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The Paramagnetic Species Formed on the Surfaces of Various Oxides by Naphthalene Derivatives

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The ESR intensities from the paramagnetic species formed by mixing a naphthalene derivative with an oxide powder were studied after the mixture had been heated at various temperatures. The measurements were made at 20°C. As additives 1-nitronaphthalene, 1-naphthol, 1,4-naphthoquinone, naphthalic acid, 1-naphthylamine, 1-nitroso-2-naphthol, naphthalene, triphenylene, and anthracene were used. As oxides, alumina, Al_2O_3-MoO_3, silicagel, TiO_2, MgO, MoO_3, CuO, and $ZnCrO_4$ were used. The ESR intensities obtained by the first six oxides depended only on the ionization potential of the additives, while those obtained by CuO and $ZnCrO_4$ did not. The ESR intensities obtained when 1-naphthol was mixed with alumina samples with various surface areas were exactly proportional to the surface areas of the alumina specimens used. It was concluded that, in the first six oxides, the additives are chemisorbed by the oxides at the active-oxygen anion sites on the surface. The introduction of either NH_3 or N_2O onto the adsorbed species formed on Al_2O_3-MoO_3 particles decreased (in the case of NH_3) or increased (in the case of N_2O) the ESR intensities. From these facts, it is concluded that a cationic complex, (naphthalene derivative$^+$-O^{2-}), is formed on the surface of these six oxides. In the case of CuO, the presence of (Cu^+-naphthylamine$^+$) is concluded.

The effects of various additives on the ESR intensities of zinc oxide were previously studied by the present author;[1] it was found that the surface ionization of the aromatic additive on the particle of zinc oxide, $Ar+ZnO \rightarrow Ar^+ + (ZnO)^-$, is in an equilibrium with the transfer of the hole from Ar^+ to Zni (interstitial zinc atom), $Ar^+ + Zni \rightarrow Ar + Zni^+$. Though the surface ionization of the aromatic compound on silica-alumina has long been established using perylene, diphenylethylene, and diphenylamine as additives,[2,3] the detailed mechanism has not yet been made clear. In some recent studies, the formation of a negative ion is claimed for the system consisting of an oxide and nitrobenzene.[4-6] Therefore, some criterion is strongly desired with which it is possible to predict the type of paramagnetic species to be formed on the surface from an additive compound with a particular type of molecular structure or functional group. Hoping to obtain a generalized solution for this problem, we have tested systems consisting of various oxides and naphthalene derivatives with various substituted functional groups together with anthracene and triphenylene, which it is also possible to consider as naphthalene derivatives. Naphthalene derivatives have been selected because (1) their ionization potentials are lower than those of the benzene derivatives with the same functional groups; (2) the desired substituted compounds are easier to acquire than those of anthracene or other, larger condensed-ring compounds, and (3) the ionization energies may be calculated as a problem of the variation in h and k by a proper molecular orbital theory.

Experimental

The additive compounds were used after recrystallization. Benzene, the solvent for the additive solution (0.2 mmol of a solute in 2.0 m*l* of the solvent), was used after having been shaken with concentrated sulfuric acid and by subsequent distillations. Special reagent-grade oxides, shown in Table 3, were used without further purification. The additive solution (2.0 m*l*) was poured on the oxide (1.0 g) and the solvent was evaporated in air. After the evaporation of the benzene, the mixture was placed in an ESR sample tube and was then evacuated to at least 10^{-2} mmHg (or to the vapor pressure of the additive). The sample thus prepared was examined first at room temperature. After the measurement, the tube was placed in a copper block with a hole to fit the diameter and the length of the sample tube, heated to 50°C for three minutes, and then cooled to 20°C. Then the measurement was made. Identical operations were repeated at different heating

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[1] H. Ueda, *Can. J. Chem.*, **46**, 891 (1968).

[2] D. M. Brower, *Chem. Ind.*, (London) **1961**, 177.

[3] J. J. Rooney and R. C. Pink, *Proc. Chem. Soc.*, **1961**, 70.

[4] V. V. S. Rao, R. D. Iyenger and A. C. Zettlemoyer, *J. Catal.*, **12**, 278 (1968).

[5] R. D. Flockhart, I. R. Leith and R. C. Pink, *Chem. Commun.*, **1966**, 885.

[6] A. J. Trench and R. L. Nelson, *Trans. Faraday Soc.*, **63**, 2254 (1967).

temperatures, 100, 150, 200, and 250°C. The ESR intensity measurements were made using the same microwave power and at the same crystal current. Carbon powder ground with alumina and sealed in a vacuum was used as the intensity standard by measuring it between each ten measurements of the additive-oxide samples.

Results

In Table 1 the relative values of the ESR intensities obtained from Al_2O_3-MoO_3 (10%) containing various additives, after the sample had been heated at 250°C, x_1, x_2, x_3, u_1, u_2, and u_3, are shown. In the table, x denotes the intensity of the line with $g=2.004\pm0.001$ and with δH_{msl} smaller than 10 gauss, and u denotes the intensity of the line with $g=1.9328$. Both x and u are relative values, and so they are shown on different scales. The suffix 1 denotes the value for the sample in vacuum, 2 that for the sample in N_2O (350 mmHg), and 3 that for sample in NH_3 (300 mmHg). In Fig. 1, the x_1 values of Table 1 and the corresponding values for different oxides, *i.e.*, Al_2O_3, MoO_3, MgO, TiO_2 and silicagel, are plotted against the light absorption wave number in kilo Kaiser of the additve. The wave number value used here is equal to $10^7/\lambda_{max}$, where λ_{max} denotes the maximum peak wavelength in mμ of the absorption peaks observed below 500 mμ.[*1] Figure 2 shows the spin concentration obtained by γ-alumina with 1-naphthol at room temperature *versus* the surface area of the alumina sample, which was measured by the helium-nitrogen BET method. The results show that unpaired electrons are formed on the surface and that the concentration is 3.3×10^{11} spins/cm², which may be compared with the value reported by Rooney and Pink, 2×10^{11} spins/cm² for perylene-silica-alumina. Table 2 shows the line-width at the maximum slope of the singlet ESR absorption, with $g=$

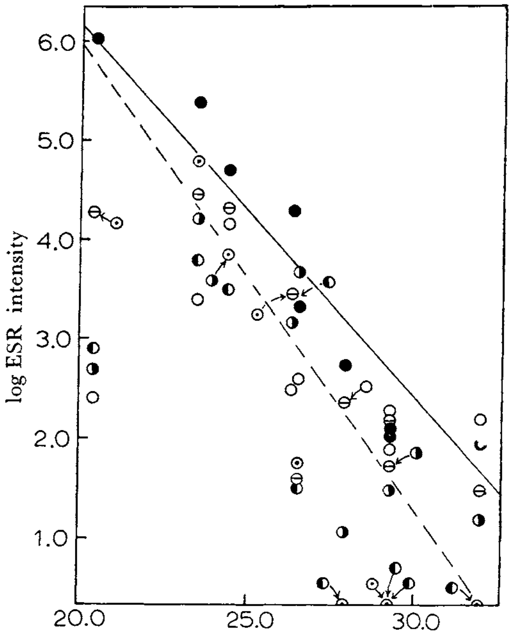

Fig. 1. Relative ESR intensities of Al_2O_3-MoO_3 *vs.* absorption wave number of additives.
● Al_2O_3-MoO_3, ⊖ Al_2O_3, ○ MoO, ⊙ MgO, ◐ TiO_2, ◑ Silicagel

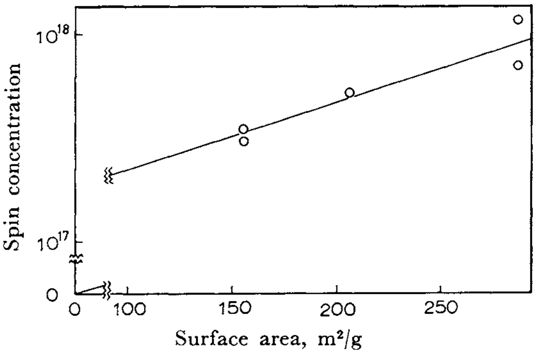

Fig. 2. Spin concentration (per gram) *vs.* surface area. Oxide: γ-Alumina. Additive: 1-Naphthol.

Table 1. Relative ESR intensities observed

Additive	x_1	x_2	x_3	u_1	u_2	u_3
1-Naphthol	1.11×10^6	2.20×10^6	2.60×10^4	1.49×10^3	1.57×10^3	1.41×10^3
1,4-Naphthoquinone	2.48×10^5	8.10×10^5	4.95×10^4	3.90×10^3	4.80×10^3	3.10×10^3
1-Nitroso-2-naphthol	6.55×10^4	2.46×10^5	4.50×10^4	1.15×10^3	9.35×10^2	1.38×10^3
1-Nitronaphthalene	2.00×10^4	2.25×10^5	2.27×10^3	3.92×10^2	3.50×10^2	4.33×10^2
Anthracene	2.32×10^3	6.25×10^4	2.65×10^2	1.50×10^3	5.65×10^3	7.40×10^2
1-Naphthylamine	5.80×10^2	2.67×10^5	2.20×10^2	2.00×10^3	8.87×10^3	1.18×10^3
Triphenylene	1.24×10^2	4.10×10^2	2.45×10^2	8.12×10^2	1.30×10^3	3.23×10^2
1,8-Naphthalene-dicarboxylic acid	1.20×10^2	1.20×10^2	1.20×10^2	5.26×10^2	7.75×10^2	2.78×10^2
Naphthalene	92	1.50×10^2	95	4.39×10^2	5.90×10^2	2.88×10^2

[*1] Some of the additives absorb in the near IR region; this phenomenon must be due to a different type of transition and so was ignored.

2.004±0.001, for the species formed by various additives. It can be seen that both the δH_{msl} and g values depend upon the additives. In Table 3 the same quantities as in Table 2 are shown for various oxides mixed with 1-nitroso-2-naphthol as the additive. The results show that the oxides also slightly affect the spectroscopic constants. In the case of perylene-silica-alumina, the hyperfine splitting was partly resolved in the spectrum. In the present study only 1-nitroso-2-naphthol gave a

TABLE 2. THE LINE WIDTHS AT MAXIMUM SLOPE OF THE ESR ABSORPTION SPECTRA FROM THE SPECIES ON Al_2O_3-MoO_3

Additive	δH_{msl}, gauss	δg, $\times 10^{-4}$
1,4-Naphthoquinone	7.3	+0.6
1-Nitronaphthalene	8.8	+3.6
1,8-Naphthalene-dicarboxylic acid	8.7	−2.4
1-Naphthylamine	8.8	−4.2
1-Naphthol	8.0	0.0
1-Nitroso-2-naphthol	8.4	0.0
Naphthalene	7.3	−4.2
Triphenylene	5.5	−9.0
Anthracene	6.5	−9.0

TABLE 3. THE LINE WIDTHS AT MAXIMUM SLOPE OF THE ESR ABSORPTION SPECTRA FROM THE SPECIES FORMED BY 1-NITROSO-2-NAPHTHOL AND VARIOUS OXIDES

Oxide	δH_{msl}	δg, $\times 10^{-4}$
Al_2O_3-MoO_3	8.4	0.0
Al_2O_3	7.3	+6.6
TiO_2	6.6	0.0
Silicagel	5.5	+6.6
MoO_3	6.2	0.0
MgO	5.5	−6.6
CuO	5.5	−3.5
$ZnCrO_4$	8.8	+5.4

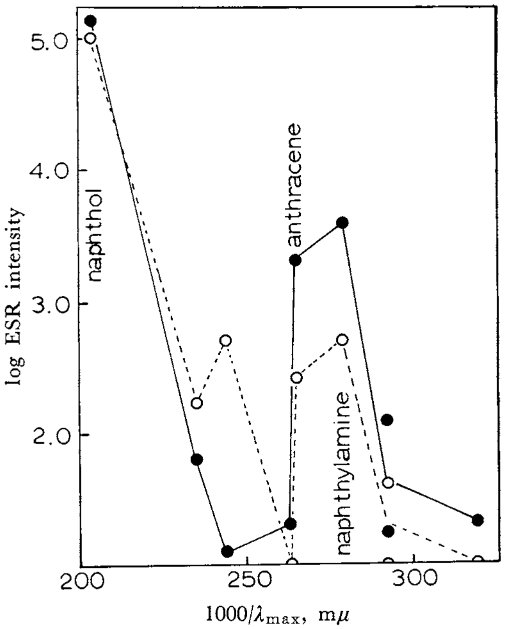

Fig. 3. Relative ESR intensities of CuO and $ZnCrO_4$ vs. $1000/\lambda_{\max}$ of additives.
○ $ZnCrO_4$, ● CuO

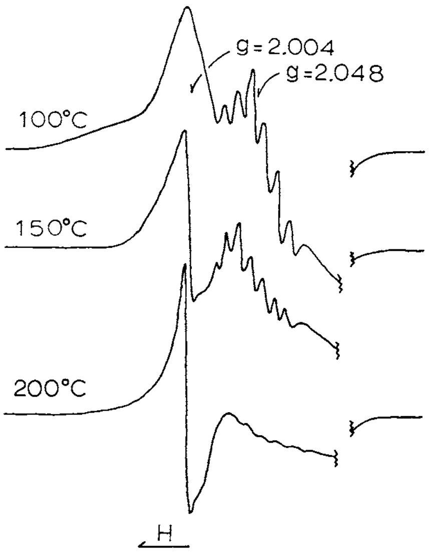

Fig. 4. First derivatives of the ESR spectra from CuO - 1-naphtylamine.

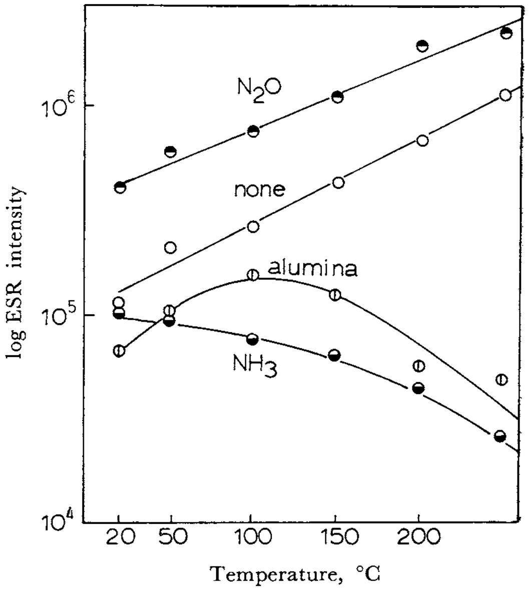

Fig. 5. Temperature dependence of the ESR intensities of Al_2O_3 and Al_2O_3-MoO_3 containing 1-naphthol with and without N_2O or NH_3.
○ Al_2O_3-MoO_3 in vacuum, ⦶ Al_2O_3 in vacuum, ◓ Al_2O_3-MoO_3 in N_2O, ◒ Al_2O_3-MoO_3 in NH_3

hyperfine structure in the spectrum (three lines), but this structure disappeared when the specimen was heated at higher temperatures. Figure 3 shows the same quantities as those in Fig. 1 except for CuO (filled circles) and $ZnCrO_4$ (white circles). In this figure, the ESR intensities are stronger only for the additives which have either –OH or a $-NH_2$ group, or which are Lewis bases. Figure 4 shows the dependence of the relative ESR intensities for the sample consisting of CuO and 1-naphthylamine on the temperature of the heat treatment at 100, 150 and 200°C. The vertical amplitude of the spectrum at 200°C is six times as strong as that at 100 or 150°C. In Fig. 5 the temperature dependence of the relative (all on the same scale) ESR intensities for alumina and Al_2O_3-MoO_3, with 1-naphthol as the additive and with or without N_2O or NH_3 are shown. It can be seen that when both N_2O and Mo^{6+} exist on the surface they give the same type of activity to the surface of alumina, while NH_3 gives the opposite activity.

Discussion

The determination of the sign of the electric charge on an organic ionic species is often difficult[7,8] if the available information is limited to the spectroscopic data. Such difficulty increases if the spectroscopic measurement is made for a solid sample. In the case of zinc oxide[1] the presence of the electron donor, Zni, which gave the line with $g=1.96$ and which could easily be identified, has already been established. By using this fact, the sign of the aromatic ionic species on zinc oxice was determined. In some studies, the criterion that the electronegativity of the functional group attached to the aromatic ring determines the sign of the ionic species to be formed by that compound, has been used. However, it seems that this criterion is not as good as the one stating that the type of environment, in which the ionization occurs, determines the sign of the ionic species. This latter criterion can be written, alternatively, as stating that the atmosphere, the solvent, the matrix or the nature of the surface where the ionization occurs determines the type of the ionic species to be formed, rather than the intrinsic nature of the additive or the solute. Generally speaking, an aromatic compound with a low ionization potential, typically represented by perylene, also has a large electron affinity. In other words, it is equally easy to form an anion and a cation. The results obtained by radiation chemical studies of rigid glass solid solutions of aromatic compounds in solvents of various chemical structures have indicated that the matrix determines the sign of the electric charge of the ionic species to be formed.[9] In the present work, the additives with lower ionization potentials gave stronger ESR intensities, as is shownin Fig. 1. It cannot directly be concluded, for the foregoing reason, that cations were giving the ESR signals. However, the facts in Fig. 1 at least indicate that ionic species are formed.

Recently many studies have been made of ionic intermediates in radiation chemistry. Probably the most reliable method for the discrimination of ions in condensed phases has been the addition of N_2O or NH_3 to observe its effects on the formation of ionic intermediates. If an aromatic hydrocarbon is dissolved in an aliphatic ether and if this solution is irradiated, the electron primarily formed by ionizing radiation is captured by the solute molecule to form its negative ion. This formation of the negative ion can be effectively prevented by adding a small amount of N_2O to the solution, since N_2O scavenges the electron primarily formed.[10] If N_2O is added to a system in which a cation is to be formed, it increases the amount of the cation.[8] On the other hand, if NH_3 is added, it scavenges the positively-charged molecular species.[8] The results in Table 1 show that, for all the additives studied, the ESR intensities are partly cancelled by NH_3 and increased by N_2O. It seems that Table 1 provides enough evidence to establish the formation of a cation or a cation-like species in these systems. The results in Fig. 2 show that the phenomenon is a surface process.

In the case of the silica-alumina-perylene system, a carefully-created anaerobic environment was needed for the formation of the cation. This also indicates that the ionization is a surface process. The ESR data in Tables 2 and 3 show that the molecular orbital for the unpaired electron is made by an admixture of the wave functions of both the oxide and the additive orbitals. In other words, the unpaired spin is both on the oxide and the additive sides. Therefore, the additive is adsorbed by the oxide particles by chemisorption. The fact that the positive ions of the oxides shown in Fig. 1 (for example, the Mg^{2+} of MgO) do not affect the spectrum indicates that the chemisorption takes place at the O^{2-} site of the surface by an overlapping of its $2p$ orbital and the π-orbital of the aromatic additive molecule. If the cation of the oxide, *e.g.*, Mg^{2+}, accepts the electron directly from the additive molecule, what determines the ESR intensity will be both the electron affinity of the cation of the oxide and the ionization potential of the additive molecule. The results in Fig. 1 indicate that only the ionization potential of the additive determines the ESR intensity. The difference in the total intensities of the

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[7] For example, H. Ueda, *J. Phys. Chem.*, **68**, 1304 (1964).

[8] H. Ueda, This Bulletin, **41**, 2578 (1968).

[9] T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375, 4372 (1966).

[10] G. Scholes and M. Simic, *Nature*, **202**, 895 (1964); S. Sato, T. Terao, M. Kono and S. Shida, This Bulletin, **40**, 1818 (1967).

ESR signal for different oxides indicates that the ionization which follows the chemisorption takes place on those O^{2-} ions which are in or which occupy certain active sites on the surface, probably somehow extruding above the surface. This assumed O^{2-} is written as O^{*2-} in this paper. Therefore, the nature of the surface-active sites at which the chemisorption occurs may be concluded to be quite similar for all the oxides shown in Fig. 1, while their relative concentrations are different for different oxides.

In the case of CuO and $ZnCrO_4$, the ESR intensities are strong only for the additives which have either $-NH_2$ or -OH groups. This is probably due to the fact that, in these oxides, the bond between the metal cation and oxygen is weak; as a result, there are few active O^{*2-} ions on the surface because the O^{*2-} ions can escape from the surface more easily than O^{2-} ions. Incidentally, it is assumed that a chemical bond is formed between the lone pair of the $-NH_2$ or -OH group and the metal cation of the oxide, *e.g.*, Cu^{2+}. A good piece of evidence to support this speculation is the spectrum shown in Fig. 4. At room tmeperature (CuO-1-naphthylamine) gives a broad ESR spectrum with $g=2.050$. When the sample is subjected to heat treatment at 100°C, a hyperfine splitting consisting of seven lines with an approximate intensity ratio of 1 : 2 : 2 : 2 : 2 : 2 : 1 appears, with its absorption center at $g=2.050$. If the splitting factor due to the amino-nitrogen is twice as large as that of amino hydrogen, these seven lines can most reasonably be interpreted by $a_H=14.6$ gauss and $a_N=29.2$ gauss. The large *s*-character or isotropy of this unpaired spin shows that one of the sigma lone-pair electrons is donated to the 3*d* orbital of Cu^{2+}. Between 100°C and 150°C, naphthylamine approaches Cu^{2+}; directing its $-NH_2$ group toward the Cu^{2+} ion. The (Cu^{2+}-naphthylamine) weak complex thus formed becomes a more strongly-combined charge-transfer complex (Cu^+-naphthylamine$^+$) at 200°C, giving rise to the strong ESR absorption at $g=2.004$; this indicates that the unpaired electron is mostly on the (naphthylamine$^+$) side.

In the past literature, the formation of the positively-charged species has been handled as a hole transfer from an active site or acid center to the adsorbed (it is not certain if a chemisorption or a van der Waals adsorption has been assumed) aromatic molecule. This theory does not, however, work well when the following two facts are to be interpreted. Firstly, if there are such holes (naturally having unpaired electrons), they and their counterparts (electrons or anions) should be observed even when no additives are added, provided that the electrons are not in the conduction band. Secondly, by such a mechanism the increment in the signal intensity in the presence of N_2O cannot be interpreted. If the active site consists of a proton, the counter anion should be O^{2-} or OH^-. For such systems, the effect of N_2O on the ESR intensity cannot be expected. The fact that the quenching of the ESR intensity by NH_3 is not done thoroughly also indicates that such a hole transfer is not true. If the active site consists of a proton, it should be very effectively scavenged by NH_3. These facts suggest that the formation of the positively-charged species is governed by several equilibrium reactions among O^{*2-}, trapped electrons (T^-), the aromatic additive (Ar), N_2O, and NH_3 (if these are added).

The existence of some electron traps can be concluded from Fig. 5. In the naphthol-alumina sample, the ESR intensity begins to decrease if the temperature of the heat treatment is above 100°C. This is not due to the thermal decomposition of the positively-charged species, for in the naphthol-Al_2O_3-MoO_3 system no such decrease in intensity is found as far as to a heat treatment temperature of 250°C. In the latter sample, a signal due to Mo^{5+} ($g=1.9328$) appears together with the line $g=2.004$. By these facts, the decrease in the ESR intensity in alumina is concluded to be caused by a recombination of the trapped electron and the cation complex formed. If Mo^{6+} is present, the electron is also trapped by Mo^{6+} to form Mo^{5+}; therefore, the recombination between the trapped electron and the cation complex, though it is probably still taking place, is far slower than that in the alumina-naphthol sample.

The following equilibrium equations describe the surface reactions leading to the cation complex:

$$ArO^{*2-} \rightleftarrows Ar^+O^{*2-} + e^-;\ K_i \qquad (1)$$

$$e^- + T \rightleftarrows T^-;\ K_t \qquad (2)$$

$$T^- + Ar^+O^{*2-} \rightleftarrows T + ArO^{*2-};\ K_r \qquad (3)$$

Ar denotes an additive, T denotes an electron trap such as Mo^{6+} and T^- denotes the trapped state, *e.g.*, Mo^{5+}. Only two of (1), (2) and (3) are independent; therefore, (1′) and (3′) are used for the analysis of the data. In (1′) and (3′), x denotes $[Ar^+O^{*2-}]$, u denotes $[T^-]$, and t denotes $[T]$.

$$[ArO^{*2-}]\cdot K_i = x\cdot[e^-] \qquad (1')$$

$$u\cdot x\cdot K_r = t\cdot[ArO^{*2-}] \qquad (3')$$

As the total concentration of the positively-charged species is equal to that of the negatively-charged species (the suffixes used are those in Table 1):

$$x_1 = u_1 + [e^-] \qquad (4)$$

From (1′), (3′) and (4), we obtain:

$$x_1^2 = [ArO^{*2-}]\cdot K_i + t_1\cdot[ArO^{*2-}]/K_r$$

is derived. As K_r is large, and as $t_1/K_r\cdot K_i$ can be neglected,

$$x_1 = \sqrt{[ArO^{*2-}]\cdot K_i}$$

$$t_1 = u_1\cdot x_1\cdot K_r/[ArO^{*2-}]$$

are obtained. If N_2O is added to this system,

$$N_2O + T^- \rightleftarrows N_2O^- + T;\ K_s \qquad (5)$$

is expected in addition to (1), (2) and (3).[*2] Then,

$$u_2\cdot[N_2O]\cdot K_s = t_2\cdot[N_2O^-]$$

is derived. In this case, (4) should be altered:

$$x_2 = u_2 + [e^-] + [N_2O^-] \qquad (6)$$

Together with (1′) and (3′), and neglecting $t/K_r\cdot K_i$, (6) gives:

$$x_2 = \sqrt{[ArO^{*2-}]\cdot(K_i + [N_2O]\cdot K_s/K_r)}$$

Therefore,

$$(x_2/x_1)^2 - 1 = [N_2O]\cdot K_s/K_i\cdot K_r \equiv Y_{21}$$

$$1/Y_{21}\cdot x_1{}^2 = K_r/[N_2O]\cdot[ArO^{*2-}]\cdot K_s$$

are obtained. As $[ArO^{*2-}]\cdot[N_2O]$ will be equal for all the additives used, the value on the left side gives the relative value of K_r. t_2 is shown in the same way as t_1:

$$t_2 = u_2\cdot x_2\cdot K_r/[ArO^{*2-}]$$

If NH_3 is added,

$$Ar^+O^{*2-} + NH_3 \rightleftarrows ArO^{*2-} + NH_3{}^+ \ ; \ K_c$$

$$x_3\cdot[NH_3]\cdot K_c = [ArO^{*2-}]\cdot[NH_3] \qquad (7)$$

take place instead of (3). The equation corresponding to (4) or (6) is:

$$x_3 + [NH_3{}^+] = u + [e^-] \qquad (8)$$

From (7), (8), (1′), and (3′), and neglecting $t/K_r\cdot K_i$,

$$x_3{}^2 = [ArO^{*2-}]\cdot K_i/(1+[NH_3]\cdot K_c/[ArO^{*2-}])$$

$$(x_1/x_3)^2 - 1 = [NH_3]\cdot K_c/[ArO^{*2-}] \equiv Y_{13}$$

are obtained. Since $K_c/[ArO^{*2-}]$ should be equal for all the additives, Y_{13} gives the relative value of K_c. The relative values of $[ArO^{*2-}]\cdot K_i$, t_2, $K_r/[ArO^{*2-}]\cdot[N_2O]\cdot K_s$, and $[NH_3]\cdot K_c/[ArO^{*2-}]$ are shown in Table 4.

It is well-known that the $-NO_2$ group in an aromatic nitro compound deaccelerates a nucleophillic substitution reaction, while an amino group on an aromatic amine accelerates it. These facts show that these groups greatly change the electron densities on some particular carbon atoms of the aromatic ring. The drawing of a direct analogy between such facts and the criterion for the determination of the sign of the electric charge in an ionic species on the oxide surface seems to be wrong for the following reasons. It is not the free cation, Ar^+, but the chemisorbed species, Ar^+O^{*2-}, that is formed by the charge transfer from Ar to T. The cation complex, Ar^+O^{*2-}, can also be written as $(ArO^*)^-$, which it is possible to describe as an anion. This view may also be related to the fact that a strictly anaerobic condition was needed for the observation of the "perylene cation" on silica-alumina. The rate constants of O_2 and N_2O when reacting with a hydrated electron are comparable and are very large. Therefore, O_2 has a strong ability to destroy an anion, but not a cation. On the other hand, the cation of perylene has been observed in a mixture of O_2 and anhydrous HF.[11] Therefore, the "perylene cation" previously reported might not have been the free cation. Perylene$^+O^{*2-}$ or (perylene-$O^*)^-$ might be a more proper form to describe the paramagnetic species observed. Therefore, to use the electron density distribution function of "Ar" and not that of "ArO^{*2-}" to predict the formation of either a cation or an anion on an oxide surface is not right.

As is shown in Table 4, the activities of Mo^{6+}, *i.e.*, t_2, are not the same for different additives, though its chemical concentrations are all the same.

TABLE 4. RELATIVE VALUES OF SURFACE REACTION CONSTANTS FOR Al_2O_3-MoO_3

Additive	For ArO^{*2-}		For Ar^+O^{*2-}	
	$[ArO^{*2-}]\cdot K_i$	t_2	$\dfrac{K_r}{[ArO^{\circ 2-}]\cdot[N_2O]\cdot K_s}$	$\dfrac{[NH_3]\cdot K_c}{[ArO^{*2-}]}$
1-Naphthol	3.02×10^3	1.23×10^{-3}	2.89×10^{-5}	2.4×10
1,4-Naphthoquinone	1.54×10^2	8.40×10^{-3}	1.73×10^{-4}	3.2×10^{-1}
1-Nitroso-2-naphthol	1.05×10	5.25×10^{-3}	1.85×10^{-3}	1.4×10^{-2}
1-Nitronaphthalene*	1.00	1.00	1.00	1.00
Anthracene	1.35×10^{-2}	1.39×10^2	3.16	1.00
1-Naphthylamine	8.35×10^{-4}	4.50×10^{-2}	1.46×10^{-3}	7.9×10^{-2}
Triphenylene	3.80×10^{-5}	4.61	6.95×10^2	$\simeq0$
1,8-Naphthalenedicarboxylic acid	3.52×10^{-5}		7.39×10^2	$\simeq0$
Naphthalene	2.10×10^{-5}	8.44	7.50×10^3	$\simeq0$

* The values for this compound are put to be the standard values.

[*2] It may be more proper to use the chemical equations, $N_2O+e^-\rightleftarrows N_2+O^-$, and so on, instead of (5). Though the negative-charge transfer to N_2O itself has been established, the behavior and fate of N_2O on the solid surfaces investigated in this study have not yet been made clear. Therefore, further discussion or theoretical treatment, beyond (5), of the fate of N_2O after scavenging an electron or an anion has been omitted in the present report.

11) W. Ij. Aalbersberg, G. J. Hoijtink, E. L. Mackor and W. P. Weijland, *J. Chem. Soc.*, **1959**, 3049.

This is partly due to the fact that the system studied is not a homogeneous solution; therefore, the equilibria in (2), (3) and (5) are more involved than those to be found with a homogeneous system like an equeous solution of Mo^{6+}. From (5) and (3),

$$N_2O + ArO^{*2-} \rightleftarrows Ar^{+}O^{*2-} + N_2O^{-};\ K_s/K_r$$

is derived. In this reaction, Mo^{6+}-Mo^{5+} functions as a catalyst. The different activities of Mo^{6+} for different kinds of Ar mean that the catalytic activities of Mo^{6+}-Mo^{5+} are different for different kinds of Ar. This is due to the heterogeneous nature of the system.

In my previous paper,[1] no rule was found for the relation between the physical properties of the additives and the ESR intensities obtained by use of them. This is partly due to the fact that the compounds used in the previous paper consisted of rather varied types of substances. Such complexity has been avoided in the present work by using naphthalene derivatives.

The measurement of the active sites in a catalyst by means of the "additive-ESR-method" cannot be done so simply as has been thought possible. The selection of a proper additive with known equilibrium constants, a proper temperature, and a proper atmosphere to "develop" the paramagnetic species seems to be important.

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