Electron-transfer Reactions between Neutral Cobalt Complexes

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Electron transfer occurs between the acetylacetone complexes of cobalt(II) and cobalt(III) in toluene at 98 °C. The slow reaction follows second-order kinetics with $k = 2{\cdot}36\ \mathrm{l\ mol^{-1}\ h^{-1}}$. A mechanism involving an acetylacetonate ion bridge is suggested for the transfer of ligand which accompanies the electron-transfer process. A similar mechanism is believed to account for electron transfer between *N*-arylsalicylideneimine complexes of cobalt although these reactions show only first-order dependence on the concentrations of the cobalt(III) complexes.

Most previous studies of electron-transfer reactions between co-ordination compounds have involved species which were either cations or anions. In a few cases one of the reactants has been a neutral molecule, *e.g.* ferrocene–ferricinium[1] ion, tetraphenylporphin cobalt(II)–tetraphenylporphine cobalt(III) cation.[2] A study has now been made of the electron-transfer reactions between neutral complexes of cobalt(III) and cobalt(II) using acetylacetone and several *N*-substituted salicylaldimines as ligands. Each system examined consists of a four-co-ordinate cobalt(II) complex and a six-co-ordinate cobalt(III) so that formally ligand exchange must accompany electron transfer to keep the net chemical constitutions of the systems unaltered.

$$\mathrm{CoL_2} + \overset{*}{\mathrm{Co}}\mathrm{L_3} \rightleftharpoons \overset{*}{\mathrm{Co}}\mathrm{L_2} + \mathrm{CoL_3}$$

Some initial work was carried out on the $\mathrm{Co^{II/III}}$ acetylacetonate system using acetylacetone as a solvent since this would make an interesting comparison with reactions between hydrated ions in aqueous solution. However, although reaction occurred, the kinetic behaviour was complex, the rate apparently depending on fractional powers of the concentrations of the complexes. Subsequent experiments were carried out in toluene where kinetic behaviour appeared simpler.

EXPERIMENTAL

Bis(acetylacetonato)cobalt(II).—This compound was prepared by heating the dihydrate *in vacuo* at 116 °C followed by sublimation of the product at 10^{-3} mmHg to give ruby-red prisms which were extremely hygroscopic. The compound was handled in a dry atmosphere and prepared as required.

Tris(acetylacetonato)cobalt(III).—This compound was prepared by the oxidation of cobalt acetate in the presence of acetylacetone with hydrogen peroxide in aqueous ethanol solution. The complex was labelled with $^{60}\mathrm{Co}$ by the addition of $^{60}\mathrm{CoCl_2}$ to the reaction mixture. The product was purified by chromatography on alumina in ethanol solution. Cobalt(II) ions were adsorbed strongly at the top of the column while the cobalt(III) complex was easily eluted and crystallised.

Bis(N-*arylsalicylaldiminato*)*cobalt*(II)[3] and *tris*(N-*arylsalicylaldiminato*)*cobalt*(III)[4] complexes, where the aryl group was phenyl or *p*-tolyl, were prepared as previously described. The cobalt(III) complexes were labelled by the addition of $^{60}\mathrm{CoCl_2}$ to the reaction mixtures. Purification from traces of cobalt(II) complexes was accomplished by chromatography on alumina.

Reaction Technique.—Solutions of the reactants in toluene were prepared with careful exclusion of oxygen and moisture. Aliquots of the solutions were mixed under nitrogen in a flask from which 5—10 ml samples could be dispensed into glass reaction tubes cooled to −78 °C. Nitrogen could be passed through the reaction tubes during the filling procedure. The tubes were finally sealed and placed in a thermostat at the required temperature from whence they were removed at suitable time intervals, the reaction being stopped by placing the tubes in a slurry of ethanol and solid $\mathrm{CO_2}$. The tubes were opened and the reactants separated by rinsing the contents onto a short column of chromatographic grade alumina (5 in × $\frac{3}{4}$ in), slurried with ethanol. Gentle suction applied at the base of the column aided a rapid separation into a pink cobalt(II) band held firmly at the head of the column and an easily eluted green or yellow band due to the cobalt(III) complexes lower on the column. The cobalt(II) compound was subsequently removed by elution with ethanolic ammonium thiocyanate. Both fractions were made to constant volume for chemical analysis and radio-assay. Cobalt was determined colorimetrically as the blue thiocyanato-complex.

Irreversible Oxidation or Reduction Reactions.—Trial experiments showed that cobalt(II) acetylacetonate slowly oxidised in toluene solution at the temperatures used in the experiments even when the most stringent precautions were taken to exclude oxygen and moisture from the system and when all oxidising impurities had been removed from toluene by distilling the solvent first over sodium and then in the presence of the anhydrous cobalt complex. The rate of oxidation was considerably slower than the measured rate of electron transfer but the change in cobalt(II) concentration was significant over the period of reaction. Each sample was therefore analysed for both cobalt(II) and cobalt(III) in order to determine the fraction F of $^{60}\mathrm{Co}$ exchanged at time t for use in the Mackay equation.[5] All exchange data were expressed in terms of the change in activity of a cobalt(II) fraction following the treatment of Leuhr, Challinger, and Masters[6] for exchange systems containing a component undergoing an irreversible reaction. A very much slower irreversible reduction of the cobalt(III)–acetylacetone complex was observed in separate experiments but the correction for this was less than the overall experimental error of the method and it was ignored.

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[1] D. R. Stranks, *Discuss. Faraday Soc.*, 1960, **29**, 73.

[2] G. D. Dorough and R. W. Dodson, Quarterly Progress Reports, Brookhaven National Laboratory, BNL 132(5-11), 1951, p. 68.

[3] B. O. West, *J. Chem. Soc.*, 1962, 1374.

[4] B. O. West, *J. Chem. Soc.*, 1960, 4944.

[5] H. A. C. McKay, *Nature*, 1938, **142**, 997.

[6] C. P. Leuhr, G. E. Challinger, and B. J. Masters, *J. Amer. Chem. Soc.*, 1956, **78**, 1314.

The error involved in the overall experimental method was assessed to be ±7% made up of contributions from the separation procedures, the measurements of concentration and radioactive assay, and the final graphical determination of k.

The cobalt(II)-*N*-arylsalicylaldiminato-complexes did not show irreversible oxidation in purified toluene and although a very slow reduction of the cobalt(III) compounds was observed it was again within experimental error compared to the time of reaction and a correction was not applied.

RESULTS AND DISCUSSION

Acetylacetone Complexes.—The determination of the half-times for electron-transfer reactions at various initial concentrations of the two cobalt acetylacetonate complexes enabled a series of second-order rate constants to be calculated from the expressions

$$R = \frac{[\mathrm{Co^{II}}][\mathrm{Co^{III}}]\ln 2}{([\mathrm{Co^{II}}] + [\mathrm{Co^{III}}])t_{\frac{1}{2}}} = k[\mathrm{Co^{II}}][\mathrm{Co^{III}}]$$

$$k = \frac{\ln 2}{([\mathrm{Co^{II}}] + [\mathrm{Co^{III}}])t_{\frac{1}{2}}}$$

The values are given in Table 1 and their constancy indicates that the reaction obeys second-order kinetics and that the rate expression is first order with respect to each component. The activation energy for the reaction, determined over the range 55·9—98·7 °C is 59·4 kJ mol^{-1} and the entropy of activation calculated at 372 K is −148 kJ mol^{-1} K^{-1}.

The overall electron-transfer reaction may be represented as follows, an asterisk indicating the cobalt initially labelled.

$$\mathrm{Co^{II}(acac)_2} + \overset{*}{\mathrm{C}}\mathrm{o^{III}(acac)_3} \rightleftharpoons \overset{*}{\mathrm{C}}\mathrm{o^{II}(acac)_2} + \mathrm{Co^{III}(acac)_3}$$

Any mechanism that is suggested for the overall reaction must account for the exchange of a mole of the ligand between the complexes as well as providing a pathway for electron transfer in order to keep the chemical composition of the system unchanged.

Cotton and Elder [7] have established that the cobalt(II) complex is tetrameric in the solid state but determinations of the molecular weight of the compound in various non-polar solvents by Cotton and Soderberg [8] has shown that considerable dissociation occurs in solution. The published data indicates that the degree of association should be less than 1·1 at cobalt(II) acetylacetonate concentrations comparable with those used in the kinetic experiments (*i.e.* 0·01M or less) and at the temperature used, 98 °C. Both higher concentrations and lower temperatures have been used in obtaining an activation energy for the reaction and the proportion of dimeric or other polymeric species will be greater in these experiments.

The fit of the data to a second-order law with each component having a first-order concentration dependence has led to the assumption that the reaction does not involve polymeric species at least at low concentrations. The stereochemistry of the monomer is uncertain since magnetic data are unavailable for solutions of the compound at high temperatures but one may predict on the basis of the general properties of cobalt(II) four-co-ordinate species that it will be a tetrahedral molecule with a spin-free electron configuration for cobalt. The cobalt(III) compound is octahedral and spin-paired.[9]

The requirements of the Franck–Condon principle make it necessary that two metal complexes taking part in an electron-transfer reaction adjust their electronic energy states to being equal except for the exchanging electron, before electron transfer can take place. This is normally interpreted to mean that metal–ligand bond distances and the spin states of the metal ions must change to some intermediate values between those of the ground states of the complexes before transfer can occur.[10]

An optimum situation should exist when, in the intermediate state, the stereochemistries of the two complexes can become equal as well as their electronic configurations.

These considerations suggest that direct electron exchange between four-co-ordinate $\mathrm{Co^{II}(acac)_2}$ and six-co-ordinate $\mathrm{Co^{II}(acac)_3}$ species would not be a favoured mechanism for exchange. Not only would the reactants have very different stereochemistries which would make it difficult to attain the necessary similarity of energy states, but the products arising from passage of an electron would also have the ' wrong ' stereochemistries for the valence states of the metal ions formed, requiring further substantial reorganisation.

$$\mathrm{Co^{II}(acac)_2} + \overset{*}{\mathrm{C}}\mathrm{o^{III}(acac)_3} \xrightarrow{\text{v. slow}} [\mathrm{Co^{III}(acac)_2}]^+ + [\overset{*}{\mathrm{C}}\mathrm{o^{II}(acac)_3}]^-$$

$$[\overset{*}{\mathrm{C}}\mathrm{o^{II}(acac)_3}]^- \xrightarrow{\text{fast}} \overset{*}{\mathrm{C}}\mathrm{o^{II}(acac)_2} + \mathrm{acac}^-$$

$$[\mathrm{Co^{III}(acac)_2}]^+ + \mathrm{acac}^- \longrightarrow \mathrm{Co^{III}(acac)_3}$$

An alternative mechanism could involve the dissociation of the $\mathrm{Co^{III}}$ compound followed by electron transfer between the two resulting four-co-ordinate species.

$$\overset{*}{\mathrm{C}}\mathrm{o^{III}(acac)_3} \rightleftharpoons [\overset{*}{\mathrm{C}}\mathrm{o^{III}(acac)_2}]^+ + \mathrm{acac}^-$$

$$[\overset{*}{\mathrm{C}}\mathrm{o^{III}(acac)_2}]^+ + \mathrm{Co^{II}(acac)_2} \longrightarrow \overset{*}{\mathrm{C}}\mathrm{o^{II}(acac)_2} + [\mathrm{Co^{III}(acac)_2}]^+$$

Such a complete dissociation seems most unlikely in a non-polar solvent such as toluene while the observation that the addition of free acetylacetone to the system increases the rate of electron transfer is evidence against this hypothesis since this should restrict ionisation of the $\mathrm{Co^{III}}$ complex and hence retard the reaction. The

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[7] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1965, **4**, 1145.

[8] F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, 1964, **3**, 1.

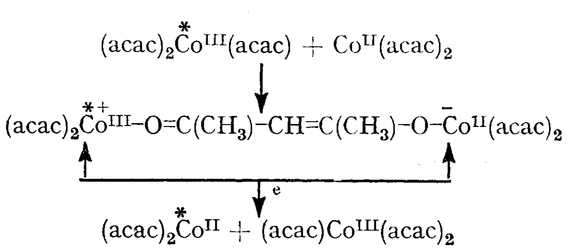
[9] R. O. Whipple, R. West, and K. Emerson, *J. Chem. Soc.*, 1953, 3715.

[10] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' Wiley, New York, 1967, 2nd ed., ch. 6.

possible reason for the rate increase observed is dealt with later in this paper.

A more plausible mechanism involves the dissociation of one of the two Co–O bonds connecting an acetylacetonate ion to a Co^{III} ion followed by co-ordination of this ' free end ' of the ligand to the Co^{II} ion in a $\text{Co}^{\text{II}}(\text{acac})_2$ molecule. A bridged transition-state complex is thereby formed in which each cobalt ion becomes five-co-ordinate thus allowing an optimum reorganisation of the electronic configurations of the two cobalt ions and adjustment of all Co–O distances to take place prior to passage of an electron. This hypothesis also provides a route for exchange of ligand which must accompany electron transfer in order to preserve the stoicheiometry of the reaction.

The conjugated structure of the bridging acetylacetonate ion should also assist the passage of an electron from Co^{II} to Co^{III}. After this has occurred, dissociation of the remaining end of the bridging ligand can occur followed by its co-ordination to the newly created cobalt(III) species.



$$(\text{acac})_2\overset{*}{\text{Co}}{}^{\text{III}}(\text{acac}) + \text{Co}^{\text{II}}(\text{acac})_2$$
$$\downarrow$$
$$(\text{acac})_2\overset{*+}{\text{Co}}{}^{\text{III}}\text{–O=C(CH}_3\text{)–CH=C(CH}_3\text{)–O–}\overset{-}{\text{Co}}{}^{\text{II}}(\text{acac})_2$$
$$\downarrow e$$
$$(\text{acac})_2\overset{*}{\text{Co}}{}^{\text{II}} + (\text{acac})\text{Co}^{\text{III}}(\text{acac})_2$$

Support for this hypothesis is also found in the work of Fay and Piper [11] who have suggested that *cis–trans* isomerisation in Co^{III} derivatives of trifluoroacetylacetone proceeds by rupture of one Co–O bond and formation of a symmetrical five-co-ordinate intermediate.

Cobalt(II)–acetylacetone can readily co-ordinate with additional oxygen-containing ligands as indicated by its polymeric nature in the solid state [7] and in concentrated solution [8] while Dwyer and Sargeson [12] have also shown that a third acetylacetonate ion can be attached, though weakly, to the neutral four-co-ordinate complex in 80% dioxan. The formation of a bridged intermediate may thus be aided by the electrophilic attack of the cobalt in a cobalt(II) complex on an oxygen atom of an acetylacetonate ion attached to cobalt(III) thus encouraging dissociation of a Co^{III}–O bond. The high degree of organisation represented by the postulated transition state agrees with the large negative entropy of activation found for the reaction. It should be noted however that other electron-transfer reactions between charged cobalt complexes of different spin multiplicities in which bridged intermediates have not been postulated also show negative entropies of activation.[10] It is certain that the slow rates of electron transfer observed with such cobalt systems are related to the change in spin multiplicities involved and the activation entropy values no doubt contain components relating to the reorganisation of both electronic configurations prior to an electron moving between the cobalt species.

When the reaction is carried out in mixtures of toluene and acetylacetone the rate of electron transfer increases as the proportion of acetylacetone is increased up to *ca.* 60% (w/v) acetylacetone. Further increase in acetylacetone until the pure solvent is used does not produce a marked increase in rate. Preliminary experiments on the rate of reaction in acetylacetone show that it is not markedly influenced by a two-fold variation in the concentrations of the metal complexes. This indicates that the mechanism of exchange differs from that suggested for reaction in toluene, when substantial amounts of acetylacetone are present or when the pure ligand is used alone as the solvent.

It is not possible to present firm evidence for an alternative mechanism at this stage but the following comments may be made. First the ease with which $\text{Co}^{\text{II}}(\text{acac})_2$ can co-ordinate other ligands which have Lewis base properties suggests that acetylacetone itself can no doubt co-ordinate to the complex to produce a five- or six-co-ordinate species in solution. Secondly acetylacetone will certainly undergo exchange with the Co^{III} complex at 98 °C since Palmer, Fay, and Piper [13] have established that it will exchange with the trifluoroacetylacetonatocobalt(III) complex at 100°. Such an exchange presupposes breaking of a Co–O bond and co-ordination of a ' free ' acetylacetone molecule at the vacant co-ordination site so formed. This may be followed by release of the previously co-ordinated group and completion of the co-ordination of the incoming ligand. A proton must be lost from the exchanging ligand in this process and it may be readily envisaged as being transferred to the acetylacetonate ion being replaced.

Those processes would be expected to aid in the formation of bridged complexes with $\text{Co}^{\text{II}}(\text{acac})_2$ species since co-ordination of an acetylacetone molecule to a Co^{III} vacant site would prevent the reformation of the Co–O bond first broken, thus increasing the chance of such a free ' end ' co-ordinating with a neighbouring Co^{II} species. There will also be expected very ready exchange between co-ordinated acetylacetonate ligands and solvent acetylacetone in view of the labile nature of such d^7 spin-free compounds. All these considerations suggest that acetylacetone may play an important role in the electron-transfer process when it is present in sufficiently high concentration. More detailed studies of this and other systems, having as solvent the group co-ordinated to the metal, should prove of considerable interest because of the formal analogy with aquated ions reacting in water.

N-*Arylsalicylaldimine Complexes*.—The combined electron- and ligand-transfer reactions of these complexes are slow as expected for electron-transfer reactions between spin-free Co^{II} (ref. 3) and spin-paired Co^{III} (ref. 4) compounds. However they occur more rapidly in toluene

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[11] R. C. Fay and T. S. Piper, *Inorg. Chem.*, 1964, **3**, 348.

[12] F. P. Dwyer and A. M. Sargeson, *Proc. Roy. Soc., N.S.W.*, 1956, 141.

[13] R. A. Palmer, R. C. Fay, and T. S. Piper, *Inorg. Chem.*, 1964, **3**, 875.

than between the acetylacetone complexes and were consequently studied at a lower temperature (55 °C). The McKay equation was used to calculate the rate of exchange. Its variation with change in concentration of each component indicated only a first-order dependence on the Co^{III} complexes, being independent of Co^{II} (Table 3). The addition of a four-fold excess of *N*-*p*-tolylsalicylideneimine to the reaction system involving the complexes of that ligand did not alter the first-order rate constant significantly and this is evidence against a dissociation mechanism involving the cobalt complexes. Larger amounts of the free base could not be added to the system because it lowered the retention of cobalt(II) on the alumina columns used in separating the two reactants and made separation very difficult. Thermal decomposition of both cobalt(III) complexes to cobalt(II) species occurred in solution at the reaction temperature but the rates of decomposition were far slower than the measured rates of electron transfer.

TABLE 1

The electron-transfer reaction between acetylacetonates in toluene

10^3c/M				
Co^{II}	Co^{III}	$t_{\frac{1}{2}}$/h	k/l mol^{-1} h^{-1}	t/°C (±0·1 °C)
9·65	4·75	20·0	2·40	98·7
10·0	10·0	14·5	2·39	98·7
4·80	4·90	31·1	2·29	98·7
4·60	5·15	28·3	2·51	98·7
9·50	9·75	16·3	2·20	98·7
17·9	19·3	28·2	0·66	91·0
25·5	24·7	58·0	0·238	81·0
17·9	19·3	2540	0·00733	55·9

TABLE 2

The electron-transfer reaction between cobalt(II) and cobalt(III) acetylacetone complexes in toluene–acetylacetone mixtures at 98·7 °C

10^2c/M			
Co^{II}	Co^{III}	Acetylacetone (%)	$t_{\frac{1}{2}}$/h
0·50	0·50	0	31·1
0·50	0·50	20	10·3
0·50	0·50	40	6·8
0·50	0·50	60	5·9
0·50	0·50	80	5·2
0·48	0·48	100	4·4
0·96	0·96	100	3·9
0·48	0·96	100	3·8
0·96	0·43	100	4·4

It is suggested that bridged intermediates are involved in these reactions, just as has been suggested for the acetylacetone exchange. Dissociation of a cobalt(III)–ligand bond can occur and the 'free end' can co-ordinate to a nearby cobalt(II) complex thus establishing a conjugated bridge across which an electron can move once cobalt–ligand bond distances and electron configurations have adjusted to appropriate intermediate values. The reaction is completed by the final dissociation of the remaining bond of the ligand to the 'original cobalt(III)' (now Co^{II}) and its co-ordination to the 'new' cobalt(III) (original Co^{II}). Cobalt(II) in salicylaldimine-type complexes co-ordinates other groups only weakly [3] in contradistinction to bis(acetylacetonato)cobalt(II) and it appears unlikely that attack of the cobalt(II) complex on an oxygen or nitrogen atom bonded to cobalt(III) could significantly aid the dissociation of the Co^{III}–ligand bond as was suggested in the reaction of the acetylacetone compounds. Further, any Co^{II}/Co^{III} bridge formed by such a ligand should dissociate readily because of the low co-ordinating power of the cobalt(II) species.[3] It may therefore be suggested that the rate-determining step for this reaction is the breaking of the first cobalt(III)–ligand bond, hence the first-order dependence on cobalt(III) observed. The experimental activation energy for the reaction involving the *N*-*p*-tolyl complexes is 54·3 kJ mol^{-1} with $\Delta S^{\ddagger} = -107$ kJ mol^{-1} K^{-1}, and for the *N*-phenyl compounds 56·0 kJ mol^{-1}, with $\Delta S^{\ddagger} = -104$ kJ mol^{-1} K^{-1}; both activation entropies were calculated at 328 K. These values are of similar orders of magnitude to those derived from the Co^{II}/Co^{III} acetylacetone exchange and reflect the similar mechanistic basis proposed.

TABLE 3

The electron-transfer reaction between Co^{II} and Co^{III} *N*-arylsalicylaldimine complexes in toluene

10^2c/M					
Co^{II}	Co^{III}	$t_{\frac{1}{2}}$/min	10^5R/ mol l^{-1} min^{-1}	10^3k/ min^{-1}	t/°C (±0·1 °C)
N-*p*-Tolylsalicylaldimine complexes					
0·50	0·49	61·0	2·80	5·70	55·0
0·25	0·49	47·0	3·15	6·44	55·0
0·76	0·48	67·0	3·06	6·28	55·0
1·00	0·48	72·0	3·17	6·50	55·0
0·50	0·73	54·0	3·80	5·20	55·0
0·50	0·24	85·0	1·30	5·60	55·0
0·50	0·11	86·0	0·762	6·56	55·0
0·50	0·29	81·0	1·58	5·44	55·0
0·50	0·48	114·0	1·50	3·08	50·0
0·50	0·25	35·0	3·23	13·30	60·0
N-Phenylsalicylaldimine complexes					
0·99	0·50	77·0	3·00	6·00	55·0
0·25	0·50	38·5	2·99	5·98	55·0
1·99	0·50	92·5	2·99	5·98	55·0
0·50	1·00	40·0	5·78	5·78	55·0
0·50	0·25	77·0	1·49	5·96	55·0
0·50	0·12	92·0	0·753	6·02	55·0
0·50	0·50	26·5	6·53	13·05	60·0
0·50	0·50	125·0	1·38	2·76	50·0

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