Radical Intermediates in the Photoinduced Formation of Benzene Cation-Radicals over H-ZSM-5 Zeolites

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Received: November 29, 1993; In Final Form: May 10, 1994*

Radical particles are shown to appear under irradiation ($h\nu \ge 2.8$ eV) of H-ZSM-5 zeolites with adsorbed benzene. The particles appeared to be benzene cation-radical precursors over the zeolite. Heating resulted in irreversible destruction of the particles and emergence of a benzene cation-radical spectrum. The obtained radicals have no detectable hyperfine splittings on the protons, their spectrum remaining almost the same when deuterobenzene was used. The possible structure of the particles is discussed.

Introduction

Photostimulated benzene cation-radical (CR) formation was previously shown to follow a monophotonic mechanism under irradiation of H-ZSM-5 zeolite with adsorbed benzene starting from photon energies of $h\nu = 2.8 \text{ eV}.^{1,2}$ The process involves formation of electron donor-acceptor complexes between benzene molecules and zeolite strong surface acceptor centers (A_S) and, thus, can be described by the following scheme:

$$A_{S} + C_{6}H_{6} \rightleftharpoons [A_{S} \cdot C_{6}H_{6}] \stackrel{h\nu}{\rightleftharpoons} [A_{S} \cdot C_{6}H_{6}]^{*} \rightarrow A_{S}^{-} + C_{6}H_{6}^{+}$$
(1)

Only cation-radicals $C_6H_6^+$ managed to be registered by means of ESR at temperatures higher than 150 K. A proposed counter ion (A_S-) failed to be observed, the nature of acceptor centers (A_S) responsible for the photoprocesses remaining unclear.

In the present paper photoinduced radical formation with participation of benzene molecules adsorbed over H-ZSM-5 zeolite was studied at lower temperatures (down to 93 K).

Experimental Procedure

Research was carried out on an ESR "in situ" installation on the basis of the "ERS-221" spectrometer. A scheme of the installation is given in Figure 1.

A quartz ampule with a catalyst connected to a high-vacuum apparatus is placed in the spectrometer resonator. The catalyst temperature (90–835 K) in the course of the pretreatment and the experiments is controlled by a special thermostat. The vacuum apparatus allows one to carry out a prolonged pretreatment and gas adsorption both under dynamic vacuum (10⁻⁷ Torr) and under controlled pressure (up to 800 Torr). The presence of a monochromator mounted in the lightning device makes it possible for one to study the spectral characteristics of the photostimulated processes in the range of quantum energies of 1–5 eV. This installation permits one to record ESR spectra and obtain other information on the state of the adsorption layer at any step of the treatment and in the course of a catalytical process. The installation is also equipped with a computer that is used for ESR spectrum analysis.

A ZSM-5 zeolite sample in H-form prepared by the hydrothermal synthesis was obtained from NPO "Grosneftechim". The zeolite aluminosilicate composition corresponded to the molar ratio $SiO_2/Al_2O_3 = 60$; the iron content was 0.14 wt % Fe₂O₃.



Figure 1. Scheme of the experimental installation: (1) ampule with a catalyst; (2) cavity of the "ERS-221" spectrometer; (3) thermostat; (4) monochromator; (5) mercury lamp; (6,9) traps cooled by liquid nitrogen; (7,8) pressure meter; (10) mercury pump; capacities for storage of (11) liquids and (12) gases; (13) metal valves.

The sample had been studied earlier with respect to benzene adsorption leading to CR formation.¹⁻³

Standard sample pretreatment consisted of oxygen-vacuum treatments at 823 K followed by a freezing-out of the products in a trap cooled by liquid nitrogen. Finally the sample was heated in oxygen (20 Torr, 2 h) with further cooling to 573 K in oxygen followed by evacuation at this temperature for an hour.

To avoid isotopic exchange effects during deuterobenzene adsorption, these experiments were preceded by surface deuteration in D_2 gas at 823 K for 4 h, the gas being changed after 2 h.

Benzene and benzene-*d* adsorption was carried out at 373 K with further evacuation for 30 min. The amount of adsorbed substance obtained after the procedure was 0.4 wt % (3 × 10¹⁹ molecules/g)². It was measured by an amount of benzene desorbed upon heating the zeolite to 673 K.

The sample was irradiated directly in the ESR spectrometer cavity, a high-pressure 1-kW mercury lamp being the irradiation source. The intensity of the monochromatized irradiation of the sample was about 10^{16} photons/s.

Results

1. Photostimulated Formation of Primary Radicals R_X . Irradiation of the zeolite with adsorbed benzene at 93 K starting with photon energies of 2.8 eV leads to an appearance of new paramagnetic particles (R_X). Their ESR spectrum is presented in Figure 2 (spectrum 1). An analogous spectrum was obtained upon deuterobenzene adsorption (Figure 2, spectrum 2).

In the spectrum two doublets symmetric with respect to the free electron g-factor (g_e) can be seen, the splitting value in the

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[•] Abstract published in Advance ACS Abstracts, June 15, 1994.



Figure 2. ERS spectra obtained after irradiation ($h\nu = 3.4 \text{ eV}$) of H-ZSM-5 zeolite with adsorbed C₆H₆ (spectrum 1) and C₆D₆ (spectrum 2) at 93 K.



Figure 3. ESR spectra of photoinduced benzene and deuterobenzene CR at 173 K. In both cases the spectrum stick diagrams are shown.

doublets being 8 and 24 mT. The outer doublet components look like parallel components in an anisotropic spectrum, whereas those of the inner doublet (8 mT) are like perpendicular ones. The high-field components of the doublets are more poorly resolved than the low-field ones and have lower pick intensities. Both doublets have an additional doublet splitting, the magnitude for the outer one being 1.9 mT. As already mentioned, the values are the same for an ordinary and a deuterated benzene. That makes it possible to assert that they are not associated with the hyperfine coupling on protons.

Analysis of the emergence and disappearance conditions for the radicals R_X^{\bullet} verifies that the spectra concern mainly an individual particle. Only low-intensity CR spectra can be seen additionally (Figure 2).

2. Formation of Benzene Cation Radicals. Upon a temperature rise, the spectrum intensity of R_X^{\bullet} radicals was observed to fall simultaneously with the benzene CR concentration growth. ESR spectra of $C_6H_6^+$ and $C_6D_6^+$ cation-radicals are presented in Figure 3. It should be noted that even at such a low temperature benzene CRs possess a fairly high mobility that averages the g-and A-tensor anisotropy. It manifests in an extremely low line width and makes it possible to observe a well-resolved spectrum of $C_6D_6^+$ CR (Figure 3).

In order to find out a correlation between R_X^* radical disappearance and benzene CR emergence, the following experiment was conducted. The zeolite with adsorbed benzene was irradiated at 93 K with subsequent momentary heating of the sample, the heating temperature varying from 123 to 173 K. Afterward the sample was cooled down to 93 K with the following ESR spectrum registration.

The changes in the R_X^{\bullet} concentration were determined from the spectrum pick intensity changes in respective units since a direct numerical integration of the spectra could lead to



Figure 4. Dependence of benzene CR concentration on the R_X spectrum intensity. The temperature of ESR spectrum registration was 93 K.



Figure 5. Kinetics of photostimulated benzene CR destruction at 293 K (1) and calculated dependences for a bimolecular reaction with $\alpha = 0.95$ (2) and $\alpha = 1.05$ (3).

considerable mistakes. The mistakes were caused primarily by the big width of the spectrum, its low intensity, and a superposition of the spectra belonging to other particles. A computer analysis showed the spectra from both R_X radicals and C_6H_6 CR remain constant during the experiment.

The results of the experiment are shown in Figure 4. One can see the dependence of the benzene CR concentration growth upon the R_X^* spectral intensity falls, being almost linear. That makes it possible to conclude that the radicals R_X^* discovered by us are precursors of benzene CRs in their photostimulated formation over H-ZSM-5 zeolites. Thus, the appearance of benzene CRs in this process is caused by primary destruction of radical particles R_X^* and no irradiation is needed.

$$R_{X}^{*} \xrightarrow{T > 120 \text{ K}} C_{6}H_{6}^{+}$$
(2)

If H-ZSM-5 zeolite with adsorbed benzene is irradiated at temperatures higher than 150 K, the R_X^{\bullet} stationary concentration is low and only benzene CRs are observed by means of ESR.^{1,2}

3. Benzene Cation-Radical Destruction. At temperatures higher than 200 K the benzene CRs were destroyed, with no paramagnetic products being formed. The kinetics of the photoinduced benzene CR concentration decrease at 293 K is given in Figure 5. The data show the kinetic dependence of the decrease to be well described by a straight line in logarithmic coordinates with an incidence tangent equal to -1. With the dependence being characteristic for bimolecular reactions, such a reaction is supposed to be a limiting stage of the CR destruction in the studied temperature range:

$$C_6H_6^+ + P \rightarrow \text{products}$$
 (3)

where P is a particle reacting with the radical, with products being unobservable by ESR.

It is essential that the initial concentrations of the reagents should be equal ($\alpha = [P]_0/[C_6H_6^+]_0 \approx 1$). Figure 5 also shows a calculated kinetics of a bimolecular reaction for a lack and surplus of the reagent P ($\alpha = 1.05$ and $\alpha = 0.95$). Small changes in the ratio of the initial concentrations are shown to lead to a substantial deviation of the kinetic dependence. Thus, given that the reaction is bimolecular, equal amounts of the initial reagents should be used to describe the kinetics ($\alpha = 1.0$). It seems hardly probable that there could exist upon the surface any other particles besides the counter ions with concentrations so close to that of the benzene CRs. We believe P to be either the counter ion itself or a product of its chemical transformations. So, the process represents a recombination between a benzene CR and its counter ion.

It should be noted that the disappearance mechanism of photoinduced benzene CRs obtained with a low concentration of adsorbed benzene (3×10^{19} molecules/g) substantially differs from that of thermoinduced CRs appearing under the filling of all zeolite channels (10^{21} molecules/g)⁴. In the former case their destruction is most probably caused by a recombination process resulting in the disappearance of all paramagnetic particles, whereas in the latter case the benzene CRs were shown to take part in a polycondensation process to give CRs of biphenyl and terphenyl that are precursors of coke paramagnetic centers. In this process the concentration of the paramagnetic particles remains constant.

Discussion

The CR formation process must involve at least the following stages: formation of an excited stated due to a photon absorption, relaxation of the excited state, separation of charges, and stabilization of an ion-radical state.

The observation of the benzene CR ESR spectrum with a small width for an individual spectral component (ΔH) verifies that the nearest paramagnetic center is situated relatively far from the CR. For $C_6D_6^+$, the line width does not exceed 0.05 mT. So, supposing paramagnetic centers are distributed evenly over the surface, one can estimate the distance between them to be more than 30 Å.⁵

One can suppose that separation of the charges resulting in CR formation can be preceded by a state with charges not yet entirely separated, i.e. a radical pair state. The discovered particle R_X^* can be supposed to correspond to a state with no separation of charges. In this case an electron could be stabilized on a trap close to the positive charge. Two appearing paramagnetic particles can interact to form a radical pair.

The ESR spectra of the particles R_X° obtained by us resemble those of the radical pairs with the structure $[RO_2^{\circ} \dots RO^{\circ}]$ observed upon γ -irradiation of diphenylethane peroxide.⁶ The formation of the radical pair $[O_2^{\circ} \dots R^+]$ was proposed as an outcome of the interaction of aniline with zeolite active sites.⁷ Active sites of ZSM-5 zeolites participating in benzene CR formation are known to incorporate molecular oxygen.^{3,8,9} Thus, a radical pair in our system may have an analogous structure $[O_2^{\circ} \dots C_6H_6^+]$.

If the particle R_X^* observed by us is a radical pair, a doublet with a 24-mT (D_{\parallel}) splitting corresponds to parallel orientation ($\theta = 0^\circ$) of the vector connecting the radical centers in the pair with respect to the external magnetic field, whereas a doublet with an 8-mT (D_{\perp}) splitting corresponds to the perpendicular one ($\theta = 90^\circ$). So, in this particle the D_{\parallel}/D_{\perp} ratio approximately equals 3. But for isotropic pairs this ratio is known to be 2.¹⁰

Observed deviation of this parameter from the canonical one may be accounted for either by a large value of the asymmetry parameter E in the Hamiltonian of $(4)^{10}$ or by a large g-tensor anisotropy of one of paramagnetic species in the pair.¹¹ In order to evaluate parameters required for such a deviation of the



Figure 6. Simulated ESR spectra of radical pairs in polyoriented systems: (A) for particles with a small g-tensor anisotropy (calculated with the following parameters in the Hamiltonian of (4): $g_1^{(1)} = 2.045$; $g_1^{(2)} = 2.010$; $g_{\perp}^{(1)} = g_{\perp}^{(2)} = 2.002$; D = -128 G; E = 27 G); (B) for particles with a large g-tensor anisotropy (calculated with the following parameters characterizing paramagnetic particles in the pair: $g_1^{(1)} = 1.99$; $g_{\perp}^{(1)} = 0.61$; $g_1^{(2)} = 2.0045$; $g_{\perp}^{(2)} = 2.002$; r = 5.3 Å; $\theta = 70^{\circ}$; $\beta = 60^{\circ}$; $\gamma = 115^{\circ}$. Here θ is an angle between the g-tensor symmetry axis of the first particle and a vector \tilde{r} connecting the centers of the particles; β and γ are polar and azimuthal angles setting the second particle g-tensor symmetry axis direction with respect to a coordinate system where the Z-axis coincides with the first center symmetry axis, with the vector \tilde{r} lying in the XZ plane.

spectrum, we have conducted computer simulations of ESR spectra of radical pairs in terms of these two different models.

The first model supposed that paramagnetic centers possess a small g-tensor anisotropy with respect to the dipole interaction. Such a pair may have the structure $[O_2 - - C_6 H_6^+]$. The Hamiltonian for such a pair neglecting hyperfine interaction and spin exchange can be written as¹⁰

$$H = \beta \mathbf{H}_0 \mathbf{g}^{(1)} \mathbf{S}^{(1)} + \beta \mathbf{H}_0 \mathbf{g}^{(2)} \mathbf{S}^{(2)} + D(S_z^2 - S(S+1)/3) + E(S_x^2 - S_y^2)$$
(4)

The second model supposed the radical pair incorporates an ion with a large g-tensor anisotropy, for example, Fe^{3+} . These ions are present in the zeolite, and their possible role in benzene CR formation is discussed by Kazansky and co-workers.¹²

Figure 6 presents calculated ESR spectra of radical pairs that describe the experimental spectra fairly well. It is essential that the main features of the observed spectra can be accounted for in the terms of both models.

The spectrum of Figure 6A was calculated within the first model. A program worked out earlier for calculation of ESR spectra of nitroxyl biradicals was modified for the computations. To simulate the spectrum, values of the g-tensor parallel components, parameters D and E for a dipole-dipole interaction tensor, its orientation with respect to the g-tensor principal axes, and the effective line width were selected. The distance between the radical fragments in the pair corresponding to the D value is about 6 Å. To account for the anisotropy parameter E, one might assume one of the radical particles has a correlated movement perpendicular to a line connecting the average positions of the radical centers. The spatial amplitude of the movement should be at least 3-4 Å, its correlation time being very low.

To simulate spectra within the second model, theoretical formulas in the first order of perturbation and a computer program

were worked out. The pair was supposed to have a fixed structure, the sample consisting of pairs with a chaotic respective orientation. Systematic investigation of the g-tensor anisotropy influence on the ESR spectrum parameters of radical pairs is to be published separately.

Figure 6B presents a calculated spectrum satisfactorily describing the main peculiarities of the experimental spectrum. $g_{\parallel}^{(1)}/r^3$, $g_{\parallel}^{(1)}/g_{\perp}^{(1)}$, $g_{\parallel}^{(2)} - g_{\perp}^{(2)}$, θ , β , and γ values were adjusted. The detailed structure of the central part of the spectrum can be calculated in the second order of the perturbation.

It is essential that a hyperfine interaction with CR protons in the radical pair, if taken into account, might result within both models in an additional broadening of its ESR spectrum with respect to the spectrum obtained using deuterobenzene.

The calculations made it possible to simulate the experimental spectrum fairly well and achieve the required D_{\parallel}/D_{\perp} ratio. Thus, they showed that the radical intermediate in photoinduced benzene CR formation can be a radical pair. But, they neither allow to declare it unambiguously nor to choose a single pair model. Observation of these ESR spectra in the Q-band is likely to help in the choice.

Conclusion

In the present paper radical precursors of benzene cationradicals over zeolites have been discovered. The conditions of their formation and destruction have been studied. The decrease in their concentration under a temperature rise has been shown to be accompanied by an adequate concentration increase of benzene CRs. This particle has been proposed to consist of two interacting radicals with a distance of 5.3-6 Å between them.

Destruction of photoinduced benzene CRs has been studied. It has been shown to result from a recombination with a particle unobserved by means of ESR. The particle appeared to be either a counter ion itself or a product of its chemical transformations.

With the results of the present paper taken into account, the process of the photostimulated formation of cation-radicals $C_6H_6^+$ and their destruction over H-ZSM-5 zeolites can be described by the following scheme:

$$A_{S} + C_{6}H_{6} \rightleftharpoons [A_{S} \cdot C_{6}H_{6}] \stackrel{h_{\nu}}{\rightleftharpoons} [A_{S} \cdot C_{6}H_{6}]^{*} \rightarrow [A_{S}^{-} \cdots C_{6}H_{6}^{+}] \rightarrow A_{S}^{-} + C_{6}H_{6}^{+} \rightarrow \text{products} (5)$$

Formation of an electron donor-acceptor complex seems to be the first stage of the process, its photochemical activation being the second one. The activated state with a partial electron transition may transform into a pair of interacting radicals, its dissociation resulting in the formation of a benzene CR. Recombination of the radicals leading to nonparamagnetic products is the final stage.

Acknowledgment. We are pleased to thank Prof. V. F. Yudanov and Dr. A. G. Maryasov for helpful discussions and interesting ideas.

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