intermediate occurs in the lowest excited singlet state of 5(E)-SDU. This is consistent with very small quantum yield of intersystem crossing of 5(E)-SDU.

As shown in Table 5, Φ_i increases slightly with increasing the concentration of benzophenone suggesting that the excited triplet state of 5(E)-SDU can undergo the same type of reaction, even though with low efficiency. The quantum yield of pure triplet photoreaction(Φ_t) of 1.03×10^{-3} is estimated from extrapolation of the quantum yield to the point where only the benzophenone absorbs the exciting radiation (i.e., $1-\alpha=1$). Total quantum yield(Φ_i) is expressed by the following:

$$\Phi_i = \Phi_s + \Phi_{isc} \times \Phi_t$$

where Φ_s and Φ_t represent the quantum yields of photoreaction occurring via the excited singlet state and triplet state, respectively, and $\Phi_{isc} \times \Phi_t$ is the quantum yield of triplet state photoreaction on direct irradiation. Φ_s of 3.5×10^{-4} is obtained from $\Phi_i(4 \times 10^{-4})$, $\Phi_{isc}(0.052)$, and $\Phi_t(1.03 \times 10^{-3})$. Photoreaction to form the intermediate, therefore, occurs mainly via the excited singlet state with small participation of triplet state reaction.

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Reaction of Methylenethioxanthene with Thiyl Radical: Formation of A Vinyl Sulfide

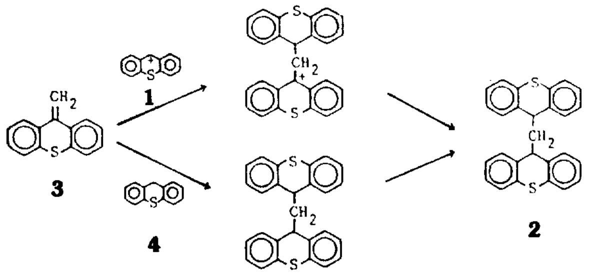
Eun Kyung Kim, Kyongtae Kim*, and Jung Hyu Shin

Department of Chemistry Seoul National University Seoul, 151. *Received June 8, 1987*

Reactions of methylenethioxanthene (**3**) with n-propanethiol in the presence of di-t-butyl peroxide(DTBP) afforded preferentially propyl 9-thioxanthenylidenemethyl sulfide(**8**) rather than propyl 9-thioxanthenylmethyl sulfide(**9**) regardless of the concentration of n-propanethiol. On the other hand reactions of **3** with a low concentration of n-propanethiol in the presence of dibenzoyl peroxide(DBPO) gave **8**, 1,2-bisthioxanthenylidene ethane(**11**), and thioxanthenylidenemethyl benzoate(**12**) but only **8** was formed at high concentration of the thiol. The formations of these products were rationallized by an electron transfer mechanism.

Introduction

The reaction of thioxanthylium ion (**1**) with diphenyl- and dibenzylmercury under nitrogen atmosphere afforded 9-phenyl- and 9-benzylthioxanthene, respectively. However, bis-9,9^1-thioxanthenylmethane (**2**) was obtained from the analogous reaction with dimethylmercury instead of 9-methylthioxanthene.[1] The formation of **2** suggests inevitably the involvement of methylenethioxanthene (**3**) as key intermediate. Therefore, it was assumed that **2** would be formed via a carbenium mechanism by an addition of **1** and/or a radical mechanism by an addition of thioxanthene radical (**4**) to **3**(Scheme 1).



Scheme 1

The possibility of the former mechanism was tested and indeed **2** could be obtained from the reaction of **3** with **1** in the presence of thioxanthene (**5**).[2]

In order to ascertain the possible involvement of the latter mechanism, **4** must be generated from a precursor which may be 9-thioxanthenylcarbonyl peroxide or 9-azothioxanthene. Syntheses of these precursors are now under progress. In connection with this work, we have investigated the reactions of **3** with n-propanethiol using two different radical initiators in order to obtain some information about the addition of a radical to **3**. The results are described in this paper.

Experimental

9-Methylenethioxanthene (**3**) was prepared using the reported method.[2] Thioxanthene(Pfaltz and Bauer), triphenylphosphine (Sigma), n-propanethiol(Aldrich), and dibenzoyl peroxide(Matheson, Colman and Bell) were used as obtained. Thioxanthone was prepared according to the literature method.[3] Nitromethane(Junsei) was dried with anhydrous calcium chloride and distilled. Dried nitromethane was stored over calcium chloride in a septum-capped bottle. Thin layer chromatography(tlc) was performed on a glass plate (2 × 8 cm) with Merck Kiesel 60 PF_{254}(Art. 7751). The slurry of the adsorbent was made in a mixture of chloroform and methanol (2:1, v/v). The chromatogram was visualized by mineral uv lamp. Column chromatography was performed with Meck silica gel (Art. 7734). Ultraviolet spectra were obtained using Beckman Model 5270 spectrophotometer. ^1H NMR spectra were recorded using Varian EM-360A spectrometer. Chemical shifts were measured in ppm relative to an internal standard TMS. Melting points were taken with Fisher-Jones melting point apparatus and were not corrected.

Reaction of thioxanthene(5) with di-t-butyl peroxide (DTBP). To a stirred solution of 0.365 g(1.84 mM) of **5** in 25 ml of dried acetonitrile was added 2.1 ml(11.4 mM) of DTBP under nitrogen. The reaction mixture was refluxed for 52 h to give a brown solution. The solvent of the reaction mixture was evaporated to dryness and the residue was chromatographed on silica gel column(2 × 15 cm). Elution with hexane (300 ml) gave 0.333 g(1.68 mM) of **5**. Next three acetone fractions gave 0.010 g(0.025 mM) of a white solid, identified as bithioxanthyl (**6**); mp>300°C(p-xylene)[4]

Reaction of 3 with DTBP. To a stirred solution of 0.151 g(0.716 mM) of **3** in 30 ml of dried acetonitrile was added 0.6 ml(3.25 mM) of DTBP under nitrogen atmosphere. The reaction mixture was refluxed for 18 h to give a brown solution. The reaction mixture was worked up as before. Elution with hexane(300 ml) gave 0.098 g(0.466 mM) of **3**. Next fractions gave thioxanthone(**7**) and other unidentified products, of which yields were very low.

Reaction of 3 with n-propanethiol(n-PrSH) in the presence of DTBP. (a) **3**: n-PrSH(1:2.7, molar ratio). To a stirred solution of 0.086 g(0.41 mM) of **3** in 30 ml of dried nitromethane was added 0.1 ml(0.084 g, 1.1 mM) of n-PrSH and 1.0 ml(5.4 mM) of DTBP under N_2. The reaction mixture was refluxed for 21 h to give a yellow solution, which showed very weak spot of **3** on thin layer chromatogram(hexane). The reaction mixture was worked up after 41 h reflux. After removal of the solvent under vacuum, the residue was chromatographed on silica gel column(3 × 12 cm). First five hexane fractions (300 ml) gave 0.045 g of yellowish liquid: IR (KBr) 3045, 2950, 2860, 1620, 1775, 1545, 1455, 1430, 1370, 1115, 1060, 755, 730 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.90-1.13 (t, 3H, CH_3), 1.45-1.90(q, 2H, CH_2), 2.67-2.94(t, 2H, CH_2), 6.56(s, 1H, =CH–), 7.20-7.86(m, 8H, aromatic); UV λ_{max}^{MeOH} 336, 294, 234 nm; MS m/e(rel. int.), 285(12.6), 284(63.4), 243(10), 242(21.7), 240(100), 239(5.0), 223(6.1), 213(6.5), 212(30.8), 210(6.0), 208(10.8), 198(4.1), 197(26.9), 163(6.4), 152(7.8), 139(6.0), 18(18.1). This compound was assigned to be propyl 9-thioxanthenylidenemethyl sulfide(**8**). Next three hexane fraction(100 ml) gave a mixture of **3** and propyl 9-thioxanthenylmethyl sulfide(**9**), which was unable to be separated(vide infra). Elution with a mixture of hexane and ether(10:1, v/v, 20 ml) gave 0.017 g(0.08 mM) of **7**. Finally elution with acetone(200 ml) gave 0.043 g of an unknown brown solid(**10**); mp, 104-105.5°C (hexane-ether, 1:1, v/v); IR(KBr) 3140(broad), 2950, 2860, 1680, 1600, 1450, 1400, 1270, 1235, 915, 835, 635 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.9-1.13(t), 1.08-1.92(m), 2.66-2.9(t), 7.18-7.3(d), 8.18(s). A singlet at δ8.18 ppm was exchangeable with D_2O and shifted to δ4.72 ppm. UV λ_{max}^{MeOH} 270(sh), 232 nm; MS m/e(rel. int.) 197 (0.1), 152(0.1), 119(38.8), 86(11.1), 78(24.7), 77(100), 75(19.3), 60(14.5), 59(32.4), 47(50.1), 46(27.8), 45(63.3), 44(32.9), 43(48.9), 42(23), 41(74.4).

(b) **3**: PrSH(1:16, molar ratio). Using the same procedure as in (a), a mixture of **3**(0.210 g, 1.0 mM) in 30 ml of nitromethane, n-PrSH(1.5 ml, 16.6 mM), and DTBP(2 ml, 10.8 mM) was refluxed under N_2 for 24 h at which time tlc showed still the presence of **3**. The mixture was refluxed for an additional 43 h and resulted in a brown solution, which was worked up as before. First two hexane fractions(200 ml) gave 0.023 g(0.11 mM) of **3**, while next three fractions of a hexane-ether mixture(150:1, v/v, 300 ml) gave 0.201 g(0.71 mM) of **8**, and 0.034 g(0.12 mM) of **9**. Using the same solvent mixture as in the above was obtained 0.016 g(0.74 mM) of **7**. Finally acetone fraction afforded 0.148 g of **10**.

Reaction of 3 with n-propanethiol in the presence of dibenzoyl peroxide(DBPO). (a) **3**: n-PrSH(1:2.1, molar ratio). To a stirred solution of 0.470 g(2.23 mM) of **3** in 50 ml of dried nitromethane was added 0.531 g(2.20 mM) of DBPO and 0.42 ml(4.64 mM) of n-PrSH under N_2. The mixture was refluxed for 38 h under N_2 to give a brown solution, which was worked up as before. First hexane fraction(150 ml) gave a mixture: 0.069 g(0.46 mM) of dipropyl disulfide, 0.002 g(9.6×10^{-3} mM) of **3** and 0.020 g of **9**. Second hexane fraction (200 ml) gave 0.274 g(0.96 mM) of **9** and 0.010 g (0.024 mM) of yellow solid; mp 262-265°C; IR(KBr) 3050, 1590,

Table 1. Reaction of 5 with DTBP

Reactants (mM)		Products (mM)		
5	DTBP	**5**	**6**	**7**
1.84	11.4	1.68 (91.2)	0.025 (1.4)	0.073 (4.0)

Number in the parenthesis represents a percent yield based on **5**.

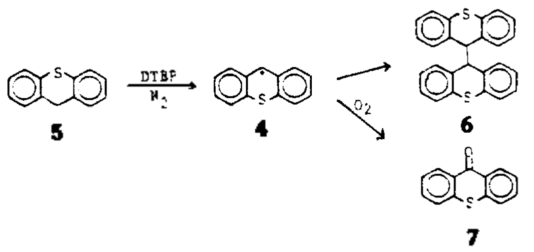
1575, 1550, 1450, 1430, 1380, 1150, 1105, 1060, 930, 770, 760, 730, 620 cm^{-1}; ^1H NMR($CDCl_3$) δ 7.1(s, 1H, =CH–), 7.2-8.0 (m, 8H, aromatic); UV λ_{max}^{MeOH} 380(sh), 338, 290(sh), 232 nm; MS m/e(rel. int.) 420(6.2), 419(13.8), 418(43.5), 417(8.7), 197(100). This compound was assigned to be 1,2-bisthioxanthenylidene ethane(**11**). Elution with benzene (100 m*l*) gave 0.542 g(4.4 mM) of benzoic acid and 0.020 g(0.048 mM) of **11**. Next benzene fraction(70 m*l*) gave a traceable amount of **7** and an orangish tar which was recrystallized from ethanol to give thioxanthenylidenemethyl benzoate(**12**): mp 121.5-123°C; IR(KBr) 3080, 3050, 1730, 1700, 1630, 1590, 1570, 1545, 1445, 1430, 1260, 1240, 1180, 1110, 1060, 750, 723, 690 cm^{-1}; ^1H NMR($CDCl_3$) δ 7.15-8.30(m, 14H); UV λ_{max}^{MeOH} 335, 283(sh), 258(sh), 231 nm; MS m/e(rel. int.) 332(0.2), 331(0.5), 330(1.6), 105(100).

(b) **3**: n-PrSH(1:21, molar ratio). Using the same procedure as in (a), **3**(0.261 g, 1.24 mM) in 50 m*l* of dried nitromethane and n-PrSH(3.01 g, 12.3 mM) were refluxed under N_2 for 41 h, followed by chromatography. First hexane fraction(100 m*l*) gave 0.129 g(0.86 mM) of dipropyl disulfide. Second hexane fraction(120 m*l*) gave a mixture of **8**(0.058 g, 0.28 mM) and a traceable amount of **9**. Elution with benzene afforded a mixture of benzoic acid, **7**, and **11** which were identified by ^1H NMR spectra. Compound **12** was obtained in small amount.

Results and Discussion

(A) Generation of thioxanthene radical (4). In order to generate **4**, **5** in the nitromethane was refluxed for 52 h in the presence of DTBP under N_2. The results are shown in Table 1.

The formation of **6** can be explained by the coupling of two **4** and that of **7** by the reaction of **4** with oxygen remained in the solvent, which is consistent with the previous results[1,5] (Scheme 2). Since more than 91% of **5** was recovered, t-butoxy radical was not conceived energetic enough to abstract a hydrogen atom from **5**.



Scheme 2

(B) Stability of 3 in the presence of DTBP. Refluxing of a mixture of **3** and DTBP for 18 h in dried nitromethane under N_2 led to 65% recovery of **3**, small amount of **7**, and some unidentified compounds. Since **3** is readily oxidized to give **7** even in the air, **7** must be formed by the oxidation of **3**[6] for the prolonged refluxing period. Recovery of **3** in 65% yield indicates that **3** decomposes substantially at the solvent refluxing temperature.

Table 2. Reactions of 3 with n-propanethiol in the presence of DTBP

Entry	Reactants (mM)			Products (mM)			
	3	n-PrSH	DTBP	**3**	**7**	**8**	**9**
I	0.41	1.1	5.4	Trace	0.08 (19.6)	0.16 (38.2)	Trace
II	1.0	16.5	10.8	0.019 (11.0)	0.07 (7.4)	0.71 (71.9)	0.12 (12.0)

Number in the parenthesis represents a percent yield based on **3**.

Table 3. Reactions of 3 with n-propanethiol in the presence of DBPO

Entry	Reactants (mM)			Products (mM)			
	3	n-PrSH	DBPO	**8**	**9**	**11**	**12**
III	2.23	4.64	2.20	1.28 (57.4)	0	0.07 (5.43)	0.06 (2.7)
IV	1.24	26.0	12.3	0.51 (41.3)	Trace	Trace	Trace

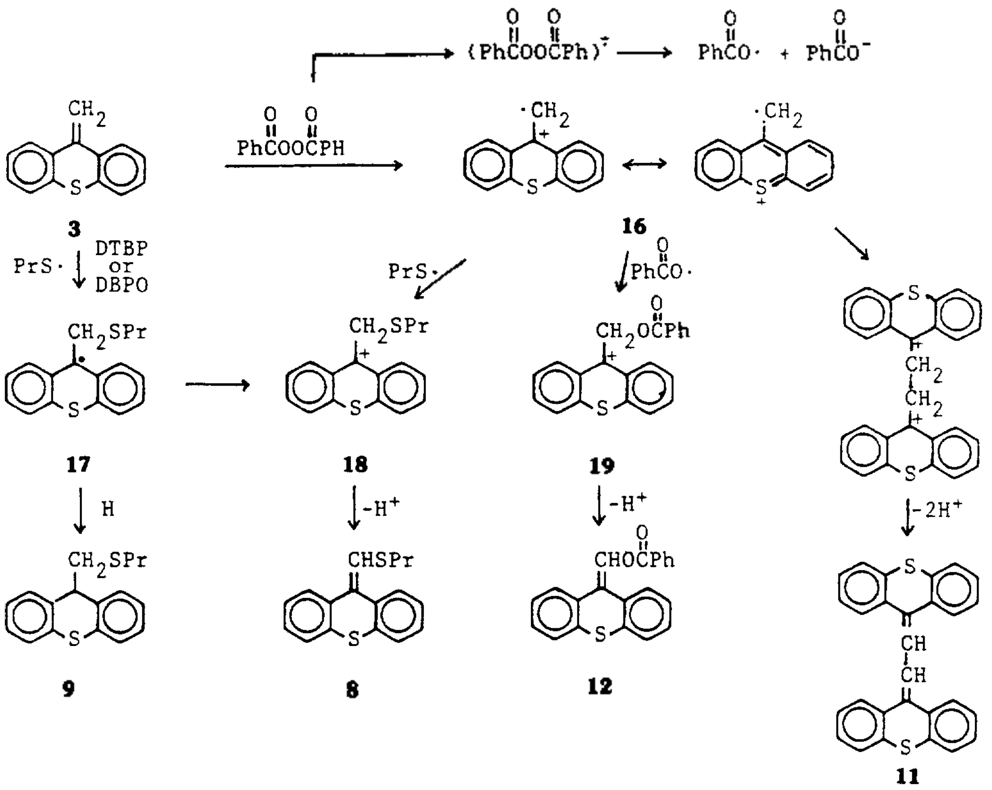
Number in the parenthesis represents a percent yield based on **3**.

(C) Reactions of 3 with n-PrSH in the presence of radical initiators. n-Propanethiyl radical was generated from thiol using DTBP, and the fate of thiyl radical in the presence of **3** was investigated. Table 2 shows the results at two different thiol concentrations.

A noteworthy thing is that yield of **8**, a vinyl sulfide, is higher than that of **9**, an addition compound regardless of the concentration of n-PrSH. This is contrast with the result obtained from the reaction of 1,1-diphenylethene with benzenethiol in the presence of AIBN, in which 100% of 2,2-diphenylethyl phenyl sulfide was produced.[8] In our case as the concentration of n-PrSH was increased(Entry II), the yield of **9** was increased to 12%. Decreased yield of **7** from 19.6% to 7.4% can be rationalized by the increased amounts of **3** dissolved in the same volume(30 m*l*) of the solvent, where oxygen content was supposed to be almost equal in both reactions.

The same trend was obtained from the reaction with n-PrSH in the presence of DBPO. Table 3 summarized the results.

When molar ratio of n-PrSH to **3** was 2.08(Entry III), a major product was **8** and no addition product (**9**) was detected. In addition, a diene (**11**) and a vinyl benzoate (**12**) were isolated. When molar ratio of n-PrSH to **3** increased to 1:20.9(Entry IV), a major product was **8**(41.3%) and the other products (**9**, **11**, **12**) were only detectable by tlc. The results summarized in Table 2 and Table 3 suggest that the major reaction pathway is not an addition of thiyl radical to **3**, followed by a hydrogen atom abstraction. The formation of a vinyl sulfide (**8**) or a vinyl ester (**12**) might not be due to losing a hydrogen atom after an addition of thiyl or a benzoyloxy radical to **3** because loss of hydrogen atom from an intermediate radical (**19**) is expected to be much higher energetic process compared with a loss of thiyl radical from **19** back to **3**, which is a well-known reversible process for addition of thiyl radicals to olefins.[9] Therefore, the formation of **8** and **12** are explained



Scheme 3

by a loss of proton from the corresponding cationic intermediates, **18**, and **19**, as shown in Scheme 3. The formation of **11** suggests that methylenthioxanthene cationi radical (**16**) is involved in this reaction. The structure of **11** was confirmed by an independent synthesis. There are some reports about one electron oxidation of olefins. For example, antimony pentachloride converts 1,1-diphenylethene into its cation radical which then dimerizes into dication.[10]

Analogously one electron transfer from **3** to DBPO produces **16** and DBPO anion radical, which then decomposes to give benzoyloxy radical and benzoate ion. Dimeriazation of **16**, followed by deprotonation affords **11**. Coupling between **16** and benzoyloxy radical, followed by deprotonation affords **12**. There have been many reports showing the role of DBPO as an electron acceptor.[11] It is possible for DBPO to be an electron acceptor since it has an accessible lowest unoccupied molecular orbital of the peroxide oxygen to which an electron can be transferred.[12]

When a large excessive n-PrSH was used(Entry IV), **8** was a major product and the amounts of **9**, **11**, and **12** were negligible. This result indicates that benzoyloxy radical is trapped by n-PrSH to give benzoic acid so that **16** may not have chance to react with benzoyloxy radical. Furthermore, dimerization of **16** is expected to be strongly repressed by the large concentration of thiyl radical. However, in the case of the reaction with DTBP, no **11** was isolated regardless of the concentration of DTBP. To our knowledge, an electron transfer between olefins and DTBP has not been reported. However, DTBP can be an electron acceptor since it also has the lowest antibonding orbital of the peroxide oxygen as DBPO. Indeed, ESR and optical evidence for the formation of the anion radical of DTBP has been reported.[13] Grignard reagents and organolithiums[14] are known as facile electron transfers to DTBP. Since **3** is a different type of compound compared with the organometallic compounds, and electron affinities of DTBP and DBPO and ionization potential of **3** are not available, it is difficult to elucidate the initial step of the reaction of **3** having DTBP. The formation mechanism of **8** in the presence of DTBP might not be the same as that in the presence of DBPO. The increased yield of **9** in the presence of a large excess of n-PrSH(Entry II) when DTBP was used suggests the involvement of a radical intermediate (**17**) as shown in Scheme 3. Although oxidation of a radical by either metallic oxidants[15] or cation radicals[16] to generate a cation is a well-known process, it is uncertain in this case what the oxidant is. Nevertheless, oxidation of **17** is expected to occur readily because the positive charge of **18** is stabilized by delocalization through the thioxanthene ring.

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zene with $NOPF_6$. However, we assumed that oxygen molecule might be an oxidizing agent in this reaction, since **3** was stable under vacuo. The oxidation mechanism of **3** by oxygen is currently uncertain. An electron transfer from **3** to oxygen, followed by the formation of 1,2-dioxetane might be a possible route to lead **7** and formaldehyde. Refer to the following references: G. A. Olah and N. Friedman, *J. Am. Chem. Soc.*, **88**, 5330 (1966); W. H. Richardson, F. C. Montgomery, M. B. Yelvington, and H. E. O' Neal, J. Am. Chem. Soc., **96**, 7525 (1974); W. H. Richardson, F. C. Montgomery, P. Slusser, and M. B. Yelvington, *J. Am. Chem. Soc.*, **97**, 2819 (1975).

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Simulation of the Solution EPR Spectra of Mixed-Valence Heteropolyanions Containing Vanadium(IV) and Vanadium(V)†

Hyunsoo So*, Chul Wee Lee, and Duckhwan Lee

Department of Chemistry, Sogang University, Seoul 121. Received June 22, 1987

Modified Bloch equations were used to simulate the solution EPR spectra of mixed-valence heteropolyanions containing vanadium(IV) and vanadium(V). Simulated are the 15-, 22-, 36- and 43-line spectra of α-1,2-$[PV(IV)VW_{10}O_{40}]^{6-}$, $[P_2V(IV)\,V_2W_{15}O_{62}]^{10-}$; $[HP_2V(IV)V_2W_{15}O_{62}]^{9-}$ and α-1,2,3-$[HSiV(IV)V_2W_9O_{40}]^{7-}$; respectively. The transition probabilities for the intramolecular electron transfer were determined from the simulations.

Introduction

Recently we have simulated the temperature-dependent EPR spectra of mixed-valence copper(II)-copper(I) complexes,[1] using the modified Bloch equations.[2,3] The simulation made it possible to determine the transition probability for the intramolecular electron transfer, and the activation energy when spectra at several different temperatures were available.

We have applied the same method to the simulation of the EPR spectra of mixed-valence heteropolyanions containing vanadium(IV) and vanadium(V), which show a variety of interesting EPR spectra. So far four types of solution spectra have been observed: a 15-line spectrum for $[SiV(IV)VW_{10}O_{40}]^{7-}$, $[P_2V(IV)VW_{16}O_{62}]^{9-}$, and α-1,2-$[PV(IV)VW_{10}O_{40}]^{6-}$;[4-6] a 22-line spectrum for $[P_2V(IV)V_2W_{15}O_{62}]^{10-}$;[5] a 36-line spectrum for $[HP_2V(IV)V_2W_{15}O_{62}]^{9-}$ in which the VO_6 octahedra are edge-shared;[5] and a 43-line spectrum for α-1,2,3-$[HSiV(IV)V_2W_9O_{40}]^{7-}$ in which the VO_6 octahedra are corner-shared.[4] The simulation of these spectra is reported in this paper.

Simulation of the Spectra

The 15-Line Spectrum. When a heteropolyanion containing two equivalent vanadium(V) atoms connected by a bridging oxygen atom is reduced, it shows a 15-line spectrum.[4-6] In order to simulate the spectrum, we first calculate the positions of eight hyperfine lines expected when the

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† Dedicated to Professor Nung Min Yoon on the occasion of his 60th birthday.