Configurational Effects in the Reaction of Cobalt(I) Schiff-base Complexes with Alkyl Bromides

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Electrogenerated diasteroisomeric cobalt(I) chelate complexes of quadridentate Schiff bases derived from substituted ethylenediamines and salicylaldehyde react with Pr^nBr, Bu^nBr, and Bu^tBr at different rates. The difference in the second-order rate constant can be attributed to the various distortions of the cobalt(I) complex in different configurations. The rate-limiting step is independent of the formation of the cobalt–carbon bond and it is proposed that the reaction occurs *via* an inner-sphere alkyl-bridged electron transfer, with a $[Co^I(chelate)]^- \cdots R^+ \cdots X^-$ transition state. The reaction is sensitive to purely stereochemical perturbations of the co-ordination sphere of the metal atom.

THE use of model compounds is a technique which has been extensively employed in order to gain information about the mechanism of reaction at co-ordination sites on cobalt and iron atoms in coenzyme B_{12} chemistry and in oxygen transport and activation chemistry respectively.[1] Previously, most work has been devoted to the rationalization of the behaviour of model and naturally occurring compounds as regards the electronic effects of ligands, manifest in redox potentials and the thermodynamics and kinetics of chemical reactivity. However, steric factors are an essential element in the control of biochemical functions, *e.g.* through conformational changes due to ligand binding. Hence, the ' intrinsic ' kinetic barriers deserve as much attention as the thermodynamic aspects of reactivity. Knowledge of the mechanism which leads to selectivity is relevant not only to the understanding of enzymatic reactions, but also in the development of new catalysts.

Special steric features were introduced in model compounds for oxygen transport and activation with the aim of reproducing the obstacle to axial ligation which prevents dimerization of the chelate, as in the naturally occurring oxygen carrier.[2,†]

A series of cobalt chelates which can be obtained in different configurations involving only minor changes in the electronic structure was prepared by Ugo and co-workers.[3] Enantiomers, and diastereoisomeric, optically active, and *meso* forms, were synthesized from quadridentate Schiff-base ligands formed by the condensation of salicylaldehyde with mono- and di-substituted ethylenediamine. The equilibrium and kinetic parameters of the reversible formation of oxygen adducts of these chelates were discussed in terms of the structural distortions, as induced by different conformations.[4,5]

We have found significant differences in redox potentials between diastereoisomers [6,7] which can be related to differences in chemical reactivity. Electrochemical techniques can be used to investigate the mechanisms involving heterogeneous electron transfer(s) and homogeneous chemical reaction undergone by cobalt chelates and their organometallic derivatives.[8,‡] We have also reported [8a] an approximately linear relationship between the polarographic half-wave potential ($E_{\frac{1}{2}}$) of the reversible, heterogeneous one-electron reduction (1) and the

$$[Co^{II}(chelate)] \xrightarrow{+e} [Co^{I}(chelate)]^- \qquad (1)$$

$$[Co^{I}(chelate)]^- + RX \xrightarrow{k_2} [CoR(chelate)] + X^- \qquad (2)$$

log of the rate constant of the reaction (2) where the chelate is a quadridentate Schiff base formed from salicylaldehyde or *o*-hydroxyacetophenone and ethylenediamine or *o*-phenylenediamine, and $R = CH_3$. The methyl-donor compound, RX, can be a methyl halide, methylsulphonium, or methylammonium ion. This reaction of nucleophilic low-valent metal complexes is one of the more general routes to the preparation of cobalt(III)–alkyl complexes.[1,§]

The present work attempts to evaluate the influence of steric factors on the rate of reaction (2) and to separate the kinetic components from the driving force of the reaction.[¶] The second-order rate constants of the reactions of Pr^nBr, Bu^nBr, and Bu^tBr with a range of optically active and diastereoisomeric model cobalt(I) chelates obtained *in situ* by electrochemical reduction of the corresponding cobalt(II) chelates have thus been determined. The $E_{\frac{1}{2}}$ value of reaction (1) is related to the driving force of reaction (2) to show that the changes in the free energies of activation and of reaction are independent of the formation of the organocobalt derivative. The Marcus model [9] as extended to group transfer reactions [10] is applied in order to obtain information about the nature of the transition state and the reaction mechanism.

EXPERIMENTAL

Materials.—The cobalt complexes, $[Co^{II}(chelate)]$, were kindly donated by Professor R. Ugo. The parent ligand,

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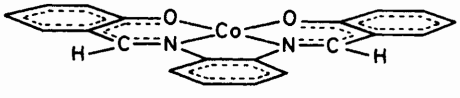
[†] The axial ligation constants of the ' capped ' metal porphyrins differ from those of the flat porphyrins, although small molecules, *e.g.* CO and O_2, can co-ordinate in the axial position inside the cap (P. E. Ellis, jun., J. E. Linard, T. Szymanski, R. D. Jones, J. R. Budge, and F. Basolo, *J. Am. Chem. Soc.*, 1980, **102**, 1889; J. E. Baldwin, T. Klase, and M. Peters, *J. Chem. Soc., Chem. Commun.*, 1976, 881).

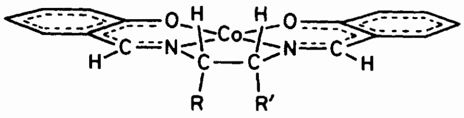
[‡] A ' quantitative ' comparison of vitamin B_{12} model compounds was carried out recently with electrochemical techniques by R. G. Finke, B. L. Smith, M. W. Droege, C. M. Elliott, and E. Hershenhart, *J. Organomet. Chem.*, 1980, **202**, C25.

[§] The synthesis of organocobalt derivatives by chemical reduction of $[Co^{II}(salen)]$ has been reported (G. Costa and G. Mestroni, *J. Organomet. Chem.*, 1968, **11**, 333).

[¶] In the study of charge transfer between alkylmetals and oxidants it was proposed that the separation of polar from steric effects is possible by *meta*, *para*, and *ortho* substitution in the organic moiety (C. L. Wong and J. K. Kochi, *J. Am. Chem. Soc.*, 1980, **102**, 2928).



$[\mathrm{Co^{II}(salphen)}]$



$[\mathrm{Co^{II}(chelate)}]$

Chelate	R	R
NN'-Ethylenebis(salicylideneiminate): salen	H	H
NN'-Propane-1,2-diylbis(salicylideneiminate): sal(+)pn or sal(±)pn	H	CH_3
NN'-1-Phenylethylenebis(salicylideneiminate): sal(−)pen	H	C_6H_5
NN'-Butane-2,3-diylbis(salicylideneiminate): sal(+)bn or sal(*m*)bn	CH_3	CH_3
NN'-1,2-Diphenylethylenebis(salicylideneiminate): sal(+)dpen or sal(*m*)dpen	C_6H_5	C_6H_5
NN'-1,2-Cyclohexylenebis(salicylideneiminate): sal(+)chxn, sal(*m*)chxn, or sal(−)chxn	$-(CH_2)_4-$	

NN'-ethylenebis(salicylideneiminate) (salen), was obtained from ethylenediamine while from *o*-phenylenediamine, the corresponding ligand, *NN'*-*o*-phenylenebis(salicylideneiminate) (salphen), was obtained. The synthesis and characterization of the complexes have been described in detail elsewhere.[3]

Dimethylformamide (dmf) (Erba) was dried over 4 Å molecular sieves before use. Sodium perchlorate (Erba) was dried at 50 °C *in vacuo*. t-Butyl bromide was purified by successive distillations.

Apparatus.—The apparatus used for cyclic voltammetric measurements has already been described.[8]

Kinetic Measurements.—Reactions between the electrogenerated $[\mathrm{Co^I(chelate)}]^-$ complexes and alkyl bromides were followed by cyclic voltammetry as previously reported.[8] The kinetic measurements were performed under pseudo-first-order conditions in the presence of an excess of substrate RX and the second-order rate constants were calculated as before [11] from the rate of disappearance of $[\mathrm{Co^I(chelate)}]^-$ by Nicholson's method.[11,12] The reaction with $\mathrm{Bu^tBr}$ is electrocatalytic and was investigated as previously described.[13]

Catalysis of alkyl halide reduction by vitamin B_{12} was reported by Hill *et al.*[14] and was subsequently investigated by Lexa *et al.*[15] in their studies on electrochemistry and electrocatalysis of vitamin B_{12} derivatives and porphyrins. We independently reported the electrocatalytic reduction of $\mathrm{Bu^tBr}$ by $[\mathrm{Co^I(salen)}]^-$.[13]

Half-wave potentials of irreversible two-electron reductions of saturated aliphatic monobromides in dmf–$[\mathrm{NBu_4}][\mathrm{ClO_4}]$ (0.01 mol dm^{-3}) are likely to be much more negative than the standard potential (although not known precisely).[16-18] On the other hand, cobalt(I) and nickel(0) complexes occasionally show a one-electron reduction potential which is less cathodic than the actual irreversible reduction potential of the alkyl halides but more cathodic than their standard potential for a hypothetical one-electron reduction of the latter.[19-22]

RESULTS AND DISCUSSION

The differences in the $E_{\frac{1}{2}}$ data for reaction (1) are significant not only between compounds with chelating agents bearing different substituents in the ethylenediamine ring, but also between diastereoisomers differing only in their configuration.

In the presence of $\mathrm{Pr^nBr}$ and $\mathrm{Bu^nBr}$ in dmf solution, the electrogenerated $[\mathrm{Co^I(chelate)}]^-$ yields the corresponding organometals according to reaction (2),[8a] while reaction with $\mathrm{Bu^tBr}$ yields isobutene and hydrogen together with $[\mathrm{Co^{II}(chelate)}]$ according to reactions (3) and (4).[13]

$$[\mathrm{Co^I(chelate)}]^- + \mathrm{Bu^tBr} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{CoBu^t(Br)(chelate)}]^- \quad (3)$$

$$[\mathrm{CoBu^t(Br)(chelate)}]^- \xrightarrow{k_4} [\mathrm{Co^{II}(chelate)}] + \mathrm{C_4H_8} + \tfrac{1}{2}\mathrm{H_2} + \mathrm{Br^-} \quad (4)$$

The second-order rate constants of reactions (2) and (3) are given in the Table. The data span a range of *ca.* 1.7

Polarographic half-wave potentials for reaction (1) and kinetic data for reactions (2) and (3) in dmf–$NaClO_4$ (0.1 mol dm^{-3}) at 0 °C

$[\mathrm{Co^{II}(chelate)}]$	$(E_{\frac{1}{2}})_1$/V for $\mathrm{Co^{II}} \longrightarrow \mathrm{Co^I}$	k_2 */dm^3 mol^{-1} s^{-1} R = $\mathrm{Pr^n}$	k_2 */dm^3 mol^{-1} s^{-1} R = $\mathrm{Bu^n}$	k_3 */dm^3 mol^{-1} s^{-1} R = $\mathrm{Bu^t}$
[Co(salen)]	−1.119	1 041 (3.02)	1 436 (3.16)	1 019 (3.01)
[Co{sal(±)pn}]	−1.124	731 (2.86)	946 (2.98)	
[Co{sal(−)pen}]	−1.084	464 (2.67)	531 (2.73)	
[Co{sal(+)bn}]	−1.126	191 (2.28)	210 (2.32)	118 (2.07)
[Co{sal(*m*)bn}]	−1.146	945 (2.98)	1 250 (3.10)	1 176 (3.07)
[Co{sal(+)dpen}]	−1.044	40 (1.60)	75 (1.88)	146 (2.16)
[Co{sal(*m*)dpen}]	−1.067	213 (2.33)	190 (2.28)	176 (2.24)
[Co{sal(−)chxn}]	−1.171	2 095 (3.32)	3 174 (3.50)	3 140 (3.50)
[Co{sal(*m*)chxn}]	−1.154	1 542 (3.19)	2 100 (3.32)	2 200 (3.34)
[Co(salphen)]	−1.043	506 (2.70)	762 (1.79)	

* log *k* Values are given in parentheses.

logarithmic units but allow a meaningful discussion of differences and trends. A plot of log *k* against $E_{\frac{1}{2}}$ is shown in Figure 1.

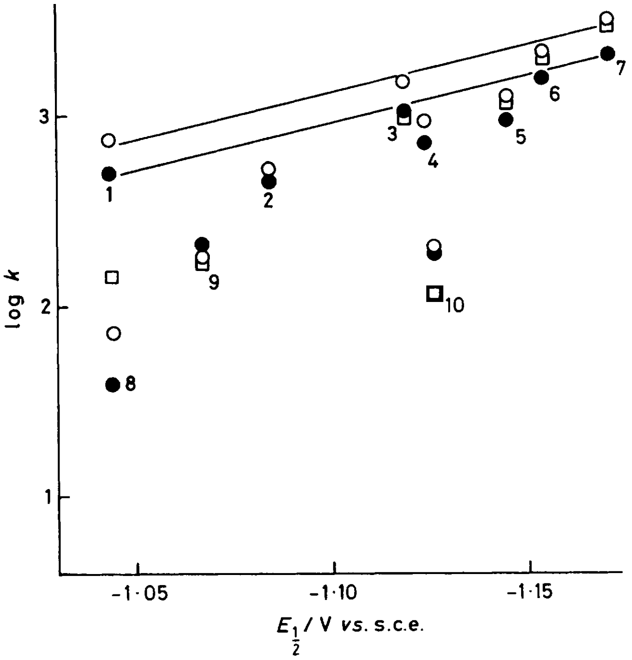


FIGURE 1 Relationship between the rates (log *k*) of reactions (2) and (3) and the half-wave potentials, $E_{\frac{1}{2}}$. Data from the Table: (●) $\mathrm{Pr^nBr}$, (○) $\mathrm{Bu^nBr}$, (□) $\mathrm{Bu^tBr}$; salphen (1), sal(−)pen (2), salen (3), sal(±)pn (4), sal(*m*)bn (5), sal(*m*)chxn (6), sal(−)chxn (7), sal(+)dpen (8), sal(*m*)dpen (9), sal(+)bn (10)

It can be seen that log *k* increases with $E_{\frac{1}{2}}$ for the complexes [Co(salphen)], [Co(salen)], the monosubstituted derivatives [Co{sal(±)pn}], [Co{sal(−)pen}], and the cyclohexyl derivatives. With the exception of [Co{sal(+)dpen}], all the chelates examined show similar reaction rate constants with $\mathrm{Pr^nBr}$, $\mathrm{Bu^nBr}$, and $\mathrm{Bu^tBr}$, within 0.2 logarithmic units. Thus, the log *k* values appear to be influenced by the structure of the metal chelate to the same extent for all substrates.

Moreover, an approximately linear relationship between log *k* and $E_{\frac{1}{2}}$ is found for [Co(salphen)], [Co(salen)], and the two diastereoisomers [Co{sal(−)chxn}] and [Co{sal(*m*)chxn}]. Deviations from linearity are observed for the monosubstituted complexes, [Co{sal(±)pn}] and [Co{sal(−)pen}], as well as for the *meso* form [Co{sal(*m*)bn}], stronger deviations being found for both the diastereoisomers [Co{sal(+)dpen}] and [Co{sal(*m*)dpen}] and for [Co{sal(+)bn}].

Significant differences are found between the reaction rate constants of diastereoisomers: the *meso* forms are reduced at *more* cathodic potentials and with higher rate constants than the optically active forms of the butanediamine and the diphenylethylenediamine derivatives. An opposite trend is observed for the cyclohexyldiamine derivatives, whose *meso* form is reduced at *less* cathodic potentials and with smaller rate constants than the optically active forms.

These results are in agreement with the variations in the circular dichroism (c.d.) spectra in the 350-nm region.[3d] A complete inversion of the sign of the c.d. spectrum was observed for [Co{sal(−)chxn}] with respect to all optically active species. This is attributed to the fact that the most stable conformation of [Co{sal(+)bn}] and [Co{sal(+)dpen}] has the substituents on the ethylenediamine carbon atoms in axial positions with respect to the Co–N–C–C–N ring which is in the half-chair conformation due to steric repulsion between the substituents and the hydrogen atoms of the azomethine group. In the optically active species, [Co{sal(+)chxn}], the only possible conformation is bis-equatorial due to the steric requirements of the cyclohexyl ring fused with the Co–N–C–C–N ring.

As regards the difference in log *k* values between two diastereoisomers, it is observed that the [Co{sal(+)bn}]–[Co{sal(*m*)bn}] couple show the greatest difference while that for the [Co{sal(+)chxn}]–[Co{sal(*m*)chxn}] couple is the least.

The position of the various chelates relative to the approximately linear plot of Figure 1 can be rationalized in terms of the distortion caused by substitution and in terms of conformation of the Co–N–C–C–N ring in the chelate macrocycle. The strongest deviations, observed for [Co{sal(+)bn}] and [Co{sal(+)dpen}], can be attributed to the bis-axial conformation which presumably causes a strong distortion from the planar geometry of the equatorial co-ordination bonds, unlike the *meso* forms with axial–equatorial conformations, which are likely to be less distorted. The smaller deviations from linearity shown by [Co{sal(−)pen}] and [Co{sal(±)pn}] can be explained by the less constrained geometry of the monosubstituted Co–N–C–C–N ring. Conversely, in the cyclohexylenediamine derivatives the less distorted geometry is likely to be that of the optically active diastereoisomer which has the bis-equatorial conformation. Moreover, the cyclohexyl derivatives are probably more rigid than the other chelates, preventing major distortion of the co-ordination bonds around the cobalt atom.

Apart from the evidence for conformational effects of the ligands on the rate constant of reaction (2), the above results can also be examined with reference to the reaction mechanism. The formation of alkylcobalt compounds from cobalt(I) chelates of bis(dimethylglyoximato)-dianions, quadridentate Schiff bases, and vitamin $\mathrm{B_{12}}$ itself is generally classified as a nucleophilic substitution at the α-carbon atom of the alkyl group, occurring with a classical S_N2 mechanism.[1f,23] This mechanism was also proposed for the alkylation of tetra-aza-macrocycles.[24] However, the high rate constant found for the reaction of MeI with $[\mathrm{Co^IL}]$ (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclodeca-4,11-diene) led Tait *et al.*[25] and Endicott and co-workers[26] to suggest that this species and other Curtis-type macrocycles which fail to give easily isolable cobalt(III)–alkyl compounds do not follow the classical S_N2 mechanism but rather react *via* an electron-transfer mechanism generating $\mathrm{Co^{II}}$, $\mathrm{CH_3^{\bullet}}$, and $\mathrm{I^-}$. Further information concerning the detailed mechanism of this process was obtained from analysis of the relationship between the free energy of activation, $\Delta G^\ddagger$, and the driving force of the reaction, $\Delta G^\ominus$, assuming the validity of the Marcus model [9] extended to the methyl, and more generally, to the saturated primary alkyl group transfer reactions.[10,27,*] The linear relationship previously found between reaction rate constants of a series of $[Co^I(chelate)]^-$ with EtBr, PhBr, and $(Me_2SC_6H_4Me)^+$ and the reversible redox potentials of the Co^{II}–Co^I couple [8a] suggests that when bulky substituents are not present on the quadridentate equatorial ligand the $E_{\frac{1}{2}}$ value for the Co^{II}–Co^I process is related to the thermodynamics of the reaction. The driving force of the reaction may thus be assumed to be linearly proportional to the difference between the standard potential of the one-electron oxidation of the cobalt(I) species and that of the one-electron reduction of the substrate RX. Unfortunately, the electrochemical reduction of alkyl halides occurs with electron transfer before and after bond cleavage and the standard potential of the first reversible one-electron transfer cannot be measured.

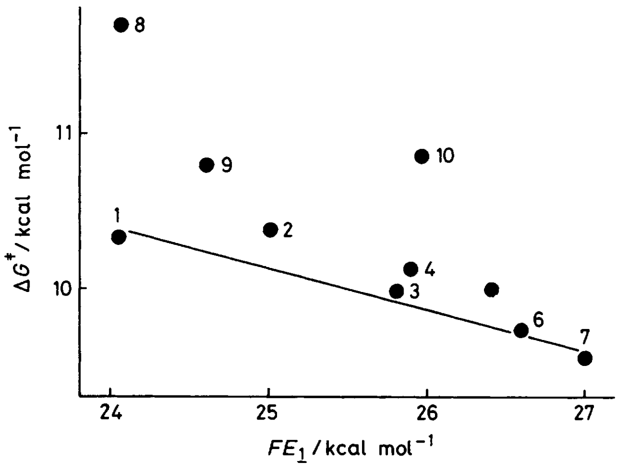


FIGURE 2 Relationship between the free energy of activation for reaction (2) and the half-wave potentials (1 cal = 4.184 J); RX = Pr^nBr. $\Delta G^\ddagger$ is calculated from the equation: $k = Z \exp(-\Delta G^\ddagger/RT)$ where $Z \approx 10^{11}$ dm^3 mol^{-1} s^{-1}; key as in Figure 1

Nevertheless, for a series of reactions of $[Co^I(chelate)]^-$ with the same organic halide, the ***difference*** in the driving force, $\Delta G_1 - \Delta G_2$, of two such reactions can be assumed to be linearly related to the ***difference*** in the heterogeneous one-electron transfer potentials, $(E_{\frac{1}{2}})_1 - (E_{\frac{1}{2}})_2$. The slope of the relationship between the free energies, $\Delta G^\ddagger$ and $\Delta G^\ominus$, can be found from a plot of $FE_{\frac{1}{2}}$ against $\Delta G^\ddagger$, as calculated from the second-order rate constant (Figure 2). The main result obtained from such a plot is the value of the symmetry factor, α, which is related to the location of the transition state along the reaction co-ordinate in the electron, atom, or group transfer. In equation (5) $\Delta G_{1.1}^\ddagger$ and $\Delta G_{11.11}^\ddagger$ are the free energies of

$$\alpha = \left(\frac{\partial \Delta G^\ddagger}{\partial \Delta G^\ominus}\right)_{\Delta G^\ddagger} = \frac{1}{2}\left[1 + \frac{\Delta G^\ominus}{2(\Delta G_{1.1}^\ddagger + \Delta G_{11.11}^\ddagger)}\right] \quad (5)$$

activation of the symmetrical transfer reaction between the same donor and acceptor system.

A linear dependence of $\Delta G^\ddagger$ on $\Delta G^\ominus$ is only found, in principle, when changes in $\Delta G^\ominus$ along the reaction series are limited. In the present case, the range of $\Delta G^\ominus$ is relatively small; one of the $\Delta G^\ddagger$ terms for the symmetrical reaction ($RBr + Br^-$) remains constant while the other changes only slightly when the less distorted $[Co^I(chelate)]^-$ nucleophiles are considered. An approximately linear relationship between log k and $E_{\frac{1}{2}}$ or between $\Delta G^\ddagger$ and $\Delta G^\ominus$ is thus expected in these cases.

For the reactions of $[Co^I(salen)]^-$, $[Co^I(salphen)]^-$, $[Co^I\{sal(m)chxn\}]^-$, and $[Co^I\{sal(-)chxn\}]^-$ with Pr^nBr a linear relationship between $\Delta G^\ddagger$ and $FE_{\frac{1}{2}}$ is found with a slope of $\alpha = 0.27$. This value is below the lowest found [10] for the reaction of $C_6H_5SO_3Me$ with conventional nucleophiles such as OH^- ($\alpha = 0.33$) and CN^- ($\alpha = 0.34$) and, hence, is in accord with the ' downhill ' process due to the strong nucleophilicity of $[Co^I(chelate)]^-$. Moreover, this value of α suggests a reactant-like character of the transition state.

The similar kinetic behaviour of primary and tertiary alkyl substrates, irrespective of the formation of organocobalt derivatives, is also relevant to the understanding of the reaction mechanism. This feature suggests that the rate-determining step and its transition state are not qualitatively different when either primary or tertiary carbon atoms are involved. This confirms that the transition state precedes the formation of the cobalt–carbon bond, which is stable only with primary and secondary carbon atoms. Furthermore, an ion-pair intermediate ensuing from the rate-limiting electron transfer can be envisaged.

The nature of the transition state of the rate-determining step of an S_N2 reaction has been the subject of extensive discussion.[10b,28] If the transition state is more reactant- than product-like, the possibility of charge separation within the substrate and the formation of an ion pair is suggested. A pictorial representation of the S_N2 ion-pair mechanism was proposed by Bordwell and co-workers; [29] in the present case it can be represented by equations (6) and (7). The transition state leads to

$$[Co^I(chelate)]^- + RBr \longrightarrow \underset{\text{transition state}}{\{[Co^I(chelate)]^- \cdots R^+ \cdots Br^-\}} \quad (6)$$

$$\{[Co^I(chelate)]^- \cdots R^+ \cdots Br^-\} \xrightarrow[\text{determining}]{\text{rate}} \underset{\text{intermediate}}{\{[Co^{II}(chelate)] \cdots R^\bullet \cdots Br^-\}} \quad (7)$$

the rate-determining step which involves electron transfer from the nucleophile to the carbon atom. Only if R

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[*] Recent work of S. Fukuzumi, C. L. Wong, and J. K. Kochi, *J. Am. Chem. Soc.*, 1980, **102**, 2928, points to the potential of the Marcus model together with the charge-transfer theory of Mulliken in evaluating steric effects as quantitative probes for outer- and inner-sphere electron transfer between organometals and various oxidizing agents. The application of the Marcus model to atom and group transfer reactions was recently reviewed by Albery [10a] and was adopted by Endicott *et al.*[30] in studies of energetics and dynamics of methyl-bridged electron transfer for the methylcobalamin–cobalamin(II) couple and model chelates.

is a primary or secondary alkyl group is the organocobalt product formed from the intermediate electron-transfer product. In the case of Bu^{t}Br, the bulkiness of the radical prevents the formation of a stable Co–C bond and the reaction proceeds with elimination of hydrogen. The intermediate formation of a cobalt hydride cannot be ruled out.*

Conclusion.—Our results obviously have a bearing on current studies of methyl transfer between $[\mathrm{Co^{II}(chelate)}]^{2+,0}$ and $[\mathrm{Co^{III}Me(chelate)}]^{2+,0}$ (chelate = non-charged tetra-aza-macrocyclic ligands, corrin, or dimethylglyoximato-dianion). Endicott *et al.*[30] recently suggested a transition state involving a three-centre–three-electron bond, $[\mathrm{Co^{II}}\text{–}(\mathrm{R^{\bullet}})\text{–}\mathrm{Co^{II}}]$, relating the activation barrier to the transition-state binding energy for these reactions. Within the context of a three-centre–four-electron, $\{[\mathrm{Co^{I}(chelate)}]^{-}\text{–}(\mathrm{R^{+}})\text{–}\mathrm{X^{-}}\}$, transition-state binding model as in the present study, the critical parameters may be the same as those examined by Endicott, *i.e.* the transition-state bond energy and the critical distance of separation in the transition state.

A significant increase in the Co–C bond distance has been attributed to the geminal methyl groups in the macrocycle 5,7,7,12,14,14-hexamethyl-,1,4,8,11-tetra-azacyclotetradeca-4,11-diene relative to the less encumbered tetra-aza-macrocycle, corrin, or dimethylglyoximato-dianion. The lengthening of the Co–C bond contributes in turn to an increase in the intrinsic barrier to the methyl-mediated inner-sphere electron transfer.

Present results show that even in the case of $[\mathrm{Co^{I}(chelate)}]^{-}$ with alkyl bromides, the separation between the donor and acceptor centres in the transition state is increased by the presence of methyl substituents on the Co–N–C–C–N ring. This increase may be sufficient to prevent the formation of a stable bond in the final products, as in the case of the reaction with Bu^{t}Br.

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* A rate-limiting electron transfer leading to a common ion-pair intermediate $\mathrm{Ni^{I}RX^{\bullet -}}$ has been proposed in the reaction of nickel(0) complexes with aromatic halides leading to mixtures of nickel(I) and organometallic nickel(II) products (T. T. Tsou and J. R. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 6319).

[1/1489 *Received, 24th September*, 1981]

REFERENCES

[1] (*a*) J. M. Pratt, ' Inorganic Chemistry of Vitamin B_{12},' Academic Press, London, 1972; (*b*) G. Costa, *Pure Appl. Chem.*, 1972, **30**, 335; (*c*) G. Costa, *Coord. Chem. Rev.*, 1972, **8**, 63; (*d*) H. A. O. Hill, in ' Inorganic Biochemistry,' ed. G. L. Eichorn, Elsevier, Amsterdam, 1973, p. 1076; (*e*) J. Halpern, *Ann. N.Y. Acad. Sci.*, 1974, **239**, 1; (*f*) G. N. Schrauzer, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 417; (*g*) M. W. Witman and J. H. Weber, *Inorg. Chim. Acta*, 1977, **23**, 263.

[2] J. P. Collman, *Acc. Chem. Res.*, 1977, **10**, 205; J. Almog, J. E. Baldwin, R. L. Dyer, and M. Peters, *J. Am. Chem. Soc.*, 1975, **97**, 226; J. Almog, J. E. Baldwin, and J. Huff, *ibid.*, p. 227.

[3] (*a*) M. Gullotti, A. Pasini, P. Fantucci, R. Ugo, and R. D. Gillard, *Gazz. Chim. Ital.*, 1972, **102**, 855; (*b*) C. Busetto, F. Casiati, A. Fusi, M. Gullotti, F. Morazzoni, and A. Pasini, *J. Chem. Soc., Dalton Trans.*, 1973, 754; (*c*) M. Gullotti, L. Casella, A. Pasini, and R. Ugo, *ibid.*, 1977, 339; (*d*) A. Pasini, M. Gullotti, and R. Ugo, *ibid.*, p. 346; (*e*) E. Cesarotti, M. Gullotti, A. Pasini, and R. Ugo, *ibid.*, p. 757.

[4] M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1973, 420; N. Bresciani, M. Calligaris, G. Nardin, and L. Randaccio, *ibid.*, 1974, 498, 1606.

[5] A. Puxeddu and G. Costa, *J. Chem. Soc., Dalton Trans.*, 1981, 1115.

[6] J. Hanzlik, A. Puxeddu, and G. Costa, *J. Chem. Soc., Dalton Trans.*, 1977, 542.

[7] A. Puxeddu and G. Costa, *J. Chem. Soc., Dalton Trans.*, 1977, 2327.

[8] (*a*) G. Costa, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc., Dalton Trans.*, 1973, 2034; (*b*) G. Costa, A. Puxeddu, and E. Reisenhofer, *Bioelectrochemistry, Bioenergetics*, 1974, **1**, 29; (*c*) E. Reisenhofer and G. Costa, *J. Chem. Soc., Dalton Trans.*, 1976, 521; (*d*) E. Reisenhofer and G. Costa, *Inorg. Chim. Acta*, 1981, **49**, 121.

[9] R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155; *J. Phys. Chem.*, 1963, **67**, 853; *Faraday Discuss. Chem. Soc.*, 1960, **29**, 21.

[10] (*a*) W. J. Albery, *Annu. Rev. Phys. Chem.*, 1980, **31**, 227; (*b*) W. J. Albery and M. M. Kreevoy, *Adv. Phys. Org. Chem.*, 1978, **16**, 87.

[11] R. S. Nicholson, *Anal. Chem.*, 1965, **37**, 1406.

[12] R. S. Nicholson and I. H. Shavin, *Anal. Chem.*, 1964, **36**, 706.

[13] A. Puxeddu and G. Costa, *J. Chem. Soc., Dalton Trans.*, 1980, 1489.

[14] H. A. O. Hill, J. M. Pratt, M. P. O'Riordan, F. R. Williams, and R. J. Williams, *J. Chem. Soc. A*, 1971, 1859.

[15] D. Lexa, J. M. Salveant, and J. P. Soufflet, *J. Electroanal. Chem. Interfacial Electrochem.*, 1979, 159.

[16] M. R. Rifi, in ' Organic Electrochemistry,' ed. M. M. Baizer, M. Dekker, New York, 1973, ch. 6.

[17] O. R. Brown and J. A. Harrison, *J. Electroanal. Chem. Interfacial Electrochem.*, 1969, **21**, 387.

[18] A. J. Fry and R. L. Krieger, *J. Org. Chem.*, 1976, **41**, 54.

[19] G. Cosden, K. P. Healy, and D. Pletcher, *J. Chem. Soc., Dalton Trans.*, 1978, 972.

[20] K. P. Healy and D. Pletcher, *J. Organomet. Chem.*, 1978, **161**, 109.

[21] G. Schiavon, G. Bontempelli, and B. Corain, *J. Chem. Soc., Dalton Trans.*, 1981, 1074.

[22] S. Margel and F. Anson, *J. Electrochem. Soc.*, 1978, **125**, 1234.

[23] G. N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc.*, 1969, **91**, 3341.

[24] E. Ochiai, K. M. Long, C. R. Sperati, and D. H. Busch, *J. Am. Chem. Soc.*, 1969, **91**, 3201.

[25] A. M. Tait, M. Z. Hoffmann, and E. Hayton, *J. Am. Chem. Soc.*, 1976, **98**, 86.

[26] D. P. Rillema, J. F. Endicott, and E. Papaconstantinon, *Inorg. Chem.*, 1971, **10**, 1739.

[27] J. H. Elson, D. G. Morrell, and J. K. Kochi, *J. Organomet. Chem.*, 1975, **84**, C7.

[28] T. W. Bentley and P. von R. Schleier, *Adv. Phys. Org. Chem.*, 1977, **14**, 1.

[29] F. G. Bordwell and T. G. Mecca, *J. Am. Chem. Soc.*, 1975, **97**, 123, 127; F. G. Bordwell, P. F. Wiley, and T. G. Mecca, *ibid.*, p. 132.

[30] J. F. Endicott, K. P. Balakrishnan, and Chung-Lai Wong, *J. Am. Chem. Soc.*, 1980, **102**, 5519.