Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

MASS SPECTRA AND BOND ENERGIES OF LANTHANIDE TRICYCLOPENTADIENYL COMPLEXES

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(Received December 29th, 1969)

SUMMARY

Ionization potentials and appearance potentials for Cp_3Nd, Cp_3Sm, Cp_3Yb, and Cp_2Yb are reported. Using this information, the first bond dissociation energy of Cp_3Yb is calculated to be 58 ± 5 kcal. Also, fragmentation patterns of these compounds are discussed in relationship to the type of bonding involved.

The mass spectra and related energetics of various metal sandwich compounds have been examined by several investigators[1-6]. These investigations have included fragmentation patterns and appearance potentials of dicyclopentadienylmetal compounds[1-2], cyclopentadienylmetal carbonyls[3], dibenzenechromium derivatives[4], dicyclopentadienylmetal dichlorides[5], tricyclopentadienylmetal complexes[6], and tetracyclopentadienylmetal complexes[6]. The present work presents further data on the lanthanide tricyclopentadienides and provide the first direct measurement of a metal–cyclopentadienide bond energy for the rare earths.

Thermochemical bond energies of a few organometallics, such as Cp_2ZrCl_2[5], Cp_2TiCl_2[5], Cp_2Fe[7] and Cp_2Ni[8] ($Cp = C_5H_5$), have been reported. Average bond energies of several dicyclopentadienylmetal complexes also have been determined by mass spectrometry[1]. The accuracy of this method, however, is seriously hampered by "tailing" effects and other problems associated with the determination of the

TABLE 1

IONIZATION POTENTIALS AND APPEARANCE POTENTIALS OF RARE EARTH CYCLOPENTADIENIDES
Values in eV.

Compound	$AP(P)^+$	$AP(P-Cp)^+$	$AP(P-2Cp)^+$	$AP(P-3Cp)^+$
Cp_3Nd	8.3 ± 0.1	10.0 ± 0.2	17.8 ± 0.3	23.2 ± 0.4
Cp_3Sm	8.0 ± 0.1	10.0 ± 0.2	14.4 ± 0.3	22.2 ± 0.4
Cp_2Yb	7.62 ± 0.09	10.4 ± 0.2	15.6 ± 0.3	
Cp_3Yb	7.72 ± 0.09	10.1 ± 0.2	12.2 ± 0.2	17.8 ± 0.4[a]

[a] By private communication Dr. Müller confirmed that his reported value[6] for the appearance potential of this ion was a typographical error and should be 19.0 ± 0.5 eV.

appearance potential of an uncomplexed metal ion. Moreover, all values reported are only average bond energies and not the first bond dissociation energy of the molecule. In contrast, we have been able to obtain a measurement of the first bond dissociation energy of Cp_3Yb because of the existence of ytterbium cyclopentadienides in two oxidation states.

The appearance potentials of the compounds studied are listed in Table 1. Metastable peaks were observed for the indicated successive loss of cyclopentadienyl groups for both ytterbium compounds, but not for the neodymium or samarium compounds. Using the appearance potentials listed in Table 1, values for the following processes can be obtained:

$$Cp_3Yb \rightarrow Cp_2Yb^+ + Cp \qquad \Delta H = 10.1 \text{ eV} \qquad (1)$$

$$Cp_2Yb \rightarrow Cp_2Yb^+ \qquad \Delta H = 7.62 \text{ eV} \qquad (2)$$

Subtracting eqn. (2) from eqn. (1) gives eqn. (3) and thus the first bond dissociation energy of Cp_3Yb.

$$Cp_3Yb \rightarrow Cp_2Yb + Cp \qquad \Delta H = 58 \pm 5 \text{ kcal} \qquad (3)$$

This value is quite accurate since the processes measured are those of lowest energy and hence of highest accuracy. Although readily available from the existing metal ionization potential data[9] and the measured appearance potentials of M^+ from the Cp_xM compounds, the average metal–cyclopentadienide bond energies were not calculated due to the inherent inaccuracies previously mentioned.

The ions in the mass spectrum of the rare earth tricyclopentadienides are listed in Table 2. The data were corrected for isotopic distribution and the relative abundances of the ions calculated from peak heights. Despite careful scrutiny of the higher mass region, no polymeric material of any kind was observed. Also, no identifiable peaks other than those listed in Table 2 were detected. Finally, an absolute identification of the less abundant ions was occasionally difficult since various isotopic species overlapped each other by the successive loss of protons.

TABLE 2

MASS SPECTRUM OF Cp_xM COMPOUNDS

Ion	Relative intensities at 70 eV			
	Cp_3Nd	Cp_3Sm	Cp_3Yb	Cp_2Yb
M^+	4	7	15	15
C_2HM^+	2	1.3	2	2
$C_3H_2M^+$	1	0.7	1	1
CpM^+	26	32	30	43
Cp_2M^+	50	41	34	39
Cp_3M^+	17	18	18	

Using data such as those in Table 2, Friedman *et al.*[1] have characterized the mass spectra of ionically bound dicyclopentadienylmetal sandwich complexes by an abundance of lower *m/e* ions. Relative abundances in covalently bound complexes exhibited the opposite character. We infer from our abundances that the complexes we studied are ionically bound as previously suggested by Calderazzo[10] and Wilkinson[11].

EXPERIMENTAL

All measurements and mass spectra were obtained by using an A.E.I. MS 902. In a typical experiment the ionizing voltage was 70 V, the accelerating potential 8000 V, the ionizing current 20 μA, the source pressure 4×10^{-7} mm and the spectrum was scanned magnetically. Samples were introduced by using a direct insertion probe. The source temperature was maintained at 70° for all compounds except Cp_2Yb which required 215°*. To determine appearance potentials, the vanishing current method was used with xenon as a reference. The preparation of all compounds has been previously reported[12,13].

ACKNOWLEDGEMENT

The partial support of this work by the National Science Foundation (Grant N. GP-7881) is gratefully acknowledged.

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* The compounds are well-known for their extreme thermal stability. Also, experience in this laboratory has shown that Cp_2Yb can be sublimed repeatedly at 360° at 10^{-3} mm with no noticeable decomposition. Moreover, all of the compounds studied have been sealed under vacuum in closed tubes and have been subjected to 200–400° for several days and have shown no significant decomposition.