

Electron Paramagnetic Resonance Measurements of Dibenzenechromium Cations on Silica Gel and in Y-Type Zeolites

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The EPR spectra of $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ cations on silica gel and in Y-type zeolite were studied. The spectra show a well resolved proton hyperfine structure due to interactions between the unpaired electron and twelve equivalent protons of the benzene rings. An analysis of the ^{53}Cr hyperfine structure indicates that the unpaired electron is mainly localized in the $3d_z^2$ orbital of the chromium(I). The thermal stability of the dibenzenechromium complexes was greater in the Y-type zeolites than on silica gel. It was not possible to achieve either the reversible formation of the complex or ligand exchange with mesitylene. Furthermore, the dibenzenechromium complex did not form new π -arene complexes with acetylenes.

INTRODUCTION

The structure and properties of π -complexes of chromium have attracted considerable attention in view of their catalytic activity (1, 2). Karol (1) observed that chromocene on silica gel forms a highly active catalyst for polymerization of ethylene. This polymerization process is believed to occur by a coordinated anionic mechanism. Similar observations were found by Ermakov *et al.* (2) for the tris- π -alkylchromium complexes on a number of carriers.

The dibenzenechromium complexes were discovered by Hein (3) and subsequent work by Fischer *et al.* (4) and Tsutsui *et al.* (5) led to methods which are most generally applicable for the preparation of bis- π -arene complexes. Since the dibenzenechromium complexes are diamagnetic and have a zero dipole moment when chromium is in the zero valence state, these workers suggested a ferrocene-like sandwich structure. In order to verify the structure a number of X-ray studies on the bis- π -arene complexes were carried out (6).

The $\text{Cr}(\text{O})$ complex may be easily

oxidized to the paramagnetic Cr(I) complex, and a number of EPR studies have been carried out in liquid (7-9) and solid solutions with both C_6H_6 and C_6D_6 as ligands (10). According to Feltham *et al.* (7) the bonding between the benzene rings and the chromium atom involves a hybridization of the π orbitals of the rings and the d orbitals of the metal atom. In addition, Prins *et al.* (10) conclude from molecular orbital calculations that the benzene rings interact mainly with the $3d_z^2$ orbital of the chromium and that the contribution of the $4s$ orbital is small.

The possibility that these dibenzenechromium complexes in zeolites and on silica gel may be active catalysts for dimerization and trimerization reactions, has led to the present study of the properties, specific interactions and stabilities of the $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ cations.

EXPERIMENTAL

Two Linde NaY zeolite samples and one silica gel sample were exchanged by shaking these samples with an aqueous solution of $\text{Cr}(\text{C}_6\text{H}_6)_2$ or with $\text{Cr}(\text{C}_6\text{H}_6)_2$ in a 1:1

mixture of methanol/benzene. The silica gel was obtained from E. H. Sargent and the dibenzene chromium from Alpha Inorganics. It was observed from the EPR spectra that $\text{Cr}(\text{C}_6\text{H}_6)_2$ undergoes an irreversible 1-electron oxidation in methanol/benzene mixtures or in aqueous solutions. The solubility of $\text{Cr}(\text{C}_6\text{H}_6)_2$ in water, however, was very small so that the exchange level of $\text{Cr}(\text{C}_6\text{H}_6)_2$ in the NaY zeolite (0.75 ions per unit cell) and on silica gel (0.69×10^{19} ions/g) was low. The solubility of the dibenzenechromium was greater in methanol/benzene which results in a greater exchange in the NaY zeolite (7.1 ions per unit cell). After the exchange the samples were repeatedly washed with pure solvent to remove the excess complex and were dried under vacuum at room temperature.

Both types of samples were degassed briefly at room temperature and at temperatures up to 200°C for 1 h. EPR spectra were taken following evacuation at several degassing temperatures. Desorption of benzene from the dibenzenechromium samples was carried out at different temperatures by heating the sample under vacuum. In several experiments this was followed by a reabsorption of benzene or of mesitylene. Alternately the exchanged complex was heated in an atmosphere of deuterated acetylene, methylacetylene, or dimethylacetylene. The EPR measurements were made at 77 K using a Varian E6S spectrometer with a TE_{102} mode microwave cavity. The instrument was operated in the X-band region at about 9.1 GHz. The g values were measured by comparison with a DPPH sample ($g = 2.0036$) attached to the outside of the sample tube.

RESULTS

The EPR spectra of the $(\text{C}_6\text{H}_6)_2\text{Cr}^+$ cations on the silica gel and in the low-exchanged Y-type zeolite are shown in Figs. 1a and 1b. The EPR spectra are characteristic of an axially symmetric molecule localized on the silicate carriers. The hyperfine structure due to the protons can be resolved for the x and y directions, as well as for the z direction when the co-

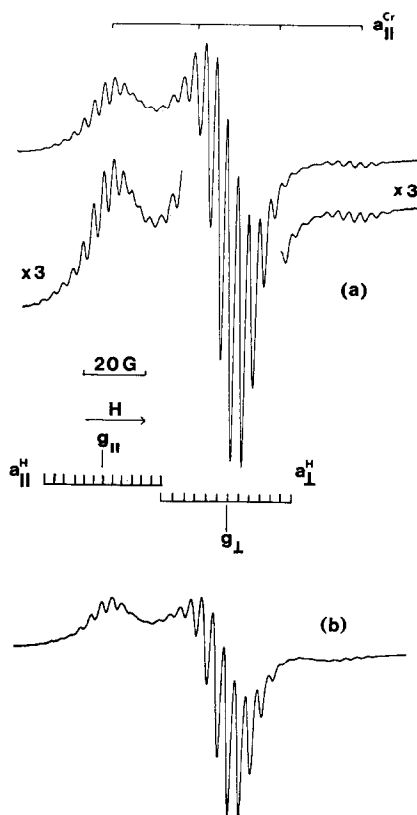


FIG. 1. EPR X-band spectra of $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ cations (a) on silica gel and (b) in a Y-type zeolite after a brief evacuation at room temperature.

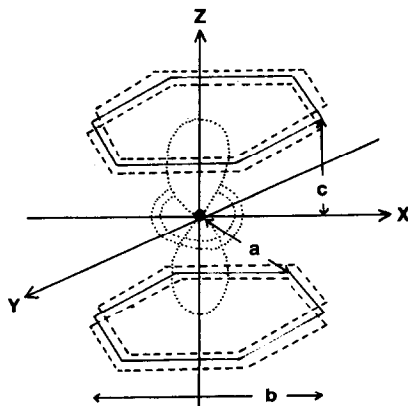


FIG. 2. Representation of A_{1g} configuration of benzene and the metal orbitals in $\text{Cr}(\text{C}_6\text{H}_6)_2^+$.

TABLE 1
THE g VALUES AND HYPERFINE SPLITTINGS (IN GAUSS) FOR $\text{Cr}(\text{C}_6\text{H}_6)_2^+$

	$\text{Cr}(\text{C}_6\text{H}_6)_2\text{Y}(1)^a$	$\text{Cr}(\text{C}_6\text{H}_6)_2\text{Y}(2)^b$	Silica gel	$\text{Cr}(\text{C}_6\text{H}_6)_2^+$ in solid solutions ^c	$\text{Cr}(\text{C}_6\text{H}_6)_2^+$ in liquid solutions ^c
g_{\parallel}	2.0039	2.0032	2.0038	2.0023	—
g_{\perp}	1.9790	1.9791	1.9790	1.9785	—
g	—	—	—	—	1.9865
$ a_{\parallel}^{\text{Cr}} $	—	—	—	~ 0.5	—
$ a_{\perp}^{\text{Cr}} $	26.7	26.7	26.7	26.9	—
$ a_{\parallel}^{\text{H}} $	3.6	3.6	3.6	3.64	—
$ a_{\perp}^{\text{H}} $	3.2	3.2	3.2	3.1	—
$ a_{\text{iso}}^{\text{H}} $	—	—	—	—	3.46

^a Exchanged from aqueous solution.

^b Exchanged from $\text{CH}_3\text{OH}/\text{C}_6\text{H}_6$ solution.

^c Ref. (10).

ordinate system is defined as in Fig. 2 (10). The apparent axial symmetry can be explained either by a rotation around the z axis, which averages out the anisotropy between the protons in the x and y directions, or by a rigid $(\text{C}_6\text{H}_6)_2\text{Cr}^+$ cation adsorbed in a manner such that the x and y directions are magnetically equivalent.

At the high-field region of the $(\text{C}_6\text{H}_6)_2\text{Cr}^+$ spectrum the hyperfine component, belonging to one of the four ^{53}Cr ($I = 3/2$) lines, was observed. According to Prins *et al.* (10) these four ^{53}Cr lines must be centered around the x, y peak. In the spectra no axial ^{53}Cr hyperfine structure was found. The magnetic parameters derived from the spectra of the $(\text{C}_6\text{H}_6)_2\text{Cr}^+$ cations on silica gel and in the Y zeolite are given in Table 1.

The thermal stability of the complex on the two silicates differs greatly. As shown in Fig. 3 the complex begins to decay upon evacuation at 25°C on the silica gel; however, it is reasonably stable up to 80°C in the zeolite. In one zeolite sample the cation was exchanged from a pure methanol solution. The desorption products were determined as a function of temperature, and it was observed that the evolution of C_6H_6 began at 85–90°C.

Attempts to remove the benzene ligands and to add the benzene back at temperatures from 25 to 150°C were unsuccessful. Furthermore, it was not possible to ex-

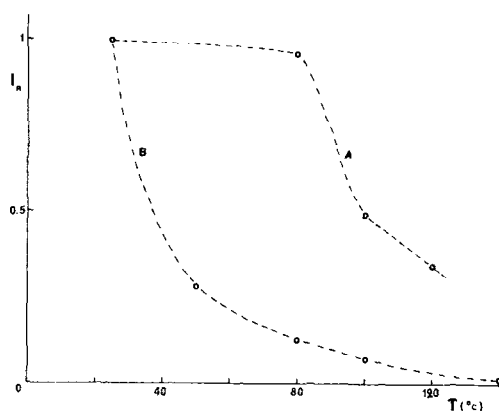


FIG. 3. The thermal stability of the dichromium complexes (A) in a Y-type zeolite and (B) on silica gel.

change the benzene ligand with mesitylene which would have given a distinctly different spectrum. Likewise, reacting the adsorbed complex with deuterated acetylene, methylacetylene, or dimethylacetylene did not result in the formation of a new π -arene complex.

DISCUSSION

The dibenzenechromium cation has a structure as shown in Fig. 2. The dimensions of the dibenzenechromium complexes are approximately 4.97, 4.97, 4.76 Å in the x, y and z directions. This indicates that the complex can enter easily the large cavities through the 9 Å twelve-membered

ring; hence, steric hindrance during the exchange is not important. The complexes must be localized in the large cavities of the zeolite.

The molecule has D_{6h} symmetry and the six $p\pi$ -electrons of benzene form six molecular orbitals. The superhyperfine structure, appearing in Fig. 1, is attributed to hyperfine interaction between the unpaired electron and the twelve equivalent protons on the benzene rings. Such an interaction would give rise to $2NI + 1$ lines, where I is the nuclear spin and N the number of equivalent nuclei, or 13 lines. The fact that the 13 proton hyperfine lines are observable, together with the fact that the observed g values are approximately the same as those obtained from chromium salts (7, 10) indicates that the bonding between the benzene rings and the chromium atoms involves some degree of hybridization of the π orbitals of the rings and the d orbitals of the chromium atom.

Following the analysis of Prins *et al.* (10) the unpaired electron is taken to be in the a_{1g} orbital, for which the total wave function may be written as

$$\psi_{(a_{1g})} = \alpha_1\psi_{(3d_{z^2})} + \alpha_2\psi_{(4s)} + \alpha_3\psi_{(\text{ligand orbitals})}, \quad (1)$$

where α_1 , α_2 and α_3 are the coefficients of the respective atomic wave functions. For the unpaired electron in the d_{z^2} orbital McGarvey (11) derived the following equations for the hyperfine terms a_{\perp} and a_{\parallel} :

$$a_{\perp} = A_{\text{iso}} + \frac{4}{7}\alpha_1^2P - \frac{1}{7}(g_{\perp} - 2.0023)P, \quad (2)$$

$$a_{\parallel} = A_{\text{iso}} - \frac{2}{7}\alpha_1^2P + \frac{15}{14}(g_{\perp} - 2.0023)P, \quad (3)$$

where $P = g_e g_n \beta_e \beta_n \langle r^{-3} \rangle$. Here β_e and β_n are the Bohr and nuclear magneton, respectively, g_e and g_n are the free electron and nuclear g factors and A_{iso} is the isotropic hyperfine coupling constant.

The value of a_{\perp}^{Cr} was evaluated knowing the center of the $M_I = -\frac{3}{2}$ band in the high-field region and the field corresponding to g_{\perp} . Although no $a_{\parallel}^{\text{Cr}}$ hyperfine structure was observed, Prins *et al.* (10)

were able to calculate that $a_{\parallel}^{\text{Cr}} = 0.5$ G for the $(C_6H_6)_2Cr^+$ cations from values of a_{\perp}^{Cr} and $A_{\text{iso}}^{\text{Cr}}$. The latter was obtained from the spectrum of the cation in liquid solution. The small splitting of $a_{\parallel}^{\text{Cr}} = 0.5$ G is approximately equal to the line width, therefore it is not directly observable.

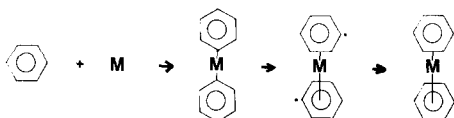
Using the values of $|a_{\parallel}|$, $|a_{\perp}|$, and g_{\perp} given in Table 1, one may show from Eqs. (2) and (3) that $(\alpha_1^2 - 0.0409)P = \pm 30.52$. Since the magnetic moment, μ_N , for ^{53}Cr is negative, P is negative. The only possible sign choice is that a_{\parallel} and a_{\perp} are positive; thus, $(\alpha_1^2 - 0.0409)P = -30.52$. McGarvey (11) has tabulated values of P for different valence states of chromium. For Cr^+ , $P = -31.5$ G or $\alpha_1 = 0.93$, which confirms that the unpaired electron is highly localized in the $3d_{z^2}$ orbital.

Information on the contribution of the ligand orbitals can be drawn from the proton hyperfine splitting. Within experimental error, isotropic proton hyperfine splittings were observed. From the experimental splitting constant a spin density of 0.0068 per proton, or a total density of 0.0816 was found.

As shown in Table 1 the magnetic parameters of the dibenzene chromium complexes in the zeolite framework or on silica gel are remarkably similar to those reported for the $(C_6H_6)_2Cr^+$ cations in liquid and solid solutions (10). This suggests that the environment has only a small influence on the electronic configuration of the complex. The silicate framework, however, has a significant influence on the stability of the complex, as shown in Fig. 3. In the zeolite, where the π -complex is hidden in a system of cavities, the complex was more stable to temperature changes than on the outer silicate surface of the silica gel. The π -complex is tightly locked into the zeolite by electrostatic forces and the decreased mobility may increase the thermal stability. Desorption experiments at different temperatures showed that the dibenzenechromium decomposed.

Upon readsorption of benzene or mesitylene in a partially decomposed sample no π -complexes were formed, even in the pres-

ence of water. Moreover, after a reduction with hydrogen at 400°C no π -complexes were reformed upon addition of benzene and water. The formation of the π -complex occurs through a σ -dibenzene chromium complex which transforms into a π -complex via a π -radical hybridization (5):



The failure to reform the dibenzene π -complex in the zeolite and on silica gel may be due to the stabilization of the σ -dibenzene chromium complexes on the silicate surface.

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