.

Sample G was a sample of $(HGe)_2O_3$ which had been stirred in D_2O for one week. As expected, the Ge-H bonds were replaced by Ge-D bonds; hence the band at 2000 cm^{-1} was replaced by one at 1450 cm^{-1}. The spectrum of G in the low frequency region shows new features similar to those which appear when $(HGe)_2O_3$ is stirred for long periods with either H_2O or D_2O. Apparently $(HGe)_2O_3$ undergoes degradation during such treatment.

A Raman spectrum of sample F showed broad bands at 2030 and 560 cm^{-1}, probably due to Ge-H and Ge-O stretching, respectively. No bands could be found in the Raman spectrum of sample A.

<u>Pyrolysis</u>. When ordinary germanium(II) hydroxide is heated in vacuo

to 400°, the principal reaction is the dehydration to GeO,[10,11] although a small amount of hydrogen gas is evolved during the process.

$$Ge(OH)_2 \longrightarrow GeO + H_2O$$

On the other hand, when germynyl sesquioxide is similarly heated, most of the hydrogen in the compound is evolved as hydrogen gas, and the residue is a mixture of GeO and GeO_2.

$$(HGe)_2O_3 \longrightarrow H_2 + GeO + GeO_2$$

Evidence supporting these reactions is presented in Table II.

Solubility Studies. The solubility of germanium(II) hydroxide in water and in sodium hydroxide solutions has been studied by various workers.[1,2,4] The results are somewhat discordant; however there is general agreement that the solubility is very low, i.e. <0.03 M. We believe that previous workers have not fully recognized that the nature of the solid phase changes at a measureable rate when germanium(II) hydroxide is suspended in alkaline solutions, that the rate of this change is a function of hydroxide concentration, and that consequently the measured solubility changes with hydroxide concentration and with time.

We measured the solubility of germanous hydroxide (i.e., the concentration of Ge(II) in solutions saturated with germanous hydroxide) as a function of the concentration of sodium hydroxide in the solutions and as a function of time. After initial equilibration periods of one half hour, the concentration of Ge(II) decreased with time - the rate of decrease being greatest in the more concentrated hydroxide solutions.

The solubilities determined for several equilibration times are plotted vs hydroxide ion concentration in Figure 2. From the curves for equilibration times of 45 minutes and 5 hours, it can be seen that the solubility of relatively fresh $Ge(OH)_2$ increases with increasing hydroxide concentration. The measured solubilities decrease with time at all hydroxide concentrations, but especially rapidly at concentrations of 5 M and higher. The conversion of freshly precipitated, yellow, germanium(II) hydroxide to brown $(HGe)_2O_3$ is rapid (hours) in highly concentrated hydroxide solutions and slow (days) in dilute hydroxide solutions. The color of germanous hydroxide suspended in sodium hydroxide solutions appears to be closely correlated with the solubility -- the dark material having a lower solubility than the light material.

These results indicate that ordinary germanium(II) hydroxide reacts with the hydroxide ion to form a soluble species, perhaps a complex such as $OGeH(OH)_2^-$. The conversion of $Ge(OH)_2$ to the relatively insoluble $(HGe)_2O_3$ appears to be catalyzed by this dissolved species or by hydroxide ions, perhaps through a mechanism such as the following.[12-15]

$$Ge(OH)_2 + OH^- \longrightarrow :Ge(OH)_3^- \rightleftharpoons (HO)_2\overset{H}{\overset{|}{Ge}}O^-$$

$$(HO)_2\overset{H}{\overset{|}{Ge}}O^- + HO-\overset{H}{\underset{\underset{O}{|}}{Ge}}-O- \longrightarrow (HO)_2\overset{H}{\overset{|}{Ge}}-O-\overset{H}{\underset{\underset{O}{|}}{Ge}}-O- + OH^-$$

Experimental Section

Germanium(II) hydroxide was precipitated by the addition of aqueous ammonia to a solution of Ge(II) in hydrochloric acid.[16] This and all subsequent operations were carried out under a nitrogen atmosphere. The

$Ge(OH)_2$ was collected on a sintered-glass funnel and washed with deoxygenated water. The conversion to $(HGe)_2O_3$ was effected most conveniently by stirring damp $Ge(OH)_2$ (prepared from 5 g of GeO_2) with 35 ml of 10 M NaOH at 70° for 1 hr. The resulting dark brown solid was washed on a coarse sintered-glass funnel with deoxygenated water until the filtrate was neutral. The sample was dried to constant weight by pumping through a liquid nitrogen trap (20 hrs. generally sufficing). To avoid splattering of the sample, it was cooled to 0° during the initial pumping. Yield, 1.2 g (26%).

The purity of the $Ge(OH)_2$ was established by determining the equivalents of reducing power per mole of germanium. The hydrogen evolved during digestion of the material in 10 M NaOH at 120° for 3 days, followed by analysis for Ge by the mannitol method,[17] corresponded to 1.996 equiv./mol (theory, 2.000 equiv./mol). The $(HGe)_2O_3$ was analyzed for Ge by the mannitol titration method (after treatment with acid and peroxide). Calcd: Ge, 74.4 Found: Ge, 75.7.

Infrared spectra were obtained using mulls in Nujol or chlorofluorocarbon oil (Series 14-25, Halocarbon Products Corpn., Hackensack, N.J.) between NaCl or KBr plates and a Perkin-Elmer Model 337 Grating Infrared Spectrophotometer. Raman spectra were obtained using a Coherent Radiation Co. Spectrometer (Model 1401).

Pyrolyses were carried out in a glass tube in a tube furnace. The samples were heated while continuously Toepler-pumping the evolved hydrogen through liquid nitrogen-cooled traps. Germanium in the pyrolyzed residues was determined as described above.

All manipulations involved in the solubility measurements were carried out under nitrogen. Each $Ge(OH)_2$ slurry was stirred for a measured time; a portion of the slurry was centrifuged, and an aliquot of the clear supernatant was acidified, treated with excess standard triiodide solution, and titrated with thiosulfate.

Acknowledgements. This work was supported largely by the U. S. Energy Research and Development Administration.

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(12) The pK of the Ge-H proton of $HGe(OH)_3$ may be roughly estimated by the method of Branch and Calvin[13] to be equal to the pK of GeH_4[14] (25) less 3 times the inductive factor for oxygen, i.e., $25 - 3 \times 4 = 13$. The pK of an O-H proton of $HGe(OH)_3$ can be estimated to be equal to the pK of $Ge(OH)_4$[15] (8.6) plus a correction of 4/2.8 for the replacement of an OH group by H, i.e. $8.6 + 1.4 = 10.0$. Although these estimates are very rough, they do indicate that the $OGeH(OH)_2^-$

tautomer should have a stability at least comparable to that of the $Ge(OH)_3^-$ tautomer.

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Table I. Physical and Chemical Treatment of Germanium(II) Hydroxide Samples Examined as Mulls by Infrared Spectrometry.

Sample	Treatment[a]	Color[b]
A	Untreated[a]	yellow
B	Digested in boiling water for 4 hours.	brown
C	Boiled with 1 M H_2SO_4 for 1 hour.	dark brown
D	Stirred with 7 M NaOH for 3 days at 25°; then washed thoroughly with water by repeated centrifugation and decantation.	brown
E	Same as D; then stirred with 1 M H_2SO_4 for 30 min. and finally washed again with water as above.	brown
F	Digested in 7 M NaOH at 75° for 1 hour; washed as above.	dark brown
G	Digested in 7 M NaOH at 75° for 1 hour; washed thoroughly; dried in vacuo overnight; then stirred for 1 week in D_2O.	dark brown

[a]Each sample of germanous hydroxide was precipitated and washed as described in the Experimental Section. After the indicated treatment, the sample was pumped on overnight at 0°. The mull was made using the resulting dried material. [b]Color before vacuum drying. The colors darkened upon drying.

Table II. The Pyrolysis of Germanium(II) Hydroxide and Germynyl Sesquioxide at 400° in Vacuo.

Compound	Residue weight, g.	H_2 formed, mmol	Ge, mmol	Calcd. Ratio H_2/Ge	Calcd. Ratio O/Ge in residue
$Ge(OH)_2$	0.0378	<0.01	0.416	<0.02	1.1
$Ge(OH)_2$	0.1422	0.035	1.590	0.02	1.1
$(HGe)_2O_3$	0.0143	0.064	0.157	0.41	1.2
$(HGe)_2O_3$	0.0606	0.276	0.643	0.43	1.4
$(HGe)_2O_3$	0.0819	0.396	0.854	0.46	1.5

Figure Captions

Fig. 1. Infrared spectra of mulls of $Ge(OH)_2$ and $(HGe)_2O_3$. See Table I for significance of letter notations. All spectra are for Nujol mulls except F^* and G^*, which are for halocarbon mulls.

Fig. 2. The solubility of $Ge(OH)_2$ as a function of time and of hydroxide concentration.

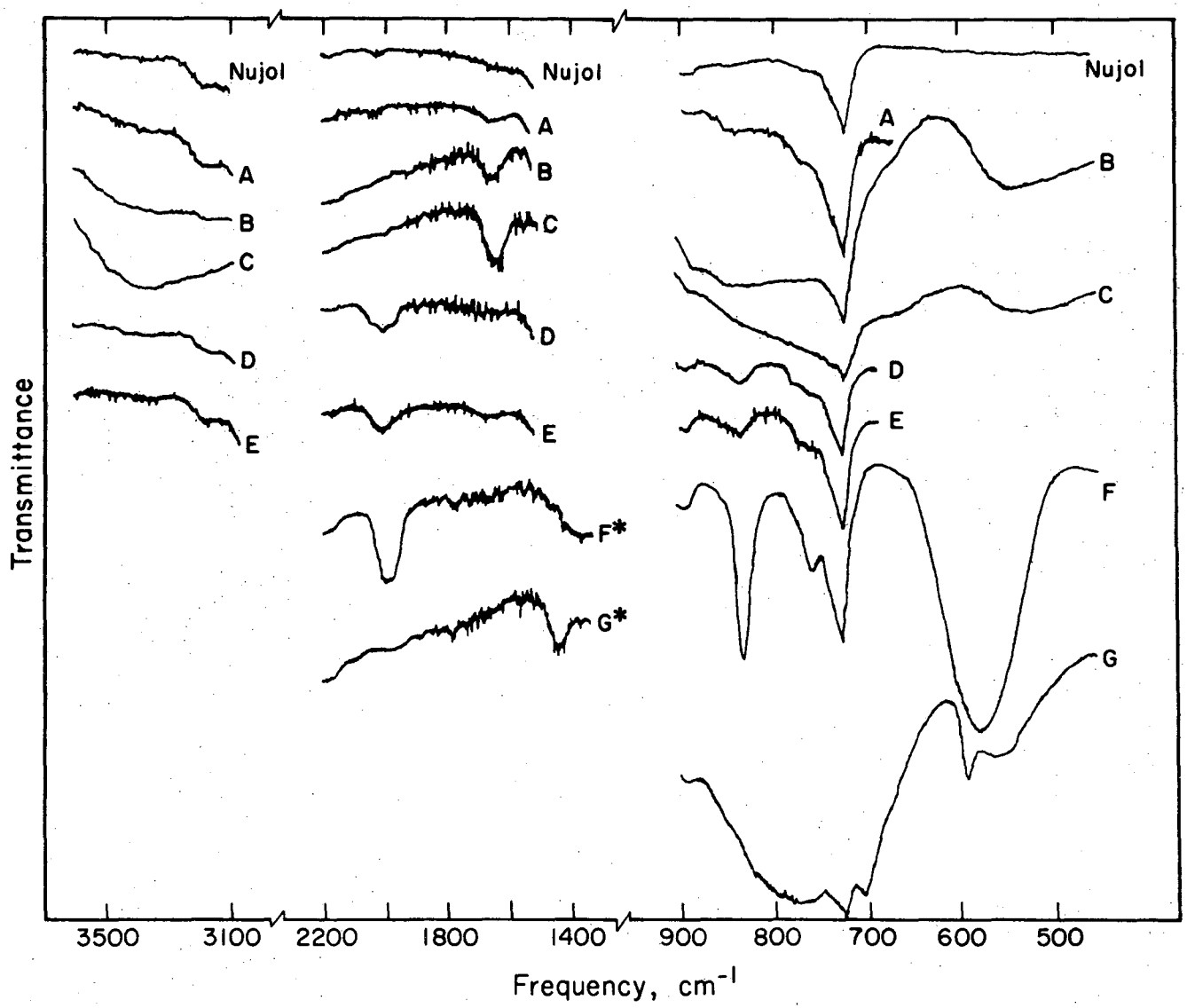
Nujol
A
B
C
D
E
F*
G*
Nujol
A
B
C
D
E
Nujol
A
B
C
D
E
F
G
Transmittance
3500
3100
2200
1800
1400
900
800
700
600
500
Frequency, cm^{-1}

FIG. 1

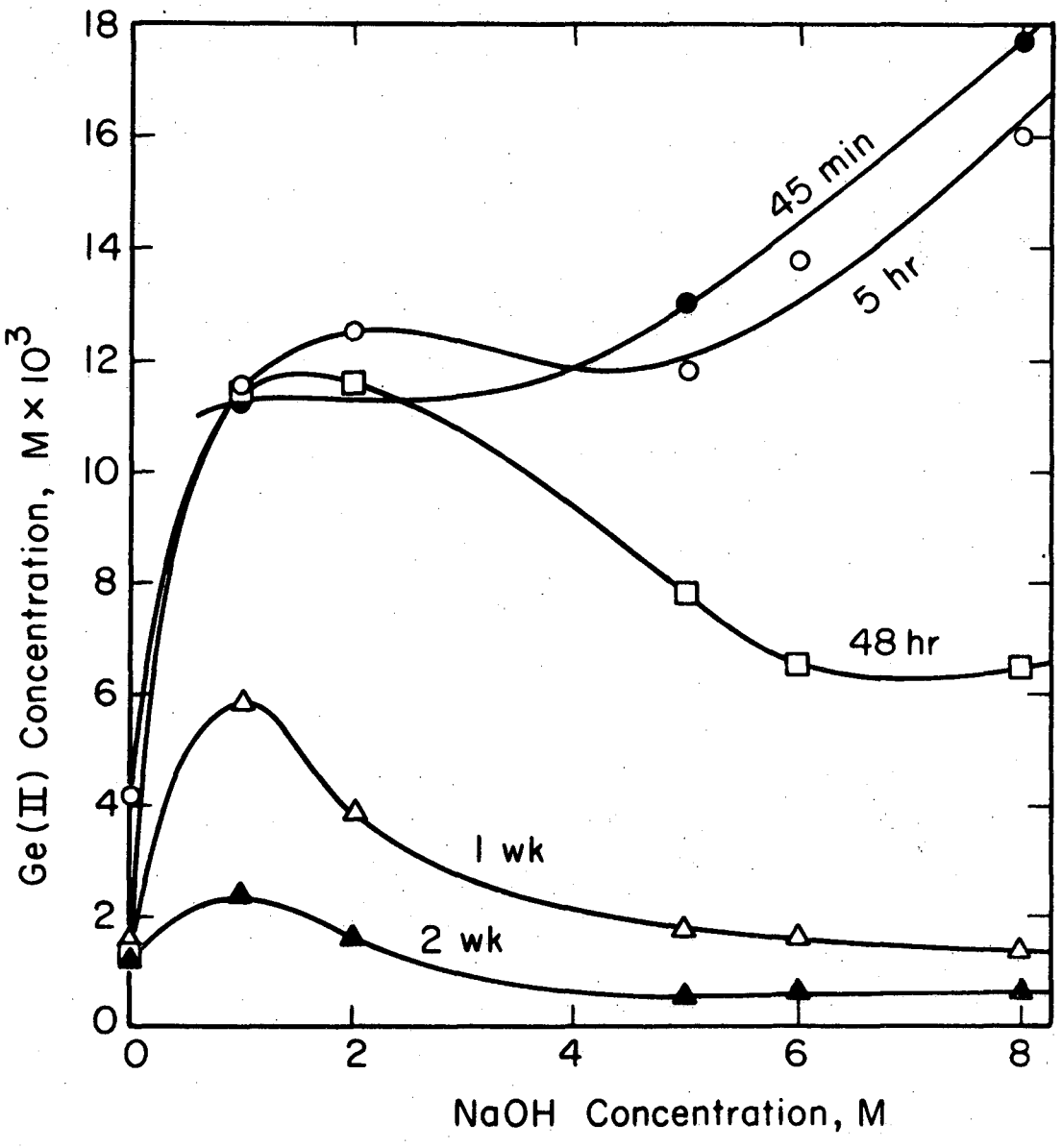
18
16
14
12
10
8
6
4
2
0
Ge(II) Concentration, M × 10^3
0
2
4
6
8
NaOH Concentration, M
45 min
5 hr
48 hr
1 wk
2 wk

FIG. 2

0 0 0 0 4 7 1 1 3 3 7

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