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Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

THERMAL DECOMPOSITION OF THE SOLVENT EXTRACTED MOLYBDENUM(VI) COMPLEXES FROM HYDROCHLORIC ACID SOLUTIONS WITH TRIOCTYLAMINE AND TRIOCTYLMETHYLAMMONIUM CHLORIDE

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The complexes of molybdenum(VI) with trioctylamine (TOA, R_3N) and trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$) were prepared by drying in vacuo the organic solutions for the extraction of molybdenum(VI) from hydrochloric acid solutions at low and higher acidities, respectively, by TOA and TOMAC in benzene. The resulting complexes were examined by thermal analysis (TG and DTA) in air and under the atmosphere of nitrogen, and their thermally decomposed products such as volatile matters and residues by gas chlomatography, X-ray diffraction study and infrared spectrophotometry. It was found that their complexes decompose thermally to MoO_3 by cracking of alkyl groups combined with molybdenum(VI) ion. Accordingly the thermal decomposition process of those complexes is discussed and the probable structure of the complexes is proposed on the basis of the results obtained.

In order to obtain further information concerning the compositions of the complexes isolated from the organic solutions in the solvent extraction of metals with long-chain aliphatic amines, the thermal decomposition of the

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solvent extracted chloro complexes of copper(II) [1], zirconium(IV) [2], vanadium(IV) [3] and uranium(VI) [4] has been examined in air, and of divalent manganese, cobalt, copper and zinc [5], trivalent gallium, indium and thallium [6] and vanadium(IV) [7] under an atmosphere of nitrogen. Besides the present author has investigated the extraction of molybdenum(VI) from hydrochloric acid solutions by trioctylamine (TOA, R_3N) and trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$) in a previous paper [8]. Thus this study extends the work to an examination of the thermal decomposition of the complexes of molybdenum(VI) extracted from hydrochloric acid solutions with TOA and TOMAC in air and under the atmosphere of nitrogen.

Experimental

Chemicals

TOA and TOMAC of high purity (both >99%, Koei Chemical Co., Ltd., Osaka) were used without further purification and diluted with benzene. Aqueous solutions of molybdenum(VI) were prepared by dissolving sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) and molybdic acid ($H_2MoO_4 \cdot H_2O$) in hydrochloric acid. All chemicals used were of analytical reagent grade.

Preparation of complexes

The results for the extractions of molybdenum(VI) from hydrochloric acid solutions by TOA and TOMAC suggest that the composition of the complexes formed in the extraction at low aqueous acidity are different from those at higher acidity [8]. Accordingly the respective complexes with TOA and TOMAC were prepared by drying in vacuo ($<60^\circ$ at 1 Torr) the organic solutions from the extractions at low and higher aqueous acidities. The organic solutions saturated with molybdenum were prepared as follows. (1) The complexes formed at low aqueous acidity: equal volumes of $0.01\ mol \cdot dm^{-3}$ TOA or TOMAC in benzene and of aqueous solution containing $0.0062\ mol \cdot dm^{-3}$ sodium molybdate in $0.015\ mol \cdot dm^{-3}$ hydrochloric acid (*pH* 2.36) were shaken for 10 min at 20°, and the organic phase was used repeatedly several times (total seven) for such extraction of molybdenum from fresh aqueous acid solution. (2) The complexes formed at higher aqueous acidity: equal volumes of $0.05\ mol \cdot dm^{-3}$ TOA or TOMAC in benzene and of aqueous solution containing $0.2\ mol \cdot dm^{-3}$ molybdic acid in

6 mol·dm^{-3} hydrochloric acid were shaken for 10 min at 20°, and the organic phase obtained was freed from benzene. The organic extracts so obtained contain the composition in the molar ratios, as shown in Table 1.

Table 1 Molar ratios of $[R_3N]$ or $[R_3R'N]$ / [Mol] / [Cl] / $[H_2O]$ in the complexes formed in the solvent extraction of molybdenum(VI) from hydrochloric acid solutions with TOA and TOMAC

$[HCl]_{init}$ aq'	Molar ratio	
mol·dm^{-3}	$[R_3N]$ / [Mo] / [Cl] / $[H_2O]$	$[R_3R'N]$ / [Mo] / [Cl] / $[H_2O]$
0.015	0.49 / 1.0 / – / 1.96	0.52 / 1.0 / – / 2.10
6.0	0.92 / 1.0 / 2.81 / 3.03	0.95 / 1.0 / 2.71 / 2.83

Analyses

The complexes were examined by thermogravimetry (TG) and differential thermal analysis (DTA), and the products of their thermal decompositions such as volatile matters and residues were checked by gas chromatography, X-ray diffraction study and infrared spectrophotometry [6]. The TG and DTA were performed under an atmosphere of nitrogen at a heating rate of 5 deg·min^{-1} and a flow rate of 50 cm^3·min^{-1} with alumel-chromel thermocouples, using 0.04 g of the sample and α–alumina as reference material for the measurement of differential thermal electromotive force. The residues were derived from the complexes by heating to the required temperatures at a rate of 5 deg·min^{-1} under the same atmosphere. Infrared spectra were recorded on Japan Spectroscopic Co., Ltd. models IRA–1 (4000–650 cm^{-1})and IR-F (700–200 cm^{-1}) grating spectrometers. The absorption spectra of the complexes dissolved in 1,2–dichloroethane were determined on a Shimazu model QV–50 spectrophotometer using matched 1.0·1.0 cm fused silica cells. X-ray powder diffraction diagrams were obtained on a Geigerflex recording X-ray diffractometer with filtered copper radiation [3]. The volatile matters were collected with a 2 cm^3 syringe at the gas outlet of the DTA apparatus and analysed with a Shimazu model GC–6AMPTF gas chromatograph under the following analytical conditions: carrier gas, helium at 40 cm^3·min^{-1}; column, Porapak Q of 80 / 100 mesh; column temperature, 140°; detector, FID. Each component detected was identified by gas chromatography-mass spectrometry (GC–MS). Hydrogen chloride in the volatile matter was trapped in 0.05 mol·dm^{-3} silver nitrate solution in an interval of 10° at a temperature between 200 and 350° by passing it through the solution for 3 min. For chemical analysis, the resulting materials were dissolved in benzene, and the chloride concentration and water content in proportions of the solution were determined by Volhard's and Karl Fisher titrations. Additionally, the benzene solutions were washed with 1 mol·dm^{-3} sodium hydroxide solution, and then the molybdenum concentrations were determined by titration with CyDTA using xylenol orange as indicator [9]. The apparent molecular weight of complex was determined in benzene on a Hitachi model 115 isothermal molecular weight apparatus.

Results and discussion

Thermal decomposition of the complexes formed at low aqueous acidity

The infrared spectra of the organic extracts from hydrochloric acid solutions at low acidity exhibit the absorptions as shown in Table 2. In those complexes, however, the Mo–Cl stretching band is not observed in correspondence to the results for chloride concentration. Besides the absorption spectra of the organic extracts show three absorptions at 225, 255 and 325 nm, suggesting that the organic species contains the group $MoO_3 \cdot 2H_2O$. Further the measurement of apparent molecular weight indicated that the complexes with TOA and TOMAC exist in the polymerized species. Although the degree of their polymerization depends on the condition of preparation, the complexes formed in this experiment were observed to be the dimeric species: the observed values were in 1490 and 1510 for the theoretical values of 713 and 727, respectively. Accordingly it is considered that those complexes have the respective stoichiometric compositions such as $(R_3NH)Mo_2O_6(OH) \cdot 3H_2O$ and $(R_3R'N)Mo_2O_6(OH) \cdot 3H_2O$.

The TG and DTA curves of the complexes with TOA and TOMAC are shown in Fig. 1. For the complex with TOA, the TG curve exhibits the weight-loss of 53.5% at 175–750°, while the DTA curve under the atmosphere of nitrogen reveals the endothermic reactions at 65, 100, 220, 240, 265, 300 and 410°. The complex with TOMAC exhibits the weight-loss of 51.5% at 165–520° in the TG curve, and the endotherms at 55, 80, 165, 260, 270, 305 and 410° in the DTA curve. In Fig. 1 it is observed that the endothermic reactions in the DTA curves occur at points near the changes of shape in the TG curves. However, since the endotherms which appear at 65 and 125° for the complex with TOA and at 55, 80 and 165° for the complex with TOMAC are not accompanied with the weight-losses, it is assumed that their reactions arise from the liquefaction and/or dissociation of the complexes. Additionally, it seems that the thermal stabilities of the complex with TOA resembles that of the complex with TOMAC.

Table 2 Infrared spectral data for the complexes of molybdenum(VI) with TOA and TOMAC

Frequency, cm^{-1}		Probable assignment
TOA-complex	TOMAC-complex	
3560–3200 (wb)*	3400 (wb)	γOH
3020–2520 (mb)		γNH^+
2920 (s)	2920 (s)	γCH (sym. and asym.)
2850 (ms)	2850 (ms)	
1635 (vw)	1630 (vw)	δOH
1470 (m)	1465 (m)	δCH3 degenerate CH2 scissoring
1375 (w)	1375 (w)	δCH3 (sym.)
965 (m)	970 (s)	γMo=O
950 (w)	940 (s)	
920 (w)	915 (ms)	
910 (w)		
850 (w)	860 (m)	γMo–O–Mo (asym.) and/or γMo–O
810 (w)	800 (s)	
730 (w)	725 (ms)	
665 (w)	665 (w)	
575 (w)		γMo–OH (sym. and asym.)
550 (m)	550 (m)	
520 (m)	520 (m)	γMo–O–Mo (sym.)
470 (w)		δMoO2
440 (w)	435 (m)	
410 (m)	425 (m)	
370 (m)	375 (m)	
355 (m)	360 (m)	

* s = strong, ms = medium strng, m = medium, w = weak, vw = very weak

The volatile matters generated in the thermal decomposition of the complexes with TOA and TOMAC contain aliphatic compounds such as allene, ethylene, ethane, propane, 1–butene, 2–butene and methyl alcohol, identified by GC–MS. However, since those complexes have no chlorine, the release of methyl chloride or hydrogen chloride is not observed like the other instance [5]. Some representative gas chromatographic data are illustrated in Tables 3–4, where the relative peak heights in gas chromatogram of the components are indicated as a function of the heating temperature. The complexes with TOA and TOMAC reveal the formation of methyl alcohol at 350° and 275–300°, respectively and the maximum in the production of hydrocarbon at 400–475° and 400–450°, respectively. It is thus thought that in the DTA curves of the complexes with TOA and TOMAC, the endothermic reactions at 220–300° result from the relase of the hydroxyl group, co-ordinated to molybdenum(VI) ion, and at 410–475° from cracking of alkyl groups.

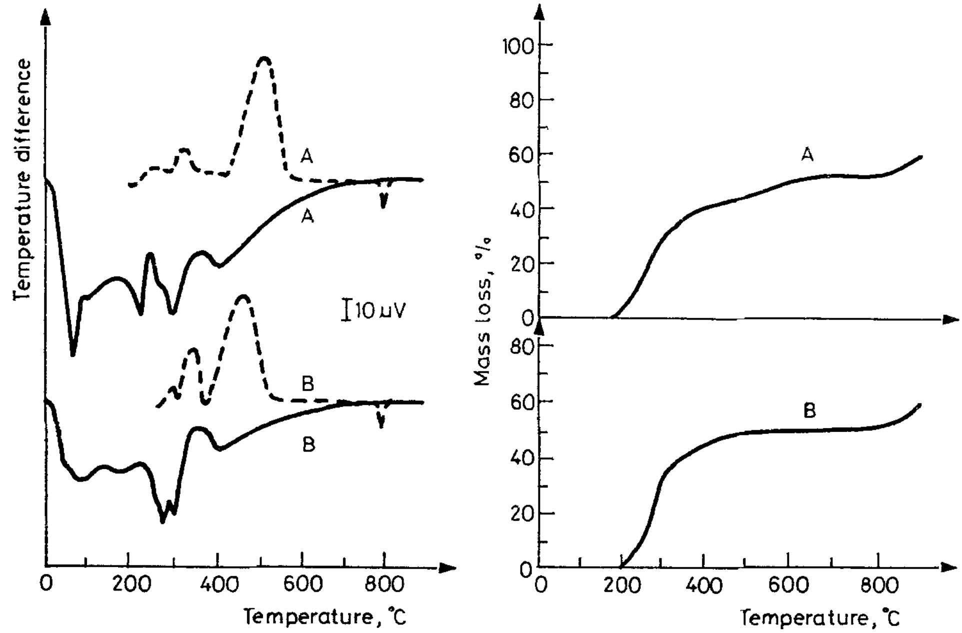


Fig. 1 DTA and TG curves for the complexes of Mo(VI) with TOA and TOMAC formed at low aqueous acidity (A, TOA complex; B, TOMAC complex; Continuous and broken lines represent the examinations under atmospheres of nitrogen and air, respectively)

When the complexes are heated under the atmosphere of nitrogen, their infrared spectra show the following patterns: for the complex with TOA (Fig. 2), on heating at 200° the absorptions due to the alkyl groups, the νMo=O and Mo–O–Mo and/or νMo–O decrease in intensity, and the δMoO$_2$ band almost disappears, and at 300° the νMo–O and νMo–O appear at 960 and 720 cm^{-1}, respectively; for the complex with TOMAC (Fig. 3), at 200° the spectrum retains a pattern similar to that of the starting material, although the absorptions decrease slightly in intensity, and then at 300° the νMo=O and νMo–O appear at 980 and 730 cm^{-1}, respectively. The changes in the infrared spectra of the thermal decomposition residues from the TOMAC complex are almost the same as those in the case of the

TOA complex residues. In the thermal decomposition of the complexes with TOA and TOMAC, the X-ray diffraction results reveal the amorphous pattern on heating at 200–700° under the atmosphere of nitrogen, although the crystallization progresses with increasing the temperature (Figs 4–5). However, since the products at above 600° in air exhibit the pattern of MoO_3 and the TG curves show the weight-loss at above 790°, it is presumed that MoO_3 is formed by the thermal decomposition of the complexes. Accordingly it is

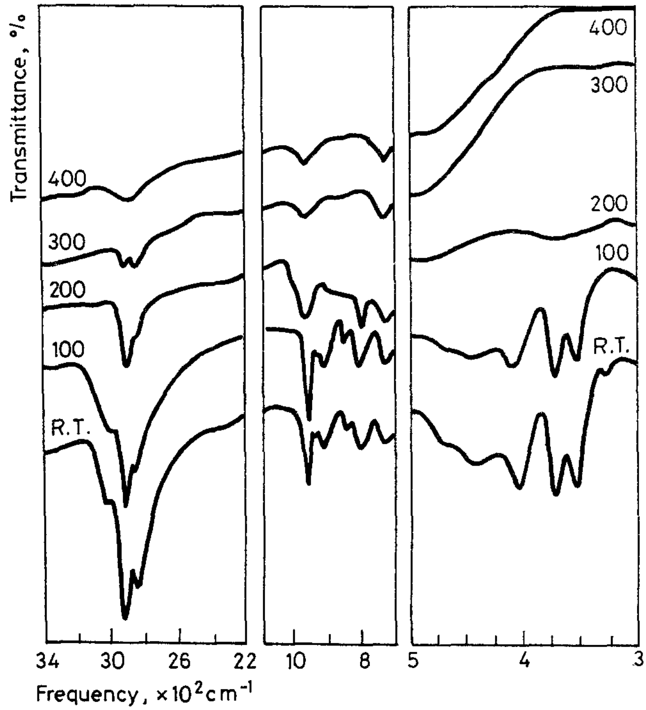


Fig. 2 Infrared spectra of the residues derived under atmospheres of nitrogen from the complex of molybdenum(VI) with TOA formed at low aqueous acidity by heating to the stated temperature (Numerals on curves are heating temperatures, °C)

explained that for the DTA curves of the complexes in air, the large exotherms which appear at 515 and 460° for the complexes with TOA and TOMAC, respectively arise from the combustion of remaining carbon and the endotherm at 790° from the sublimation of MoO_3.

Hence the endothermic reactions in the DTA curves of the complexes with TOA and TOMAC formed at low aqueous acidity under an atmosphere of nitrogen are interpreted as shown in Table 5. It is considered that the thermal decompositions of their complexes which proceed in the sequences

$$(R_3NH)Mo_2O_6(OH)\cdot 3H_2O \xrightarrow[\text{liquefaction and/or dissociation}]{65-125\,^{\circ}C}$$

$$R_3NHOH\cdot 2MoO_3\cdot 3H_2O \xrightarrow[\text{dehydroxylation}]{220-300\,^{\circ}C} R_3N\cdot 2MoO_3$$

$$\xrightarrow[\text{cracking}]{410-475\,^{\circ}C} Mo + MoO_3$$

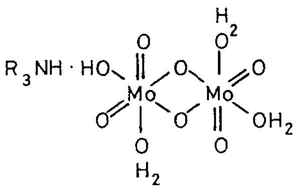
and

$$(R_3R'N)Mo_2O_6(OH)\cdot 3H_2O \xrightarrow[\text{liquefaction and/or dissociation}]{55-165\,^{\circ}C}$$

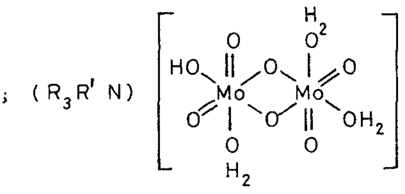
$$R_3R'NOH\cdot 2MoO_3\cdot 3H_2O \xrightarrow[\text{dehydroxylation (and }-CH_3OH\text{)}]{260-305\,^{\circ}C}$$

$$R_3N\cdot 2MoO_3 \xrightarrow[\text{cracking}]{410-475\,^{\circ}C} Mo + MoO_3\,,$$

suggesting the proposed structures [I] and [II] for the complexes of molybdenum(VI) with TOA and TOMAC:



[I]



[II]

Thermal decomposition of the complexes formed at higher aqueous acidity

The infrared spectra of the organic extracts from hydrochloric acid solutions at higher acidity exhibit the patterns similar to the absorption bands given in Table 2, except for the absorptions due to the Mo – Cl stretching frequency at 331 and 340 (and / or 334) cm^{-1} for the extracts by TOA and TOMAC, respectively, suggesting the formation of chloro complexes. In contrast, as the organic extracts from hydrochloric acid solutions at higher

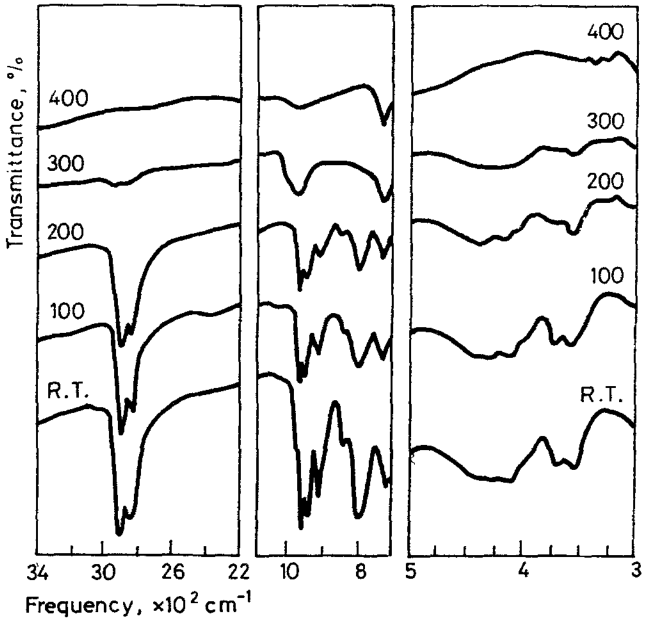


Fig. 3 Infrared spectra of the residues derived under atmosphere of nitrogen from the complex of molybdenum(VI) with TOMAC formed at low aqueous acidity by heating to the stated temperature (Numerals on curves are heating temperatures, °C)

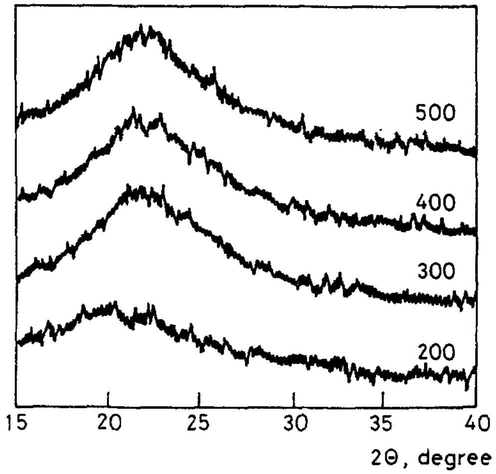


Fig. 4 X-ray diffraction diagrams of the residues derived under atmosphere of nitrogen from the complex of molybdenum(VI) with TOA formed at low aqueous acidity (Numerals on curves are heating temperatures, °C)

aqueous acidity by TOA and TOMAC exhibit a maximum absorption at 304 nm, it is inferred that a species of the type $MoO_2Cl_3^-$ is formed in both organic phases. Thus Table 1 indicates that the chloro complexes with TOA and TOMAC having the respective stoichiometric compositions such as $(R_3NH)MoO_2Cl_3\cdot 3H_2O$ and $(R_3R'N)MoO_2Cl_3\cdot 3H_2O$ are formed at higher aqueous acidity. Although these compositions are not changed by the variation in the condition of preparation, it is found that the chloro complexes with TOA and TOMAC exist in the dimeric species by the measurement of apparent molecular weight: the observed values were in 2640 and 2720 for the theoretical values of 1285 and 1313, respectively.

Table 3 Relative peak heights of some components in the gas chromatogram of the complex of molybdenum(VI) with TOA formed at low aqueous acidity as a function of heating temperature

Temp.,	Relative peak height*, mm						
°C	C_3H_4	C_2H_4	C_2H_6	C_3H_6	CH_3OH	1–C_4H_8**	2–C_4H_8**
150	7						
175	5			2			
200	6			1			
225	3			1			
250							
275	12	2	2	2	2	2	1
300	33	4	2	1	2	1	5
325	13	2	3	5	2	1	3
350	14	7	10	1	12	6	13
375	39	30	74	2	42	32	63
400	64	38	128	3		34	102
425	236	6	213			31	97
450	208	8	300	2		4	20
475	600	10	180		3		2
500	122	3	2	4	1		3

*Sensitivity range $4\cdot 10^3$ μV

**1– or 2–C_4H_8 denotes 1– or 2–butene

The TG and DTA curves of the chloro complexes with TOA and TOMAC are indicated in Fig. 6. For the chloro complex with TOA, the TG curve reveals the weight-losses of 69.3 and 13.9% at 140–350 and 350–550°, respectively, and the DTA curve under the atmosphere of nitrogen shows the endothermic reactions at 80, 125, 190, 275, 315, 370 and 435°. The chloro complex with TOMAC gives the weight-losses of 60.2 and 15.0% at 85-350° and 350–650°, respectively, in the TG curves, and the endotherms at 80, 115, 200, 270, 315, 360 and 435° in the DTA curve. In both complexes, the endothermic reaction at 80° is attributed to the liquefaction of the complexes, because there are no accompanying the weight-losses in the TG curves. In addition, the endotherms at 125 and 115° for the chloro complexes with TOA and TOMAC, respectively are considered to be ascribed to the release of water molecule.

Table 4 Relative peak heights of some components in the gas chromatogram of the complex of molybdenum(VI) with TOMAC formed at low aqueous acidity as a function of heating temperature

Temp., °C	Relative peak height*, mm						
	C_3H_4	C_2H_4	C_2H_6	C_3H_6	CH_3OH	1–C_4H_8**	2–C_4H_8**
150	3						
175	3						
200	6				4		
225	8	2	1		3		
250	3	1	2	1	20	2	
275	22	2	2	2	119	2	2
300	53	3	2	3	131	3	3
325	68	12	8	2	14	10	6
350	98	26	23	3	13	17	9
375	116	60	52	5		52	28
400	117	82	84	4		54	56
425	354	37	36	4		6	10
450	340	26	15	3		1	3
475	93	16	7	2			
500	40	5	3	4		3	1

*Sensitivity range $4 \cdot 10^3$ μV

**1– or 2–C_4H_8 denotes 1– or 2–butene

The volatile matters generated in the thermal decomposition of the chloro complexes with TOA and TOMAC contain aliphatic compounds such as allene, ethylene, ethane, propene, propane, 1–butene, 2–butene, methyl alcohol and methyl chloride, identified by GC–MS, and hydrogen chloride, trapped in silver nitrate solution. Some representative gas chromatographic

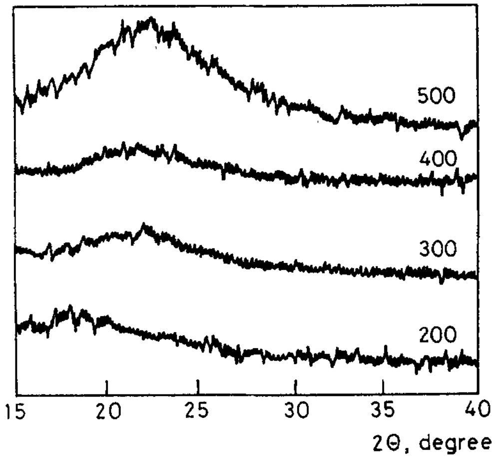


Fig. 5 X-ray diffraction diagrams of the residues derived under atmosphere of nitrogen from the complex of molybdenum(VI) with TOMAC formed at low aqueous acidity (Numerals on curves are heating temperatures, °C)

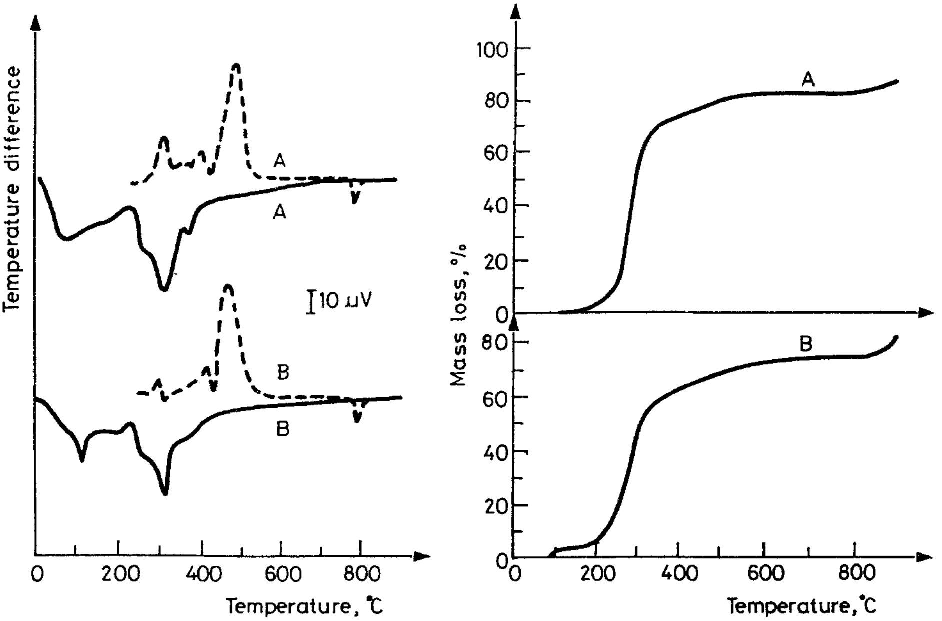


Fig. 6 DTA and TG curves for the complexes of Mo(VI) with TOA and TOMAC formed at higher aqueous acidity (A, TOA complex; B, TOMAC complex; Continuous and broken lines represent the examinations under atmospheres of nitrogen and air, respectively)

data are illustrated in Tables 6–7 as well as shown in Tables 3–4. On the other hand, hydrogen chloride evolved from the chloro complex with TOA is detected above 200° (before the detection of the organic components) and its maximum amount is obtained at about 250°, as observed in the thermal decomposition of divalent metal complexes [5]. This implies that the thermal decomposition is initiated by the release of hydrogen chloride at 275°, followed by the decomposition of TOA. Accordingly it is supposed that the endotherms at 315, 370 and 435° for the chloro complex with TOA arise from the cracking of the alkyl group. The volatile matter from the chloro complex with TOMAC contains the same organic components as those for the complex with TOA, although the former complex yields much more methyl alcohol and methyl chloride than the latter. In Table 7, it is apparent that the distribution of methyl alcohol and methyl chloride is different from that of hydrocarbons: the maximum amounts of methyl alcohol and methyl chloride are detected at 225 and 275°, respectively, and those of hydrocarbons at 375–425°. These components are almost generated in the beginning of the thermal decomposition, implying that the decomposition of the chloro complex with TOMAC releases methyl alcohol at first and then methyl chloride. It is therefore inferred that the endotherms at 200° corresponds to the dissociation that at 270° to dechlorination due to the evolution of methyl chloride, and those at 315 and 345° to cracking of alkyl groups.

Table 5 Probable assignment of the endothermic reactions in the DTA curves of molybdenum(VI) complexes with TOA and TOMAC formed at low aqueous acidity

Temperature, °C		Probable assignment
TOA	TOMAC	
65	55	Dissolution and / or dissociation
	80	
125	165	
220		Dehydroxylation
240	260	
265	270	
300	305	Cracking
410	410	
475	475	

When the chloro complex with TOA is heated at 200°, the absorpition pattern due to the νMo=O is changed and the Mo–O–Mo stretching bands disappear (Fig. 7). However, since the other absorption bands are little changed, it is assumed that the dimeric complex with TOA is dissociated at 200°. On heating at 300°, the absorption due to the alkyl groups decrease in intensity, and the broad band due to the $\nu Mo=O$ appears newly. For the chloro complex with TOMAC, the OH bands disappears at 200°, but the variation in the other absorptions is similar to that for the complex with TOMAC (Fig. 8). The X-ray diffraction results for the thermal decomposition of the chloro complexes show the amorphous pattern on heating at 200-700° under the atmosphere of nitrogen, while the thermally decomposed products of the chloro complexes with TOA and TOMAC in air at above 600 and 500°, respectively indicate the patterns of MoO_3 (Figs 9–10). This is also supported by the infrared results shown in Figs 7–8. In addition, as the TG curves exhibit the weigh-loss at above 800°, it is expected that MoO_3 is formed by the thermal decomposition of the chloro complexes.

Table 6 Relative peak heights of some components in the gas chromatogram of the chloro complex of molybdenum(VI) with TOA formed at higher aqueous acidity as a function of heating temperature

Temp.,	Relative peak height*, mm							
°C	C_3H_4	C_2H_4	C_2H_6	C_3H_6	CH_3OH	CH_3Cl	1–C_4H_8**	2–C_4H_8**
150	3							
175	3							
200			1				1	
225					1			
250	26	3	2	1		5	2	4
275	28	7	11	2	3	15	5	7
300	30	13	21	1	13	6	10	15
325	25	23	30	1	22	23	22	23
350	80	77	108		2	30	76	78
375	183	140	280	3	7		150	205
400	103	40	145	1		62	3	12
425	26	3	14	1		3		
450	42	14	7	1		5		
475	15	21	3					
500	18	7	1					

*Sensitivity range $4\cdot10^3$ µV

**1– or 2–C_4H_8 denotes 1– or 2–butene

Table 7 Relative peak heights of some components in the gas chromatogram of the chloro complex of molybdenum(VI) with TOMAC formed at higher aqueous acidity as a function of heating temperature

Temp.,	Relative peak height*, mm							
°C	C3H4	C2H4	C2H6	C3H6	CH3OH	CH3Cl	1–C4H8**	2–C4H8**
150					1			
175					55			
200		1		1	680	5		
225	13	1	1	2	1800	2		
250		1	1		690	1		
275	172	1	1	3		1400	1	2
300	168	2	1	4		800		
325	117	6	8	5		540	3	7
350	112	13	17	4	2	174	11	13
375	120	47	42	3		19	42	37
400	47	36	52	4	3	72	28	56
425	218	24	280	3			28	54
450	196	9	147		2	23	1	3
475	34	1	2	2				
500	155	7	3	2		2		1

*Sensitivity range $4 \cdot 10^3$ μV

**1– or 2–C4H8 denotes 1– or 2–butene

Table 8 Probable assignment of the endothermic reactions in the DTA curves of molybdenum(VI) chloro complexes with TOA and TOMAC formed at higher aqueous acidity

Temperature, °C		Probable assignment
TOA	TOMAC	
80	80	Dissolution
125	115	Release of water
190	200	Dissociation
275	270	Release of HCl or CH3Cl
315	315	Cracking and dechlorination
370	345	
435	435	

Thus the large exotherms, which appears at 485 and 470° in the DTA curves in air of the chloro complexes with TOA and TOMAC, respectively and the

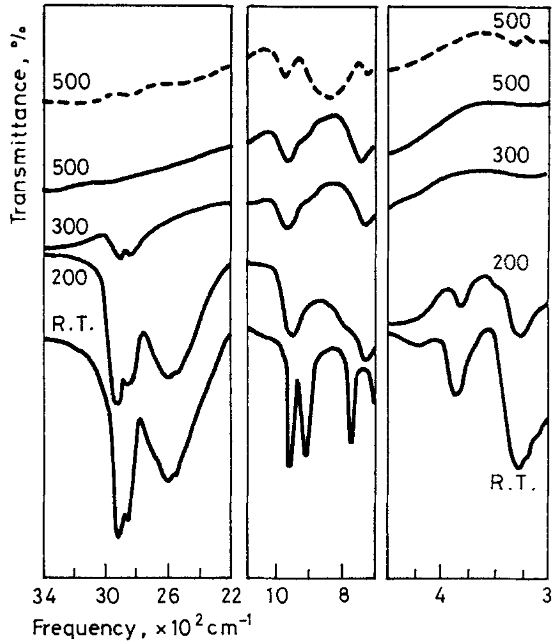


Fig. 7 Infrared spectra of the residues derived from the chloro complex of molybdenum(VI) with TOA by heating temperature (Numerals on curves are heating temperatures, °C; Continuous and broken lines represent under atmospheres of nitrogen and air, respectively)

endotherm at 790° are explained to be attributed to the combustion of remaining carbon and the sublimation of MoO_3, respectively.

Accordingly the endotherms in the DTA curves of the chloro complexes with TOA and TOMAC under an atmosphere of nitrogen are interpreted as in Table 8. Hence it is considered that the thermal decompositions of the chloro complexes with TOA and TOMAC proceed in the sequences

$$(R_3NH)_2Mo_2O_4Cl_6\cdot 6H_2O \xrightarrow[\text{liquefaction, }-H_2O]{80-115\,^{\circ}C} (R_3NH)_2Mo_2O_4Cl_6$$

$$\xrightarrow[\text{dissociation}]{200\,^{\circ}C} R_3NH\,MoO_2Cl_3 \xrightarrow[-HCl]{275\,^{\circ}C} R_3N\cdot MoO_2Cl_2$$

$$\xrightarrow[\text{cracking, }-Cl^{-}]{315-435\,^{\circ}C} Mo+MoO_3$$

and

$$(R_3R'N)_2Mo_2O_4Cl_6\cdot 6H_2O \xrightarrow[\text{liquefaction}-H_2O]{80-125\,^\circ C}$$

$$(R_3R'N)_2Mo_2O_4Cl_6 \xrightarrow[\text{dissociation}]{200\,^\circ C} R_3R'N\,MoO_2Cl_3 \xrightarrow[-CH_3Cl]{270\,^\circ C}$$

$$R_3N\cdot MoO_2Cl_2 \xrightarrow[\text{cracking},\ -Cl]{315-435\,^\circ C} Mo+MoO_3\,,$$

supporting the proposed structures [III] and [IV] for the complexes with TOA and TOMAC:

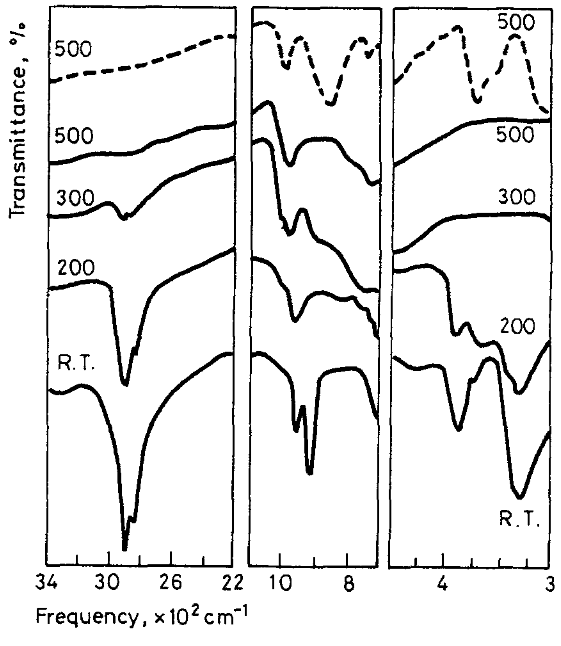


Fig. 8 Infrared spectra of the residues derived from the chloro complex of molybdenum(VI) with TOMAC by heating temperature (Numerals on curves are heating temperatures, °C; Continuous and broken lines represent under atomosphers of nitrogen air, respectively)

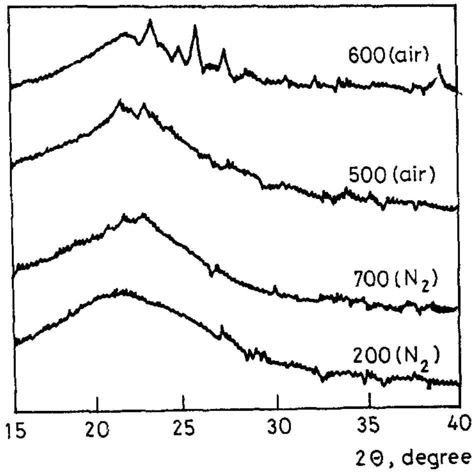


Fig. 9 X-ray diffraction diagrams of the residues derived from the chloro complex of molybdenum(VI) with TOA formed at higher aqueous acidity (Numerals on curves are heating temperatures, °C; N_2 or air in parenthesis denotes under the respective atomospher)

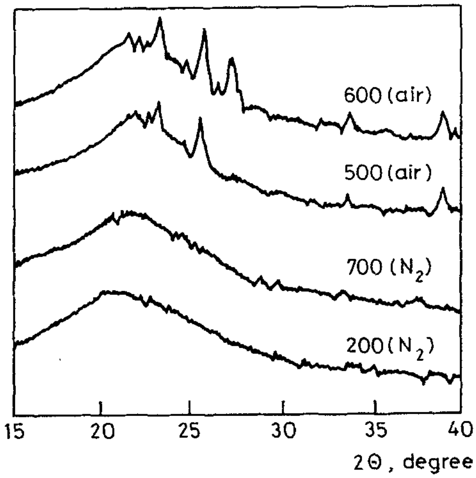
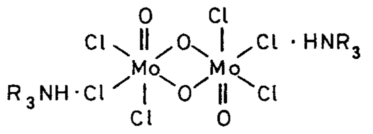
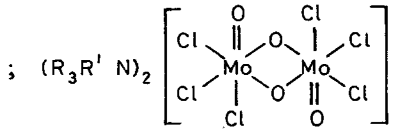


Fig. 10 X-ray diffraction diagrams of the residues derived from the chloro complex of molybdenum(VI) with TOMAC formed at higher aqueous acidity (Numerals on curves are heating temperatures, °C; N_2 or air in parenthesis denotes under the respective atomospher)



[III]



[IV]

* * *

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Zusammenfassung — Komplexe von Molybdän(VI) mit Trioktylamin (TOA, R_3N) und Trioktylmethylammoniumchlorid (TOMAC, $R_3R'NCl$) wurden hergestellt, mittels TG und DTA in Luft und in Stickstoffatmosphäre untersucht. Die thermischen Zersetzungsprodukte der Komplexe (flüchtige Substanzen und Rückstände) wurden mittels Gaschromatographie, Röntgendiffraktion und IR-Spektroskopie untersucht. Es wurde gezeigt, daß die Komplexe thermisch zu MoO_3 zerfallen, indem die an das Molybdän(VI)-Ion gebundenen Alkylgruppen abgekrackt werden. Die Ergebnisse der thermischen Zersetzungsprozesse wird diskutiert und auf der Basis der erhaltenen Ergebnisse die wahrscheinliche Struktur der Komplexe dargelegt.