

## MASS SPECTROMETRY OF $\pi$ -COMPLEXES OF TRANSITION METALS

### V\*. DIMERIC ( $\pi$ -CYCLOPENTADIENYL)DICARBOXYLATOVANADIUM COMPLEXES

Yu.S. NEKRASOV\*, D.V. ZAGOREVSKII and V.F. SIZOI

*Institute of Organo-Element Compounds, Academy of Sciences, Vavilova St. 28, Moscow, 117312 (U.S.S.R.)*

V.T. KALINNIKOV and A.A. PASYNSKII

*Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR, Moscow (U.S.S.R.)*

(Received April 24th, 1975)

#### Summary

Mass spectra of dimeric ( $\pi$ -cyclopentadienyl)dicarboxylatovanadium complexes  $[\pi\text{-C}_5\text{H}_5\text{V}(\text{OOCR})_2]_2$ , have been studied. The principal paths of fragmentation of the trihaloalkyl derivatives involve the formation of V—Hal bonds, whereas V—O bonds are formed during decomposition of acetato and formato complexes. An unusual increase in stability of dimeric and monomeric ions of the alkyl derivatives is observed in going from R = CH<sub>3</sub> to R = CF<sub>3</sub>. With aromatic complexes, only ions containing a single metal atom occur.

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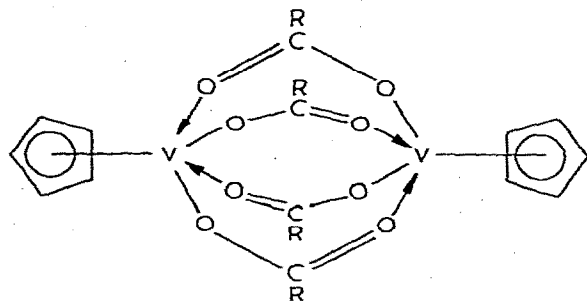
#### Introduction

Recently studied ( $\pi$ -cyclopentadienyl)dicarboxylatovanadium complexes [2-6] differ from other dimeric dicarboxylato complexes of transition metals [7] in that the former contain no V—V bonds (V—V bond distance 3.7 Å), with metal atoms linked by four bridging carboxylato groups (X-ray data).

In this paper we report a further investigation of these compounds by means of mass spectrometry intended to clarify structural features and the nature of chemical bonding in compounds of this "lantern" structure type. The complexes  $[\pi\text{-C}_5\text{H}_5\text{V}(\text{OOCR})_2]_2$  (I-VIII) have been synthesized according to the procedure cited previously [4].

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\* For part IV see ref. [1].



(I, R = H; II, R = CH<sub>3</sub>; III, R = CCl<sub>3</sub>; IV, R = CF<sub>3</sub>;

V, R = C<sub>6</sub>H<sub>5</sub>; VI, R = *m*-C<sub>6</sub>H<sub>4</sub>F; VII, R =  $\alpha$ -furyl; VIII, R =  $\alpha$ -thienyl)

All the compounds behave as antiferromagnetics and show the same temperature dependence of magnetic susceptibility. So the same molecular structure may be suggested for all of them.

### Results and discussion

Fragmentation pathways and stability of molecular ions I-VIII depend to a considerable degree on the nature of the substituent R. Thus, only the mass spectra of alkyl carboxylates I-IV\* indicate the presence of molecular ions,  $[\pi\text{-C}_5\text{H}_5\text{V}(\text{OOCR})_2]_2^+(P_2^+)$ , whereas monomeric ions,  $[\pi\text{-C}_5\text{H}_5\text{V}(\text{OOCR})_2]^+(P_1^+)$ , are the heaviest units observed in the spectra of aryl carboxylates V-VIII.

#### *Fragmentation of molecular ions of dimeric ( $\pi$ -cyclopentadienyl)di-alkylcarboxylatovanadiums I-IV*

All the alkyl carboxylates studied (I-IV) yielded mass spectra indicating the presence of molecular ions  $[\pi\text{-C}_5\text{H}_5\text{V}(\text{OOCR})_2]_2^+(P_2^+)$ . Their dependence of stability, under electron impact ( $W = P_2^+/\Sigma F_i$  [8]), on the substituent R increases across the series CH<sub>3</sub> < H < CCl<sub>3</sub> < CF<sub>3</sub>, i.e., with the electronegativity of the substituent (Table 1). This result appears unexpected, since as a rule stability of molecular ions changes in the opposite direction, cf. mass spectrometric data on copper carboxylates Cu<sub>2</sub>(OOCR)<sub>2</sub> [9,10].

The predominant path of  $P_2^+$  fragmentation involves the formation of monomeric ions  $[\pi\text{-C}_5\text{H}_5\text{V}(\text{OOCR})_2]^+(P_1^+)$ . The latter decompose to yield a number of ions containing a single metal atom. Similar to the stability of  $P_2^+$ , the probability of the formation of  $P_1^+$  ( $P_1^+/\{\Sigma P_1 + \Sigma P_2\}$ ) increases in going from R = CH<sub>3</sub> to R = CF<sub>3</sub> (Table 1). Other fragmentation paths include elimination of RCOO $\cdot$ , C<sub>5</sub>H<sub>5</sub> $\cdot$ , CX<sub>2</sub>COO and X, (X = Cl, F; see Schemes 1-3 and Table 2). Elimination of RCO $\cdot$  is a feature characteristic of the decomposition of  $[P_2 - \text{RCOO}]^+$  ions together with quite a number of other ions in the mass spectra of I-IV. The resulting ions (Schemes 1-3) contain highly stable V—O—V bonds [11]. Elimina-

\* Mass spectrum of ( $\pi$ -cyclopentadienyl)diacetatovanadium was reported by King [2]. However, he did not observe ions containing two metal atoms.

TABLE 1

SOME RATIOS CHARACTERISTIC OF STABILITIES OF MOLECULAR IONS ( $P_2^+$ ) AND PROBABILITIES OF MONOMERIC IONS ( $P_1^+$ ) AND IONS  $[P_1 - RCOO^-]^+$  IN THE MASS SPECTRA OF  $[\pi-C_5H_5V(OOCR_2)]_2$  I-IV

Characteristic	R = CH <sub>3</sub> (II)	R = H (I)	R = CCl <sub>3</sub> (III)	R = CF <sub>3</sub> (IV)
1	2	3	4	5
Stability of molecular ions $P_2^+/\Sigma P_2^a + \Sigma P_1$	$8 \times 10^{-5}$	$1.1 \times 10^{-2}$	$2.3 \times 10^{-2}$	$1.5 \times 10^{-1}$
Ability of molecular ions to decompose yielding monomers $P_2^+/\Sigma P_1$	$8 \times 10^{-5}$	$6 \times 10^{-3}$	$3 \times 10^{-2}$	$2.6 \times 10^{-1}$
Relative contributions of dimetallic ions to summary ion current $(\Sigma P_2/\Sigma P_2 + \Sigma P_1) \times 10^2$	1.1	2.5	26	40
Probabilities of monomeric ions $(P_1^+/\Sigma P_2 + \Sigma P_1) \times 10^2$	4.4	7.7	16	20
Ability of monomeric ions to fragmentation $(P_1^+/\Sigma P_1) \times 10^2$	4.5	4.0	21	34
Probabilities of ions $[P_1 - RCOO^-]^+$ $([P_1 - RCOO^-]^+/\Sigma P_2^+ \Sigma P_1) \times 10^2$	11.5	5.3	5.2	1.8
$([P_1 - RCOO^-]^+/\Sigma P_1) \times 10^2$	12.0	5.5	7.1	3.1
$[P_1 - RCOO^-]^+/P_1^+$	2.5	0.69	0.33	0.09

<sup>a</sup>  $\Sigma P_n$  is the overall ion current intensity from ions containing  $n$  metal atoms ( $n = 1$  or  $2$ ) including  $P_1^+$  and  $P_2^+$  ions.

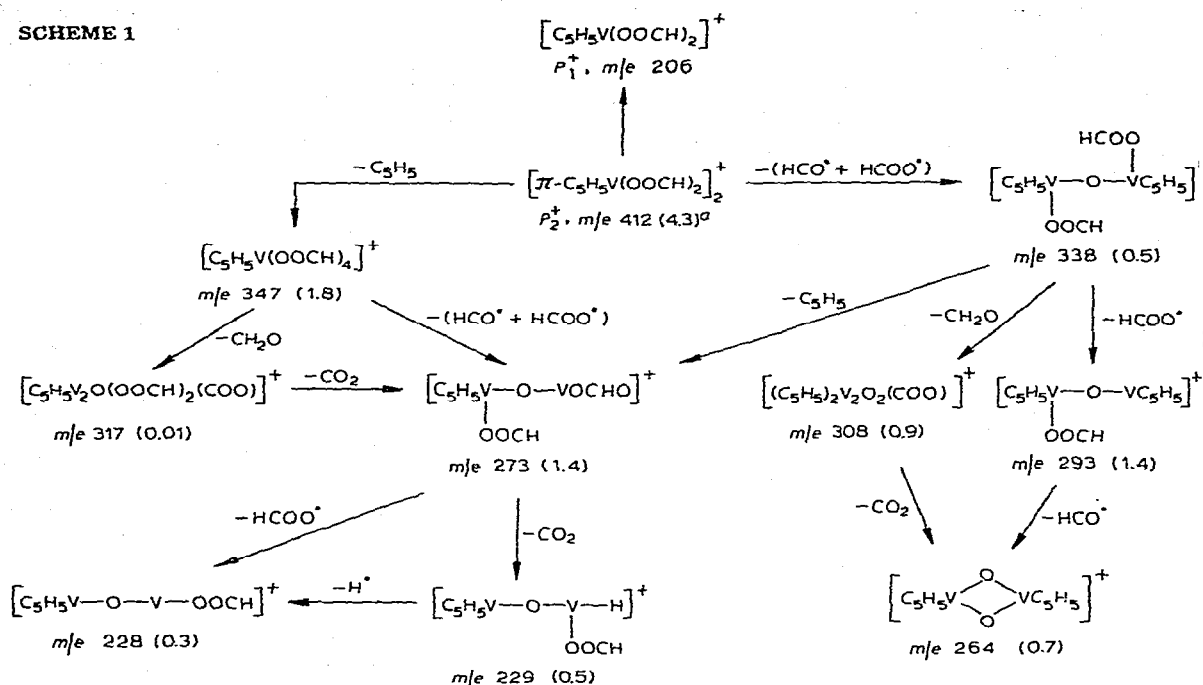
TABLE 2

DIMETALLIC IONS IN MASS SPECTRUM OF  $[\pi-C_5H_5V(OOCCl_3)_2]_2$

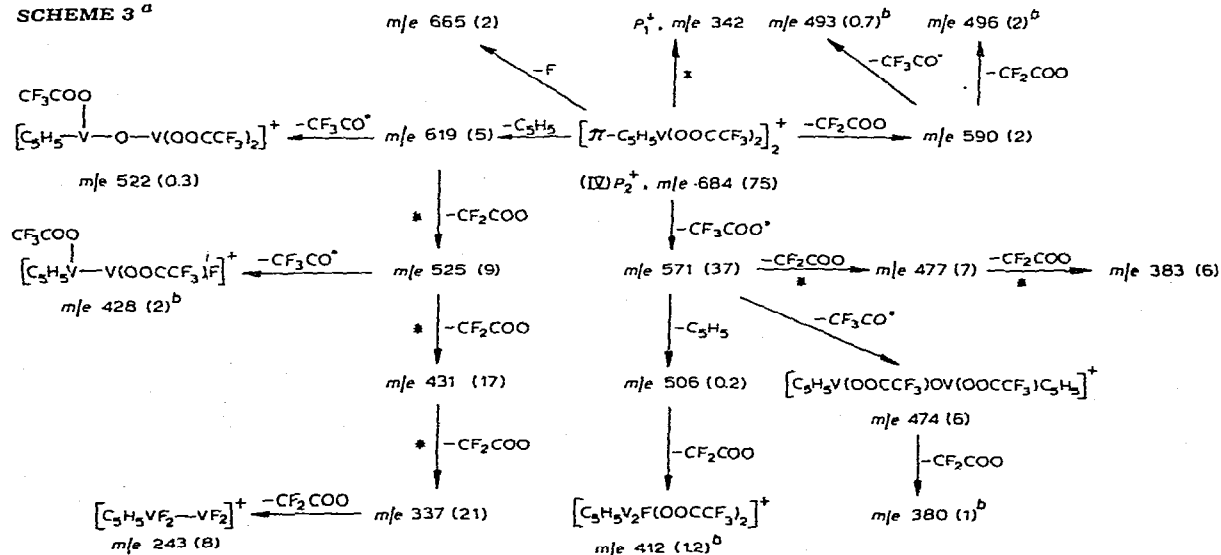
Ion	$m/e$	Intensity
$(C_5H_5)_2V_2(OOCCl_3)_4^+, P_2^+$	876 <sup>a</sup>	10.5
$(C_5H_5)_2V_2(OOCCl_3)_3(OOCCl_2)^+$	841	0.8
$(C_5H_5)_2V_2(OOCCl_3)_2(OOCCl_2)_2^+$	806	0.1
$(C_5H_5)_2V_2Cl(OOCCl_3)_3^+$	750	0.1
$(C_5H_5)_2V_2(OOCCl_3)_3^+$	715	7
$(C_5H_5)_2V_2(OOCCl_3)_2(OOCCl_2)^+$	680	0.1
$(C_5H_5)_2V_2Cl_2(OOCCl_3)_2^+$	624	11
$(C_5H_5)_2V_2Cl(OOCCl_3)_2^+$	589	26
$(C_5H_5)_2V_2Cl(OOCCl_3)(OOCCl_2)^+$	554	6
$(C_5H)_2V_2Cl_3(OOCCl_3)^+$	498	19
$(C_5H_5)_2V_2Cl_2(OOCCl_3)^+$	463	24
$(C_5H_5)_2V_2Cl(OOCCl_3)^+$	428	8
$(C_5H_5)_2V_2Cl(OOCCl_2)^+$	393	2
$(C_5H_5)_2V_2Cl_3^+$	337	11

<sup>a</sup> The values of  $m/e$  cited for the mass spectrum of III correspond to ions containing <sup>35</sup>Cl atoms.

SCHEME 1



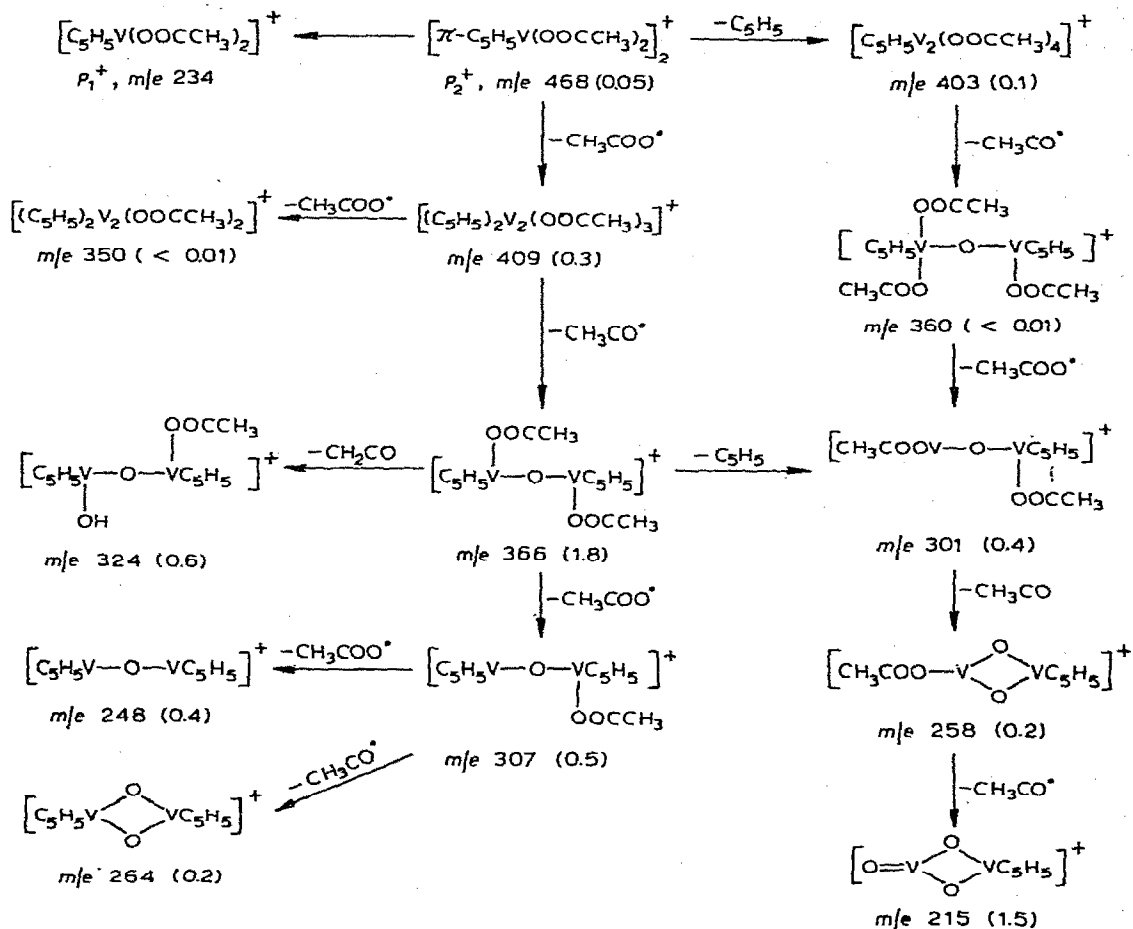
<sup>a</sup> Ion intensities (% of the maximum intensity peak) are given in brackets, after *m/e* values.

SCHEME 3<sup>a</sup>

<sup>a</sup> Processes substantiated by the corresponding metastable peaks are labelled by asterisks in this and following Schemes.

<sup>b</sup> Further fragmentation of these ions involve elimination of  $CF_2COO$ ,  $CF_3COO^+$  or  $CF_3CO^+$  and lead to ions with intensities below 0.2%.

SCHEME 2



tion of  $\text{CX}_2\text{COO}$  is characteristic of haloalkyl derivatives only ( $\text{X} = \text{Cl}, \text{F}$ ); the process appears to involve halogen migration to the metal atom [9,10,12]. Under the mass spectrometric experimental conditions, the formation of the  $\text{V}-\text{X}$  bond is characterized by lower activation energy than the competitive process for  $\text{V}-\text{O}$  bonding. This follows from the comparison of ion current intensities which correspond to eliminating  $\text{CF}_2\text{COO}^\bullet$  or  $\text{CF}_3\text{CO}^\bullet$  from the same precursor (cf. peak intensities at  $m/e$  525 and 522, 431 and 428, 477 and 474, 496 and 493 resulting from fragmentation of ions with  $m/e$  of 619, 525, 571 and 590, respectively, Scheme 3).

#### Fragmentation of monomeric ions ( $P_1^+$ ) of ( $\pi$ -cyclopentadienyl)di-alkylcarboxylatovanadiums I-IV

Monomeric ions I-IV are directly formed from molecular ions, as evidenced by the corresponding metastable peak in the mass spectrum of IV [ $m/e$  171.0: 684 ( $P_2^+$ )  $\rightarrow$  342 ( $P_1^+$ )].

The mass spectra show that the most important processes involved in fragmentation of mononuclear ions are elimination of ketene in the case of the

TABLE 3

VALUES OF  $m/e$  AND INTENSITIES (% WITH RESPECT TO  $I_{\max}$ ) OF IONS OCCURRING IN MASS SPECTRA OF MONOMERIC UNITS I-IV  $C_5H_5V(OOCR)_2$  <sup>a</sup> [I, R = X = H; II, R = CX<sub>3</sub> (X = H); III, R = CX<sub>3</sub> (X = Cl); IV, R = CX<sub>3</sub> (X = F)]

Ion	II	I	III	IV
1	2	3	4	5
$C_5H_5V(OOCR)_2, P_1^+$	234(28)	206(29)	438(71)	342(100)
$P_1 - X^+$			403(26)	233(1)
$P_1 - 2X^+$			368(6)	
$P_1 - CX_2COO^+$		162(29)	312(42)	248(98)
$P_1 - RCOO^+$	175(69)	161(20)	277(24)	229(9)
$P_1 - RCOO - X^+$	174(15)			
$C_5H_5VX(OX)^+$		134(33)		
$C_5H_5VOX^+$	133(71)	133(11)		151(<0.1)
$C_5H_5V(X)(OOCX)^+$				198(3.5)
$C_5H_5VX_3^+$			221(17)	
$C_5H_5VX_2^+$			186(100)	154(48)
$C_5H_5V(OOCX)^+$				179(4)
$C_5H_5VX^+$		117(25)	151(53)	135(24)
$C_5H_5VO^+$	132(100)	132(100)		132(<0.1)
$VO^+$	67(28)	67(16)		67(4)
$P_1 - (R-X)CO^+$	192(82)	178(18)		
$P_1 - RCO^+$	191(11)			
$C_5H_5V(OH)_2^+$	150(72)	150(9)		
$C_5H_5VO(OH)^+$	149(34)	149(2)		
$V(OOCR)_2^+$	169(4)	141(1.5)		
$VOOCR^+$	110(4)	96(4)		
$HOVOOCR^+$	127(18)	113(3)		
$OVOOCR^+$	126(5)			
$V(OH)_2^+$	85(9)	85(4.5)		
$VO(OH)^+$	84(8)			
$VOH^+$	68(7)	68(2.5)		
$C_5H_5V^+$	116(19)	116(60)		

<sup>a</sup> Only metal containing ions are included.

acetato complex, of CO in the case of the formato complex and of CX<sub>2</sub>COO in the case of the trihaloacetato derivatives (Table 3).

The principal pathways for the decomposition of monomeric ions ( $P_1^+$ ) of aliphatic carboxylates I-IV resemble those characteristic of transition metal carboxylato complexes studied earlier [9,10,12]. As in the case of  $P_2^+$ , a general feature of  $P_1^+$  decomposition is elimination of the RCOO<sup>•</sup> radical.

The acetato and formato complexes are characterized by cyclopentadienyl radical elimination which occurs with  $P_1^+$  and some other fragment ions, e.g.,  $[P_1 - RCOO]^+$ ,  $[P_1 - (R-H)CO]^+$ ,  $[C_5H_5VO]^+$  etc. With haloacetato derivatives, a general path of fragmentation of  $P_1^+$  involves elimination of the halogen atom and CX<sub>2</sub>COO, as is the case with the corresponding molecular ions (Tables 2 and 3, Scheme 3).

With the acetato and formato derivatives, the principal fragmentation pathways lead to the formation of the  $[C_5H_5VO]^+$  ion which gives rise to the greatest intensity peak in the mass spectrum. In the first case it is formed via successive elimination of ketene and acetic acid molecules and in the second via HCOO<sup>•</sup> and HCO<sup>•</sup> radicals respectively. It should be noted that the  $[C_5H_5VO]^+$  ion

never occurs in mass spectra of trihaloacetato complexes. In this case the principal fragmentation path involves the formation of  $[C_5H_5VX]^+$  and  $[C_5H_5VX_2]^+$  ions containing V—X bonds. This may be due to lower energy losses of the process and/or higher stability of the ions, as compared to those involved in the formation of  $[C_5H_5VO]^+$ .

Stability of monomeric ions ( $P_1^+/\Sigma P_1$ , Table 1) changes similarly to the stability of molecular ions, i.e., an increase with electron-withdrawing power of the substituent R. The relative ion current intensity of  $[P_1 - RCOO]^+$  ( $[P_1 - RCOO]^+/P_1^+$ ) decreases in the same series (Table 1). The degree of the process under electron impact conditions is determined by:

- (i) energy of the bond that undergoes rupture,
- (ii) stability of the ions formed,
- (iii) stability of the eliminated radical.

The intensities of  $[P_1 - RCOO]^+$  ions follow the RCOO<sup>•</sup> stability series [13]. As for  $[P_1 - RCOO]^+$ , their stability should decrease when passing from electron donor to electron acceptor substituents [14], in agreement with our

TABLE 4

MASS SPECTRA OF ( $\pi$ -CYCLOPENTADIENYL)DICARBOXYLATOVANADIUMS V-VIII CONTAINING AROMATIC AND HETEROCYCLIC SUBSTITUENTS,  $C_5H_5V(OOCR)_2$  (V, R =  $C_6H_5$ ; VI, R =  $C_6H_4F$ ; VII, R =  $\alpha$ -Furyl; VIII, R =  $\alpha$ -Thienyl<sup>a</sup>)

Ion	V	VI	VII	VIII
1	2	3	4	5
$C_5H_5V(OOCR)_2^+, P_1^+$	358(100)	394(100)	338(100)	370(73)
$C_5H_5V(OR)(OOCR)^+$			310(2)	342(100)
$C_5H_5V(OOCR)R^+$	314(2)		294(30)	326(15)
$V(OOCR)_2^+$	293(1)	329(1)	273(1)	
$C_5H_5V(OR)_2^+$			282(4)	
$C_5H_5VR(OR)^+$			266(3)	
$C_5H_5VR_2^+$	270(27)		250(6)	
$V(OR)(OOCR)^+$	265(3)	301(3)		277(24)
$C_5H_5V(OH)(OOCR)^+$	254(5)	272(10)	244(6)	260(34)
$C_5H_5VO(OOCR)^+$	253(3)	271(3)	243(3)	
$VR(OOCR)^+$	249(2)	285(3)	229(4)	
$C_5H_5VH(OOCR)^+$	238(2)		227(7)	244(19)
$C_5H_5V(OOCR)^+$	237(9)	255(9)	226(3)	243(10)
$V(OR)_2^+$	237(9)		217(6)	
$C_5H_5VO(OR)^+$				231(30)
$VR(OR)^+$	221(48)			233(49)
$C_5H_5VOR^+$	209(4)	227(4)	199(16)	
$VR_2^+$	205(30)			
$C_5H_5VR^+$	193(18)	211(11)	183(25)	199(7)
$VO(OR)^+$				166(45)
$V(OOCR)^+$			178(1)	
$C_5H_5VO(OH)^+$				149(63)
$VOR^+$		162(3)		
$VR^+$			145(7)	
$C_5H_5VO^+$	132(4)	132(10)	132(19)	
$C_5H_5V^+$	116(19)	116(16)	116(63)	
$VOH^+$			68(8)	
$VO^+$	67(8)	67(18)	67(44)	67(4)
$V^+$	51(2)	51(3)	51(16)	

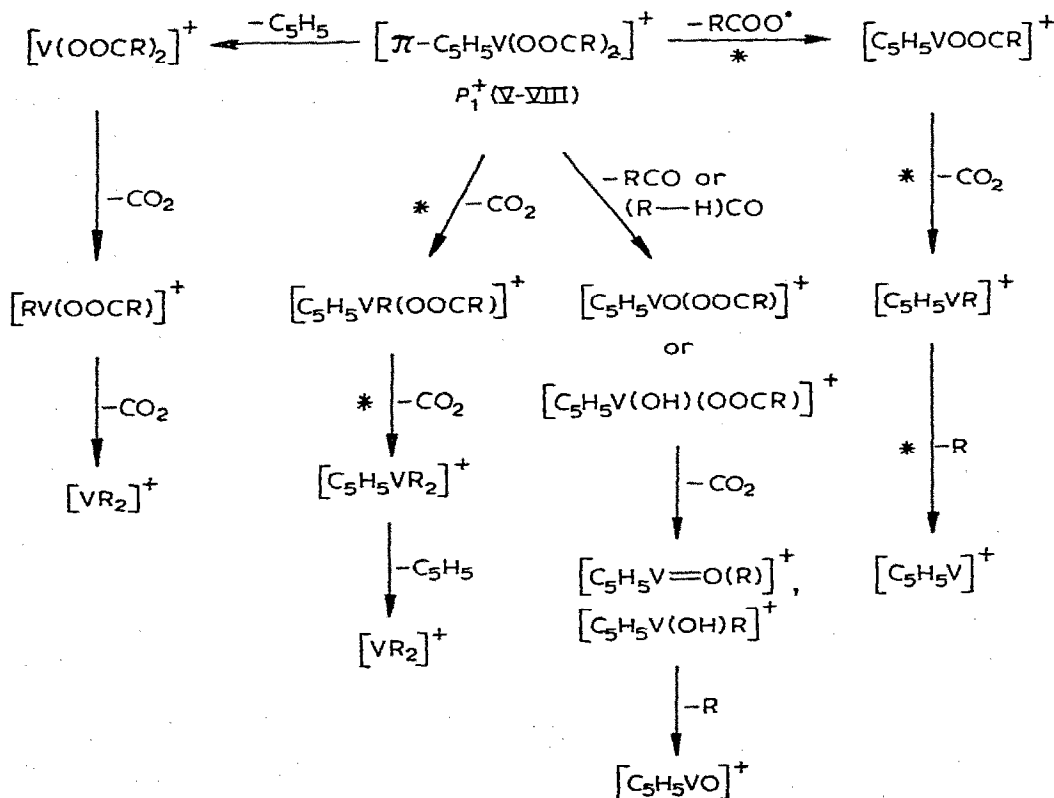
<sup>a</sup> Only metal containing ions are included.

observations (Table 1). Thus, the enhancement of  $P_1^+$  and  $P_2^+$  stabilities on going from  $R = CH_3$  to  $R = CF_3$  seems to be due to a decrease of the stability of the  $RCOO^{\cdot}$  type radicals and/or to an increase in the  $V-OOCR$  bond strength. When discussing rearrangement processes, one should consider in addition the ability of hydrogen, halogen and oxygen atoms to undergo migration, also the strengths of the resulting bonds,  $V=O$ ,  $V-OH$ ,  $V-Cl$ ,  $V-F$  etc.

An increase in dimetallic ion contribution to the general fragmentation scheme when going from  $R = CH_3$  to  $R = CF_3$  may result from some difference between molecular ion structures of I and II on the one hand and III with IV on the other.

In particular, it is possible that in the latter case direct  $V-V$  bonding occurs. In this connection, it is important to note that III and IV give mass spectra indicating ions that should necessarily contain  $V-V$  bonds:  $[(C_5H_5)_2V_2Cl_3]^+$ ,  $[(C_5H_5)_2V_2F_3]^+$ ,  $[(C_5H_5)_2V_2F_4]^+$  and so on. However, a further investigation is needed to find out whether this bond is formed at the step of the molecular ion or at some other step, and we will not discuss this question here. It seems possible that the variable stability of molecular ions I-IV may be due to some variation in the nature of vanadium-oxygen bonds in molecular ions possessing structures of neutral molecules.

SCHEME 4



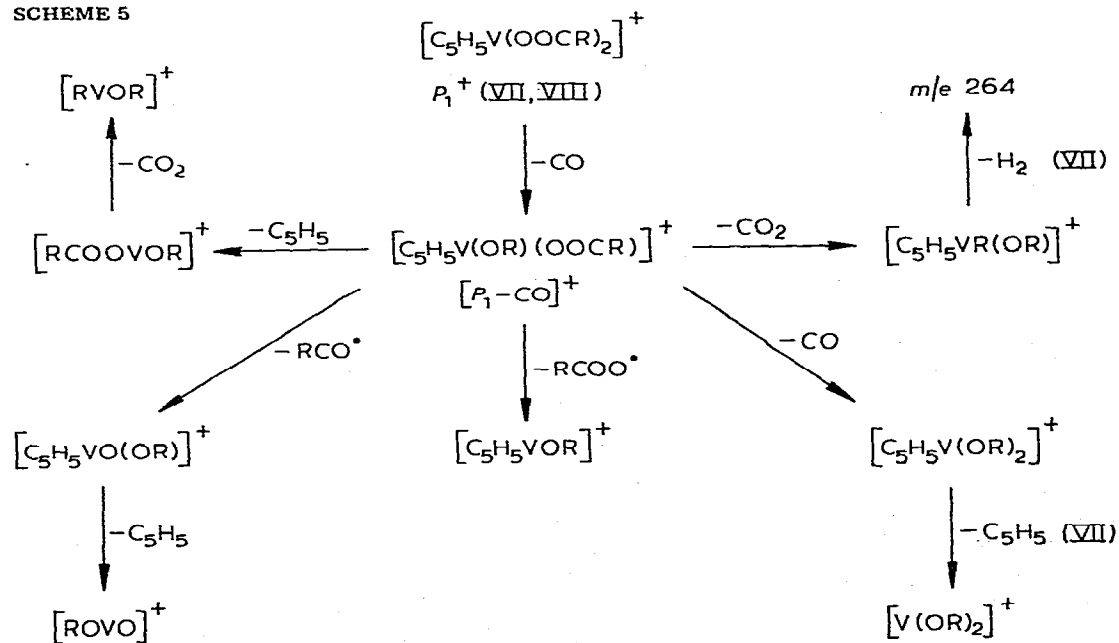


*Fragmentation of monomeric ions of ( $\pi$ -cyclopentadienyl)dicarboxylatovanadiums V-VIII containing aromatic and heterocyclic substituents*

There are no peaks due to molecular ions in the mass spectra of aromatic and heterocyclic carboxylates V-VIII. The heaviest ions that occur in this case are monomeric units ( $P_1^+$ ), which indicates an exceedingly low stability of molecular and other dimetallic ions. Similar to the corresponding ions from alkylcarboxylato complexes,  $P_1^+$  ions from V-VIII decompose via elimination of  $\text{RCOO}^\cdot$  or  $\text{C}_5\text{H}_5$  radicals. The amount of fragmentation via the first process is lower and via the second higher than in the case of the acetate or formate. A distinguishing feature characteristic of fragmentation of aromatic carboxylates lies in elimination of  $\text{CO}_2$  molecules and the associated migration of the substituent R towards a vanadium atom which results in the  $[\text{C}_5\text{H}_5\text{VR}_n]^+$  and  $[\text{VR}_n]^+$  ions ( $n = 1, 2$ ) (Scheme 4, Table 3).

The mass spectra of ( $\pi$ -cyclopentadienyl)dicarboxylatovanadiums containing aromatic or heterocyclic substituents are characterized by the occurrence of intensive (frequently the most intensive in the spectrum) peaks corresponding to carboxylic acid ions. Poor reproducibility of the peak intensities, which depend on the inlet temperature as well as on the time the sample is kept in the ion source, allowed us to suppose that  $\text{RCOOH}^+$  ions originate from ionization of the corresponding acids which are formed owing to thermal or hydrolytic decomposition of initial compounds; earlier, McDonald and Shannon [15] pointed to the same possibility in their study on metal acetylacetonates. To check this assumption, we have measured the mass spectrum of VII using the instrument flushed through with  $\text{D}_2\text{O}$  vapour and observed an intensive peak at  $m/e$  113 corresponding to deuterofuran carboxylic acid  $\text{C}_4\text{H}_3\text{OCOOD}^+$  along with a peak at  $m/e$  112 ( $\text{C}_4\text{H}_3\text{OCOOH}^+$ ). This indicates that carboxylic acid ions present in

SCHEME 5



mass spectra of ( $\pi$ -cyclopentadienyl)dicarboxylatovanadiums result mainly from thermal or hydrolytic decomposition of initial compounds in the ion source.

### Experimental

Mass spectra were obtained with an MX-1303 instrument equipped with a direct inlet system using 30 eV electrons at an accelerating voltage of 2 kV; the ionization chamber temperature was 200°C and the inlet system kept at temperatures 10 to 25°C higher than the temperature at which sample vaporization begins.

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