

Use of Electron Spin Resonance Spectroscopy To Study the Photochemistry of Adsorbed Dibenzyl Ketone on Porous Silica

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Contribution No. 4498, E. I. du Pont de Nemours and Company, Central Research & Development, Experimental Station, Wilmington, Delaware 19898

Received June 30, 1987. In Final Form: December 30, 1987

With electron spin resonance (ESR) spectroscopy, it was possible to observe benzyl radicals formed photochemically in situ from dibenzyl ketone (DBK) adsorbed on porous silica samples. The spectra showed different shapes and g values as a function of surface coverage and silica pore diameters. With large pores (95 Å), spectral broadening at low coverages suggests intraradical interactions, which become more profound with intermediate pore sizes (40 Å) due to the smaller intraradical distances. With still smaller pore sizes (20 Å), benzyl radicals are immobile and relatively unreactive. In each case, the presence of water vapor leads to the same solution-like spectrum. The g values indicate that substantial crystal field distortions occur on binding, which allows spin-orbit coupling due to mixing of the partially filled molecular orbital with unfilled orbitals. Two binding orientations are indicated, characterized by different g values. The more highly shifted value ($g \approx 1.93$) is observed with pore- and surface-bound 20-Å silica and with all silicas in the presence of water vapor, while the other binding mode ($g \approx 1.99$) is observed with 95- and 40-Å. With 95-Å silica, the ESR spectra show average behavior between the surface and bound forms, indicating rapid equilibration. With 40- and 20-Å silicas, the spectra show superpositions of the two extreme spectra, indicating slow equilibration of binding sites.

Photochemistry of small molecules has been used extensively to study confined environments. In general, these studies have employed such techniques as flash photolysis, resonance Raman, NMR, and ESR spectroscopy. From such studies, it has been possible to describe interfaces in terms of probe mobilities and effective environmental polarities. The reactivity and mobility of small molecules on solids have been studied by using photochemically or radiolytically produced radicals and radical pairs.¹ In particular, electron spin resonance (ESR) spectroscopy has been used to study radical pairs formed on photoexcitation of peroxides in crystals of the same peroxide² and in urea channels.³ A recent study reported the ESR spectra of photochemically generated radicals from dimethyl 2,2'-azodiosbutyrate adsorbed on silicas and zeolites.⁴ We were interested in using a similar methodology to study randomly adsorbed molecules on silica gels of various pore sizes and thereby probe the vapor-solid interface. The study of silica gel surfaces has involved bulk property techniques such as BET surface areas, electron microscopy, ESCA, and laser flash photolysis of adsorbed molecules.⁵ A combination of these techniques has shown that porous silica contains an internal surface which can be described in terms of a distribution of pores of various diameters. The study of the adsorption and subsequent photochemistry of small molecules on silica gel surfaces of different average pore sizes has been investigated previously by using product studies.⁶ In the current investigation, ESR spectroscopy is used to directly observe photochemically generated radicals formed on photodecomposition of dibenzyl ketone (DBK) adsorbed at different sites on dif-

ferent silicas and thereby more directly probe the effects of adsorption on photochemistry. To complement this, we use photochemistry to investigate the internal surfaces of porous silica. Upon photoexcitation, DBK undergoes cleavage to give benzyl radicals (PhCH_2^*) and phenylacetyl radicals (PhCH_2CO^*). Under most conditions, the phenylacetyl loses carbon monoxide rapidly ($6.4 \times 10^6 \text{ s}^{-1}$ at 300 K)⁷ to produce a second benzyl radical. The ESR spectrum of benzyl radicals under conditions where the DBK precursor is adsorbed on silica gel can therefore be used as a probe of the adsorption sites on the silica gel.

Experimental Section

Silica gel samples were prepared by diluting a solution of sodium silicate (Du Pont, "Solution F"; mole ratio $\text{SiO}_2:\text{Na}_2\text{O} = 3.25$; 29% SiO_2 by weight) with water to give a 6% solution of SiO_2 by weight. This solution (3 L) was passed through a 6-L Rexyn 101 (acid form) ion-exchange resin to give 3 L of silicic acid solution (pH 3.0). Addition of 10 mL of 1 N NH_4OH raised the pH to 5.5. After 20 min, the solution gelled and the mixture was aged for 4 h more. The mixture was cooled for 12 h with dry ice, warmed to room temperature, filtered through a coarse fritted disk, washed 4 times with 1 L of concentrated hydrochloric acid,

(1) See, for example: (a) Sohma, J.; Shiotani, M. *ACS Symp. Ser.* 1976, 34, 141-156. (b) McBride, J. M.; Vary, M. W.; Whitsel, B. L. *ACS Symp. Ser.* 1978, 208-223. Yakimchenko, O. E.; Lebedev, Y. S. *Russ. Chem. Rev.* 1978, 47, 531-548. (d) Cichowlas, A. A.; Krzyzanowski, S. Z. *Phys. Chem. Neue Folge* 1982, 129, 119-128. (e) Kasai, P. H.; Gaura, R. M. *J. Phys. Chem.* 1982, 86, 4257-4260. (f) Kasai, P. H.; Bishop, R. J., Jr. *J. Am. Chem. Soc.* 1972, 94, 5560-5566. (g) Lunsford, J. H. *J. Phys. Chem.* 1968, 72, 4163. (h) Huang, Y.; Vansant, E. F. *J. Phys. Chem.* 1973, 77, 663-337. (i) Avnir, D. *J. Am. Chem. Soc.* 1987, 109, 2931-2938.

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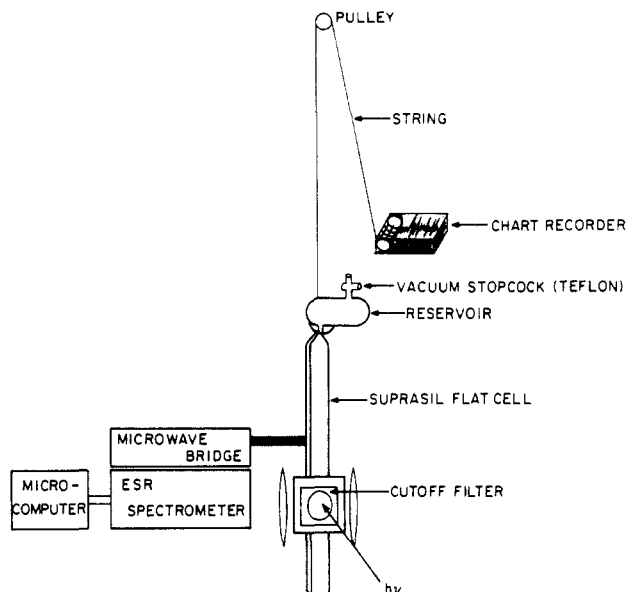


Figure 1. Schematic representation of the instrumentation used in measuring the ESR spectra of photochemically generated radicals adsorbed on silica.

washed with water, and dried in air at 150 °C for 8 h. The resulting 180 g of silica had a composition of $\text{Si}_3\text{O}_5(\text{OH})_2$ with less than 1 ppm of Fe. BET measurements showed a surface area of 888 m^2/g , an average pore diameter of 21.5 Å, and a median pore diameter of 20 Å.

A 50-g portion of this silica was slurried in 500 mL of H_2O , and the pH was adjusted to 8 with 3 mL of 1 N NH_4OH . After 7 days, the silica was filtered, washed with H_2O , and dried at 140 °C for 4 h. BET measurements indicated a surface area of 703 m^2/g , an average pore diameter of 57 Å, and a median pore diameter of 40 Å.

Another 50-g portion of the 20-Å silica was slurried in 1 L of H_2O with 50 mL of 1 N NH_4OH (pH 9.0), aged 9 days at room temperature, filtered, washed, and dried at 150 °C. This product had a surface area of 571 m^2/g and an average and median pore diameter of 95 Å. The pore distributions of these silicas have been described previously.⁶

DBK was obtained from Fluka Corp. and used without further purification. Samples were prepared by adding the appropriate amount of DBK in 75 mL of pentane to 10 g of oven-dried (150 °C) silica gel covered by 50 mL of pentane. The solvent was removed first with crude vacuum or by air stream, and then the sample was transferred to a $0.3 \times 0.8 \times 60$ cm Suprasil flat cell equipped with a reservoir and O-ring vacuum seal; the cell was then evacuated to better than 5×10^{-4} Torr. In cases where water vapor was added to the system, the evacuated sample was exposed to pure water vapor for 20 min before resealing. Measurements were carried out by using a Bruker 100D ESR X-band spectrometer interfaced with an IBM 9002 microcomputer. Irradiations were carried out with an Oriol 6141 1000-W HgXe lamp with aqueous and 300-nm cutoff filters. Samples were irradiated in the ESR cavity with the flat cell drawn evenly through the cavity at a rate of 1–2 cm/min as shown in Figure 1. The g values were estimated with the same cell and instrumentation assuming a g value of 2.002 for DPPH adsorbed on silica gel.

Results and Discussion

Photolysis of DBK in homogeneous solution produces benzyl radicals that show a characteristic ESR spectrum (Figure 2) where all lines can be attributed to the benzyl radicals.⁸ The product of the reaction is diphenylethane produced as two benzyl radicals collide. Similarly, irradiation of DBK adsorbed on silica gels is found to produce diphenylethane quantitatively.⁶ The ESR spectral be-

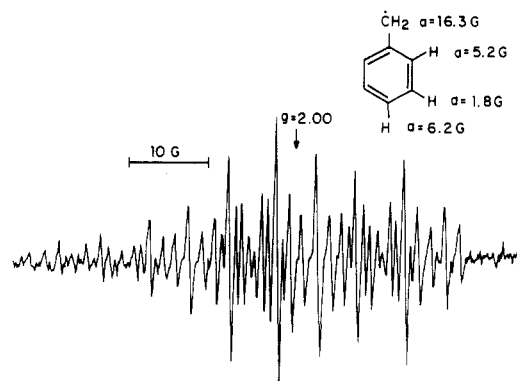


Figure 2. ESR spectrum of benzyl radical formed on photolysis of DBK in cyclohexanol with a flowing solution.

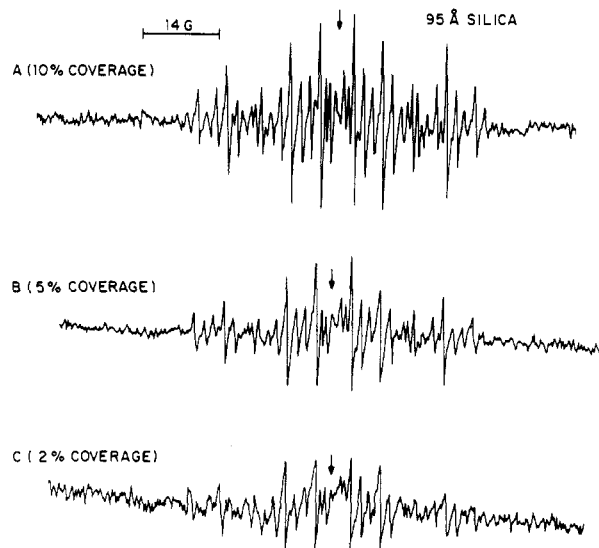


Figure 3. ESR spectra obtained on photolysis of DBK adsorbed on 95-Å silica (surface area = 571 m^2/g). In each case, the center position ($g = 1.99$) is marked by an arrow: (A) 10% of the surface covered by DBK; (B) 5% coverage; (C) 2% coverage.

havior of irradiated DBK varies upon adsorption on silica as a function of pore size and surface coverage. We found that to obtain good spectra, especially at low coverages, it is necessary to constantly photolyze fresh sample in the ESR cavity. To accomplish this, the sample tube was drawn through the cavity at a slow, steady rate by using the apparatus shown in Figure 1. In this way, product development and DBK consumption do not affect the spectra. In contrast, earlier investigations of photochemically generated radicals adsorbed on silica found spectral changes as a function of irradiation times.⁴ With large-pore-diameter silica (95 Å), the ESR spectra of the adsorbed benzyl radicals as a function of percent DBK loading (Figures 3A–C) show an increase in line widths at lower DBK coverages, though the hyperfine coupling constants remain the same as observed in solution. The value of g remains constant at approximately 1.99 between 10% (31.4 mg of DBK/1.32 g of silica) and 2% (6.5 mg of DBK/1.44 g of silica) of the surface covered by DBK (assuming a molecular surface area for DBK of 84 Å²). Such broadening of the lines can be rationalized in the following manner: the large pores can easily accommodate more than one benzyl radical formed either in the cage or from different DBK precursors. At lower coverages, a greater proportion of these radicals will be in smaller pores, where interradsical interactions (collisions) will be more common than on the surface (i.e., in larger pores). Such interactions could lead to spin exchange⁹ or dipolar cou-

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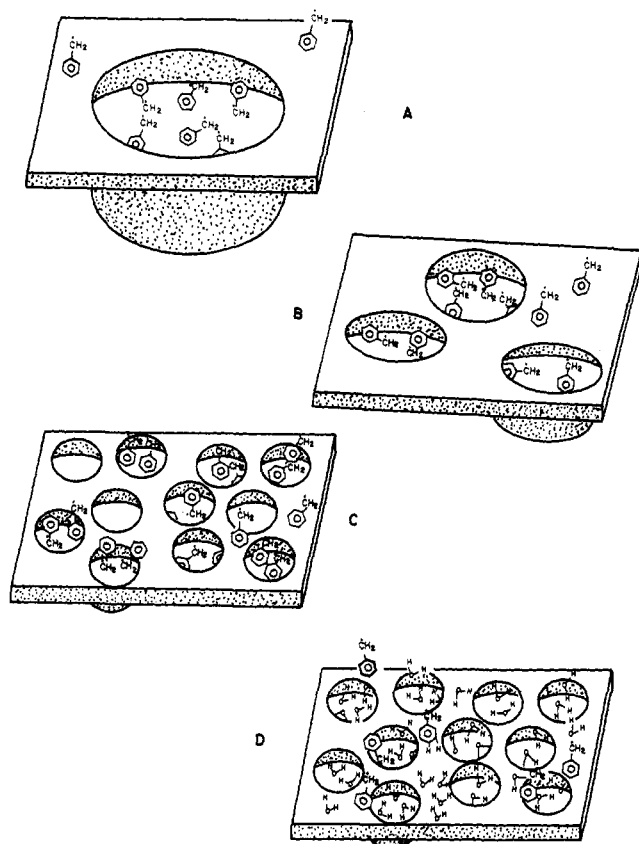


Figure 4. Schematic representation of the binding of benzyl radicals adsorbed on silica: (A) with large pore sizes (95 Å), the benzyl radicals interact slightly in the pores; (B) with 40-Å silica, inter-radical interactions within the pores are increased due to the smaller average distance between radicals in the pores; (C) with 20-Å silica, the benzyl radicals bind tightly in the pores and are unable to dimerize; (D) in the presence of water vapor, DBK is displaced from the pores such that the benzyl radicals see the same environment independent of pore size or percent coverage. The orientations of the benzyl radicals adsorbed on the surface were not determined in this investigation and therefore are arbitrarily represented here. Note also that "surface" binding may actually represent binding within large pores.

pling, which provide electronic relaxation and concomitant line-broadening. That the spectrum does not appear to be a superposition of two spectra may indicate that equilibration of the benzyl radicals occurs rapidly on the ESR time scale. This model is shown schematically in Figure 4A. Alternatively, the binding in the smaller pores could allow less rotational freedom for the radicals than for radicals adsorbed in large pores. The resulting anisotropy could cause apparent spectral broadening. Again, equilibration between sites must be fast on the ESR time scale. It has been noted that smaller pores contain a greater amount of active silanol sites on the silica surface compared to the less strongly adsorbing siloxane sites.⁵ Therefore, DBK will tend to partition to the more active smaller pores at low coverages.

With 40-Å silica gel, a solution-like DBK spectrum is observed at high DBK coverages with a g value of 1.99 and hyperfine splitting the same as in homogeneous solution (Figure 5A). At lower coverages (below 5% of the surface covered by DBK; 30 mg of DBK/2.1 g of silica), a broad, structureless component dominates (Figure 5B-D) with the g value remaining constant. This broad component

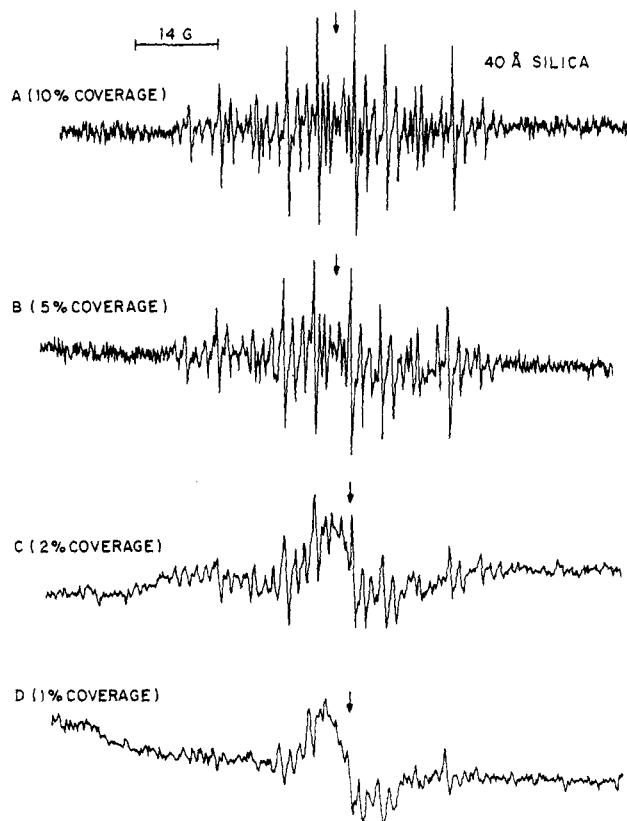


Figure 5. ESR spectra obtained on photolysis of DBK adsorbed on 40-Å silica (surface area = 703 m²/g). The arrow indicates the position of $g = 1.99$: (A) 10% DBK coverage of the surface; (B) 5% coverage; (C) 2% coverage; (D) 1% coverage.

may have similar origins to the less substantial broadening observed with the 95-Å silica gel. That is, spin exchange (or dipolar coupling) of two radicals within a small pore could lead to broadening in the ESR spectrum. In the 40-Å silica case, there will be a greater proportion of pores of small diameters, and therefore, the average distance between the radicals in these small pores will be lower than in the relatively larger pores found in the 95-Å case. The net result is greater spin exchange and increased spectral broadening to give a single ESR peak in the 40-Å silica case. The ESR spectrum in this case appears to be a superposition of two spectra (solution type and broadened) rather than an average. This suggests that, unlike the adsorbed benzyl radicals on 95-Å silica, the radicals on the 40-Å silica cannot equilibrate between sites within the ESR lifetime. This situation is shown schematically in Figure 4B. Again, broadening could also result from relatively rigid binding of the radicals in the pores, which results in an anisotropic spectrum.

On 20-Å silica gel, a similar pattern (Figure 6A) is obtained by using high loading of DBK (37 mg of DBK/1 g of silica; 10% surface coverage) as obtained in solution, again with the same hyperfine splitting as in solution; however, the g value is shifted considerably, from the free electron value of 2.00 to 1.93. As the surface coverage of DBK is decreased, a secondary broad structured spectral component begins to dominate (Figure 6B-D), though the g value remains constant. Moreover, this broad spectrum remains apparent several seconds after irradiation, whereas the sharper spectrum (as well as the solution spectrum) disappears rapidly (less than 1 s) after irradiation.¹⁰ The

(9) See, for example: Molin, Y. N.; Salikhov, K. M.; Zamarayev, K. I. *Spin Exchange*; Springer Series in Chemical Physics; Springer-Verlag: Berlin, 1980; Vol. 8.

(10) Note that no half-field transitions, evidence for a triplet biradical, were observed at room temperature with high or low coverage on 20-Å silica.

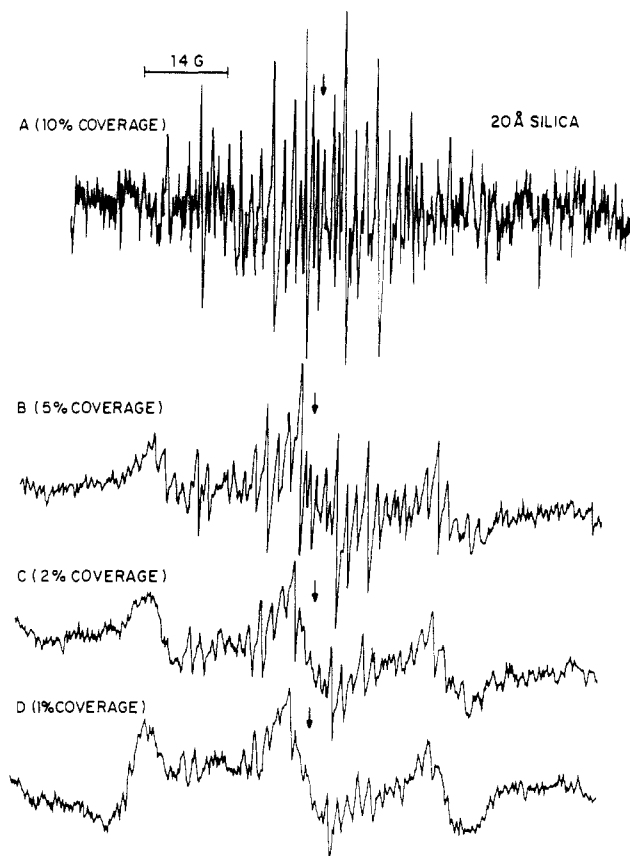


Figure 6. ESR spectra obtained on photolysis of DBK adsorbed on 20-Å silica (surface area = 888 m²/g). The arrow indicates the position of $g = 1.93$: (A) 10% DBK coverage of the surface; (B) 5% coverage; (C) 2% coverage; (D) 1% coverage.

radical species giving the broad spectrum therefore is stabilized considerably with respect to the solution radical species. Although it is possible that the spectrum observed at low coverages results from spin exchange of interacting radicals in the radical pair, the shape of the spectrum suggests that the benzyl radicals, at low coverages, are essentially immobilized within the pores. The resulting anisotropic spectrum is similar to those reported for randomly oriented, immobilized radicals where the three g tensor components are unequal.¹¹ This idea is further supported by the long lifetime of the radical: the benzyl radicals are protected from each other by rigid binding within the silica pores. Interaction between the radicals need not be eliminated if the geometry for radical combination cannot be obtained. With 20-Å silica, there will be a balance between geometrical restriction of binding and minimizing the pore size of binding to obtain maximum active silanol sites for interaction with the DBK. Apparently these active sites form such tight fits with the DBK at low coverages that rotational mobility of the generated benzyl radicals is essentially eliminated. That the spectra show superposition rather than averaging again suggests that equilibration between sites is slow. The behavior of DBK on photolysis in 20-Å silica is shown schematically in Figure 4C.

The idea that the above behavior of benzyl radicals on different pore size silicas is associated with binding in small, active pores was tested by adding water vapor. Water adsorbs preferentially to the silanol sites of the pores, effectively preventing the hydrophobic DBK from

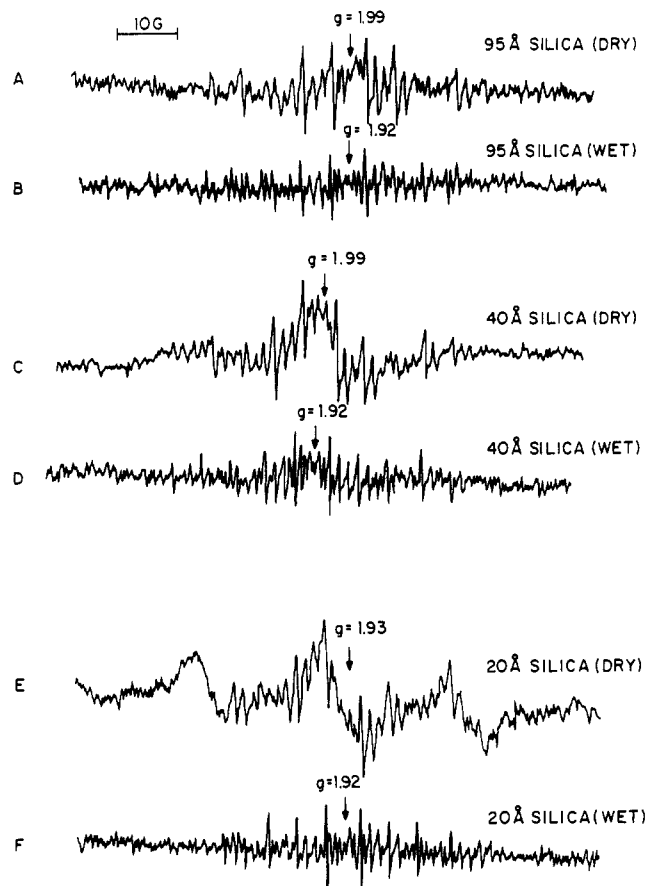


Figure 7. ESR spectra of 2% surface coverage of DBK on silicas.

binding in the smaller pores. Upon addition of water vapor to each of the above systems, solution-type spectra were obtained independent of surface coverage or pore size with all hyperfine splitting being the same as obtained in homogeneous solution (Figure 7). This suggests that the structured ESR spectra observed at high DBK coverages with each silica correspond to surface (large pore) adsorbed benzyl radicals, while the broader spectra result from intrapore radicals as shown in Figure 4. The g value in the presence of water vapor was in each case found to be 1.92.

Changes in g values can result from indirect interactions between electron spins and an applied magnetic field due to orbital angular momentum interactions (spin-orbit coupling).¹² Though such effects are often associated with degenerate orbitals,¹³ they can occur whenever an applied magnetic field allows mixing of electronically excited states with the ground state. Since the g values of the adsorbed benzyl radicals are lower than the free electron value of 2.00, the predominant interaction must involve mixing of the singly occupied molecular orbital with vacant orbitals (rather than mixing with filled orbitals). This mixing may occur by distortion of the crystal field of the molecule upon adsorption.

The g value shifts observed with the different pore size silicas at different coverages suggest that the benzyl radicals do not bind with the same orientation in each case. In particular, the mode of binding with dry 20-Å silica, and with all three silicas (95, 40, and 20 Å), in the presence of water vapor appears to be the same. In this mode of binding, the largest g value shift is observed ($g \approx 1.93$), indicating a large degree of spin-orbit coupling. With 95- or 40-Å silicas, a second mode of binding is observed, where

(11) See, for example: Ayscough, P. B. *Electron Spin Resonance in Chemistry*; Methuen: London, 1967; pp. 323-332.

(12) See, for example, ref 1b.

(13) See, for example, ref 1f.

g is shifted less dramatically from the free electron value ($g \approx 1.99$). These different binding modes appear to have little direct effect on other ESR spectral parameters (e.g., hyperfine splittings, line shapes). These g values do indicate that there are at least two binding modes on the surface: one adopted in the presence of water vapor or with 20-Å silica and the other with 40- and 95-Å silicas.

Conclusion

In this study, ESR spectroscopy was used to study the behavior of photochemically generated radicals adsorbed on silica surfaces by using both the shape of the spectra and the g value. The spectral behavior of the radicals was found to be distinctly different as a function of pore size and surface coverage. With large pore sizes (95 Å), the benzyl radicals equilibrate between sites with either spin exchange between radicals occurring within smaller pores or tighter binding of the radicals in these pores than in large pores. With intermediate size pores (40 Å), equilibration between sites is slow. Radicals within the smaller pores of this silica interact more strongly with each other than in the case of the larger pores of 95-Å silica, resulting in a large amount of spin exchange at low coverages (or the rotational motion is more limited, resulting in an anisotropic spectrum with only one resolved peak). With small-pore silica (20 Å), intraradical interactions are decreased. Intrapore radicals are isolated, motionally restricted, and relatively unreactive. The ESR spectrum

indicates a powder pattern where the rotational motion of the radical is extremely hindered. The g values of benzyl radicals in the different silicas indicate the presence of two types of binding orientations. In one orientation, crystal field distortions allow greater spin-orbit coupling due to interactions of the unpaired electron with unfilled orbitals. The resulting g value (1.93) is found in case of surface binding in the presence of water vapor for all three silicas and pore and surface binding in the case of 20-Å silica. With benzyl radicals on 95- and 40-Å silicas, a second mode of binding is observed, characterized by a g value of 1.99. While the shapes of the ESR spectra suggest different radical-radical interactions and rotational mobilities with the different pore size silicas, the g values suggest different orientations of the radicals adsorbed on the surfaces and in the pores. The methodology reported here represents a novel technique for the study of porous solids using the ESR spectroscopy of photochemically generated radicals. This method provides information on the structure and dynamics of adsorbed molecules on solids and allows different types of adsorption to be distinguished.

Acknowledgment. K.C.W. acknowledges the NIH for a postdoctoral fellowship (National Cancer Institute PHS Grant CA07957). We thank the NSF, AFOSR, and IBM Corp. for financial support.

Registry No. benzyl radical, 2154-56-5; dibenzyl ketone, 102-04-5.

Hyperthermal Scattering of Atoms from Disordered Surfaces

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Received November 11, 1987

We present an analysis of hyperthermal elastic and inelastic scattering of an atom from a surface. The analysis, which represents the properties of the surface via use of its dynamic structure function, is well suited to describe the scattering of an atom from a disordered surface. The approach used is an adaptation of the pioneering work of Micha on the description of hyperthermal atom-molecule collisions. Three model atom-disordered surface-scattering problems are briefly described.

Introduction

Although there exists a formal theory of scattering of atoms from an arbitrarily complicated many atom target, such as a surface, reduction of that theory to yield predictions of the properties of specific systems remains a challenge. The difficulties attendant to reduction of the formal theory arise in part from lack of detailed knowledge of the potential energy functions of complicated many body systems and in part from the complexity of the dynamics. This paper examines the use of a correlation function representation of hyperthermal atom-surface scattering. Our analysis is an adaptation of the important work of Micha¹⁻⁶ on hyperthermal atom-polyatomic molecule scattering.

The traditional theory of atom-polyatomic molecule scattering starts with a potential energy surface for the system, calculated by using the Born-Oppenheimer approximation. Since this potential energy surface is a complicated function of the spatial degrees of freedom of the system, it is convenient to expand the atom-polyatomic molecule interaction in a set of basis functions with origin at the center of mass of the molecule and with coefficients

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