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The Oxygenation-deoxygenation of Cobalt(II) Complexes on Polymers

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Three cobalt(II) complexes, bis-(salicylaldehyde)-ethylenediimine-cobalt(II), bis-(salicylaldimino)cobalt(II), and di-(salicylal)-3,3′-diimino-di-*n*-propylamine-cobalt(II), were mixed with poly-4-vinylpyridine. These mixtures showed ESR signals which reversively appeared under oxygen. We tried to identify these signals on the basis of the electonic structure, cobalt(III)-O_2^{-1}. The oxygenation-deoxygenation rates were also observed and found to obey the Elovich rate equation.

Many oxygen-carrier cobalt(II) chelates have been investigated,[1] of these, bis-(salicylaldehyde)-imine-cobalt(II) complexes have long been investigated, especially by Calvin *et al.*[2,3] These complexes, however, do not seem to have been studied from the viewpoint of technological designs for producing solid-state oxidizing catalysts from them.

It is known that the paramagnetic bis-(salicylaldehyde)-ethylenediimine-cobalt(II) yields a diamagnetic-oxygenated complex ($Co/O_2=2/1$).[3] The present authors found that an ESR signal appeared when a mixture of this chelate and poly-4-vinylpyridine (PVP) was exposed to oxygen; on the other hand, the signal disappeared when the mixture was placed in a vacuum. Several cycles were successfully tried; they have already been reported briefly.[4]

The paramagnetic species in mixtures of a cobalt(II) chelate with a polymer have been identified, and also the properties of oxygenation-deoxygenation rates have been investigated in this study. The chelates which have been tried successfully are: bis-(salicylaldimino)cobalt(II) (Complex B-1 and Complex B-2; the abbreviations are explained in the Experimental part), and di-(salicylal)-3,3-diimino-di-*n*-propylamine-cobalt(II) (Complex C), as well as the above bis-(salicylaldehyde)-ethylenediimine-cobalt(II) (Complex A).

Results

The four mixtures, Complex A-PVP, Complex B-1-PVP, Complex B-2-PVP, and Complex C-PVP, each showed an ESR signal which appeared (or

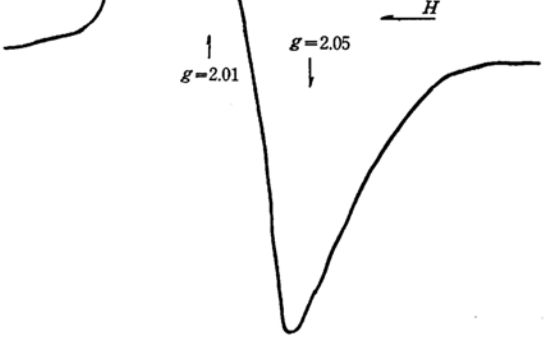

Fig. 1. The ESR signal on A-PVP with O_2. $P_{O_2}=1$ atm, Co/pyridine ring = 1/100, at room temp.

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1) L. H. Vogt, Jr., *Chem. Revs.*, **63**, 269 (1963).

2) A. E. Martell and M. Calvin, "The Chemistry of the Metal Chelate Compounds," Prentice Hall, N. Y. (1956), p. 337.

3) M. Calvin, R. H. Bailes and W. K. Wilmarth, *J. Am. Chem. Soc.*, **68**, 2254 (1946).

4) A. Misono, S. Koda and Y. Uchida, This Bulletin, **42**, 580 (1969).

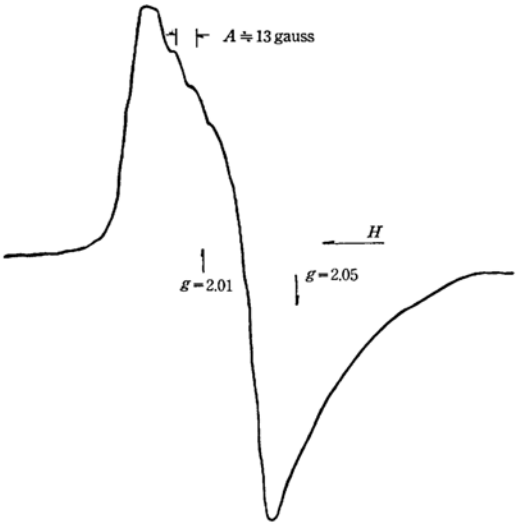

Fig. 2. The ESR signal on B-2-PVP with O_2. P_{air} = 494 mmHg, Co/pyridine ring = 1/90, at room temp.

increased) under oxygen (or air) and disappeared (or decreased) *in vacuo*. The ESR signals are shown with their approximate *g* and *A* values in Figs. 1—3. (These *g* values were roughly estimated so as to explain the signal shapes (and are, therefore, not very accurate) according to the method for randomly-oriented particles in a fixed position.[5] The *A* values were approximate intervals (in gauss) between two appropriate hfs signal peaks). The PVP itself and the mixture of cobalt(II) acetylacetone with PVP showed no corresponding ESR signal, even under oxygen.

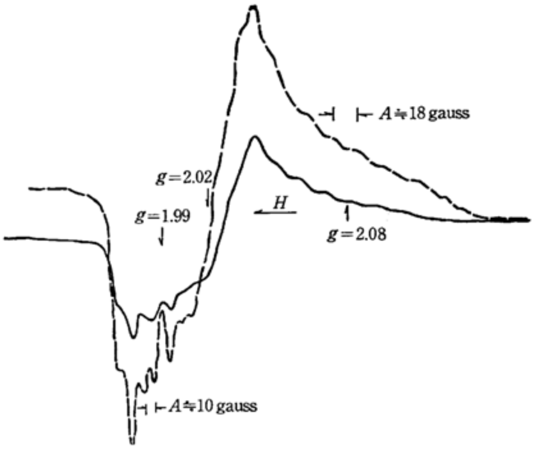

Fig. 3. The ESR signal on C-PVP with O_2. P_{air} = 1 atm, Co/pyridine ring = 1/160, at room temp. (——) and at −130°C (– – –)

Polyacrylonitrile was also tried as a chelate-carrier instead of PVP, but the chelates could not be successfully carried on the polymer by any means tried.

The ESR signal shapes (investigated in the case of A-PVP) were almost independent of the temperature over the range from about 40 to −140°C. The signal in the case of the Complex C became a little sharper at a lower temperature.

The shape was almost independent of the oxygen pressure over the range from 1 atom to several mmHg (investigated in the case of A-PVP) and also of the relative mole ratio of cobalt(II) *vs.* the pyridine ring in the polymer over the range from 1/20 to 1/400 (investigated in the case of B-2-PVP).

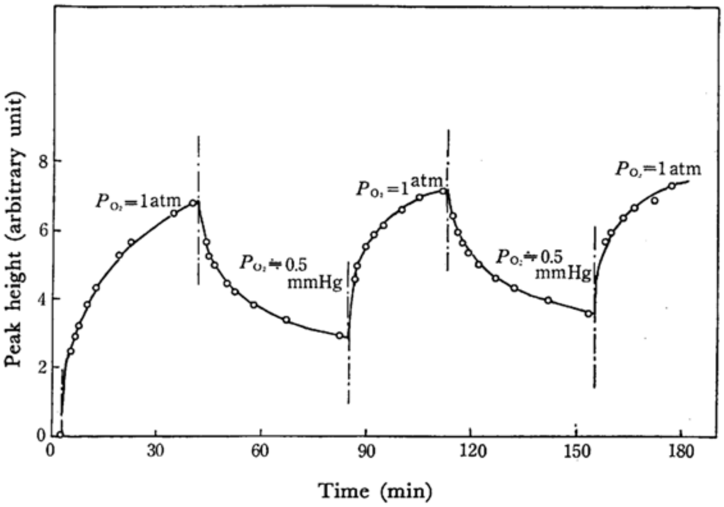

Fig. 4. Oxygenation-deoxygenation cycle (for A-PVP). Co/pyridine ring = 1/110, at room temp.

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[5] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

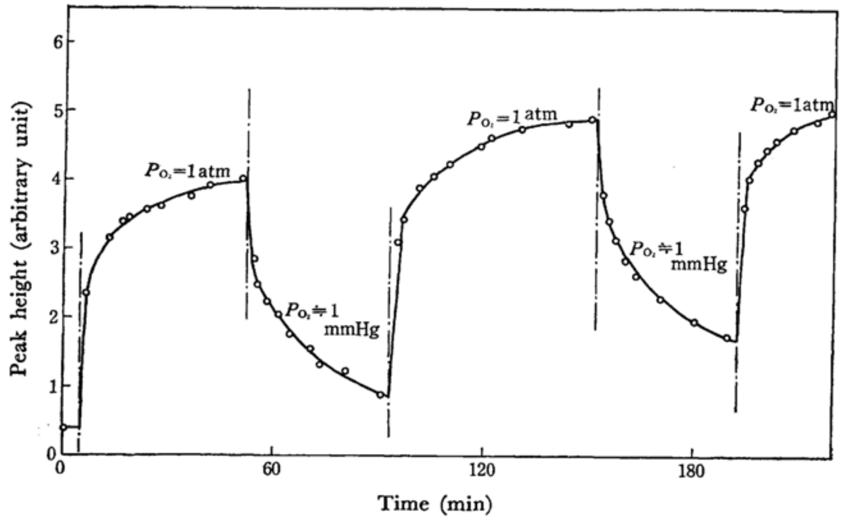

Fig. 5. Oxygenation-deoxygenation cycle (for B-1-PVP). Co/pyridine ring=1/50 at room temp.

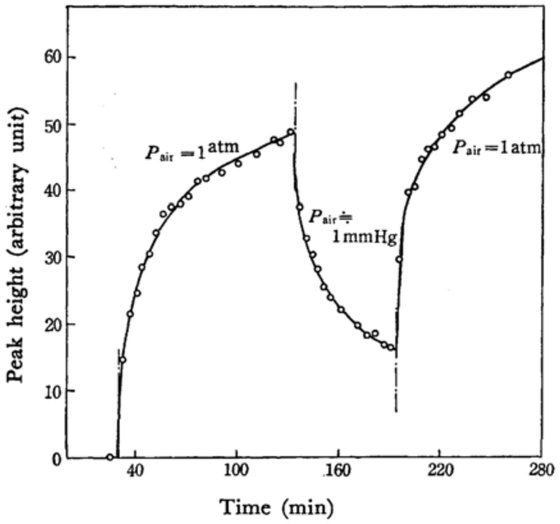

Fig. 6. Oxygenation-deoxygenation cycle (for C-PVP). Co-pyridine ring = 1/160, at room temp.

The changes in the relative strength of the ESR signal (which was considered to be proportional to the amounts of the corresponding paramagnetic species, as will be explained in the Experimental part) upon the introduction and exhaustion of oxygen (or air) are illustrated in Fig. 4 (for A-PVP), in Fig. 5 (for B-1-PVP), and in Fig. 6 (for C-PVP).

The rate of the increase and decrease of the signal strength seems to obey the Elovich rate equation (Figs. 7—9); that is,

increasing:

$$\log(t + t_0) = av - b$$

decreasing:

$$\log(t + t_0) = cv + d$$

t_0, a, b, c, d: constants independent of the contact time

v: signal strength

t: contact time

The signal strength is not proportional to $t^{1/2}$. Here, the strength proportionate to $t^{1/2}$ can be expected at an earlier stage if the rate is determined by gas diffusion through a polymer film.[6] Moreover, the first derivative of the signal strength against the contact time (Fig. 10) sufficiently obeyed the equation derived from the above Elovich equation:

$$dv/dt = Ae^{-Bv}$$

$$A = e^{2.303b}/2.303a$$

$$B = 2.303a$$

Moreover, it did not follow the equation:

$$dv/dt = k(v_e - v) \qquad k,\ v_e: \text{constants}$$

This equation can be expected to hold in the case of Langmuir adsorption,[7] and also at a later stage when the adsorption is determined by gas diffusion through a polymer film.[6]

The constants, a, b, c, and d, seemed, however, not to be independent of the previous history of the mixture (*cf.* Table 1). Above all, the enlargement of the b values agrees with the observation that the oxygenation rate increases with the repetition of the oxygenation-deoxygenation.

The relative signal strength changed easily with the temperature (Fig. 11). The signal strength seemed to decrease more rapidly with the rise in

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[6] Y. Wada (editor), "Kobunshi no Bussei Kogaku," Ohm Co., Tokyo (1967), p. 255.

[7] T. Keii, "Kyuchaku," Kyoritsu Shuppan Co., Tokyo (1965), p. 50.

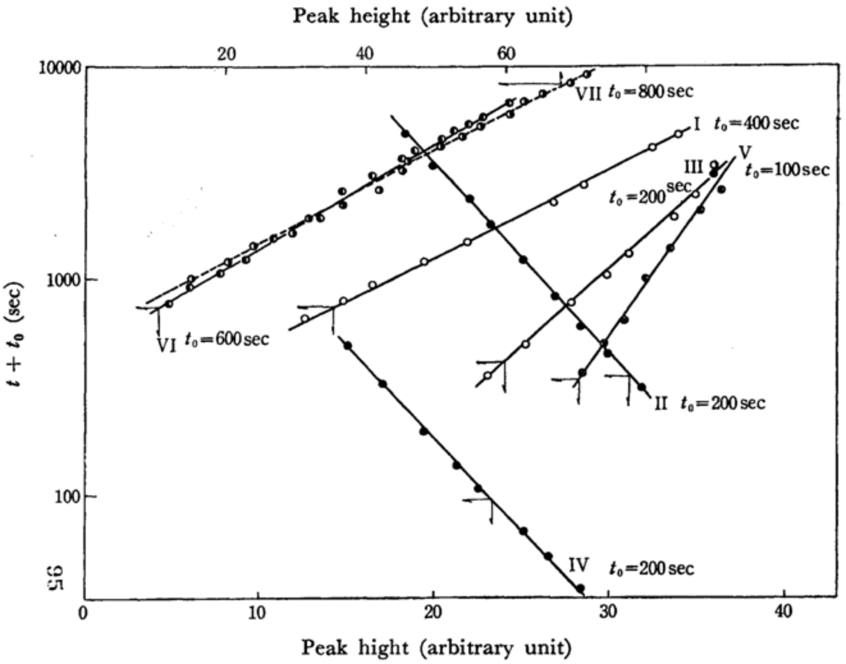

Fig. 7. Elovich plot (for A-PVP).
From the data of Fig. 4 for I—V, Co/pyridine ring=1/110, at room temp.
I, III, V: the first, second and third oxygenation stage, respectively, $P_{O_2}=1$ atm
II, IV: the first and second deoxygenation stage, respectively, $P_{O_2}\fallingdotseq 0.5$ mmHg
VI: Co/pyridine ring=1/90, at room temp., the first oxygenation stage, $P_{air}=60$ mmHg
VII: Co/pyridine ring=1/50, at room temp., the first oxygenation stage, $P_{air}=1$ atm

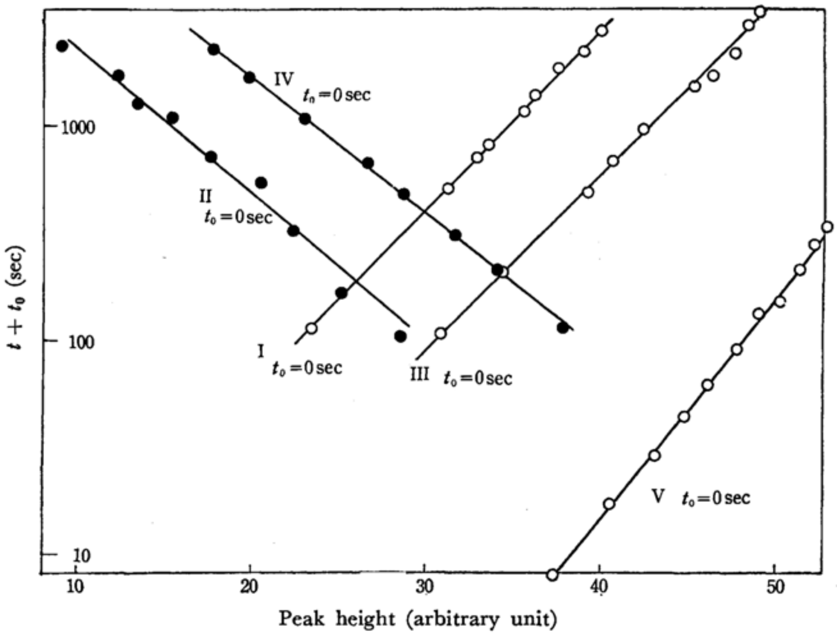

Fig. 8. Elovich plot (for B-1-PVP).
From the data of Fig. 5; Co/pyridine ring=1/50, at room temp.
I, III, V: the first, second and third oxygenation stage, respectively, $P_{O_2}=1$ atm
II, IV: the first and second deoxygenation stage, respectively, $P_{O_2}=1$ mmHg

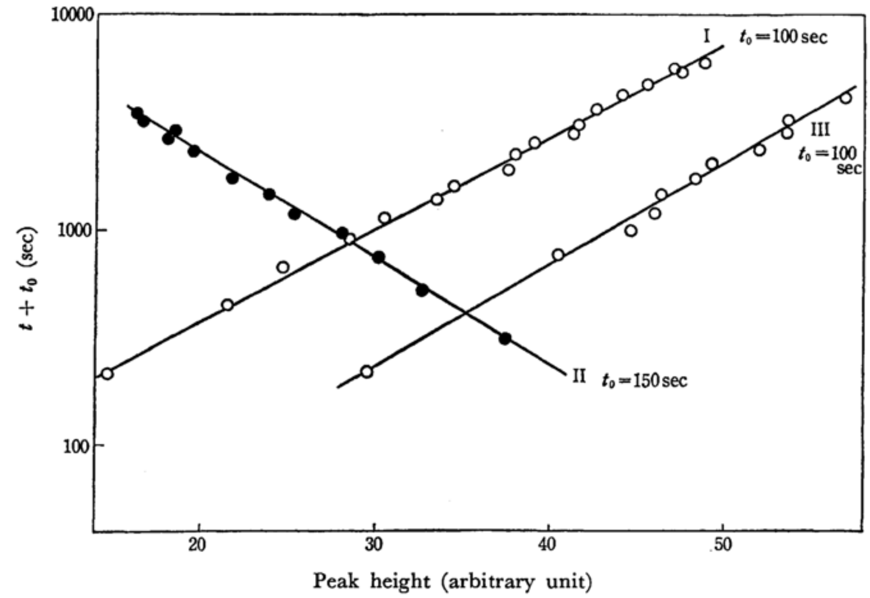

Fig. 9. Elovich plot (for C-PVP).
From the data of Fig. 6; Co/pyridine ring=1/160, at room temp.
I: the first oxygenation stage, $P_{\mathrm{air}}=1$ atm
II: the first deoxygenation stage, $P_{\mathrm{air}} \fallingdotseq 1$ mmHg
III: the second oxygenation stage, $P_{\mathrm{air}}=1$ atm

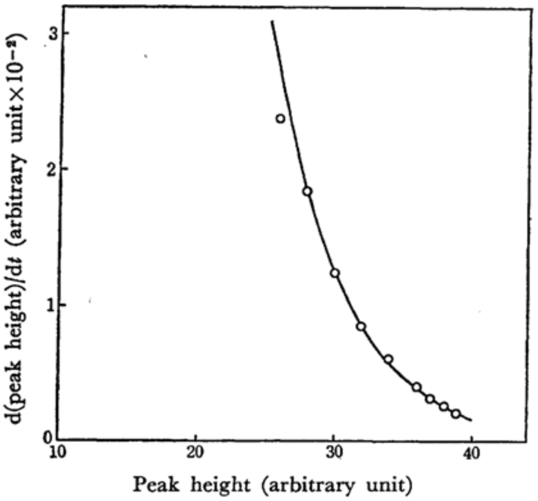

Fig. 10. The relation between the peak height and the first derivative of the peak height against contact time.
This example is the first oxygenation stage of B-1-PVP; the full line is calculated by the equation $\log(t+t_0)=av-b$, where, $t_0=0$, $a=0.085$, $b=-0.055$; the particles are observed values.

the temperature than can be expected when the signal strength fits the Curie law (the ESR strength of a paramagnetic ion $\propto 1/T$). This perhaps indicates that the equilibrium is more declined to the dissociated state at higher temperatures.

Discussion

The ESR signals, shown in Figs. 1—3, can be considered for the following reasons to be caused by a 1 : 1 adduct of molecular oxygen with the cobalt complex. The signals are observed only when the cobalt complexes on PVP are exposed to oxygen. Even if a 1 : 2 adduct ($Co/O_2=2/1$) of molecular oxygen with the chelate is made, the adduct may be diamagnetic. In fact, bis-(salicylaldehyde)-ethylenediimine-cobalt(II) (which is paramagnetic) forms a 1 : 2 oxygen adduct which is diamagnetic, and di-(salicylal)-3,3′-diimino-di-*n*-propylamine-cobalt(II) (which is paramagnetic) forms a 1 : 1 oxygen adduct which is paramagnetic, in the solid state.[2] Apparently a 1 : 2 adduct can be identified as $Co(III)$-O_2^{-2} -$Co(III)$ which has no free spin, while a 1 : 1 adduct can be schematically considered to be $Co(III)$-O_2^{-1} or $Co(II)$-O_2, and therefore paramagnetic (one unpaired electron).

All three ESR signals can be explained as apparently caused by a paramagnetic species which has three different *g* values (one *g* value is larger than the other two *g* values, which are almost equal to each other). The hyperfine structures were found only on the high-magnetic-field side in the cases of A-PVP and B-PVP. In the signal for C-PVP, the hf structures were a little clearer. The hf structures can be considered to be caused by the mononucleus cobalt atom ($I=7/2$). Only a few lines appeared, although eight lines were expected.

Table 1. The constants of Elovich equations

		a	*b*	*c*	*d*	t_0 (sec)
A-PVP	I	0.041	−2.291			400
	II			−0.086	4.984	200
	III	0.071	−0.914			200
	IV			−0.089	5.335	200
	V	0.110	+0.541			100
B-1-PVP	I	0.085	−0.055			∼0
	II			−0.071	4.052	∼0
	III	0.083	+0.548			∼0
	IV			−0.064	4.483	∼0
	V	0.106	+3.081			∼0
C-PVP	I	0.043	−1.706			400
	II			−0.050	0.601	150
	III	0.048	−0.917			100

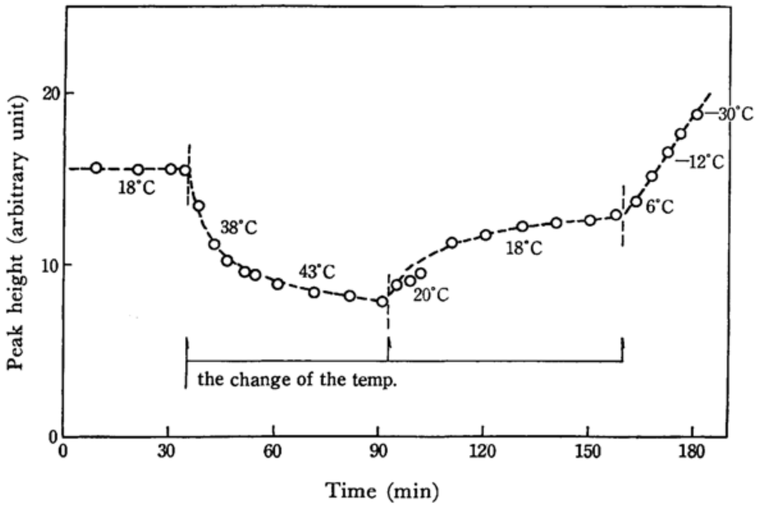

Fig. 11. The effect of the temperature (for A-PVP).
Co/pyridine ring=1/50, $P_{\mathrm{air}}=1$ atm
The described temp. show the temp. of the atmosphere.

There could be two ways of analysing these ESR signals; one way is based on the electronic structure, Co(II)-O_2 (in this structure, the valence d electrons of cobalt are considered to localize in metal orbitals), while the other is based on the electronic structure, Co(III)-O_2^{-1} (in this structure, one of the valence d electrons of cobalt is considered to migrate in a molecular orbital of oxygen).

There are several low-spin cobalt(II) complexes, for example, cobalt(II) phthalocyanine,[8] $Co(CH_3NC)_5^{2+}$,[9] and $Co(CN)_5^{3-}$.[9] These low-spin cobalt(II) complexes have *g* values which are relatively close to 2 (for example, $g_\parallel=2.000$, and $g_\perp=2.117$ for $Co(CH_3NC)_5^{2+}$, and $g_\parallel=1.992$, and $g_\perp=2.157$ for $Co(CN)_5^{3-}$). In general, however, the *A* values caused by the cobalt atom of these complexes are relatively large (for example, $A_\parallel=87$ gauss, and $A_\perp=57$ gauss for $Co(CH_3NC)_5^{2+}$, and $A_\parallel=87$ gauss, and $A_\perp=28$ gauss for $Co(CN)_5^{3-}$). From a con-

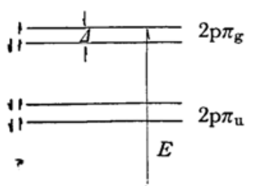

Fig. 12. Occupation of the electronic levels of O_2^- in the ground state.

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[8] J. M. Assour, *J. Am. Chem. Soc.*, **87**, 4701 (1965).

[9] J. J. Alexander and H. B. Gray, *ibid.*, **89**, 3356 (1967); M. E. Kimball, D. W. Pratt and W. C. Kaska, *Inorg. Chem.*, **7**, 2006 (1968).

sideration of these reports, the Δ values of the adducts of oxygen with the chelates on PVP may be much larger than the approximately-estimated values if the electronic structure of the adduct is considered to be mainly Co(II)-O_2.

On the contrary, the method based on the Co(III)-O_2^{-1} electronic structure is more fruitful. The radical anion of molecular oxygen is analysed as having the following three different g values[10] (here, the Δ and E are illustrated in Fig. 12. g_e, λ and l have the ordinary meaning):

$$g_1 = g_e + 2(\lambda^2/\lambda^2 + \Delta^2)^{1/2}l$$

$$g_2 = g_e\left(\frac{\Delta^2}{\Delta^2 + \lambda^2}\right)^{1/2} - (\lambda/E)\cdot\left[-\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \frac{\Delta}{(\lambda^2 + \Delta^2)^{1/2}} + 1\right]$$

$$g_3 = g_e\left(\frac{\Delta^2 + \lambda^2}{\Delta^2}\right)^{1/2} - (\lambda/E)\cdot\left[\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \frac{\Delta}{(\lambda^2 + \Delta^2)^{1/2}} - 1\right]$$

When the oxygen molecule (as a radical anion) coordinates to the cobalt chelate (the structure is not clear now; for example, a structure in which the oxygen molecule coordinates to the cobalt chelate with its molecular axis oblique against the cobalt hf tensor is a common one for binuclear cobalt complexes bridged by molecular oxygen[11]), there may be some interaction between the antibonding 2pπ orbital of oxygen and one of the d orbitals (perhaps d_{z^2}, though this identification is tentative) of the chelate. The larger interaction makes Δ larger. When the following values are assumed: $l=1$, $\lambda=226\ \text{cm}^{-1}$ (taken from atomic oxygen[10]) E is considered to be enough large to neglect λ/E, because the energy interval between 2pπ_g and 2pσ_g (as one-electron orbitals) are calculated to be 2.25 Rydberg.[12]

The g values are to be calculated as follows:

$$g_1 = 2.09,\ g_2 = g_3 = 2.00,\ \text{when}\ \Delta = 5000\ \text{cm}^{-1}$$

$$g_1 = 2.05,\ g_2 = g_3 = 2.00,\ \text{when}\ \Delta = 10000\ \text{cm}^{-1}$$

These estimated values seem to agree roughly with the observed values. Moreover, only a small migration of the free spin into the metal orbitals may be sufficient to result in the observed hf structures, in which the Δ values are quite small, according to Kon and Sharpless.[13]

The rates of oxygenation and deoxygenation seem to obey the Elovich equation, at least in the earlier stages. Theoretically speaking, the Elovich equation can be derived when the rate of adsorption is determined by the reaction of gases and the adsorption sites, with, in general, one of the following conditions (1) or 2)) being satisfied:[14]

1) $N_s(E)/N_s$=constant (heterogeneous surface)
   $N_s(E)$: the number of sites having E as the adsorption heat
   N_s: the total number of sites existing
2) $\varepsilon(\theta)=\varepsilon_0-c\theta$ (homogeneous surface)
   θ: percentage covered
   $\varepsilon(\theta)$: adsortpion heat
   ε_0: constant
   $c\theta$: interaction energy between the adsorbed molecules

The chelates are perhaps coordinated on PVP in miscellaneous states. Also, small molecules such as methanol (which is used as the solvent in preparing the complex-polymer mixtures) may be left behind in the neighborhood of the chelates; then the adsorption heat on the chelate (the chelate with its neighborhood is considered to constitute the adsorption site) could be distributed over a wide range.

The constants of the Elovich equation seem not to be independent of the repeating number of the oxygenation-deoxygenation cycle. This may be the result of small changes in the structure of the adsorption site (for example, such molecules as methanol, which have been left behind in the neighborhood of the metal ion, though perhaps small in amount, may evaporate in the deoxygenation cycle), of the resulted changes in the adsorption heat distribution, and/or of some irreversible oxygenation. The stage of gas diffusion itself through the polymer film may have little effect on the changes of the constants.

It has been reported[13] that the ESR signal of the oxygen adducted to di-(salicylal)-3,3′-diimino-di-*n*-propylamine-cobalt(II) disappeared at lower temperatures in solution; this was attributed to the assumed dimerization of the cobalt(II)-oxygen adduct (paramag.) to yield cobalt(II)-oxygen-cobalt(II) (diamag.). However, the ESR signals on the mixtures investigated in the present paper did not disappear at lower temperatures. This may mean that the cobalt-oxygen adduct on the polymer does not dimerize to give cobalt-O_2-cobalt even at lower temperatures, because the chelates are fixed on hardly-moving polymer chains; this is perhaps the most important reason why the paramagnetic mononuclear cobalt-oxygen adduct is formed on the polymer.

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[10] W. Känzig and M. H. Cohen, *Phys. Rev. Lett.*, **3**, 509 (1959).

[11] F. Basolo and R. G. Peason, "Mechanisms of Inorganic Reactions," Second Ed., John Wiley & Sons, Inc. (1967), p. 641.

[12] T. Shimanouchi, "Kozo-kagaku Kogi-shiryo," Shokabo Co., Tokyo (1965), p. 35.

[13] H. Kon and N. E. Sharpless, *Spectrosc. Lett.*, **1**, 49 (1968).

[14] "Shokubai Kogaku Koza," Vol. 4, ed. by Y. Yoneda, Chijin Shokan Co., Tokyo (1964), p. 233; Ref. 7, p. 45; T. Keii, *Shokubai (Catalyst)*, **3**, 77 (1961).

Experimental

Reagents. *Poly-4-vinylpyridine (PVP).* Commercially-obtained 4-vinylpyridine was polymerized by copper acetate (the molecular weight was considered to be about 4000).[15] Found: C, 71.81; H, 7.32; N, 11.88%. Calcd for $(C_7H_7NO\cdot 0.67H_2O)_n$: C, 71.74; H, 7.18; N, 11.95%.

It was also polymerized by $K_2S_2O_8$ in water (the molecular weight was abut 50000).[16] Found: C, 76.88; H, 7.23; N, 12.43%. Calcd for $(C_7H_7NO\cdot 0.30H_2O)_n$: C, 76.05; H, 6.93; N, 12.67%.

These two polymers were found to have no detectable differences when used as chelate carriers.

Bis-(salicylaldehyde)-ethylenediimine-cobalt(II). This chelate was synthesized according to the litetrature[17] and was recrystallized from methanol. Found: C, 58.85; H, 4.08; N, 8.62%. Calcd for $C_{16}H_{14}N_2O_2Co$: C, 59.10; H, 4.30; N, 8.63% (Complex A).

Bis-(salicylaldimino)cobalt(II). This chelate was synthesized according to Endo.[18] At first as a dihydrate (Found: C, 50.94; H, 4.86; N, 7.91%. Calcd for $C_{14}H_{12}N_2O_2Co\cdot 2H_2O$: C, 50.16; H, 4.81; N, 8.36%); then it was dehydrated at 130°C for 2.5 hr *in vacuo.* Found: C, 56.18; H, 3.93%. Calcd for $C_{14}H_{12}N_2O_2Co$: C, 56.20; H, 4.04% (Complex B-1).

Also according to Yamada:[19] Found: C, 56.20; H, 4.13; N, 9.12, 9.43%. Calcd for $C_{14}H_{12}N_2O_2Co$: C, 56.20; H, 4.04; N, 9.36% (Complex B-2).

The infrared spectra of B-1 agreed with those of B-2. The B-1 and B-2 complexes showed no differences in the present experiments.

Di-(salicylal)-3,3′-diimino-di-n-propylamine-cobalt(II). This chelate was synthesized according to the literature[17] and was purified by reprecipitating it by water from an ethanol solution as a monohydrate. Found: C, 57.81; H, 6.21; N, 10.21%. Calcd for $C_{20}H_{.3}N_3O_2Co\cdot H_2O$: C, 58.00; H, 6.09; N, 10.14% (Complex C).

Cobalt(II)-acetylacetone. This complex was obtained commercially and was used without further purification.

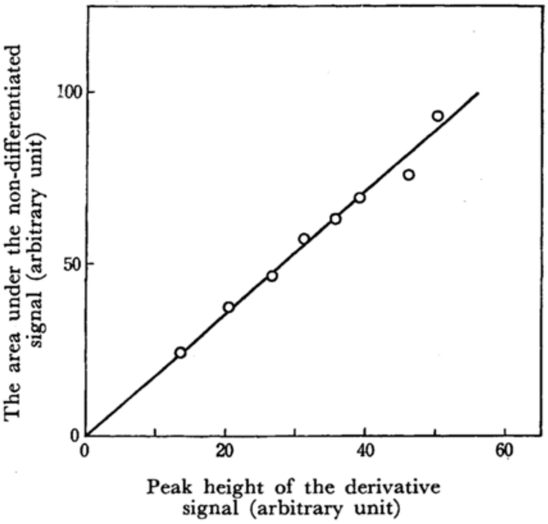

Fig. 13. The relation between the peak height of a first derivative signal and the area under the corresponding non-differentiated signal (in the case of B-1-PVP). Co/pyridine ring=1/50, P_{O_2}=1 atm.

Methanol. Commercial methanol was dehydrated by anhydrous calcium sulfate and was distilled under nitrogen.

Preparation of the Chelate-polymer Mixtures. These mixtures were made as thin, transparent films by mixing one of the complexes with PVP in methanol under nitrogen, and by then evaporating the solvent methanol.

ESR Measurements. The ESR spectra were observed with a Japan Electron Optics Laboratory Co., EPR spectrometer, Model JES-3BS-X (X-band). The value of the field strength was calculated from the observed signal of the manganese marker. The estimation of the g values were based on accurate measurements of the changes in field strength from the point of view of approximate calibration.

The relative amounts (arbitrary unit) of paramagnetic species of a given sample were measured as the peak heights of the first derivative signals, because the peak heights were found to be proportionate to the areas under the non-differentiated signal (Fig. 13), which are themselves considered to be proportionate to the amounts of paramagnetic species at a given temperature.

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[15] S. Tazuke and S. Okamura, *J. Polymer Sci.*, **A4**, 141 (1966).

[16] P. F. Onyon, *Trans. Faraday Soc.*, **51**, 400 (1955).

[17] R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.*, **69**, 1886 (1947).

[18] J. Endo, *Nippon Kwagaku Kwaisi (J. Chem. Soc. Japan)*, **65**, 424 (1944).

[19] H. Nishikawa and S. Yamada, This Bulletin, **37**, 8 (1964).