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THE MARCUS CROSS RELATION FOR HYDROGEN-TRANSFER REACTIONS

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The Marcus cross relation provides a tool to calculate cross rates from the corresponding identity rates and the equilibrium constant. Assumptions made in deriving the Marcus cross relation and conclusions which can be drawn from agreement or disagreement between experimental and calculated cross rates are discussed. For a small variation in identity rate constants, agreement between experimental and calculated cross rates simply means that the rate constant of a hypothetical thermoneutral cross reaction has a value within the range covered by the identity rates. Whether or not this value corresponds to the mean value of logarithmic identity rate constants can only be checked for a large variation in identity rates. Therefore, a newly defined index *M* is used to relate the difference in experimental and calculated logarithmic rate constants to the variation in the logarithmic identity rates. Provided that the Marcus cross relation is not obeyed, this indicates non-additivity of kinetic parameters. Applying this analysis to proton-transfer reactions between different transition metal acids and between 9-alkylfluorenes and (9-alkylfluorenyl)lithium shows that claims about agreement or disagreement of experimental rate constants with the rate constants calculated by means of the Marcus cross relation have to be revised in part.

INTRODUCTION

Marcus rate theory[1] continues to be a very useful tool for analysing electron- and hydrogen-transfer reactions and also other reaction types as well.[2–4] It is now clear that this theoretical approach to chemical reactivity constitutes a classical approximation to a more general quantum rate theory.[2,3,5,6] This seems to be generally recognized in the field of electron-transfer reactions but not to the same extent as far as hydrogen-transfer reactions are concerned. In many cases, however, given that quantum effects are of no importance, the simple Marcus model is still the method of choice.

The Marcus cross relation is one minor part of this theory which predicts that the rate constant of a cross reaction, k_{AB}, can be calculated from the corresponding exchange or identity rates (k_{AA}, k_{BB}) and the equilibrium constant, K_{AB}, by means of the equation

$$\log k_{AB} = (1/2)(\log k_{AA} + \log k_{BB} + \log K_{AB}) \quad (1)$$

Recently, Kristjánsdóttir and Norton[7] reported on proton-transfer cross and identity reaction rates between transition metal acids of Cr, Mo and W.[7] They thus directly compare the rate constants measured experimentally and calculated from equation (1). The differences found were not very pronounced and therefore they concluded that their experimental data obeyed the Marcus cross relation (1). Their further claim was that in this manner 'Marcus theory passes the first real test of its applicability to proton-transfer reactions.' This statement and the discussion on the Marcus cross relation in other papers[4,8,9] seem to indicate that the real meaning of this relation remains to be clarified.

MARCUS CROSS RELATION

According to Marcus and Sutin,[1] the rate expression for a cross reaction is given by

$$\log k^{AB} = \log Z^{AB} - (1/2\cdot 3RT)\{w_r^{AB} + \lambda^{AB}/4 + (\Delta G_0')^{AB}/2 + [(\Delta G_0')^{AB}]^2/4\lambda^{AB}\} \quad (2)$$

where Z is the pre-exponential factor, w_r and w_p are the work terms, $\lambda/4$ is the intrinsic barrier and $\Delta G_0'$ is given by

$$\Delta G_0' = w_p - w_r + \Delta G_0 \quad (3)$$

where ΔG_0 is the reaction free energy.

On the other hand, for an identity reaction, $\Delta G_0' = 0$ holds by definition and therefore the corresponding rate expression is given by

$$\log k^{AA} = \log Z^{AA} - (1/2\cdot 3RT)\{w_r^{AA} + \lambda^{AA}/4\} \quad (4)$$

In order to derive equation (1) from equations (2)–(4), one has to neglect the quadratic term in equation (2) and to assume that $w_p^{AB} - w_r^{AB} = 0$ holds. Further, the

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hypothetical logarithmic rate constant of a thermoneutral cross reaction [equation (2) with $\Delta G_0^{\circ} = 0$] is assumed to correspond to the mean value of the corresponding logarithmic identity reaction rate constants. Neglecting the quadratic term in deriving the Marcus cross relation is certainly justified provided that the equilibrium constants are not too large. In this case the relationship between logarithmic rate and equilibrium constants can be assumed to be linear. The assumption $w_p^{AB} - w_r^{AB} = 0$ is also very likely to be obeyed. Therefore, in the following any discussion on the correctness of the Marcus cross relation refers to the remaining kinetic parameters. Kinetic parameters are all parameters in the Marcus rate expression affecting the rate constant except for the reaction free energy. Note that averaging of the kinetic parameters includes not only the intrinsic barrier, but also w_r and the pre-exponential factor. The latter quantity is assumed to be constant in the classical Marcus approach. On the other hand, it is one of the results of quantum-statistical rate theory that the value of the pre-exponential factor may vary, for example, for a varying intermolecular interaction, owing to, say, steric hindrance.[6,10,11] The assumption of a constant pre-exponential factor is also responsible for the fact that the classical Marcus approach cannot account for a non-Arrhenius behaviour of rate constants.

What is the real meaning of the Marcus cross relation? At first glance one realizes that it does not constitute a general test of the Marcus theory as claimed by Kristjánsdóttir and Norton.[7] Whether or not an experimental system fulfils equation (1) simply depends on whether certain relationships between kinetic parameters involved in the Marcus rate expressions for cross and identity rates are obeyed. This does not refer at all to the roots from which Marcus theory was developed. Disagreement is simply a hint that the parameter relationships assumed to hold in deriving equation (1) are not obeyed.

The next question is what conclusions can be drawn if experimental cross rates agree or disagree with the rates calculated according to equation (1). One of the most useful ideas introduced by the Marcus model into the discussion on chemical reactivity is the quantitative separation of thermodynamic and kinetic effects on rate constants [see equation (2)]. In answering the question raised it proves useful to make this separation.

Imagine a diagram in which rate constants are plotted against equilibrium constants such as those shown in Figures 1 and 2. The calculation of cross rates according to the Marcus cross relation can be viewed as consisting of two steps. In the first the mean value of the logarithmic identity rates is calculated. This step is related to the kinetic parameters in the Marcus rate expression. It fixes a point on the ordinate of the diagram ($\log K_{AB} = 0$), which represents the rate constant of a hypothetical 'thermoneutral' cross reaction k_{AB}^0. Then this point is used as a reference for taking into account the effect of the equilibrium constant, the thermodynamic effect, in a second step. This latter step, however, is not a peculiarity of Marcus rate theory. It simply follows from microscopic reversibility [see equation (5)]. The quantity k_{BA} is the rate constant of the back reaction.

$$\log K_{AB} = \log k_{AB} - \log k_{BA} \qquad (5)$$

The condition of microscopic reversibility is, of course, always fulfilled by definition. In other words, whether

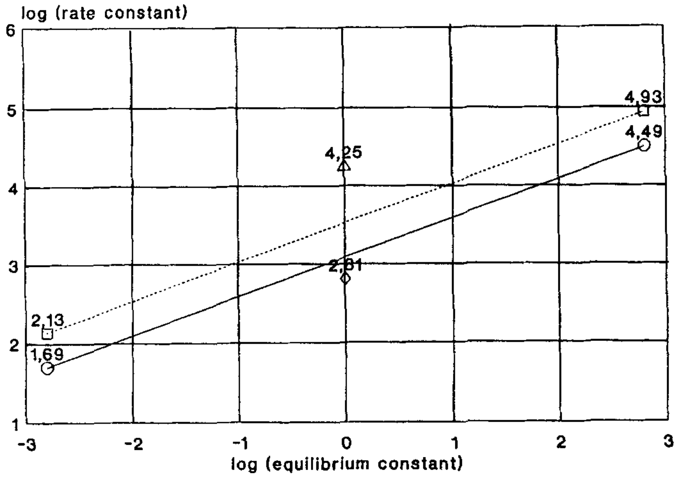

Figure 1. Experimental endergonic and exergonic cross rate constants (○) and identity rate constants (△, Cr; ◇, W) for the proton-transfer reaction between transition metal acids of Cr and W after Ref. 7, and endergonic and exergonic cross rate constants (□) calculated according to the Marcus cross relation, equation (1)

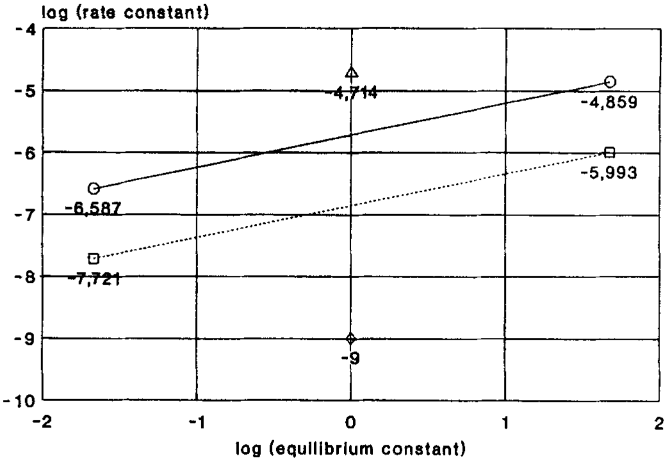

Figure 2. Experimental endergonic and exergonic cross rate constants (○) and identity rate constants (△, H; ◇, *t*-Bu) for the proton-transfer reaction between 9-alkylfluorenes and (9-alkylfluorenyl)lithium (H, *t*-Bu) after Ref. 8, and endergonic and exergonic cross rate constants (□) calculated according to the Marcus cross relation, equation (1)

or not the Marcus cross relation is obeyed this is in any case a statement on kinetic parameters. Note that a 'Brønsted plot' of forward and backward reaction rates of a single equilibrium has always a slope $\alpha = 0{\cdot}5$. If equation (5) is introduced into equation (1), one arrives at

$$\begin{aligned}\log k_{AB}^{0} &= (1/2)(\log k_{AB} + \log k_{BA})\\ &= (1/2)(\log k_{AA} + \log k_{BB})\end{aligned} \qquad (6)$$

According to equation (6), the mean value of the logarithmic identity rate constants should be identical with the mean value of the logarithmic cross rate constants. This is the basic assumption of the Marcus cross relation. Note that the left-hand side of equation (6) corresponds to the logarithmic rate constant of the hypothetical thermoneutral cross reaction $\log k_{AB}^{0}$. On a $\log k$ versus $\log K$ diagram it corresponds to the crossing point of a straight line connecting the exergonic and endergonic cross rate constants with the ordinate axis at $\log K = 0$. If equation (6) is fulfilled then the calculated and observed cross rates are also identical. If there is a difference between the two sides of equation (6) the value of this difference is identical with the difference between the calculated and observed cross rates. It is recommended to use equation (6) for deciding whether or not the Marcus cross relation is obeyed, because this equation directs attention to the basic assumption of the cross relation referring to the kinetic parameters. It leaves out the thermodynamic effect, whose contribution is not questionable. This is, of course, only correct for the analysis of the Marcus cross relation and not for the Marcus rate theory in general.

The usual criterion for comparing calculated and observed values is the ratio of rate constants or the difference in logarithmic rate constants, see Ref. 7 and Tables 1 and 2. This measure is identical for the comparison of cross rates and for the deviation between the mean value of logarithmic identity rate constants and $\log k_{AB}^{0}$. Even though it cannot be claimed, in general, it is certainly very likely that the value of $\log k_{AB}^{0}$ is within the range covered by the identity rates. In this case, however, the possible deviation between calculated and experimental rates decreases with decreasing difference in the identity rates. This does not indicate a better agreement between experimental and calculated values but is rather an outcome of the more stringent restraint on the possible variation in k_{AB}^{0}. In order to take this effect into account it is therefore useful to define a measures which relates the difference in calculated and experimental logarithmic rate constants to the difference in the logarithmic identity rate constants. This is done by the index M defined as

$$M = (\log k_{AB}^{calc} - \log k_{AB}^{exp})/(\log k_{AA} - \log k_{BB}) \qquad (7)$$

where k_{AA} represents the faster identity reaction. Note that $\log k_{AB}^{exp}$ can also be written as

$$\begin{aligned}\log k_{AB}^{exp} &= (1/2)(\log k_{AB} + \log k_{BA} + \log K_{AB})\\ &= \log k_{AB}^{0} + (1/2)\log K_{AB}\end{aligned} \qquad (8)$$

Inserting equations (1) and (8) into equation (7) leads to

$$M = \left[\frac{(1/2)\log k_{AA} + (1/2)\log k_{BB} - \log k_{AB}^{0}}{(\log k_{AA} - \log k_{BB})}\right] \qquad (9)$$

From equation (7), one can see that $M = 0$ provided that the calculated and experimental rate constants are identical. If one assumes that the maximum and minimum values of $\log k_{AB}^{0}$ are $\log k_{AA}$ and $\log k_{BB}$,

Table 1. Experimental and calculated exergonic cross rates (k_{AB}^{exp} and k_{AB}^{calc}), equilibrium constants (K_{AB}), identity rates (k_{AA}, k_{BB}) and criterion M for proton transfer between transition metal acids of Cr, Mo and W[7]

A/B	Log k_{AB}^{exp}	Log $k_{AB}^{calc\,a,b}$	Log K_{AB}	Log k_{AB}^{calc} − log $k_{AB}^{exp\,b}$	Log k_{AA} − log k_{BB}[c]	M
Cr/Mo	4·22	4·125	0·60	−0·095	0·85	−0·11
Mo/W	3·93	4·205	2·20	0·275	0·59	0·46
Cr/W	4·49	4·93	2·80	0·44	1·44	0·30

[a] Even though we used exactly the same identity rates and equilibrium constants we could not exactly reproduce the calculated rate constants reported by Kristjánsdóttir and Norton.[7] The general trend, however, is the same and therefore this discrepancy does not affect the conclusions drawn. All rate constants are given in $\mathrm{l\,mol^{-1}\,s^{-1}}$.

[b] The corresponding logarithmic endergonic rate constants can simply be calculated from the exergonic rate constants by subtracting log K_{AB}. The difference between calculated and experimental values is the same for exergonic and endergonic rates.

[c] Identity rates: log $k_{Cr} = 4{\cdot}25$, log $k_{Mo} = 3{\cdot}40$, log $k_{w} = 2{\cdot}81$.

Table 2. Experimental and calculated endergonic cross rates (k_{AB}^{exp} and k_{AB}^{calc}), equilibrium constants (K_{AB}), identity rates (k_{AA}, k_{BB}) and criterion M for proton transfer between 9-alkylfluorenes and (9-alkylfluorenyl)-lithium[8]

A/B	Log k_{AB}^{exp}	Log k_{AB}^{calc}	Log K_{AB}[a]	Log k_{AB}^{calc} − log $k_{AB}^{exp\,b}$	Log k_{AA} − log k_{BB}[b]	M
H/*t*-Bu	−6·587	−7·721	−1·728	−1·134	4·286	−0·26
Me/*t*-Bu	−7·293	−8·180	−1·878	−0·887	3·518	−0·25
Et/*t*-Bu	−8·086	−8·276	−1·260	−0·190	2·708	−0·07
i-Pr/*t*-Bu	−8·300	−8·456	−0·594	−0·156	1·682	−0·09

[a] The equilibrium constants K_{AB} were calculated by the ratio of the statistically corrected endergonic and exergonic cross reactions given in Table V in Ref. 8. They are slightly different from the equilibrium constants given in the same table.

[b] Logarithmic identity rates: log $k_{H} = -4{\cdot}714$, log $k_{Me} = -5{\cdot}482$, log $k_{Et} = -6{\cdot}292$, log $k_{i\text{-}Pr} = -7{\cdot}318$, log $k_{t\text{-}Bu} = -9{\cdot}000$.

then the following inequality can be derived from equation (9):

$$-1/2 < M < 1/2 \qquad (10)$$

This means that M may vary between $-1/2$ and $+1/2$. M values smaller than $-1/2$ or larger than $+1/2$ would indicate that k_{AB}^{0} is not within the range covered by the identity rates. M scales the difference in calculated and experimental logarithmic rate constants by the difference in the logarithmic exchange rates. Positive M values are obtained if the calculated rate constants are larger than the experimental values. The calculation of M is not possible if two different identity reactions have equal rate constants by chance. A further problem in applying M as a criterion for the Marcus cross relation is related to the statistical significance of small rate constant changes. In general, the error limits of the rate constants should be used for M. Nevertheless, being aware of these possible pitfalls, the index M may be useful in evaluating rate constants in view of their agreement with the Marcus cross relation.

RELATION TO EXPERIMENTAL DATA

Tables 1 and 2 and Figures 1 and 2 show the rate data for proton-transfer between transition metal acids of Cr, Mo and W reported by Kristjánsdóttir and Norton[7] and for proton-transfer between 9-alkylfluorenes and (9-alkylfluorenyl)lithium reported by Murdoch *et al.*[8] As already noted, Kristjánsdóttir and Norton claimed that their data should obey the Marcus cross relation. On the other hand, both Kristjansdóttir and Norton and Murdoch *et al.* pointed out that the fluorene data do not obey the Marcus cross relation. In this case the mean value of the logarithmic identity rate constants is approximately equal to the logarithmic endergonic rate constant.[8]

At first glance, one realizes that by adopting the difference in calculated and observed logarithmic rate constants as a criterion the pattern mentioned above is found. The calculated difference decreases with decreasing variation in identity rates. It is not surprising that there may be exceptions to this rule as for the Mo/W and for the Cr/Mo cases. Adopting the difference in the calculated and experimental logarithmic rate constants as criterion, it turns out that there is no clear difference between the transition metal acid and the fluorene data as claimed by the authors. For example, if a difference in the logarithmic rate constants within a range of ±0·3 is assumed to indicate agreement, both the Cr/W combination of transition metal acids and the H/*t*-Bu and Me/*t*-Bu combinations of the fluorenes do not obey the Marcus cross relation, whereas the remaining combinations do. This result is confirmed and slightly modified if the quantity M is used as a criterion. Let as assume that M values within a range of $\pm 0{\cdot}15$ indicate agreement with the Marcus cross relation (the cut-off values $\pm 0{\cdot}3$ for the logarithmic rate constant and $\pm 0{\cdot}15$ for M are only a first guess; more reliable values can be obtained from a combination of statistical techniques and further experience in applying M). In this case neither the combinations Mo/W and Cr/W of the transition metal acids nor the combinations H/*t*-Bu and Me/*t*-Bu obey the Marcus cross relation. The largest deviations by the M criterion are found for the combinations Mo/W and Cr/W of the transition metal acids. Note, however, that in the Mo/W case the variation in the identity rate constants is only 0·59 logarithmic units. It is certainly very likely that the rate constant of a hypothetical thermoneutral cross rate has a value within the range covered by the identity rates. On the other hand, it is by no means certain that this rate constant corresponds exactly to the mean value. If, however, the variation in the identity rates is small it does not play any role if the logarithmic hypothetical thermoneutral cross rate is exactly identical with the mean value of the corresponding identity rates. In this case equation (1) is always obeyed. This simply means that the rate constant k^0_{AB} is not outside the range covered by the identity rate constants. A full test of the Marcus cross relation thus requires experimental systems for which the variation in identity rates is not too small. Let us assume that a difference in the logarithmic identity rate constants of 1 is a minimum value. In this case only the Cr/W combination of the transition metal acids and all examples of the fluorenes given in Table 2 are appropriate. If further a value of M within the range of $\pm 0{\cdot}15$ is assumed to indicate agreement, then the Cr/W combination and the H/*t*-Bu and Me/*t*-Bu combinations of the fluorenes do not obey the Marcus cross relation, whereas the Et/*t*-Bu and *i*-Pr/*t*-Bu combinations do. Contrary to the pattern displayed by the difference in experimental and calculated logarithmic rate constants, the index M shows that the largest deviation is found for the Cr/W combination of transition metal acids (see also Figures 1 and 2).

Therefore, the conclusions drawn in Refs 7 and 8 on agreement or disagreement of the experimental rate data with data calculated by means of the Marcus cross relation have to be revised in part. If the Marcus cross relation is not obeyed, the question arises of why the calculated rate constants are larger (Figure 1) or smaller (Figure 2) than the experimental values.

For reaction series of 9-alkylfluorenes with one alkyl substituent kept fixed and the alkyl groups in the other reagent varying from H through Me, Et, *i*-Pr and *t*-Bu, anomalous Brønsted coefficients between 0·7 and 1·8 were obtained.[8] Even though it seemed tempting to attribute this anomaly to steric effects, the authors excluded this possibility and proposed a two-step mechanism. On the other hand, an alternative interpretation claimed that the anomalous Brønsted coefficients can be understood by non-additive steric effects.[12] According to this interpretation, increasing kinetic deuterium isotope effects were predicted for the identity reactions in passing from H/H to *t*-Bu/*t*-Bu (increasing steric hindrance). So far, however, only a value of $k_H/k_D = 9{\cdot}5$ for the H/H case is known. Hence, the question of which of these interpretations is correct is open to discussion.

As can be seen from Figures 1 and 2, the reason for not obeying the Marcus cross relation is non-additivity of kinetic parameters. Non-additive in this sense means for the fluorenes that the effect on the kinetic parameters in passing from H/H to H/*t*-Bu by replacement of H by *t*-Bu is different from the effect exerted by the replacement of the other hydrogen by the second *t*-Bu group in passing from H/*t*-Bu to *t*-Bu/*t*-Bu. Introduction of the first *t*-Bu has a smaller effect than introduction of the second *t*-Bu group. In other words, the effect of a substituent in one of the reactants is dependent on the substituent in the other one. In Ref. 12 an explanation of this non-additivity was given in terms of steric effects. For the transition metal acids studied by Kristjánsdóttir and Norton[7] there is a different situation (see Figure 1). In this case, passing from Cr/Cr to Cr/W has a larger effect than passing from Cr/W to W/W. An explanation for this effect remains to be given, even though steric effects are probably the origin of this pattern.

Another example which refers, however, to methyl transfer provides further support for our analysis of the Marcus cross relation. Lewis and Hu[9] reported an almost perfect agreement between cross rates calculated according to this relation and observed experimentally for methyl transfer between arenesulphonates. This is not surprising if one realizes that the variation in logarithmic rate constants of identity reactions is only 0·61 (see Table 1 in Ref. 9; 55 °C). Hence this experimental example simply confirms the fact that k^0_{AB} is within the range covered by the identity rate constants. It is not possible to check in this case whether or not it corresponds to the mean value of logarithmic identity rate constants.

CONCLUSION

An analysis of the Marcus cross relation leads to the following results. For a small variation in identity rate constants, agreement between experimental and calculated cross rates simply means that the rate constant of a hypothetical thermoneutral cross reaction has a value within the range covered by the identity rates. Whether or not this value corresponds to the mean value of logarithmic identity rate constants can only be checked for a large variation in identity rates. Therefore, an index M is proposed, which relates the difference in experimental and calculated logarithmic rate constants to the variation in the logarithmic identity rates. Provided that the Marcus cross relation is not obeyed, this indicates non-additivity of kinetic parameters. Applying this analysis to the proton-transfer reaction between different transition metal acids and between 9-alkylfluorenes and (9-alkylfluorenyl)lithium shows that claims on agreement or disagreement of experimental rate constants with the rate constants calculated by means of the Marcus cross relation have to be revised in part. This work has shown further that the Marcus cross relation continues to be a useful tool in analyzing hydrogen-transfer reactions.

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