[September, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (9), 2343—2345 (1976)

The Simulation of the ESR Spectra of the Perylene Cation on Solid Surfaces

Hisashi Ueda
National Chemical Laboratory for Industry, Mita, Meguro-ku, Tokyo 153

(Received July 2, 1975)

The simulation of the ESR spectra of the perylene cation formed on the surface of silica gel (with MoO_3), silica–alumina, and γ-alumina (with MoO_3) was studied. These oxides were pretreated in a vacuum of 10^{-5} Torr and at 300 °C, and were then brought into contact with a purified perylene solution in benzene. The main parameters which determine the shape of spectra were investigated. By comparing the experimental spectra with the simulated ones, it was concluded that unpaired electron-spin densities on the carbon atoms of the perylene cation are identical to those of the perylene cation in the H_2SO_4 solution. However, the number of γ-protons which have spin-nuclear interactions with the unpaired electron is three or less. It was found that a considerable part of the line-width is caused by g-unisotropies. If the perylene cation is bound more strongly on the surface, more g-unisotropy is observed and the half-width becomes wider. When the perylene cation is prepared in the air, O_2 and H_2O molecules coordinate to the perylene cation formed. It was found that the complex cations thus formed have different g-unisotropies and that the ESR spectrum of this cation mixture is structureless, smooth, and a continuous curve.

The perylene cation is formed when a benzene solution of perylene is added to pretreated silica gel, on which MoO_3 is supported. The pretreatment consists of heating the oxide at 300 °C and under a vacuum of 10^{-5} Torr. The ESR spectra of the perylene cations formed on those oxides which have been thus pretreated have hyperfine structures which are not found in the spectra of untreated oxides.[1–3] The present work was undertaken in order to ascertain what simulation parameters will simulate those hyperfine structures. The combinations of parameters which fit the experimental spectra well were found, and upon those parameters the probable structures of the perylene cation on oxide surfaces are discussed.

Experimental

The perylene cation is formed when a benzene solution of perylene is mixed with inorganic oxide powders which have positively charged points on their surfaces. In the present work three mixed oxides were used: (1) γ-alumina, on which 8.5% of MoO_3 was supported, (2) silica–alumina, consisting of 25% Al_2O_3 and 75% SiO_2, and (3) silica gel, on which 8.5% of MoO_3 was supported. All the oxides except the alumina sample for Fig. 4 were pretreated before mixing with a perylene solution (5 mg/ml). The pretreatment consisted of heating the mixed oxide in a Pyrex tube at 300 °C while it was evacuated to 10^{-5} Torr. After one hour the oxide was cooled and mixed with a perylene solution in benzene which had been prepared in the vacuum line. In the sample for Fig. 4 the perylene cation was prepared in the air. A benzene solution of perylene and alumina with MoO_3 were mixed and then the benzene was evaporated in the air. After the evaporation of the benzene the ESR spectra of the perylene cation (Fig. 4, solid line) were obtained. The evacuation of the sample to 10^{-5} Torr had no effect on the spectrum. After recording the spectrum, benzene was added to the sample and the ESR spectrum was taken again. Again no solvent effect was observed.

Results

In Fig. 1 the ESR spectrum of the perylene cation formed on the surface of γ-alumina (solid line) is shown. One of the simulated spectra is also shown (dotted line).

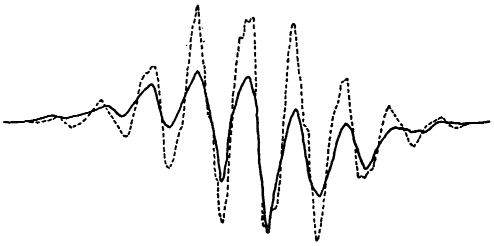

Fig. 1. ESR spectra of perylene cation on pretreated alumina (MoO_3) surfaces. The dotted curve is a simulated spectrum.

The parameters used for the simulation spectrum were $a_\alpha=4.10$, $a_\beta=3.10$, and $a_\gamma=0.46$ G, which are common through Figs. 1—5.[4,5] In the case of Fig. 1, $NA=4$, $NB=4$, $NC=3$, and $W=1.84$ G were used. NC and W could not be decided separately. $NC=3$ was selected in connection with Fig. 3, after which $W=1.84$ G was adopted.

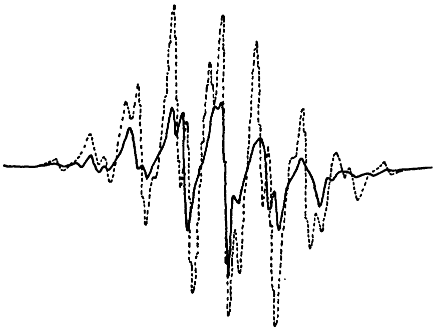

Fig. 2. ESR spectra of perylene cation on pretreated silica–alumina surfaces. The dotted curve is a simulated spectrum.

In Fig. 2 the ESR spectrum of the perylene cation formed on the surface of silica–alumina (solid line) is shown. One of the simulated spectra is also shown (dotted line). The parameters used for Fig. 2 were $NA=4$, $NB=4$, $NC=0$, and $W=2.98$ G. The further splitting of the 9-line spectrum is caused by $a_\alpha-a_\beta=1.0$ G. The line widths of the 9-line (or 18-line)

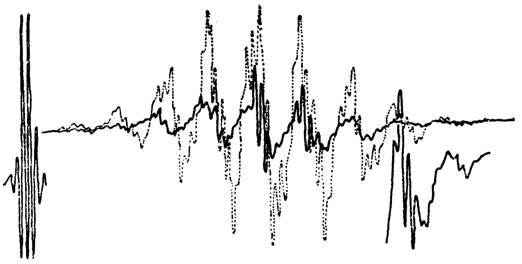

Fig. 3. ESR spectra of perylene cation on pretreated silica gel (MoO_3) surfaces. The dotted curve is a simulated spectrum.

spectrum of Fig. 2 are determined by both NC and W. Therefore, $NC=0$ and $W=2.98$ G should not be accepted with their face values.

In Fig. 3 the ESR spectrum of the perylene cation formed on the surface of silica gel (solid line) is shown. One of the simulated spectra is also shown (dotted line). The parameters used for Fig. 3 were $NA=4$, $NB=4$, $NC=3$, and $W=1.33$ G. The total number of the hyperfine lines to be obtained theoretically is $(NA+1)(NB+1)(NC+1)=100$. The central part of the second derivative curve of the experimentally obtained spectrum is shown to the left of the first derivative curves. In the second derivative curve, the variations in the curvatures of the spectral line are more intensified than the first derivative curve. An important point found in the experimental spectrum is that the total number of hyperfine lines is an even number. The two equally strong, most intense lines in the center of the spectrum typically demonstrate this fact. In the case of Fig. 3, therefore, $NC=3$ is an essential parameter. Considering this fact, $NC=3$ was used in the simulation of Fig. 1. In order to see the less intense hyperfine lines, a part of the 10-times-amplified spectrum is shown to the right of the figure.

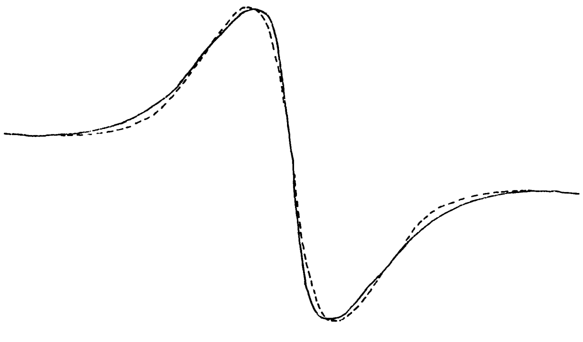

Fig. 4. ESR spectra of perylene cation prepared in the air. The dotted curve is a simulated spectrum which was calculated by assuming a half width of 8.20 G.

In Fig. 4 the ESR spectrum of the perylene cation which was prepared in the air on the alumina surface (solid line) is shown. As a mathematical problem, $NA=4$, $NB=4$, and $W=8.20$ G give a satisfactorily simulated spectrum (dotted line). However, $W=8.20$ G, considering $a_\alpha=4.10$ G, is too large to interpret. Therefore, some other simulations must be tried. For this reason the spectra in Fig. 5 were calculated.

In Fig. 5 three simulated spectra, 5A, 5B, and 5C, are shown. The 5A spectrum was obtained by $a_\alpha=a_\beta=$ 3.60 G (a g-unisotropy of 1.0 G or $\delta g=0.0006$ is included in these values), $NA=4$, $NB=4$, and $W=1.82$ G. This is similar to the one in Fig. 1. On the base of 5A, the 5B spectrum was calculated assuming g-unisotropy. The unisotropic principal values of g, g_1(2.0009), g_2(2.0030), and g_3(2.0051) were assumed. In 1800 directions uniformly distributed in the three-dimensional space, the g-factors were computed from those three principal values. The 1800 spectra obtained by these g-factors were then averaged. The 5B spectrum thus obtained shows that the assumption of only one set of unisotropic g-factors is not enough to get a smooth simulation curve in Fig. 4. If two perylene cations with different principal values of the g-factor are assumed, a smoother curve, 5C, is obtained. In the 5C spectrum, g_{11}(2.0009), g_{12}(2.0030), g_{13}(2.0051), and g_{21}(2.0019), g_{22}(2.0040), and g_{23}(2.0061) were assumed. In practice, the 5B′ spectrum was computed from g_{21}, g_{22}, and g_{23} in the same way as that for 5B. The 5B and 5B′ spectra were then averaged.

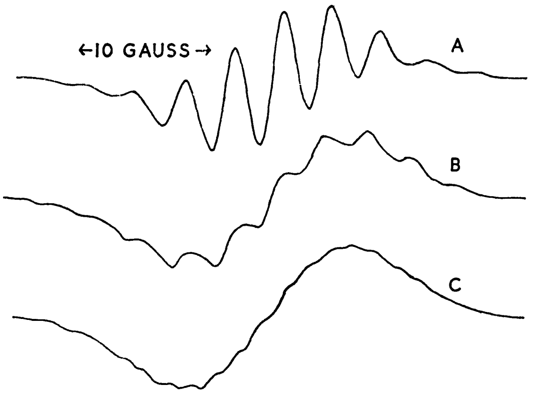

Fig. 5. The simulated ESR spectra for the perylene cation prepared in the air. A: Single g-factor with line width of 1.0 G. B: A spectrum obtained by averaging the spectrum A by a set of unisotropic g-factors. C: A spectrum obtained by averaging two of B-type spectrum different g-tensors.

Discussion

The Unpaired Electron-spin-density Distribution in the Perylene Cation. One of the γ-protons of the perylene cation on the silica gel surface, as is shown by the simulation in Fig. 3, does not have a hyperfine interaction with the unpaired electron. If one of the γ-protons is removed from the perylene molecule, and if the cation becomes a $C_{20}H_{11}\cdot$ radical, the molecular symmetry changes and the a_α and a_β values should change from 4.10 G and 3.10 G respectively. In the present simulations, $a_\alpha=4.10$ and $a_\beta=3.10$ G gave satisfactory results. This suggests that the migration of the proton was not so large as to cause a great change in the π-electron orbital.

The Factors Affecting the Linewidth. There are three main sources which contribute to the magnitude of the half-width, W: (1) the magnetic dipole-dipole interactions, (2) the unaveraged unisotropic hyperfine splitting caused by the restricted motions of the cation, and (3) the unisotropy in the g-factor.

The contribution of (1) is estimated from the linewidth of Fig. 3 to be about 0.2 G. The contribution from (2) will be about 2 G because it will be about 50% of a_α (4.10 G). The contribution from (3) apparently becomes quite large in some cases. In Fig. 5, if two of the principal values differ from the third value $+0.0021$ and -0.0021 respectively, the half-width becomes so wide that the entire spectrum looks continuous. A half-width of 8.2 G can give a simulated spectrum which resembles the experimentally obtained spectrum.

The Different States of the Perylene Cation on Three Oxides.

Silica Gel: If a completely degassed and dehydrated sample is used, the half-width can be reduced to 0.2 G and the detailed structure of the spectrum can be observed. The motions of the perylene cation are quite free in this case, and as a result the unisotropy in the g-factor is considerably reduced.

Silica–Alumina: In Fig. 2, $NC=0$ and $W=2.98$ G were used as simulation parameters. In the W value the width caused by $NC=3$ and $a_\gamma=0.46$ G may be hidden. The reason why a_γ is not observed is the unisotropy in the g-factor. If unisotropy of 0.0003 in the principal values of the g-factor is assumed, the resulting linewidth is 0.46 G. Therefore, a_γ becomes invisible. On silica–alumina surfaces, the motions of the perylene cation are more restricted than those on silica gel. However, the linewidth caused by the unisotropy of the g-factor is not so large as to submerge the 1.0 G difference between a_γ and a_β.

γ-Alumina: *In the Presence of Air and Humidity.* The perylene cation prepared in the presence of air and humidity gives the ESR spectrum shown in Fig. 4. If we assume two different states of the perylene cation, which have differently unisotropic g-factors, a spectrum like Fig. 5C may be obtained. This holds true if, for example, we assume (P^+O_2), a perylene cation to which O_2 is weakly bonded, and (P^+OH_2), a perylene cation to which H_2O is weakly bonded. If (P^+O_2) has the g-factor of (g_{11}, g_{12}, g_{13}) and (P^+OH_2) has the g-factor of (g_{21}, g_{22}, g_{23}) used for Fig. 5C, and if there is an equal mixture of those two species, a spectrum just like Fig. 5C is observed. It will also be possible to use alternate species, such as P^+O (an atomic oxygen is adsorbed by the cation) or P^+O_2-1 and P^+O_2-2 (two differently coordinated oxygen molecules to a perylene cation) as well as P^+O_2 and P^+OH_2. It remains for future study to determine which of them are really present.

γ-Alumina: *Cation Formation in a Vacuum.* When a perylene solution is mixed with calcined alumina with MoO_3 in a vacuum line, the effects of O_2 and H_2O will be mostly removed from the spectrum. However, even after repeating the pretreatment several times, the ESR spectrum of the perylene cation cannot be resolved any more than that in Fig. 1. The reason for this is that the motions of the perylene cation are more restricted than those on silica–alumina. If the motion of the cation is more restricted, the unisotropy of the hyperfine structure can be observed more; also, the unisotropy of the g-factor will be observed still more. For these reasons, the half-width value, 1.84 G, for Fig. 1 includes the width due to the g-factor unisotropy. Seeing that, in the case of silica–alumina, $a_\alpha - a_\beta = 1.0$ G was detected in the experimental spectrum, while in the case of alumina it was almost unobservable, the half-width due to the g-unisotropy is 1.0 G. This corresponds to a g-unisotropy of 0.0006.

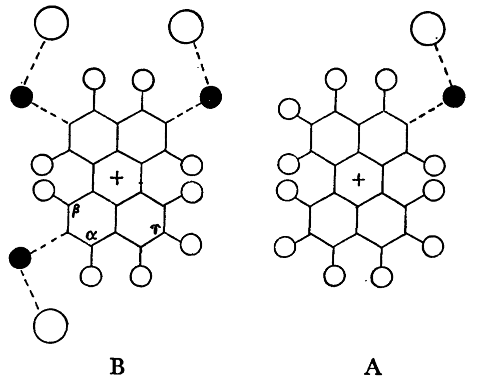

Fig. 6. Perylene cation on oxide surfaces. A: Fixed at one point and has relatively free motions. The cation on silica gel surface. B: Fixed at several points, and has restricted motions. The cation formed in the air on alumina surface. A large circle signifies an oxygen atom (anion) and a small filled circle signifies a fixed proton.

Conclusion. An oxygen atom, an oxygen ion, or molecules containing oxygen will bond weakly to the perylene cation, formed and stabilized on an oxide surface. The unpaired electron of the perylene cation migrates slightly to the atomic or molecular orbital of oxygen. The spin-orbit coupling in the oxygen orbitals affects the energy level of the unpaired electron and causes the g-factor to become slightly more unisotropic. The unisotropy of the g-tensor is averaged by the motion of the perylene cation allowed on the surface. The degree of averaging depends on the oxide carriers used. The pictures shown in Fig. 6 illustrate some aspects of the perylene cation formed on oxide surfaces.

References

1) H. Ueda, *J. Chem. Phys.*, **62**, 3362 (1975).

2) H. Ueda, *Nippon Kagaku Kaishi*, **1975**, 422.

3) H. Ueda, *Can. J. Chem.*, **46**, 891 (1968); *Bull. Chem. Soc. Jpn.*, **43**, 319 (1970); **47**, 1338 (1974); H, Ueda and N. Todo, *Can. J. Chem.*, **51**, 885 (1973).

4) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

5) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964).