Some Metal Alloxides

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Tetraalloxygermanium(IV), $(CH_2:CH \cdot CH_2 \cdot O)_4Ge$, has been synthesized from germanium tetrachloride, allyl alcohol, and ammonia. The alloxides $[(CH_2:CH \cdot CH_2 \cdot O)_4Ti]_2$ and $[(CH_2:CH \cdot CH_2 \cdot O)_5M]_2$ (M=Nb and Ta) have been synthesized by reactions of the corresponding metal isopropoxides with allyl alcohol followed by removal of the isopropanol by azeotropic distillation with benzene. These four metal alloxides can be purified by distillation under reduced pressure. The spectroscopic properties of these new compounds are discussed.

Introduction

During the past two decades the chemistry of metal alkoxides has received considerable attention.[1] The interest in this class of compounds has arisen both from their industrial applications[2] and from the novel effects of changes in the alkoxy groups on the volatility, molecular association, and metal coordination number in the corresponding metal alkoxides.[1,3,4,5]

Despite this considerable amount of work with metal alkoxides in general, metal alkoxides containing unsaturated alcohols have received almost no attention. The only known metal alkoxide derived from a vinylic alcohol is a vinoxytitanium derivative which can be obtained from tetraisopropoxytitanium and acetaldehyde according to the following equation:

$$Ti(OCHMe_2)_4 + 2\ CH_3CHO \rightarrow$$
$$Ti(OCH:CH_2)_2(OCHMe_2)_2 + 2\ Me_2CHOH$$
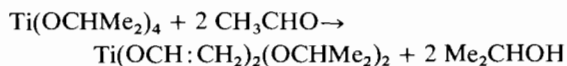
This reaction was suggested to proceed by alcohol interchange involving the vinyl alcohol formed by enolization of the acetaldehyde.[6]
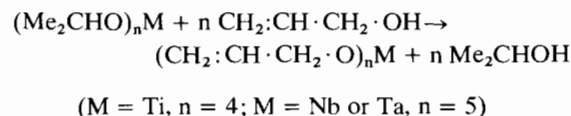
One difficulty in the preparation of metal alkoxides derived from vinylic alcohols is the instability of such alcohols relative to the tautomeric aldehydes or ketones. The preparations of metal alkoxides derived from allylic alcohols do not have this difficulty since allylic alcohols are perfectly stable compounds. This paper describes the preparation and properties of some metal alloxides derived from the readily available allyl alcohol.

The titanium derivative $(CH_2:CH \cdot CH_2 \cdot O)_4Ti$ has been previously mentioned in the literature[7] but its spectroscopic properties have not been reported.

Results and Discussion

Reaction of germanium tetrachloride with allyl alcohol in the presence of excess gaseous ammonia gives tetraalloxygermanium(IV), $(CH_2:CH \cdot CH_2 \cdot O)_4Ge$, as a distillable colorless liquid. The molecular weight indicates this compound to be monomeric in accord with its formulation as a normal tetrahedral germanium(IV) derivative.

An analogous preparative method was avoided for the alloxides of titanium, zirconium, niobium, and tantalum, since the halides of these metals in the desired oxidation states are strong Lewis acids which might be expected to destroy the carbon–carbon double bond of the allyl alcohol or alloxide groups through addition or polymerization. The alloxides $[(CH_2:CH \cdot CH_2 \cdot O)_4Ti]_2$ and $[(CH_2:CH \cdot CH_2 \cdot O)_5M]_2$ (M = Nb or Ta) were instead prepared by reactions of the corresponding metal isopropoxides with allyl alcohol according to the following equation:

$$(Me_2CHO)_nM + n\ CH_2:CH \cdot CH_2 \cdot OH \rightarrow$$
$$(CH_2:CH \cdot CH_2 \cdot O)_nM + n\ Me_2CHOH$$

$$(M = Ti, n = 4; M = Nb\ or\ Ta, n = 5)$$

They were all colorless liquids which could be purified by vacuum distillation. The formulation of these alloxides as dimers is supported by ebullioscopic molecular weight determinations in benzene solution. An attempt to prepare a similar zirconium alloxide by the same general method led to a yellow viscous liquid of approximate stoichiometry $[(CH_2:CH \cdot CH_2 \cdot O)_4Zr]_n$, but this material could not be obtained pure since it decomposed upon attempted distillation at 180°/0.5 mm.

The infrared spectra of all of these metal alloxides exhibited a sharp ν(C:C) frequency at 1640–1645 cm^{-1} indicating the expected retention of the uncomplexed carbon–carbon double bond in going from allyl alcohol

to the metal alloxides. In addition, strong bands at 1110–1070 and at 1020 cm^{-1} may be assigned to the ν(C–O) frequency in accord with previously published[8] infrared studies on metal alkoxides.

The proton n.m.r. spectrum of an allyl group contains a large number of closely spaced lines and thus is relatively difficult to analyze.[9] The proton n.m.r. data on the metal alloxides are summarized in Table I where the vinylic protons are labelled as in structure I. In order

I
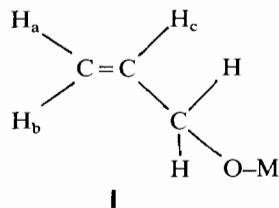
to make these assignments, the largest coupling constants J(ac), J(bc), and J(c–CH$_2$) were first determined from the symmetrical H$_c$ resonance which was separated clearly from the other resonances. These coupling constants were then used to sort out the remaining peaks from H$_a$, H$_b$, and the CH$_2$ group, which generally overlapped.

The coupling constants and most of the chemical shifts changed relatively little from allyl alcohol to any of the metal alloxides. The CH$_2$ resonance changed the most upon changing the element to which the alloxy group is bonded in accord with expectations based on the fact that the CH$_2$ protons are closer to the bonding end of the alloxy group than are the vinylic protons. The CH$_2$ resonance at ambient temperature could not distinguish between terminal and bridging alloxy groups in the compounds [(CH$_2$:CH·CH$_2$·O)$_4$Ti]$_2$ and [(CH$_2$: CH·CH$_2$·O)$_5$M]$_2$ (M = Nb and Ta) which must contain both types of alloxy groups. Furthermore, the single CH$_2$ resonances in [(CH$_2$:CH·CH$_2$·O)$_4$Ti]$_2$ and [(CH$_2$:CH·CH$_2$·O)$_5$Nb]$_2$ failed to separate into two or more resonances upon cooling to –60°C. The present data are insufficient to establish whether the

inability to observe more than one CH$_2$ resonance at ambient temperature or down to –60°C in the cases of the titanium and niobium derivatives is due to fluxional properties of these metal alkoxides involving rapid interchange of the terminal and bridging alloxy groups or simply to insufficient chemical shift differences between the CH$_2$ protons in terminal and bridging alloxy groups. The chemical shift of the CH$_2$ protons in the germanium derivative (CH$_2$:CH·CH$_2$·O)$_4$Ge is significantly higher ($\tau \sim 5.6$) than the chemical shifts of the CH$_2$ protons in the titanium, niobium, and tantalum derivatives ($\tau \sim 5.1$) suggesting that the strong Lewis acidic nature of these latter metals deshields the CH$_2$ protons by removing electron density from the intermediate oxygen atom.

The mass spectrum of (CH$_2$:CH·CH$_2$·O)$_4$Ge did not exhibit a molecular ion of significant intensity but exhibited the ions (C$_3$H$_5$O)$_n$Ge$^+$ (n = 3,2, and 1), C$_3$H$_5$OGeO$^+$, and GeOH$^+$ indicating fragmentation involving both germanium–oxygen and carbon–oxygen bond cleavage. Metastable ion evidence was observed for the stepwise loss of two alloxy groups from (C$_3$H$_5$O)$_3$Ge$^+$ to give C$_3$H$_5$OGe$^+$ despite complications from the multiisotopic nature of germanium. Satisfactory mass spectra of the titanium, zirconium, niobium, and tantalum alloxides could not be obtained on the available mass spectrometer despite numerous attempts.

This work indicates that germanium forms an alloxide (CH$_2$:CH·CH$_2$·O)$_4$Ge with a degree of polymerization close to 1 (Found: 1.08); titanium, niobium, and tantalum form alloxides with degrees of polymerization close to 2 (Found: 2.19, 1.88, and 1.91 for Ti, Nb, and Ta, respectively); and zirconium forms a less volatile alloxide with a higher, still unknown, degree of polymerization. Comparison of these observations with reported[1] degrees of polymerization of metal alkoxides from saturated alcohols indicates a close similarity between the degrees of polymerization of metal alloxides and these of the corresponding metal ethoxides consistent with the similar steric requirements of ethyl and allyl groups.

TABLE I. Proton N.m.r. Spectra of Metall Alloxides.

Compound	Chemical Shifts, τ, Vinyl Protons[a]				Coupling Constants, Hz					
	Solvent	H$_a$	H$_b$	H$_c$	CH$_2$	J(ab)	J(ac)	J(bc)	J(a–CH$_2$)	J(b–CH$_2$)	J(c–CH$_2$)
CH$_2$=CHCH$_2$OH	CCl$_4$	4.70	4.76	3.94	5.92	2	10	18	2	2	5
(CH$_2$=CHCH$_2$O)$_4$Ge	CDCl$_3$	4.89	4.72	4.06	5.59	2	10	18	2	2	5
[(CH$_2$=CHCH$_2$O)$_4$Ti]$_2$	CCl$_4$	5.03	4.83	4.04	5.14	2	10	17	2	2	5
[(CH$_2$=CHCH$_2$O)$_4$Zr]$_n$	CCl$_4$	~4.8 to	5.0	~4.1	~5.5	spectrum very broad; no fine structure resolved					
[(CH$_2$=CHCH$_2$O)$_5$Nb]$_2$	CCl$_4$	4.92	4.79	4.10	5.12	b	~10	~17	b	b	~5
[(CH$_2$=CHCH$_2$O)$_5$Ta]$_2$	CDCl$_3$	4.92	4.78	4.07	5.03	b	~10	~18	b	b	~5

[a] See structure I for these designations of the vinyl protons of the allyl group.
[b] The splittings could not be resolved because the peaks were too broad.

Experimental

Carbon and hydrogen analyses were performed by the University of Melbourne, CSIRO, Australia. The metals were analyzed gravimetrically as their oxides. Infrared spectra were taken of the neat liquids and recorded on a Perkin–Elmer Model 337 spectrometer with KBr optics. Proton n.m.r. spectra (Table I) were taken in CCl_4 or $CDCl_3$ solutions and recorded on a Varian HA–100 spectrometer at 100 MHz. Mass spectra were taken at 70 ev on the University of Georgia Perkin–Elmer Hitachi RMU-6 mass spectrometer. Molecular weights were determined in benzene solutions with a semimicroebulliometer (Gallenkamp) using thermistor sensing. All reactions were carried out in glass apparatus with interchangeable joints. Extreme care was taken to exclude moisture during all of the experiments.

Allyl alcohol was distilled over sodium before use. Titanium, zirconium, niobium, and tantalum alkoxides were prepared by methods described in the literature.[1]

Tetraalloxygermanium(IV)

A solution of germanium tetrachloride (8.7 g, 40.5 mmol) in benzene (60 ml) was treated with allyl alcohol (18 g, 310 mmol). A current of anhydrous ammonia gas was passed slowly for 3 hr. The precipitated ammonium chloride was then removed by filtration. The filtrate was concentrated under reduced pressure to give a colorless liquid. Vacuum distillation of this liquid gave *tetraalloxygermanium(IV)* (6.1 g, 50%), b.p. 110° C at 5.0 mmHg (Found: C, 47.0; H, 6.4; Ge, 23.5; *M*, 321.4. $C_{12}H_{20}O_4Ge$ requires C, 47.9; H, 6.7; Ge, 24.1; *M*, 300.8). Infrared spectrum (cm^{-1}): ν(CH) frequencies at 3095 (sh), 3070 (s), 3010 (m), 2970 (m), 2920 (m), 2870 (vs); ν(C:C) frequency at 1640 (s); other bands at 1450 (s), 1420 (vs), 1370 (s), 1350 (s), 1280 (m), 1250 (m), 1160 (w), 1110 (vs), 1020 (vs, br), 920 (vs), 755 (vs), 700 (sh), 600 (s, br), 540 (m, br).

Octaalloxydititanium(IV)

Titanium(IV) isopropoxide (3.4 g, 12 mmol as monomer), benzene (60 ml), and allyl alcohol (8.7 g, 150 mmol) were boiled for 6 hr under a fractionating column. The azeotrope was collected slowly during this period. Solvent was removed in vacuum. The residue was distilled under reduced pressure to give colorless liquid *octaalloxydititanium(IV)* (2.8 g, 85%), b.p. 142–143° C at 0.5 mmHg (Found: C, 52.3; H, 7.4; Ti, 17.4; *M*, 608.6. $C_{24}H_{40}O_8Ti_2$ requires C, 52.2; H, 7.3; Ti, 17.3; *M*, 552.2). Infrared spectrum (cm^{-1}): ν(CH) frequencies at 3090 (vs), 3020 (m), 2990 (m), 2910 (sh), 2840 (vs), 2790 (w); ν(C:C) frequency at 1645 (s); other bands at 1415 (m), 1405 (s), 1340 (s), 1270 (m), 1235 (m), 1110 (vs), 1020 (vs,

br), 920 (vs), 790 (w), 690 (vs, br), 600 (w), 540 (vs, br).

Attempted Preparation of Zirconium(IV) Alloxide

Allyl alcohol (13 g, 224 mmol), $Zr(OCHMe_2)_4$, Me_2CHOH (3.6 g, 9.3 mmol), and benzene (50 ml) were boiled together for 6 hr under a fractionating column with slow removal of the azeotrope. Excess of the solvent was distilled and the residue was dried under reduced pressure to give a pale yellow viscous liquid (2.3 g, 92% based on $(CH_2{:}CH \cdot CH_2 \cdot O)_4Zr$). Upon attempted vacuum distillation this liquid decomposed at 180° C and 0.5 mmHg to give pale yellow vapors which passed into the pump. Found: Zr, 29.7. $C_{12}H_{20}O_4Zr$ requires Zr, 28.6. Infrared spectrum (cm^{-1}): ν(CH) frequencies at 3070 (vs), 3005 (m), 2970 (m), 2900 (m, sh), 2830 (vs); ν(C:C) at 1638 (s); other bands at 1445 (m), 1405 (vs), 1345 (m), 1280 (m), 1250 (w), 1180 (sh, br), 1130 (vs), 1020 (vs, br), 990 (sh), 920 (vs), 790 (w), 670 (m).

Decaalloxydiniobium(V)

Pentaisopropoxyniobium(V) (2.9 g, 7.5 mmol), benzene (70 ml), and allyl alcohol (8 g, 138 mmol) were boiled together for 12 hr under a fractionating column with slow removal of the azeotrope. Solvent was removed under reduced pressure. The residue was purified by vacuum distillation to give colorless viscous liquid *decaalloxydiniobium(V)* (2.1 g, 74.5%), b.p. 198° C at 0.1 mmHg (Found: C, 47.3; H, 6.7; Nb, 24.7; *M*, 710. $C_{30}H_{50}O_{10}Nb_2$ requires C, 47.6; H, 6.7; Nb, 24.6; *M*, 756.4). Infrared spectrum (cm^{-1}): ν(CH) frequencies at 3095 (sh), 3090 (m), 3020 (m), 2995 (m), 2910 (m), 2850 (vs), 2700 (w); ν(C:C) at 1640 (m); other bands at 1440 (s), 1410 (s), 1390 (sh), 1350 (s), 1330 (sh), 1280 (m), 1240 (w), 1110 (vs, sh), 1070 (vs, br), 1020 (s), 920 (vs), 835 (m), 680 (vs), 630 (w), 540 (m, br).

Decaalloxyditantalum(V)

Decaethoxyditantalum(V) (4.5 g, 5.55 mmol), benzene (70 ml), and allyl alcohol (8.0 g, 138 mmol) were boiled together for 12 hr under a fractionating column with slow removal of the azeotrope. Solvent was removed under reduced pressure. The residue was purified by vacuum distillation to give colorless liquid *decaalloxyditantalum(V)* (4.0 g, 91%), b.p. 178° C at 0.3 mmHg (Found: C, 38.0; H, 5.4; Ta, 39.0; *M*, 887.2. $C_{30}H_{50}O_{10}Ta_2$ requires C, 38.6; H, 5.4; Ta, 38.8; *M*, 932.4). Infrared spectrum (cm^{-1}): ν(CH) frequencies at 3095 (sh), 3085 (m), 3010 (m), 2990 (m), 2900 (sh), 2850 (vs), 2690 (w); ν(C:C) at 1645 (s); other bands at 1460 (m), 1420 (s), 1410 (sh), 1350 (m), 1340 (m), 1280 (m), 1245 (w), 1140 (sh), 1090 (vs, br), 1020 (s), 980 (vs), 920 (vs), 800 (w), 680 (vs), 630 (w), 520 (sh), 490 (vs).

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