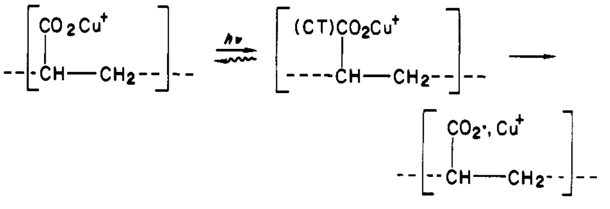
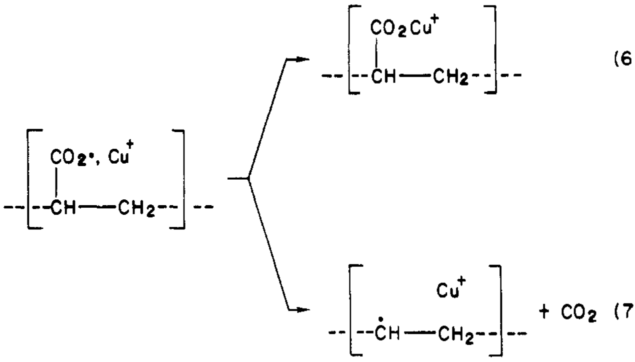
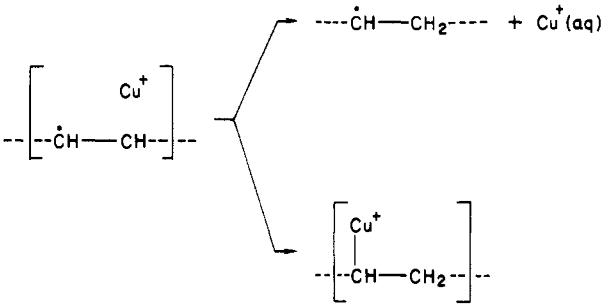

(5)

other related radicals.[11] On the basis of the reported spectra of alkyl–copper intermediates,[1–3,5,6] it is possible to assign the species produced with low-intensity flashes ($\lambda_{max} \sim 400$ nm, Figure 1) as an alkyl–copper complex, eq 7.


(6)

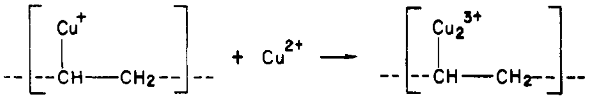
(7)

Moreover the short time that is required for the formation of such an alkyl–copper complex, $t < 50$ ns, suggests that it must be the product of geminate and secondary reactions of the decarboxylated radical and cuprous ions. The fact that spearation of the cuprous ions and methyl radicals from the bulk of the solution proved to be insignificant in the photodecomposition of $CuOCOCH_3{}^+$,[2] shows that a similar process, eq 8, under the attractive electrostatic potential of the poly(acrylic acid) must also lack relevance in photolysis of copper–poly(acrylic acid) complexes.

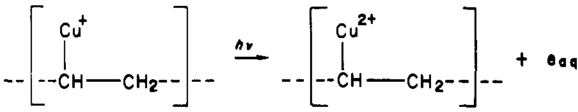

(8)

(9)

In this context, the spectral transformations observed in a 0.1–10 μs time domain, Figure 4, and the kinetics of such transformations, e.g. the dependence of the rate on free Cu(II) concentration, point to the formation of a dimeric alkyl complex when Cu(II) ions add to the monomeric alkyl–copper complex, eq 10.[12,13]

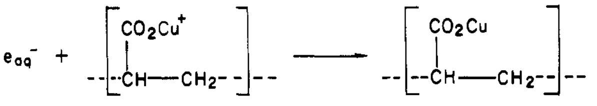

(10)

The spectrum and reactivity of the short lived species ($\lambda_{max} \sim 700$ nm, Figure 1) agree with those reported for the solvated electron.[14] The second-order dependence of the solvated electron concentration on light intensity, Figure 2, signals that such species is not a primary photochemical product and that it must be formed in a biphotonic process.[8] Such a biphotonic process can be associated with the secondary photolysis of the alkyl–copper intermediate, eq 11.[15]


(11)

The fast decay of the solvated electron in our experiments must be related to various competitive reactions with scavengers that are present in solutions of the copper-polyacrylic acid complexes, eq 12–16. In this regard, the increase of the optical density at 400 nm during the decay of the electron in the absence of N_2O can be attributed to the regeneration of some of the primary alkyl–copper intermediate, eq 16. Since the formation of solvated electrons can be related to secondary photolysis of the monomeric alkyl–copper species and since Cu(I)–halide complexes have reactive CTTS states that decay in solvated electrons and Cu(II) species,[16,17] the photochemical properties of the monomeric alkyl–copper intermediate seem to be closer to those of the cuprous complexes than to those of the corresponding cupric compounds, a fact that signals a very high electronic density in the metal center.

$$e_{aq}^- + Cu^{2+}(aq) \longrightarrow Cu^+(aq) \qquad (12)$$


(13)

$$e_{aq}^- + H^+ \rightarrow H\bullet \qquad (14)$$

$$H^+ + e_{aq}^- + N_2O \longrightarrow N_2 + OH\bullet \qquad (15)$$


(16)

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2744 from the Notre Dame Radiation Laboratory.

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Contribution from the National Bureau of Standards,
Gaithersburg, Maryland 20899

Solid-State ^{13}C NMR Molecular Structure of Microcrystalline, Polymeric Me_2SnHPO_4

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Received August 26, 1985

Interest in the structure and bonding of organotin(IV) oxyphosphorus acid derivatives and in their possible use as commercial biocides has prompted the synthesis of a number of these compounds.[2–7] For the most part, they are high-melting, polymeric,

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Table I. Analytical Data for Reaction Products of Me_2SnCl_2 with Na_2HPO_4[a] and NaH_2PO_4[b]

			elemental anal. data	
entry	compd	source/ref	% C	% H
1	$(Me_2Sn)_3(PO_4)\cdot 8H_2O$	calcd	9.24	4.39
2	Me_2SnHPO_4	calcd	9.81	2.88
3	$(Me_2Sn)_3(PO_4)\cdot 8H_2O$	7a	9.82, 9.59	3.55, 3.19
4	Me_2SnHPO_4	2	9.98	3.08
5	Me_2SnHPO_4	8	9.71	2.57
6	Me_2SnHPO_4	11	9.68[c]	2.88[c]
7	Me_2SnHPO_4	*c*	9.93	2.88

[a] Entries 3–6 with Na_2HPO_4. [b] Entry 7 with NaH_2PO_4. [c] This work.

intractable powders unsuited for X-ray crystallography. Organosubstitution on the phosphorus ligand (i.e., R_nPO_{4-n}) has provided several slightly soluble crystalline polymeric di- and triorganotin(IV) compounds, some of which have been characterized by X-ray methods. Chivers, Kerr, and co-workers[7] have reported the X-ray structure of $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$, the only organotin(IV) bearing an inorganic oxyphosphorus acid ligand to be obtained in a form suitable for crystallographic analysis. Interestingly, this insoluble, polymeric compound was obtained as the product of the combination of equimolar amounts of Me_2SnCl_2 and Na_2HPO_4; in earlier studies,[2,8] the white powders isolated from this reaction were identified by elemental analysis as the expected Me_2SnPO_4H.

Recently, we described[9] solid-state ^{13}C NMR studies of a variety of structurally characterized crystalline methyltin(IV) compounds that revealed a simple relationship (eq 1) between the magnitude

$$|^1J| = 11.4\theta - 875 \qquad (1)$$

of $^1J(^{119}Sn,^{13}C)$ ($|^1J|$, in Hz) and the Me–Sn–Me angle, θ (deg). Tin–carbon J coupling is also measurable from solid-state ^{13}C NMR spectra of methyltin(IV) polymers[10] and, in combination with the methyltin resonance multiplicity, provides considerable insight into the molecular structure of these materials. In this paper we report solid-state ^{13}C NMR, IR, and elemental analysis data for powders obtained in the reaction of Me_2SnCl_2 with Na_2HPO_4 and NaH_2PO_4. Comparison of the NMR structure of the powders with the X-ray structure reported for $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$ demonstrates the ability of solid-state NMR studies to complement and extend X-ray structural analyses.

Results and Discussion

Although crystalline, polymeric $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$ was isolated[7] from the reaction of equimolar amounts of Me_2SnCl_2 and Na_2HPO_4 in aqueous solution, in our and others' hands[2,8,11] the same reaction conditions have yielded white powders. Analysis data for these powders, along with calculated % C and % H for Me_2SnHPO_4 and $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$ are collected in Table I. The last entry, 7, was obtained in a reaction substituting NaH_2PO_4 for Na_2HPO_4. The similarity of the data for the powders (entries 4–7) indicate that they are of identical composition and suggests that they differ from $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$, entry 3 (poor analyses for the latter compound were attributed[7a] to the lability of the waters of hydration). The % C and % H data for the powders are inconsistent with a 3:2 $Me_2Sn:PO_4$ ratio and instead agree well with the composition Me_2SnHPO_4. We modified the synthetic procedure in an attempt to obtain crystalline $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$, but the products of these reactions were consistent only with Me_2SnHPO_4 as determined by elemental and/or solid-state NMR analysis.

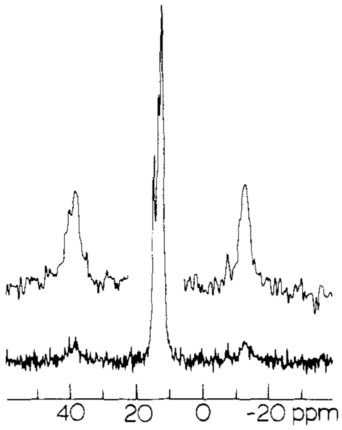

Figure 1. Solid-state ^{13}C NMR spectrum of microcrystalline Me_2SnHPO_4 powder at 15.08 MHz. Inset spectrum with sensitivity enhancement (line broadening = 3 Hz, amplitude × 4) shows fused ^{117}Sn, ^{119}Sn satellites.

While most bands in the IR spectra of the Me_2SnHPO_4 solids we have isolated are also present in the spectrum reported for $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$,[7a] several distinct differences were noted: a band of medium-to-strong intensity at 1425 cm^{-1} in Me_2SnHPO_4 appears as a weak signal in the IR of $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$, and strong bands at 910 and 823 cm^{-1} correspond to strong bands at 888 and 795 cm^{-1} for $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$. These results indicate that the bulk of the reaction product from which the crystal of $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$ was isolated for X-ray analysis differed from our products.

The solid-state ^{13}C NMR spectrum of a sample of microcrystalline Me_2SnHPO_4 is shown in Figure 1 (the NMR spectra of all of our reaction products were identical). Three ^{13}C resonances, at 13.0, 11.5, and 10.6 ppm, and the tin–carbon J coupling interaction are clearly distinguishable in the spectrum. The appearance of more than one ^{13}C methyl resonance is not unexpected, since small differences in methyl environments can give rise to significant differences in chemical shift.[10b] The narrow group of tin satellites indicates similar bonding geometry of the different tin centers. From eq 1 and the observed tin–carbon J coupling ($|^1J|$ = 780 ± 20 Hz), Me–Sn–Me angles of about 143–147° are estimated. Interestingly, this Me–Sn–Me angle resembles those of two of the three unique tin centers in polymeric $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$ (Me–Sn–Me angles = 145, 151°). The third Me_2Sn unit in $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$ adopts an almost regular octahedral configuration (Me–Sn–Me angle = 178°) for which $|^1J|$ = 1154 Hz is predicted. The absence of such a large J coupling (which would have been clearly visible) in the NMR spectra of the powders reinforces the distinction between the microcrystalline powders obtained in the reaction of Me_2SnCl_2 with Na_2HPO_4 and Me_2SnHPO_4 and crystalline $(Me_2Sn)_3(PO_4)_2\cdot 8H_2O$.

The ambient-temperature Mössbauer spectrum of Me_2SnHPO_4[2] and its insolubility and high melting point indicate a polymeric

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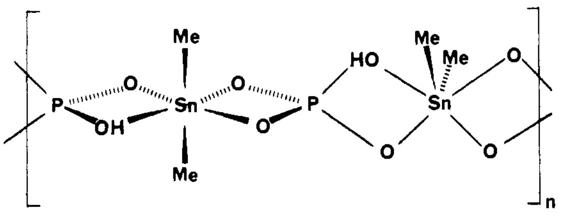
(11) A sample of Me_2SnHPO_4 was generously provided us by Prof. J. J. Zuckerman (University of Oklahoma).

structure. Structure **1** is tentatively proposed on the basis of analogies to $(Me_2Sn)_3(PO_4)_2{\cdot}8H_2O$ and other dimethyltin(IV) compounds, which adopt distorted octahedral geometries at tin.[7,12-14] In **1** the tin methyls of Me_2SnHPO_4 lie on either side of a distorted square plane (two long, two short Sn–O bonds) containing tin and four phosphate oxygens. In view of the apparent importance of hydrogen-bonding interactions in other organotin(IV) solids,[3a,7,15] the linear polymeric chains of Me_2SnHPO_4 likely associate via hydrogen bonds to produce a two- or three-dimensional network.



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Conclusions

Elemental analysis, IR, and solid-state NMR data establish the difference between the usual microcrystalline product of the reaction of Me_2SnCl_2 with Na_2HPO_4 and NaH_2PO_4 and the apparently untypical crystalline product that was previously isolated and characterized by X-ray diffraction. Earlier identifications of the microcrystalline product as Me_2SnHPO_4 are strongly supported. Further, the tin-carbon *J* coupling observed in the solid-state ${}^{13}C$ NMR spectra of microcrystalline Me_2SnHPO_4 provides insight into its molecular structure and allows comparison with the structure of X-ray characterized $(Me_2Sn)_3(PO_4)_2{\cdot}8H_2O$ to be made.

Experimental Section

Materials. Me_2SnCl_2, $Na_2HPO_4{\cdot}7H_2O$, and $NaH_2PO_4{\cdot}H_2O$ were obtained from commercial sources and used without purification. Aqueous solutions of Me_2SnCl_2 and Na_2HPO_4 or NaH_2PO_4 were combined at room temperature and allowed to stand undisturbed during product (Me_2SnHPO_4) formation.[2,8] At higher concentrations of reagents (0.3 M) a powder (microcrystalline needles or plates) formed shortly after mixing, and precipitation was essentially complete within 24 h; at lower concentrations (to 0.002 M) the product (macroscopic needles) appeared after 1 or more days, and several weeks were required for a good conversion to product. Under no conditions were crystals of Me_2SnHPO_4 with cross-sections sufficient for X-ray crystallography obtained. The product was isolated by suction filtration and rinsed with methanol. Isolated yields ranged from 50 to 90% for reactant concentrations between 0.3 and 0.03 M. No melting was observed up to temperatures of 340 °C. FT-IR (solid state, diffuse reflectance): 3250 (s, br), 2994 (m), 2906 (m), 2762 (w), 2217 (br, w), 1728 (w), 1600 (w), 1425 (m), 1214 (s), 1193 (s), 1132 (s), 1106 (s), 1054 (br, s), 910 (s), 823 (s), 669 (m), 607 (m), 566 (s) cm^{-1}. All attempts to obtain $(Me_2Sn)_3(PO_4)_2{\cdot}8H_2O$, by varying the concentration of reagents, adjusting the pH between 3 and 7,[7a] or changing the stoichiometry to 3:2 Me_2SnCl_2:Na_2HPO_4 (or NaH_2PO_4) provided only Me_2SnHPO_4.

NMR Spectroscopy. Solid-state ${}^{13}C$ NMR spectra were obtained on samples of ca. 0.4 g at 15.08 MHz with a homebuilt instrument with a probe temperature of 304 K. The high-resolution spectra were acquired with 60-MHz high-power proton decoupling, spin-locking cross-polarization with ${}^1H$ and ${}^{13}C$ fields matched at 57 kHz for 2 ms, and magic angle spinning at 2300 Hz. Dwell times of 50 μs and repetition rates of 9 s were used. ${}^{13}C$ chemical shifts are relative to the internal secondary standard Delrin (89.1 ± 0.3 ppm). Spectra revealing chemical shift information could be obtained in about 200 scans; 2–3K scans were required to observe the tin satellites clearly. Because of the similar gyromagnetic ratios of the spin-${}^1/_2$ isotopes ${}^{117}Sn$ and ${}^{119}Sn$ (1:1.046) and their similar natural abundances (7.6 and 8.6%, respectively), the magnitude of ${}^1J({}^{119}Sn,{}^{13}C)$ was calculated by multiplying the separation of the fused ${}^{117}Sn$ and ${}^{119}Sn$ satellite resonances by 1.023.

Acknowledgment. We thank Professor T. Chivers (University of Calgary) for helpful suggestions and for providing us with the IR spectrum of $(Me_2Sn)_3(PO_4)_2{\cdot}8H_2O$ and Professor J. J. Zuckerman for a critical reading of this manuscript.

Registry No. (Me_2SnHPO_4), 100485-80-1; Me_2SnCl_2, 753-73-1; Na_2HPO_4, 7558-79-4; NaH_2PO_4, 7558-80-7.

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Contribution from Ames Laboratory
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Iowa State University, Ames, Iowa 50011

Flash-Photolytic Study of the Kinetics and Mechanism of the Reduction of Halocobaloximes by 1-Hydroxy-1-methylethyl Radicals[1]

Philip Connolly, James H. Espenson,* and Andreja Bakac

Received June 18, 1985

This work was begun with two objectives in mind. First, we sought to study the kinetics of reduction of some members of a family of cobalt(III) complexes by an aliphatic radical; several other examples have been explored,[2-6] but not cobaloximes.[7] Second, we sought to develop a method that would allow the flash-photolytic formation of the radical and monitoring of product buildup (rather than reactant loss, with its attendant limitations). The α-radical from 2-propanol, $\cdot C(CH_3)_2OH$, seemed like an ideal test case for both objectives, since its chemistry has been widely explored by pulse radiolysis. This radical was found to react with the complexes $X(H_2O)Co(dmgH)_2$ (X = Cl, Br) as in eq 1.

$$X(H_2O)_2Co(dmgH)_2 + \cdot C(CH_3)_2OH \rightarrow (H_2O)_2Co(dmgH)_2 + (CH_3)_2CO + H^+ + X^- \quad (1)$$

Experimental Section

The complexes $X(H_2O)Co(dmgH)_2$ (X = Cl, Br) were prepared by the literature method[8] and characterized by cobalt analysis. Other chemicals were reagent grade materials or standard preparations.

The flash photolysis experiments were performed with the Xenon Corp. Model 710 flash photolysis unit described previously.[9] The photomultiplier voltages were collected and digitized by a Nicolet Model 2090-3A digital oscilloscope with a Model 206-1 plug-in unit, interfaced with an Apple II computer. The reactions were monitored by recording the growth in absorbance at 462 nm, an absorption maximum of $(H_2O)_2Co(dmgH)_2$ (ϵ 3400 M^{-1} cm^{-1}).[10]

The flash photolysis equipment has a dead time of about 70 μs. Since the reactions between $\cdot C(CH_3)_2OH$ and $X(H_2O)_2Co(dmgH)_2$ occur rapidly ($k \approx 10^8$ M^{-1} s^{-1}), the cobalt(III) concentration must be $< \sim 10^{-4}$ M. The disproportionation of the radical (eq 2) cannot be avoided,

$$2\cdot C(CH_3)_2OH = (CH_3)_2CO + (CH_3)_2CHOH \quad 2k_2 \qquad (2)$$

however, since it has a rate constant $k_2 = 7 \times 10^8$ M^{-1} s^{-1}.[11] *This*

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