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A Study on Electron Spin Resonance of the Complex between Metal Ions of Group II and *o*-Quinone Anion*[1]

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An electron spin resonance study on the complex formation between *o*-quinone anion and metal ions of group II was undertaken, and the change in *g*-factor and proton hyperfine splittings of *o*-quinone anion by the complex formation were examined in detail. The change in *g*-factor was closely related to both the change in the unpaired electron distribution and the change in energy difference between lone pair orbital of oxygen and unpaired electron orbital. The stabilization of the quinone anion against its coupling reaction was seemed to be related to the shift in *g*-factor by complex formation. The interaction between quinone anion and metal ions was deduced to be partly ionic. An open shell SCF calculation with CI for the free quinone anion was carried out in order to discuss the electronic spectra of the complex.

Besides the electron spin resonance study on the complexes of paramagnetic metal ions, such study on the complex between free radicals or radical ions and diamagnetic metal ions is also efficient in the investigations into the nature of the interaction between ligands and metal ions.

It is well known that the mixture of poly-phenol and alkaline earth metal ion yields green colored complex, and this fact was applied to the qualitative analysis of these ions. During this reaction, a kind of complex between *o*-quinone anion and the metal ions is thought to be produced.

Eaton[1] studied on the effect of complex formation of *o*-quinone anion with diamagnetic ions of group II and III by the ESR spectra, and found the change in proton hyperfine splitting of the ligand, and the appearance of additional hyperfine splittings due to the nuclear magnetic moment of metal ions in the cases of Y^{3+} and La^{3+} ions.

Since *g*-factor of the ESR spectrum is closely related to the change in the lone pair orbital of oxygen atom in semiquinone anion, it is useful to examine the effects of complex formation of both *g*-factor and proton hyperfine splitting for the investigation into the nature of interaction between ligand and metal ion.

The present work was undertaken in order to examine the change in *g*-factor of *o*-quinone anion and also to reexamine the change in hyperfine splittings in detail, and to make a theoretical discussion on the nature of the interaction between ligand and metal ion.

An attempt to analyze the electronic spectra of *o*-quinone anion was made using an open-shell SCF method of Pople and Nesbet with CI. The effects of complex formation on the reactivity of *o*-quinone anion were also studied.

Experimentals

o-Benzoquinone was prepared by the oxidation of catechol.

The electron spin resonance spectra were measured using a home-made X-band spectrometer of 455-kc/sec field modulation and with a 30 cm electromagnet of

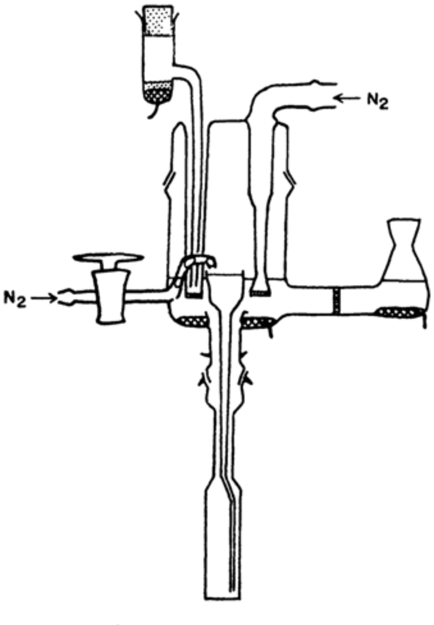

Fig. 1. The electrolytic reduction cell for the measurements of electronic absorption spectra.

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*1 This work was presented at the Fourth Symposium on Electron Spin Resonance in 1965, Nagoya.

[1] D. R. Eaton, *Inorg. Chem.*, **3**, 1268 (1964).

Japan Electron Optics Laboratory Co. The samples for ESR and UV measurements were prepared as follows. In the case of quinone anions with alkali metal ions, the radicals were prepared using a flow system at a flow rate of about 0.5 m*l*/sec. In the case of quinone anions with alkaline earth metal ions, three different methods were used: a) the flow method at a flow rate of about 3 m*l*/min, b) aerial oxidation by shaking the dilute ammonia solution of hydroquinone in contact with air, and deaeration of the solution, c) the electrolytic reduction, the cell for which is shown in Fig. 1.

The electronic absorption spectra were measured using a Hitachi spectrophotometer model EPS-2, under the same condition as that for the measurement of ESR spectra.

For magnetic field calibration, peroxylamine disulfonate was used as a reference with a dual mode (H_{014}) ESR cavity. ^{14}N hyperfine splitting constant and *g*-factor of peroxylamine disulfonate were taken to be 13.0 G and 2.00550, respectively.[2)]

Calculation of Spin Density and *g*-Factor in Quinone Anion. Hückel MO method and McLachlan's method[3)] were used for the calculation of spin density for free and complex quinone anion. In addition, the iterative simple MO method,[4)] and the open-shell SCF MO method of Pople and Nesbet[5)] with CI were used for free quinone anion.

In the iterative method, the coulomb integrals and the exchange integrals were repeatedly modified according to the values of the total charges and bond orders under the assumption that coulomb and exchange integrals were proportional to the electronegativity of the atom and to the overlap integral between atoms, respectively. The iteration was repeated until the mutual consistency of the assumed set with the calculated set was achieved.

The variation of *g*-factor in complex quinone anions was analyzed on the basis of theory given by Stone.

Writing the *n*th molecular orbital ϕ_n as linear combination of atomic orbitals, $\phi_n = \sum_k \chi_k^{(n)}$, where $\chi_k^{(n)}$ is an (un-normalized) atomic orbital on atom *k*, and using second order perturbation theory with neglecting differential overlap integral, Stone had derived the following expression for *g*-factor:[6)]

$$g_{zz} = 2.00232 + 2\sum_{n \neq p} \frac{\sum_k \langle \chi_k^{(p)} | l_{kz} | \chi_k^{(n)} \rangle \sum_{k'} \zeta_{k'} \langle \chi_{k'}^{(n)} | l_{k'z} | \chi_{k'}^{(p)} \rangle}{E_p - E_n} \tag{1}$$

where l_{kz} is the *z*-component of angular momentum about the *k*th atom, ζ_k is the spin orbit coupling constant for the *k*th atom, E_p is the energy of the odd electron orbital and E_n is the energy of the *n*th molecular orbital in the molecule.

For the case of quinone anion, Δg can be divided into three parts as follows:

$$\Delta g = g - g_e = \Delta g_{hc} + \Delta g_{co} + \Delta g_n$$

where Δg_{hc}, Δg_{co} and Δg_n are the contributions to Δg from the parts of C–C and C–H σ-orbitals of the skeleton, CO σ-orbitals, and the oxygen lone-pair orbitals, respectively.

In the present study, the iterative simple MO method and the modified extended Hückel MO method were used for π-system and for CO σ-bond, respectively. For simplicity, the bonding between SP^2 hybrid orbital of carbon atom and 2P atomic orbital of oxygen atom was taken as CO σ-bonding. With the above-mentioned orbitals, Δg was calculated using Eq. (1).

Δg_{hc} was estimated from the following equation,[6)]

$$\Delta g_{hc} = \sum_i^{\text{carbon}} \rho_i (24.7 - 19.3\Lambda) \times 10^{-5} \tag{2}$$

where Λ is the coefficient of the odd-electron orbital energy, $\alpha + \Lambda\beta$, and ρ_i is the odd-electron density on the *i*th carbon.

Δg_n could be estimated on the basis of the $n \rightarrow \pi^*$ transition process in quinone anion, so that the contribution from *i*th lone-pair orbital to Δg_n was given by the following equation, derived from Eq. (1).

$$\Delta g_n{}^i = \frac{2}{3} \frac{\langle \chi_z^{(p)} | l_y | \chi_x^{(n)} \rangle \zeta_O \langle \chi_x^{(n)} | l_y | \chi_z^{(p)} \rangle}{E_p - E_n} = \frac{2}{3} \frac{\zeta_O \rho_O}{E_p - E_n} \tag{3}$$

here, the subscripts *x*, *y* and *z* represent the *x*, *y* and *z*-components of the quantities, respectively, ρ_O is the spin density on oxygen atom and $E_p - E_n$ is the $n \rightarrow \pi^*$ transition energy.

Results

Whereas the hyperfine coupling constants in ESR spectra and the stability of *p*-benzoquinone anion were not affected by the presence of metal ions, *o*-benzoquinone anion was fairly affected under the same condition.

The alkali metal ions did not change the hf coupling constants, but slightly increased its signal intensity of the ESR spectrum. Notable effects of the presence of metal ions were seen in the case of alkaline earth metal ions. The coupling constants and *g*-factor were changed in accordance with the cation species.

Observed hyperfine splittings and *g*-factors for *o*-quinone anion are listed in Table 1, together with spin densities derived from experimental proton hyperfine splitting constants using McConnell's relationship: as, $a = Q \cdot \rho$. Here *Q* was chosen to be 23 gauss.

In addition to the primary *o*-quinone anion the spectrum which had been attributed to secondary radical was observed in methanol. The latter radical was identified with 4, 5-dimethoxy benzosemiquinone anion radical formed through the substitution of 4 and 5 position of *o*-quinone anion by methoxy groups.[1)]

The observed electronic absorption spectra of

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2) J. Q. Adams and J. R. Thomas, *J. Chem. Phys.*, **39**, 1904 (1964).

3) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

4) Y. Kurita and M. Kubo, This Bulletin, **24**, 13 (1951); S. Nagakura, *ibid.*, **25**, 164 (1952); S. Nagakura and T. Hosoya, *ibid.*, **25**, 179 (1952).

5) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).

6) A. J. Stone, *Mol. Phys.*, **6**, 509 (1963).

TABLE 1. OBSERVED HYPERFINE SPLITTINGS AND g-FACTORS, TOGETHER WITH SPIN DENSITIES DERIVED FROM EXPERIMENTAL PROTON HF-SPLITTING CONSTANTS BY USING MCCONNELL'S RELATIONSHIP

Counter ion	Solvent	a_3 (gauss)	a_4 (gauss)	ρ_3	ρ_4	g-Factor
NH_4^+	H_2O	0.76	3.77	0.033	0.164	2.00467
Mg^{2+}	H_2O	0.53	4.03	0.023	0.175	2.00423
Ca^{2+}	H_2O	0.66	3.89	0.029	0.169	2.00433
Sr^{2+}	H_2O	0.70	3.82	0.030	0.166	2.00435
Ba^{2+}	H_2O	0.73	3.85	0.032	0.167	2.00400
Zn^{2+}	H_2O	0.49	3.98	0.021	0.173	2.00389
Cd^{2+}	H_2O	0.53	3.93	0.023	0.171	2.00347
Mg^{2+}	DMSO	0.90	3.83	0.039	0.167	2.00442
Ca^{2+}	DMSO	1.03	3.76	0.045	0.163	2.00447
Sr^{2+}	DMSO	1.07	3.67	0.046	0.160	2.00430
Ba^{2+}	DMSO	1.15	3.62	0.050	0.157	2.00386
Zn^{2+}	DMSO	0.77	3.78	0.033	0.164	2.00412

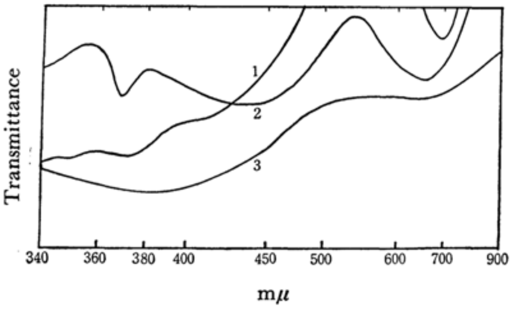

Fig. 2. The electronic absorption spectra of quinone anions.
(1) quinone anion with Mg^{2+} in DMSO
(2) quinone anion with Mg^{2+} in acetonitrile
(3) free quinone anion in acetonitrile

complex radical using an electrolytic reduction are shown in Fig. 2. Three peaks at 370—380 mμ (I), 400—440 mμ (II) and 650—700 mμ (III) were assigned to the complex o-quinone anion radical.

The contour plots of spin densities calculated varying the coulomb integral of oxygen in Hückel MO method and McLachlan's method are shown in Fig. 3.

The spin densities and the odd-electron orbital energy of quinone anion calculated by the iterative simple MO method were as follows.

$$\rho_1 = 0.173,\ \rho_3 = 0.018,\ \rho_4 = 0.104,\ \rho_7 = 0.205,$$
$$\text{and}\quad E_p = \alpha + 0.574\beta. \qquad \beta = -2.39\ \text{eV}$$

The unrestricted SCF calculation was carried out until the spin densities became mutually consistent to three decimal places, and the result is shown diagrammatically in Fig. 5, together with the experimental values.

The bonding and antibonding orbitals of a C–O σ-bond were obtained: as,

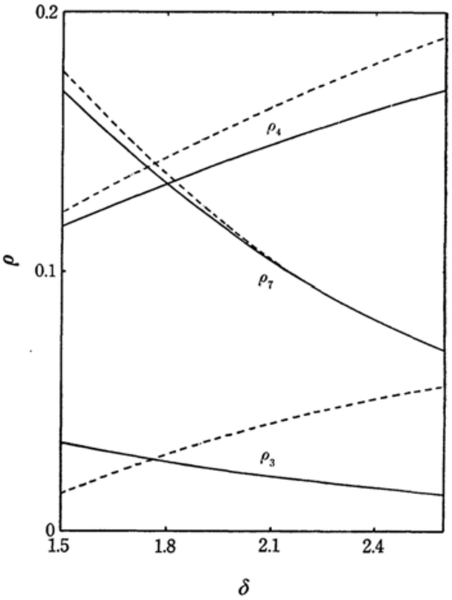

Fig. 3. The contour plots of calculated spin densities.
—— by Hückel MO, ---- by McLachlan's method, in which λ was taken to be 1.2. The axis of abscissa represents δ in coulomb integral $\alpha_O = \alpha + \delta\beta$.

$$\phi^b{}_{CO} = 0.549\chi_{sp^2} + 0.708\chi_p \quad E^b{}_{CO} = -22.46\ \text{eV}$$
$$\phi^a{}_{CO} = 0.851\chi_{sp^2} - 0.783\chi_p \quad E^a{}_{CO} = 2.46\ \text{eV}$$

Accordingly, Δg_{hc} and Δg_{co} for the free quinone anion were estimated to be 3.3×10^{-5}, -41.1×10^{-5}, respectively. In aqueous solution, g-factor of the free quinone anion was 2.00467, so that to have such value, the contribution from the lone-pair orbitals, Δg_n should be 273×10^{-5}, and the absorption band for $n\rightarrow\pi^*$ transition was estimated to be at $ca.$ 662 mμ using Eq. (3).

Discussion

Hyperfine Coupling Constants of the Complex Radical. As shown in Table 1, hyperfine coupling constants for the ring protons at ortho position decreased as those of meta position increased. The contour plots of calculated spin densities using Hückel MO treatment showed that ρ_4 increased as the δ increased whereas the spin density ρ_3 (at position 3) decreased. Here δ denotes the coefficient of coulomb integral of oxygen atom, $\alpha_O = \alpha + \delta\beta$. This tendency was consistent with that of the change in experimental spin density, accordingly the effect of chelation on the spin density seemed to be equivalent to the value of coulomb integral of oxygen atom where assuming it to be more negative.

Fraenkel *et al.*,[7] showed that McLachlan's method led to an excellent agreement between the observed proton hyperfine splittings and the calculated ones for free *o*-quinone anion, where $\lambda = 1.2$, $\alpha_O = \alpha_B + 2.1\beta$ and $\beta_{CO} = \beta_{CC}$ were taken as molecular parameters. And in their calculation, while ρ_4 was positive, ρ_3 was negative.

As shown in Fig. 3, McLachlan's method, however, led to such result that not only ρ_4 but also the absolute value of ρ_3 (in this case, ρ_3 was negative) increased as the δ increased. Thus the McLachlan's method was seemingly unsuitable to analyze the experimental result. The present result possibly showed that ρ_3 and ρ_4 were both positive.

In general, spin polarization has a tendency to enhance the spin density at the position where high spin density would be expected by Hückel MO calculation, while it would diminish the spin density at the position where low spin density would be expected by Hückel MO calculation. In fact such tendency was observed so far as ρ_3 and ρ_4 were concerned.

The semiempirical parameter λ in McLachlan's method controls the amount of spin polarization in the radical. If λ is taken to be less than 0.3, the effect of spin polarization still remains small, both ρ_3 and ρ_4 remain positive in the case of δ value less than 2.3 and the tendency of decrease in a_3 and increase in a_4 as δ increases is evident. The turning point of spin density ρ_3 from positive to negative depends on not only λ but δ, *e. g.*, with $\lambda = 0.5$, the turning point was at $\delta = 1.9$.

On varying the counter ions in the sequence of NH_4^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, ρ_3 decreased, whereas ρ_4 increased. The observed values of ρ_3 and ρ_4 correlated smoothly with electronegativity of the metal atom as shown in Fig. 4, or in other expression the coulomb integral of oxygen in the complex quinone anion seemed to correlate to the electronegativity of metal ion changed. It is noted here that this sequence agreed with the sequence of the stability of the complex quinone anion in solution. This is discussed again in later section.

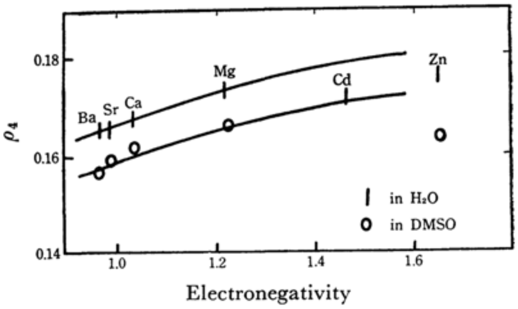

Fig. 4. The relationship between the observed spin density on position 4 and the Pauling's electronegativity of metal atom.

As to the solvent effects, a fact that the complex radical was more stable in DMSO than in water was found. And this was understood by the difference in electrostatic interactions as follows. The dielectric constant of water is larger than that of DMSO, thus in water the radical ion has weaker interaction with metal ion, or the dissociation constant of the complex should be larger than in DMSO. The difference in electrostatic interaction could also relate to the difference in the amount of increase in δ. Figure 4 shows that the oxygen atom had larger value of δ in water than in DMSO, or in other word, in the solvent of larger dielectric constant the value of δ became larger.

***g*-Factor of Complex Radical.** The solvent effect on *g*-factor of diphenyl nitric oxide has been treated as a perturbation of increase in coulomb integral of the oxygen atom through the hydrogen-bonding between solute and solvent.[8] On the other hand, in the present case the addition of metal ion to the oxygen atoms of quinone anion made the coulomb integral of oxygen atom more negative and thus affected on *g*-factor of the anion. Although both the lone pair orbitals of oxygen atom and C–O σ-bond would be likely affected, as the first step of approximation, an assumption that σ-system remains unchanged in the complexes was made. Then the effect of complex formation on *g*-factor could be regarded as a perturbation only on π-electron system. The effect of a change in α_o on the spin density on the rth atom ρ_r, the odd-electron orbital bond order between rth and sth atoms P_{rs} and the odd-electron orbital energy E_p will be expressed using atom-atom polarizability as follows.

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[7] G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961); G. Vincow, *ibid.*, **38**, 917 (1963).

[8] T. Kawamura, S. Matsunami, T. Yonezawa and K. Fukui, This Bulletin, **38**, 1935 (1965).

TABLE 2. g-FACTORS FOR COMPLEX QUINONE ANIONS

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Zn^{2+}	Cd^{2+}	NH_4^+
$g_{obs.}$	2.00423	2.00433	2.00435	2.00400	2.00389	2.00347	2.00467
$g_{calc.}$	2.00416	2.00448	2.00454	2.00461	2.00408	2.00420	2.00467
$(g_{obs.}-g_{calc.})\times 10^{+5}$	7	−15	−19	−61	−19	−73	−0

With the molecular orbital calculated by the interative method, these quantities are as follows.

$$\left.\begin{aligned}
\delta E_p &= \rho_7\delta\alpha_7 + \rho_8\delta\alpha_8 = 0.4096\times\delta\alpha_O \\
\delta\rho_1 &= \pi^p{}_{1,7}\delta\alpha_7 + \pi^p{}_{1,8}\delta\alpha_8 = 0.1376\times\delta\alpha_O/\beta \\
\delta\rho_3 &= \pi^p{}_{3,7}\delta\alpha_7 + \pi^p{}_{3,8}\delta\alpha_8 = -0.0184\times\delta\alpha_O/\beta \\
\delta\rho_4 &= \pi^p{}_{4,7}\delta\alpha_7 + \pi^p{}_{4,8}\delta\alpha_8 = 0.0936\times\delta\alpha_O/\beta \\
\delta\rho_7 &= \pi^p{}_{7,7}\delta\alpha_7 + \pi^p{}_{7,8}\delta\alpha_8 = -0.2128\times\delta\alpha_O/\beta \\
\delta P_{17} &= \pi^p{}_{17,7}\delta\alpha_7 + \pi^p{}_{18,8}\delta\alpha_8 = 0.0224\times\delta\alpha_O/\beta
\end{aligned}\right\} \quad (4)$$

Here, the same notation as that in the reference was used.[8)]

The effect of complex formation on g-factor could be divided into three parts as mentioned in the preceding section, that is to say, $\delta\Delta g_{hc}$, $\delta\Delta g_{co}$ and $\delta\Delta g_n$, which could be expressed by the amount of change in α_O.

$$\left.\begin{aligned}
\delta\Delta g_{hc} &= 1.1\times 10^{-5}\times\delta\alpha_O/\beta \\
\delta\Delta g_{co} &= 9.3\times 10^{-5}\times\delta\alpha_O/\beta
\end{aligned}\right\} \quad (5)$$

$$\begin{aligned}
\delta\Delta g_n &= \frac{4}{3}\frac{\zeta_O(\rho_O+\delta\rho_O)}{E_p+\delta E_p-E_n} - \frac{4}{3}\frac{\zeta_O\rho_O}{E_p-E_n} \\
&= -140.7\times 10^{-5}\times\delta\alpha_O/\beta \\
&\quad -72.9\times 10^{-5}\times(\delta\alpha_O/\beta)^2
\end{aligned}$$

Using Eq. (4), the increase in coulomb integral of oxygen atom could be estimated by the deviation of observed hyperfine coupling constants for complex quinone from that for free quinone anion, thus the change in $\delta\Delta g$ was calculated using Eq. (5). Calculated values of g-factor are listed in Table 2 together with observed ones.

As seen in Table 2, a trial to explain the variation of g-factor of complex quinone anion by considering only about the change in π-system was not necessarily carried out successfully. In the cases of Ba^{2+} and Cd^{2+} there was fairly large disagreement between $g_{cal.}$ and $g_{obs.}$, so that it seemed necessary to consider some additional contributions coming from the change in σ-system.

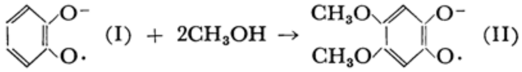
The contributions from Δg_{hc} and Δg_{co} were estimated to be 3.3×10^{-5} and -41.1×10^{-5}, respectively, and these values are so small that they can be disregarded as compared with Δg_n: the contribution from lone pair orbital.

If the addition of metal ion to oxygen atoms of quinone anion stabilizes lone pair orbital energies of oxygen atoms, the difference between lone pair orbital energy and unpaired electron orbital energy will be enhanced and as a result, the estimated value of g-factor will decrease as expected from Eq. (3). Therefore, it may be reasonable to take the difference between the observed value and the calculated one of g-factor in Table 2 as the measure of stabilization in lone pair orbital energy of oxygen atom.

The quantity, $g_{obs.}-g_{calc.}$, increased with the stabilization of E_n, so that in this study among the ions of IIa and IIb group elements, the stabilization of lone pair orbital energy was found to increase in the order of $Ba^{2+}>Sr^{2+}>Ca^{2+}>Mg^{2+}$ and $Cd^{2+}>Zn^{2+}$, respectively.

As a conclusion, following mechanisms of the variation of g-factor were approved. The change in distribution of unpaired electron in complex quinone anion coming from the increase in coulomb integral of oxygen is partly the origin of the variation of g-factor, and the change in energy difference between lone pair orbital of oxygen and unpaired electron orbital is also responsible for the variation of g-factor.

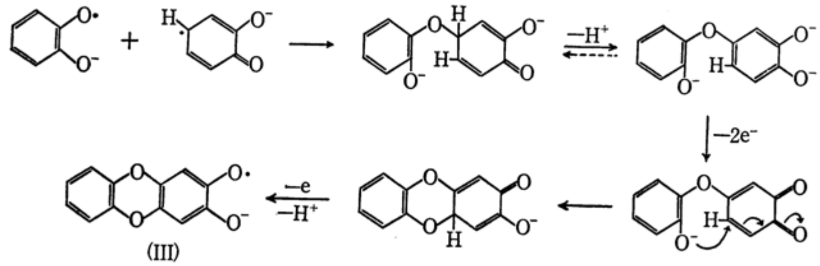
Reactivity and Structure of Complex Quinone Anion. Using the alkaline methanol as a solvent for o-quinone anion-metal ion system, the spectrum for a secondary radical superimposing on that of primary radical was observed and the secondary radical had been identified as a methoxylated radical (II). This secondary radical was formed by a reaction of primary radical (I) with methanol[1)] in the presence of metal ions as catalyst.



It was shown in Hückel MO treatment that the complex formation brought about the increase in unpaired electron density at position 4 and 5, and also the decrease in total π-electron density at these positions. As a result, the increase in unpaired electron density would make the radical reaction favorable at these positions, and the decrease in total π-electron density would make the negatively charged species more easily to attack at these position too.

The nature of the attacking species was not known at the present stage of experiment, however, it may be suggested that the attacking species is radical or has neagtive charge.

On the other hand, in the absence of metal ions, when the spectrum of o-quinone anion in alkaline solution was recorded, the gradual appearance of a triplet spectrum superimposed on the center of original spectrum was observed. This triplet



(III)

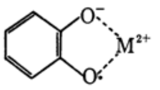
spectrum was assigned to dibenzo-1,4-dioxin-2,3-quinone anion (III) which was formed through dimerization of *o*-quinone anion.[9]

In this study, however, dimer anion was not observed in the presence of alkaline earth metals. This is probably due to the restriction against dimerization reaction for the complex quinone anion, since oxygen atoms in the complex anion are hindered by a metal ion and are prevented to react with another anion. Upon the addition of various metal ions, the stability of complexed anion against such dimerization reaction increased as the ability of enhancing δ in the coulomb integral of oxygen increased, thus the interaction between oxygen atoms of quinone anion and metal ion played an important role in the selectivity of reaction.

The hyperfine splitting due to the metal nuclei had been observed,[1] and this shows confirmatively that metal ion has an interaction with *o*-quinone anion and the unpaired electron flows into the metal ion, but this amount is estimated to be very small.

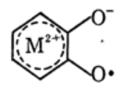
For the complex quinone anion, following two structures are possible. a) Metal ion is in the plane of benzene ring and attaches to two oxygen atoms of the quinone anion. b) Metal ion is located above the benzene ring and interacts with whole of the π-electrons of benzene ring.

(a)



(IV)

(b)



(V)

In the latter case, the metal ion makes coulomb integrals of all carbon atoms more negative, and this is equivalent to the decrease in δ in coulomb integral of oxygen atoms, and this effect does not agree with experiment, or it will give the wrong tendency in the variation of unpaired electron distribution. Thus, it could be suggested that the *o*-quinone anion-metal complex takes the structure of the former case (a).

Energy Levels of *o*-Quinone Anion. The studies on the electronic spectra of *o*-benzoquinone were reported already,[10] and such an approximate information about the energy levels of the anion tha one or two absorption bands seemingly appear in the wavelength region of 500—800 mμ was derived.

For the detailed discussion on the electronic state of the anion, a calculation based on unrestricted SCF-MO method (UHF) was performed, and three absorption bands in visible region were expected. The energies of the allowed transitions and the oscillator strengths for those transitions are shown in Fig. 5.

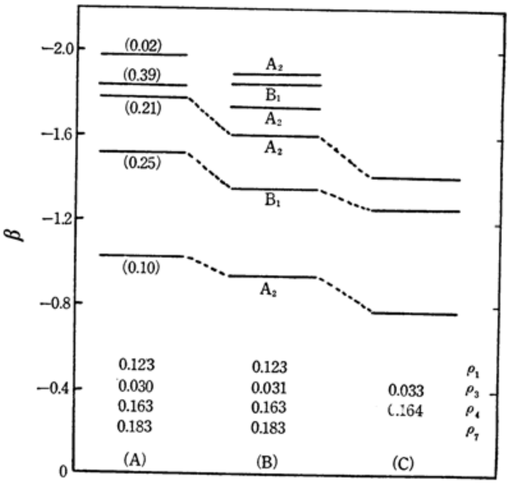


Fig. 5. The spin density and the excitation energy of free quinone anion. (A) by open shell SCFMO (B) by open shell SCFMO-CI. (C) observed values. The numerals in the parentheses indicate the calculated oscillator strengthes.

While the experimental value of oscillator strength could not be determined because of the difficulty in determination of the concentration of the anion, the relative intensities of observed spectra were compared with the calculated oscillator strength, and three observed absorption bands at 370—380 mμ, 400—440 mμ, and 650—760 mμ were assigned to $\pi \rightarrow \pi^*$ transitions.

Figure 5 also shows the result obtained by considering on configuration interaction among twenty

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[9] F. R. Hewgill, T. J. Stone and W. A. Waters, *J. Chem. Soc.*, **1964**, 408.

[10] S. Nagakura and A. Kuboyama, *J. Am. Chem. Soc.*, **76**, 1003 (1954); A. Kuboyama and K. Wada, This Bulletin, **38**, 1709 (1965).

low lying excited doublet states. Since the wave function obtained here was not true eigenfunction of $S=1/2$ state, we should use the annihilation operator and remove the components of higher spin states. The wave function obtained after applying annihilation operator, however, does not satisfy the condition of energy minimum, on the contrary. Even if the higher spin states are excluded, the drastic change of spin density distribution will not be expected because those states are lying in high energy states and the effect from those states will be small. For that reason, only single determinant wave function was used at the starting point. In this CI calculation, we also made an approximation, in which the singly excited states had the same form as those in closed-shell SCF-MO.

In open-shell SCF-MO, electron correlation is already partly included so that the configuration interaction in UHF has different significance from that in restricted HF.

In this study, the result that the configuration interaction scarcely affected on the spin density, whereas it considerably affected on the transition energy was also shown.

The weak absorption band for $n \rightarrow \pi^*$ transition, the energy of which estimated to be approximately 1.8—3.7 eV from the observed values of g-factor using Eq. (3), might be masked by the strong π-π^* transition bands in this region.

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Appendix

An Unrestricted SCF MO-CI Calculation of *o*-Quinone Anion. In the closed shell Hartree-Fock wave function, the repulsion between electrons is not accounted for properly because electrons affect each other through their instaneous potentials, not just by their average potentials. The antisymmetry of the wave function itself acts as if there would be a rather strong repulsion between particles with the same spin at small distances, but further correlative effects associated with particles having different spins cannot be treated properly.

On the other hand, in the open shell SCF MO, the orbitals associated with different spins will automatically try to arrange themselves in such a way that particles having antiparallel spins will tend to avoid each other due to their mutual repulsion.

In the present study, the unrestricted Hartree-Fock method (UHF) of Pople and Nesbest was used for free *o*-quinone anion. The ground state wave function was described by:

$$\Psi_g = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_n\bar{\phi}_n\phi_{n+1}| \tag{6}$$

where $N(=2n+1)$ is the number of π-electrons. The molecular orbitals given by the linear combination of atomic orbitals were chosen to minimize the electronic energy.

$$E=\sum_i^{\alpha+\beta} H_i+\frac{1}{2}\sum_i^{\alpha+\beta}\sum_j^{\alpha+\beta} J_{ij}-\frac{1}{2}\Big(\sum_i^{\alpha}\sum_j^{\alpha}+\sum_i^{\beta}\sum_j^{\beta}\Big)K_{ij}$$

In the calculation of H_i, J_{ij} and K_{ij}, the coulomb repulsion integrals, $(\mu\mu|\mu\mu)$ and $(\mu\mu|\nu\nu)$, and the core integrals, α and β were evaluated by the semiempirical procedure analogous to that of Pariser and Parr.[11)]

The core integrals were calculated from the next equations:

$$\alpha_\mu = -w_\mu - \sum_{\mu\neq\nu}(\mu\mu|\nu\nu)$$

$$\beta_{\mathrm{CC}} = -\frac{17.464}{r^6{}_{\mathrm{CC}}}\mathrm{eV}, \quad \beta_{\mathrm{CO}} = -\frac{8.8086}{r^6{}_{\mathrm{CO}}}\mathrm{eV}^{12)}$$

where w_μ and $(\mu\mu|\nu\nu)$ were the valence state ionization potential and the coulomb repulsion integral under the neutral electron distribution.

It was assumed that the free *o*-quinone anion was planer and that the ring part and r_{CO} of the radical had the same molecular dimension as that of benzene and 1.23Å, respectively. The one-center coulomb repulsion integral $(\mu\mu|\mu\mu)$ and the two-center coulomb repulsion integral $(\mu\mu|\nu\nu)$ were evaluated from the same procedure as that in Harada's paper.[13)]

The best result of calculation, in which core integrals were calculated assuming that each atom of the molecule was neutral but repulsion integral was modified by the result of the iterative simple MO method, is given in Fig. 5.

The configuration interaction between the ground state and the singly excited states in the same spin state as the ground state was considered.

The singly excited states were represented by Slater determinants of the form under our approximation.

$$\left.\begin{aligned}
\psi^{(\mathrm{I})}_{i\to k} &= |\cdots\phi_i\phi_k\phi_0|(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)/\sqrt{6}\\
\psi^{(\mathrm{II})}_{i\to k} &= |\cdots\phi_i\phi_k\phi_0|(\alpha\beta\alpha-\beta\alpha\alpha)/\sqrt{2}\\
\psi_{i\to o} &= |\cdots\phi_i\phi_0\bar{\phi}_0|\\
\psi_{o\to l} &= |\cdots\phi_i\bar{\phi}_i\phi_l|
\end{aligned}\right\} \tag{7}$$

The electronic ground state function was approximated by a linear combination of doublet functions, (6) and (7).

$$\Phi = \sum_i A_i\psi_i$$

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