Journal of Organometallic Chemistry, 99 (1975) 107—114

PROPERTIES AND LIGAND EXCHANGE REACTIONS OF TRIMETHYL(OXINATO)ANTIMONY(V) COMPLEXES

YOSHIKANE KAWASAKI and KATSUYA HASHIMOTO

Department of Applied Chemistry, Osaka University, Yamadakami, Suita, Osaka 565 (Japan)

(Received April 15th, 1975)

Summary

The rate constant, k, activation energy, E_a, and activation entropy, $\Delta S^{\neq}$, were determined by the NMR line broadening technique for the ligand exchange reactions, $(CH_3)_3SbL[X—Y]$ (X, Y = Cl, Br, NO_3, $OC_6H_4NO_2$-*p*, O_2CCH_3, O_2CCH_2Cl, O_2CCHCl_2, and O_2CCCl_3; L = oxinato and 2-methyl-8-hydroxyquinolinato). Most of the ligand exchange reactions in these systems were found to proceed through a bridging intermediate. The rate constants, k, of these reactions are mainly decided by the activation entropy, $\Delta S^{\neq}$, rather than the activation energy, E_a. The lability of the ligands in these reactions increases in the following order: $O_2CCH_3 \lesssim OC_6H_4NO_2\text{-}p < O_2CCH_2Cl < O_2CCHCl_2 < O_2CCCl_3 < Cl < Br$.

Introduction

Several structural studies on organo(oxinato)antimony(V) complexes have been reported from the standpoint of the coordination of the oxinato ligands [1-3]. There are, however, very few investigations on the kinetics and mechanisms of the ligand-exchange reactions in organoantimony compounds, although considerable thermodynamic data have been reported for the redistribution reactions of several organometallic compounds of Group VB elements [4-8].

In this study, the rate constant, k, and the activation parameters, E_a, $\Delta S^{\neq}$, and $\Delta G^{\neq}$, were obtained by analyzing the temperature-dependent PMR spectra of the methyl groups for the ligand-exchange reaction 1 (Ox = oxinato ligand).

$$(CH_3)_3Sb(Ox)X + (CH_3)_3Sb'(Ox)Y \rightleftharpoons (CH_3)_3Sb(Ox)Y + (CH_3)_3Sb'(Ox)X \quad (1)$$

The solvent dependence of the k, E_a and $\Delta S^{\neq}$ values also was studied.

Experimental

Preparation of $(CH_3)_3Sb(Ox)X$ ($X = NO_3$, $OC_6H_4NO_2$-p, $OC_6H_2(NO_2)_3$-2,4,6, and O_2CR; $R = H$, CH_3, $CH(CH_3)_2$, CH_2CN, CH_2Cl, $CHCl_2$, CCl_3, CBr_3, and C_6H_5)

All of these complexes were prepared in an essentially identical manner [2], so that only one typical procedure is given. A mixture of trimethylantimony dibromide (9.8 mmol) in benzene and sodium methoxide (19.6 mmol) in methanol was refluxed for 30 min. After distilling off some portion of solvent, the precipitated sodium bromide was filtered off. To the filtrate was added dilute aqueous nitric acid (9.8 mmol), and the azeotrope of water and benzene was distilled off. 8-Hydroxyquinoline (9.8 mmol) in benzene was added to the reaction mixture and the solution was refluxed for about 30 min*. The yellow solid, obtained after removing the solvent under reduced pressure, was crystallized from acetone to give pale-yellow crystals of $(CH_3)_3Sb(Ox)NO_3$.

Most of the complexes were purified by recrystallization from acetone, but for the complexes based on $X = OC_6H_4NO_2$-*p* and O_2CCBr_3, n-hexane and dichloromethane, respectively, were used in the recrystallization.

Preparation of $(CH_3)_3Sb(2MeOx)X$ (X = Cl and Br)

A mixture of trimethylantimony dichloride (9.8 mmol), 2-methyl-8-hydroxyquinoline (2MeOx) (9.8 mmol) in benzene and sodium methoxide in methanol was refluxed for 30 min. After filtering off sodium chloride, the solvent was removed under reduced pressure and the residual solid crystallized from acetone to give white crystals of $(CH_3)_3Sb(2MeOx)Cl$. The corresponding bromide was prepared from trimethylantimony dibromide by the same method. The properties of these complexes are listed in Table 1.

Physical measurements and method of calculation

The UV spectra were recorded with a Hitachi 124 spectrometer using 0.1 cm length quartz cells. The results are shown in Table 2. The IR spectra were obtained in Nujol mulls and in dichloromethane with Hitachi EPI-L and 225 spectrometers equipped with gratings. Some relevant frequencies are shown in Table 3 and in Table 4.

The PMR spectra were measured on a JEOL JNM-PS-100 spectrometer operating at 100 MHz. TMS was used as internal standard. The chemical shift of the methyl groups attached to antimony and the 2 and 4 protons of the oxinato ligand are shown in Table 2. The temperatures were calibrated with a thermocouple immersed in an open, nonspinning NMR tube, partially filled with solvent.

Known amounts of $(CH_3)_3SbLX$ ($[C_A]$) and $(CH_3)_3SbLY$ ($[C_B]$) (X, Y = Cl, Br, $OC_6H_4NO_2$-*p*, O_2CCH_3, O_2CCH_2Cl, O_2CCHCl_2, and O_2CCCl_3; L = Ox and 2MeOx) were dissolved in a 1 ml volumetric flask. The solution prepared in this way was sealed in an NMR tube in vacuo, after degassing several times by the freeze-thaw-freeze method.

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* Addition of a small amount of acetylacetone accelerates the reaction when X is the carboxylato group.

TABLE 1

ANALYTICAL DATA FOR $(CH_3)_3Sb(Ox)X$ AND $(CH_3)_3Sb(2MeOx)X$

Compound	M.p. (°C)	Analysis: found (calcd.) (%)		
		C	H	N
$(CH_3)_3Sb(Ox)X$				
$X = NO_3$	167 (dec)	38.32	4.22	7.66
		(38 64)	(4.05)	(7.51)
$OC_6H_4NO_2$-*p*	82	48.24	4.47	6.20
		(48.14)	(4.26)	(6.24)
$OC_6H_2(NO_2)_3$-2,4,6	178 (dec)	39.82	3.19	10.28
		(40.10)	(3.18)	(10.39)
O_2CCH_3	138-140	45.58	4.58	3.83
		(45 42)	(4.90)	(3.79)
O_2CCH_2Cl	140-141	41.37	4.30	3.52
		(41 57)	(4.24)	(3.46)
O_2CCHCl_2	144-146	38.36	3.76	3.31
		(38.31)	(3.67)	(3.19)
O_2CCCl_3	129 (dec)	35.32	3.16	3.14
		(35.52)	(3.19)	(2.96)
O_2CCBr_3	100 (dec)	27.93	2.64	2.35
		(27.71)	(2.49)	(2.31)
O_2CCH_2CN	135-136	45.37	4.40	7.29
		(45.60)	(4.34)	(7.09)
O_2CH	113	43.37	4.50	4.09
		(43.85)	(4.53)	(3.93)
$O_2CC_6H_5$	100	52.27	4.70	3.35
		(52.81)	(4.67)	(3.24)
$O_2CCH(CH_3)_2$	58-60	48.25	5.61	3.62
		(48.27)	(5.57)	(3.52)
$(CH_3)_3Sb(2MeOx)X$				
$X = Cl$	165-167	43.39	4.60	4.00
		(43.32)	(4.75)	(3.89)
Br	154-155	38.26	4.33	3.64
		(38.56)	(4.23)	(3.46)

The theoretical spectra for the ligand-exchange reaction 1 were calculated by using the method reported in the literature [9]. The rate constant, k, was calculated by eqn. 2,

$$k = 1/(\tau_A \times [C_B]) = 1/(\tau_B \times [C_A]) \qquad (2)$$

where the τ_A and τ_B are mean residence times of the species A and B, respectively and $[C_A]$ and $[C_B]$ are their concentrations. The τ_A and τ_B were determined by visual comparison of observed and calculated PMR line shapes of the methyl groups attached to the antimony atoms. Figure 1 shows a typical Arrhenius plot for the $(CH_3)_3SbOx[Cl—Br]$* system measured in CH_2Cl_2, in which different values were taken for $[C_A]$ and $[C_B]$. Table 5 gives the rate constants, k, and activation parameters, E_a, $\Delta S^{\neq}$ and $\Delta G^{\neq}$, for the several ligand-exchange systems $(CH_3)_3SbL[X—Y]$.

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* We use the abbreviation $(CH_3)_3SbL[X—Y]$ for eqn. 1.

TABLE 2

PMR- AND UV-SPECTRAL DATA FOR $(CH_3)_3Sb(Ox)X$ AND $(CH_3)_3Sb(2MeOx)X$ IN CH_2Cl_2

Compound	PMR δ (ppm)			UV (nm) λ_{max}
	Sb—CH_3	2—H	4—H	
$(CH_3)_3Sb(Ox)X$				
X = Cl	1.91	8.69	8.16	353
Br	2.07	8.73	8.20	352
NO_3	1.84	8.92	8.34	342
$OC_6H_4NO_2$-*p*	1.73	8.75	8.17	[a]
$OC_6H_2(NO_2)_3$-2,4,6	1.90	9.02	8.18	[a]
O_2CCH_3	1.64	9.06	8.20	340
O_2CCH_2Cl	1.69	9.10	8.23	338
O_2CCHCl_2	1.72	9.07	8.22	334
O_2CCCl_3	1.80	9.03	8.24	334
O_2CCBr_3	1.74	9.13	8.22	334
O_2CCH_2CN	1.72	9.03	8.22	332
O_2CH	1.69	8.95	8.13	332
$O_2CC_6H_5$	1.72	9.26	8.22	335
$O_2CCH(CH_3)_2$	1.62	9.10	8.19	341
$(CH_3)_3Sb(2MeOx)X$				
X = Cl	1.93		8.10	329
Br	2.07		8.04	328

[a] Obscured by the other absorption.

TABLE 3

RELEVANT IR FREQUENCIES OF THE NO_3 GROUP OF $[(CH_3)_3Sb(NO_3)]_nX$ AND CH_3NO_3

CH_3NO_3 [a]	X			Assignment
	n = 1	*n* = 1	*n* = 2	
	NO_3 [b]	Ox	O [b]	
1672	1536	1475	1450	$\nu_{asym}(NO_2)$
1287	1282	1275	1290	$\nu_{sym}(NO_2)$
854	954	1002	1018	ν(N—O)

[a] Ref. 13. [b] Ref. 14.

TABLE 4

RELEVANT IR FREQUENCIES OF $(CH_3)_3Sb(O_2CR)X$ (in cm^{-1})

R = H X =		R = CH_3 X =		R = C_6H_5 X =		Assignment
O_2CH [a]	Ox	O_2CCH_3	Ox	$O_2CC_6H_5$ [a]	Ox	
1653	1621	1650	1622	1642 1631	1605	ν_{asym}(O—C—O)
1233	1250	1286	1355 1313	1323 1299	1328	ν_{sym}(O—C—O)
365	340	287 270	257	347	272	ν(Sb—O)

[a] Ref. 14.

TABLE 5

ACTIVATION PARAMETERS FOR THE LIGAND-EXCHANGE SYSTEM $(CH_3)_3Sb(L)[X—Y]$ AT 25° C [a]

System			Solvent	log *k*	E_a (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)	$\Delta G^{\neq}$ (kcal mol^{-1})
L	X	Y					
Ox	Cl	Br	CH_2Cl_2	4.47 ± 0.15	9.3 ± 0.6	—8 ± 3	11.3 ± 0.2
Ox	Cl	NO_3	CH_2Cl_2	4.44 ± 0.44	7.5 ± 1.4	—15 ± 7	11.4 ± 0.6
Ox	Br	O_2CCCl_3	$CHCl_2CHCl_2$	2.94 ± 0.08	6.0 ± 0.6	—27 ± 2	13.4 ± 0.1
Ox	Br	O_2CCHCl_2	$CHCl_2CHCl_2$	2.77 ± 0.06	5.5 ± 0.6	—29 ± 2	13.7 ± 0.1
Ox	Br	O_2CCH_2Cl	$CHCl_2CHCl_2$	2.69 ± 0.06	4.5 ± 0.6	—33 ± 2	13.8 ± 0.1
Ox	Br	O_2CCH_3	CH_2ClCH_2Cl	2.39 ± 0.06	4.4 ± 0.9	—35 ± 3	14.2 ± 0.1
Ox	Br	$OC_6H_4NO_2$-*p*	$CHCl_2CHCl_2$	2.40 ± 0.02	7.0 ± 0.3	—26 ± 1	14.2 ± 0.03
Ox	Cl	O_2CCH_3	$CHCl_2CHCl_2$	1.68 ± 0.04	5.7 ± 0.4	—34 ± 2	15.2 ± 0.1
			CH_3NO_2	4.38 ± 0.42	8.5 ± 2.5	—12 ± 10	11.9 ± 0.6
2MeOx	Cl	Br	CH_2Cl_2	1.87 ± 0.02	5.6 ± 0.3	—33 ± 1	14.9 ± 0.03
Cl	Cl	NO_3 [b]	CH_2Cl_2 [c]	1.78			
			$C_6H_5NO_2$ [d]	1.66 ± 0.03	10.6 ± 2.1 [e]	—16 ± 6	

[a] Error estimated at the 95% confidence level. [b] Ref. 8. [c] Value at 64° C. [d] Values at 32°C. [e] $\Delta H^{\neq}$ value.

Results and discussion

UV- and IR-spectra

As is shown in Table 2, the λ_{max} of the longest wave length for $(CH_3)_3Sb(Ox)Cl$ and $(CH_3)_3Sb(Ox)Br$ appears at 353 and 352 nm, respectively*. These

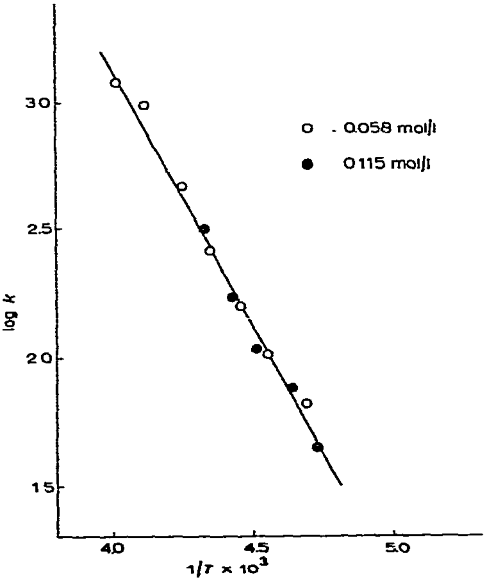

Fig. 1. Arrhenius plot for the $(CH_3)_3SbOx[Cl—Br]$ system.

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* These values are different from those reported previously [2,3]. The reason is that the reported values were obtained by using 1 cm quartz cells and therefore at a concentration of about 10^{-4} mol/l. The present values, however, were obtained at the concentration of about 10^{-3} mol/l.

values give an indication that there is an interaction between the Sb atom and the N atom of the oxinato ligand according to the criterion given by Moeller et al. [10]. However, in the corresponding 2-methyloxinato complexes, the band appears in the region where chelation would not be expected. In $(CH_3)_3Sb(Ox)OC_6H_4NO_2$-*p*, the band due to the oxinato ligand is overridden by a strong band of the $OC_6H_4NO_2$-*p* group. The UV criterion, therefore, cannot be used for the chelation of the oxinato ligand. However, in this compound also, Sb—N interaction is to be expected, since in an analogous compound, $(CH_3)_3Sb(Ox)OH$, the UV-spectrum exhibits a band at 350 nm [11]. In every carboxylato complex, $(CH_3)_3Sb(Ox)O_2CR$, studied and in the nitrato complex, $(CH_3)_3Sb(Ox)NO_3$, the band appears in the region 330-340 nm. This region lies between that of the typically chelated complexes at 350-430 nm and that of the non-chelated compounds at 320-300 nm [2,12]. Therefore, in these carboxylato and nitrato complexes, the Sb—N interaction is probably weak if present at all.

As can be seen from Table 3, the separation between the $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ values increases in the order: $[(CH_3)_3SbNO_3]_2O < (CH_3)_3Sb(Ox)NO_3 < (CH_3)_3Sb(NO_3)_2 < CH_3NO_3$. This result indicates that the deviation from the C_{3v} symmetry of the NO_3 group increases in the above order and is the smallest in $[(CH_3)_3SbNO_3]_2O$. If we assume that the ν(N—O) value reflects bonding between the NO_3 group and the Sb atom, as is in transition-metal nitrato complexes [13], the Sb—O bond in $(CH_3)_3Sb(Ox)NO_3$ is more ionic than that in $(CH_3)_3Sb(NO_3)_2$ and is similar to that in $[(CH_3)_3SbNO_3]_2O$ [14]. This conclusion is in agreement with that resulting from the behavior of the $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ values.

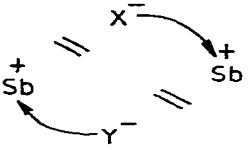
In Table 4, some relevant IR data for the carboxylato complexes of trimethylantimony, $(CH_3)_3Sb(Ox)O_2CR$ and $(CH_3)_3Sb(O_2CR)_2$, are shown. The ν_{asym}(O—C—O) always appears at a low frequency and the ν_{sym}(O—C—O) exhibits a high frequency for the former as compared to the latter [14]. The ν(Sb—O) value between the carboxylato group and the antimony atom is shifted to low frequency by substitution of one of the carboxylato groups of $(CH_3)_3Sb(O_2CR)_2$ by the oxinato group. These results suggest that the Sb—O bond becomes more ionic and probably weaker in the oxinato—carboxylato complexes than that in the dicarboxylato complexes. Similar results have been reported for the M—O—C(=O)R type complexes [15].

Similarly, the ν(Sb—Cl) band is shifted to red in $(CH_3)_3Sb(Ox)Cl$ (234 cm^{-1}) in comparison with that in $(CH_3)_3SbCl_2$ (280 cm^{-1}). These observations imply that the oxinato group has the effect of making the Sb—X bond more ionic in the $(CH_3)_3Sb(Ox)X$ complexes. One of the reasons for this effect of the oxinato group is found in the coordination of the N atom of the oxinato group to the Sb atom.

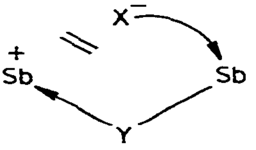
Ligand exchange reaction

As can be seen from Table 5, the $\Delta S^{\neq}$ values are negative in all of the ligand-exchange reaction systems $(CH_3)_3SbOx[X—Y]$ studied; and the system which shows a larger negative $\Delta S^{\neq}$ value gives, in general, a smaller E_a value. In most of the systems, the rate constant, *k*, becomes small when the $\Delta S^{\neq}$ value becomes more negative and the E_a value becomes small. The rate constant, *k*, therefore, is mainly affected by the entropy term, $\Delta S^{\neq}$, rather than the activation energy, E_a. By comparing the k values in Table 5, the lability of the ligands as revealed from the rate constant is seen to increase in the same order as the acid strength of the free carboxylic acid: $O_2CCH_3 \lesssim OC_6H_4NO_2\text{-}p < O_2CCH_2Cl < O_2CCHCl_2 < O_2CCCl_3 < Cl < Br$.

The relatively large E_a and $\Delta S^{\neq}$ values for the $(CH_3)_3SbOx[Br—Cl]$ system are probably due to the fact that the ligand exchange takes place through solvent-separated ion pairs I or II, as was proposed for the $(CH_3)_3SbCl[Cl—NO_3]$ system in nitrobenzene [8] in the transition state. In contrast to this system, a bridging intermediate III may be a probable path for the halogen exchange in the $(CH_3)_3Sb(2MeOx)[Br—Cl]$ system, since the E_a and $\Delta S^{\neq}$ values are very small. In $(CH_3)_3SbOx[Br—O_2CR]$ systems, the bridging intermediate IV may also be a preferential path for the ligand exchange for the same reason as in the $(CH_3)_3Sb(2MeOx)[Br—Cl]$ system. The relatively large negative $\Delta S^{\neq}$ values for the $(CH_3)_3SbOx[Cl—NO_3]$ and $(CH_3)_3SbOx[Br—OC_6H_4NO_2\text{-}p]$ systems suggest a possibility of the bridging of the NO_3 and $OC_6H_4NO_2\text{-}p$ groups in the transition state, respectively.



(I)



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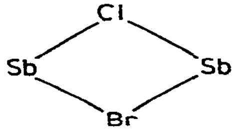

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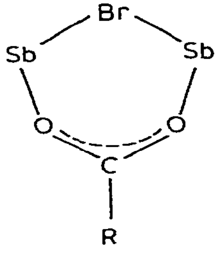

(IV)

Some of the results for the solvent dependence of the activation parameters for the $(CH_3)_3SbOx[Cl—O_2CCH_3]$ system are shown in Table 5. One notable result is that the $\Delta S^{\neq}$ value becomes less negative and at the same time the E_a value becomes large on changing the solvent from $CHCl_2CHCl_2$ to CH_3NO_2. The $\Delta S^{\neq}$ term is again the main factor which decides the rate constant. The rate constant and the activation parameters for this system in CH_3NO_2 are very similar to those for the $(CH_3)_3SbOx[Br—Cl]$ system in CH_2Cl_2. Therefore, the above results indicate that in the polar solvent the Sb—X bond is highly polarized so that it is easy to form solvent-separated ion pairs in the transition state.

Acknowledgement

Thanks are due to Professor R. Okawara of Osaka University for his continuous encouragement.

References

1 Y. Matsumura and R. Okawara, Inorg. Nucl. Chem. Lett., 4 (1968) 521.
2 Y. Kawasaki, Inorg. Nucl. Chem. Lett., 5 (1969) 805.
3 H.A. Meinema, E. Rivarola and J.G. Noltes, J. Organometal. Chem., 17 (1969) 71.
4 J.C. Lockhart, Chem. Rev., 65 (1965) 131.
5 H. Weingarten and J.R. Van Wazer, J. Amer. Chem. Soc., 88 (1966) 2700.
6 C.G. Moreland, M.H. O'Brien, C.E. Douthit and G.G. Long, Inorg. Chem., 7 (1968) 834.
7 K. Moedritzer, Organometallic Reactions, Wiley—Interscience, New York, N.Y., 1971.
8 C.G. Moreland and R.J. Beam, Inorg. Chem., 11 (1972) 3112.
9 C.S. Johnson, Jr, Advances in Magnetic Resonance, Vol. 1, Academic Press, New York, N.Y., 1965.
10 (a) T. Moeller and A.J. Cohen, J. Amer. Chem. Soc , 72 (1950) 3546; (b) T. Moeller and F.L. Pundsack, J. Amer. Chem. Soc., 76 (1954) 617.
11 Y. Kawasaki, to be published.
12 M. Wada and R. Okawara, Inorg. Nucl. Chem. Lett., 5 (1969) 355.
13 B.M. Gatehouse, S.E. Livingston and R.S. Nyholm, J. Chem. Soc., (1957) 4222; idem, J. Inorg. Nucl. Chem., 8 (1958) 75.
14 M. Shindo and R. Okawara, J. Organometal. Chem., 5 (1966) 537.
15 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley—Interscience, New York, N.Y., 1970.