

The Axially Fixed Phenanthrene Cation on Oxide Surfaces as Studied by Electron Spin Resonance

HISASHI UEDA

Tokyo Kogyo Shikenjo, 2-19-19 Mita, Meguro-ku, Tokyo 153, Japan

Received May 13, 1976; revised January 17, 1977

A benzene solution of phenanthrene, which had been purified by zone melting method, was mixed with γ -alumina (with 10.5% of MoO_3 supported on it), or silica gel (with 8.5% of MoO_3 supported on it), both of which had been treated at 300°C in a vacuum of 10^{-5} Torr. The phenanthrene cation thus produced was observed by esr method. In the case of silica gel, the number of protons interacting with the unpaired electron was: 1 proton with a splitting of 1.41 G, 2 with 1.97 G, 2 with 4.09 G, and 4 with 2.79 G, and the half-width was 0.07 G. In the case of γ -alumina, the number of protons interacting with the unpaired electron was: 1 proton with a splitting of 1.50 G, and 8 with 3.00 G, and the half-width was 0.57 G. The analysis of the obtained spectra has shown that a combination of four $\text{RCH}_2\cdot$ radicals and a $\text{RCHR}'\cdot$ radical interprets them. It has been concluded that the phenanthrene cation has restricted rotational motions on an oxide surface. It has also been shown that there are three significant points in the studies of the aromatic hydrocarbon cations on the catalyst surface by esr method. (A) The interaction between adsorbed O_2 or H_2O and the cation can be observed. (B) The exact point of the molecule at which the cation is adsorbed on the oxide surface can be known. (C) The differences in the states of adsorption of the aromatic cation on different oxides are found.

It is well known that cations of aromatic hydrocarbons are formed on the surface of solid oxides (1-7). Detailed discussions of the esr spectra observed from cations of aromatic hydrocarbons on oxide surfaces have been tried (8). The present author studied the effects of oxides on the esr of the hydrocarbon cation formed on the oxide, using Al_2O_3 on which 10.5% of MoO_3 was supported, SiO_2 on which 8.5% of MoO_3 was supported, and silica-alumina (25% Al_2O_3 -75% SiO_2). The results obtained showed that a new esr spectrum, having a hyperfine structure which had never been resolved before, can be observed if the solid inorganic oxide had been pretreated at 300°C in a vacuum of 10^{-5} Torr (9). The analysis of the hyperfine structure in the esr spec-

trum thus observed may give some light to the interactions between the oxide surface and the aromatic cation formed on it. The effect of a third substance (such as O_2 or H_2O) which is adsorbed to the surface on the esr spectrum can be studied as well. In the case of perylene, the molecular symmetry of the cation formed on SiO_2 surface was found to be lower than that of a neutral molecule. Since the molecular symmetry of phenanthrene is lower than that of perylene, the lowering of molecular symmetry when a neutral phenanthrene molecule is converted to the cation is expected to be more apparent than that observed in perylene. For this reason phenanthrene was studied in this work.

It seems there is almost no published results of the esr spectrum of phenanthrene

cation. The material purity may be responsible for the difficulty to get esr spectra of phenanthrene cation in or on any medium. In the present work, therefore, several trials to obtain phenanthrene cation on the surface of Al_2O_3 or SiO_2 on which MoO_3 was supported were made using phenanthrene purified by zone melting method. Two different esr spectra were obtained subsequently and are reported in this paper.

EXPERIMENTAL METHODS

1. Materials

Phenanthrene: Purified by zone melting method. **Mixed oxides:** The oxides on which MoO_3 was supported was prepared by the following procedure. γ -Alumina powder of Shokubai Kasei Co. was mixed with an aqueous solution of ammonium molybdate. The mixture was shaken at 40°C for 1 hr. The solution was then separated from alumina by a centrifuge. The alumina was dried at 100°C , was then heated at 300°C in air, and then was calcined at 500°C for 1 hr. After preparation the MoO_3 content was analyzed and was found to be 10.5%. Silica gel powder of Fuji-Davison Co. was treated in the same way as above. The MoO_3 content in this case was 5.8%. Both alumina- MoO_3 and silica gel- MoO_3 had surface areas of 200 m^2/g . The purity of both alumina and silica gel used were not particularly high. **Benzene:** Special reagent grade benzene was shaken with concentrated sulfuric acid. This was then distilled three times in a vacuum line and was stored in it. Within 1 hr of the purification it was introduced into the sample tube connected to the vacuum line and then the sample tube was sealed off.

2. Measurement of esr

ME-3X type esr spectrometer of JEOL was used. The first derivative form of the

true resonance curve was recorded on the chart paper. The output voltages were simultaneously converted to digital numbers (0-255)₁₀, by JEC-5 spectrum computer of JEOL, in which they were stored. They were then punched out on a paper data tape. The sampling points were 1024 for each spectrum. The second derivative function was obtained from this paper tape by a computer differentiation.

3. Computation

The spectral simulation was made by means of a Fortran system program using a minicomputer having 8K memory. The simulation spectrum was printed out on a paper data tape in the same way as that used for esr measurement. The unpaired electron spin density distribution in the phenanthrene cation molecular orbital was computed by Hückel molecular orbital method and by McLachlan molecular orbital method.

RESULTS

The second derivative esr spectrum, centered at $g = 2.00$ obtained from the mixture of the benzene solution of phenanthrene and the silica gel on which 5.83% of MoO_3 had been supported and which had been pretreated at 300°C and at 10^{-5} Torr, is shown as 1E in Fig. 1. The simulated spectrum, in the second derivative

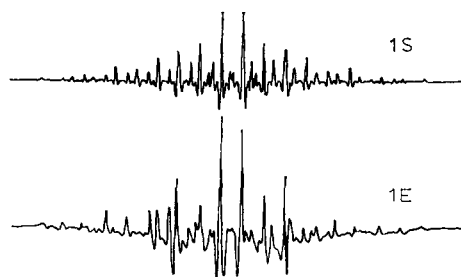


FIG. 1. The second derivative esr absorption spectra of phenanthrene cation formed on SiO_2 surfaces. 1S is by simulation, and 1E is by experiment. The functional form of 1S line is $\exp(-100 H^2)$.

form, is also shown as 1S in Fig. 1. In the simulation, $y = 1/\exp(cx^2)$, a Gaussian function, was used in which x was the magnitude of the magnetic field in Gauss and c was 100 G^{-2} . This value gives a half-width of 0.07 G . The second derivative form was obtained by computer differentiation. The numbers of protons, which were assumed to give hyperfine structures to the spectrum were; 1 proton with 1.41 G , 2 with 1.97 G , 2 with 4.09 G , and 4 with 2.79 G of hyperfine splitting values, respectively. The intensity ratio of the three absorption lines which are generated by an equal interaction between an unpaired electron and two identical protons, which it is necessary to decide in the process of calculation, is assumed to be $1:3:1$ rather than to be $1:2:1$. The reason for it is discussed below. The second derivative esr spectrum, centered at $g = 2.00$, obtained from the mixture of the benzene solution of phenanthrene and the γ -alumina on which 10.5% of MoO_3 had been supported and which had been pre-treated at 300°C and at 10^{-5} Torr, is shown as 2E in Fig. 2. The simulated spectrum, in the second derivative form, is also shown as 2S3 and 2S6 in Fig. 2. The spectrum 2S3 was computed by the formula, $y = (1 + cx^2)^{-1}$, a Lorentzian function, in which x was the magnitude of the magnetic field in Gauss and c was

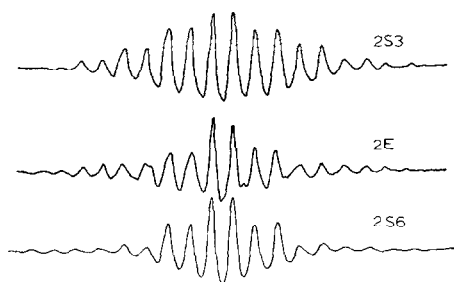


FIG. 2. The second derivative esr absorption spectra of phenanthrene cation formed on $\gamma\text{-Al}_2\text{O}_3$ surfaces. 2S3 and 2S6 are by simulation, and 2E is by experiment. The functional form of 2S3 and 2S6 lines is $1/(1 + 3H^2)$.

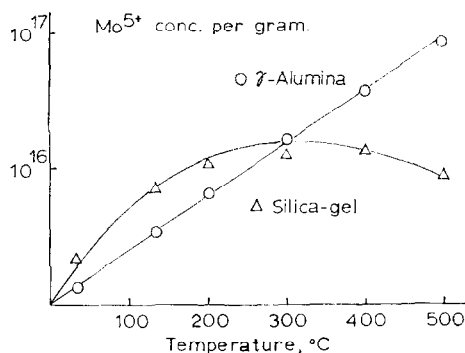


FIG. 3. The relation between Mo^{5+} concentration and the heating temperature when MoO_3 , 9.58% - SiO_2 , 90.42% , and MoO_3 , 10.5% - Al_2O_3 , 89.5% were heated, while they were evacuated to 10^{-5} Torr. Neither phenanthrene nor benzene was added to those mixed oxides.

3.0 G^{-2} . This gives a half-width of 0.57 G . The numbers of the hyperfine protons were: 1 proton with 1.50 G , and 8 protons with 3.00 G . In the 2S3 simulation, the intensity ratio of a triplet esr spectrum caused by two equivalent protons (the RCH_2 -radical, see Discussion section) was assumed to be $1:3:1$, and in the 2S6 simulation, the intensity ratio assumed was $1:6:1$. Magnetic field increases from left to right in both Figs. 1 and 2. In Fig. 3, the concentration of Mo^{5+} , observed from the oxide on which MoO_3 was supported is plotted against heat treatment temperature. The heat treatment was made in a vacuum of 10^{-5} Torr without adding any organic substances such as benzene or phenanthrene. One of the oxides used for Fig. 3 was silica gel on which 9.58% of MoO_3 was supported. The other oxide was alumina on which 10.5% of MoO_3 was supported. The spectral shape of Mo^{5+} esr absorption depended on the oxide carrier used. In the calculation of Mo^{5+} concentration, the area enclosed by the true absorption curve and the base line was taken into account (11). The highest Mo^{5+} concentration from γ -alumina (10.5% MoO_3) was obtained at 500°C and was $7.8 \times 10^{16}/\text{g}$, and that from silica gel (9.58% MoO_3) was obtained at 300°C

TABLE 1
Spin Densities in Phenanthrene Cation

Position	HSPIN	MSPIN	1E1	1E2	2E1	2E2
1	0.003	0.023	— ^a	— ^a	— ^a	— ^a
2	0.054	0.037	0.087	0.066	0.133	0.100
3	0.099	0.110	0.124	0.093	0.133	0.100
4	0.001	-0.041	-0.062 ^b	-0.047 ^b	-0.066 ^b	-0.050 ^b
5	0.115	0.146	0.124	0.093	0.133	0.100
6	0.026	-0.011	— ^a	— ^a	— ^a	— ^a
7	0.172	0.235	0.182	0.136	0.133	0.100
Total	0.993	0.998				

^a No proton is attached to those carbon atoms.

^b Only one proton was found for this position.

and was $1.2 \times 10^{16}/\text{g}$. The Mo^{5+} ratios to the total molybdenum ions supported at their peaks were, therefore, 0.018% for alumina and 0.003% for silica gel. The distribution of the unpaired electron spin in a phenanthrene cation molecule computed is shown in Table 1. HSPIN denotes the spin densities obtained by Hückel MO and MSPIN denotes those by McLachlan MO. The relation $A = Q|\rho|$ holds between A , the hyperfine splitting caused by a proton, and ρ , the unpaired spin density on the carbon atom to which the proton is attached. The experimental spin density values 1E1 were obtained by using 22.5 G as Q . The experimentally obtained splitting values, A , were assigned to the numbered carbon atoms, see Fig. 4, so as to give the best agreement between the calculated spin densities and the experimentally obtained spin densities. The values shown as 1E2 were obtained when 30.0 G was used for Q , the reason for it is discussed below. The values shown as 2E1 and 2E2 in Table 1 were obtained from the 2E spectrum of Fig. 2 in a similar manner. In Fig. 4 the numbering of carbon atoms in phenanthrene cation conveniently defined in this paper is shown. The directions of X , Y , and Z axes, which were set to consider the anisotropies in the esr spectra, are also shown in Fig. 4.

DISCUSSION

1. The Characteristics of esr Spectra of phenanthrene Cation on Oxide Surfaces

The following three conclusions may be obtained from the experimental results. (I) There is a discrepancy between the number of protons which really give the hyperfine structure to the esr spectrum and that expected from a neutral molecule. In other words, one of the protons is missing in the cation. From Table 1 the missing position is concluded to be one of the 4-position carbon atoms in Fig. 4. A similar phenomenon has already been found in the case of perylene (9). (II) The shape of the esr spectrum obtained from phenanthrene cation depends on the oxide carrier used. In the silica gel carrier, the functional form

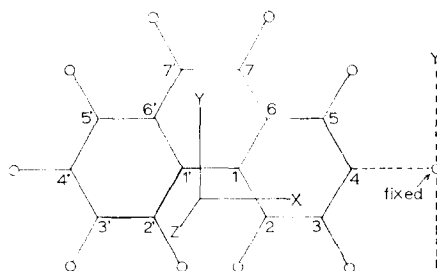


Fig. 4. The numbering of the carbon atoms in a phenanthrene molecule used for spin density calculation. The X , Y , and Z axes shown were used for the simulation of esr spectra, Fig. 6, considering their anisotropies; $Y' \parallel Y$.

is a Gaussian and the half-width is 0.07 G, while on the γ -alumina carrier, the functional form is a Lorentzian and the half-width is 0.57 G. The unpaired electron spin density distribution varies with the carrier on which the cation is formed, too. (III) The unpaired electron is interacting equally with each set of the two protons of identical symmetry, except with those at 4- and 4'-positions. Normally expected intensity ratio of hyperfine lines obtained from two identical protons is 1:2:1. However, in the present study, the intensity ratio of 1:3:1 or 1:6:1 was necessary to get better simulated spectra.

2. Irregular Intensity Ratio

The magnetic interaction between a proton and an unpaired electron has two terms. The one which does not depend on the external magnetic field, isotropic term, and the one which depends on the external magnetic field, anisotropic term. Only the isotropic term is observed when an aromatic hydrocarbon ion is in a rapid motion. If only the isotropic term is considered, the intensity ratio of the hyperfine lines observed from an unpaired electron and two protons equally interacting with it is 1:2:1. However, if the anisotropic splittings are superposed on the isotropic splittings, the intensity ratio may deviate from 1:2:1. Considering this fact, spectral simulation assuming slow molecular motions of phen-

anthrene cation was carried out in the present work. As shown in Fig. 4, the X , Y , and Z axes were chosen. The Z -axis is perpendicular to the molecular plane. If we look at the 2C-2H and 2'C-2'H bonds, it will be seen that both replace each other with each other if 180° rotation of the Y -axis is made. As the spin densities on 2C and 2'C are equal, the hyperfine splitting caused by these two protons, 2H and 2'H, is equivalent to that caused by a $\text{RCH}_2\cdot$ radical. However, the angle $\angle \text{HCH}$ in this hypothetical $\text{RCH}_2\cdot$ radical should be 60° , and is different from the same angle in the normal $\text{RCH}_2\cdot$ radical, which is 120° . In Fig. 5 the direction of the magnetic field is shown by the arrow MF, and the angle between the X -axis and the arrow MF is denoted by α , and the angle between the line formed by the normal projection of the MF vector on the Y - Z plane and the Y -axis is denoted by β . If the hyperfine splitting by 5H is considered, one of the principal values (whose anisotropic part is some positive value), A_{11} , lies in the direction of 5C-5H. One of the other two principal values (whose anisotropic part is some negative value) also lies in the X - Y plane, and is perpendicular to A_{11} . This value is denoted by A_{12} . The third principal value (whose anisotropic part is approximately 0) is parallel to the Z -axis, which is denoted by A_{13} . If we let A_{21} , A_{22} , and A_{23} denote the corresponding principal values of the hyperfine splitting by 5'H, A_{21} lies in the direction -60° from that of A_{11} , A_{22} in the direction -60° from that of A_{12} , A_{23} in the direction parallel to A_{13} . Let the angle between A_{11} and the arrow MF be denoted by θ_1 , and the angle between A_{12} and the line obtained by the normal projection of MF on the A_{12} - A_{13} plane be denoted by ϕ_1 . If A_{21} , A_{22} , and A_{23} are used instead of A_{11} , A_{12} , and A_{13} in the above expression, the corresponding angles θ_2 and ϕ_2 are obtained. By applying the same procedure, corresponding principal values and angles

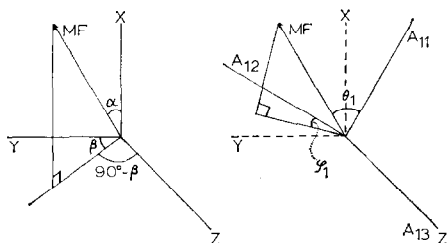


FIG. 5. The parameters α , β , θ_1 , and ϕ_1 are illustrated. The XY plane coincides with the molecular plane. A_{11} and A_{12} also lie in the molecular plane or the XY plane.

can be obtained from the combinations of hydrogen atoms, (2H, 2'H), (3H, 3'H), and (7H, 7'H). Therefore, the esr spectrum of the phenanthrene cation on an oxide surface is interpreted by a structural model in which several hypothetical methylene radicals are conjugated to each other. The experimental results indicate that there are no effects of 4H on the esr spectrum, while 4'H gives a doublet structure to the spectrum. The intensity ratio of this doublet line is 1:1, which requires no particular attentions when the intensity ratio is considered. The values of A_{11} , A_{12} , and A_{13} are estimated to be $90 \cdot x$ MHz, $30 \cdot x$ MHz, and $60 \cdot x$ MHz, where x is the spin density on the C-H carbon atom and $60 \cdot x$ MHz is the isotropic hyperfine splitting value of the tensor (12). In the case of perylene cation formed on the surface of SiO_2 on which MoO_3 was supported, it was concluded from the analysis of the esr spectrum obtained that only one of the protons had no hyperfine interactions with the unpaired electron. The reason for it has been interpreted as that perylene molecule is chemisorbed on the oxide surface through the hydrogen atom, which gives no hyperfine splitting, and therefore the C-H bond is lengthened here (9). Thus, as one particular point of the cation molecule is strongly bonded to the oxide surface, the three dimensional free rotational motions of the cation are not possible, and the permitted motion is the one around one axis only, such as around X-axis. If the rotational motion is very fast, the anisotropy is averaged, but if the rotational motion is not fast, the anisotropy is not averaged. As a result, a sum of the spectra each of which corresponds to different values of α and β angles designated in Fig. 5 is observed. Let us consider the case in which the cation is fixed on the oxide surface by an axis parallel with the X-axis. In Fig. 5, let H_1 denote the magnetic field for the hyperfine line with m_1 and H_0 denote the field

for $m_1 = 0$, then $H_1 - H_0$ is written as,

$$H_1 - H_0 = m_1(A_{11}^2 \sin^2 \theta_1 \sin^2 \phi_1 + A_{12}^2 \sin^2 \theta_1 \cos^2 \phi_1 + A_{13}^2 \cos^2 \theta_1)^{\frac{1}{2}}$$

In this equation m_1 is the nuclear spin quantum number of the 5H proton. Identical equation can be written for the 5'H proton,

$$H_2 - H_0 = m_2(A_{21}^2 \sin^2 \theta_2 \sin^2 \phi_2 + A_{22}^2 \sin^2 \theta_2 \cos^2 \phi_2 + A_{23}^2 \cos^2 \theta_2)^{\frac{1}{2}}$$

$(H_1 + H_2 - 2H_0)$ then gives the positions of the hyperfine lines of RCH_2 -measured from the center of the spectrum. In Fig. 5 the equations $\cos \theta_1 = (\frac{3}{2})^{\frac{1}{2}} \cos \alpha + 0.5 \sin \alpha \cos \beta$, $\cos \theta_2 = (\frac{3}{2})^{\frac{1}{2}} \cos \alpha - 0.5 \sin \alpha \cos \beta$, and $\cos \phi_1 = \cos \phi_2 = \sin \alpha \sin \beta$ holds. Let's consider the case in which α takes the discrete angle values from 0 to 90° by 5° intervals, and in which β takes the same discrete values for each value of α . In this case phenanthrene cation occupies $19 \times 19 = 361$ different orientations in the magnetic field. The distribution of the resonance positions of these 361 spectra give a simulated spectrum, shown X in Fig. 6. In Fig. 6, the left part shows the magnetic field region from -32 G to -20 G measured from the center of the spectrum, and the right part shows the central region of the spectrum. The

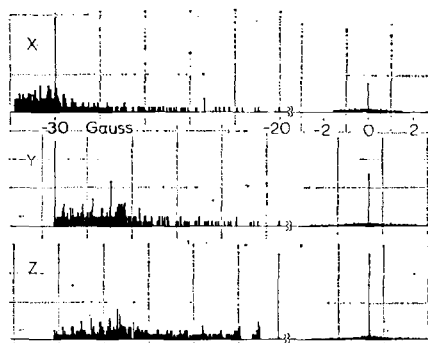


Fig. 6. The simulation of the anisotropic esr spectra of RCH_2 -radical which is rotating slowly. The intensities in the left parts (-32 G, -20 G), are magnified to 10 times of those in the right parts or the absorption center (0 G, ± 3 G).

intensities of (-32 , -20 G) region is multiplied by 10 if compared with those of the central region. ($m_1 + m_2 = 0$) gives the central absorption lines, while ($m_1 + m_2 = 1$) gives the absorption lines in the (-32 , -20 G) region. For simplicity, 30 MHz is approximated by 10 G. The entire magnetic field region, namely, -35 to 35 G was divided into 3500 subregions of 0.02 G width. The intensity of the absorption occurring in each subregion should be proportional to the total number of lines whose resonance positions fall in the subregion. In the case in which the rotation axis is assumed to be parallel to the X -axis, the intensity ratio between the line at -30 G and the central line is 1:3.14, which is approximately equal to the simulation parameter used for 2S3 in Fig. 2, 1:3. Therefore, it will be possible to say that the phenanthrene cation formed on the surface of silica gel is adsorbed on the surface by an axis parallel to the X -axis and therefore by the 4C-4H bond. This cation should have a freedom of spinning motion around this 4C-4H bond. The same calculations were made with respect to the axes parallel to the Y (or Y') and the Z axes assuming fixed rotations of $\text{RCH}_2\cdot$ on the oxide surface. They are shown as Y and Z in Fig. 6. The intensity ratios obtained in these cases for the triplet line are 1:6:1 and 1:10:1, respectively. The relative intensities of the outer lines at ± 30 G (or at ± 20 G) in these two cases are far smaller than the X -axis case. The (1:6:1) intensity ratio is approximately equal to the intensity parameter used for the 2S6 simulation in Fig. 2. Among the intensities of the lines of 2S3, the ratio of the central two lines and the adjacent two lines is approximately 1:0.8. This ratio to be obtained from the cation having complete freedom of motion is 1:0.8. However, this ratio found in the 2E spectrum is approximately 2:1. This 2:1 ratio cannot be explained if one considers the presence of only one cation having a

complete freedom of motion. It will be unnatural to assume more than two cations to explain the 2E spectrum. Therefore, the restricted motion model described above, in which the phenanthrene cation rotates around Y' axis will be the only explanation of the 2E spectrum. In other words, the phenanthrene cation formed on the surface of γ -alumina is adsorbed on the surface by the 4C-4H bond, which is in common with the cation on the surface of silica gel, except the fact that on the surface of γ -alumina, the cation has no freedom of spinning motion and it can rotate around the Y' axis only.

It is possible to conclude from above considerations that the adsorption model, in which the phenanthrene cation is bonded on the oxide surface by the 4C-4H group, interprets the obtained esr spectra best.

3. The Significance of Studying the esr Spectra from an Aromatic Hydrocarbon Cation Formed on the Surface of Pre-treated Inorganic Oxides

*a. The effects of the adsorbed substances on the ESR of the cations formed.*¹ As it was shown in a previous paper (9), the adsorbed species which easily becomes an electron donor on the oxide surface broadens the hyperfine lines of the esr spectrum and submerge most of the hyperfine lines. From a reverse point of view, some information of the adsorbed species on oxide surfaces may be obtained from the esr spectrum observed from a hydrocarbon-oxide mixture. The heat treatment at 300°C (10^{-5} Torr) produces the maximum

¹ In addition to the effects of the adsorbed species, some effects of the impurities contained in the oxide carriers used or the impurities in ammonium molybdate, if there are any, on the esr of the hydrocarbon cation might be detected. The present author, however, could not relate these possibilities with the axial motions of the phenanthrene cation. For this reason, those impurity effects were omitted in this paper.

concentration of Mo^{5+} in $\text{SiO}_2\text{-MoO}_3$. As this maximum concentration of Mo^{5+} is merely 30 ppm of the total supported Mo^{6+} concentration, it is impossible to say if the phenanthrene cation is formed in the neighborhood of Mo^{5+} ions. The actual meaning of the heat treatment at 300°C and at 10^{-5} Torr seems to remove the mobile oxygen anions which have surrounded the Mo^{6+} ions in the process of calcination. Therefore, the presence of those mobile oxygen anions will be one of the major causes which make the hyperfine esr lines of phenanthrene cation unobservable.

b. Chemisorption through the C-H bond at 4-position. Experimental results are reasonably interpreted, with respect to both calculated spin densities and the simulated spectra, if an adsorption model in which phenanthrene cation is fixed on oxide surfaces by the axis parallel to the 4C-4H bond. Therefore, some detailed knowledge about the state of hydrocarbon adsorption on oxide surfaces can be expected by analyzing the hyperfine structures in the esr spectrum of the hydrocarbon cation.

c. Different states of hydrocarbon adsorption on the two carriers. The difference between the carrier effect of SiO_2 and that of Al_2O_3 may be interpreted in terms of the different temperature dependent stabilities of Mo^{5+} ion formed on these carriers, see Fig. 3. In addition to it, a clear difference in the spin density distribution is found between the phenanthrene cation formed on SiO_2 and that formed on Al_2O_3 , as shown in Table 1. The calculated spin densities, MSPIN, is closer to the experimental values of 1E1 or 1E2 than to those of 2E1 or 2E2. These facts indicate that a

stronger surface force is extended to the phenanthrene cation formed on Al_2O_3 than that formed on SiO_2 , and that the electronic state of the phenanthrene cation is, accordingly, more complicated in the one formed on Al_2O_3 than on SiO_2 . From the analysis of the intensity ratio of the hyperfine lines, the phenanthrene cation formed on the surface of γ -alumina is concluded not to have the freedom of spinning motion. The reason for it is that the π -orbital of the cation and the atomic orbitals of the oxygen anion on the surface of alumina overlap with each other to form a more extended molecular orbital. This inhibition of the spinning motion proves the stronger chemisorbing power of γ -alumina carrier. It is possible to discuss the carrier effects of SiO_2 and Al_2O_3 by comparing the hyperfine structures in the esr spectra of hydrocarbon cations formed on the surface of oxides which are used as carriers for catalysts.

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