

## Aromatic Radical Cation Formation on Catalytic Materials

### INTRODUCTION

Electron paramagnetic resonance (EPR) experiments have conclusively demonstrated that the interactions of organic molecules with a number of amorphous and crystalline aluminosilicate catalysts generate molecular species containing at least one unpaired electron spin. Most of the published research (1-3) has been concerned with the spectra of polynuclear aromatics on silica-alumina catalysts. This research, together with optical studies (4), confirmed the suspicion that the catalyst abstracts a  $\pi$  electron from the molecule producing an aromatic radical cation. However, radical cation formation was not observed when benzene, toluene, *o*-xylene, or hexamethylbenzene were sorbed on silica-alumina (1).

The formation of radicals from parent molecules whose ionization potentials exceed those of the polynuclear aromatics has been accomplished with the catalytically more active rare-earth faujasites of the X type (5, 6), and calcium-exchanged Y zeolite (5). Experiments in this laboratory with aromatic and aliphatic molecules on the commercial catalyst hydrogen Zeolon (Norton Chemical Products, Worcester, Massachusetts), hereinafter denoted HZ, have revealed an abundance of hyperfine structure, whose successful interpretation promises a deeper understanding of the nature of the interactions between molecules and catalysts. This note presents a preliminary report of some results obtained with benzene and its methyl derivatives.

### EXPERIMENTAL METHODS

The catalyst was obtained as "Lot 47" from the Norton Company; its analysis, on a weight percent basis, following ignition, was (%): Fe, 0.30; Na, 0.34;  $\text{Al}_2\text{O}_3$ , 12.3;  $\text{SiO}_2$ , 85.4.

The catalyst was pretreated with oxygen for 1 hr at 500°C and evacuated at the same temperature for about 3 hr. After cooling to room temperature the catalyst was transferred, under vacuum, to standard EPR sample tubes and sealed. Hydrocarbons were deposited on the catalyst by submerging the sample tube in larger tubes containing the liquid hydrocarbon, and then opening the EPR tube. In the case of solid hydrocarbons, the catalyst samples were immersed in tubes containing a bed of the hydrocarbon, heated to the melting point of the hydrocarbon, and then opened.

EPR spectra were obtained immediately from all samples, but it was frequently a matter of 1 or 2 days before well-resolved spectra were obtained. The optimum line width in equilibrated systems was about 3 gauss (G). All spectra were observed at room temperature in a magnetic field of 3300 G.

### RESULTS AND DISCUSSION

#### *Benzene*

The hyperfine couplings of unpaired spins to nuclei with nonvanishing spin are given approximately by the McConnell relation  $a = Q\rho$ , where  $Q$  is a constant and  $\rho$  is the unpaired spin density at the nucleus. Reasonable  $Q$  values for directly bonded protons and methyl group protons in radical cations are  $Q_{\text{H}} = 26.6$  G and  $Q_{\text{CH}_3} = 40$  G. Thus the spectrum anticipated for the radical cation of benzene consists of 7 uniformly-spaced lines with hyperfine splitting  $a_{\text{H}} = \frac{1}{6}(26.6) = 4.4$  G and relative signal intensities in the ratios 1:6:15:20:15:6:1. The spectrum initially observed when benzene is deposited on HZ is shown in Fig. 1a. The splittings resolved in the central region of the spectrum are 2.2 G, just half the value anticipated for the radical cation of

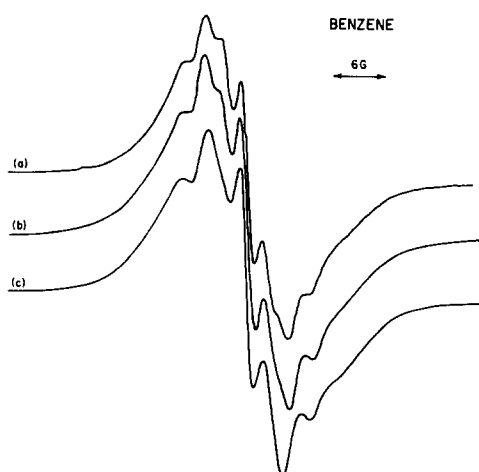


FIG. 1. EPR spectra of benzene on hydrogen Zeolon (HZ): (a) initially observed spectrum; (b) spectrum observed after 10 min; (c) after a time lapse of 1 hr.

benzene. The full breadth of the spectrum is approximately 30 G, so that if the 2.2-G splitting persists throughout this breadth, the spectrum would include about  $30/2.2 \approx 14$  lines.

The spectra observed after time lapses of 10 and 60 min are shown in Fig. 1b and c. These spectra show a gradual diminution of the intensities of several lines. The apparent increase in resolution in the wings of the spectrum shows that lines in these regions are also decreasing in intensity. The average value of the large splitting in the central region is 3.8 G.

The simplest interpretation of these observations is that, initially, the radical cation dimer of benzene is formed, that is, a single unpaired spin equally shared between two benzene rings, presumably in a sandwich-like configuration. This system would exhibit a 13-line spectrum with uniform spacing one-half that of the monomeric radical cation. The subsequent changes in the spectrum are attributed to a fairly rapid approach to an equilibrium distribution of the dimeric and monomeric radical cation forms.

This interpretation is supported by recently reported (7) observations of radical cation dimers of a number of aromatic molecules in solution and, especially, by the reported observation of the radical cation

dimer of benzene when benzene sorbed on silica-alumina is subjected to  $\gamma$ -irradiation at 77°K (8).

#### Durene

The spectrum of the durene/HZ system is shown in Fig. 2. The splitting of the prominent lines is 10.8 G, which, because of its magnitude, is attributed to a coupling of the unpaired spin to methyl group protons ( $\rho_{\text{CH}_3} \approx 1/4$ ). Since the most intense line appears in the center of the spectrum, there must be an odd number of lines; hence, the unpaired spin must be coupled to an even number of methyl group protons. As 11 lines are clearly resolved, the coupling must involve four equivalent methyl groups, the relative intensities of the twelfth and thirteenth lines being too weak to detect. The line width of 3 G precludes the detection of the small (<1 G) triplet splittings from the two-ring protons. The observed spectrum is consistent with that observed in solution (9, 10).

Under higher resolution, additional lines are detected in the durene spectrum. It is speculated that these lines arise from an isomerization product. The possibility that radical cations of pentamethylbenzene are also present cannot be excluded on the basis of the EPR spectra alone.

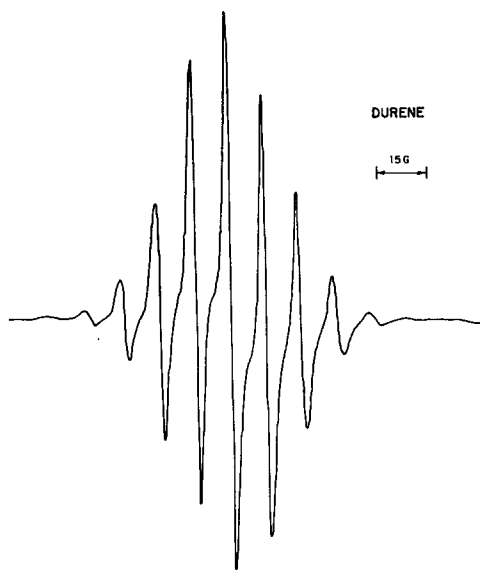


FIG. 2. EPR spectrum of durene adsorbed on HZ.

### Pentamethylbenzene

The EPR spectrum of pentamethylbenzene/HZ is shown in Fig. 3. The splitting of the prominent lines of the spectrum is 10.6 G, and these lines are attributed to the radical cation of pentamethylbenzene. The splittings arising from the ring proton and the methyl group *para* to this proton are less than the line width, and, hence, are not resolved. Since the spectrum of the radical cation of durene cannot, under these experimental conditions, be distinguished from that of the pentamethylbenzene, the prominent lines of Fig. 3 may also include a contribution from the durene radical cation.

The subsidiary lines in the spectrum of Fig. 3 are separated from the prominent lines by 5.3 G. An intriguing possibility is that the additional lines arise from the radical cation dimer of pentamethylbenzene. This explanation brings the splitting of 5.3 G precisely in line with the monomer splitting. The intensity ratios of the subsidiary lines are consistent with the dimer hypothesis.

### Hexamethylbenzene

The spectrum of hexamethylbenzene/HZ is shown in Fig. 4. There is clearly an odd number of lines, and as their splitting is 6.6 G, these lines are attributed to the radical cation of hexamethylbenzene ( $\rho_{\text{CH}_3} = 1/6$ ). Under higher resolution, the presence of additional, but poorly resolved,

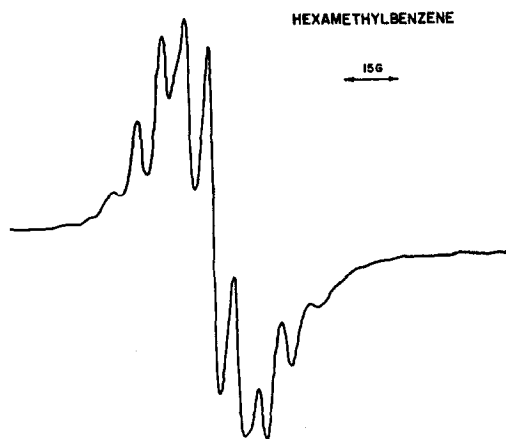


FIG. 4. EPR spectrum of hexamethylbenzene adsorbed on HZ.

lines is evident, but no speculations as to their origin will be attempted here.

### Toluene, Xylenes, Mesitylene, Tetramethylbenzenes

EPR spectra have also been observed when toluene, the xylenes, mesitylene, and the tetramethylbenzenes are sorbed on HZ. The spectra are complicated by the small aromatic proton splittings of the order of the line widths.

### ACKNOWLEDGMENTS

The authors thank Drs. E. Dempsey, R. Desau, and E. I. Heiba for some useful discussions, and Mr. O. M. Epifanio for his careful and painstaking work in preparing the samples and obtaining their spectra.

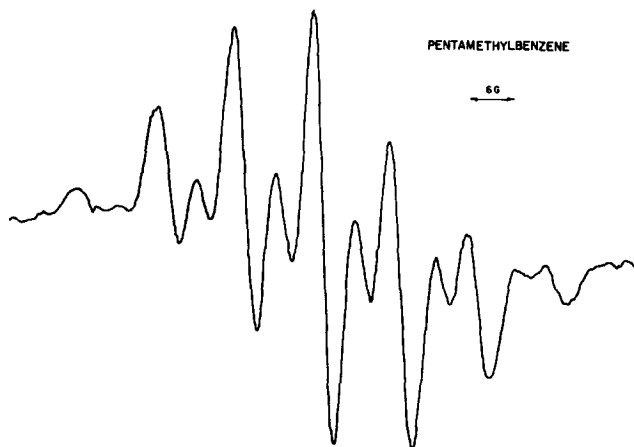


FIG. 3. EPR spectrum of pentamethylbenzene adsorbed on HZ.

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## The Structure of Metallic Particles in Dispersed Catalysts

Metallic particles dispersed in silica have been used extensively for many decades as industrial catalysts and also for fundamental laboratory investigations (1). Their usefulness lies in their good thermal stability and the high surface area of the metal. In more recent years it has been suggested that the activity depends upon the sizes of the metallic particles to an extent that exceeds the change in surface area (2-7). For instance, the adsorption of nitrogen was found to depend more on crystal size (15-70 Å) than on the type of metal, and this led to the suggestion that the nature of the surface sites exposed on small crystals is important (3). Subsequently, models of small crystals have been examined and the distributions of the various types of site computed as a function of the sizes and shapes of the crystals (8, 9).

In all this work it has been assumed that the small crystals have a FCC structure. However, it has been shown by electron microscopy that for some FCC metals very small particles formed by condensation

from the vapor in a vacuum (10, 11), or as smokes in inert gas atmospheres (12), or by precipitation from solution (13), are not necessarily FCC crystals, but frequently adopt specific multiply-twinned forms. Several such types of particles have been identified by electron diffraction and dark-field electron microscopy, and they have been shown to contain 5 (pentagonal bipyramid) and 20 (icosahedron) uniform tetrahedral units, respectively (10). These forms, particularly the latter, are attractive because their structure allows them to expose only close-packed faces in a very compact manner.

The detailed internal structure of these multiply-twinned particles can be seen in very high-resolution electron micrographs by Komoda (14), and their stability has been investigated theoretically (15, 16). It was shown that for small numbers of atoms (about 500) a pentagonal bipyramid should be more stable than a tetrahedron, and that up to cluster sizes of about 2000 atoms, an icosahedron should be about as stable as a