104. Kinetics of Extremely Fast Ligand Exchange Reactions with Methylmercury(II)-complexes of 1-Methylpyridine-2-thione and 1-Methylquinaldine-4-thione: Rate-Equilibria Correlations

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Summary

Methylmercury(II) transfer from two heterocyclic thiones to a wide variety of other ligands and the reverse reaction have been investigated by the temperature-jump method. The reactions are almost diffusion controlled, even when the free energy difference is negligible. The only exceptions are reactions to and from hydroxide. They are about hundred times slower than those with other ligands of comparable stability at zero free energy difference. This is in agreement with the behaviour of hydroxide in other methylmercury(II) exchange reactions. They follow an associative reaction mechanism. An empirical correlation of rate- and equilibrium-constants for atom transfer reactions is proposed. This equation shows some similarities to that of the *Marcus* type for atom transfer. However, the proposed equation not only describes reactions governed by an associative mechanism, but also those of dissociative type and cases between the two extremes.

1. Introduction. – The kinetics of the transfer reactions of methylmercury(II) from hydroxide to a wide variety of ligands (X = halides, CN^-, N-, P- and S-donors) according to equation (1) has been found [1] [2] to be very similar to that of

$$CH_3HgOH + X \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} CH_3HgX^+ + OH^-$$

$$\Delta \log K = \log K_{CH_3HgX} - \log K_{CH_3HgOH} = \log \frac{[CH_3HgX]\,[OH]}{[CH_3HgOH]\,[X]} \qquad (1)$$

the 'moderately fast' proton transfer reactions [3]. The *Brønsted* plot $\log k_{12}$ *vs.* $\Delta \log K$ shows a smooth change of $a = d \log k_{12}/d\,\Delta \log K$ from 1 to 0. The maximum value of k_{12}, viz. the diffusion controlled limit is reached for $\Delta \log K = 5$, whereas, at $\Delta \log K = 0$ the value of k_{12} is about 100 times lower than would be expected for a diffusion controlled reaction. To determine whether this rate-equilibria relation is typical for methylmercury transfer reactions, we replaced OH^- by the thiones Y and investigated reaction (2) for a similar variety of X as in equation (1):

$$CH_3HgY^+ + X \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} CH_3HgX^+ + Y \qquad (2)$$

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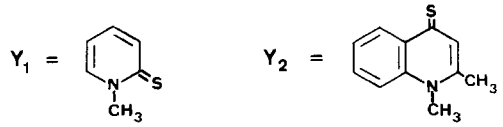


Surprisingly, the reactions where no OH^- is involved are almost diffusion-controlled, even at $\Delta \log K = 0$.

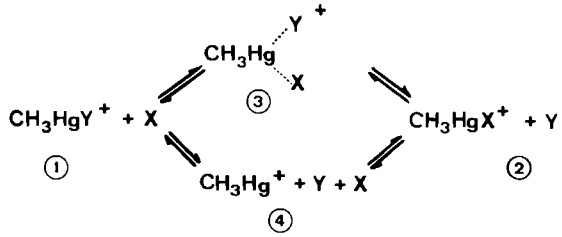
2. Experimental Part. – *Substances.* Stock solutions of methylmercury hydroxide have been prepared as previously described [2] [4]. 1-Methylpyridine-2-thione (Y_1) [5], 1-methyl-quinaldine-4-thione (Y_2) [6] and $(C_6H_5)_2PC_6H_4$-3-SO_3^- [7] have been prepared by literature methods. All other substances were available in analytical grade.

Stability constants. Literature values are generally given for 20° and I = 0.1M [1] [2] [4] [8]. As the kinetic measurements had to be carried out at I = 1M for experimental reasons, $\Delta \log K$ was photometrically redetermined for the thione Y_1. The differences to I = 0.1M are not very large compared to the accuracy of the rate constants, so the stability constants for I = 0.1M were used for the calculation of the equilibrium concentrations in the case of Y_2.

The *temperature jump experiments* for $X = OH^-$ according to equation (2) were carried out on a temperature jump relaxation spectrophotometer (Messanlagen Studiengesellschaft, Göttingen) with a time resolution of approximately 5 μs at 20° and I = 0.1M. The relaxation experiments for all other ligands were performed on a cable temperature jump apparatus (time resolution approximately 50 ns) at the *Max-Planck*-Institut für biophysikalische Chemie, Göttingen. These measurements were done at 20° and I = 1M. The reactions were directly followed at 350 nm for Y_1 and at 385 nm for Y_2. $\varepsilon(Y_1, 350\text{ nm}) = 8.3 \cdot 10^3$, $\varepsilon(CH_3HgY^+, 350\text{ nm}) = 5 \cdot 10^2$, $\varepsilon(Y_2, 385\text{ nm}) = 2.1 \cdot 10^4$, $\varepsilon(CH_3HgY_2^+, 385\text{ nm}) = 1.5 \cdot 10^3$ [$cm^{-1}\,M^{-1}$].

The solutions were freshly prepared and carefully degassed. They remained stable within the time taken for the experiments. Relaxation times, τ, given by $d\delta[MY^+]/dt = \delta[MY^+]/\tau$ (where $\delta[MY^+]$ = deviation from the equilibrium concentration) have been evaluated by visual comparison of the experimental curves with electronically simulated curves (exponential curves with allowance for the heating time).

3. Results. – Under the experimental conditions used, the methylmercury(II) transfer reactions follow mechanisms according to the simplified equation 3. The encounter complexes are omitted (but see discussion, eq. 6).



(3)

The reaction sequence ① ⇄ ③ ⇄ ② describes a concerted mechanism with ③ as an associative transition state. Route ① ⇄ ④ ⇄ ② involves the formation of the aquaion CH_3Hg^+ as an intermediate and the subsequent substitution of H_2O by the ligand X. This route is comparable with the solvent pathway, *e.g.* in square planar complexes [9]. The rate constants of the reactions ① ⇄ ④ and ④ ⇄ ② could be measured separately in some cases *(Table 1)*. These water exchanges are all diffusion controlled. If it is assumed that the same applies for the other water exchanges, estimations can easily be given. Therefore, reactions

Table 1. *Rate constants* $k_f[M^{-1}\ s^{-1}]$ *for the formation reaction and* $k_d[s^{-1}]$ *for the dissociation reaction of methylmercury(II) complexes according to* $CH_3Hg^+ + X \underset{k_d}{\overset{k_f}{\rightleftharpoons}} CH_3HgX^+$. ($I = 0.1$ M, 20°)

X	$\log k_f$	$\log k_d$	$\log K_{CH_3HgX}$
H_2O[a])	8.9	10.6	−1.7
$Co(NH_3)_5NCS^{2+}$	8.0	4.8	3.2
Cl^-[b])	9.3	4.0	5.25
2-pada[c])	9.16	3.41	5.75
Br^-	9.95	3.33	6.62
I^-	10.4	1.8	8.60
OH^-	10.7	1.3	9.37

[a]) See [2].

[b]) This value is in line with the rate constant for the reaction $HgCl^+ + Cl^- \xrightarrow{k} HgCl_2$ ($\log k = 9.8$) [22].

[c]) Pyridine-2-azo-4′-dimethylaniline.

with ④ as an intermediate could be neglected by choosing appropriate concentrations (but see [4]). For X = imidazole and NH_3 the protonation equilibria (4) had also to be taken into account.

$$\begin{aligned} HX^+ + OH^- &\rightleftharpoons X + H_2O \\ X + H^+ &\rightleftharpoons HX^+ \end{aligned} \qquad (4)$$

The rate constants of the reactions (4) are known [10]. For the concentrations used, these protonation reactions can be treated as established pre-equilibria. Therefore only one relaxation time can be detected in the temperature jump experiment at the given wavelengths.

The dependence of the reciprocal relaxation time on the concentrations and the overall rate constants is given by equation (5) for the pathway ① ⇄ ③ ⇄ ②.

$$\frac{1}{\tau} = k_{12}\left\{[CH_3HgY]\cdot s + [X] + \frac{k_{21}}{k_{12}}([CH_3HgX] + [Y])\right\} = k_{12}\cdot f(c_i) \qquad (5)$$

with

$$s = \frac{1}{1 + \dfrac{1}{[X]/[HX] + [X]/[H]}} \qquad \frac{k_{21}}{k_{12}} = \frac{K_{CH_3HgY}}{K_{CH_3HgX}}$$

This expression is valid for small perturbations and under the assumption of a transition state or a steady state intermediate for ③ [11]. A graph of $1/\tau$ *vs.* $f(c_i)$ yields a straight line with slope k_{12}. The experimental conditions are listed in *Table 2*, resulting rate constants in *Table 3*.

4. Discussion. – The transfer of methylmercury(II) between the *S*-donating heterocyclic thiones (Y_1 and Y_2) and the series of investigated ligands X – except hydroxide – belong to the fastest ligand exchange reactions at metal centers (*Fig. 1* and *2*). This enormous mobility is all the more astonishing as the

Table 2. *Experimental conditions: ranges of concentrations and relaxation times,* I = 1M, 20°

X	$[CH_3Hg]_t \cdot 10^4$	$[Y]_t \cdot 10^4$	$[X]_t$	pH	τ [μs]
Y = 1-Methylpyridine-2-thione					
CH_3COO^-	1.3–5.0	1.2–5.0	0.44–1.0	6.6	1.8–7.2
Cl^-	1.0–6.0	1.0–7.0	$3.3 \cdot 10^{-2}$ – 0.66	3	0.23–3.9
NCS^-	2.8–7.0	2.8–7.0	$(3.3–5.0) \cdot 10^{-2}$	3	0.28–2.7
Br^-	2.0–4.9	2.4–5.0	$(1.0–3.6) \cdot 10^{-2}$	3	0.37–1.7
Imidazole	2.0	5.0	$4.9 \cdot 10^{-3}$	7	1.2–1.9
NH_3	3.0	3.3	1.0	5.0–5.8	7.4–17
$(C_6H_5)_2PC_6H_4$-3-SO_3^-	2.0	10.0	$2 \cdot 10^{-4}$	3	2.0–3.0
OH^-	1.9–6.2	1.2–4.9	–	9.0–9.7	36–105
Y = 1-Methylquinaldine-4-thione					
Cl^-	0.65–1.9	0.65–1.9	0.17–1.0	4	2.6–10.2
Br^-	0.23–1.9	0.23–1.9	$(0.74–6.1) \cdot 10^{-2}$	4	2.1–17.0
Imidazole	0.5–1.0	0.5–1.0	$(2.7–5.4) \cdot 10^{-2}$	6.9–7.4	3.0–7.7
NH_3	0.7–2.0	0.7–2.0	0.35–1.0	7.0	3.1–8.3
I^-	0.5–2.0	0.5–2.0	$(1.9–7.5) \cdot 10^{-4}$	4	1.8–11.5
$(C_6H_5)_2PC_6H_4$-3-SO_3^-	0.8–2.0	0.8–2.0	$(0.8–2.0) \cdot 10^{-4}$	4	5.1–12.0
OH^-	0.5–0.75	0.5–0.75	–	9.6–10.0	3.25–5.8
$S_2O_3^{2-}$	0.5–2.0	0.5–2.0	$(0.5–2.0) \cdot 10^{-4}$	4	6.8–26

exchange takes place between very stable complexes with formation constants as high as 10^{10} [M^{-1}]. These $CH_3Hg(II)$ transfers are as fast as the proton transfers between *N*- and *O*-donors. They also show very similar rate equilibria relations. As the range of complexes investigated was very large, we can expect that all ligands not undergoing serious structural changes [12] [13] during the course of the reaction behave similarly, viz. they are diffusion controlled. A similarly high reactivity[1]) is found for the methylmercury(II) exchange at glutathione, where the rate constant for the selfexchange is $k_{12} = k_{21} = 10^{8.8}\,M^{-1}\,s^{-1}$ [15].

The mechanism of the above mentioned ligand exchanges at methylmercury(II) according to equation (6) cannot be described satisfactorly in terms of the

$$\underset{①}{CH_3HgY^+ + X} \rightleftharpoons \underset{ⓐ}{(CH_3HgY^+ \cdots X)} \rightleftharpoons \underset{ⓑ}{(CH_3HgX^+ \cdots Y)} \rightleftharpoons \underset{②}{CH_3HgX^+ + Y} \quad (6)$$

with

$$\frac{1}{k_{12}} = \frac{1}{K \cdot k_{2b}} + \frac{k_{a1}}{k_{1a} \cdot k_{ab}} + \frac{1}{k_{1a}} \quad \text{and} \quad K = \frac{k_{12}}{k_{21}} = \frac{k_{1a} \cdot k_{ab} \cdot k_{b2}}{k_{2b} \cdot k_{ba} \cdot k_{a1}}$$

ⓐ, ⓑ = encounter complexes

classical nomenclatures for metal complex reactions [9]. These classifications have been mainly developed for cases where the step ⓐ → ⓑ is rate determining.

[1]) The high reactivity of the $CH_3Hg(II)$-complexes is probably one of the reasons for their well known toxicity [14]. Other reasons are: a) the pronounced softness of Hg(II); b) the very stable C-Hg-Bond; this bond will not break under ordinary conditions [2]; c) the excellent solubility of the biologically relevant form CH_3HgCl in both lipophilic and hydrophilic solvents.

Table 3. *Rate constants* [$M^{-1}\,s^{-1}$] *for the direct exchange of methylmercury(II) according to*

$$CH_3HgY^+ + X \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} CH_3HgX^+ + Y \quad (I = 1M,\ 20°)$$

X	$\log k_{12}$	$\log k_{21}$	$\Delta \log K$
Y = 1-Methylpyridine-2-thione			
CH_3COO^-	4.74	9.37	−4.63
Cl^-	6.53	9.45	−2.92
NCS^-	7.45	9.69	−2.24
Br^-	7.68	9.33	−1.65
Imidazole	7.9	8.8	−0.90
NH_3	7.94	8.43	−0.49
$(C_6H_5)_2PC_6H_4$-3-SO_3^-	9.2	8.2	1.00
OH^-	8.00	6.78	1.22
Y = 1-Methylquinaldine-4-thione			
Cl^-	5.01	9.46	−4.45
Br^-	6.30	9.42	−3.12
Imidazole	6.76	9.46	−2.70
NH_3	6.93	9.03	−2.10
I^-	8.29	9.39	−1.10
$(C_6H_5)_2PC_6H_4$-3-SO_3^-	8.43	8.98	−0.55
OH^-	7.40	7.69	−0.29
$S_2O_3^{2-}$	9.15	7.95	1.20

If the overall rate constant shows that the reaction is diffusion controlled, then $k_{ab} > k_{a1}$ for $K > 1$ and $k_{ba} > k_{b2}$ for $K < 1$. When the charge product of the reacting species is zero k_{1a}, k_{a1}, k_{2b} and k_{b2} will be about $10^{9.5}$ if a reaction distance (= contact of Hg(II) with the incoming ligand) of about 3 Å is assumed [10b]. According to transition state theory, the free activation energy $\Delta G^{\ddagger}_{ab} = RT(\ln kT/h - \ln k_{ab})$ will be less than 4 kcal/mol for the step (a)→(b) for an exergonic reaction and the same maximum value will hold for $\Delta G^{\ddagger}_{ba}$ for an endergonic reaction. This low activation barrier again demonstrates the excellent bridging ability of $CH_3Hg(II)$ and the intimate mechanism of the step (a)→(b) could most likely be termed I_a [9a], but the overall behaviour is of course determined by diffusion processes.

However, a different behaviour is observed with hydroxide as one of the exchanging ligands (see *Fig. 3*, where the results for other exchanges to and from OH^- are included [2]). In this case, diffusion is no longer rate determining for $-4 < \Delta \log K < 4$ and the observed rate constant k_{12} yields (eq. 6) k_{ab}, because, as already mentioned, k_{1a} and k_{a1} can be calculated for a given charge type and assumed reaction distances [10b]. The reverse reaction can be treated in the same way.

To determine the type of mechanism when hydroxide is involved, the intuitively developed equation (7) was used.

$$\Delta G^{\ddagger} = \frac{1}{2}\left[p \cdot \Delta G + \sqrt{(p \cdot \Delta G)^2 + (2\Delta G_0^{\ddagger})^2}\right] \tag{7}$$

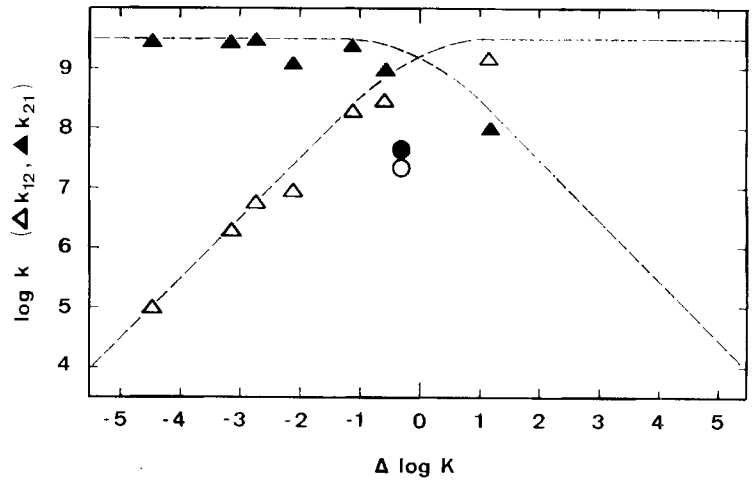


Fig. 1. *log*k$-\Delta$*log*K*-dependence for the* $CH_3Hg(II)$*-exchange between* $Y=$ *1-methylquinaldine-4-thione and* X (from left to right: X= Cl^-, Br^-, imidazole, NH_3, I^-, $(C_6H_5)_2PC_6H_4$-3-SO_3^-, OH^- (circles) and $S_2O_3^{2-}$ according to equation (2)). Broken lines calculated for diffusion controlled reactions with $k_{1a}=k_{a1}=k_{2b}=k_{b2}=10^{9.5}$ [M^{-1} s^{-1}, s^{-1}]. I= 1M, 20°.

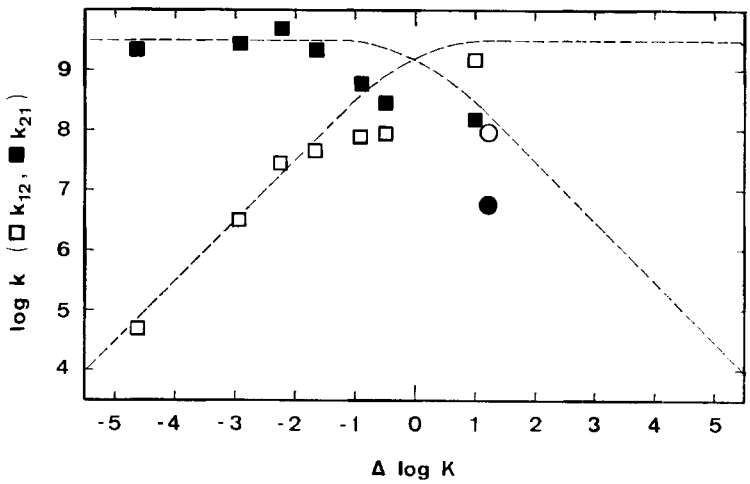


Fig. 2. *log*k$-\Delta$*log*K*-dependence for the* $CH_3Hg(II)$*-exchange between* $Y=$ *1-methylpyridine-2-thione and* X (from left to right: X= acetate, Cl^-, NCS^-, Br^-, imidazole, NH_3, $(C_6H_5)_2PC_6H_4$-3-SO_3^- and OH^- (circles) according to equation (2)). Calculation of broken lines as in *Figure 1*. I= 1M, 20°.

This equation describes the free energy of a transfer step as a function of the standard free energy difference ΔG of the reaction (a)→(b) in equation (6). Two parameters, p and $\Delta G_0^{\ddagger}$ are required. The features of equation (7) are as follows:

a) For p= 1 it is a direct translation of *Hammond*'s postulate [16]: a symmetrical hyperbola with the axis $\Delta G^{\ddagger}=0$ and $\Delta G^{\ddagger}=\Delta G$. The value of $\Delta G^{\ddagger}$ at $\Delta G=0$ is called 'intrinsic barrier', $\Delta G_0^{\ddagger}$ (*Marcus* [17]). It is characteristic for a particular reaction series.

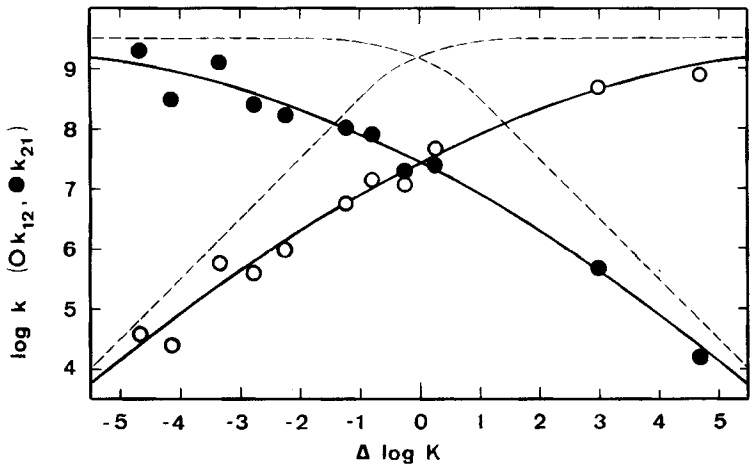


Fig. 3. *log*k$-\Delta$*log*K*-dependence for the* $CH_3Hg(II)$*-exchange between* OH^- *and X* (from left to right: X=pyridine, Cl^-, NCS^-, Br^-, imidazole, 1-methylpyridine-2-thione, I^-, $(C_6H_5)_2PC_6H_4SO_3^-$, 1-methylquinaldine-4-thione, 4-nitrothiophenolate and CN^- according to equation (1)). Calculation of broken lines as in *Figure 1*. Full lines calculated with equations (6) and (7): p=1, $\Delta G_0^{\neq} = 7.2$ kcal/mol, $k_{1a} = k_{a1} = k_{2b} = k_{b2} = 10^{9.5}$ [$M^{-1}\,s^{-1}$, s^{-1}], I=0.1 M, 20°.

b) It allows for the experimentally determined fact of varying participation of an incoming or leaving ligand in the transition state (factor p). In *dissociative* reactions, a variation of the incoming ligand does not alter the exchange rate, hence p=0 ($\alpha=0$, $\beta=-1$ for constant k_{1a}, k_{a1}, k_{2b}, k_{b2}). This holds of course only for $\Delta G^{\neq} > \Delta G$. In *associative* reactions, the incoming ligand participates fully (p=1) according to its coordination tendency. For $\Delta G=0$ and $k_{1a}=k_{2b}$, $k_{a1}=k_{b2}$, the *Brønsted* coefficients will be $\alpha=0.5$ and $\beta=-0.5$. With p-values between 0 and 1 all intermediate cases between the extreme associative and dissociative mechanisms can be described. Equation (7) can equally well be used for two-step mechanisms, if an additional assumption concerning the free energy of the intermediate is made [2].

Applying the transition state theory, the $\Delta G^{\neq}$-values of equation (7) yield exchange rate constants k_{ab}. In combination with diffusion rates, overall rate constants k_{12} and k_{21} respectively can be calculated. Results for a few examples are given in *Figure 4*. Comparison with experimental log*k vs.* Δ log*K* graphs allows a distinction between various reaction types. For the special case p=1, equation (7) yields results numerically comparable to those of *Marcus* [17], *Murdoch* [18], *Agmon & Levine* [19], *Kurz* [20] and many others cited in [20].

The reactivity-stability graph for methylmercury(II) transfer to and from hydroxide *(Fig. 3)* can best be fitted with p=1, $\Delta G_0^{\neq} = (7.2 \pm 0.3)$ kcal/mol and $k_{1a} = k_{2b} = k_{a1} = k_{2b} = 10^{9.5}$ (charge influences are not considered). This indicates an associative one-step mechanism for these reactions. In contrast to most other cases of ligand exchange reactions at metal centers, $CH_3Hg(II)$ is not responsible for this particular intrinsic barrier. It is due rather to the specific structure of the hydrated OH^-. Therefore we propose the term I_{al} for this type of reaction (l meaning activation energy caused by the ligand).

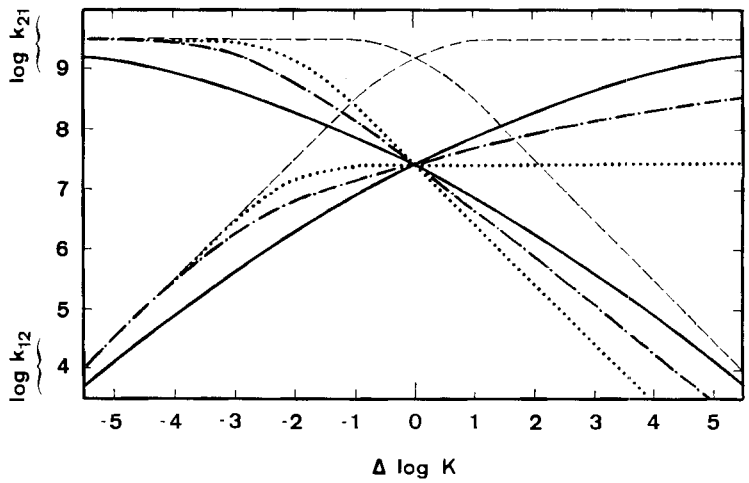


Fig. 4. *Calculated log*k – *Δlog*K*-correlations according to equations (6) and (7) for* $\Delta G_0^{\neq} = 7.2$ *kcal/mol,* $k_{1a} = k_{a1} = k_{2b} = k_{b2} = 10^{9.5}$ [$M^{-1}s^{-1}$, s^{-1}] *and variable p:* p = 1 ————, p = 0.5 – · – · –, p = 0 · · · · · · Calculation of broken lines as in *Figure 1.*

The relatively large activation energy may be explained by the fact that the rather strongly hydrated OH^- can react as $H_7O_4^-$. This is in contrast to other ligands which form complexes (a) and (b) with a direct contact to $CH_3Hg(II)$. The 'ligand' $H_7O_4^-$ is of course a much weaker nucleophile than the finally bound OH^-. Hence, reactions of CH_3HgX with OH^- are only diffusion controlled when X is rather weakly bound. For $-4 < \Delta \log K$, $H_7O_4^-$ must partly dehydrate and for very large $\Delta \log K$ it must fully dehydrate before X can be substituted. The partial dehydration energy appears as activation energy in the region of intermediate $\Delta \log K$ values. If X is very strongly bound, the entry of OH^- is however no longer rate determining, but the reverse reaction, viz. the substitution of OH^- in CH_3HgOH by X, will be diffusion controlled.

We believe that ligand specific activation can be of importance for reactions of many other metal complexes. Because of the same curvature of $\log k$ *vs.* $\Delta \log K$ graphs for I_a as well as I_{al} mechanisms, only sufficient variations of the ligand allow a clear distinction between these types of activation.

Similar rate-equilibria relationships are found in other cases where the free and the methylmercurated ligand differ markedly in structure [12] [13]. In such situations the activation energy of the exchange step is mainly determined by the structural changes of the ligand. Depending on whether this reorganisation of the incoming ligand is assisted by the metallic center or not, p in equation (7) has to be fixed between 1 and 0. The rate-equilibrium correlation for the exchange of such a ligand against various 'uncomplicated' ligands looks like that of classical I_a, I_d and in-between mechanisms where the activation energy is due to the metal center at which the exchange takes place. Again, only sufficient variation of the exchanged ligands can tell whether the coordination center, the ligands or both are responsible for a needed activation.

The equations (6) and (7) would also be useful for the description of proton transfer reactions as well as ligand exchange processes at other metal centers. In the latter case we believe that our analysis of ($\log k - \Delta \log K$)-relations is a useful and transparent extension of the well known *Marcus* treatment [17]. *Marcus* assumes a fully associative transfer step in his treatment[2]) of atom transfer reactions. The transfer step for ligand exchange processes is obviously very often not of an associative type [21]. Therefore, *Marcus* treatment cannot be used in such cases without additional terms. This terms should have a similar function as our p in equation (7). The factor p permits an analysis of all types of ligand exchanges: I_a, I_d, A, D, I_{al} and intermediate cases.

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2) The work required to bring the reactants (or products) together is allowed for with w^r (w^p). However, this treatment is not valid for very fast reactions (see footnote (3) in [17b]). It has to be replaced by a stepwise mechanism as in equation (6). Work terms and eventual steric factors are then included in the calculation of the diffusion rate constants k_{1a}, k_{a1}, k_{2b} and k_{b2}.