ported by the Italian National Research Council (CNR).

Registry No. **1**, 66945-55-9; **2** (isomer 1), 72656-95-2; **2** (isomer 2), 72656-96-3; **3**, 72581-96-5; **4** (isomer 1), 72581-97-6; **4** (isomer 2), 72598-31-3; **5**, 71930-15-9; **6**, 72581-98-7; **7**, 72581-99-8; **8**, 72598-32-4; **9**, 71930-13-7; **10**, 72582-00-4; $PtBrCl(C_2H_4)(R,R\text{-mben})$, 71930-14-8; PtBrCl(FN)(R,R-mben), 72582-01-5; potassium trichloro(ethene)platinate(1−), 12012-50-9; potassium tribromo(ethene)platinate(1−), 12175-83-6.

Supplementary Material Available: Listings of observed and calculated structure factors for $[PtCl_2(C_2H_4)(R,R\text{-mben})]$ and $[PtCl_2(CH_3CH{=}CH_2)(R,R\text{-mben})]$ (8 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois,
the Chemistry Department, Nuclear Research Centre Negev, Beer-Sheva, Israel,
and the Institut für Anorganische Chemie, Technische Universitat Hannover, Hannover, Federal Republic Germany

Activation Energies for an Intramolecular Electron Transfer Reaction[1]

JAMES V. BEITZ,[2a] JOHN R. MILLER,[2a] HAIM COHEN,[2b] KARL WIEGHARDT,[2c] and DAN MEYERSTEIN*[2a,d]

Received May 14, 1979

Activation energies and solvent effects for the intramolecular electron transfer reaction from a ligated p-nitrobenzoate radical anion to a cobalt(III) center in the complexes formed by the reduction of I and II were measured. The rate of the intramolecular electron transfer reaction decreases with increasing solvent polarity. The activation energies range between 9.0 and 12.5 kcal/mol for complex I and between 13.3 and 19.5 kcal/mol for complex II. The rates always followed Arrhenius temperature dependence, even with 10^4 changes in rate from room temperature to 203 K. Very large preexponential factors, 2×10^{11}–10^{18} s^{-1}, are calculated for these rate constants.

Introduction

Recently several groups have reported the kinetics of intramolecular electron transfer, ET, reactions in complexes of the type M_1LM_2[3-13] (where M_1 and M_2 represent the oxidizing and reducing metal cations with their ligand spheres and L is the bridging ligand). The study of such ET reactions is of importance as it represents one of the elementary steps in inner sphere intramolecular ET reactions[14,15] and as it presents an opportunity to study the factors affecting ET through ligands of different chemical nature.

In some cases the ET reaction in M_1LM_2 is directly from M_1 to M_2 without a "coupling mechanism" through the ligand.[4,7] In these cases the ET reaction can be viewed as proceeding via an outer sphere mechanism. The ligand L serves mainly to keep the two reacting centers in close proximity. However in most systems studied orbital coupling through the bond systems of the ligands supplies the route for the ET process. In many of these cases the ET can be described as a two-step process: reduction of L by M_2 followed by the reduction of M_1 by the anion radical $L^-\cdot$. This is known as the "chemical mechanism".[15]

$$M_1{}^{n+}LM_2{}^{m+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M_1{}^{n+}L^-\cdot M_2{}^{(m+1)+} \xrightarrow{k_1'} M_1{}^{(n-1)+}LM_2{}^{(m+1)+} \qquad (1)$$

Evidently the measurement of the kinetics of ET in the latter case supplies information on a relatively complex system. It is therefore of interest that recent studies have shown that it is possible to reduce $Co^{III}L$, where L ≡ p-nitrobenzoate[16,17] or pyrazinecarboxylate[18] bound to the cobalt through the carboxylate, by free radicals, e.g., e_{aq}^-, $CO_2^-\cdot$, $(CH_3)_2\dot{C}OH$ via the mechanism

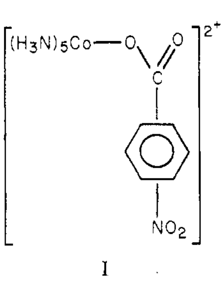
$$Co^{III}L + \cdot R \xrightarrow{k_2} Co^{III}L^-\cdot + R^+ \qquad (2)$$

$$Co(III)L^-\cdot \xrightarrow{k_3} Co^{II}L \qquad (3)$$

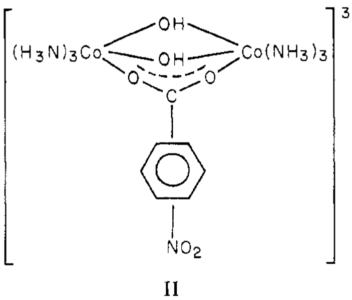
and that k_3 can thus be directly measured.

This and predictions, by modern radiationless transition theories of electron transfer, of non-Arrhenius behavior[19,20] stirred us to study reaction 3 over a wide temperature range. A hoped for result of decreased or even zero activation energies at low temperature, less than 150 K, was not found. The reactions we studied remained strongly activated and became too slow for our measurement techniques at about 200 K.

The compounds chosen for this study (I and II) were previously shown to be reduced by $(CH_3)_2\dot{C}OH$ radicals via reactions 2 and 3.[16,17] The rate of reaction 3 was found to be



I



II

---

[1] Work performed in part under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy.

[2] (a) Chemistry Division, Argonne National Laboratory. (b) Nuclear Research Centre Negev. (c) Institut fur Anorganische Chemie, Technische Universitat, Hannover. (d) Visiting Scientist from the Chemistry Department of the Nuclear Research Centre Negev and Ben-Gurion University of the Negev, Beer-Sheva, Israel.

[3] D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **93**, 7347 (1971).

[4] S. S. Isied and H. Taube, *J. Am. Chem. Soc.*, **95**, 8198 (1973).

[5] J. K. Hurst and R. H. Lane, *J. Am. Chem. Soc.*, **95**, 1703 (1973).

[6] R. D. Cannon and J. Gardiner, *Inorg. Chem.*, **13**, 390 (1970).

[7] H. Fischer, G. M. Tom, and H. Taube, *J. Am. Chem. Soc.*, **98**, 5512 (1976).

[8] J. Iwo and A. Haim *J. Am. Chem. Soc.*, **98**, 1172 (1976).

[9] L. A. A. Olivera, H. E. Toma, and E. Giesbrecht, *Inorg. Chim. Acta*, **22**, 269 (1977).

[10] H. Spiecker and K. Wieghardt, *Inorg. Chem.*, **16**, 1290 (1977).

[11] K. Rieder and H. Taube, *J. Am. Chem. Soc.*, **99**, 7891 (1977).

[12] H. Bertram and K. Wieghardt, *Angew. Chem.*, **90**, 218 (1978).

[13] J. M. Malin, D. A. Ryan, and T. V. O'Halloran *J. Am. Chem. Soc.*, **100**, 2097 (1978).

[14] A. Haim, *Acc. Chem. Res.*, **8**, 264 (1975).

[15] H. Taube, "Electron Transfer Reactions of Complex Ions in Solution", Academic Press, New York, 1970.

[16] M. Z. Hoffman and M. G. Simic, *J. Am. Chem. Soc.*, **94**, 1757 (1972), and M. G. Simic, M. Z. Hoffman, and N. V. Brezniak *ibid.*, **99**, 2166 (1977).

[17] K. Wieghardt, H. Cohen, and D. Meyerstein, *Ber. Bunsenges. Phys. Chem.*, **82**, 388 (1978).

[18] K. Wieghardt, H. Cohen, and D. Meyerstein, *Angew. Chem.*, **90**, 632 (1978).

[19] J. J. Hopfield, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 3640 (1974).

[20] J. Jortner, *J. Chem. Phys.*, **64**, 4860 (1976).

0020-1669/80/1319-0966$01.00/0

Table I

solvent[a]	complex	temp range, K	k_2(295 K),[b] M s^{-1}	$\Delta H_2^{\ddagger}$, kcal mol^{-1}	k_3(295 K),[c] s^{-1}	$\Delta H_3^{\ddagger}$, kcal mol^{-1}	A_3,[d] s^{-1}	$\Delta S_3^{\ddagger}$, eu
99% H_2O + 1% 2-propanol	II	273–306	1.4×10^9	3.1 ± 2.0	2.3×10^3	18.4 ± 1.0	1×10^{17}	19.4
	I	273–306			1.3×10^4	12.5 ± 1.0	2×10^{13}	2.9
99% D_2O + 1% 2-propanol	II	295	1.25×10^9		1.4×10^3			
90% H_2O + 10% 2-propanol	II	273–306	1.3×10^9	3.2 ± 2.0	3.5×10^3	19.5 ± 1.0	1×10^{18}	24.0
	I	273–306			1.3×10^4	12.2 ± 1.0	1.5×10^{13}	1.9
50% H_2O + 50% 2-propanol	II	230–313			1.0×10^4	14.5 ± 0.7	6×10^{14}	9.1
	I	230–313			5.0×10^4	9.0 ± 0.5	2×10^{11}	−6.3
10% H_2O + 90% 2-propanol	II	213–295	4.3×10^8	9.3 ± 0.5	6.0×10^4	13.3 ± 0.4	5×10^{14}	8.6
	I[e]	295			~1.0×10^5			
50% H_2O + 50%[f] ethylene glycol	II	203–295	8×10^7	5.4 ± 0.3	5.8×10^3	17.0 ± 0.6	3×10^{16}	16.5
	I	203–295			2.0×10^3	10.7 ± 0.5	2×10^{11}	−6.9

[a] Expressed as v/v %. [b] Accuracy ±25%, due to small amount weighed. [c] Accuracy ±15%, due mainly to uncertainty in temperature. [d] Preexponential factor for k_3. [e] In this system very small signals were observed, it might be that k_2[complex] < k_3, and/or that the reductant, $(CH_3)_2\dot{C}OH$, reacts, under these conditions, faster with Co(III) than with nitrobenzoate. [f] Reducing radical $HO\dot{C}HCH_2OH$.

very similar in aqueous solutions, though the structure of the complexes is different.[17] It seemed therefore of interest to check whether the activation parameters were also similar for the two reactions. As our preliminary results also indicated that there was a strong solvent effect on reactions 2 and 3, this aspect was also studied.

Experimental Section

Materials. Complexes I and II were prepared as their perchlorate salts according to procedures decribed in the literature and characterized by elemental analysis and their UV–visible spectra.[17,21] All other chemicals used were of analytical grade and were used without further purification. Triply distilled water and D_2O were used throughout the study.

Procedure. Evacuated solutions of 1–20 mM of I or II in different solvents in 1 × 1 cm optical quartz cells were irradiated by single 10–40-ns pulses of 15 MeV electrons from the Argonne linear accelerator. The pulse produced $1-3 \times 10^{-5}$ M free radicals (e_{aq}^- and $(CH_3)\dot{C}OH$ or $HO\dot{C}HCH_2OH$).

Temperature control was provided by an Oxford CF204 cryostat in which the sample cell was immersed in 1 atm of helium exchange gas thermostated at the temperature of interest. Analyzing light from a xenon arc lamp passed through monochromators both before and after the sample. The transmitted light fell on a photomultiplier tube whose anode current was digitized by a transient recorder (Biomation 8100).

When the electron transfer rate became very slow ($k_3 \ll 1$ s^{-1}), it was necessary to reduce the intensity of our monochromatic analyzing light to avoid photochemical contributions to the measured rate. For $k_3 > 1$ s^{-1} a 20-fold reduction in light intensity produced no change in the observed rate.

Results

When solutions containing I or II were irradiated, the formation and disappearance of an absorption due to unstable intermediates was observed (followed at 350 nm for compound I and at 370 nm for compound II in most experiments which contained 2 mM of I or II). This absorption is attributed to the ligated *p*-nitrobenzoate radical anion.[16,17] The kinetic data are summarized in Table I. k_2 was calculated from the rate of formation of the unstable intermediates by the reaction of the free radicals $(CH_3)_2\dot{C}OH$ or $HO\dot{C}HCH_2OH$, with I or II. This reaction obeyed a first-order dependence on the concentrations of the complex and the free radical. The rate of the intramolecular electron transfer process, k_3, was independent of pulse intensity or complex concentration. Plots of $1/T$ vs. ln k_2 and ln k_3 for compound II in 10% H_2O + 90% 2-propanol and in 50% H_2O + 50% ethylene glycol are given in Figure 1.

Discussion

Solvent Effect and Activation Energy for the Reduction of the Nitrobenzoate Group by Free Radicals. The results in Table I clearly indicate that the rate of reaction of the $(CH_3)_2\dot{C}OH$ radical with compound II decreases with increasing concentration of 2-propanol. In parallel the activation energy for this reaction increases. These observations are in accordance with the fact that, due to stabilization of the nitrobenzoate anion radical by solvation, the free energy gain in reaction 2 decreases with decreasing polarity of the solvent.[22] The observation that k_2 is considerably slower for reactions of $HO\dot{C}HCH_2OH$ than of $(CH_3)_2\dot{C}OH$, though measured in different media, is in accord with the fact that the former is a considerably weaker reducing agent.[26]

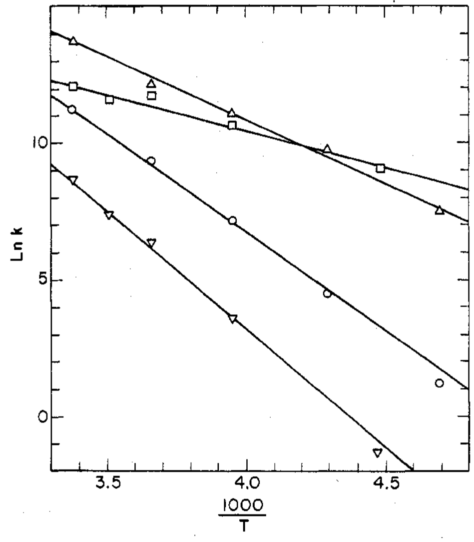


Figure 1. Arrhenius plots are shown for 2 mM solutions of complex II in 50% ethylene glycol–50% H_2O (▽ and □) and in 90% 2-propanol–10% H_2O (△ and ○). Measured rate constants, k_2, for ligated *p*-nitrobenzoate anion formation are shown as △ and □. Measured rate constants, k_3, for intramolecular electron transfer are shown as ○ and ▽. See Table I for the activation parameters calculated from the slopes of these and other Arrhenius pots. The values of k_2 were shifted six units down the ordinate.

---

(21) E. S. Gould, *J. Am. Chem. Soc.*, **88**, 2983 (1966).

(22) The reduction potential of nitrobenzene in water at neutral pH is −0.486 V vs. NHE[23a] compared to −1.147 V vs. SCE in acetonitrile.[23b] The larger stabilization of the nitrobenzene radical anion by solvation in polar media can be also deduced from the effect on the UV–vis spectra[24] and EPR[24] spectra of $C_6H_5NO_2^{-}\cdot$ and on the self-exchange rate between $C_6H_5NO_2$ and $C_6H_5NO_2^{-}\cdot$[25] on adding H_2O to DMF solutions.

(23) (a) D. Meisel and P. Neta, *J. Am. Chem. Soc.*, **97**, 5198 (1975); (b) A. Maki and D. Geske, *ibid.*, **83**, 1852 (1961).

(24) J. Q. Chambers and R. N. Adams, *Mol. Phys.*, **9**, 413 (1965).

(25) P. A. Malachesky, T. A. Miller, T. Layloff, and R. N. Adams, IAEA Proceedings of Symposium at Brookhaven National Laboratories, 157 (1965).

(26) K. D. Asmus, H. Mockel, and A. Henglein, *J. Phys. Chem.*, **77**, 1218 (1973).

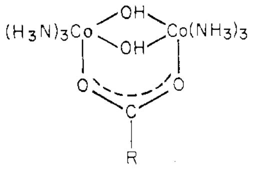
Solvent Effect on the Intramolecular Electron Transfer Reaction. The results in Table I clearly indicate that k_3 increases with decreasing polarity of the solvent, i.e., with increasing 2-propanol concentration. This increase in rate is accompanied by a parallel decrease in $\Delta H_3^{\ddagger}$. Both these effects are attributed to an increased free energy gain, ΔG_3°, due to the lower redox potential of the $^{-}O_2CC_6H_4NO_2/{}^{-}O_2CC_6H_4NO_2^{-}\cdot$ couple in the less polar solvents and to decreased solvent rearrangement energies in the less polar media.[27] If selective solvation occurs in the mixed solvents used, the local composition of the solvent around the cobalt and nitrobenzoate moieties would change less rapidly than the bulk solvent composition.

Activation Parameters for the Intramolecular Electron Transfer Reaction. The results clearly indicate that the intramolecular ET reactions are strongly temperature activated and obey the Arrhenius law over a wide temperature range. The activation energies for compound II are larger than for compound I in a given solvent.

Preexponential factors, A_3, obtained by extrapolation to $T \to \infty$ of the expression $k_3 = A_3 \exp[-(\Delta H_3^{\ddagger}/RT)]$ vary from 2×10^{11} to 2×10^{13} s^{-1} for compound I and from 5×10^{14} to 10^{18} s^{-1} for compound II. (It should be mentioned that these preexponential factors are obtained by extrapolation over many orders of magnitude, assuming that $\Delta H^{\ddagger}$ remains constant. It is, however, possible to envisage conditions under which $\Delta H^{\ddagger}$ is a function of temperature, thus causing a larger than evident error in $\Delta H_3^{\ddagger}$ or $\Delta S_3^{\ddagger}$). By use of the preexponential factors, $\Delta S_3^{\ddagger}$ was calculated; see Table I. For compound I, $\Delta S_3^{\ddagger}$ is about 0 eu, whereas for compound II we find that $\Delta S_3^{\ddagger}$ has large positive values. The latter values are even more surprising if it is remembered that the carboxylate group binding the nitrobenzoate radical anion to the Co(III) center is believed to act as an insulating group,[16,18,28] a fact which might result in nonadiabacity and therefore negative contribution to $\Delta S_3^{\ddagger}$.

Kinetic data indicated that the intramolecular ET reactions reported here can be considered as an "outer sphere" ET process.[17] Therefore, the preexponential factors obtained can be also compared with those estimated from experiments[29,30] and theoretical [19,20,31-36] consideration of ET processes in glasses. For exothermic reactions with Franck–Condon barriers, both experiments and theory point to preexponential factors of about 10^{15} s^{-1} for species in contact.[30] Rates decrease about a factor of 10 for each ~1.5 Å separation, r, between the donor and acceptor.[30] The rate constant according to this theory can be written as $k_3 = 10^{(15-r/1.5)}e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}$. If one assumes that in compounds I and II the electron is transferred over a distance of 3–4.5 Å from the aromatic ring to the Co(III) center, then $k_3 = 10^{12.5\pm0.5}e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}$ is obtained and $\Delta S^{\ddagger}$ values similar to those derived from transition-state theory are found.

It is of interest to note that both the activation energies, $\Delta H_3^{\ddagger}$, and the positive entropies of activation, $\Delta S_3^{\ddagger}$, are considerably larger for compound II than for compound I. As it is reasonable to assume that ΔG_3° is at least as large for II as for I, the results suggest that the larger activation parameters are due to the more rigid structure of II which requires a larger reorganization accompanied by a larger $\Delta S_3^{\ddagger}$. Large positive $\Delta S^{\ddagger}$ values similar to those in Table I have been reported for intramolecular ET in complexes of the type M_1LM_2, where $M_1 \equiv$ Co(III)[12,37]. These large $\Delta S^{\ddagger}$ values occurred for complexes with similar structures to II, i.e., having the structure



$\Delta S^{\ddagger} \sim 0$[6,7,10,11] was reported for mononuclear cobalt complexes (with one exception[13]). For both types of complexes larger activation energies, $\Delta H^{\ddagger}$, than observed in this study were reported.[6,7,10-12,37] This observation is explained by the smaller free energy gain, ΔG°, in the M_1LM_2 processes.

Mechanism of Reduction of Cobalt(III) Centers. It should be pointed out that the present results clearly indicate that the previous observation that k_3 has a similar value for compounds I in 99% H_2O + 1% 2-propanol[16] and II in 93% H_2O + 7% 2-propanol[17] at room temperature was incidental. The ET reaction in complex II has about 6 kcal more activation energy. However, recently reported work[16,18,28] lends support to the idea that the carboxylate group is a poor lead-in group for an ET from a ligand to a cobalt(III) center.

Two alternative mechanisms have been suggested to explain the very slow electron-transfer reactions of cobalt(III/II) complexes: (a) activation of molecular vibrations to overcome large inner sphere rearrangements around the cobalts;[39-41] (b) a two-step mechanism in which an electronic excited state of Co(II) ($t_{2g}^6\ e_g^1$ configuration) is an intermediate.[11,38,42]

The activation parameters found in the present study could not be used to distinguish which of these two mechanisms was operative. In principle, mechanism a leads to a temperature-dependent $\Delta H^{\ddagger}$,[20,31] in contrast to our observations. However, this temperature dependence is expected to be very small over the temperature range in which these reactions could be studied, due to the very low frequencies of the vibrational modes involved.[41]

Acknowledgment. We thank Don Ficht and Lee Rawson for excellent linac operation. Financial support for the synthetic work from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Registry No. I, 36445-08-6; II, 58482-16-9.

---

(27) R. D. Cannon, *Chem. Phys. Lett.*, **49**, 299 (1977).
(28) H. Cohen and D. Meyerstein, *J. Chem. Soc., Dalton Trans.*, 2477 (1975).
(29) J. R. Miller, *Science*, **189**, 221 (1975).
(30) J. V. Beitz and J. R. Miller in "Tunneling in Biological Systems", B. Chance, Ed., Academic Press, New York, 1978.
(31) J. Ulstrup and J. Jortner, *J. Chem. Phys.*, **13**, 4358 (1975).
(32) N. R. Kestner, J. Logan, and J. Jortner, *J. Phys. Chem.*, **78**, 2148 (1974).
(33) R. P. Van Duyne and S. F. Fischer, *Chem. Phys.*, **5**, 183 (1974).
(34) S. Efrima and M. Bixon, *Chem. Phys. Lett.*, **25**, 34 (1974); *J. Chem. Phys.* **64**, 3639 (1976); and *Chem. Phys.*, **13**, 447 (1976).
(35) W. Schmickler, *J. Chem. Soc., Faraday Trans. 2*, **72**, 307 (1976).
(36) P. P. Schmidt, *J. Chem. Phys.*, **56**, 2775 (1972); **58**, 4384 (1973).
(37) H. Bertram and K. Wieghardt, *Chem. Ber.*, **111**, 832 (1978).
(38) H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).
(39) D. P. Rillema, J. F. Endicott, and N. A. P Kane-Maguire, *J. Chem. Soc., Chem. Commun.*, 495 (1972).
(40) M. D. Glick, J. M. Kuszaj, and J. F. Endicott, *J. Am. Chem. Soc.*, **95**, 5097 (1973)
(41) E. Buhks, M. Bixon, J. Jortner, and G. Navon, *Inorg. Chem.*, **18**, 2014 (1979).
(42) G. Schonobuch and T. Strekas, *Inorg. Nucl. Chem. Lett.*, **13**, 591 (1977)