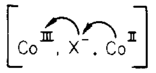
bonding may play a role in promoting electron transfer in these systems, these effects seem to be relatively small.[32]

We propose that the mechanism for the perturbation of nonadiabatic electron-transfer rates by charge-transfer interactions can be described as a super-exchange interaction



$$\left[\mathrm{Co}^{\mathrm{III}}, \mathrm{X}^{-}. \mathrm{Co}^{\mathrm{II}}\right]$$

and that the perturbation is weighted as the sum of the inverse of the vertical transitions to the ion-pair charge-transfer state $^*[\mathrm{Co^{II}(phen)_3, X}]$ and the ionized reductant $^*[\mathrm{Co(sep)^{3+}, e^-(aq)}]$. The effect of the perturbation is to increase donor–acceptor overlap between the reactants (here $\mathrm{Co(phen)_3}^{3+}$ and $\mathrm{Co(sep)^{2+}}$) in the collision complex. The preferred geometrical arrangement for these outer-sphere interactions is by no means clear. We suspect that several arrangements contribute and that the net perturbation can conveniently be regarded as a correction to the spherical-wave approximation on which (1) is based.[22]

We deliberately selected a weak but simple and well-defined charge-transfer interaction for this study. The effect we have found may be useful as a probe of nonadiabaticity in electron-transfer reactions. Contingent on the values of α, straightforward application of (1) implies that nearly all electron-transfer reactions are significantly nonadiabatic. That many reactions seem adiabatic suggests that a large number of effects contribute to the electronic matrix element; most likely among these are the large orbital radii of heavy metals (i.e., leading to small values of α), the collective effect of a large number of high-energy charge-transfer perturbations (e.g., involving H_2O, $\mathrm{TFMS^-}$, $\mathrm{ClO_4^-}$, etc.), and exchange coupling of electronically degenerate systems.

The complexes $\mathrm{Co(phen)_3(ClO_4)_3}$,[33] $\mathrm{Co(sep)Cl_3}$,[34] and $\mathrm{Ru(NH_3)_6Cl_3}$ were prepared and purified according to standard procedures; purity was established by electronic absorption spectra and elemental analysis. Solutions containing $\mathrm{Co(sep)^{2+}}$ or $\mathrm{Ru(NH_3)_6}^{2+}$ were prepared from the trivalent salts by reduction with Zn.

The kinetics of the reactions

$$[\mathrm{Co(phen)_3}^{3+}, \mathrm{X}^-] + \mathrm{M(II)} \rightarrow [\mathrm{Co(phen)_3}^{2+}, \mathrm{X}^-] + \mathrm{M(III)}$$

were monitored at 305 nm since a following reaction ($t_{1/2} \sim 5$ s), tentatively identified as

$$\mathrm{Co(phen)_3}^{2+} + 3\mathrm{H}^+ \rightarrow \mathrm{Co}^{2+} + 3\mathrm{phenH}^+$$

complicated infinite time measurements at other wavelengths. Pseudo-first-order conditions were used with $[\mathrm{M(II)}] > [\mathrm{Co(phen)_3}^{3+}]$. Ionic strength was maintained at 0.10 M with $\mathrm{LiCF_3SO_3}$. The slow reaction of ascorbate with $\mathrm{Co(phen)_3}^{3+}$ was not a complicating feature since this counterion was kept with the reductant until the electron-transfer reaction was initiated by stopped flow mixing.

Registry No. $\mathrm{Co(sep)^{2+}}$, 63218-22-4; $\mathrm{Ru(NH_3)_6}^{2+}$, 19052-44-9; $\mathrm{Co(phen)_3}^{3+}$, 18581-79-8.

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(29) Based on the Marcus square-root relation.[4] Thus, for $k_{\mathrm{ab}} = (k_{\mathrm{aa}}k_{\mathrm{bb}}K_{\mathrm{ab}}f_{\mathrm{ab}})^{1/2}$ and $k_{\mathrm{cb}} = (k_{\mathrm{cc}}k_{\mathrm{bb}}K_{\mathrm{cb}}f_{\mathrm{cb}})^{1/2}$, $k_{\mathrm{ab}}/k_{\mathrm{cb}} \simeq (k_{\mathrm{aa}}K_{\mathrm{ac}}/k_{\mathrm{cc}})^{1/2}$. We have used $k_{\mathrm{exch}}[\mathrm{Co(sep)^{3+,2+}}] = 5\ \mathrm{M^{-1}\ s^{-1}}$,[30] $k_{\mathrm{exch}}[\mathrm{Ru(NH_3)_6}^{3+,2+}] = 3 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$,[31] and $K_{\mathrm{ac}} = 1.2 \times 10^6$. Note that if the $\mathrm{Co(sep)^{3+,2+}}$ is nonadiabatic, one expects $k_x(\mathrm{Co})/k_x(\mathrm{Ru}) > 45$.

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(32) Note that $\mathrm{NO_2^-}$ and ascorbate are basic and the protons on $\mathrm{Co(sep)^{3+}}$ may be relatively acidic. We do find a 4.5-fold rate enhancement for the $\mathrm{Co(phen)_3}^{3+}/\mathrm{Co(sep)^{2+}}$ reaction in acetate medium (but no effect for the $\mathrm{Ru(NH_3)_6}^{2+}$ reductions) as compared to the rate in a NaTFMS medium at the same pH (viz., 1×10^{-5} M $\mathrm{H^+}$). This effect may originate in a hydrogen-bonding interaction. Such an interaction with the ground-state species necessarily results in a shift in the M(III)–M(II) potential, and 25–40 mV shifts to more negative potentials are observed for the $\mathrm{Co(sep)^{3+,2+}}$ couple, but not for $\mathrm{Ru(NH_3)_6}^{3+,2+}$, in nitrite, ascorbate, and acetate media (the largest shift is for acetate) compared to TFMS. We have not corrected for these apparent hydrogen-bonding effects because their kinetic significance is unknown (hydrogen bonding to the 3+ ion, as manifested in E^f, should tend to increase the "solvent" reorganizational barrier) and because the effects seem relatively small. That the charge-transfer effects dominate the rate patterns we have reported is substantiated by predictable responses in $k_x[\mathrm{Co(sep)^{2+}}]/k_x[\mathrm{Ru(NH_3)_6}^{2+}]$ when E^f for the $\mathrm{Co(PP)_3}^{3+,2+}$ couple is altered by using substituted polypyridyls (PP = 5-nitro-1,10-phenanthroline, 1,10-phenanthroline, or 3,4,7,8-tetramethyl-1,10-phenanthroline) and $\mathrm{Co(phen)_2(chn)^{3+}}$ (chn = cyclohexanediamine) oxidants (work in progress).

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Trialkyl Phosphite Complexes of Cobalt

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Hydrogenation, carbonylation, and oligo- and polymerization reactions over cobalt(0) complexes are of current interest. Carrying on our investigations[2–5] on the reactivity of mononuclear d^9 metal complexes, we have studied the partial or total ligand displacement of bis(ethyl fumarate)bis(acetonitrile)cobalt(0) (I). This paper deals with the preparation of the paramagnetic complexes tris(trialkyl phosphite)(fumarate)cobalt(0) (II) and tris(trialkyl phosphite)(maleic anhydride)cobalt(0) (III). Complexes II were prepared according to

$$\underset{\mathrm{I}}{\mathrm{Co(CH_3CN)_2L_2}} + 3\mathrm{P(OR)_3} \rightarrow \underset{\mathrm{II}}{\mathrm{CoL[P(OR)_3]_3}} + 2\mathrm{CH_3CN} + \mathrm{L} \qquad (1)$$

$$\mathrm{L} = \text{ethyl fumarate};\ \mathrm{R} = \mathrm{CH_3},\ \mathrm{C_2H_5},\ \mathrm{CH(CH_3)_2}$$

All operations were run in N_2 or Ar atmosphere. The reaction was carried out by addition of a slight excess (10%) of phosphite to a solution of I in degassed toluene. Ligand exchange took place immediately and was accompanied by a change from red to greenish yellow. Vacuum distillation of solvent and excess phosphite left a dark solid residue which was extracted with degassed hexane and filtered. The filtrate was cooled at −78 °C and gave a good yield of II in the form of yellow plates.

When the above reaction was run in the presence of 1 equiv of maleic anhydride (MA) a further ligand substitution led to III, as follows:

$$\underset{\mathrm{I}}{\mathrm{Co(CH_3CN)_2L_2}} + 3\mathrm{P(OR)_3} + \mathrm{MA} \rightarrow \underset{\mathrm{III}}{[\mathrm{P(OR)_3}]_3\mathrm{CoMA}} + 2\mathrm{L} + 2\mathrm{CH_3CN}$$

In case of IIIa, $R = CH_3$ the product separated almost quantitatively when the reaction mixture cooled. Recrystallization from toluene gave a crop of pure compound (mp 134–135 °C) as dark red prismatic crystals suitable for X-ray studies. Microanalytical data and cryoscopic determinations of the molecular weight in benzene are consistent with the above mentioned mononuclear nature of the molecules. Considerable NMR line-broadening shows that the compounds are paramagnetic. The EPR spectrum of the powdered sample of IIIa (at 298 K) shows a broad signal centered at $g_{\mathrm{iso}} \approx 2.10$ due to the d^9 system with $s = {}^1/_2$.

Since only rather few examples of mononuclear d^9 complexes of cobalt have been prepared[5–10] and in view of the paucity of

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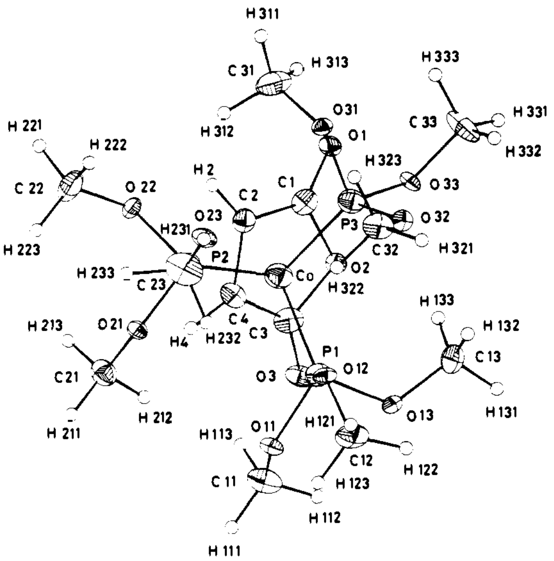

Figure 1. Molecular structure of tris(trimethyl phosphite)(maleic anhydride)cobalt(0).

molecular structural data,[5,9] an X-ray investigation of complexes such as II and III is meaningful. The crystal structure of IIIa was determined from counter data, solved by direct and Fourier methods, and refined by least-squares techniques to $R = 0.07$ for 2726 independent reflections. Crystals are monoclinic, space-group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 9.517$ (4) Å, $b = 15.432$ (14), c 16.915 (8) Å, β 113.17 (6)°.

The crystal structure of IIIa consists of the packing of discrete mononuclear molecules separated by normal van der Waals forces. As may be seen from Figure 1, the molecular structure, which is devoid of any idealized symmetry, may be described in terms of a pseudotetrahedrally coordinated Co atom, by assuming one coordination site for the olefin ligand with mean bond distances Co–P 2.172 (2) Å and Co–C(olefinic) 2.033 (7) Å and mean bond angles P–Co–P 99.4 (4)° and P–Co–B 117.4° (B is the midpoint of the olefinic bond). The significant departure from the ideal tetrahedral value is not surprising as in d^9 complexes Jahn–Teller instability causes distortions away from the most regular structures. The Co(0)–P bond distance is comparable to that of 2.167 Å in $CoH(N_2)(P(C_6H_5)_3)_3$,[11] whereas the agreement with the Co(0)–C distances of 2.06 (1) Å in I is satisfactory.

Viewing down the MA plane, we may also describe the coordination of the cobalt(0)–maleic anhydride complex in terms of a deformed tetragonal pyramid with an apical trimethyl phosphite ligand. However, it is stressed that this formal description would require a difference in apical and basal Co–P bonds, at variance to the observations.

The parameters and bonding of the trimethyl phosphite–cobalt part of the molecule are not significantly different from those observed in trimethyl phosphites,[12] phosphates, or phosphines.[13] In particular, the mean P–O distance of 1.594 (6) Å is close to bond lengths frequently found in tetrahedral organophosphine and orthophosphate esters[13] with P–O–C groupings (average 1.590 Å, range 1.56–1.64 Å) and indicates a certain degree of π bonding. The mean O–C bond length (1.443 (12) Å) is also close to standard (1.44 Å).[13] As usual in these ligands, the M–P–O angles are larger and the O–P–O angles less than tetrahedral; the mean Co–P–O and O–P–O angles are 117.1 and 100.6°, respectively. The latter is close to the standard value (100°).[13] The conformations of the three asymmetric trimethyl phosphite groups with tetrahedrally coordinated pentavalent phosphorous are of the common "two down, one up" arrangement.[12] The orientations of the $P(OCH_3)_3$ groups with respect to the metal do not appear to be influenced appreciably by packing forces.

The most significant structural feature is the conformational change of the maleic anhydride ring in IIIa from the C_{2v} configuration in free maleic anhydride[14] to an idealized C_s configuration in the ligand. The deformation results from the two carbonyl groups bending out of the mean plane of the ring away from the cobalt atom by an average of 0.2 Å. Similar distortions have frequently been observed, as in cyclopentadienyl(duroquinone)-cobalt dihydrate.[15] The mean bond lengths of the ring (C–C 1.435 Å, C=C 1.451 Å, C=O 1.200 Å, C–O 1.418 Å), as compared to those of free maleic anhydride (1.470, 1.303, 1.189, and 1.388 Å, respectively),[14] indicate complete π-electron delocalization. Migration of electrons from cobalt to the olefin may be interpreted as strong back-donation from a d orbital of cobalt to the antibonding π^* orbital of the olefin. This is confirmed by the large decrease of the C=O stretching frequencies from 1780 and 1850 cm^{-1} in free MA to 1722 and 1787 cm^{-1} (Nujol mull) in IIIa. Similar features have been described for other MA complexes.[16–21] The IR spectral evidence confirms that the C=O groups are not directly involved in π coordination because the shifts in ν(C=O) would have been much higher.[22,23] This is also in accordance with the greater mean distance of Co–C(O) as compared to Co–B (see Figure 1).

Our results are in line with the findings of Klein[6] that paramagnetic cobalt(0) compounds with phosphorous ligands are stable and amenable to replacement reactions with retention of the valence state.

Registry No. I, 63372-41-8; II (R = CH_3), 82555-92-8; II (R = C_2H_5), 82555-93-9; II (R = $CH(CH_3)_2$), 82571-33-3; III (R = CH_3), 82555-94-0.

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Iron(III) Phenoxide Complexes: Models for Iron(III)-Tyrosine Coordination

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The reaction of phenols with $FeCl_3$, which was reported more than a century ago, has remained the classic qualitative test for the hydroxyarene functionality.[1] However, in no instance has the isolation and structural characterization of a Fe(III) complex

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