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MASS SPECTRA OF THE β-DIKETONE CHELATES OF 1,6-DICHLORO-1,5-CYCLOOCTADIENERHODIUM

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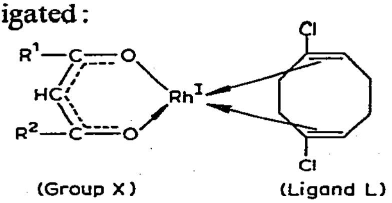
SUMMARY

The mass spectra of a number of complexes of general formula XRh^IL, where X is 1,3-propanedione substituted at positions 1 and 3 with CH_3, C_6H_5, p-$C_6H_4CH_3$, p-$C_6H_4OCH_3$, p-C_6H_4Cl and p-$C_6H_4NO_2$ groups respectively and L is 1,6-dichloro-1,5-cyclooctadiene, have been measured. The spectra were used to characterize the fragmentation patterns of the molecular ions of the complexes under investigation and to explain the character of the Rh–L bond in the molecular ion-radicals $[XRhL]^{+\cdot}$ and in the fragments $[RhL]^+$. The molecular ion-radicals of all complexes decompose to yield the fragments X^+ and $[RhL]^+$, but not $[RhX]^{+\cdot}$. The appearance potential values (*AP*) of the fragment $[RhL]^+$ obtained from various $[XRhL]^{+\cdot}$ ions appear to depend on the character of the 1,3-substituents in the ligand X. The difference in the *AP* values of $[RhL]^+$ for the *n*th and first complex is identical with the difference in dissociation energies of the X–Rh bond in the complex [XRhL] and may be related to the rates of polymerization of chloroprene initiated with the complexes studied here.

INTRODUCTION

Recently, we have prepared a number of new complexes of monovalent rhodium, recorded their IR and NMR spectra and followed their effects on the dimerization and polymerization of chloroprene[1,2]. The following complexes have been investigated:



(I) $R^1=R^2=CH_3$
(II) $R^1=CH_3, R^2=Ph$
(III) $R^1=R^2=Ph$
(IV) $R^1=R^2=p$-$CH_3C_6H_4$
(V) $R^1=R^2=p$-$CH_3OC_6H_4$
(VI) $R^1=R^2=p$-ClC_6H_4
(VII) $R^1=R^2=p$-$NO_2C_6H_4$

In this study, the mass spectra of the complexes described have been recorded and the nature of their fragmentation in the ion source of a mass spectrometer characterized. At the same time, the ionization potential values (*IP*) of the individual complexes and the appearance potentials (*AP*) of the $[RhL]^+$ ion have been determined. The differences between the appearance potentials of the $[RhL]^+$ ion have been used to characterize the differences in the bond energy $X–Rh^IL$ which appear to depend on the nature of the ligand X. It has been found that the differences in this bond energy for the complexes (I)–(VII) may be related to the relative rates of polymerization of chloroprene when initiated with these complexes. The rates of polymerization have also been correlated with the values of the Hammett constants of the substituents R^1 and R^2 in the ligand X as determined mass spectrometrically.

METHODS

The mass spectra were measured with an A.E.I. MS-902 apparatus, the electron energy being 70 eV, by using a direct input system at ion source temperatures within the range 120–200° depending on the vapour tension of the complexes under investigation. The elementary compositions of some fragments of complexes (II), (III) and (VI) were measured using a resolution of 10000/10% by using the peak matching

TABLE 1

THE COMPOSITION OF SOME FRAGMENTS OF COMPLEXES (II), (III) AND (VI) DETERMINED BY THE PEAK MATCHING METHOD

Determined (m/e)	*Composition*	*Calcd. (m/e)*	*Determined (m/e)*	*Composition*	*Calcd. (m/e)*
Complex (II)					
439.9816	$C_{18}H_{19}O_2Cl_2Rh$	439.9818	205.9594	C_8H_7Rh	205.9604
405.0129	$C_{18}H_{19}O_2ClRh$	405.0146	204.9522	C_8H_6Rh	204.9525
369.0380	$C_{18}H_{18}O_2Rh$	369.0378	180.9524	C_6H_6Rh	180.9525
368.0301	$C_{18}H_{17}O_2Rh$	368.0300	179.9448	C_6H_5Rh	179.9447
242.9450	C_8H_9RhCl	242.9449	a 105.0343	C_7H_5O	105.0340
241.9343	C_8H_8RhCl	241.9347	b 105.0706	C_8H_9	105.0704
240.9287	C_8H_7RhCl	240.9293	a 103.0547	C_8H_7	103.0548
239.9114	C_8H_6RhCl	239.9114	b 102.9058	Rh	102.9056
206.9674	C_8H_8Rh	206.9682			
Complex (III)					
403.0562	$C_{22}H_{20}RhO$	403.0570	267.9765	$C_{13}H_9Rh$	267.9761
374.0536	$C_{21}H_{19}Rh$	374.0543	224.0829	$C_{15}H_{12}O_2$	224.0837
360.9863	$C_{16}H_{15}OClRh$	360.9867	223.0761	$C_{15}H_{11}O_2$	223.0759
326.0178	$C_{16}H_{15}ORh$	326.0179	191.9431	C_7H_5Rh	191.9447
297.9840	$C_{14}H_{11}ORh$	397.9866	180.9523	C_6H_6Rh	180.9525
282.9990	$C_{14}H_{12}Rh$	282.9995	165.0699	$C_{13}H_9$	165.0704
278.9214	$C_8H_{10}Cl_2Rh$	278.9215	147.0455	C_9H_7	147.0446
269.9915	$C_{13}H_{11}Rh$	269.9917			
Complex (VI)					
469.9656	$C_{22}H_{17}Cl_2ORh$	469.9676	241.9371	C_8H_8ClRh	241.9371
357.9644	$C_{16}H_{12}ClORh$	357.9655	225.9060	C_7H_4ClRh	225.9058
352.9360	$C_{14}H_{12}Cl_2Rh$	352.9372	a 181.0051	$C_9H_6ClO_2$	181.0045
290.9980	$C_{15}H_9O_2Cl_2$	290.9980	b 180.9519	C_6H_6Rh	180.9525
278.9208	$C_8H_{10}Cl_2Rh$	278.9215	138.9952	C_7H_4ClO	138.9951

method (Table 1). All complexes were stable under the experimental conditions used; only complex (VII), which required the highest source temperature, underwent any apparent thermal decomposition. Some metastable ions of complexes (II) and (III) were also measured using the defocussing method. The appearance and ionization potentials were recorded with an accuracy ±0.1 eV by means of the semilogarithmic method suggested by Lossing *et al.*[3] and were calibrated with respect to the ionization potential of argon ^{40}Ar for which $I=15.75$ eV. The values thus obtained are summarized in Table 2.

TABLE 2

IONIZATION POTENTIALS (*IP*) OF THE XRhL COMPLEXES AND THE APPEARANCE POTENTIALS (*AP*) OF THE $[RhL]^+$ ION

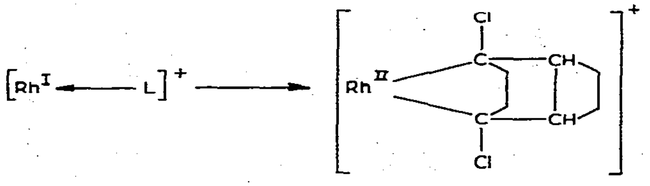
Complex	*IP* (*eV*)	*AP* (*eV*)	$AP_n - AP_I$	$AP - IP$	$\log\left(\frac{I[RhL]^+}{I[XRhL]^+}\right)+2^a$
(I)	8.80	12.45	0	3.65	1.901
(II)	8.60	13.15	0.70	4.55	1.613
(III)	8.70	13.65	1.20	4.95	1.316
(IV)	8.75	14.05	1.60	5.30	1.113
(V)	8.30	13.85	1.40	5.55	0.948
(VI)	8.45	12.85	0.40	4.40	1.674[b]
(VII)	9.50	12.65	0.20	3.15	2.398

[a] $I[RhL]^+$ and $I[XRhL]^+$ = relative intensities of the fragment (a) and of the molecular ion M^+; $M^+ = [XRhC_8H_{10}{}^{35}Cl^{35}Cl]^+$. [b] $I[XRhL]^+ = I_M + \frac{1}{2}I_{M+2} + \frac{1}{6}I_{M+4}$.

RESULTS AND DISCUSSION

1. *Fragmentation of molecular ions*

The mass spectra (Figs. 1–4) are characterized by a number of intense molecular peaks but a basically similar fragmentation pattern, the characteristic feature of which is the formation of fragments of the type $[RhL]^+$ (*m/e* 279). The ions $[RhL]^+$ are present amongst the fragmentation products of all the complexes studied, their relative intensity decreasing in the series (VII) > (I) > (VI) > (II) > (III) > (IV) > (V). On the other hand, no ions of type $[RhX]^+$, whose nominal *m/e* masses would correspond to the values 202 (I), 264 (II), 326 (III), 354 (IV), 386 (V), 394 (VI) and 416 (VII), could be detected. The greater stability of the $[RhL]^+$ fragments is obviously due to an electron re-distribution involving the rhodium atom and the dichlorocyclooctadiene ligand and possibly to a change in the valency of the rhodium atom. This change may be depicted schematically as follows:



(1)

(a)

(*continued on p. 359*)

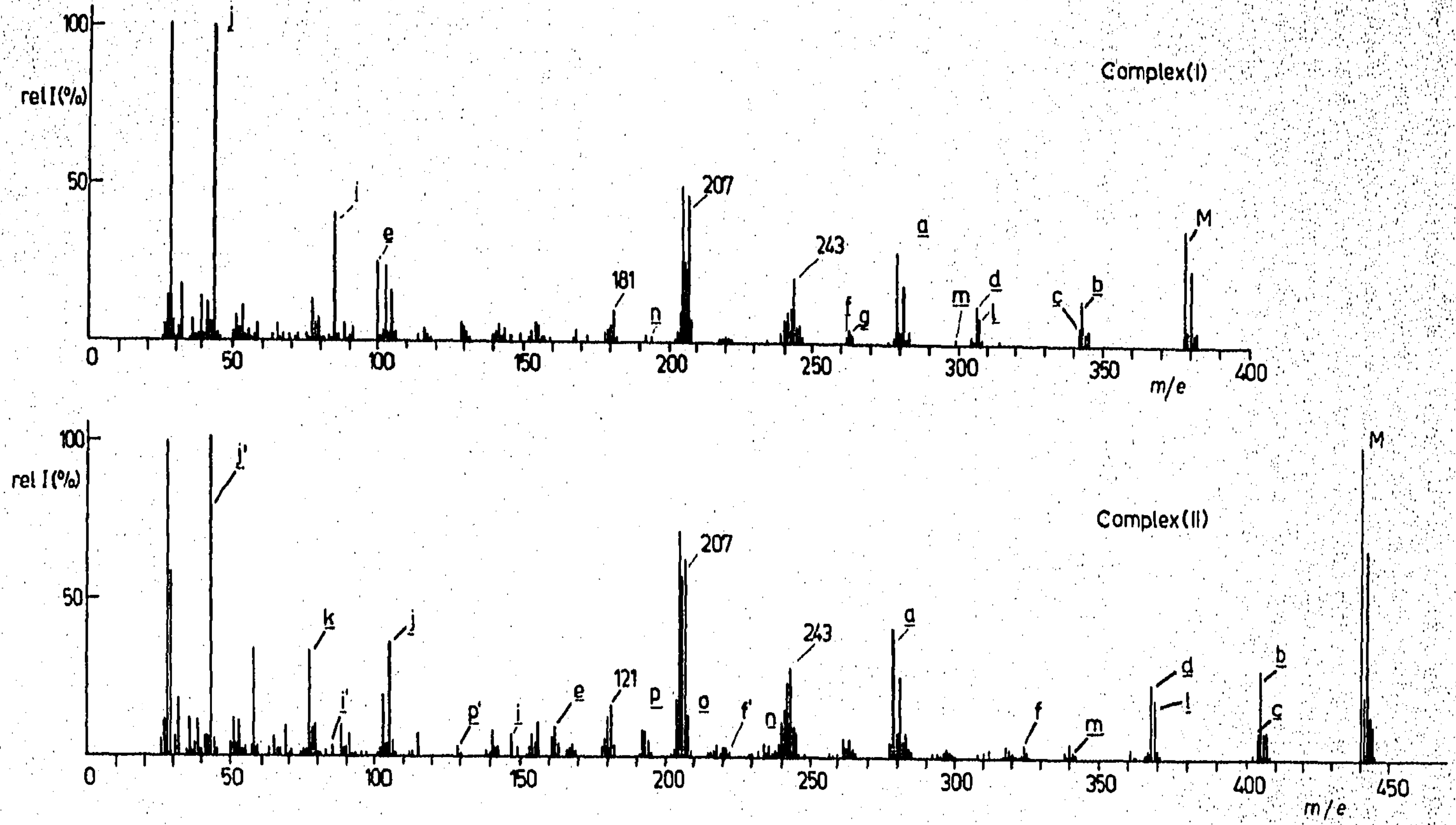


Fig. 1. Mass spectra of complexes (I) and (II); electron energy 70 eV, emission 500 μA, temperature of ion source, 135° (I) and 140° (II).

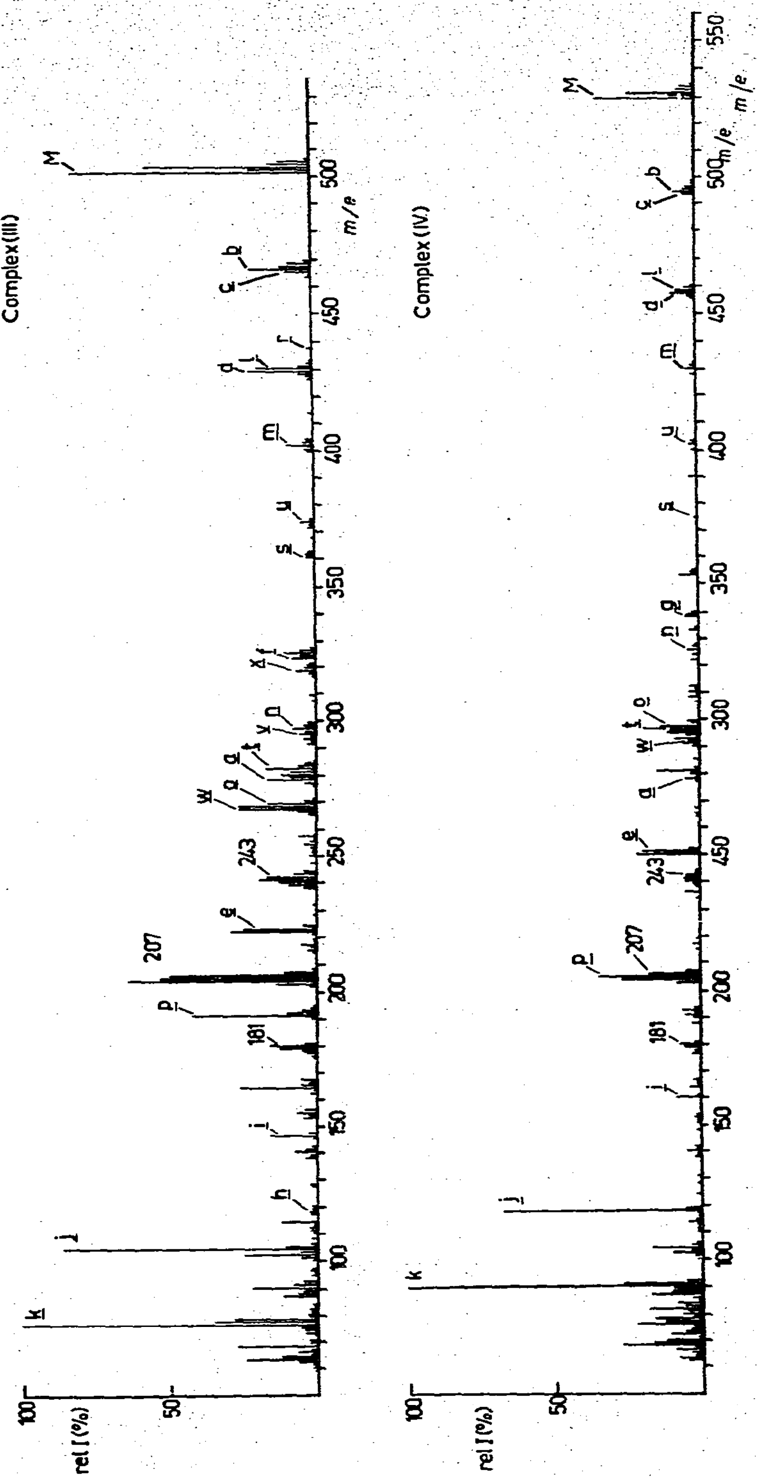


Fig. 2. Mass spectra of complexes (III) and (IV); electron energy 70 eV, emission 500 μA, temperature of ion source, 145° (III) and 165° (IV).

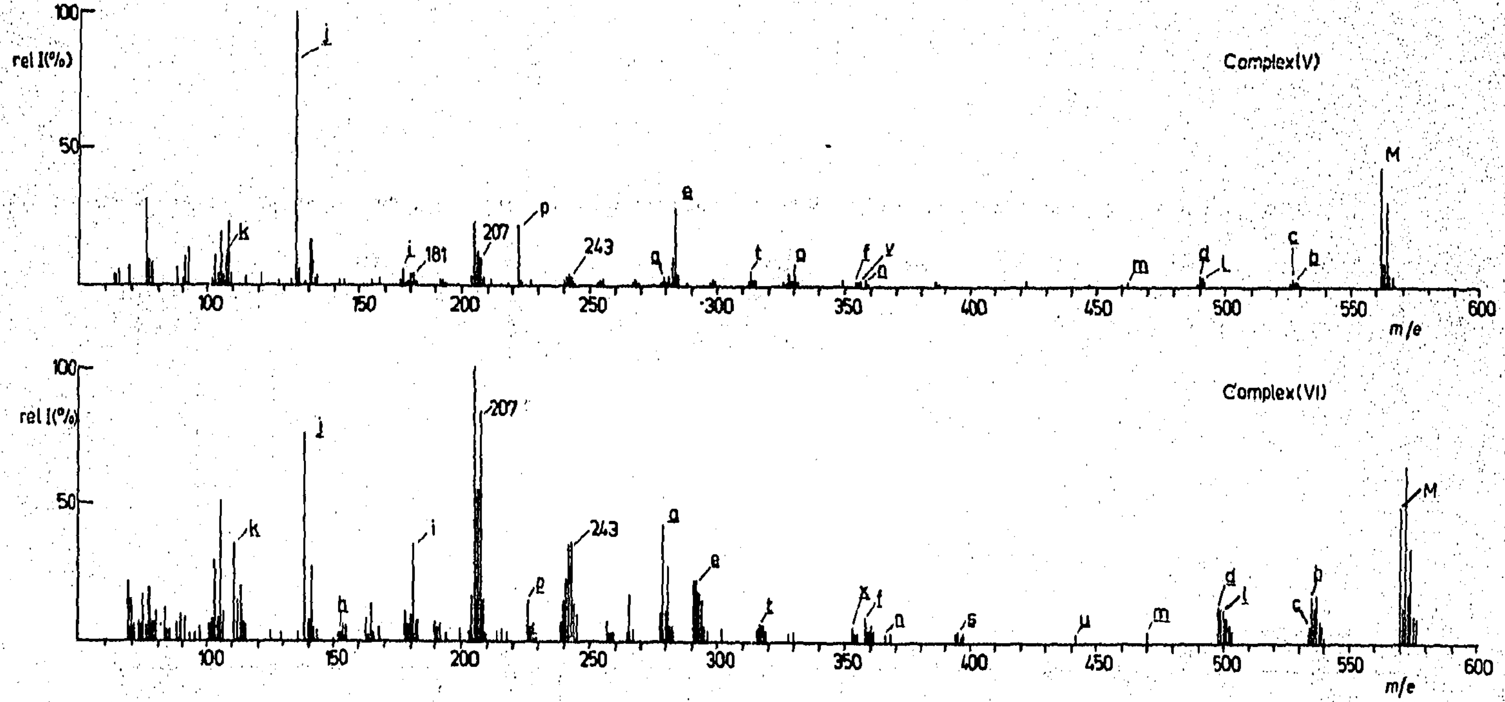


Fig. 3. Mass spectra of complexes (V) and (VI); electron energy 70 eV, emission 500 μA, temperature of ion source, 160° (V) and 170° (VI).

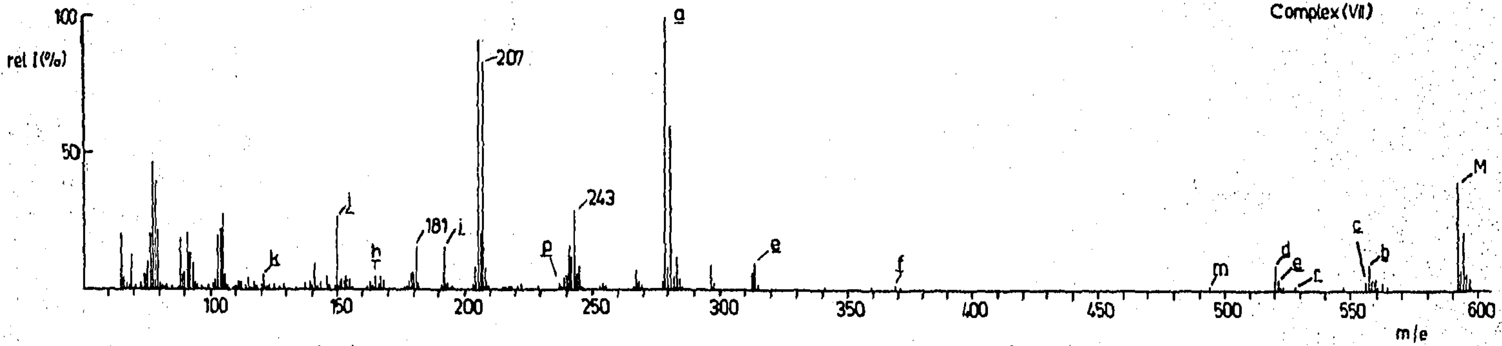
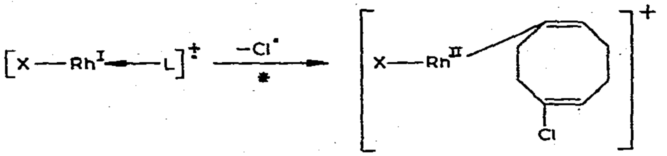


Fig. 4. Mass spectrum of complex (VII); electron energy 70 eV, emission 500 μA, temperature of ion source 200°.

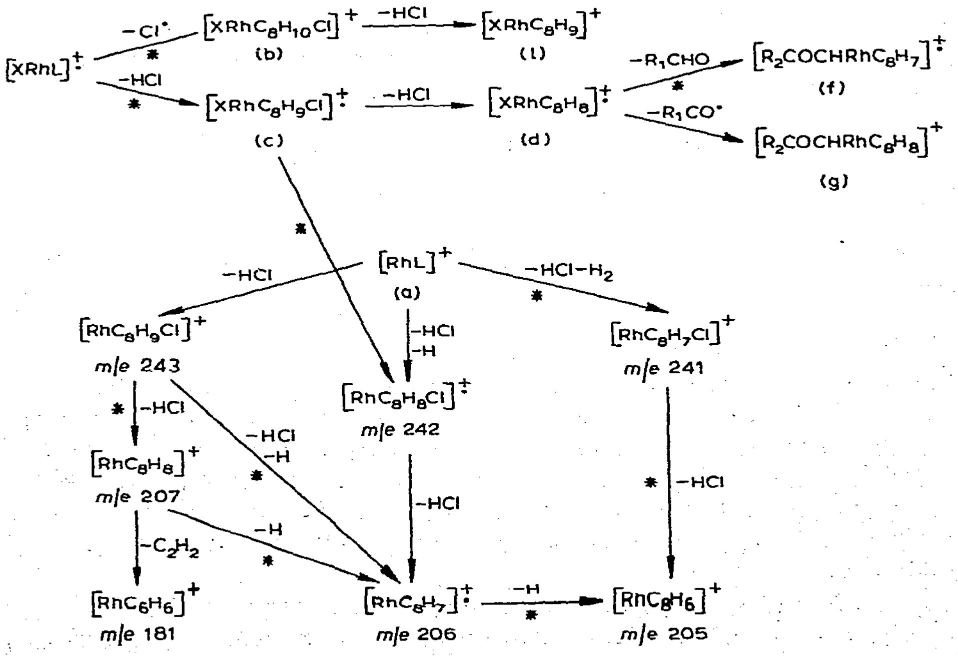
The different character of the Rh–L bond in the molecular ion and in the fragment (a) is also demonstrated by the somewhat different fragmentation patterns of the ligand L when present as a component of the molecular ion $[XRhL]^{+\cdot}$ and of the fragment (a). For example, the intensity of the ions (b) (*cf.* Scheme 1) is generally higher than that of the fragments (c). On the other hand, the intensity of the ions (a) $-$Cl which are similar to the ions (b) is virtually zero. This may be explained on the basis that the change in the valency of the rhodium atom in the molecular ion and the corresponding increase in the strength of the Rh–L bond are preferred to the step involving the splitting-off of a chlorine atom, which from the above discussion may be depicted by the equation:



(2)

Following from Scheme 1, the fragments (a) are probably the precursors of a number of ions which were found in the spectra of all the complexes studied in the present investigation, and which, in some cases, are those exhibiting the most intense peaks (*m/e* 239–243, 205, 206, 207, 181). Splitting-off of hydrogen chloride and hydrogen from ion (a) leads to the presence of intense peaks corresponding to the fragments $[C_8H_8Rh]^+$, $[C_8H_7Rh]^+$ and $[C_8H_6Rh]^+$ (*m/e* 207, 206 and 205). In agreement with the metastable ions detected during this investigation, their decomposition pattern is written as shown in Scheme 1, thus enabling an explanation of the

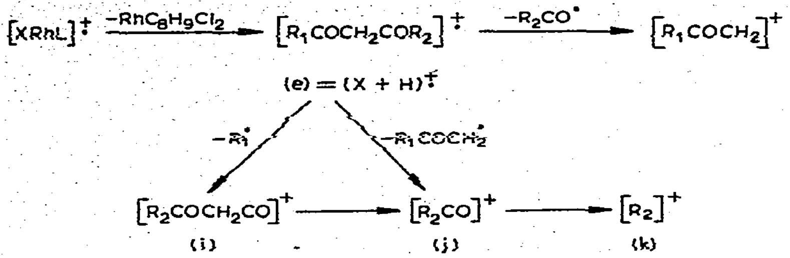
SCHEME 1



different intensities observed for these fragments when the latter are formed from the different complexes studied in this investigation.

No $[XRh]^{+\cdot}$ ions were detected in the spectra, but participation of the fragments arising from the ligand X but not containing the rhodium atom occurred to a considerable extent. The formation of these fragments and of their decomposition products is partly depicted in Scheme 2:

SCHEME 2



Those complexes in which the bond strength between X and the central atom, Rh, is greatest *i.e.* complexes (III), (V) and (IV), fragment to form ions of medium intensity which contain groups arising from the ligand X in addition to the rhodium atom. Their formation and fragmentation patterns are shown in Scheme 3.

2. *Ionization potentials of the complexes and appearance potentials of the $[RhL]^+$ ion*

The ionization potentials (*IP*) of the complexes investigated in this study vary over the range 8.30–8.80 eV (Table 2). Complex (VII) is an exception; the nitro group present in this complex causes a considerable decrease in the electron density in the region of the central Rh atom leading to an *IP* value of 9.50 eV.

From the definitions of the ionization potential of the [XRhL] molecule and the appearance potential of the $[RhL]^+$ ion expressed in equations (3) and (4) it

$$IP[\mathrm{XRhL}] = \Delta H[\mathrm{XRhL}]^{+\cdot} - \Delta H[\mathrm{XRhL}] \tag{3}$$

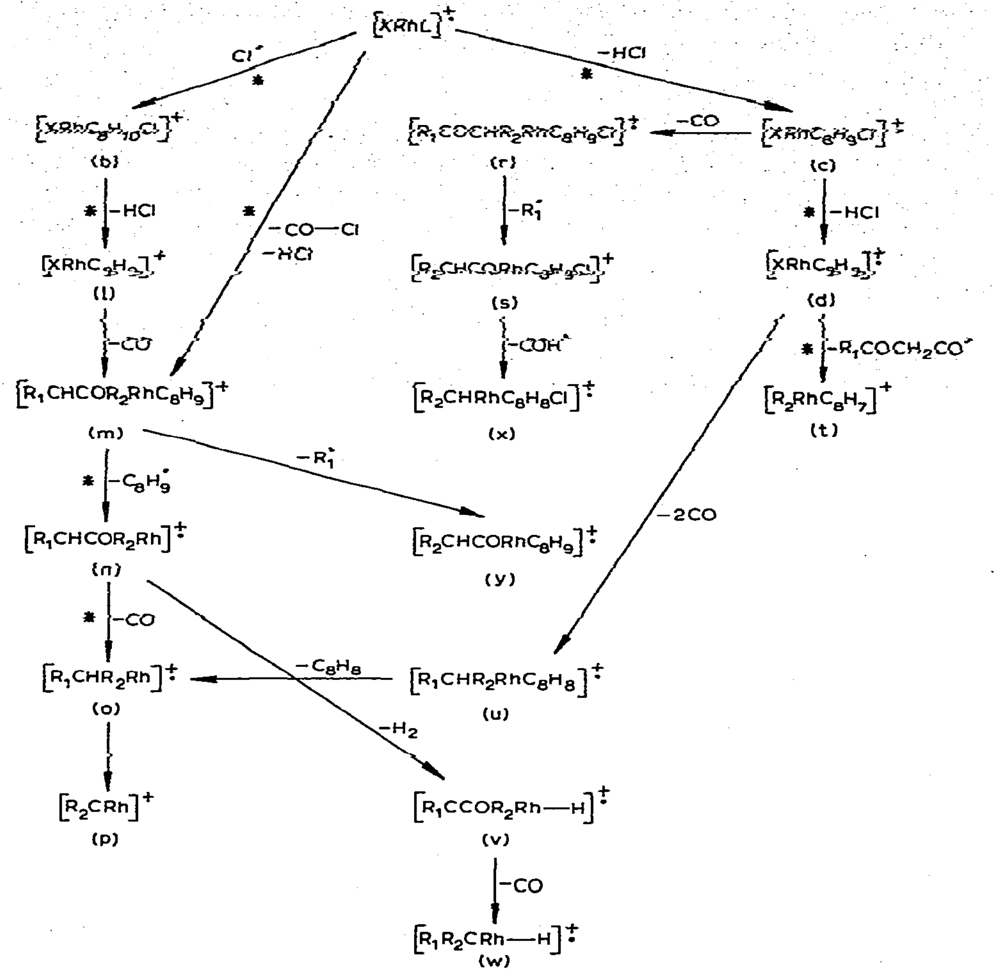
$$AP[\mathrm{RhL}]^{+} \geqslant \Delta H[\mathrm{RhL}]^{+} + \Delta H(\mathrm{X})\cdot - \Delta H[\mathrm{XRhL}] \tag{4}$$

follows that the difference $AP\,[\mathrm{RhL}]^+ - IP\,[\mathrm{XRhL}]^{+\cdot}$ may be put equal to the dissociation energy of the molecular ion which decomposes according to the reaction:

$$[\mathrm{XRhL}]^{+\cdot} \rightarrow [\mathrm{RhL}]^{+} + \mathrm{X}\cdot \tag{5}$$

The magnitude of $AP - IP$ increases in the series (VII) < (I) < (VI) < (II) < (III) < (IV) < (V), (see Table 2). From Table 2 it will be seen that an inverse linear dependence exists between the above differences and the logarithm of the intensity ratio of the peaks $I[\mathrm{RhL}]^+/I[\mathrm{XRhL}]^{+\cdot}$ for all complexes studied here, thus suggesting that the decomposition reaction (5) is a simple process. In fact, the relatively simple nature of this reaction may, in some cases, be directly confirmed by the presence of of metastable ions.

The homolytic dissociation of the complex [X–RhL] into radical fragments X· and RhL·, a reaction which involves the absorption of the dissociation energy *D*, SCHEME 3



may be expressed by the equation

$$[\text{X-RhL}] + D \rightarrow [\text{X}]^{\cdot} + [\text{RhL}]^{\cdot} \qquad (6)$$

According to eqn. (6), the dissociation energies of the first and the nth complex may be calculated from the heats of formation of the various components involved:

$$D_1 = \Delta H[\text{X}_1]^{\cdot} + \Delta H[\text{RhL}]^{\cdot} - \Delta H[\text{X}_1\text{RhL}] \qquad (7)$$

$$D_n = \Delta H[\text{X}_n]^{\cdot} + \Delta H[\text{RhL}]^{\cdot} - \Delta H[\text{X}_n\text{RhL}] \qquad (8)$$

Similarly, the appearance potentials for the formation of the $[\text{RhL}]^+$ ion can also be calculated from the first and the nth complex via eqn. (4):

$$AP[\text{RhL}]_1^+ \geqslant \Delta H[\text{RhL}]^+ + \Delta H[\text{X}_1]^{\cdot} - \Delta H[\text{X}_1\text{RhL}] \qquad (9)$$

$$AP[\text{RhL}]_n^+ \geqslant \Delta H[\text{RhL}]^+ + \Delta H[\text{X}_n]^{\cdot} - \Delta H[\text{X}_n\text{RhL}] \qquad (10)$$

If it is assumed that the excitation energy of the ion $[\mathrm{RhL}]^+$ is the same for each of the complexes (I)–(VII) under investigation, then insertion of this eqns. information into (7)–(10) leads to the relationship:

$$AP[\mathrm{RhL}]_n^+ - AP[\mathrm{RhL}]_\mathrm{I}^+ = D_n - D_\mathrm{I} \tag{11}$$

The difference between the appearance potentials of the $[\mathrm{RhL}]^+$ ion arising from the nth and the first complex is thus equal to the difference between the dissociation energies for the homolytic decomposition of these complexes. The dissociation energy of the complexes increases in the series (I) < (VII) < (VI) < (II) < (III) < (V) < (IV) (see Table 2), and for complex (IV) it is greater by a factor of 1.60 ± 0.20 eV, *i.e.* 36.9 ± 4.6 kcal·mole^{-1}, than for the first complex.

A plot of the difference $AP\ [\mathrm{RhL}]_n^+ - AP[\mathrm{RhL}]_\mathrm{I}^+$, or $D_n - D_\mathrm{I}$ *vs.* $\log (r_n/r_\mathrm{I})_p$, where r_n and r_I denote the polymerization rates (p) of chloroprene when initiated with the nth and the first complex, (Fig. 5) is essentially linear. This dependence is similar to the relationship between $\log(r_n/r_\mathrm{I})_p$ and the σ_I values of the substituents in the phenyl groups of complexes (III)–(VII) mentioned earlier[2]. Hence, from the mass spectra of the individual complexes it is possible to directly obtain overall values for the Hammett constants of the various substituents by using the logarithm of the ratio of the intensities of the fragment and of the ion from which it is derived[4]:

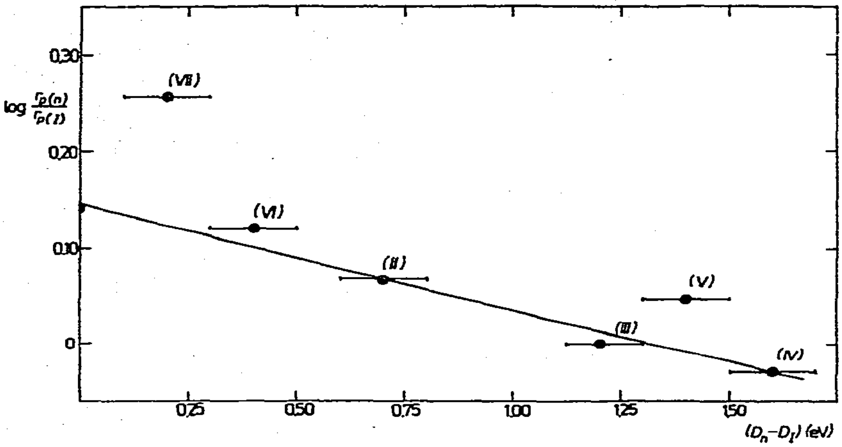


Fig. 5. Relationship between the logarithm of the relative rates of polymerization (r_p) of chloroprene in the presence of the nth and first complex and the difference between the dissociation energies (D) of the bond Rh–X in the nth and the first complex.

$$\log(I_{[\mathrm{RhL}]^+}/I_{[\mathrm{XRhL}]^+}) = \rho \cdot \sigma \tag{12}$$

The σ values thus obtained agree well with the rates of polymerization of chloroprene[2] for all the complexes studied, with the exception of complex (V) (Fig. 6). It follows, therefore, that the previous correlation between the polymerization rates and the Hammett constants of the substituents present in the complexes may be extended to include complexes (I) and (II) where a direct determination of these constants is not possible. Hence it is possible to use mass spectral measurements for the

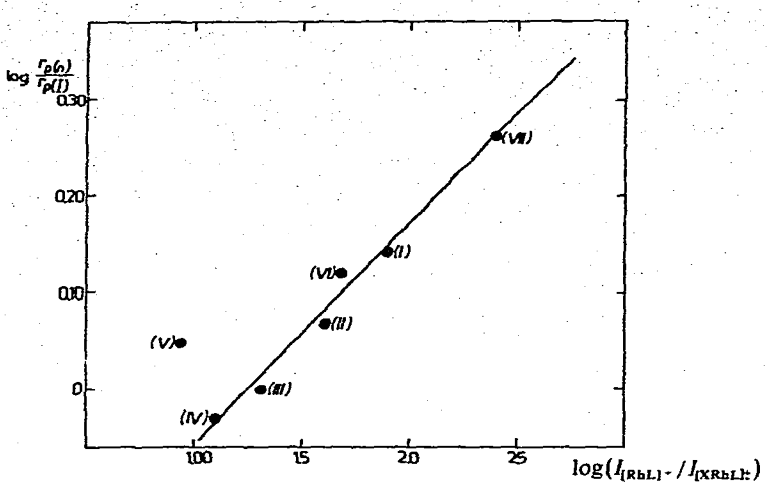


Fig. 6. Relationship between the logarithm of the relative rates of polymerization (r_p) of chloroprene in the presence of the *n*th and first complex and the logarithm of the intensity ratio (*I*) of the ions $[\text{RhL}]^+$ and $[\text{XRhL}]^{+}$ in the spectrum of the *n*th complex.

rapid estimation of the relative efficiencies of complexes such as those investigated in this study as initiators in the polymerization of chloroprene without resorting to time-consuming polymerization experiments.

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