ESR Studies of Reduced Molybdovanadophosphoric Heteropoly Acids. II. Homogeneous Reduction

Masayuki Otake and Tadaaki Otaki
The Central Research Laboratories, Mitsubishi Chemical Industries Ltd.,
Hisamoto 290, Takatsu-ku, Kawasaki 213

(Received January 31, 1974)

ESR spectra of the chemically reduced molybdovanadophosphoric heteropoly acids ($H_{3+x}Mo_{12-x}V_xPO_{40}\cdot nH_2O$, where $x=1$ and 2) were observed in the solution and glassy state in various organic solvents. On addition of equimolar amounts of reductants such as $SnCl_2\cdot 2H_2O$, $HSCH_2CH_2SH$, and CH_3SCH_3, a transient ESR signal(B) appeared with eight hfs lines referred to as V(IV), $I=7/2$, and with $\langle g\rangle=1.96$ and $\langle T\rangle=-0.83\times 10^{-2}$ cm^{-1}. However, it disappeared within *ca.* 5 hr at 20 °C and another signal(C) with $\langle g\rangle=1.962$ and $\langle T\rangle=-1.00\times 10^{-2}$ cm^{-1} gradually increased in intensity. The hyperfine coupling constant of the transient species was thus unusually small as compared with that of the ordinary V(IV) species and the C species. The mechanistic pathways of the reduction were discussed. The splitting observed in the low-field parallel components of the B signal was satisfactorily explained by a "geometrical charge isomerism" characteristic of the structure of the heteropoly anion. The origin of the unusually small hfs constant was discussed in the light of its molecular structure.

In a previous paper,[1)] it was demonstrated that partial substitution by vanadium ions for the molybdenum in molybdophosphoric acid is effective for clarifying the mechanism of the reduction and the nature of the reduced species. The results might be summarized as follows:

A) Localization of an electron on the vanadium ions giving rise to an ESR signal was confirmed.

B) In the low stage of reduction, only one paramagnetic center exists in the heteropoly cage, *i.e.*, Mo(V) for molybdophosphoric and V(IV) for vanadium substituted heteropoly acids.

C) As with usual vanadyl complexes, the terminal oxygen of the octahedral oxyanions in the heteropoly cage plays an important part in the localization of the electron on the V=O moiety.

D) As a reduction mechanism, a modified Pottkamp and Umland scheme[2)] was proposed, in which almost all the reduced molybdenum ions are tetravalent, Mo(IV)–OH.

The present study was undertaken to obtain more advanced knowledge on the mechanism of the reduction. The polarographic reduction of the above compounds has been extensively studied.[3)] However, discrepancies were observed in the results, apparently arising from failure to take into account the hydrolytic instability of the heteropoly anion in the dilute aqueous solution. In order to prevent hydrolysis we chose several organic compounds. Reduction was carried out at room temperature in various organic solvents, using stannous chloride, ethylene dithioglycol and several other sulfur compounds as reducing agents. The difference in the redox potential and the functional groups was expected to allow the formation of a different reduced state corresponding to the individual reductant. Large coupling constants and the strong anisotropic nature of the vanadium(IV) ion, introduced in the cage structure, were useful in the present study.

Experimental

Molybdovanadophosphoric acids $H_{3+x}Mo_{12-x}V_xPO_{40}$, where $x=1$ and 2, were prepared as reported[1)] according to the method of Tsigdinos and Hallada.[4)] The acids are soluble in organic compounds such as nitrile (acetonitrile), ketones (acetone and methyl ethyl ketone) and esters (methyl isobutyrate and *n*-butyl acetate). In order to avoid contamination with water, the heteropoly acids were evacuated at 100 °C to less than 10^{-3} mmHg, most of the water being removed. Commercial reagents of guaranteed grade were used without further purification. Contamination of the solvents with water was estimated to be less than 0.1%. The reductant solution was added to a solution of the heteropoly acid with the aid of a calibrated microsyringe. An X-band ESR spectrometer, JES-P-10, Japan Electron Optics Lab. Co., was used. Measurements were carried out both at 293 and 77 K. Analysis of the spectra was carried out as described.[1)]

Results

Reduction with $SnCl_2\cdot 2H_2O$ in Acetonitrile. The original molybdovanadophosphoric acids gave weak ESR signals both in their solid state and in solution. When a solution of the heteropoly acid and the reductant were mixed, the original orange solution turned blue and a new ESR signal(B), consisting of eight hfs lines referred to as vanadium(IV) ion with $I=7/2$, appeared with remarkably enhanced intensity. How-

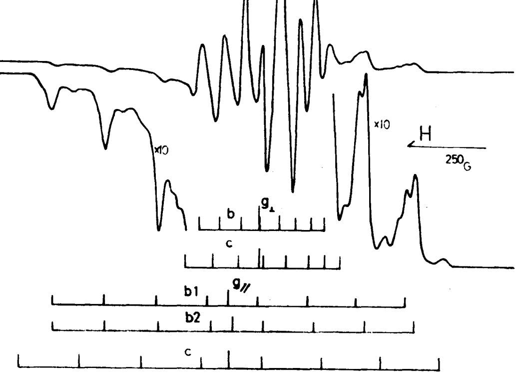

Fig. 1. ESR spectrum (1st derivative, 77 K) of $H_4Mo_{11}V_1PO_{40}$ reduced with $SnCl_2$ in acetonitrile, 0.1 M.

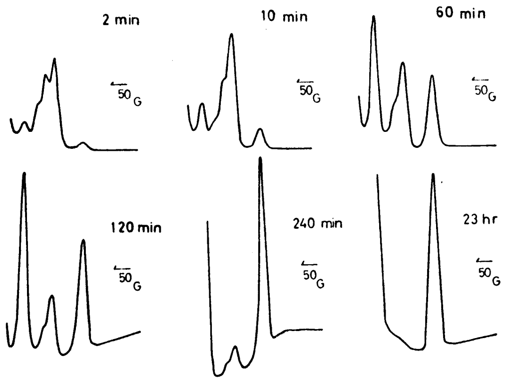

Fig. 2. The change with time of the ESR spectrum (1st derivative, 77 K) of $H_4Mo_{11}VPO_{40}$ reduced with $SnCl_2$ in acetonitrile ($m_n=-7/2$ and a part of $m_n=-5/2$, parallel hfs components)

ever, the spectral pattern changed with time, and another signal(C) gradually grew in intensity, superimposing on the former one which finally disappeared in *ca.* 5 hr at 20 °C. An illustration of the first-derivative spectrum ($x=1$ acid) is given in Fig. 1, in which both signals B and C are superimposed on each other. Splittings are observed in the low-field parallel components of signal B, which indicates that there are at least two kinds of B species. Its hfs coupling constants differ from those of C, while the g-values of both signals are almost the same. Signal C was found to be identical with that of a solution of the heteropoly acid reduced in a stream of hydrogen at 280 °C. The rate of formation and decay of the transient species B were measured more precisely by freezing the solution at liquid nitrogen temperature, after keeping the mixture for several minutes at 20 °C. Figure 2 shows how the parallel $m_n=-7/2$ hfs components of signals B and C change with time. The splitting of the parallel component of signal B is most remarkable in this spectral region. Results of the analysis of the spectrum are summarized in Table 1.

Reduction with $HSCH_2CH_2SH$ in Acetonitrile. Various amounts of ethylene dithioglycol were added to a 0.1 M solution of the $x=1$ acid in acetonitrile, but the effect of the quantity of reductant on the ESR spectral pattern was almost negligible except for that on signal intensity. The spectrum, like that in Fig. 1, indicates again the spontaneous formation of species B which disappears within a few hours. The line shape changed gradually, leaving only eight hfs lines of species C. Results of the analysis are given in Table 1. No Mo(V) signal, such as that of dithioglycol-Mo(V) complex ($\langle g\rangle=2.002$, $\langle T\rangle=32$ G)[5] was detected.

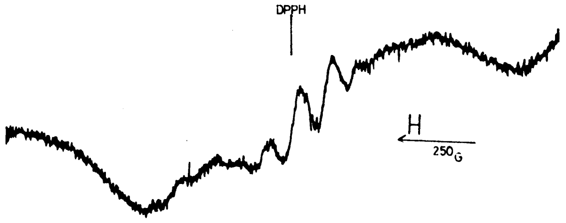

Fig. 3. ESR Spectrum (1st derivative, 20 °C) of $H_5Mo_{10}V_2PO_{40}$ reduced heterogeneously with hydrogen at 280 °C, n-butyl acetate solution, 0.1 M.

Other Sulfur Compounds as Reductant. Dimethyl sulfide and thiomalic acid dissolved in acetonitrile caused reduction of the $x=1$ heteropoly acid, giving ESR spectra similar to the spectrum of dithioglycol. The ESR parameters obtained are listed in Table 1.

Reduction with $SnCl_2\cdot 2H_2O$ in Other Solvents. Reduction in a solution of acetone and methyl ethyl ketone gave ESR signals similar to those in Fig. 1. However, the splitting of low-field parallel components of signal B was not so marked as in the case of the spectrum in the acetonitrile solution. Figure 3 illustrates an effect of the solvents on the ESR spectrum of the reduced $x=2$ heteropoly acid, in which the partly reduced acid is dissolved in n-butyl acetate. Separation of the hfs components is obviously incomplete.

Discussion

The reduction of molybdovanadophosphoric heteropoly acids with chemical reagents was found to proceed *via* a two step reaction. A number of polarographic studies of molybdophosphoric or other heteropoly acids have been reported[2,3] but not dealing with the forma-

TABLE 1. ESR PARAMETERS OF THE REDUCED $x=1$ HETEROPOLY ACID[a)]

Reductants	Species	$g_\perp$	$g_{//}$	$\langle g\rangle$	$T_\perp$[b)]	$T_{//}$[b)]	$\langle T\rangle$[b)]
$SnCl_2$	B_1	1.978	1.932	(1.963)	−0.520	−1.467	(−0.836)
	B_2	1.978	1.926	(1.961)	−0.520	−1.424	(−0.821)
	C	1.982	1.930	(1.964)	−0.648	−1.707	(−1.001)
DSH[c)]	B_1	1.978	1.931	(1.962)	−0.525	−1.473	(−0.841)
	B_2	1.978	1.925	(1.960)	−0.525	−1.429	(−0.827)
	C	1.981	1.923	(1.962)	−0.662	−1.731	(−1.018)
DMS[c)]	B_1	1.979	1.930	(1.963)	−0.532	−1.473	(−0.845)
	B_2	1.979	1.923	(1.960)	−0.532	−1.432	(−0.832)
	C	1.981	1.923	(1.962)	−0.654	−1.715	(−1.008)
TMA[c)]	B_1	1.978	1.940	(1.966)	−0.537	−1.440	(−0.838)
	B_2	1.978	1.934	(1.963)	−0.537	−1.394	(−0.822)
	C	1.981	1.934	(1.965)	−0.657	−1.701	(−1.005)

a) acetonitrile solution, 0.1 M, 77 K, b) unit in 10^{-2}cm^{-1} c) DSH; ethylene dithioglycol, DMS; dimethyl sulfide, TMA; thiomalic acid, ( ) indicates calculated values.

tion and decay of transient species. Pottkamp and Umland[2] reported a very slow change in the polarogram of 12-molybdophosphoric acid in *n*-butyl acetate. However, their observation in the polarogram seems to have no connection with ours in ESR, since the rate of appearance of signal B was very fast, and the signal was retained for *ca.* 5 hr at 20 °C.

If the reaction is assumed to follow the first-order kinetics, and $k_1 \gg k_2$, as follows,

$$\begin{array}{ccccc} \mathrm{A} & \xrightarrow{k_1} & \mathrm{B} & \xrightarrow{k_2} & \mathrm{C} \\ \text{(non-reduced)} & & \text{(Transient)} & & \text{(Final)} \\ \text{Diamagnetic} & & \text{Paramagnetic} & & \text{Paramagnetic} \end{array} \qquad (1)$$

then we obtain the relation

$$C_\mathrm{B}/(C_\mathrm{C}-C_0+C_\mathrm{B}) = \exp{(-k_2 \cdot t)} \qquad (2)$$

where C_B and C_C are the concentration of species B and C, respectively, at time t, and C_0 is the initial concentration of C. The time-dependency of $C_\mathrm{B}/(C_\mathrm{C}-C_0+C_\mathrm{B})$, determined from the peak heights of each $m_\mathrm{n}=-7/2$ parallel line (Fig. 2) is plotted in Fig. 4. The linear relation apparently supports Scheme (1).

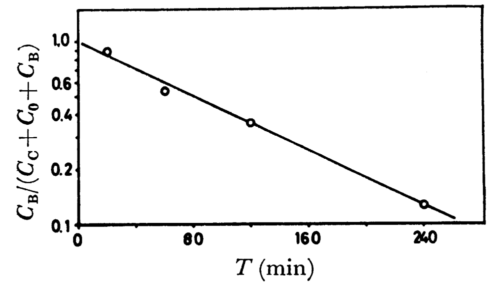

Fig. 4. The change with time of the relative peak heights of the transient (B) and the final (C) species, see text.

The mechanism for satisfying the present observation can be explained as follows.

(a) Species B is assigned as a reduced heteropoly acid and species C as a hydrolysed product from B with such a form as $[\mathrm{VO(H_2O)}_x(\mathrm{Solvent})_y]^{2+}$. According to Flynn and Pope,[6] hydrolysis of 5-tungstovanadate(IV) occurs in an aqueous solution to form hydrated vanadyl ion, $[\mathrm{VO(H_2O)_5}]^{2+}$. The T value of the hydrate (-1.06×10^{-2} cm^{-1}) is somewhat larger than that of the original heteropoly anion (-0.94×10^{-2} cm^{-1}). The T value of signal C in the present study ($\approx -1.00\times10^{-2}$ cm^{-1}) is close to but difinitely smaller than that of the hydrated vanadyl ion. Assumption of the solvation to form $[\mathrm{VO(H_2O)}_x(\mathrm{Solvent})_y]^{2+}$ may explain, even partly, such a shift of T. However, the remarkably small $g_{//}$ of species C is closer to that of both B and 11-tungstovanado(IV)phosphate polyanion[7] rather than to that of the usual $\mathrm{VO^{2+}}$ complexes whose $g_{//}$ lies in the range 1.93—1.96 (Table 2). Smith and Pope[8] further disclosed the "hydrolytic disproportionation" of the $x=1$ tungstovanadophosphate anion into the $x=0$ and $x=2$ anions. This model partly supports the present observation that g-values of B ($x=1$, in this model) and C ($x=2$) are nearly the same, but it is not suitable for kinetics or for explaining the large difference in the hfs constants. Another contradiction in this decomposition scheme is that ESR spectra of the heteropoly acids reduced with a variety of chemical reagents show a formation of species B with similar rates of formation and similar ESR parameters and its decay into species C. The ESR signal of this species is identical with that of a fresh solution of the heterogeneously reduced heteropoly acid, while reduction with hydrogen at 280 °C never causes decomposition of the compounds.

(b) Another explanation is to assign species B as an intermediate of the reduction and C as the final reduced state of the heteropoly acid in scheme (1), which can remove the contradictions of the first mechanism. It is very probable that the rate of heterogeneous reduction is too fast for the intermediate B to coexist with the final reaction product C, and thus only signal C is observed in the ESR of the reduced mass or its solution. It is of interest to investigate how the two species differ structurally or electronically from each other. If the McConnel linear relation between the hfs parameters and the electron density is also applicable in the present compounds, the hfs constant of signal B, unusually smaller than that of the ordinary vanadyl(IV) compounds as exemplified in Table 2, would indicate that the electrons are much more delocalized over the entire species. There are at least two or three isomers in each of species B and C as is obvious in the low-field splitting of their ESR spectra (Fig. 1 and Figs. 1 and 2 of the previous paper.[1]). They give a hint to elucidating the structure of the two species. An abbreviated scheme of the Keggin-type heteropoly anion structure is given in Fig. 5. Part A represents how the corner-sharing[12] bonds constitute the tetrahedral environment of the central phosphate anion with $(\mathrm{Mo_3O_9})^\mathrm{E}$, meaning an edge-sharing unit[12] whose structure is illustrated in part B. Each molybdenum oxyanion has one terminal oxygen with double-bond nature that serves as the main site for the electron-exchange in the chemical redox reactions. Thus we can count and characterize the

TABLE 2. ESR PARAMETERS OF SEVERAL VANADIUM(IV) COMPOUNDS

Compounds	$g_\perp$	$g_{//}$	$\langle g \rangle$	$T_\perp$[a]	$T_{//}$[a]	$\langle T \rangle$[a]
$\mathrm{H_4Mo_{11}VPO_{40}}$[b] B	1.978	1.928	(1.96)	52.5	145.0	(83.0)
C	1.981	1.923	(1.962)	66.2	173.1	(101.8)
$\mathrm{H_4W_{11}VPO_{40}}$[c]	1.968	1.9232	(1.953)	59.6	169.3	(96.2)
$\mathrm{VOCl_2}$[d]	1.981	1.932	1.965	71.8	182.6	106.3
$\mathrm{VO(acac)_2}$[e]	1.981	1.945	1.967	61.8	169.0	97.5
VOPC[f]	1.985	1.966	(1.979)	55.0	161.0	(109.0)

a) In unit 10^{-1}cm^{-1}, negative signs were omitted. b) Present result, dithioglycol reduction in acetonitrile. c) Authentic sample, Ref. 7. d) In 3M HCl solution, Ref. 11. e) Vanadyl acetylacetonate in tetrahydrofuran solution, Ref. 11. f) Vanadylphthalocyanine in $\mathrm{H_2SO_4}$ solution, Ref. 11.

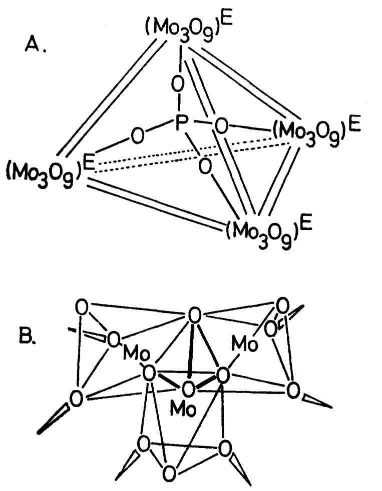

Fig. 5. Skeletal model of the Keggin structure for a) corner sharing bonds, and b) edge-sharing trimer unit, $(Mo_3O_9)^E$.

neighboring oxyanions for one molybdenum (or vanadium substituting for it) ion as is given in Table 3. Since every Mo–O bond is of highly covalent nature as is understandable from their IR spectra,[13] it is reasonable to expect that all the oxyanions are bound by the electron delocalization through the edge- and corner-sharing oxygen ions. In this respect, the edge-sharing oxyanions can make greater contribution to the delocalization of the electron brought into the heteropoly anion by reduction, since they share the d_{z^2} atomic orbital of the molybdenum ions which is directly connected with the terminal oxygen ion contributing to the electron exchange reaction. Intermediate B would then have the same molecular structure as the original heteropoly anion A, but with one reduced molybdenum(V) or vanadium(IV) ions, and one or two molybdenum(IV) ions in the neighboring positions. The difference in the position and nature of the reduced ions in relation to the paramagnetic ion can cause a different contribution to the delocalization of the paramagnetic electron. This can be regarded as the geometrical charge isomerism in the heteropoly anion. In the final reduced species C, the localization of the electron on the paramagnetic ion is more marked and its electronic state is similar to the vanadyl(IV) ion. Such a decrease in the delocalization of electron is understandable if we assume the protonation of the molybdenum(V or IV) ions coexisting in the heteropoly cage with V(IV) ion. The protonation or abstraction of hydrogen can occur at the terminal oxygen ion with double-bond nature, so that delocalization of the electron in the neighbouring ions is disturbed. This model for species C is what was proposed previously. However, a theoretical investigation based on the molecular orbital describing the heteropoly anion seems necessary for a more complete explanation for the difference in hfs parameters of the two species.

TABLE 3. CONSTRUCTION OF A HETEROPOLY CAGE IN KEGGIN STRUCTURE

Type of connection[a]	Number of neighbors
Nearest neighbor	
Edge-sharing	2
Corner-sharing	2
Next nearest neighbor	
Edge—Corner	4 or 2
Corner—Edge	2 or 4
Third neighbor	
Edge—Corner—Edge	1

a) Shortest path from one molybdenum oxyanion.

The low-field parallel lines of species B were found to be split into two or three components. The splitting (≈35 G) is nearly twice as large in magnitude as that in the reduced species in the solid spectrum (≈15 G).[1] In the solution, however, the splitting of signal C disappears, since it is not large enough for detection due to the line broadening of the solution spectrum. In the ESR spectrum of the authentic tungstovanado(IV)phosphate anion,[7] the splittings are not observed. They are thus characteristic of the chemically reduced heteropoly anion in which both V(IV) and Mo(IV) ions coexist in the heteropoly cage. The splittings are completely due to the "geometrical charge isomerism", the larger splitting in species B being related to the larger electron delocalization.

Organic solvents have been found to show an interesting effect on the spectrum. All the line-widths were somewhat larger than that of the solid. The spectrum in Fig. 3 differs from that in Fig. 1, particularly in the line-width. The line-width of the former is estimated to be *ca.* 150 G[9] and that of the latter *ca.* 25 G. This increase (solvents being *n*-butyl acetate and acetonitrile, respectively) is much larger than that in the solvent viscosity, 0.732 and 0.359 cp, respectively. This is related to the specific interaction of the heteropoly acids with esters,[10] in which hydrogen-bonding between the carboxyl group and the heteropoly acid forms a strongly solvated species.

Conclusion

Homogeneous reduction of the molybdovanadophosphoric heteropoly acids dissolved in organic solvents was investigated in order to clarify the mechanism of the reduction. Two kinds of ESR signals, B and C, were observed with a substantially different hfs parameter but with nearly equal *g*-tensor. The first-order kinetics of the decay and formation of these species was observed. A mechanism based on the assignment of species C to be some decomposition product from B had several contradiction. Signal B, which appeared just after mixing the reductant and disappeared within *ca.* 5 hr, had unusually small *T*-tensor values and was assigned to be the intermediate of the reduction. Signal C, whose intensity increased gradually, was assigned to be the final reduced species. A small structural difference in the heteropoly cage of the two species was assumed.

There are at least two isomers in both species B and C, which gave a complicated splitting in the low-field ESR spectra. This observation was characteristic of the chemically reduced heteropoly anion and was explained by the "geometrical charge isomerism".

The authors are indebted to the director of the Central Research Laboratories, Mitsubishi Chemical Industries Ltd., for permitting publication of this paper, to Dr. K. Wada for helpful discussions, and to Miss Y. Komiyama for her help in the measurement of the ESR spectra.

References

1) M. Otake, Y. Komiyama, and T. Otaki, *J. Phys. Chem.*, **24**, 2896 (1973).

2) F. Pottkamp and F. Umland, *Z. Anal. Chem.*, **260**, 185 (1972).

3) G. A. Tsigdinos, Molybdenum Chemicals Bulletin Cdb-12a (Revised), Climax Molybdenum Co., November, 1969.

4) a) G. A. Tsigdinos and C. J. Hallada, *Inorg. Chem.*, **7**, 437 (1968); b) *Inorg. Syn.*, **1**, 127 (1939).

5) T. J. Huang and G. P. Haight Jr., *J. Amer. Chem. Soc.*, **92**, 2236 (1970).

6) C. M. Flynn, Jr. and M. T. Pope, *Inorg. Chem.*, **12**, 1626 (1973).

7) D. P. Smith, H. So, J. Bender, and M. T. Pope, *ibid.*, **12**, 685 (1973).

8) D. P. Smith and M. T. Pope, *ibid.*, **12**, 331 (1973).

9) H. Takahashi, M. Shiotani, H. Kobayashi, and J. Sohma, *J. Catal.*, **14**, 134 (1969).

10) E. M. Ivashkovich, *Ukr. Khim. Zh.*, **38**, 185 (1972).

11) B. A. Goodman and J. B. Raynor, *Advan. Inorg. Radiochem.*, **13**, 135 (1970).

12) P. C. Mitchell and F. Trifiro, *J. Chem. Soc. A*, **1970**, 3183.

13) G. Lange, H. Hahn, and K. Dehnicke, *Z. Naturforsch.*, **24b**, 1498 (1969).