CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200902632

# Substantial Inverse Isotope Effects in the Hydrogen Atom Abstraction from $[(L)ClRh^{III}-H/D]^+$ Macrocyclic Complexes by Methyl Radicals in Aqueous Solutions

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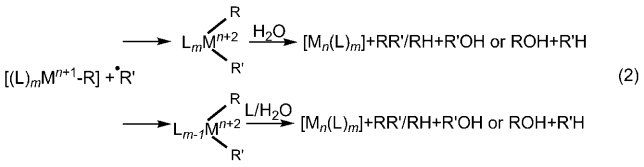
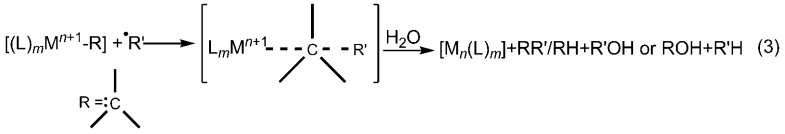
The reaction given in Equation (1) is of importance in a large variety of radical-induced processes. The mechanism of such reactions has been studied only for $R=R'$ and has still not been fully elucidated. All the reactions studied are relatively fast with $k_1 \geq 1\times10^7\,M^{-1}s^{-1}$.[1–5]

$$[(L)_mM^{n+1}-R] + {}^{\bullet}R' \xrightarrow{H_2O} [M^n(L)_m] + RR'/RH + R'OH \text{ or } ROH + R'H \quad (1)$$

In principle, such reactions might proceed by means of either of the following mechanisms [Eq. (2) or (3)]:




(2)




(3)

Recent results[4] for the reaction given in Equation (4) were interpreted as indicating that the reaction proceeds by means of the mechanism outlined in Equation (3). It seemed of interest to check whether this is generally true.

$$[(NH_3)_5Co^{III}-CH_3]^{2+} + {}^{\bullet}CH_3 \xrightarrow{H_2O} [Co(H_2O)_6]^{2+} + 5\,NH_4^+ + C_2H_6 \quad (4)$$

For this purpose it was decided to study the reactions of a variety of radicals, $^{\bullet}R'$ (with a stable $[(L)_mM^{n+1}-R]$ complex). It was decided to choose as a first example an $[(L)_mM^{n+1}-H]$ complex as the hydride ligand imposes no steric hindrance. The first reaction chosen was that given in Equation (5) in which L = 1,4,8,11-tetraazacyclotetradecane (cyclam).

$$[(L)ClRh^{III}-H]^+ + {}^{\bullet}CH_3 \xrightarrow{H_2O} [(L)ClRh^{II}(H_2O)]^+ + CH_4 \quad (5)$$

## Experimental Section

**Materials**: All solutions were prepared from analytical-grade chemicals and distilled water that was passed through a Millipore setup, the final resistance being above $10\,M\Omega\,cm^{-1}$. The *trans*- and *cis*-$[(L)ClRh^{III}-H]^+$ complexes were synthesized according to published procedures.[6,7]

**Irradiation**: The samples were irradiated by a short pulse from the electron linac of the Hebrew University of Jerusalem or in a G-220 Gammacell $^{60}Co$–$\gamma$ source with a dose rate of $16.5\,Gy\,min^{-1}$.

**Gas chromatography analysis**: GC analyses were performed on a HP 5890 gas chromatograph on a pack Q column with FID and TCD detectors.

**Formation of methyl radicals**: When ionizing radiation is absorbed by a dilute aqueous solution the process can be described by Equation (6):[8]

$$H_2O \xrightarrow{\gamma,e^-} e^-_{aq}(2.65);\cdot OH(2.65);H\cdot(0.60);H_2(0.45);H_2O_2(0.75);H_3O^+(2.65) \quad (6)$$

The values in the parentheses are the relative yields of the products as expressed by their $G$ values ($G$ values are defined as the number of

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molecules/species of each product formed per 100 eV radiation absorbed in the solution). The distribution of these products in the solution after $1\times10^{-7}$ s is homogeneous.[8] In $N_2O$ saturated solutions, $[N_2O]=2\times10^{-2}$ M, $e^-_{aq}$ is converted into $^{\bullet}OH$ radicals through Equation (7).[9] Thus, $G(^{\bullet}OH)=6.0$ in $N_2O$ saturated solution is obtained.

$$e^-_{aq} + N_2O \rightarrow N_2 + {}^{\bullet}OH + OH^- \quad k = 8.7\times10^9\ M^{-1}\,s^{-1} \tag{7}$$

The reaction in Equation (7) competes with that given in Equation (8); therefore, one has to work at pH ≥ 3.0 in order to not affect $G(^{\bullet}OH)$ too much.

$$e^-_{aq} + H_3O^+ \rightarrow {}^{\bullet}H + H_2O \quad k = 2.2\times10^{10}\ M^{-1}\,s^{-1}\ [9] \tag{8}$$

When $(CH_3)_2SO$ is added to $N_2O$ saturated solutions the reactions given in Equations (9) and (10) convert the $^{\bullet}OH$ radicals into $^{\bullet}CH_3$ radicals, with $G(^{\bullet}CH_3)=6.0$.[10]

$$^{\bullet}OH + (CH_3)_2SO \rightarrow {}^{\bullet}(CH_3)_2S^{\bullet}(O)OH \quad k = 7.0\times10^9\ M^{-1}\,s^{-1} \tag{9}$$

$$(CH_3)_2S^{\bullet}(O)OH \rightarrow CH_3S(O)OH + {}^{\bullet}CH_3 \quad k = 1.5\times10^7\ M^{-1}\,s^{-1} \tag{10}$$

In the absence of other solutes the $^{\bullet}CH_3$ radicals thus formed are transformed into $CH_4$ and $C_2H_6$ through the reactions given in Equations (11) and (12), respectively.

$$^{\bullet}CH_3 + (CH_3)_2SO \rightarrow CH_4 + {}^{\bullet}CH_2(CH_3)SO \quad k = 100\ M^{-1}\,s^{-1}\ [15] \tag{11}$$

$$^{\bullet}CH_3 + {}^{\bullet}CH_3 \rightarrow C_2H_6 \quad k = 1.2\times10^9\ M^{-1}\,s^{-1}\ [16] \tag{12}$$

The relative yields of $CH_4$ and $C_2H_6$ thus depend on the concentration of $(CH_3)_2SO$ and the dose rate of irradiation.

## Results and Discussion

First, an effort to measure $k_5$ [the rate constant for the reaction given in Eq. (5)] with the pulse radiolysis technique by following the disappearance of the absorption of the complex at 300 nm was made. However even at the highest plausible complex concentration, $1\times10^{-3}$ M, no reaction of the $^{\bullet}CH_3$ radicals with the complex was obtained, indicating that at the high dose rate used in the pulse radiolysis experiment reaction in Equation (5) is too slow to compete with that given in Equation (12).

Then the effect of *cis*- and *trans*-$[(L)ClRh^{III}–H]^+$ on the yield of $CH_4$ and $C_2H_6$ as determined by GC analysis in the considerably lower dose-rate irradiation in a γ source were measured. The results are summed up in Table 1.

It was necessary to work at pH 3.0 ($[HClO_4]=1\times10^{-3}$ M) due to the pH effect on the stability of the $[(L)ClRh^{III}–H]^+$ complexes. At pH 3.0 the radical yield is somewhat smaller than at pH 8.0 as the results demonstrate.

The results clearly demonstrate that:

1) The major product of the reaction given in Equation (5) is $CH_4$ as its yield increases with the complex concentration.
2) As $G(^{\bullet}CH_3)_{total}=G(CH_4)+2\,G(C_2H_6)$ is not affected by the complex concentration clearly reaction given in Equation (13) does not compete significantly with that given in Equation (5). Indeed the formation of $CH_3Cl$ was not observed by GC analysis.

Table 1. Products from irradiated solutions containing 0.01 M and 0.02 M $(CH_3)_2SO$ at various concentrations of $[(L)ClRh^{III}–H]^+$ complexes at pH 3.0 ($[HClO_4]=1\times10^{-3}$ M), dose rate = 16.5 Gy min$^{-1}$.[a]

| Complex [M] | $[(CH_3)_2SO]$ [M] | $CH_4/C_2H_6$ | $G(CH_4)$ | $G(C_2H_6)$ | $G(^{\bullet}CH_3)_{total}$ | $k_5$ [$M^{-1}s^{-1}$] |
|---|---|---|---|---|---|---|
| –[b] | 0.01 | 0.36 | 0.88 | 2.46 | 5.80 | |
| –[b] | 0.02 | 0.37 | 0.96 | 2.52 | 6.00 | |
| – | 0.01 | 0.29 | 0.67 | 2.33 | 5.33 | |
| – | 0.02 | 0.37 | 0.82 | 2.21 | 5.24 | |
| $1\times10^{-4}$ [c] | 0.01 | 1.42 | 2.13 | 1.50 | 5.13 | $2.4\times10^5$ |
| $2\times10^{-4}$ [c] | 0.01 | 5.28 | 3.71 | 0.70 | 5.11 | $3.1\times10^5$ |
| $6\times10^{-4}$ [c] | 0.01 | 46.5 | 5.60 | 0.12 | 5.84 | $3.8\times10^5$ |
| $1\times10^{-4}$ [c] | 0.02 | 1.52 | 2.36 | 1.55 | 5.46 | $2.4\times10^5$ |
| $2\times10^{-4}$ [c] | 0.02 | 4.28 | 3.73 | 0.87 | 5.47 | $2.7\times10^5$ |
| $6\times10^{-4}$ [c] | 0.02 | 37.0 | 5.12 | 0.14 | 5.40 | $3.2\times10^5$ |
| $1\times10^{-4}$ [d] | 0.01 | 0.72 | 1.27 | 1.89 | 5.05 | $1.20\times10^5$ |
| $2\times10^{-4}$ [d] | 0.01 | 1.09 | 1.77 | 1.62 | 5.01 | $9.3\times10^4$ |
| $6\times10^{-4}$ [d] | 0.01 | 6.51 | 3.82 | 0.59 | 5.00 | $1.15\times10^5$ |
| $1\times10^{-4}$ [d] | 0.02 | 0.89 | 1.60 | 1.81 | 5.22 | $1.47\times10^5$ |
| $2\times10^{-4}$ [d] | 0.02 | 1.73 | 2.34 | 1.38 | 5.10 | $1.30\times10^5$ |
| $6\times10^{-4}$ [d] | 0.02 | 4.62 | 3.48 | 0.75 | 4.98 | $9.1\times10^4$ |

[a] Each result is the average of at least a triplicate; error limit of the yields ±15%, of the rate constants ±25%. [b] At pH = 8.0. [c] *trans* Isomer. [d] *cis* Isomer.

$$[(L)ClRh^{III}–H]^+ + {}^{\bullet}CH_3 \xrightarrow{H_2O} [(L)(H_2O)Rh^{II}–H]^+ + CH_3Cl \tag{13}$$

The $k_5$ rate constants of reaction were determined as follows: as $C_2H_6$ is formed only from the reaction in Equation (12) and as its yield per second is measured the steady-state concentration of the $^{\bullet}CH_3$ radicals, $[^{\bullet}CH_3]_{ss}$, can be calculated from Equation (14), the yield of $CH_4$ then is given by Equation (15)

$$G(C_2H_6)\times(\text{dose rate }[Gy\,s^{-1}])\times10^{-7} = k_{12}[^{\bullet}CH_3]^2_{SS} \tag{14}$$

$$G(CH_4)\times(\text{dose rate }[Gy\,s^{-1}]) = (k_{11}[^{\bullet}(CH_3)_2SO] + k_5[\text{complex}])[^{\bullet}CH_3]_{SS} \tag{15}$$

The $k_5$ values thus obtained are summarized in Table 1. The average value of $k_5$ is $(2.8\pm0.7)\times10^5$ and $(1.2\pm0.3)\times10^5\ M^{-1}s^{-1}$ for the *trans* and *cis* isomers, respectively.

In principle $CH_4$ could be formed in the reaction given in Equation (5) through $^{\bullet}H$ atom abstraction from the ligand L. In order to rule out this possibility it was decided to repeat the experiment replacing $[(L)ClRh^{III}–H]^+$ by $[(L)ClRh^{III}–D]^+$. It was expected that this experiment will result in a relatively large kinetic isotope effect (KIE) as all $^{\bullet}H$ atom abstraction from C–H groups involve a large KIE.[11,12] The results of this experiment are summarized in Table 2.

One can see ($G(^{\bullet}CH_3)_{total}$ is not affected by the complex concentration) that as in the reaction of $[(L)ClRh^{III}–H]^+$ complexes with methyl radicals, there is no Cl atom abstraction and no $CH_3Cl$ formation.

The $k_5$ values thus obtained for the deuterated complexes are summarized in Table 2. The average value of $k_5$, that is, the rate constant for the reactions of $[(L)ClRh^{III}–D]^+$ complexes (two isomers) with methyl radical, is $(4.8\pm1.2)\times10^5$ and $(1.8\pm0.6)\times10^5\,M^{-1}s^{-1}$ for the *trans* and *cis* isomers, respectively.

From these results the kinetic isotope effects were calculated to be $k(trans\text{-}[(L)ClRh^{III}–H]^+)/k(trans\text{-}[(L)ClRh^{III}–D]^+)=0.58\pm0.20$ and $k(cis\text{-}[(L)ClRh^{III}–H]^+)/k(cis\text{-}[(L)ClRh^{III}–D]^+)=0.66\pm0.30$. Surprisingly, the results show that $k_5(D)>k_5(H)$, that is, inverse isotope effects are observed.

Table 2. Products from irradiated solutions containing 0.01 M and 0.02 M $(CH_3)_2SO$ at various concentrations of $[(L)ClRh^{III}–D]^+$ complexes at pH 3.0 ($[HClO_4]=1\times10^{-3}$ M), dose rate = 16.5 Gy min$^{-1}$.[a]

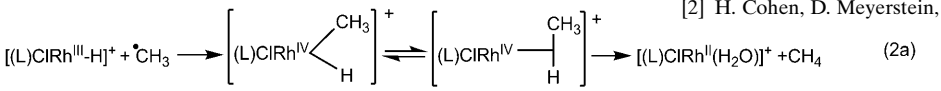
| Complex [M] | [DMSO] [M] | $CH_4/C_2H_6$ | $G(CH_4)$ | $G(C_2H_6)$ | $G(^{\bullet}CH_3)_{total}$ | $k_5$ [$M^{-1}s^{-1}$] |
|---|---|---|---|---|---|---|
| –[b] | 0.01 | 0.31 | 0.74 | 2.64 | 6.02 | |
| –[b] | 0.02 | 0.39 | 1.03 | 2.63 | 6.29 | |
| – | 0.01 | 1.09 | 1.84 | 1.68 | 5.20 | |
| – | 0.02 | 0.90 | 1.58 | 1.76 | 5.10 | |
| $1\times10^{-4}$ [c] | 0.01 | 3.69 | 3.55 | 0.96 | 5.47 | $5.00\times10^5$ |
| $2\times10^{-4}$ [c] | 0.01 | 13.8 | 5.19 | 0.37 | 5.93 | $5.95\times10^5$ |
| $6\times10^{-4}$ [c] | 0.01 | 45.6 | 4.92 | 0.11 | 5.14 | $3.46\times10^5$ |
| $1\times10^{-4}$ [c] | 0.02 | 4.03 | 4.00 | 0.99 | 5.98 | $5.44\times10^5$ |
| $2\times10^{-4}$ [c] | 0.02 | 11.6 | 5.02 | 0.43 | 5.88 | $5.28\times10^5$ |
| $6\times10^{-4}$ [c] | 0.02 | 40.4 | 5.93 | 0.15 | 6.23 | $3.56\times10^5$ |
| $1\times10^{-4}$ [d] | 0.01 | 1.39 | 2.19 | 1.57 | 5.33 | $2.56\times10^5$ |
| $2\times10^{-4}$ [d] | 0.01 | 2.10 | 2.90 | 1.38 | 5.66 | $1.68\times10^5$ |
| $6\times10^{-4}$ [d] | 0.01 | 6.04 | 3.85 | 0.64 | 5.13 | $1.11\times10^5$ |
| $1\times10^{-4}$ [d] | 0.02 | 1.77 | 2.49 | 1.41 | 5.31 | $2.76\times10^5$ |
| $2\times10^{-4}$ [d] | 0.02 | 2.21 | 2.77 | 1.25 | 5.27 | $1.64\times10^5$ |
| $6\times10^{-4}$ [d] | 0.02 | 5.60 | 3.87 | 0.69 | 5.25 | $1.06\times10^5$ |

[a] Each result is the average of at least a triplicate; error limit of the yields ±15%, of the rate constants ±25%. [b] At pH = 8.0. [c] *trans* Isomer. [d] *cis* Isomer.

Inverse apparent kinetic isotope effects are commonly attributed to the involvement of an equilibrium process[13–15] with an inverse equilibrium isotope effect, as an elementary reaction cannot involve an inverse isotope effect. Such inverse isotope effects have been observed for reductive coupling of alkyl hydrides[13–27] and less commonly aryl hydrides.[13,27–29] It is difficult to envisage an equilibrium step for the reaction given in Equation (3a).

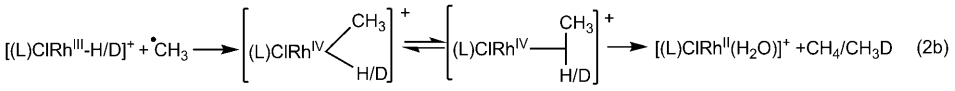
$$[(L)ClRh^{III}–H]^+ + {}^{\bullet}CH_3 \rightarrow [(L)ClRh^{II}\cdots H\cdots CH_3]^+ \rightarrow [(L)ClRh^{III}(H_2O)]^+ + CH_4 \quad (3a)$$

Therefore, the results suggest that the reaction measured involves a reductive C–H coupling, that is, the reaction given in Equation (2a):



(2a)

However, as the isotope effect is measured for a reaction in competition with reactions given in Equations (11) and (12), clearly the equilibrium step in Equation (2a), for analogous reactions of which inverse kinetic isotope effects were reported, is not sufficient as the methyl radicals react in a step that does not involve the Rh–H bond cleavage. Thus it is proposed that the hydrogen atom abstraction studied proceeds through the reaction given in Equation (2b):



(2b)

The suggestion that the first step is also an equilibrium reaction is also reasonable due to the steric constraints around the central Rh ion that has seven ligands.

## Conclusion

1) Methyl radicals abstract an hydrogen atom and not a chlorine atom from $[(L)ClRh^{III}(H_2O)]^+$.
2) The mechanism of the hydrogen atom abstraction involves formation of a Rh–C bond followed by reductive coupling and methane release as outlined in Equation (2b). This mechanism differs from that suggested for the reaction in Equation (4).[4] Clearly we cannot conclude from this study that reaction in Equation (1) always proceeds by means of the mechanism in Equation (2). Thus further studies are required to determine the precise mechanism of this reaction [Eqs. (2) or (3)].
3) This is the first hydrogen atom abstraction reaction studied with an inverse kinetic isotope effect. Thus the results suggest that the mechanism of hydrogen abstraction from M–H groups might differ considerably from that from C–H groups.

## Acknowledgements

The authors wish to thank Dr. A. Masarwa for helpful comments and assistance throughout this study. This study was supported by a grant from the Israel Atomic Energy Committee and from The Planning and Budgeting Committee of the Council of Higher Education.

**Keywords:** elimination · isotope effects · radical reactions · rhodium

[1] A. Sauer, H. Cohen, D. Meyerstein, *Inorg. Chem.* **1988**, *27*, 4578.
[2] H. Cohen, D. Meyerstein, *Inorg. Chem.* **1988**, *27*, 3429.
[3] G. Czapski, S. Goldstein, H. Cohen, D. Meyerstein, *J. Am. Chem. Soc.* **1988**, *110*, 3903.

[4] N. Shaham, A. Masarwa, Y. Matana, H. Cohen, D. Meyerstein, *Eur. J. Inorg. Chem.* **2002**, 87.
[5] A. Masarwa, D. Meyerstein, *Adv. Inorg. Chem.* **2004**, *55*, 271.
[6] A. Bakac, J. H. Espenson, *Inorg. Chem.* **1987**, *26*, 4353,.
[7] E. J. Bounsall, S. R. Korpich, *Can. J. Chem.* **1970**, *48*, 1481.
[8] M. S. Matheson, L. Dorfman, *Pulse Radiolysis*, MIT Press, Cambridge, **1969**.
[9] NIST Standard References Database, Version 2.0, A. B. Ross, W. G. Mallard, W. P. Helman, J. V. Buxton, R. E. Huie, P. Neta, **1994**.
[10] D. Veltwisch, E. Janata, K. D. Asmus, *J. Chem. Soc. Perkin Trans. 2* **1980**, 146.
[11] M. Anbar, D. Meyerstein, *J. Phys. Chem.* **1964**, *68*, 3184.
[12] E. J. Klinker, S. Shaik, H. Hirao, L. Que. Jr. , *Angew. Chem.* **2009**, *121*, 1317; *Angew. Chem. Int. Ed.* **2009**, *48*, 1291.
[13] W. D. Jones, *Acc. Chem. Res.* **2003**, *36*, 140.
[14] G. Parkin, *Acc. Chem. Res.* **2009**, *42*, 315.
[15] A. J. Esswein, A. S. Viege, M. B. Picoli, A. J. Schultz, D. G. Nocera, *Organometallics* **2008**, *27*, 1073.
[16] J. M. Buchanan, J. M. Stryker, R. G. Bergman, *J. Am. Chem. Soc.* **1986**, *108*, 1537.
[17] R. A. Periana, R. G. Bergman, *J. Am. Chem. Soc.* **1986**, *108*, 7332.
[18] M. R. Bullock, C. E. L. Headford, K. M. Hennesy, S. E. Kedley, J. R. Norton, *J. Am. Chem. Soc.* **1989**, *111*, 3897.
[19] G. Parkin, J. E. Bercaw, *Organometallics* **1989**, *8*, 1172.
[20] G. L. Gould, D. M. Heinekey, *J. Am. Chem. Soc.* **1989**, *111*, 5502.
[21] C. Wang, J. W. Ziller, J. C. Flood, *J. Am. Chem. Soc.* **1995**, *117*, 1647.
[22] S. S. Stahl, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **1996**, *118*, 5961,.
[23] D. G. Wick, K. A. Reynolds, W. D. Jones, *J. Am. Chem. Soc.* **1999**, *121*, 3964.
[24] T. J. Northcutt, D. C. Wick, A. J. Vetter, W. D. Jones, *J. Am. Chem. Soc.* **2001**, *123*, 7257.
[25] C. H. Lo, A. Hakel, M. Kapon, E. Keiman, *J. Am. Chem. Soc.* **2002**, *124*, 3226.
[26] M. A. Iron, C. H. Lo, J. M. L. Martin, E. Keinan, *J. Am. Chem. Soc.* **2002**, *124*, 7041.
[27] D. G. Churchill, K. E. Janak, J. S. Wittenburg, G. Parkin, *J. Am. Chem. Soc.* **2003**, *125*, 1403.
[28] W. D. Jones, F. J. Feher, *J. Am. Chem. Soc.* **1986**, *108*, 4814.
[29] W. H. Watson, G. Wu, M. G. Richmond, *Organometallics* **2006**, *25*, 930.

Received: September 24, 2009
Published online: November 27, 2009