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SHORT COMMUNICATION

Mass spectra and ionization potentials of $C_6H_6CrC_6H_6$ and $C_6H_6Cr(CO)_3$*

In connection with recent mass spectrometric work[1,2] on organometallic compounds, dibenzenechromium and benzenechromium tricarbonyl have been investigated. The mass spectra of the two compounds**, given in Fig. 1, show fragmentation patterns substantially the same as those reported[3-6] for similar molecules. For $C_6H_6Cr(CO)_3$, the low relative abundance of the peaks containing the CO ligand, $M(CO)_x^+$, is noteworthy. As a result the two spectra show considerable similarities. The low intensity of the *m/e* 28 peak in the spectrum of $C_6H_6Cr(CO)_3$ suggests that there was little or no thermal decomposition in the ionization chamber, and that the spectrum is probably free, therefore, from spurious features[2].

TABLE 1

IONIZATION POTENTIALS

Molecule	*IP (volts)*		*Atom IP*[8] *(volts)*		*Molecule*	*IP (volts)*	
	This work	*Lit.*				*This work*	*Lit.*
$(C_5H_5)_2Ni$		6.75[1] 7.06[3]	Ni	7.63	C_5H_5NiNO		8.50[1]
$(C_5H_5)_2Co$	5.95±0.1	6.2[3]	Co	7.86	$C_5H_5Co(CO)_2$	7.78±0.1	8.3[4]
$(C_5H_5)_2Fe$		6.99[1] 7.05[3]	Fe	7.87			
$(C_6H_6)_2Cr$	5.70±0.1		Cr	6.76	$C_6H_6Cr(CO)_3$	7.39±0.1	
$C_6H_6MnC_5H_5$		7.00[5]	Mn	7.43	$C_5H_5Mn(CO)_3$		8.3[5]

The spectrum of $(C_6H_6)_2Cr$ reported here differs in some respects from that reported recently by Denning and Wentworth[5], particularly with reference to the intensity of *m/e* 78 (C_6H_6). Although the relative intensities of the parent *m/e* 208 peak and the $C_6H_6Cr^+$ peak were about the same in the two spectra, the relative intensity of the *m/e* 78 peak in their spectrum was about six times greater than in ours. It seems probable that this difference results from the formation of less free benzene by thermal decomposition in our instrument. A further difference is the absence of *m/e* 40 ($C_3H_4^+$) in our spectrum. Four minor peaks at *m/e* 102, 104, 104.5 and 105 appear to be mainly doubly-charged parent ions, as shown by the half-integral mass, rather than $Cr(C_4H_4)^+$ ions.

The ionization potentials for $(C_6H_6)_2Cr$ and $C_6H_6Cr(CO)_3$, evaluated by a semi-logarithmic method[7] are given in Table 1, along with ionization potentials

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** The spectra were obtained with 50-V electrons, using a Hitachi–Perkin Elmer RMU-6D mass spectrometer, with magnetic field scanning. For experimental conditions see ref. 2.

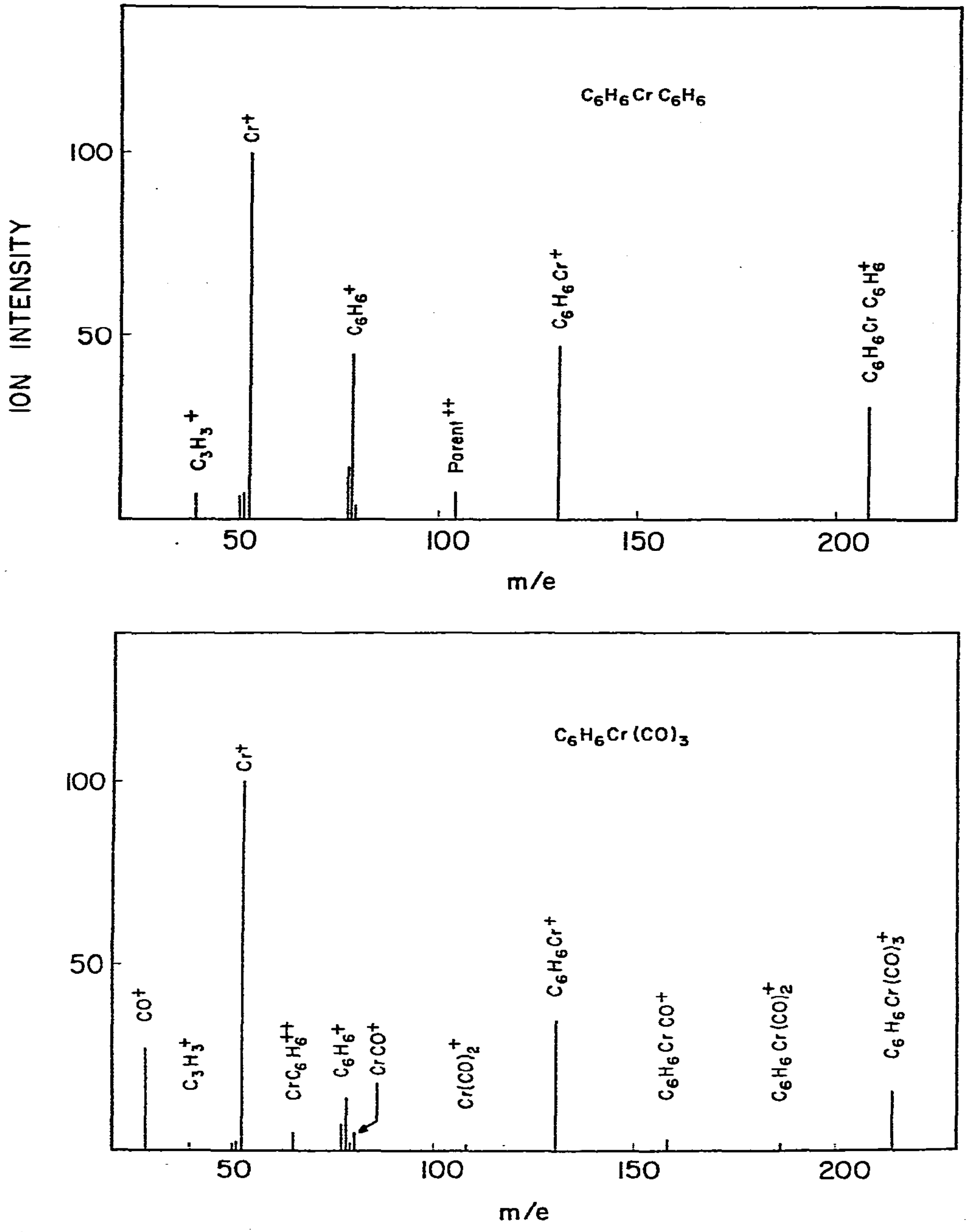

Fig. 1. Cracking patterns for $C_6H_6CrC_6H_6$ and $C_6H_6Cr(CO)_3$ at 50 eV. The relative intensities have been corrected, where necessary, for the isotopic composition of the fragments.

from the literature for analogous compounds of both types. Included also are remeasured *IP*'s for $(C_5H_5)_2Co$ and $C_5H_5Co(CO)_2$. It is clear that the ionization potentials of the "sandwich" molecules are extremely low, being generally almost a volt lower than the *IP* of the central atoms[8]. This illustrates the high stability of $(Aryl)_2M^+$ ions with respect to the neutral species[9]. By way of contrast, it can be seen that the *IP*'s of the ArylML$_n$ molecules with NO and CO ligands are 1.5–2.0 volts higher. The large difference in *IP* between $(C_6H_6)_2Cr$ and $C_6H_6Cr(CO)_3$ is consistent with the fact that only the former gives electron transfer spectra with trinitrobenzene[10,11]. The results in Table 1 suggest that only the molecules in the first column would do so.

TABLE 2

APPEARANCE POTENTIALS

Process	*AP (volts)* Present work	*AP (volts)* Lit.	*Apparent ionic bond diss. energy (kcal/mole)*	*Mean bond energy in neutral*[12] *(kcal/mole)*
$(C_5H_5)_2Fe \rightarrow C_5H_5Fe^+ + C_5H_5$	12.8 ± 1	14.38[3]	134 ± 25	69.5
$(C_5H_5)_2Ni \rightarrow C_5H_5Ni^+ + C_5H_5$	11.9 ± 1	12.67[3]	119 ± 25	56.6
$(C_5H_5)_2Co \rightarrow C_5H_5Co^+ + C_5H_5$	12.3 ± 1	14.20[3]	146 ± 25	
$(C_6H_6)_2Cr \rightarrow C_6H_6Cr^+ + C_6H_6$	9.2 ± 0.2		81 ± 8	40.5
$C_6H_6MnC_5H_5 \rightarrow C_5H_5Mn^+ + C_6H_6$		12.3[5]	122[5]	
$C_5H_5Co(CO)_2 \rightarrow C_5H_5Co^+ + 2\,CO$	10.8 ± 0.2	11.7[4]		
$C_6H_6Cr(CO)_3 \rightarrow C_6H_6Cr^+ + 3\,CO$	10.8 ± 0.2			

In Table 2 are given appearance potentials (*AP*) for ArylM$^+$ ions formed from a number of derivatives, together with corresponding literature values. Owing to the difficulty of matching the *AP* curves for the ArylM$^+$ fragment ions to those of the standard gas (Kr or Xe), the estimated error is large, but the *AP*'s appear to be appreciably lower than the literature values. In Table 2 are also given ionic bond dissociation energies $D(\text{ArylM}^+\text{–Aryl})$ estimated from the relationship

$$AP(\text{ArylM}^+) \geqslant D(\text{ArylM}^+\text{–Aryl}) + IP[(\text{Aryl})_2\text{M}]$$

Even allowing for some excess energy in the *AP* values, it is evident that the bond dissociation energies in the "sandwich" cations are much greater than the corresponding bonds in the neutral species[12], suggesting that the least firmly bound electron is anti-bonding. In this regard it may be noted[13] that theoretical calculations of the MO, SCF, and ligand field types have led to different orders for the highest filled and lowest unfilled levels for such structures. The experimental evidence for the anti-bonding nature of the least firmly bound electron would suggest that in these molecules the last occupied molecular orbital should have an energy higher than the highest atomic orbital.

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