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HALOGEN EXCHANGE REACTIONS OF TRIORGANO(8-QUINOLINOLATO)-ANTIMONY HALIDES

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Summary

The rate constants, k, and activation parameters, E_a, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$, were determined by the ^{1}H NMR line broadening technique for the following halogen exchange reactions: $(CH_3)_n(C_6H_5)_{3-n}Sb(L)[Cl \leftrightarrow Br]$ (L = 8-quinolinolato ligand and its 2-, 4-, 5-, 7-methyl, 5-chloro, 5-acetyl, 5-nitro and 5,7-dichloro derivative; n = 1—3). The rate constant and activation energy for these halogen exchange reactions were found to decrease as the number of the phenyl groups increased. The value of the activation entropy became increasingly negative in the above order. The halogen exchange reactions of the above system were found to proceed through a bridging intermediate. In the $(CH_3)_2C_6H_5Sb(L)[Cl \leftrightarrow Br]$ system, the rate constant decreased and the activation energy became large when an electron-withdrawing group was introduced into the 5-position of the 8-quinolinolato ligand. Linear relations were obtained between Taft's σ° value and $\log(k/k_o)$, and the activation entropy and activation enthalpy.

In $CH_3(C_6H_5CH_2)C_6H_5Sb(2\text{-}MeOx)O_2CCH_3$, a pentacoordinate antimony atom was found to be a chiral center (Ox = oxinato ligand).

Introduction

In a previous paper [1], we have reported ligand exchange reactions between different halogens, and between halogen and some carboxylato groups in trimethyl(8-quinolinolato)antimony compounds $(CH_3)_3Sb(Ox)[X \leftrightarrow Y]$. In this series of reactions it was found that (1) the value of the activation entropy, $\Delta S^{\ddagger}$, at 25°C has a large negative value; (2) the rate constant, k, at 25°C becomes generally small when the activation entropy becomes more negative and the activation energy becomes small, and (3) the reaction proceeds through a bridging intermediate.

In order to find a more detailed mechanism of the ligand exchange reaction in triorganoantimony(V) complexes, we have determined the rate constants and activation parameters, E_a, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$, for the following halogen exchange reaction systems by analyzing the line shapes of the temperature dependent ^{1}H NMR spectra of methyl groups (eq. 1).

$$(CH_3)_n(C_6H_5)_{3-n}Sb(L)Cl + (CH_3)_n(C_6H_5)_{3-n}Sb^*(L)Br \rightleftharpoons$$
$$(CH_3)_n(C_6H_5)_{3-n}Sb(L)Br + (CH_3)_n(C_6H_5)_{3-n}Sb^*(L)Cl \qquad (1)^*$$

(L = 8-quinolinolato ligand and its 2-, 4-, 5-, 7-methyl, 5-chloro, 5-acetyl, 5-nitro and 5,7-dichloro derivative; $n = 1$—3).

In connection with the configuration of the above triorgano(8-quinolinolato)-antimony complexes, the configuration of methylphenylbenzyl(2-methyl-8-quinolinolato)antimony acetate was studied by IR, UV and ^{1}H NMR spectra.

Experimental

Materials

Triorganoantimony compounds of the type, $(CH_3)_n(C_6H_5)_{3-n}Sb$ ($n = 1$ and 2), were obtained by cleavage of the phenyl group of triphenylantimony or diphenylmethylantimony with sodium in liquid ammonia followed by an addition of methyl chloride as reported by Sato et al. [2]. Methylbenzylphenylantimony, $CH_3(C_6H_5CH_2)C_6H_5Sb$, also was prepared by cleavage of the phenyl group of diphenylmethylantimony in liquid ammonia and addition of benzyl chloride. These compounds were oxidized by bromine or sulfuryl chloride to give corresponding triorganoantimony dihalides, $(CH_3)_n(C_6H_5)_{3-n}SbX_2$ and $CH_3(C_6H_5CH_2)C_6H_5SbX_2$.

Methyl substituted 8-quinolinols (Me-OxH) were prepared by the Skraup synthesis. 5-Acetyl-8-quinolinol(5-Ac-OxH) was obtained by the Friedel—Crafts reaction of 8-quinolinol with acetyl chloride in nitrobenzene [3]. 5-Nitro-8-quinolinol (5-NO_2-OxH) was produced by oxidation of 5-nitroso-8-quinolinol with hydrogen peroxide in sulfuric acid. 5-Chloro- and 5,7-dichloro-8-quinolinol(5-Cl-OxH and 5,7-Cl_2-OxH) were obtained from Tokyo Kasei Kogyo Co, Ltd.

Preparation of $(CH_3)_n(C_6H_5)_{3-n}Sb(L)X$ (L = Ox, 2-Me-Ox, 4-Me-Ox, 5-Me-Ox, 7-Me-Ox, 5-Cl-Ox, 5-Ac-Ox, 5-NO_2-Ox and 5,7-Cl_2-Ox; X = Cl, Br, OAc; n = 1—3)

All of these complexes were prepared in an essentially identical manner [1,4]. A mixture of equimolar amounts (2 mmol) of triorganoantimony dihalide in benzene (~60 cm^3) and sodium methoxide in methanol (~10 cm^3) was heated at reflux for 30 min. After filtering off sodium halide, 8-quinolinol or its derivative (2 mmol) was added to the filtrate and the solution was heated at reflux for 2 h. Addition of a small amount of acetylacetone generally accelerates the reaction. The solvent was removed by distillation under reduced pressure. The highly viscous yellow solution of crude product in a small amount of benzene and n-hexane solidified upon scratching the vessel with a glass rod. The resulting solid was crystallized from benzene and n-hexane to give

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* We will use hereafter an abbreviation, $(CH_3)_n(C_6H_5)_{3-n}Sb(L)[Cl \leftrightarrow Br]$, for this halogen exchange reaction.

TABLE 1

ANALYTICAL DATA OF $(CH_3)_n(C_6H_5)_{3-n}Sb(L)X$ AND $CH_3(C_6H_5CH_2)C_6H_5Sb(2\text{-}Me\text{-}Ox)O_2CCH_3$

Compound			M.p. (°C)	Analysis found (calcd.) (%)		
n	L	X		C	H	N
3	5-Ac-Ox	Cl	180—181	42.97 (43.29)	4.38 (4.41)	3.60 (3.61)
3	5-Ac-Ox	Br	160—161	38.68 (38.84)	4.02 (3.96)	3.16 (3.24)
2	Ox	Cl	113—114	49.94 (49.98)	4.26 (4.19)	3.52 (3.43)
2	Ox	Br	125—127	44.76 (45.08)	3.87 (3.78)	3.20 (3.09)
2	2-Me-Ox	Cl	170—171	51.12 (51.16)	4.46 (4.53)	3.41 (3.32)
2	2-Me-Ox	Br	174—175	46.17 (46.29)	3.97 (4.10)	2.90 (3.00)
2	4-Me-Ox	Cl	115—116	50.90 (51.16)	4.52 (4.53)	3.35 (3.32)
2	4-Me-Ox	Br	127—128	46.14 (46.29)	4.11 (4.10)	3.12 (3.00)
2	5-Me-Ox	Cl	133—134	50.94 (51.16)	4.32 (4.53)	3.42 (3.32)
2	5-Me-Ox	Br	140—141	46.06 (46.29)	3.98 (4.10)	2.99 (3.00)
2	5-Cl-Ox	Cl	106—108	46.01 (46.09)	3.69 (3.64)	3.17 (3.16)
2	5-Cl-Ox	Br	126—128	41.71 (41.89)	3.24 (3.31)	2.85 (2.87)
2	5-Ac-Ox	Cl	120—121	50.61 (50.65)	4.21 (4.25)	3.10 (3.11)
2	5-Ac-Ox	Br	125—126	46.36 (46.10)	3.89 (3.87)	3.02 (2.83)
2	5-NO_2-Ox	Cl	123—125	44.88 (45.02)	3.53 (3.56)	6.29 (6.18)
2	5-NO_2-Ox	Br	135—137	40.81 (41.00)	3.18 (3.24)	5.74 (5.62)
2	5,7-Cl_2-Ox	Cl	83— 84	42.39 (42.77)	3.11 (3.17)	2.90 (2.93)
2	5,7-Cl_2-Ox	Br	104—106	38.86 (39.13)	2.84 (2.90)	2.73 (2.68)
2	7-Me-Ox	Cl	126—127	51.29 (51.16)	4.43 (4.53)	3.36 (3.32)
2	7-Me-Ox	Br	144—145	46.29 (46.19)	4.10 (3.85)	3.00 (3.05)
1	Ox	Cl	141—142	55.97 (56.15)	4.08 (4.07)	3.04 (2.98)
1	Ox	Br	135—136	51.25 (51.30)	3.71 (3.72)	2.77 (2.72)
1	Ox	OAc	117—118	58.42 (58.33)	4.50 (4.49)	2.87 (2.83)
1	2-Me-Ox	Cl	150—152	56.95 (57.00)	4.53 (4.37)	
1	2-Me-Ox	Br	174—175	52.18 (52.21)	3.90 (4.00)	
1	5-Me-Ox	Cl	139—141	56.96 (57.00)	4.11 (4.37)	
1	5-Me-Ox	Br	153—154	51.96 (52.21)	4.10 (4.00)	
1	7-Me-Ox	Cl	127—128	57.23 (57.00)	4.37 (4.37)	
1	7-Me-Ox	Br	141—142	52.09 (52.21)	4.11 (4.00)	
$CH_3(C_6H_5CH_2)C_6H_5Sb$- $(2\text{-}Me\text{-}Ox)O_2CCH_3$			90— 91	59.89 (59.80)	4.96 (5.02)	2.65 (2.68)

pale yellow or yellow crystals of $(CH_3)_n(C_6H_5)_{3-n}Sb(L)X$. The elemental analyses and properties of these complexes are listed in Table 1.

Preparation of $CH_3(C_6H_5CH_2)C_6H_5Sb(2\text{-}Me\text{-}Ox)O_2CCH_3$

A mixture of methylbenzylphenylantimony dibromide (4 mmol) in benzene (~60 cm^3) and sodium methoxide (8 mmol) in methanol (~10 cm^3) was heated at reflux for 2 h. After filtering off sodium bromide, acetic acid (4 mmol) in benzene (20 cm^3) was added and the solution was stirred for 30 min. 2-Methyl-8-quinolinol was then added to this solution and the mixture was heated at reflux for 2 h. The solvent was removed under reduced pressure to give a pale yellow solid. After the benzene and petroleum ether solution of this solid had stood in a refrigerator over night, the crystalline product was obtained by scratching the vessel with a glass rod. It was recrystallized from benzene and petroleum ether to give $CH_3(C_6H_5CH_2)C_6H_5Sb(2\text{-}Me\text{-}Ox)$-$O_2CCH_3$ (Table 1).

Attempted preparation of $CH_3(C_6H_5CH_2)C_6H_5Sb(Ox)Br$

The preparation of this compound was tried by a method similar to the above procedure, but we could not obtain a pure compound since the product could not be crystallized. The compound decomposes gradually in dichloromethane and an odor of benzyl bromide was noticeable. The main ^{1}H NMR signals of the yellow solid obtained by evaporation of the solvent to dryness were (in dichloromethane): CH_3: 8.12, CH_2: 3.93 (J = 12 Hz, an AB quartet), 2-H: 8.65, 4-H: 8.08 ppm.

Physical measurements and sampling of complexes

The UV spectra were recorded with Hitachi 124 and 356 spectrometers using 0.1 cm length quartz cells. The λ_{max} of the longest wavelengths of the complexes in dichloromethane are shown in Table 2. The IR spectra were obtained in Nujol mulls or in benzene with Hitachi EPI-L and 225 spectrometers. The Sb—Cl stretching frequency is shown in Table 2. The ^{1}H NMR spectra were measured on a JEOL JNM-PS-100 spectrometer operating at 100 MHz. The chemical shifts of the methyl groups attached to the antimony atom and the 2- and 4-protons of the 8-quinolinolato ligand of the complexes (vs. internal tetramethylsilane) are listed in Table 2. 1,1,2,2-Tetrachloroethane or dichloromethane was used as solvent. The temperature in the NMR probe was measured by inserting a dog-legged thermometer.

Appropriate amounts of triorganoantimony complexes of chloride and bromide, $(CH_3)_n(C_6H_5)_{3-n}Sb(L)Cl$ and $(CH_3)_n(C_6H_5)_{3-n}Sb(L)Br$, were weighted into a 1 cm^3 volumetric flask and the compounds were dissolved in 1,1,2,2-tetrachloroethane. The concentration of each of the complexes was about 0.1 mol/dm^3. The solution prepared in this way was sealed in an NMR tube in vacuo after degassing several times by the freeze—thaw—freeze method.

Calculation of activation parameters of the halogen exchange reaction

The intensity of a theoretical spectrum at any frequency ω_i for the halogen exchange reaction system, $(CH_3)_n(C_6H_5)_{3-n}Sb(L)[Cl \leftrightarrow Br]$, has been given by

TABLE 2

^{1}H NMR, IR AND UV SPECTRAL DATA FOR $(CH_3)_n(C_6H_5)_{3-n}Sb(L)X$ AND $CH_3(C_6H_5CH_2)C_6H_5$-$Sb(2\text{-}Me\text{-}Ox)O_2CCH_3$

Compound			δ(Sb—CH$_3$) [a] (ppm)	δ(2-H) [a] (ppm)	δ(4-H) [a] (ppm)	ν(Sb—Cl) [b] (cm^{-1})	λ$_{max}$ [c] (nm)
n	L	X					
3	2-Me-Ox	Cl	1.93		8.10	255 [d]	328
3	2-Me-Ox	Br	2.07		8.04		329
3	Ox	Cl [e]	1.91 [c]	8.69 [c]	8.16 [c]	260 [d]	353
3	Ox	Br [e]	2.07 [c]	8.73 [c]	8.20 [c]		352
3	5-Ac-Ox	Cl	1.95	8.78	9.66	260 [d]	344
3	5-Ac-Ox	Br	2.09	9.79	9.66		339
2	2-Me-Ox	Cl	2.14		8.10	260	332
2	2-Me-Ox	Br	2.34		8.12		333
2	7-Me-Ox	Cl	2.03	8.80	8.21	263	350
2	7-Me-Ox	Br	2.20	8.85	8.23		353
2	5-Me-Ox	Cl	2.05	8.86	8.39	264	353
2	5-Me-Ox	Br	2.21	8.92	8.40		356
2	4-Me-Ox	Cl	2.02	8.71		265	341
2	4-Me-Ox	Br	2.20	8.77			342
2	Ox	Cl	2.05	8.84	8.26	266	361
2	Ox	Br	2.16	8.90	8.30		359
2	5-Cl-Ox	Cl	2.08	8.86	8.59	269	352
2	5-Cl-Ox	Br	2.24	8.91	8.61		355
2	5-Ac-Ox	Cl	2.06	8.88	9.72	271	349
2	5-Ac-Ox	Br	2.22	8.94	9.74		353
2	5-NO$_2$-Ox	Cl	2.11	8.92	9.46	275	[f]
2	5-NO$_2$-Ox	Br	2.28	8.96	9.47		[f]
2	5,7-Cl$_2$-Ox	Cl	2.13	8.86	8.54	271	356
2	5,7-Cl$_2$-Ox	Br	2.28	8.91	8.56		358
1	2-Me-Ox	Cl	2.24		8.01	270 [d]	332
1	2-Me-Ox	Br	2.47		8.02		332
1	7-Me-Ox	Cl	2.04	8.89	8.15	256 [d]	366
1	7-Me-Ox	Br	2.22	8.95	8.18		366
1	5-Me-Ox	Cl	2.04	8.91	8.33	270 [d]	369
1	5-Me-Ox	Br	2.23	8.97	8.36		370
1	Ox	Cl	2.06 [c]	8.86 [c]	8.21 [c]	260 [d]	368
1	Ox	Br	2.26 [c]	8.96 [c]	8.25 [c]		365
1	Ox	OAc	1.98 [c]	9.16 [c]	8.14 [c]		357
$CH_3(C_6H_5CH_2)C_6H_5Sb$-$(2\text{-}Me\text{-}Ox)O_2CCH_3$			1.78 [c]		7.91 [c]		346

[a] In $CHCl_2CHCl_2$. [b] In C_6H_6 using 0.5 mm cells. [c] In CH_2Cl_2. [d] In Nujol mulls. [e] Ref. 1. [f] Obscured by other absorptions.

equation 2 [5], where α_A and α_B are given by eqns. 3 and 4. τ_A and τ_B are

$$I(\omega_i) \propto \mathrm{Re}(P_A P_B) \begin{pmatrix} -(\alpha_A + 1/\tau_A) & 1/\tau_B \\ 1/\tau_A & -(\alpha_B + 1/\tau_B) \end{pmatrix}^{-1} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad (2)$$

$$\alpha_A = 1/T_{2A} + i(\omega_A - \omega_i) \qquad (3)$$

$$\alpha_B = 1/T_{2B} + i(\omega_B - \omega_i) \qquad (4)$$

values of mean life times at site A and site B, P_A and P_B are the relative populations of the species A and B, which depend on the concentration of the species A ($[c_A]$) and B ($[c_B]$), T_{2A} and T_{2B} correspond to the observed line width of

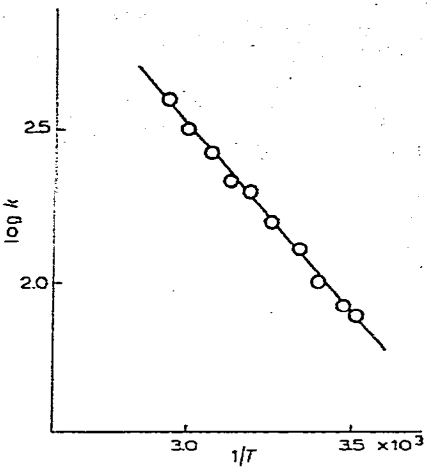


Fig. 1. Arrhenius plot for the $(CH_3)_2C_6H_5Sb(5\text{-Cl-Ox})[Cl \rightarrow Br]$ system.

the signals A and B for no halogen exchange, and ω_A and ω_B are site frequencies of the species A and B, respectively. In calculating the spectral intensity, a relation, $\tau_B = [(c_B]/[c_A]) \times \tau_A$, was used. The values of τ_A, T_{2A} and T_{2B} for the experimental spectra at any temperature were estimated by minimizing eqn. 5 by the least squares method [6], where $I^e(\omega_i)$ is the intensity of the

$$R = \sum_{i=1}^{N} (I^e(\omega_i) - I(\omega_i))^2 \tag{5}$$

observed spectrum at a frequency ω_i and N is the total number of the data points. The line-shape fitting error expressed by eqn. 6 was in a range of 2—6%.

TABLE 3

THE RATE CONSTANT AND ACTIVATION PARAMETERS FOR THE HALOGEN EXCHANGE REACTION OF THE $(CH_3)_n(C_6H_5)_{3-n}Sb(L)[Cl \rightarrow Br]$ SYSTEM AT 25°C [a]

n	L	log k	E_a (kJ mol^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta G^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J mol^{-1} K^{-1})
3	Ox [b,c]	4.46 ± 0.15	39.9 ± 2.5	37.5 ± 2.5	47.3 ± 0.9	— 33 ± 12
3	2-Me-Ox [b,c]	1.87 ± 0.02	23.3 ± 1.2	20.8 ± 1.2	62.3 ± 0.1	—139 ± 8
3	2-Me-Ox	2.63 ± 0.04	27.1 ± 1.4	24.7 ± 1.4	58.0 ± 0.2	—112 ± 6
3	5-Ac-Ox	2.46 ± 0.03	25.6 ± 1.4	23.1 ± 1.4	59.0 ± 0.2	—120 ± 5
2	7-Me-Ox	2.60 ± 0.05	17.6 ± 2.0	15.1 ± 2.0	58.1 ± 0.3	—144 ± 7
2	4-Me-Ox	2.56 ± 0.03	22.7 ± 1.8	20.2 ± 1.8	58.4 ± 0.2	—128 ± 8
2	5-Me-Ox	2.46 ± 0.05	20.7 ± 1.9	18.3 ± 1.9	59.0 ± 0.3	—137 ± 7
2	Ox	2.25 ± 0.03	23.8 ± 2.0	21.3 ± 2.0	60.1 ± 0.2	—129 ± 8
2	2-Me-Ox	2.12 ± 0.02	31.9 ± 2.1	29.5 ± 2.1	60.9 ± 0.1	—105 ± 7
2	5-Cl-Ox	2.07 ± 0.01	23.7 ± 1.2	21.2 ± 1.2	61.2 ± 0.1	—134 ± 4
2	5-Ac-Ox	1.73 ± 0.06	27.3 ± 2.2	24.9 ± 2.2	63.1 ± 0.4	—128 ± 9
2	$5\text{-}NO_2\text{-}Ox$	1.30 ± 0.10	32.8 ± 2.9	29.3 ± 2.9	65.6 ± 0.6	—122 ± 12
2	$5,7\text{-}Cl_2\text{-}Ox$	1.19 ± 0.01	30.6 ± 0.7	28.1 ± 0.7	66.2 ± 0.1	—128 ± 3
1	Ox	2.17 ± 0.02	14.2 ± 1.3	11.7 ± 1.3	60.6 ± 0.1	—163 ± 4
1	2-Me-Ox	2.04 ± 0.05	12.1 ± 2.1	9.6 ± 2.1	61.5 ± 0.3	—172 ± 8

[a] Error estimated at the 95% confidence level. [b] Ref. 1. [c] In CH_2Cl_2.

The rate constant, k, for the halogen exchange reaction of the system,

$$ERR = 1/N \cdot \sum_{i=1}^{N} |(I^e(\omega_i) - I(\omega_i))/I^e(\omega_i)| \times 100 \tag{6}$$

$$k = 1/(\tau_A \times [c_B]) \tag{7}$$

$(CH_3)_n(C_6H_5)_{3-n}Sb(L)[Cl \leftrightarrow Br]$, was calculated by eqn. 7. Figure 1 shows a typical Arrhenius plot for the system, $(CH_3)_2C_6H_5Sb(5\text{-}Cl\text{-}Ox)[Cl \leftrightarrow Br]$. From this linear plot, we calculated activation parameters, E_a, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$. These values for other halogen exchange reactions at 25° C are given in Table 3.

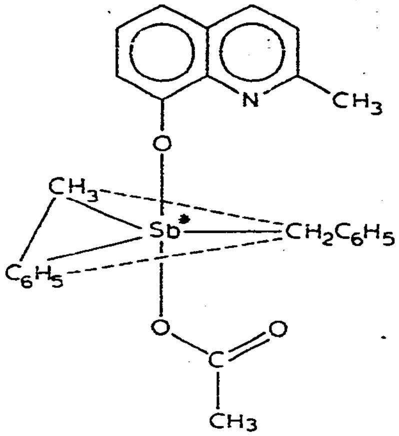
Results and discussion

UV and ¹H NMR spectra

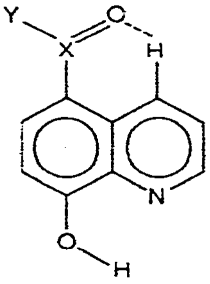
As can be seen from Table 2, the absorption maxima of the longest wave length, λ_{max}, of most of the triorganoantimony complexes, $(CH_3)_n(C_6H_5)_{3-n}$-$Sb(L)X$, studied appear in the region where the chelation by the 8-quinolinolato ligand is expected [7,8]. From this result, it seems almost certain that the antimony atom is hexacoordinated. The magnitude of the red shift of this band increases as the number of the phenyl groups increases which may indicate that the chelation by the ligand becomes stronger in this order. In $(CH_3)_2C_6H_5Sb(4\text{-}Me\text{-}Ox)X$ and $(CH_3)_3Sb(5\text{-}Ac\text{-}Ox)X$, the red shift of λ_{max} from that of the free ligands (312 and 321 nm for 4-Me-OxH and 5-Ac-OxH in dichloromethane, respectively) is rather small. Therefore, it is suspected that interaction of the nitrogen atom in the substituted 8-quinolinolato ligand with the antimony atom is very weak, if present at all. In $(CH_3)_n(C_6H_5)_{3-n}$-$Sb(2\text{-}Me\text{-}Ox)X$, the red shift of λ_{max} from the free ligand (315 nm in dichloromethane) by complex formation is small, indicating that the antimony atom has a pentacoordinated configuration.

In $CH_3(C_6H_5CH_2)C_6H_5Sb(2\text{-}Me\text{-}Ox)O_2CCH_3$, the red shift of λ_{max} is rather small and the C=O stretching band of the acetato ligand appears at 1630 cm^{-1} in a Nujol mull. The latter value indicates that the carbonyl group is almost free from interaction with the antimony atom as it is in $(CH_3)_3Sb(Ox)O_2CCH_3$ [1]. In the ¹H NMR spectrum of the methylbenzylphenylantimony complex, the methylene protons of the benzyl group show a signal having an AB quartet pattern at 3.98 ppm with J_{AB} 12 Hz. The above facts suggest that the antimony atom is a chiral center with a pentacoordinated configuration and the rate of interconversion between enantiomers at the temperature of the NMR probe is slow relative to the NMR time scale.

The values of the chemical shift of the methyl groups attached to the antimony atom and the 2- and 4-protons of the 8-quinolinolato ligand of the triorganoantimony complexes, $(CH_3)_n(C_6H_5)_{3-n}Sb(L)X$, are similar to those reported for trimethyl(8-quinolinolato)antimony complexes [1]. The 4-proton signal of the 5-acetyl- and 5-nitro-8-quinolinolato complexes of triorganoantimony halide, however, appears at very low magnetic field. This is also true for the free ligands (9.59 and 9.34 ppm for the 4-proton chemical shift for



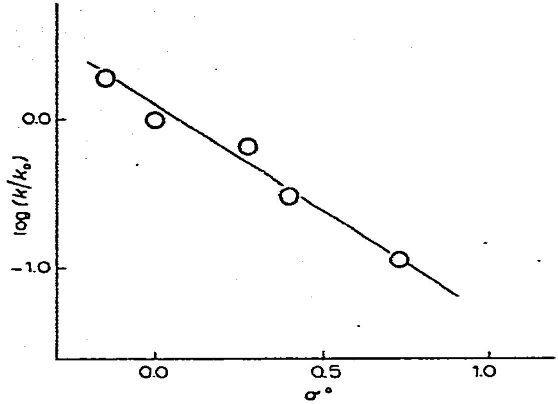
5-acetyl- and 5-nitro-8-quinolinol, respectively). This marked downfield shift of the 4-proton of these compounds may be due to the magnetic anisotropy of the acetyl and nitro groups [9]. The nitroso group at the 5-position of the 8-quinolinolato ligand does not show such an appreciable effect on the 4-proton chemical shift, but the 1-nitrogen of 6-hydroxy-1,7-diazaphenanthrene causes a notable downfield shift for the 10-proton (9.59 ppm in $CDCl_3$). The downfield shifts of the 4-proton of 5-acetyl- and 5-nitro-8-quinolinol from the 4-proton chemical shift of 8-quinolinol are 1.55 and 1.30 ppm, respectively. The corresponding downfield shifts of the 8-proton of 1-acetyl- and 1-nitro-naphthalenes from the α proton chemical shift of the naphthalene are 0.87 [10] and 0.81 [11] ppm, respectively. The relatively large downfield shift of the former as compared to that of the latter may in part be due to the fact that π-electron conjugation of the 5-acetyl or 5-nitro group with π-electrons of the quinoline ring is promoted by involvement of the lone pair of the oxygen atom at the 8-position. This probably causes the twisting angle between the acetyl or nitro group and the quinoline ring to decrease, which reduces the distance between the 4-proton and the magnetic anisotropic center of the acetyl or nitro group at the 5-position, and increases the negative charge on the oxygen atom of the acetyl or nitro group.



($X = C, Y = CH_3; X = N, Y = O$).

Halogen exchange reactions

As can be seen from Table 3, the rate constants of the halogen exchange re-



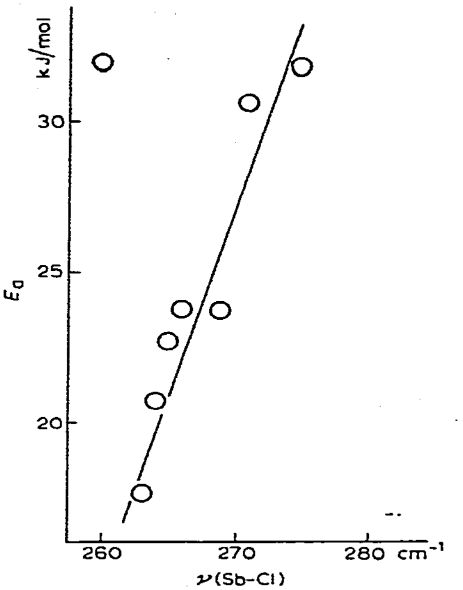


Fig. 2. Hammett plot of Taft's σ° value vs. log (k/k_0) for the $(CH_3)_2C_6H_5Sb(L)[Cl\rightarrow Br]$ system.

Fig. 3. A relation between ν(Sb—Cl) of $(CH_3)_2C_6H_5Sb(L)Cl$ and the E_a value for the $(CH_3)_2C_6H_5Sb(L)$-$[Cl\rightarrow Br]$ system.

actions for the $(CH_3)_n(C_6H_5)_{3-n}Sb(L)[Cl\leftrightarrow Br]$ system have a tendency to decrease as the number of the phenyl groups increases if the ligand L is the same. The decrease of the rate constants with increasing number of phenyl groups is due mainly to a decrease of activation entropy. The activation enthalpy causes an opposite trend to that of the rate constant. A remarkable result of the halogen exchange reactions in the present system is that the activation entropy has a large negative value and that the activation enthalpy is rather small. The result is much amplified in the $CH_3(C_6H_5)_2Sb(L)[Cl\leftrightarrow Br]$ system. The above facts imply that the halogen exchange reactions of the present system do not go through a dissociative path. The conclusion is quite similar to that of the halogen-carboxylato ligand exchange reactions of the $(CH_3)_3Sb(Ox)[X\leftrightarrow O_2CR]$ system studied in the previous paper [1].

In a series of halogen exchange reactions of the present system, $(CH_3)_2$-$C_6H_5Sb(L)[Cl\leftrightarrow Br]$, the rate constant decreases when the electron-withdrawing group is substituted at the 5-position of the 8-quinolinolato ligand. Figure 2 gives a plot of the Taft's σ° value [12] vs. the log (k/k_o) value, where k_o is the rate constant for L = Ox. A good linear relation was obtained with a slope (ρ value) of -1.31 and a correlation coefficient of 0.987. In this series of halogen exchange reactions, the rate constant decreases with increasing activation energy. The result is in marked contrast to that for the $(CH_3)_3Sb(Ox)$-$[Br\leftrightarrow O_2CR]$ system [1], in which the rate constant generally decreases with decreasing activation energy and activation entropy. A plot of activation energy for the halogen exchange reactions of the $(CH_3)_2C_6H_5Sb(L)[Cl\leftrightarrow Br]$ system vs. the Sb—Cl stretching frequency of the complex, $(CH_3)_2C_6H_5Sb(L)Cl$, in benzene is shown in Fig. 3.

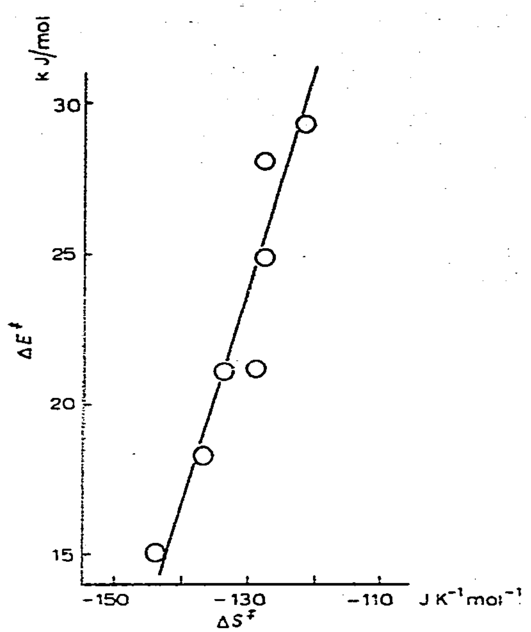
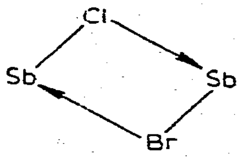
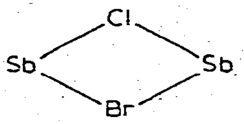


Fig. 4. A plot of $\Delta S^\ddagger$ vs. $\Delta H^\ddagger$ for the $(CH_3)_2C_6H_5Sb(L)[Cl{\rightarrow}Br]$ system.

A rather good linear relationship (correlation coefficient $r = 0.943$) was obtained when the deviating point of the 2-methyl-8-quinolinolato complex was excluded. This relationship seems to suggest that the activation energy of the halogen exchange reactions of this system depends on the strength of the antimony—halogen bond. The marked deviation of the point of the 2-methyl-8-quinolinolato complex may be due to the fact that the configuration around the antimony atom is different from that of the others as a result of the steric effect of the methyl group at the 2-position. The substituents at the 7-position of the 8-quinolinolato ligand, however, do not show any appreciable steric effect for the halogen exchange reactions. The relationship of Fig. 3 and the large negative activation entropy, together with the rather small activation energy for the $(CH_3)_2C_6H_5Sb(L)[Cl{\leftrightarrow}Br]$ system, indicate that the halogen exchange reaction pathway may involve initial loosening of the antimony—halogen bond and then association via unsymmetrical halogen atom bridging as is shown in I. On the other hand in the $CH_3(C_6H_5)_2Sb(L)[Cl{\leftrightarrow}Br]$ system, the symmetrical bridging state II may be the transition state for the halogen exchange reactions, because the activation energy is very small and activation entropy is large and negative.



(I)



(II)

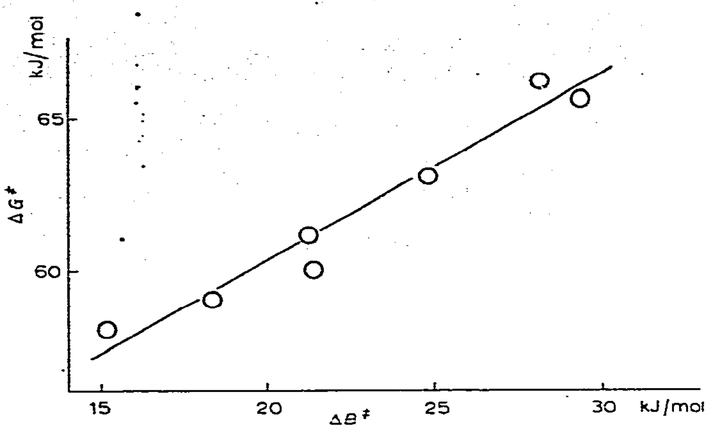


Fig. 5. A plot of $\Delta H^{\ddagger}$ vs. $\Delta G^{\ddagger}$ for the $(CH_3)_2C_6H_5Sb(L)[Cl\leftrightarrow Br]$ system.

It has been reported [13,14] that a linear relationship between the free energies for two reaction series would be expected to hold only if each series shows one of the following types of behavior; (1) ΔS is constant, (2) ΔH is constant, or (3) ΔH is linearly related to ΔS. A plot of $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ for the $(CH_3)_2C_6H_5Sb(L)[Cl\leftrightarrow Br]$ system is shown in Fig. 4. If we exclude the conspiciously deviating points for 2-methyl- and 4-methyl-8-quinolinolato complexes, which were omitted from Fig. 4, a fairly good linear relationship with a slope (β value) of 640 and a correlation coefficient of 0.931 is obtained. The β value of the present system is somewhat larger than the most frequently observed values but is not out of the range that has been reported [15]. This relation indicates that the present system belongs to the third category of the above classification. However, it may be possibile that the linear relation of the present system is fortuitous, because the uncertainty in activation entropy is rather large. A plot of $\Delta H^{\ddagger}$ vs. $\Delta G^{\ddagger}$ for the same system is shown in Fig. 5. This plot indicates that $\Delta G^{\ddagger}$ is linearly related to $\Delta H^{\ddagger}$ with a slope of 0.630 and a correlation coefficient of 0.977 (points of the 2-methyl- and 4-methyl-8-quinolinolato complexes also are excluded). This linear relationship is expected, with a slope of 0.533 $(1 - T/\beta)$, if the linear relation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ holds true [15]. The discrepancy of the calculated value from that obtained from Fig. 5 may be due mainly to insufficient accuracy of the activation entropy.

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