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Solvent Effects on the Formation of Aromatic Hydrocarbon Ions and Mo^{5+} on the Surface of Al_2O_3–MoO_3

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The formation of two aromatic hydrocarbon ions on the surface of Al_2O_3–MoO_3 has already been postulated. The concentrations of these paramagnetic species were measured for various solvents by using DPPH single crystals as the reference standard. The formation of two different aromatic ions on the surface of Al_2O_3–MoO_3 could also be confirmed by the solvent dependence. The intensity of microwave magnetic field H_1 and the modulation width were considered in this measurement. Without solvent molecules such as benzene on the oxide surface, an ESR signal without cation hyperfine structure was almost exclusively observed. The intensities and intensity ratio between the two components of the ESR absorption at $g=2.00$, with and without hyperfine structure, change with solvent. The results indicated that solvent molecules, when adsorbed on the oxide surface, form a surface structure or a surface system which makes the charge transfer from the oxide surface to the solute hydrocarbon easier.

The electron spin resonance (ESR) method is used in studies of catalysis for various purposes, being (1) to know the orbital function of the unpaired electron spin or the crystal field in the bulk or on the surface of solid catalysts,1) and (2) to detect the reaction intermediates (molecular or atomic) in a stable or in a semi-stable state.2) As another application, the interaction among the system components can also be analysed if the mixture (catalyst, reaction-substrate, reaction-intermediates, reaction products, and reaction-byproducts) is considered as a reaction system consisting of these system components.3) If such a system is treated as a reaction system, some additive added to the system, or the solvent used to dissolve the substrate should also be treated as a system component. For this reason, a study of solvent effects on the formation of the paramagnetic species is expected to clarify some facts important for the study of catalysis. In order to see some of the dynamic aspects of the system, quantitative measurements and processings of the concentrations of the system components are necessary. As intermediates paramagnetic species were chosen and quantitative ESR method was used to find the solvent effects on the perylene– (or anthracene)–Al_2O_3–MoO_3 system.

Experimental

Quantitative ESR Measurement. Quantitative ESR measurements normally employ several reference standards with which comparisons are made between these references and the samples to be measured.4) If DPPH is used as a reference, it is diluted in the form of a solution or a solid mixture to obtain the unpaired electron concentration almost equal to that of the sample.5) However, decomposition of DPPH during the course of dilution or storage is inevitable and an accurate and consistent measurement is not easy. Thus a single crystal of DPPH has been used as a reference. The maximum measurable number of unpaired electron spins obtained with the ESR instrument used, a JES-3BX, under the usual adjustment conditions of detector and amplifier, changes with input microwave power and modulation width. At 10 μW and 2.0 G modulation width at 100 kHz, 2×10^{19} unpaired electron spin gives a final first derivative output voltage of 10 mV on the recording device. A 10 mg single crystal contains 1.5216×10^{19} molecules and if weighed by a microbalance, 10.00 mg is obtained as effective figures. The number of unpaired electron spins contained in a (10.00 ± 0.005) mg crystal is $(1.5216\pm0.0008)\times10^{19}$ or 1.521×10^{19}.

The dependence of the ESR signal on the input microwave power should also be considered.6) The magnitude of the microwave magnetic field H_1 is determined by the incident power to the resonant cavity, P, and the "Q" of the cavity. Therefore, the Q value for each sample should be known to estimate the relative H_1 value. The ESR absorption energy is proportional to H_1.2,7) If we denote the Q value of an empty resonant cavity by Q_0, and the H_1 value by H_{10}, we have ${H_{10}}^2=k\cdot P\cdot Q_0$ where k is a constant. If a sample is placed in the cavity, we have ${H_1}^2=k\cdot P\cdot Q$. From these two relations we get ${H_1}^2={H_{10}}^2\cdot Q/Q_0$. Q/Q_0 is estimated by the intensity of an Mn^{2+} line from the $MnSO_2$/MgO sample fixed in the cavity. The microwave circuit is so adjusted as to give the strongest signal amplitude.

Modulation width should be taken into consideration in order to analyze an ESR spectrum having two spectral components.8) If one of the components has a hyperfine structure (hfs), the modulation width should be small enough to observe the hfs. Since the first derivative absorption function is obtained experimentally as a function of the magnetic field $H, f(H)=f_1(H)+f_2(H)$, the integral absorption function $F(H)=F_1(H)+F_2(H)$ must be derived from $f(H)$. If the amplitude of $f(H)$, A_1, is plotted against the modulation width, h, it is proportional to h until h reaches $h_{\max}$, after which A_1 shows a decreasing tendency. A_1 is directly proportional to $F_1(H_c, h_{\max})$, which is the height of $F_1(H)$ observed by $h_{\max}$ modulation width, where H_c is the value of the magnetic field for the peak point of the absorption curve. The height of $F_2(H)$ is $F_2(H_c, h'_{\max})$, where $h'_{\max}$ differs from $h_{\max}$. If the relation between the amplitude of $f_1(H)$ (or $f_2(H)$) observed with a modulation width h and $F_1(H_c, h_{\max})$ (or $F_2(H_c, h'_{\max})$) is known, the latter value can be estimated from A_1 or (A_2). From these quantities the spin concentration, y, was calculated as $y=N_2/M$, where M is the weight of the sample placed in the 45 mm×5.0 mm ϕ cylindrical section the sample tube where microwave magnetic field is the strongest, and N_2 is the total number of the paramagnetic species contained in the same space. N_2 is determined by the relation

$$N_2=\frac{N_1}{I_1}\times\frac{S(\text{sample})}{S(\text{DPPH})}\times\frac{I(P')}{J(P')}\ ,$$

where N_1 is the number of molecules in the DPPH single crystal, $I(P')$ is the intensity of $F_1(H)$ or $F_2(H)$ at P' (dimension, mV G), I_1 is that for the DPPH single crystal at 1 μW, and $J(P')$ is equal to $I(P')/I(1\ \mu W)$ determined by the power dependence curves. S(sample) or S(DPPH) is equal to

$$\int_{H=0}^{H=+\infty} h(H-H_0)\mathrm{d}H/h(0)$$

where $h(H-H_0)$ is the spectrum function written in H(dimension, mV) and the integral value is obtained by a double integration of the first derivative absorption curve. The values of S observed for DPPH (single crystal sealed in a vacuum), perylene cation, R^+O^{*2-}, and Mo^{5+} are 2.8488, 6.61, 13.75, and 108.18 G, respectively.

Preparation of Sample. If the amount of MoO_3 supported on Al_2O_3 is small, (1—3%), the amount of cation formation after contact with a hydrocarbon solution is also small.[9] A fairly large number of cations are formed when the wt% of MoO_3 is above 5%. For this reason, 8.5% of MoO_3 was supported on γ-alumina. The method of preparation is the same as that given in a previous paper.[10] The solvent well shaken with concentrated sulfuric acid, distilled twice, and then distilled into the vessel in which perylene crystals had been placed. After dissolving perylene this solution was mixed with the Al_2O_3–MoO_3 which had been evacuated to 10^{-4} mmHg in a vacuum line. Immediately after contact of the perylene solution a certain amount of perylene cation was formed, gradually increasing as shown in Fig. 2. The first spectrum was recorded at 10—12.5 min after contact of the solution and the subsequent measurements were made at 1, 2, 3, and 6 hr, 1, 2, 3 day, and so on.

It seems that the solvent molecules are working as something more than a simple dispersing medium of perylene molecules.[11] The following experiment was made to see the solvent effect. An aromatic compound was adsorbed on the surface of Al_2O_3–MoO_3, to which the solvent vapor was introduced. For this purpose, anthracene, whose vapor pressure is higher than that of perylene, is more suitable. 0.5 g of Al_2O_3–MoO_3 and 50 mg of anthracene was mixed well and placed in a sample tube, which was placed in the microwave resonant cavity and connected to the vacuum line. During evacuation, the anthracene vapor was adsorbed by the oxide and ESR absorption without hyperfine structure was gradually built up. The notation R^+O^{*2-} was used for this species.[12] Here R denotes anthracene, O^{*2-} the oxygen anion located at some particular points on the oxide surface at which the p-orbitals of an O^{2-} ion might be expected to overlap with the π-orbitals of the aromatic compound adsorbed more easily than at other positions. Various solvent vapors were introduced into the sample and the ESR spectrum after vapor introduction was recorded.

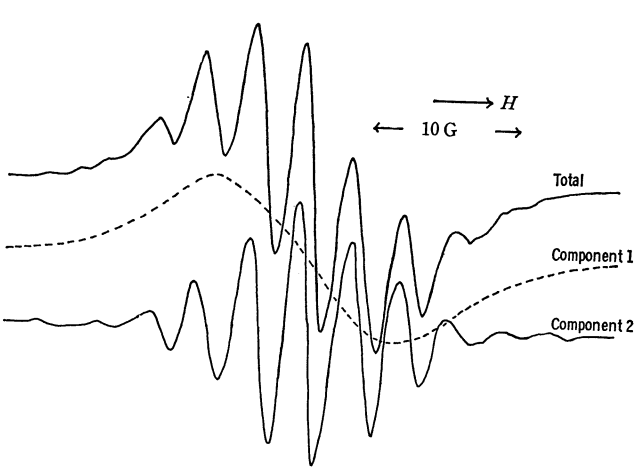

Fig. 1. The two component spectra, Component-1 and Component-2, contained in the observed spectrum, total.

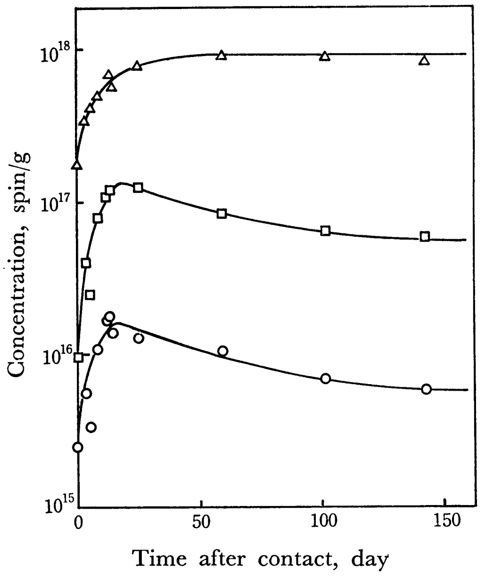

Fig. 2. The time dependence of the concentrations of the paramagnetic species observed.
△: Mo^{5+}, □: R^+O^{*2-}, ○: R^+

Results

The ESR spectrum obtained by perylene–Al_2O_3–MoO_3–solvent system is shown as "total" in Fig. 1. The total spectrum can be analyzed to consist of Component-1 and Component-2. The amplitude of the strongest hyperfine line A (or the central line) was read from the total spectrum. Using ΔH_{msl} of each hyperfine component line, amplitude A, and combination coefficients $_8C_r/70$, the first derivative hyperfine spectrum which represents a pure perylene cation on a solid surface was drawn (Component-2, Fig. 1). The difference between total and Component-2 is Component-1. Component-2 is due to perylene cation, R^+, and Component-1 to R^+O^{*2-}.[10,11,12] The absorption intensity of ESR spectrum (Fig. 1) changes with time after the formation of the paramagnetic species as shown in Fig. 2. The temperature of storage and that of the measurements was 20 °C. The results in Table 1 were calculated so as to give the values which would be obtained under the conditions, $Q=Q_0$ and input power of 1 μW, or obtained with H_{10} for 1 μW. All the data were calculated as if they were obtained with the same H_1 value and without any power saturation. The change in the ESR spectra of anthracene–Al_2O_3–MoO_3 system when a solvent vapor was introduced is shown in Fig. 3. The temperature of measurement was 20 °C. The modulation width, microwave imput power and signal amplification factors were 20 mG, 1.0 mW, 5×10^2; 32 mG, 1.0 mW, 1×10^3; 50 mG, 0.1 mW, 2×10^3; 50 mG, 0.1 mW, 2×10^3; 25 mG, 1.0 mW, 1×10^3; 10 mG, 0.1 mW, 1×10^3. Solvents used have different structures. However, they were added into the sample tube in vapor phase in small amounts making the difference in Q which was slightly affected by different solvent vapor negligibly.

TABLE 1. SOLVENT EFFECT ON THE FORMATION OF R^{+}, R^{+}O^{*2-}, AND Mo^{5+} a)

Solvent	R^{+} b)	R^{+}O^{*2-} c)	Mo^{5+} d)
n-Hexane	.59	.95	.86
Cyclohexane	1.5	3.2	.58
Benzene	1.1	2.7	8.5
Toluene	2.0	4.7	1.6
Ethylbenzene	1.0	3.4	1.5
n-Propylbene	.70	2.9	.90
Cumene	.94	3.2	1.3
t-Butylbenzene	.36	2.6	.86
p-Xylene	2.3	4.9	1.7
o-Xylene	1.1	2.0	.88
m-Xylene	.68	2.7	.70
1,2,3-Trimethylbenzene	10.8	25.5	11.7
1,2,4-Trimethylbenzene	2.4	6.6	2.6
1,3,5-Trimethylbenzene	.90	4.1	1.4
Mixtures of benzene-cyclohexane			
BZ/CH 3:1	.36	2.9	.67
BZ/CH 1:1	1.2	4.2	1.3

a) Measured 143 day after preparation.
b) $\times 10^{15}$/g. c) $\times 10^{16}$/g. d) $\times 10^{17}$/g.

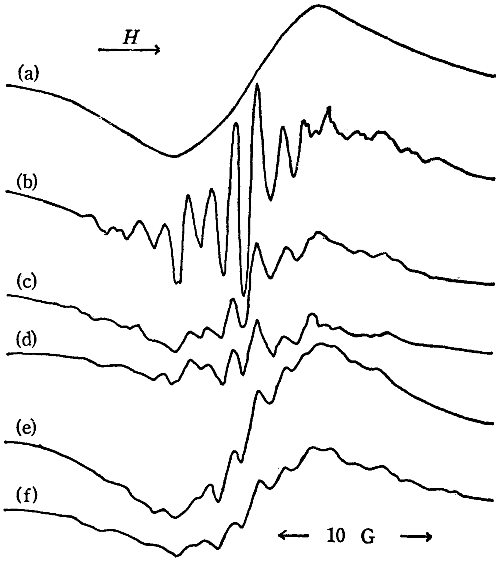

Fig. 3. The change in the ESR spectra from anthracene-Al$_3$O$_3$-MoO$_3$ after vapor of various solvents is introduced.
(a): Before solvent in, (b): C$_6$H$_6$ 80 mmHg, (c): C$_6$H$_{12}$ 70 mmHg, (d): CCl$_4$ 20 mmHg, (e): *t*-Butylbenzene 3 mmHg, (f): Aniline <1 mmHg

Discussion

Formation of Two Paramagnetic Species. Evidence to show the formation of two paramagnetic species, R^{+} and R^{+}O^{*2-}, has been given in a few cases. The reactivity of R^{+} with H$_2$O is higher than that of R^{+}O^{*2-} and with use of this R^{+}O^{*2-} was separated from R^{+}.[11] The ESR microwave saturation factor of R^{+} is larger than that of R^{+}O^{*2-} which makes the shape of the ESR spectrum of the mixture of these two paramagnetic species strongly power dependent.[13] The experimental results were analysed assuming the presence of two paramagnetic hydrocarbon species. The following assumption was found to be correct: if Component-1 is a spurious signal formed by a broadening of Component-2, the ratio between Component-1 and Compontne-2 should be the same for all the solvents used provided that the measurements are made under the same conditions, *i. e.*, the same H_1 value, and the same modulation width. However, the results (Table 1) show that the ratio greatly depends on the solvent, *viz.* 15 for *n*-hexane, 70 for *t*-butyl benzene, and 46 for 1,3,5-trimethyl benzene. Thus, the solvent effects give evidence to conclude that Component-1 and Component-2 are due to chemically different paramagnetic species.

Necessity of a Solvent in a Cation Formation. The effect of introduced benzene vapor on the ESR of Al$_2$O$_3$-MoO$_3$-anthracene system indicates that solvent molecules are necessary for observing an ESR spectrum having hfs of the anthracene cation. However, a perylene cation might give an ESR spectrum without a hyperfine structure if trapped on a solid surface. The hyperfine structure in the ESR of a hydrocarbon cation is given by two spin Hamiltonian terms, anisotropic which depends on the direction of the external magnetic field, and isotropic which does not. In solution the anisotropic term cannot be observed since it is averaged out by the tumbling motion of the molecule.[14] On a solid catalyst surface the hfs can only be partly observed because of the restricted motions.[15] However, if the sample is cooled to liquid nitrogen temperature, the hfs almost vanishes.[15] Thus, the appearance of a hfs in the ESR upon introduction of a solvent can be due to either (A) formation of the cation by the action of the solvent vapor, or (B) change of the cation, which existed but whose ESR spectrum did not show a hfs, to one which shows a hfs in the spectrum. If (B) is the case it would only be explained as motions of the cation on the surface of the oxide, which have been frozen, resume their activities because the solvent molecules defreeze them. Such defreezing should be due to a partial dissolution of the cation by the solvent molecules on the oxide surface. However, such a partial dissolution will disappear if the solvent is removed from the sample. The hfs in the ESR spectrum once formed does not change when the sample is evacuated subsequently.[11] Thus, case (B) is ruled out. It is concluded that the solvent molecule is necessary for the formation of an aromatic cation on the oxide surface.

Role of the Solvent Molecule in the Cation Formation. If solvent molecules are indispensable to the formation of a hydrocarbon cation, the question arises as to how a "solvent" molecule differs from a "solute" molecule. The solvent dealt with is a substance which is liquid at room temperature and can dissolve aromatic hydrocarbons. This indicates that the solvent molecule can move freely and occupy the oxide surface continuously, cover the narrower places like small pores, and move from one place to another on the surface. The following three roles are possible for solvents. (A) The solvent dissolves the solute and carries it to the micropores where the parent cation (or the positive electric charge source) lies. (B) The solvent molecule accepts a positive charge from the parent cation and delivers it to the solute molecule by thermal molecular motions. (C) The oxide surface combined with a certain arrangement of the adsorbed solvent molecules, as a whole, promotes the charge transfer process. In this case the aromatic cation formation occurs if an aromatic compound and a positive charge exist on both ends of this surface and solvent arrangement. The possibility for (A) will be excluded because a small amount of solvent (contact pressure$<$10 mmHg) can cause the formation of anthracene cation. It is hard to distinguish (B) from (C). An experiment carried out with mixed solvents of benzene and cyclohexane (Table 1) seems to exclude (B). If (B) holds, the total formation of the solute cation will be the sum of its formations due to benzene and cyclohexane. If (C) is correct, a small number of cyclohexane present in the surface arrangement of benzene molecules would weaken the function of this surface–benzene system and a linear relation between the composition of the mixed solvent and the cation formation could not be expected. If the solvent or the third component is a liquid at 20 °C, (B) should be more probable. However, when naphthalene which is solid at 20 °C was added as a third component, 10 mg of naphthalene to 30 mg of anthracene, a strong ESR signal of anthracene cation was observed.[16] Thus (C) is more probable.

The results obtained by alkylated benzenes are shown in Table 1. The results shown for toluene to cumene are similar. In the case of dimethylbenzenes, the formation of the paramagnetic species decreases in the order *p*-, *o*-, and *m*-. In the case of trimethyl derivatives, the formation of the paramagnetic species decreases in the order 1,2,3-trimethyl benzene (TMB), 1,2,4-TMB, and 1,3,5-TMB. It is desirable to analyze the results and know what physical factors of the solvent molecules are responsible for the difference. The results from trimethyl benzenes (Table 1) indicate that the molecule with a lower molecular symmetry produces more cation, indicating that a higher dielectric constant favors cation formation. The effect of ionization potential may be studied by computing the energy eigen-values of the molecular orbitals in the methyl substituted benzene cation molecules. The steric effects may also be seen in the series of toluene, ethyl benzene, propyl benzene, and butyl benzene, the formation of perylene cation decreasing in this order.

Paramagnetic Species other than R^+, R^+O^{*2-}, and Mo^{5+}. ESR absorption which is not due to any of these three species is always found in the spectra obtained by Al_2O_3–MoO_3 and has not been interpreted.[3,10] The observed concentration of Mo^{5+} is far greater than the sum of R^+ and R^+O^{*2-}. If benzene is used as a solvent, $(Mo^{5+})=8.5\times10^{17}$ spin/g, while the sum $((R^+)+(R^+O^{*2-}))=2.86\times10^{16}$ spin/g, and is 8.2×10^{17} spin/g less than the former. This indicates that at least this amount of static electricity is compensated by some positively charged species, T^+. Though R^+ and R^+O^{*2-}, both having net positive electric charge, decrease with time, the concentration of Mo^{5+}, having a net negative charge, increases with time. This seems to indicate that the neutralization of R^+ and R^+O^{*2-} takes place not by Mo^{5+} but by some other negatively charged species, T^-. Thus, if the Al_2O_3–MoO_3–hydrocarbon catalytic reaction system is analyzed, T^+ and T^- should be included in the system components.

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