The Application of Marcus Theory to Organometallic Reactions: Observation of the Inverted Region in the Reaction of Metal–Alkenes to form Metal–Allyls

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The activation energy of reaction of metal co-ordinated allylic alkenes to cationic metal-allyls has been measured and follows the prediction of Marcus theory for electron transfer indicative of an initial electron transfer dominating the kinetics of the reaction.

Herein the first experimental observation of the Marcus 'inverted region' for an organometallic reaction is reported. Marcus theory relates the kinetic barrier for an electron-transfer reaction to the thermodynamic driving force through equation (1).[1]† This leads to the prediction that as the driving force increases the kinetic barrier decreases to a minimum and then increases. The region in which the kinetic barrier increases with increasing thermodynamic driving force is referred to as the inverted region.[2] The inverted region in electron-transfer kinetics has only recently been observed.[3] The reaction reported here, equation (2), is formally an intramolecular oxidative addition. Oxidative addition reactions involving the cleavage of carbon–halogen bonds are known to occur by a variety of mechanisms.[4] One of these involves initial electron transfer from the metal to the alkyl halide. This is similar to the oxidative addition mechanism which operates in the addition of I_2 to $(C_5R_5)Mn(CO)_3$ (R = H or Me) and probably in similar reactions with $(C_5R_5)M(CO)_2$ (M = Co or Rh, R = H or Me).[5] If this is the case in our system the rate of the reaction should be controlled by the kinetics of electron transfer and hence be amenable to Marcus theory.

$$\Delta G^{\ddagger} = (w_{AB} + w_{BA})/2 + \lambda/4 + \Delta G_{AB}/2 + (\Delta G_{AB} + w_{AB} - w_{BA})^2/(4\lambda) \quad (1)$$

The reaction on which kinetic measurements were obtained is shown in equation (2) where, for M = Mn, $R_5 = H_5$, Me_5, or MeH_4; for M = Co or Rh, R = H or Me. Solutions of the various complexes are easily prepared by photolysis of the appropriate cyclopentadienyl metal carbonyl in allyl chloride at low temperatures (80—160 K). Following photolysis, the disappearance of the i.r. absorption due to the neutral alkene molecule is accompanied by the appearance of high energy metal carbonyl absorptions due to the cationic allyl complex. For instance photolysis of $(C_5H_5)Mn(CO)_3$ in allyl chloride at 134.2 K results in loss of i.r. absorption associated with this molecule and the appearance of absorption bands at 2132, 1965, and 1900 cm^{-1}. The new absorption bands are assigned as due to free CO (2132 cm^{-1})[6] and the new dicarbonyl alkene fragment, $(C_5H_5)Mn(CH_2CHCH_2Cl)(CO)_2$ (1965 and 1900 cm^{-1}). The assignment of this species as an alkene complex is due to the similarity of its i.r. spectrum to that of other $(C_5H_5)Mn(alkene)(CO)_2$ complexes which also exhibit metal carbonyl absorptions in this region.[7] In the dark a further reaction occurs which is characterized by loss of absorption due to the alkene complex and concomitant increase in absorption at 2032 and 1993 cm^{-1}. These new bands are associated with the known[8,9] complex, $[(C_5H_5)Mn(\eta^3\text{-}CH_2CHCH_2)(CO)_2]^+$; hence the reaction occurs according to equation (2) where M = Mn, $n = 2$. The time dependence of this change in absorption allows measurement of the rate of this reaction.‡ Plots of $\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ *vs.* time are linear for three half lives indicating that the reaction is first order in $(C_5H_5)Mn(CH_2CHCH_2Cl)(CO)_2$. Rate constants for

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† The formalism used here is that of ref. 1b.

‡ Appropriate controls ensured that the reaction rate was not influenced by the monitoring beam of the i.r. spectrometer.

Table 1. Kinetic and thermodynamic terms for reaction according to equation (2).[a]

Metal complex	$\Delta H'$[b]	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$ $\times 10^{-3}$
(1) $(C_5Me_5)Rh(CH_2CHCH_2Cl)(CO)$	6.23	0.52(2)	0.41(16)
(2) $(C_5Me_5)Co(CH_2CHCH_2Cl)(CO)$	6.31	0.43(4)	0.49(37)
(3) $(C_5Me_5)Mn(CH_2CHCH_2Cl)(CO)_2$	6.89	0.25(1)	−0.70(6)
(4) $(C_5H_5)Co(CH_2CHCH_2Cl)(CO)$	7.02	0.26(1)	−0.42(11)
(5) $(C_5H_5)Rh(CH_2CHCH_2Cl)(CO)$	7.07	0.28(1)	−1.20(9)
(6) $(C_5H_4Me)Mn(CH_2CHCH_2Cl)(CO)_2$	7.32	0.35(2)	−0.42(16)
(7) $(C_5H_5)Mn(CH_2CHCH_2Cl)(CO)_2$	7.48	0.46(4)	0.24(26)

[a] Units are all eV. Errors for the activation parameters are given in brackets and reflect the uncertainty in the last digit as derived from least squares analysis of the kinetic data. [b] The relative error is determined by the error in fitting the photoelectron spectra which is 0.02 eV.[14]

the formation of the allyl cation are then calculated from the slope of these plots. Obtaining similar measurements at a series of temperatures allowed the activation parameters to be calculated from Eyring plots.[10] This general procedure was repeated for the different metal fragments[11]§ and the results are given in Table 1. It is notable that in the Mn system increased methyl substitution at the cyclopentadienyl ring results in a lowering of the activation enthalpy whereas for the Co and Rh the opposite is true.

$$(C_5R_5)M(CH_2CHCH_2Cl)(CO)_n \rightarrow [(C_5R_5)M(CH_2CHCH_2)(CO)_n]^+ + Cl^- \quad (2)$$

Unfortunately the thermodynamics of the reactions are not available. In order to deduce the relative thermodynamics of the reactions of the different metal fragments we use a Born–Haber cycle. Initially we cleave the C–Cl bond, energy *D*(C–Cl). The next step is transfer of an electron from the metal to the free halogen, the energy of this being given by the ionization potential of the metal fragment, IP, minus the electron affinity of the halogen, EA. The last step is the energy of formation of the allyl from the alkene radical. For our purposes we will assume that this is constant for all complexes. This leaves us with the contributions from the ionization potential of the metal fragments, the electron affinity of the halogen and the carbon–halogen bond energy in the allyl halide. As the ionization potentials of the unsaturated metal complexes are not known we instead use the value of the corresponding carbonyl adduct [*i.e.* the ionization potential of $(C_5H_5)Mn(CO)_3$ is used instead of that for $(C_5H_5)Mn(CO)_2$].[12—14]¶ The value of *D*(C–Cl) and EA are available from the literature.[15,16] The contributions due to solvation of the complexes have been left out and are assumed to be constant for all the complexes. Using this scheme, approximate, relative enthalpies of reaction can be calculated for the series of reactions.

The enthalpy change for the reaction is hence given by IP − EA + *D*(C–Cl) + *c*, where the constant *c* reflects the contributions from all other terms in the Born–Haber cycle and the work terms $w_{BA} - w_{AB}$.[17]** Although the original form of Marcus theory applied to the free energy, the equation can be formulated in terms of enthalpy. Defining ΔH′ as IP − EA + *D*(C–Cl) and using equation (1) in terms of its enthalpy equivalent and substituting $\Delta H = \Delta H' + c$ gives rise to equation (3). The calculated values of $\Delta H'$ are given in Table 1.

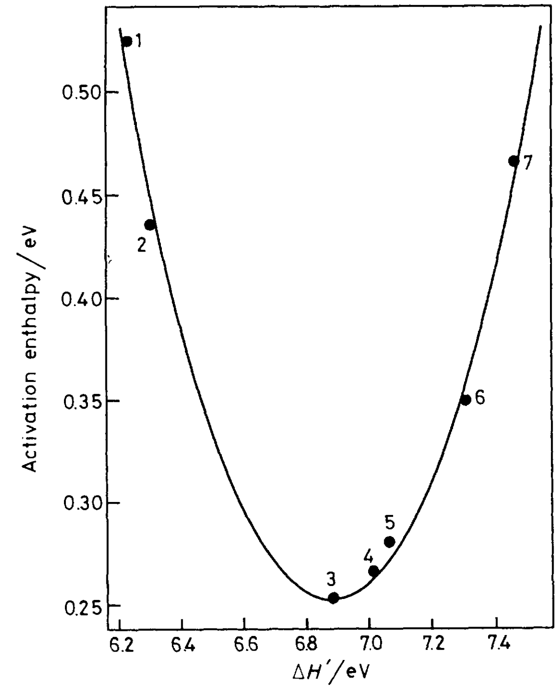

Figure 1. Fit of the enthalpy of activation and $\Delta H'$ (see text) to Marcus theory. The numerals represent the complexes as in Table 1. The line represents the best fit to Marcus theory. The derived parameters according to equation (3) are $w_{AB} = 0.25$ eV, $\lambda = 0.42$ eV, and $c = 7.30$ eV.

$$\Delta H^{\ddagger} = w_{AB} + \lambda\,[1 + (\Delta H' + c)/\lambda]^2/4 \quad (3)$$

Figure 2 shows a plot of the kinetic barrier to reaction, $\Delta H^{\ddagger}$, *vs.* $\Delta H'$. As $\Delta H'$ decreases the driving force is increasing and the barrier to reaction initially decreases to a minimum and then increases. In spite of the crude approximations used, *i.e.* that *c* is constant as we change metal complexes, the data in Figure 2 clearly describe a parabola and hence are at the classical limit of Marcus theory. The parameters derived from a best fit of our data to equation (3), the solid line in Figure 1, are $w_{AB} = 0.25$ eV, $\lambda = 0.42$ eV, and $c = 7.30$ eV.

In spite of the fit we obtain for the activation enthalpy it should be noted that a plot of the free energy does not give rise to a parabola. This is presumably a result of the change in metal fragments giving rise to similar, although shifted, potential energy surfaces along the reaction co-ordinate and different surfaces orthogonal to the reaction co-ordinate. It should be noted that the activation energy in an earlier study also fits the general trend of Marcus theory better than the free energies.||

In simple outer-sphere electron transfer w_{AB} is associated with the energy required to bring the reagents together. In our case it may be indicative of an internal rotation of the alkene prior to electron transfer. If this is correct it may occur with similar enthalpies but differing entropies as the metal frag-

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§ Cationic allyl compounds are known for both Co and Rh.

¶ Values for the ionization potential were obtained from the u.v. photoelectron spectra, see refs. 12—14.

** See for instance ref. 17 where w^r and w^p correspond to our w_{AB} and w_{BA}.

|| For instance a plot of the activation energies of Table 3 in ref. 3g shows the activation energy in phenol to be lower than in benzonitrile or biphenyl in contrast with the plot in Figure 1.

ments are changed. This possibility is currently being pursued in our laboratory.

These results indicate that the reaction of an allylic alkene to an allyl-bound system is consistent with intramolecular electron transfer from a metal orbital to the C–Cl antibonding orbital controlling the reaction rate. In the full paper we will discuss in more detail both the effects of changing the allylic halide and the interpretation of the derived constants.

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References

1 R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966; (b) G. G. Hammes 'Principles of Chemical Kinetics,' Academic Press, New York, 1978; (c) R. D. Cannon, 'Electron Transfer Reactions,' Butterworth and Co., Toronto, 1980.

2 G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, 1986, **86**, 401.

3 (a) J. R. Miller, L. T. Calcaterra, and G. L. Closs, *J. Am. Chem. Soc.*, 1983, **106**, 3047; (b) J. R. Miller, J. V. Beitz, and R. K. Huddleston, *ibid*; 1984, **106**, 5057; (c) G. L. Closs, L. T. Calcaterra, N. J. Green, K. W. Penfield, and J. R. Miller, *J. Phys. Chem.*, 1986, **90**, 3673; (d) M. R. Wasielewski, M. P. Niemczyk, W. A. Svec, and E. B. Pewitt, *J. Am. Chem. Soc.*, 1985, **107**, 1080; (e) M. P. Irvine, R. J. Harrison, G. S. Beddard, P. Leighton, and J. K. M. Sanders, *J. Chem. Phys.*, 1986, **104**, 315; (f) I. R. Gould, D. Ege, S. L. Mattes, and S. Farid, *J. Am. Chem. Soc.*, 1987, **109**, 3794; (g) A. A. H. Kadhum and G. A. Salmon, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2521.

4 J. K. Kochi, 'Organometallic Mechanisms and Catalysis,' Academic Press, London, 1978.

5 N. G. Connelly and M. D. Kitchen, *J. Chem. Soc., Dalton. Trans.*, 1977, 931; K. Broadley, N. G. Connelly, and W. E. Geiger, *ibid.*, 1983, 121; N. G. Connelly and S. J. Raven, *ibid.*, 1986, 1631.

6 CO loss has previously been shown to be the primary photochemical step for this fragment in this temperature region: R. H. Hill and M. S. Wrighton, *Organometallics*, 1987, **6**, 632.

7 J. B. Woell and P. Boudjouk, *J. Organomet. Chem.*, 1979, **172**, C43; I. B. Benson, S. A. R. Knox, R. F. D. Stansfield, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1977, 404; M. Herberhold and C. R. Jablonski, *Chem. Ber.*, 1969, **102**, 778.

8 A. P. Rosan, *J. Chem. Soc., Chem. Commun.*, 1981, 311.

9 B. Buchmann and A. Salzer, *J. Organomet. Chem.*, 1985, **295**, 63.

10 J. Sandstrom, 'Dynamic NMR Spectroscopy,' Academic Press, London, 1982.

11 E. O. Fischer and R. D. Fischer, *Z. Naturforsch., Teil B* 1961, **16**, 475; R. F. Heck, *J. Org. Chem.*, 1963, **28**, 604; A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 243.

12 D. L. Lichtenberger and R. F. Fenske, *J. Am. Chem. Soc.*, 1976, **98**, 50.

13 D. C. Calabro, J. L. Hubbard, C. H. Blevins, A. C. Campbell, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1981, **103**, 6839.

14 D. L. Lichtenberger, D. C. Calabro, and G. E. Kellogg, *Organometallics*, 1984, **3**, 1623.

15 R. T. Sanderson, 'Chemical Bonds and Bond Energy,' 2nd edn., Academic Press, New York, 1976.

16 R. C. Weast, 'Handbook of Chemistry and Physics,' 55th edn., CRC Press, Cleveland, 1974.

17 R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891.