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Reactions of 2,2,6,6-Tetramethylpiperidine Nitroxide Radical with Tin(IV) Halides

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2,2,6,6-Tetramethylpiperidine nitroxide radical (TMPNO.) has been found to react with tin tetrahalides according to the redox process and to give bis(2,2,6,6-tetramethylpiperidine-1-oxoammonium)tin hexahalides $[TMPN^+{=}O]_2SnX_6^{2-}$ *(X = Cl, Br). These ionic complexes have been characterized by elemental analyses, conductivity measurements, IR, NMR, and UV spectra. It has been observed that dimethyltin dichloride and phenyltin trichloride react easily with* $[TMPN^+{=}O]Cl^-$ *giving* $[TMPN^+{=}O][(CH_3)_2SnCl_3]$ *and* $[TMPN^+{=}O]_2[C_5H_5SnCl_5]^{2-}$*, respectively. The behavior of* $[TMPN^+{=}O][(CH_3)SnCl_3]^-$ *in solution has been investigated spectroscopically.*

Introduction

2,2,6,6-Tetramethylpiperidine nitroxide (TMPNO·) and di-tert-butyl nitroxide (DTBNO·) are stable nitroxide radicals, and recently the investigations on the interaction between these stable radicals and metal halides have been studied. Beck and Schmidtner isolated the DTBNO· complexes with cobalt and palladium halides,[1,2] in which DTBNO· was concluded to coordinate to the cobalt atom through the oxygen atom and to the palladium atom by both oxygen and nitrogen atoms, respectively. Hoffman and Eames[3,4] and Abakumov[5] reported that TMPNO· and DTBNO· interact with the group III metal halides through the oxygen atom of these stable radicals in solution on the basis of the ESR spectra where hyperfine splittings caused by ^{27}Al and ^{69,71}Ga nuclei were observed.

Although interactions of tin halides with many a Lewis base have widely been investigated, the interactions with radicals have never been studied. We have been interested in the interactions between tin halides and TMPNO·. It has been observed that the redox reactions occur between tin tetrahalides and TMPNO·, producing ionic bis(2,2,6,6-tetramethylpiperidine-1-oxoammonium)tin hexahalides. Further, some ionic oxoammonium-organotin chloride complexes have been isolated by the reaction between organotin chlorides and 2,2,6,6-tetramethylpiperidine-1-oxoammonium chloride. The configurations of these complexes will be discussed.

Experimental Section

2,2,6,6-Tetramethylpiperidine nitroxide (TMPNO·). Triacetoneamine prepared by the procedure described elsewhere[6] was reduced to 2,2,6,6-tetramethylpiperidine by means of a modified Wolf-Kishner reduction.[7] A methanol solution (1100 ml) containing 24.7 g of 2,2,6,6-tetramethylpiperidine and an aqueous solution (120 ml) containing 1 g of $Na_2WO_4{\cdot}2H_2O$ and 1.2 g of EDTA were put into the flask equipped with a stirrer, a dropping funnel and a thermometer. After 120 ml of 10% H_2O_2 was dropped with stirring, the reaction mixture was allowed to stand at room temperature for 30 hours with stirring. The red methanol solution was extracted with ether. After ether was evaporated to dryness under reduced pressure, the crude TMPNO· obtained (in a yield of 16 g, 60%) was purified by distillation or sublimation under reduced pressure. M. p. 37°C (lit.[8] 37-38°C). *Anal.* Calcd for $C_9H_{18}NO$: C, 69.18; H, 11.61; N, 8.97. Found: C, 68.86; H, 11.65; N, 8.70.

Bis(2,2,6,6-tetramethylpiperidine-1-oxoammonium)-tin hexachloride (Ia). Tin tetrachloride dissolved in acetonitrile was added to an acetonitrile solution of TMPNO· at the mole ratio 1:1, producing yellow precipitates. Recrystallization from acetonitrile gave deep yellow crystals. M. p. 150-153°C. (decomp.). *Anal.* Calcd for $C_{18}H_{36}N_2O_2SnCl_6$: C, 33.58; H, 5.64; N, 4.35. Found: C, 33.32; H, 5.76; N, 4.44.

Bis(2,2,6,6-tetramethylpiperidine-1-oxoammonium)-tin hexabromide (Ib). By the similar method the complex was obtained as brown precipitates. Recrystallization from acetonitrile yielded reddish orange crystals. M. p. 137-139°C (decomp.). *Anal.* Calcd for $C_{18}H_{35}N_2O_2SnBr_6$: C, 23.74; H, 3.99; N, 3.08. Found: C, 23.79; H, 4.05; N, 3.20.

2,2,6,6-Tetramethylpiperidine-1-oxoammonium perchlorate (II). To an nitromethane solution of 86 mg (0.33 mmole) of silver perchlorate was added 108 mg (0,17 mmole) of the compound (Ia), producing white precipitates. The reaction mixture was filtered and ether was added to the filtrate to give yellow crystals.

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Anal. Calcd for $C_9H_{18}NO_5Cl$: C, 42.28; H, 7.10; N, 5.48. Found: C, 41.99; H, 7.27; N, 5.19.

2,2,6,6-Tetramethylpiperidine-1-oxoammonium chloride (III). According to the similar method to the literature,[9] chlorine gas was bubbled into carbon tetrachloride solution containing TMPNO·, producing the yellow precipitates (III). These compounds were washed with carbon tetrachloride and dried in vacuo.

Bis(2,2,6,6-tetramethylpiperidine-1-oxoammonium)-phenyltin pentachloride (IV). To a carbon tetrachloride solution of 152 mg (0.5 mmole) of phenyltin trichloride was added 191 mg (1 mmole) of compound (III), producing yellow crystals. M. p. 120-121°C. *Anal.* Calcd for $C_{24}H_{41}N_2O_2SnCl_5$: C, 42.05; H, 6.03; N, 4.09. Found: C, 41.40; H, 6.11; N, 4.11.

2,2,6,6-Tetramethylpiperidine-1-oxoammonium dimethyltin trichloride (V). To a carbon tetrachloride solution of 220 mg (1 mmole) of dimethyltin dichloride was added 191 mg (1 mmole) of the compound (III), producing deep yellow crystals. M. p. 103-104° C. *Anal.* Calcd for $C_{11}H_{24}NOSnCl_3$: C, 32.12; H, 5.88; N, 3.41. Found: C, 32.20; H, 6.05; N, 3.35.

Spectral Measurements. ESR spectra were measured using a Japan Electron Optics JES-ME-3X. The signals were corrected against marker signals of Mn^{2+} in MnO. NMR spectra were obtained by a Japan Electron Optics JNM-3H-60 spectrometer operating at 60 MHz. Tetramethylsilane was used as an internal standard. IR spectra were recorded on a Hitachi-Perkin 225 and Hitachi EPI-L spectrophotometers, both equipped with gratings. Electronic spectra were measured in solution using a Hitachi 124 spectrophotometer and in solid using a Hitachi EPS one.

Conductivity Measurements. Electric conductivities were measured in acetonitrile at 25±0.5°C using Yokogawa Universal Bridge, Type BV-Z-13A. Acetonitrile used in the measurements was dried by phosphorus pentoxide several times and purified by fractional distillation. The specific conductance of acetonitrile used here was 1.5×10^{-7} ohm^{-1} cm^{-1}.

Results and Discussion

As is shown in Table I, in the ESR spectra the ^{14}N hyperfine splitting constants a_N of TMPNO· increase appreciably in protic solvents, especially in water, because of the formation of the hydrogen bonding with these solvent molecules, which is consistent with the results obtained by Kawamura[10] and Drago.[11] However, the a_N values do not vary by adding an excess of dimethyltin dichloride, butyltin trichloride or phenyltin trichloride in carbon tetrachloride (a_N = 15.8±0.1 G). Therefore, it is assumed that TMPNO· interacts scarcely with the organotin chlorides. On the other hand, the ESR signals disappeared slowly in the TMPNO·–$SnMr_4$ mixture and quickly in the TMPNO·–$SnCl_4$ mixture, which suggests the formation of the diamagnetic species in these solutions.

Table I. The ^{14}N hyperfine splitting constants a_N* of TMPNO· in various solvents.

Solvents	a_N(G)
n-Hexane	15.57
Cyclohexane	15.57
Carbon Tetrachloride	15.57
1,4-Dioxane	15.84
Acetone	15.86
Pyridine	16.02
Acetonitrile	16.12
Chloroform	16.14
Water/1,4-Dioxane = 1/4**	16.42
Methanol	16.62
Water/1,4-Dioxane = 2/3	16.82
= 3/2	17.30
= 4/1	17.35
Water	17.47

* Uncertainties are estimated to be ± 0.1 G for splitting constants. ** Volume ratios.

In the IR spectra of the complexes obtained by the reaction of TMPNO· with $SnCl_4$ or $SnBr_4$ in acetonitrile, the strong band appears at near 1610 cm^{-1}, accompanied with the disappearance of the N–O stretching band of TMPNO· observed at 1339 cm^{-1}. This new band is assigned to the $N^+=O$ stretching vibration, which would be supported by the $-N=O$ stretching band of alkyl nitroso compounds observed at near 1600 cm^{-1}.[12] The increase of N–O bond order in the cation $TMPNO^+=O$ is expected since the odd electron of the radical is removed from an antibonding orbital. In the far-infrared region of the complexes strong bands are observed at 295 (Ia) and 205 cm^{-1} (Ib), respectively. These are characteristic Sn–X stretching frequencies of SnX_6^{2-} (X = Cl, Br) having regular octahedral configurations around the tin atom,[13,14] which were confirmed by X-ray crystallographic analyses of K_2SnCl_6[15] and $(NH_4)_2SnBr_6$.[16] The results of the relevant IR frequencies of the 2,2,6,6-tetramethylpiperidine-1-oxoammonium complexes are summarized in Table II.

Table II. Relevant IR frequencies of 2,2,6,6-tetramethylpiperidine-1-oxoammonium complexes (in cm^{-1}).

Complexes	$\nu(\overset{+}{N}=O)$	ν(Sn-C)		ν(Sn-X)	
Ia	1613(s)	—		295(s)	
Ib	1608(s)	—		205(vs)	
II	1623(s)	—		—	
IV	1606(s)	—		295(vs)	
				257(vs)	247(sh)
V	1616(s)	571(s)	521(s)	320(vs)	230(vs)

In Figure 1 are indicated absorption spectra of TMPNO· and its complexes in acetonitrile. The bands of TMPNO· at near 240 and 460 mμ have been assigned to π–π* (or n–σ*) and n–π* transitions, re-

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(9) V.A. Golubev, E.G. Rozantsev, and M.B. Neiman, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1927 (1965).
(10) T. Kawamura, S. Matsunani, and T. Yonezawa, *Bull. Chem. Soc. Japan, 40,* 1111 (1967).
(11) Y.Y. Lim and R.S. Drago, *J. Am. Chem. Soc.*, 93, 891 (1971).
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(14) J.A. Creighton and J.H.S. Green, *J. Chem. Soc.*, (A), 808 (1968).
(15) G. Engel, *Z. Krist.*, (A), *90*, 341 (1935).
(16) G. Markstein and H. Nowotny, *Z. Krist.*, (A), *100*, 265 (1938).

Table III. NMR chemical shifts and coupling constants of ionic complexes at room temperature.[a]

Complexes	Solvents	Chemical shifts (ppm) τ(-CH$_2$-)	τ(-CH$_3$)	τ(Sn-CH$_3$)	Coupling constants (HZ) J(^{119}Sn-CH$_3$)
Ia	Liq. sulfur dioxide	7.36 br	8.17 s	—	—
Ib	Liq. sulfur dioxide	7.38 br	8.19 s	—	—
II	Liq. sulfur dioxide	7.40 br	8.21 s	—	—
IV	Liq. sulfur dioxide	7.43 br	8.24 s	—	—
V	Liq. sulfur dioxide	7.40 br	8.21 s	8.71 (8.47)[b]	80.8 (72.7)
	Chloroform	[c]	[c]	8.68 (8.80)	85.7 (67.7)
	Dichloromethane	[c]	[c]	8.74 (8.80)	86.9 (70.4)
	Nitromethane	[c]	[c]	8.81 (8.64)	91.8 (75.9)
	Acetonitrile-d$_3$	[c]	[c]	8.82 (8.81)	92.4 (81.6)

[a] The abbreviations used are as follows: br; broad, s; singlet. [b] Values in parentheses are for dimethyltin dichloride. [c] Not observed.

spectively.[17,18] The n–π* absorptions of the oxoammonium complexes are observed at the same positions as that of TMPNO· in acetonitrile. The molar extinction coefficient ε increases by about four times in Ia and twice in II that of TMPNO·, respectively. This means that TMPNO· loses an odd electron occupied in the π* orbital to form the oxoammonium cation, resulting in the enhancement of intensity of the n–π* absorption band.

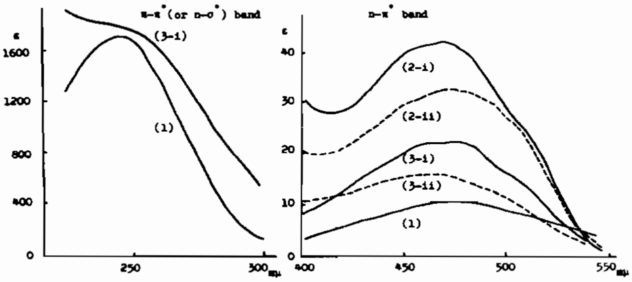
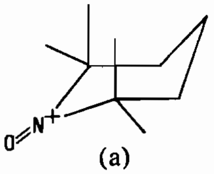


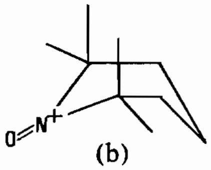
Figure 1. UV and visible spectra of TMPNO· and its complexes. (1), TMPNO· in acetonitrile; (2-i), Compound (Ia) in acetonitrile; (2-ii), Compound (Ia) in solid; (3-i), Compound (II) in acetonitrile; (3-ii), Compound (II) in solid.

The ionic character of these complexes is also confirmed by the conductivity measurements in acetonitrile; the molar conductances obtained are as follows: 295 (Ia, 1.00×10^{-3} mole/l); 250 (Ib, 1.00×10^{-3} mole/l); 177 ohm^{-1} cm^2 mole^{-1} (II, 1.02×10^{-3} mole/l).

In Table III are given the proton nmr chemical shifts of 2,2,6,6-tetramethylpiperidine-1-oxoammonium cation (TMPN$^+$=O) of these ionic complexes, in liquid sulfur dioxide at room temperature. TMPN$^+$=O may have two conformations, chair (a) and boat (b) forms.



(a)



(b)

The methyl protons exhibit a single sharp signal at room temperature and this is true even at −100°C in liquid sulfur dioxide, indicating that a flip-flop motion of the oxoammonium cation is continued even at very low temperature.

The formation of the ionic complexes by the reaction between TMPNO· and tin tetrahalides would be according to the following mechanism:

(i) the redox reaction,

$$2\text{TMPNO}^{\cdot} + \text{SnX}_4(\text{X}=\text{Cl},\text{Br}) \rightarrow 2[\text{TMP}\overset{+}{\text{N}}=\text{O}]\text{X}^- + \text{SnX}_2$$

(ii) the association reaction,

$$2[\text{TMP}\overset{+}{\text{N}}=\text{O}]\text{X}^- + \text{SnX}_4 \rightarrow [\text{TMP}\overset{+}{\text{N}}=\text{O}]_2\text{SnX}_6^{2-}$$

The process (ii) has been confirmed by the fact that [TMPN$^+$=O]Cl$^-$ (III) reacts easily with SnCl$_4$ giving the complex (Ia) containing SnCl$_6^{2-}$. In addition, it has been found that phenyltin trichloride and dimethyltin dichloride, which hardly interact with TMPNO·, react easily with (III) to form (IV) and (V).

The pentachlorophenyltin anion would also be hexacoordinated around the tin atom. In the complex containing trichlorodimethyltin anion, two strong Sn–C and two strong Sn–Cl stretching bands were observed (see Table II). The configuration is considered to be the trigonal bipyramidal one around the tin atom with two methyl groups in the equatorial position, as was pointed out in the previous paper.[19,20]

As is shown in Figure 2, the complex 2,2,6,6-tetra-

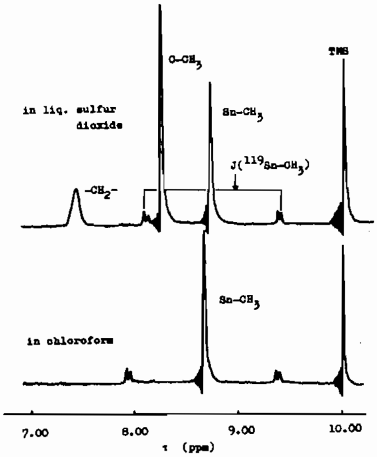


Figure 2. NMR spectra of $[\text{TMP}\overset{+}{\text{N}}=\text{O}][(\text{CH}_3)_2\text{SnCl}_3]^-$ at room temperature.

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(18) R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, 3273 (1965).

methylpiperidine-1-oxoammonium dimethyltin trichloride (V) in liquid sulfur dioxide shows a single methylene and two methyl proton signals with the intensity ratio of 1:2:1, respectively. In chloroform, however, the methylene and methyl proton signals of TMPN$^+$=O disappear and the methyl signal of $(CH_3)_2SnCl_3^-$ still remains. The disappearance of the signals of TMPN$^+$=O is explained to be due to the rapid exchange of an unpaired elecrton between TMPN$^+$=O and TMPNO· reproduced in solution.* The similar phenomena are also observed in dichloromethane, nitromethane and acetonitrile–d_3.

In Table III are represented the J(^{119}Sn–CH$_3$) values of [TMPN$^+$=O][$(CH_3)_2SnCl_3$]$^-$ together with those of dimethyltin dichloride in various solvents. The value of 92 Hz in nitromethane and acetonitrile may suggest the existence of the $(CH_3)_2SnCl_3^-$ anion having trigonal bipyramidal configuration.[20] The characteristic J(^{119}Sn–CH$_3$) values, however, decrease in the order of dichloromethane > chloroform > liquid sulfur dioxide. This may be due to the partial dissociation of the [TMPN$^+$=O] [$(CH_3)_2SnCl_3$]$^-$ complex into [TMPN$^+$=O]Cl$^-$ and dimethyltin dichloride in solution, and these species could interchange rapidly in the equilibrium, [TMPN$^+$=O][$(CH_3)_2SnCl_3$]$^-$ $\leftrightarrows$ [TMPN$^+$=O]Cl$^-$ + $(CH_3)_2SnCl_2$. Thus the observed J(^{119}Sn–CH$_3$) values are the means between those of [$(CH_3)_2SnCl_3$]$^-$ and $(CH_3)_2SnCl_2$. Further, a small amount of TMPNO· is reproduced in solution as mentioned above. It is of much interest that the TMPN$^+$=O is asily reduced to TMPNO· in solution.

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(19) F.B.W. Einstein and B.R. Penfold, *Chem. Comm.*, 780 (1966).
(20) T. Tanaka, K. Tanaka, and T. Yoshimitsu, *Bull. Chem. Soc. Japan*, *44*, 112 (1971).
* It would be due to scavenge of a small amount of the free radical reproduced that all the signals were observed clearly in liquid sulfur dioxide.