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Fourier transform ion cyclotron resonance spectroscopic studies of the chemistry of electron deficient organometallic anions: the reactions of $[Cr(CO)_3]^{\overset{\cdot}{-}}$ with alkenes and polyenes

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Abstract

Reactions of the radical anion $[Cr(CO)_3]^{\overset{\cdot}{-}}$ with a series of alkenes and polyenes in the gas phase have been examined. With straight chain alkenes the dehydrogenated main ionic product was $[C_nH_{2n-2}Cr(CO)_3]^{\overset{\cdot}{-}}$ and the minor product $[C_nH_{2n-2}Cr(CO)_2]^{\overset{\cdot}{-}}$, for $n = 4$–8, and the reactions giving these are suggested to involve η^4-conjugated alkadiene interactions with the metal centre. Similar reactions took place with the cyclic alkene C_6H_{10} and its methyl-substituted analogue C_7H_{12}. In contrast vinylbenzene, C_8H_8, and propene gave only the decarbonylated ionic products $[C_8H_8Cr(CO)_2]^{\overset{\cdot}{-}}$ and $[C_3H_6Cr(CO)]^{\overset{\cdot}{-}}$, respectively. Isomeric 1,3- and 1,4-cyclohexadienes gave the decarbonylated dehydrogenated products, $[C_6H_6Cr(CO)_2]^{\overset{\cdot}{-}}$, whereas the polyenes gave the ionic species $[(\text{Polyene})Cr(CO)_x]^{\overset{\cdot}{-}}$ with $x = 0$–3.

Introduction

A substantial number of transition metal organometallic anions have been synthesised by electron ionisation in the gas phase and identified in ion beam mass spectrometers [1], but relatively few studies have been made of the chemistry of such potentially reactive and catalytically important species. However, the use of both ion cyclotron resonance (ICR) and flowing afterglow (FA) techniques is beginning to yield new insights into negative ion/molecule substitution, displacement, and insertion reactions involving organometallic species [2–12]. More recently, Fourier transform ion cyclotron resonance (FTICR) spectroscopy has emerged as a powerful technique for the investigation of gas phase ion/molecule reactions [13–16], where use of a trapped-ion cell permits product detection for reaction times varying from a few milliseconds to seconds rather than the much shorter reaction times allowed by flowing afterglow or drift cell ICR, with measurement speed, resolution, and mass

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range also better than those for drift cell ICR. Thus, FTICR pulse/delay temporal sequences, selective ion ejection, and high mass resolution capabilities are now being used to great advantage to study numerous facets of (mainly) positive ion metal chemistry in the gas phase [13–19]. Following earlier work which identified many electron deficient organometallic anions as fragmentation products in negative ion mass spectra [20–26], a chemical study has been started of such transients in the gas phase, where ion/molecule encounters are unencumbered by solvation. Results are presented here of an FTICR study of the reactions of straight chain and cyclic alkenes and polyenes with the 13-electron radical anion $[Cr(CO)_3]^{-\cdot}$.

Experimental

Trapped-ion/molecule reactions were carried out in a Spectrospin CMS-47 Fourier transform ion cyclotron resonance spectrometer [27,28]. Details of this technique have been described previously [13–16]; for the present study a cylindrical ICR cell of radius and diameter 6 cm was used within a UHV system contained in the 15 cm bore of a 4.7 Tesla superconducting magnet in the CMS-47 instrument. The $[Cr(CO)_3]^{-\cdot}$ ions (10% relative abundance) were formed by electron ionisation of $Cr(CO)_6$ at a pressure of 5×10^{-8} mbar with 5.0 eV electrons; with $[Cr(CO)_5]^{-\cdot}$ (100%) and $[Cr(CO)_4]^{-\cdot}$ (10%) formed at the same time being ejected from the cell immediately before the reaction delay. Neutral reactants were admitted to the cell at ambient temperature, ca. 30 °C, in the pressure ratio 5/1 to the neutral metal carbonyl. Except where otherwise indicated, reaction delays of 1 s were used to establish product distributions for all ion/molecule reactions. The empirical formulae of all ionic reaction products were determined by accurate mass measurements from high resolution spectra [28]. Ion/molecule reaction pathways were deduced by selective ion ejections or plots of temporal variations of relevant product distributions. In separate experiments, mass-selected $[Cr(CO)_5]^{-\cdot}$ and $[Cr(CO)_4]^{-\cdot}$ ions were shown not to react with alkenes.

Chromium hexacarbonyl was obtained from Strem Chemicals Inc., and the organic reagents were high purity commercial samples from Matheson Gases, Phillips-66, Aldrich, Fluka and B.D.H., which were used after undergoing multiple freeze-pump-thaw cycles to remove noncondensables. Where appropriate, purities were checked by positive ion mass spectroscopy.

Results and discussion

Product distributions for the reactions between $[Cr(CO)_3]^{-\cdot}$ and the straight chain and cyclic alkenes I–XVI are given in Table 1. For the straight chain hydrocarbons III–VI, VIII–X, and XII and XIV, two competitive reaction channels were identified, leading respectively to the main product, the dehydrogenated ionic species $[C_nH_{2n\text{-}2}Cr(CO)_3]^{-\cdot}$ and the minor product, the decarbonylated and dehydrogenated ionic species $[C_nH_{2n\text{-}2}Cr(CO)_2]^{-\cdot}$. Interestingly, dehydrogenation reactions involving the formation of cobalt alkadiene complexes and H_2 in the gas phase reactions between Co^+ and alkenes have been observed recently [29]. Additionally, a reaction involving both the elimination of CO and H_2 has been shown to occur when $[Cr(CO)_3]^{-\cdot}$ reacts with n-alcohols [7]. Temporal variations of the ion abundances for a typical alkene-$[Cr(CO)_3]^{-\cdot}$ reaction between V and $[Cr(CO)_3]^{-\cdot}$ are presented

TABLE 1

PRODUCT DISTRIBUTIONS FOR REACTIONS OF $[Cr(CO)_3]^-$ WITH ALKENES [a,b]

Alkene		Isomer	Ionic products					
			$[C_nH_{2n}Cr(CO)_3]^-$	$[C_nH_{2n-2}Cr(CO)_3]^-$	$[C_nH_{2n-4}Cr(CO)_3]^-$	$[C_nH_{2n}Cr(CO)_2]^-$	$[C_nH_{2n-2}Cr(CO)_2]^-$	$[C_nH_{2n-4}Cr(CO)_2]^-$
I	C_2H_4	Ethene	0.79	0.21	–	–	–	–
II	C_3H_6	Propene	–	–	–	1.0	–	–
III	C_4H_8	1-Butene		0.55	–	0.15	0.30	–
IV		*trans*-2-Butene	0.03	0.61	–	0.15	0.21	–
V	C_5H_{10}	1-Pentene	–	0.74	–	–	0.26	–
VI		*cis*-2-Pentene	–	0.82	–	–	0.19	–
VII	C_6H_{10}	Cyclohexene	–	–	0.89	–	–	0.11
VIII	C_6H_{12}	1-Hexene	–	0.82	–	–	0.18	–
IX		2-Methyl-1-pentene	–	0.72	–	–	0.28	–
X		4-Methyl-1-pentene	–	0.78	–	–	0.23	–
XI	C_7H_{12}	1-Methylcyclohexene	–	–	0.92	–	–	0.08
XII	C_7H_{14}	1-Heptene	–	0.86	–	–	0.14	–
XIII	C_8H_8	Vinylbenzene	–	–	–	1.0	–	0
XIV	C_8H_{16}	1-Octene	–	0.53	–	–	0.38	0.09
XV		2-Methyl-4,4-dimethyl-1-pentene	< 0.01	–	–	0.34	0.66	–
XVI		2-Methyl-4,4-dimethyl-2-pentene	< 0.01	–	–	0.33	0.67	–

[a] All Cr isotopes are considered. [b] Reaction times of 1 s.

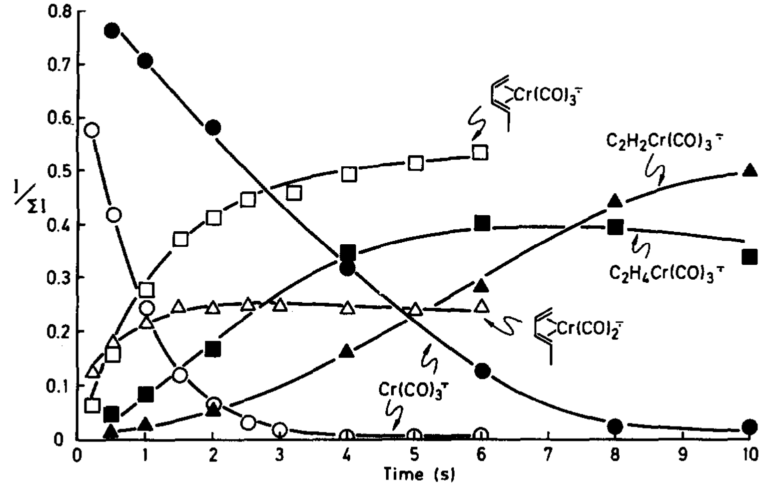
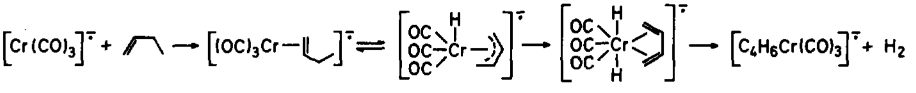


Fig. 1. Temporal variations of ion abundances for the reactions of $[Cr(CO)_3]^{-}$ with C_2H_4 (I) and with 1-pentene (V). All Cr isotopes are considered. Corrected to account for side reactions between $[Cr(CO)_3]^{-}$ and $Cr(CO)_6$ to give $[Cr_2(CO)_x]^{-}$ with $x = 5-8$ at long trapping times [4,31]. $I/\Sigma I$ = Ion abundance/Sum of product ion abundances.

in Fig. 1, and show that the reaction channels leading to main and minor products are competitive. A necessary feature of the carbon skeleton of the alkenes in these reactions appears to be their ability, after dehydrogenation, to enter into a η^4-conjugated double bond interaction with the metal, in a process which is suggested, as in Scheme 1, to occur by formation of a π-allyl metal-hydrido intermediate, and involve β-hydrogen abstraction, followed by H_2 elimination from the metal centre in a mechanism similar, at least in part, to that proposed for the dehydrogenation of alkenes by Co^+ ions [29].

The absence of dehydrogenated product ions for the reactions of the isomeric C_8H_{16} alkenes XV and XVI with $[Cr(CO)_3]^{-}$ is attributed to the structural inability of these compounds to undergo dehydrogenation and enter into a η^4-conjugated double bond interaction with $[Cr(CO)_3]^{-}$. This is consistent with the proposed mechanism and the known ligand π-acceptor stabilization of metal-containing anionic species [2]. The early straight chain members of this alkene series reacted differently with $[Cr(CO)_3]^{-}$. A single decarbonylated product ion $[C_3H_6Cr(CO)_2]^{-}$ was formed by II, but in the case of I both a 15-electron association product ion $[C_2H_4Cr(CO)_3]^{-}$ and the dehydrogenated species $[C_2H_2Cr(CO)_3]^{-}$ were formed in competing reactions which were slower than those for the other alkenes (Fig. 1). Charge retention by the metal in $[C_2H_4Cr(CO)_3]^{-}$ is likely because of the negative electron affinity of the C_2H_4 ligand, −1.55 eV [30], but small amounts, ca. 6% relative abundance, of a decarbonylated ionic product ion for this system at longer



SCHEME 1

TABLE 2

PRODUCT DISTRIBUTIONS FOR REACTIONS OF $[Cr(CO)_3]^-$ WITH POLYENES [a,b]

Polyene	Isomer	Ionic products					
		$[(polyene)Cr(CO)_3]^-$	$[(polyene)Cr(CO)_3\text{-}H]^-$	$[(polyene)Cr(CO)_2]^-$	$[(polyene)Cr(CO)_2\text{-}H_2]^-$	$[(polyene)Cr(CO)]^-$	$[(polyene)Cr]^-$
XVII C_4H_6	1,3-Butadiene	< 0.01	–	0.99	–	< 0.01	–
XVIII C_6H_8	1,3-Cyclohexadiene	0.12	< 0.01	–	0.89	–	–
XIX	1,4-Cyclohexadiene	< 0.01	0.01	–	0.98	–	–
XX C_7H_8	Bicyclo[2.2.1]hepta-2,5-diene	0.02	0.01	< 0.01	–	0.56	0.39
XXI	1,3,5-Cycloheptatriene	0.05	–	0.04	–	0.70	0.21
XXII C_8H_8	1,3,5,7-Cyclooctatetraene	0.06	–	0.16	–	0.77	0.02

[a] All Cr isotopes are considered. [b] Reaction times of 1 s.

trapping times (3 s), have also been detected. A species $[C_2H_2Cr(CO)_3]^-$ has also been identified in low abundance in reactions of $[Cr(CO)_3]^-$ with acetylene at long trapping times [31]. Reactions of the cyclohexenes VII and XI with $[Cr(CO)_3]^-$ yielded similar ionic products, with the principal ionic product $[C_nH_{2n-4}Cr(CO)_3]^-$ suggesting a mechanism involving dehydrogenation of the ring along with the formation of a charge-stabilising η^4-diene ring system able to interact with the metal centre. The identification of only the decarbonylated ionic product in the reaction of vinyl benzene XIII with $[Cr(CO)_3]^-$ indicates that H-abstraction from the aromatic ring is not an energetically favoured reaction pathway. Similar product distributions were found for the reactions of the isomeric butenes III and IV with $[Cr(CO)_3]^-$ It has been suggested that interaction of Co^+ with linear butenes induces facile isomerization to yield a common intermediate, and thus the same ionic product distributions, so the reactions of III and IV with $[Cr(CO)_3]^-$ might be accounted for the same way.

Product distributions for the reactions of $[Cr(CO)_3]^-$ with selected polyenes are given in Table 2. In all cases small abundances of association product ions were identified, but the principal products were strongly dependent upon the carbon skeleton and double bond locations in the reacting polyene. For XVII, the major ionic product $[C_4H_6Cr(CO)_2]^-$ may be regarded as involving a η^4-diene interaction with the metal in a 15-electron ionic species. For the isomeric cyclohexadienes XVIII and XIX, dehydrogenation of the ring concomitant with decarbonylation yielded the principal ionic products of formulae $[C_6H_6Cr(CO)_2]^-$. This species has been detected previously as the product of reductive decarbonylation of η^6-$C_6H_6Cr(CO)_3$ in negative chemical ionisation mass spectra [26]. Similar product distributions were obtained for the reactions of XX, XXI and XXII with $[Cr(CO)_3]^-$,

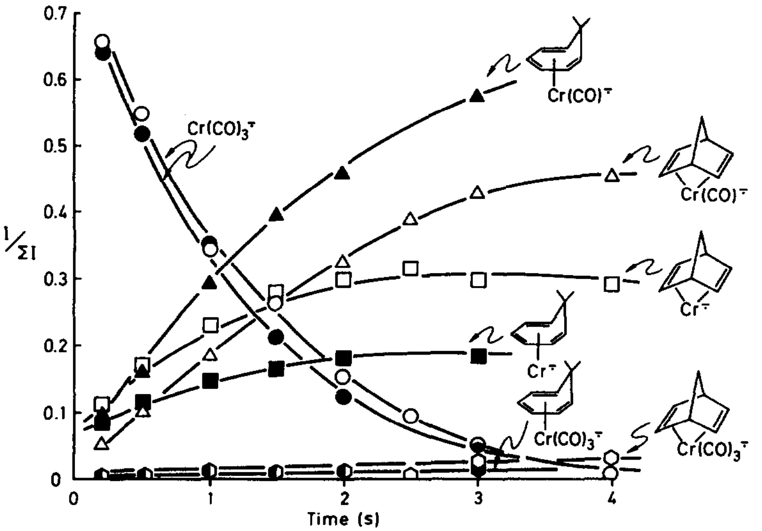


Fig. 2. Temporal variations of ion abundances for the reactions of $[Cr(CO)_3]^-$ with bicyclo[2.2.1]hepta-2,5-diene (XX) and 1,3,5-cycloheptatriene (XXI). All Cr isotopes are considered. Corrected to account for side reactions between $[Cr(CO)_3]^-$ and $Cr(CO)_6$ to give $[Cr_2(CO)_x]^-$ with $x = 5$–8 at long trapping times [4,31] $I/\Sigma I$ = Ion abundance/Sum of product ion abundances.

and Fig. 2 shows the temporal changes in product ion abundances for the reactions of XX and XXI.

All product ions for the reaction of XXI with $[Cr(CO)_3]^{-}$ have previously been identified in the negative ion mass spectrum of η^6-cycloheptatrienetricarbonylchromium(0) [24]. The suggested bonding between metal and organic ligands given for the ionic reaction products in Figs. 1 and 2 is in accord with the empirical formulae of these species obtained from accurate mass measurements of the ions, and are not necessarily indicative of the ion structures. Experimental data bearing on structures of these and other ionic products of metal carbonylate ion reactions with organic substrates will be forthcoming from collision induced decomposition studies involving pulsed valve additions of both organic reactants and collision gases to the ICR cell [32–35].

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