

THERMAL DECOMPOSITION OF THE SOLVENT-EXTRACTED CHLORO COMPLEXES OF VANADIUM(IV) WITH TRIOCTYLAMINE AND TRIOCTYLMETHYLAMMONIUM CHLORIDE

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The complexes $(R_3NHVO(OH)Cl_2)_2$ and $(R_3R'NVO(OH)Cl_2)_2$ prepared by drying in vacuo the organic solutions from the extraction into benzene of aqueous vanadyl chloride solution with trioctylamine (TOA, R_3N) and trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$), were studied by thermogravimetry and differential thermal analysis under an atmosphere of nitrogen, and the products of their thermal decomposition, such as volatile matter and residues, by gas chromatography, X-ray diffraction and infrared spectroscopy. It was found that the complexes with TOA and TOMAC thermally decompose to V_2O_3 at 200–300° by cracking of the compounds $R_3NHVO(OH)Cl_2$ and $R_3R'NVO(OH)Cl_2$ formed via dissociation of the complexes at about 150°.

The solvent extraction of metals with long-chain aliphatic amines has been investigated by a number of researchers, but the properties of the complexes isolated from their organic solutions have received little attention. In order to obtain further information concerning their compositions, the thermal decompositions of the chloro complexes of copper(II) [1], zirconium(IV) [2], vanadium(IV) [3] and uranium(VI) [4] were studied in air, and those of divalent manganese, cobalt, copper and zinc under an atmosphere of nitrogen [5]. The present paper extends the work to the thermal behaviour of chloro complexes of vanadium(IV) with trioctylamine (TOA, R_3N) and trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$) under an atmosphere of nitrogen, in comparison with air [3].

Experimental

Chemicals

TOA and TOMAC of high purity (both > 99%, Koei Chemical Co. Ltd., Osaka) were used without further purification and diluted with benzene. An aqueous solution of vanadium(IV) was prepared by dissolving vanadyl chloride, $VOCl_2$, in 0.06 mol dm⁻³ hydrochloric acid. All chemicals used were of analytical reagent grade.

Preparation and analysis of complexes

On the basis of the distribution results, the organic solutions saturated with vanadium were prepared as follows: 0.05 mol dm⁻³ TOA and TOMAC in benzene was shaken for 10 min at 20° with an aqueous solution of 0.1 mol dm⁻³ vanadyl chloride in 0.06 mol dm⁻³ hydrochloric acid containing 9.8 mol dm⁻³ lithium chloride; the organic phase was centrifuged and shaken with a fresh aqueous solution; this procedure was repeated twelve times. The organic solutions so obtained were heated in vacuo at 50–60° to remove benzene. The benzene-freed complexes with TOA and TOMAC exist as dimers of the stoichiometric compositions (R₃NHVO(OH)Cl₂)₂ and (R₃R'NVO(OH)Cl₂)₂ [6].

Analysis

The complexes were studied by thermogravimetry (TG) and differential thermal analysis (DTA), and their thermal decomposition products such as volatile matter and residues were checked by gas chromatography, X-ray diffraction and infrared spectroscopy. The TG and DTA were carried out under an atmosphere of nitrogen at a heating rate of 5 deg/min and a nitrogen flow rate of 50 ml min⁻¹, automatic recording thermobalance and DTA apparatus made by the Agne Research Centre, using alumel-chromel thermocouples, with 40 mg of sample, and α -alumina as reference material for the measurement of differential thermal electromotive force. The residues were produced from the complex by heating to the required temperatures at a rate of 5 deg/min under the same atmosphere. Infrared spectra were recorded on Japan Spectroscopic IRA-1 (4000–650 cm⁻¹) and IR-F (700–200 cm⁻¹) grating spectrometers. X-ray powder diffraction diagrams were obtained with a Geigerflex recording X-ray diffractometer with filtered copper radiation (generator operating at 30 kV and 15 mA, divergence slits 1° × 1°, receiving slit 0.3 mm, scanning speed 2° min⁻¹, chart speed 10 mm min⁻¹, time constant 2 s, scale factor 16, glancing angle 5°). The volatile matter generated during the DTA was collected with a 2 ml syringe at the gas outlet of the DTA apparatus and analyzed with a Shimadzu GC-6AMPTF gas chromatograph under the following analytical conditions: carrier gas, helium at 40 ml 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 concentrations and water contents of portions of the solution were determined by Volhard and Karl Fischer titrations. Further, the benzene solutions were washed with 1 mol dm⁻³ nitric acid, and the vanadium in the acidic layers was then determined with EDTA, with xylenol orange as indicator [7, 8].

Results and discussion

The TG and DTA curves of vanadyl complexes with TOA and TOMAC are shown in Fig. 1. For the complex with TOA, the TG curve exhibits a weight loss of 81.6% at 300° and of 3.0% at 300–450°, while the DTA curve reveals endothermic reactions at 160, 220, 230, 285 and 305°. The complex with TOMAC displays weight losses of 81.4 and 5.2% at 300 and 300–450°, respectively, in the TG curve and endotherms at 150, 210, 220, 235, 240 and 260° in the DTA curve. Additionally, from Fig. 1 it is observed that endothermic reactions occur in the DTA curves at the point near the change in shape of the TG curve.

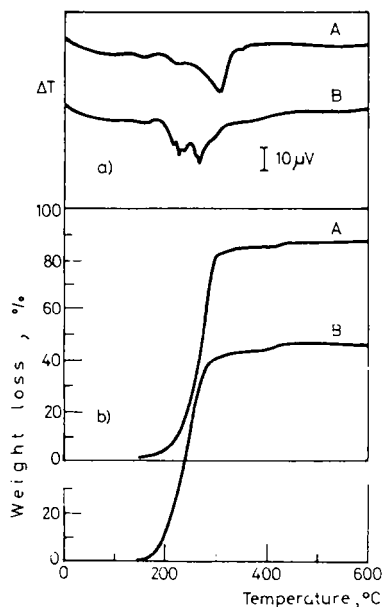


Fig. 1 DTA curves (a) and TG curves (b) of the vanadyl complexes with A, TOA; B, TOMAC

The volatile matter generated in the thermal decompositions of the vanadyl complexes with TOA and TOMAC contains 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 data are illustrated in Tables 1 and 2, where the relative peak heights in the gas chromatogram for some of the components are indicated as a function of the heating temperature. The changes in the molar ratio $[Cl]/[V]$ in the residues obtained by heating the complexes with TOA and TOMAC are given in Table 3. From these it is seen that the amount of components detected above 250° increases with increase of the temperature, in accordance with the weight loss in the TG curve, and the maximum amounts of the volatile matter correspond to

Table 1 Relative peak heights of some components in the gas chromatogram of the vanadyl complex with TOA as a function of heating temperature

Temp., °C	Relative peak height*, mm					
	C ₃ H ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	CH ₃ OH	CH ₃ Cl
150	7					
175	5				1	
200	7	1	1	2		
225				1		
250	14	2	3	2	3	1
275	13	2	3	2	2	1
300	10	3	4	3	2	1
325	37	6	10	3	9	5
350	33	12	11	2	12	3
375	28	14	12	2	12	
400	29	23	27	2		22
425	23	15	19	2		14
450	48	49	43	3		22
475	33	23	15	1		
500	27	22	13	2		

* Sensitivity range $4 \times 10^3 \mu\text{V}$

Table 2 Relative peak heights of some components in the gas chromatogram of the vanadyl complex with TOMAC as a function of heating temperature

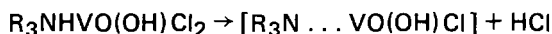
Temp., °C	Relative peak height*, mm					
	C ₃ H ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	CH ₃ OH	CH ₃ Cl
150	5				17	
175	7	1		2	336	
200	16	3		3	2500	
225	12	2	1	3	270	
250	7	3	3	3	18	1550
275	10	2	6		10	3700
300	15	6	10			420
325	33	8	12	3	12	104
350	42	14	23	3	24	50
375	62	38	54	3	47	26
400	73	61	91	3	64	12
425	53	40	77	5	53	6
450	102	57	141	2	70	9
475	26	9	12	3	7	1
500		32	36	1	8	

* Sensitivity range $4 \times 10^3 \mu\text{V}$

Table 3 Compositions of the residues from the vanadyl complexes with TOA and TOMAC after heating to the stated temperatures

Temp., °C	Molar ratio [Cl]/[V]	
	TOA	TOMAC
150	2.0	1.9
200	1.8	1.7
250	1.1	1.1
300	0.7	0.3
350	0.2	0.1
400	0	0
500	0	0

the endotherms in the DTA curve. On the other hand, hydrogen chloride evolved from the complex with TOA is detected above 200° (before the detection of the organic components) and its maximum amount is obtained at about 250°, as in the thermal decomposition of divalent metal complexes [5]. It is therefore inferred that the thermal decomposition is initiated by the release of hydrogen chloride, followed by the decomposition of TOA. This implies that the endotherms at 220 and 230° in the DTA curve are to be assigned to the release of hydrogen chloride, accompanied by the decomposition of TOA. The TG curve reveals a weight loss corresponding to the theoretical value for the thermal reaction of the complex with TOA



where the conformation of the species VO(OH)Cl may be formed during the thermal decomposition of the amine [3]. In addition, it is considered that the endotherm at 305° arises from cracking of the alkyl group.

The volatile matter from the 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 contrast, the thermal decompositions of divalent metal complexes with TOA and TOMAC do not indicate the release of methyl alcohol, attributed to the absence of hydrolyzed species [6]. In Table 2, 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 200 and 275°, respectively, and those of hydrocarbons at 400–450°. These components are largely generated at the beginning of the thermal decomposition, implying that the decomposition of the complex with TOMAC releases methyl alcohol first and then methyl chloride. From this it is deduced that the endotherms in the DTA curves correspond, in turn, to the release of methyl alcohol, methyl chloride and hydrocarbons: those at 210, 220, 235 and 240° to the release of methyl alcohol, and those at 255 and 270° to dechlorination due to the evolution of methyl chloride and/or cracking (Table 3).

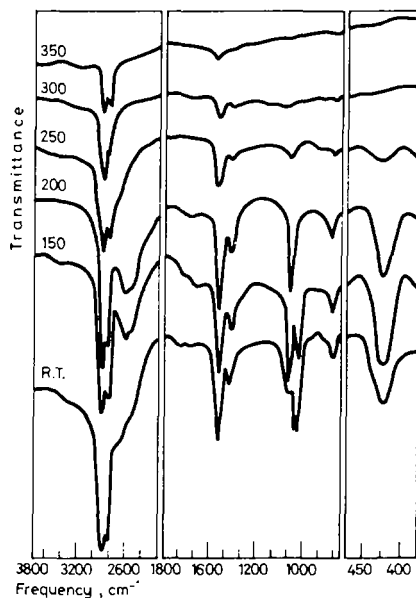


Fig. 2 Infrared spectra of the residues from the vanadyl complex with TOA after heating to the stated temperatures (numbers on curves are heating temperatures, °C)

In the infrared spectrum of the vanadyl complex with TOA (Fig. 2), the absorptions assigned to the stretching frequencies of the vanadyl group [7, 9] lie at 1005, 970, 954 and 935 cm^{-1} as a quartet band, indicating a lowering in the symmetry; the NH^+ stretching vibration at 2350 cm^{-1} for TOA hydrochloride shifts to a broad band centred at around 3000 cm^{-1} , and the $\text{V}-\text{Cl}$ stretching vibration appears at 430 cm^{-1} , confirming the formation of the chloro complex; the absorption of the OH stretching band appears at 3400 cm^{-1} and the OH bending bands at 1735 and 1620 cm^{-1} , implying the presence of hydrolyzed species. When the complex is heated at 150°, the $\text{V}-\text{O}$ stretching vibration appears at 1000 cm^{-1} , and simultaneously the vanadyl group absorptions at 1005, 970, 954 and 935 cm^{-1} decrease in intensity; further, the NH^+ stretching band at 3000 cm^{-1} shifts to lower frequency, at 2640 cm^{-1} . This is thought to result from dissociation of the dimeric complex, corresponding to the TG curve which exhibits the loss in weight. The vanadyl group absorptions and the OH bands have almost disappeared after heating at 200°. Following heating at 250°, the NH^+ band, the $\text{C}-\text{H}$ stretching bands at 2920 and 2860 cm^{-1} , the CH_3 degenerate (and CH_2 scissoring) and symmetrical bonding modes at 1465 and 1380 cm^{-1} , and the $\text{V}-\text{Cl}$ stretching band are decreased in intensity. The vanadyl complex with TOMAC (Fig. 3) gives an infrared spectrum similar to that for the complex with TOA, except for the absence of the NH^+ stretching band. However, since the splitting in the $\text{V}=\text{O}$ stretching bands at 968 and 955 cm^{-1} is less than that for the TOA complex, it is infrared that the symmetry of the latter is lower than that of the former. The changes in the infrared spectra of the thermal

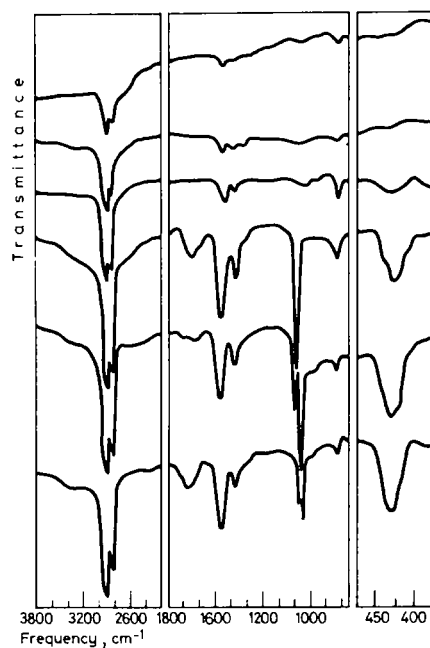


Fig. 3 Infrared spectra of the residues from the vanadyl complex with TOMAC after heating to the stated temperatures (numbers on curves are heating temperatures, °C)

Table 4 Probable assignments of the endothermic reactions in the DTA curves of the vanadyl complexes with TOA and TOMAC

Temp., °C		Probable assignment
TOA	TOMAC	
160	150	} dissociation and/or dehydration
	210	
220	220	} release of CH ₃ OH
	235	
	240	
	240	
230	255	} release of HCl
285	270	} release of CH ₃ Cl and cracking
305		} cracking

decomposition residues from the TOMAC complex are almost the same as those in the case of the TOA complex residues.

Hence, the endothermic reaction in the DTA curves are interpreted as in Table 4. Furthermore, the X-ray diffraction results (Figs 4 and 5) indicate that the residues

produced by heating the vanadyl complexes with TOA and TOMAC are of amorphous types, independently of the heating temperature. In the thermal decompositions of these complexes in air, however, the X-ray results reveal the pattern of V_2O_3 at 300° and of V_2O_5 on further heating [3]. It is thus presumed that V_2O_3 is formed during

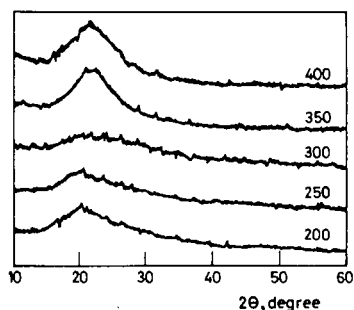


Fig. 4 X-ray diffraction diagrams of the residues from the vanadyl complex with TOA after heating to the stated temperatures (numbers on curves are heating temperatures, $^\circ\text{C}$)

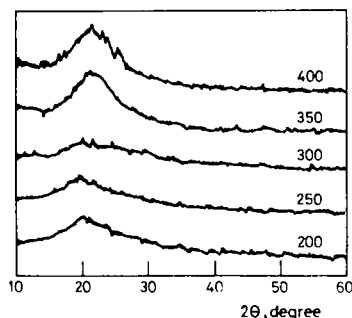
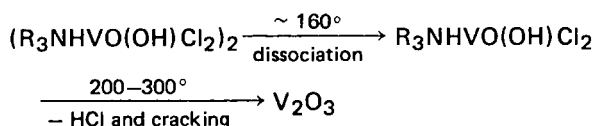
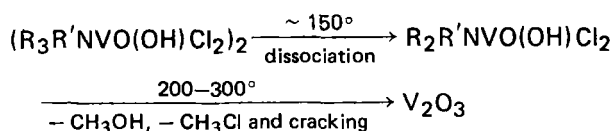


Fig. 5 X-ray diffraction diagrams of the residues from the vanadyl complex with TOMAC after heating to the stated temperatures (numbers on curves are heating temperatures, $^\circ\text{C}$)

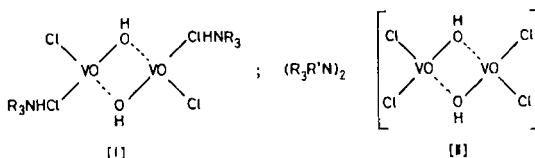
the decomposition of the complexes under an atmosphere of nitrogen. Accordingly, it is concluded that the thermal decompositions of the vanadyl complexes with TOA and TOMAC proceed in the sequences



and



supporting the proposed structures [I] and [II] for the vanadyl complexes with TOA and TOMAC:



We wish to thank the Koei Chemical Co. Ltd. for samples of TOA and TOMAC.

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Zusammenfassung — Die Komplexe $(R_3NHVO(OH)Cl_2)_2$ und $(R_3R'NVO(OH)Cl_2)_2$ wurden hergestellt, indem benzolische und wässrige Vanadylchlorid-Lösungen mit Trioctylamin (TOA, R_3N) und Trioctylmethylammoniumchlorid (TOMAC, $R_3R'NCl$) extrahiert und die erhaltenen Lösungen im Vakuum eingedampft wurden. Die Komplexe wurden in Stickstoffatmosphäre mittels TG und DTA untersucht und die thermischen Zersetzungsprodukte, und zwar sowohl die flüchtigen Verbindungen als auch die Rückstände, gaschromatographisch bzw. röntgendiffraktometrisch und IR-spektroskopisch bestimmt. Es wurde festgestellt, daß die Komplexe mit TOA und TOMAC bei 150° in die Verbindungen $R_3NHVO(OH)Cl_2$ und $R_3R'NVO(OH)Cl_2$ dissoziieren, die bei $200-300^\circ$ thermisch zu V_2O_3 zersetzt werden.

Резюме — Комплексы $(R_3NHVO(OH)Cl_2)_2$ и $(R_3R'NVO(OH)Cl_2)_2$ были получены отгонкой в вакууме бензольных экстрактов водных растворов ванадил хлорида с триоктиламином (R_3N , TOA) и с триоктилметиламмоний хлоридом (ТОМАК, $R_3R'NCl$). Термическое разложение комплексов было изучено в атмосфере азота с помощью термогравиметрии и ДТА, а летучие продукты и твердые остатки анализировались газовой хроматографией, рентгенофазовым анализом и ИК спектроскопией. Установлено, что комплексы при температуры 200–300° разлагаются до V_2O_3 с расщеплением соединений $R_3NHVO(OH)Cl_2$ и $R_3R'NVO(OH)Cl_2$, образующихся в результате диссоциации исходных комплексов при 150°.