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ESR Study of Cation Radicals Derived from Benzene and Methyl-Substituted Benzenes Adsorbed on a Synthetic Mordenite: Formation of Biphenyl Cation Radical from Benzene

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The formation of radical cations from aromatic compounds adsorbed on zeolites (*1*) and silica–alumina (*2*) has been widely studied. When an aromatic compound RH has been adsorbed, radical cations RH^+, $(RH)_2^+$, and/or R_2^+ have been observed. Radical cations R_2^+ have been found with 1,1′-binaphthyl adsorbed on silica–alumina (*3*) and with triphenylamine adsorbed on silica–alumina (*4*) or montmorillonite (*5*). ESR spectra arising from benzene and methyl-substituted benzenes have been weak and poorly resolved when adsorbed on X and Y zeolites, making identification of the radicals difficult (*6*). We have observed well-resolved ESR spectra with benzene and benzene derivatives adsorbed on a synthetic mordenite. In this paper we describe the ESR spectra of the radicals derived from benzene and methyl-substituted benzenes, identify the radical species, and discuss the mechanism of formation of biphenyl cation radical from benzene.

Ammonium mordenite (NH_4–Z) was prepared by ion exchange of Zeolon, a synthetic sodium mordenite from Norton, with ammonium chloride. The zeolite in ESR tubes (4 mm o.d.) were activated by heating in air at 520°C for 18 hr. The tubes were sealed (while still hot) with tight-fitting rubber septum caps and then neat-liquid samples or solution samples to be studied were injected through the septums. ESR measurements were carried out at room temperature with a Varian V-4501 EPR spectrometer operated at 9.5 GHz with 100 kHz field modulation. Figures 1 and 2 show observed spectra as well as theoretical spectra, which were calculated by assuming a Lorentzian line shape for the individual lines, and by taking the hyperfine (hf) coupling constants (a) and the maximum slope widths (w) given in the figures. The line width variation among the different hf lines, which arises from the restricted motion of radicals (*7*), was not taken into account in this calculation. Therefore, the complete agreement between the theoretical and the observed spectra was not attained. However, the agreement on the positions of the conspicuous peaks are excellent so that the radical species giving rise to the observed spectrum were conclusively identified. Radical concentrations were estimated by comparison of the area obtained by double integration of the first derivative curves for the sample and standard solutions of DPPH in benzene. The radical concentrations reached 6×10^{17} and 8×10^{17} radicals/g of the zeolite for neat benzene and neat toluene, respectively.

The spectrum obtained from benzene in carbon tetrachloride (Fig. 1b) agrees well with the theoretical spectrum of benzene dimer cation radical (Fig. 1a). The hf coupling constant of 2.2 G is nearly equal to that observed in sulfuric acid (*8*) or in silica–alumina (*9*). The hf coupling constants of the hydrogen atoms of the biphenyl cation radical were assumed to be

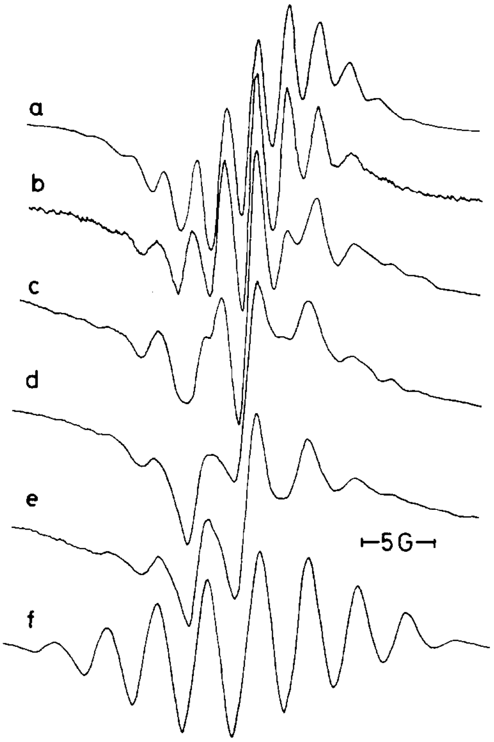


FIG. 1. ESR spectra of liquids adsorbed on NH_4–Z; (b) 1.8 mole/liter of benzene in carbon tetrachloride; (c) benzene, 5 min after mixing; (d) benzene, 24 hr after mixing; (e) 0.1 mole/liter of biphenyl in *n*-hexane. Theoretical spectra of (a) benzene dimer cation radical, $a = 2.2$ G, $w = 1.6$ G; (f) biphenyl cation radical, $a_2 = 3.37$ G, $a_3 = 0.52$ G, $a_4 = 6.74$ G, $w = 1.0$ G.

proportional to those of the corresponding hydrogen atoms observed with the biphenyl anion radical. The theoretical spectrum of the biphenyl cation radical (Fig. 1f) is in good agreement with the spectrum obtained from biphenyl in *n*-hexane (Fig. 1e). The hf coupling constants (6.74, 3.37, and 0.52 G) are 1.23 times as large as those of the biphenyl anion radical (5.46, 2.73, and 0.43 G) (*10*). The proportionality constant 1.23 is reasonable in view of the value of 1.15 for benzene (*8*), 1.13 for naphthalene (*11*), and 1.11 for anthracene (*12*). The spectra observed for neat benzene are the superposition of those for the benzene dimer cation radical and biphenyl cation radical. Immediately after the addition of benzene to the zeolite, the benzene dimer cation radical appeared together with the biphenyl cation radical (Fig. 1c). On standing at room temperature, the former decayed and eventually disappeared in a few days, while the latter persisted (Fig. 1d). The spectrum obtained from toluene (Fig. 2c) agrees well with the theoretical spectrum of 4,4′-dimethylbiphenyl cation radical (Fig. 2b). These spectra are in agreement with that obtained from 4,4′-dimethylbiphenyl (Fig. 2a), except for being different from the latter in line widths. No toluene dimer cation radical was observed even immediately after the addition of toluene to the zeolite. The spectrum obtained from *o*-xylene (Fig. 2d), quite similar to that from toluene, was assigned to 3,4,3′,4′-tetramethylbiphenyl cation radical, in which hf coupling constants of the 3 and 3′ methyl protons were too small to modify the spectrum.

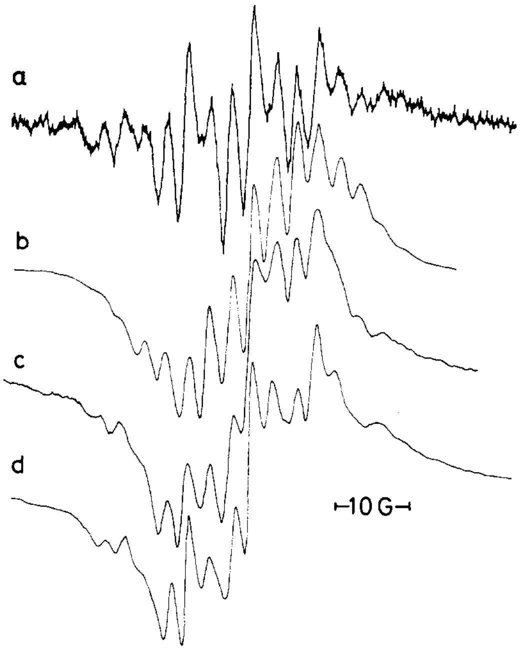
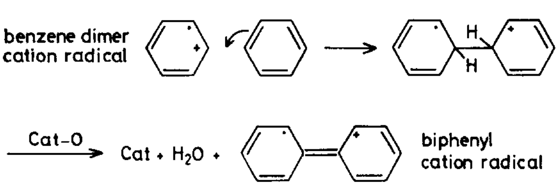


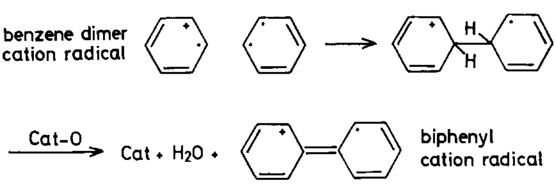
FIG. 2. ESR spectra of liquids adsorbed on NH_4–Z, (a) 4,4′-dimethylbiphenyl in carbon tetrachloride; (c) toluene; (d) *o*-xylene. Theoretical spectrum (b) of 4,4′-dimethylbiphenyl cation radical, $a_2 = 2.4$ G, $a_3 = 0.5$ G, a (CH_3) $= 6.0$ G, $w = 2.0$ G.

These findings indicate that the benzene dimer cation radical is derived from benzene and then converted to the biphenyl cation radical. Two reaction mechanisms are examined for the coupling between the cation and the neutral molecule of benzene at an oxidative site, Cat-O, on the zeolite.

The first is an ionic coupling mechanism: With a methyl-substituted benzene, the coupling must occur most readily between the carbon atom having the largest positive charge in the cation and the one having the largest negative charge in the neutral molecule. The distribution of the net charges (Q), spin densities (ρ), and free valences (F) of methyl-substituted benzenes were calculated by means of a simple Hückel MO method, in which Coulson–Crawford's parameters were used *(13)* and the overlap integrals were neglected. These values are shown in Table 1. In the case of toluene, the negative charges are mainly on the *ortho* (—0.0047) and the *para* (—0.0036) carbon atoms in the neural molecule and the largest positive charge is on the *para* carbon atom (0.330) in the cation radical. These charge distributions facilitates *para–para* and *para–ortho* coupling for toluene, however, the latter coupling must be impeded by steric hindrance effect between the methyl and the phenyl groups. Comparison of the charge distributions in the benzene cation radical (0.167) and benzene molecule (0) with those in the toluene cation radical and toluene molecule suggests that the toluene dimer cation radical undergoes coupling more readily than the benzene dimer cation radical does. Charge distributions in the *o*-xylene cation radical (0.238 and 0 on the 4 and 3 carbon atoms, respectively) and in the *o*-xylene molecule (—0.0044 and —0.0035 on the 3 and 4 carbon atoms, respectively) favor the formation of 3,4,3′,4′-tetramethylbiphenyl cation radical, the latter must be unfavorable because of the steric hindrance effect. This reaction scheme is consistent with our findings.



The second is a radical coupling mechanism:



With methyl-substituted benzenes, the coupling must occur most readily between the carbon atom having the largest spin density in the cation and the one having the largest free valence in the neutral molecule. It is found from the spin densities and free valences in Table 1 that this coupling mechanism favors the coupling between the same carbon atoms as those in the ionic coupling mechanism. Therefore, it is impossible to distinguish between these

TABLE 1

NET CHARGES (Q), SPIN DENSITIES (ρ) AND FREE VALENCES (F) CALCULATED BY A SIMPLE HÜCKEL MO METHOD

Toluene	$Q_1 = 0.0041$,	$Q_2 = -0.0047$,	$Q_3 = 0.0002$
	$Q_4 = -0.0036$,	$Q_c = -0.0763$,	$Q_x = 0.0847$
	$F_2 = 0.4083$,	$F_3 = 0.3979$,	$F_4 = 0.4011$
Toluene cation	$Q_1 = 0.3076$,	$Q_2 = 0.0932$,	$Q_3 = 0.0700$
	$Q_4 = 0.3098$,	$Q_c = 0.0142$,	$Q_x = 0.0422$
	$\rho_i = Q_i$		
o-xylene cation	$Q_1 = 0.2432$,	$Q_3 = 0.0012$,	$Q_4 = 0.2126$
	$\rho_i = Q_i$		
o-xylene	$Q_1 = 0.2468$,	$Q_3 = -0.0046$,	$Q_4 = -0.0033$
	$Q_c = -0.0762$,	$Q_x = 0.0844$	
	$F_1 = 0.2468$,	$F_3 = 0.4075$,	$F_4 = 0.4002$

two coupling mechanisms on the basis of our findings.

The spectra observed with *p*-xylene were interpreted as arising from the dimer cation radical with methyl hf coupling constants of 3.8 G (six equivalent hydrogens). The spectra observed with 1,2,3-trimethylbenzene, durene in carbon tetrachloride, and pentamethylbenzene in carbon tetrachloride were interpreted as arising from the cation radicals with methyl hf coupling constants of 10.4 G (6), 10.8 G (12), and 10.8 G (12), respectively. The hf coupling constant of 10.8 G agrees with that of 11.0 G obtained from durene cation radical in sulfuric acid (*14*). Spectra were obtained from hexamethylbenzene in carbon tetrachloride, *m*-xylene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene, but were unidentified because of their poor resolution.

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