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# Mechanistic differences between “reductive” and “oxidative” heterolysis of metal–carbon σ bonds

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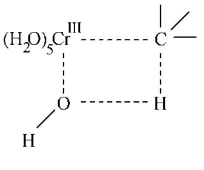
Volumes of activation, $\Delta V^{\ddagger}$, for the heterolysis reactions of copper complexes with metal–carbon σ bonds, *viz.* $[(H_2O)_5Cu^{III}\text{–}R]^{2+}$ ($R = CH_2CO_2^-$ or $CHCl_2^-$) and $[LCu^{II}\text{–}R]^+$ (L = 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane; $R = CH_2CO_2^-$), were determined using high pressure pulse-radiolysis techniques. In addition, the volume of activation for the bimolecular decomposition of $[LCu^{II}\text{–}CH_3]^+$ was determined. The results reveal the different roles of the solvent (water) in the transition states for oxidative and reductive heterolysis reactions.

## Introduction

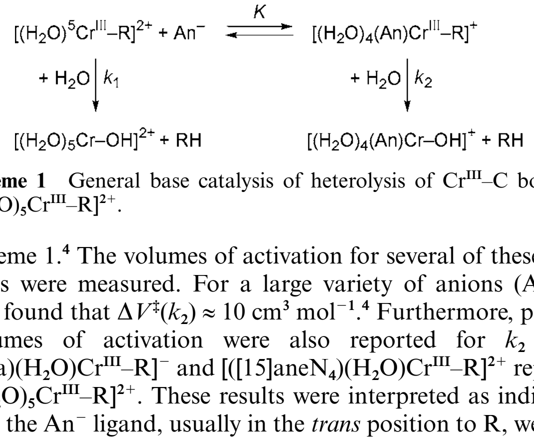
Heterolysis of the metal–carbon σ bond in transient complexes of the type $L_mM^{n+1}\text{–}R$, produced in the reaction of $L_mM^n$ with $^{\bullet}R$, proceeds *via* one of two alternative mechanisms, eqns. (1) and (2). These represent the major decomposition mechanisms

$$L_mM^{n+1}\text{–}R + H_2O \begin{cases} \rightarrow M^{n+1}L_m + RH + OH^- & (1) \\ \rightarrow M^{n-1}L_m + ROH/R_{-H} + H_3O^+ & (2) \end{cases}$$

of complexes with metal–carbon σ bonds in aqueous solutions, and formally involve an overall oxidation or reduction of the metal center during the heterolysis reaction in reference to the starting complex $L_mM^n$. In an effort to elucidate details of the underlying reaction mechanisms, activation volumes have been measured for the heterolysis of several, relatively stable complexes, *e.g.* $[(H_2O)_5Cr^{III}\text{–}CH_2OH]^{2+}$ and $[(H_2O)_5Cr^{III}\text{–}C(CH_3)_2OH]^{2+}$, with $Cr^{III}\text{–}C$ σ bonds that decompose *via* reaction (1).[1,2] These reactions are acid catalysed, *i.e.* their rate obeys the equation $k_1 = k^0 + k^H[H_3O^+]$, and it was found that $\Delta V^{\ddagger}$ for both the acid independent ($k^0$) and acid catalysed ($k^H$) pathways of these reactions is approximately zero.[1] This result was interpreted as suggesting that reaction (1) can be considered as a substitution on the central chromium(III) *via* an interchange (I) mechanism. However, it should be noted that this type of reaction couldn’t be treated as a simple ligand substitution process, since one also has to account for the large H/D solvent kinetic isotope effect observed.[3] The latter suggests that water bond cleavage plays an important role in the transition state of the process, presumably in the following way:



Reaction (1) for $M^{n+1} = Cr^{III}$ was also shown to be general base catalysed, *i.e.* proceeding *via* the mechanism described in Scheme 1.[4] The volumes of activation for several of these reactions were measured. For a large variety of anions ($An^-$) it was found that $\Delta V^{\ddagger}(k_2) \approx 10$ cm$^3$ mol$^{-1}$.[4] Furthermore, positive volumes of activation were also reported for $k_2$ when $[(nta)(H_2O)Cr^{III}\text{–}R]^-$ and $[([15]aneN_4)(H_2O)Cr^{III}\text{–}R]^{2+}$ replaced $[(H_2O)_5Cr^{III}\text{–}R]^{2+}$. These results were interpreted as indicating that the $An^-$ ligand, usually in the *trans* position to R, weakens the chromium–carbon bond, thus shifting the mechanism from pure I to $I_d$.[4] Again water bond cleavage has to be considered.



**Scheme 1** General base catalysis of heterolysis of $Cr^{III}\text{–}C$ bonds in $[(H_2O)_5Cr^{III}\text{–}R]^{2+}$.

In addition, $\Delta V^{\ddagger}$ was measured[2] for the heterolytic decomposition of $[(H_2O)_5Cr^{III}\text{–}CH_2CH(OH)_2]^{2+}$ to investigate whether the positive volume of activation is indeed due to an intrinsic effect induced by the $An^-$ ligand, and not just due to the higher rate of reaction. The rate of heterolysis of the chromium–carbon bond in this complex is considerably faster than that for the anion-catalysed reactions mentioned above. However, $\Delta V^{\ddagger}$ is only 3.3 and 1.9 cm$^3$ mol$^{-1}$ for the spontaneous and acid catalysed pathways of this reaction, respectively, such that these results are in agreement with the earlier conclusions.

A $\Delta V^{\ddagger}$ value of −8.7 cm$^3$ mol$^{-1}$ was determined[2] for reaction (3), which is the fastest of these heterolysis reactions.

$$[(H_2O)_5Cr^{III}\text{–}H]^{2+} + H_3O^+ \longrightarrow [Cr(H_2O)_6]^{3+} + H_2 \quad (3)$$

This result is consistent with the small size of the leaving group, which is outweighed by the volume decrease due to the co-ordination of the larger water molecule and the net concentration of charge.

The question remains whether the mechanistic conclusions reached for the investigated chromium systems also apply to heterolysis reactions of other metal–carbon σ bonds. For this purpose we have now studied the effect of pressure on the

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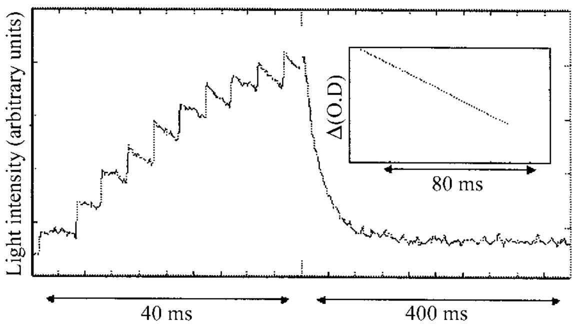


**Fig. 1** Computer output of light intensity *vs.* time. Formation and decomposition of $[LCu^{II}–CH_3CO_2^-]^+$ complex. Solution composition: $2 \times 10^{-3}$ M L, $1 \times 10^{-3}$ M $Cu^+_{aq}$ and 0.1 M Acetate, $N_2O$ saturation, pH 7.5. 10 pulses delivered, pressure = 1500 bar. Inset: kinetics of the disappearance of the $LCu^{II}–CHCO_2^-$ complex, fit to a single exponential.

heterolysis of the copper–carbon σ bond in a complex of the type $[LCu^{II}–R]^+$ (L = 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane; R = $CH_2CO_2^-$), which decomposes *via* the mechanism described by reaction (1), and in complexes of the type $[(H_2O)_5Cu^{III}–R]^{2+}$ (R = $CH_2CO_2^-$ or $CHCl_2^-$), which proceed *via* the mechanism described by reaction (2). The kinetics of formation and decomposition of these complexes was studied earlier under ambient conditions.[5,6] The reported activation volumes reveal important mechanistic information on the way in which the solvent (water) controls the oxidative or reductive character of the heterolysis mechanism.

## Experimental

### Materials

All solutions were prepared from AR grade chemicals and from triply distilled water (distilled water or ion exchange water which was further purified by passing through a Milli Q Millipore set-up, final resistivity >10 MΩ cm$^{-1}$).

### Copper(I) preparation

$Cu^+_{aq}$ was obtained *via* the comproportionation process of $Cu^0$ and $Cu(NH_3)_4^{2+}$ in concentrated $NH_3$, aliquots of which were added to acidic solutions: $Cu(s) + [Cu(NH_3)_4]^{2+} \rightleftharpoons 2[Cu(NH_3)_2]^+$.

### Instrumentation

pH was measured with a Corning 22 pH meter and adjusted by addition of $HClO_4$ and/or NaOH. The experiments were carried out at 20 °C. High pressure pulse radiolysis experiments were carried out using a Varian 7715 linear electron accelerator at the Hebrew University of Jerusalem. The experimental set-up was identical to that described in detail before.[7,8] The reported rate constants are the mean values of at least five kinetic runs, and all high pressure experiments were repeated at least two times.

## Results and discussion

### Decomposition mechanism of the complexes $[(H_2O)_5Cu^{III}–CH_2CO_2^-]$, $[(H_2O)_5Cu^{III}–CHCl_2]^{2+}$ and $[LCu^{II}–CHCO_2^-]$

$N_2O$/Ar-saturated solutions containing (3.0–10.0) × $10^{-4}$ M of $Cu^{2+}_{aq}$ or $LCu^+$, where L = 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane (the concentration of L was always twice that of $Cu^I$), 0.1 M $CH_3CO_2H$ or $CHCl_3$, pH 5.1–5.8, were irradiated by a short electron pulse from the linear accelerator. Under these conditions all the primary radicals are transformed into the desired aliphatic radicals during the pulse.[5,6] In all the systems studied two consecutive processes are observed following the formation of the aliphatic radicals; a typical example is shown in Fig. 1.

**Table 1** Rates of reaction of aliphatic radicals with $LCu^I$ and copper(II) complexes

| Reaction | $k/M^{-1}\,s^{-1}$ | Ref. |
|---|---|---|
| $Cu^{2+}(aq) + {}^{\bullet}CH_2CO_2^- \longrightarrow (Cu^{III}–CH_2CO_2^-)^+$ | $6.4 \times 10^8$ | 5 |
| $Cu^{2+}(aq) + {}^{\bullet}CHCl_2 \longrightarrow (Cu^{III}–CHCl_2)^{2+}$ | $3.0 \times 10^7$ | 5 |
| $LCu^+(aq) + {}^{\bullet}CH_2CO_2^- \longrightarrow (LCu^{II}–CH_2CO_2^-)$ | $2.7 \times 10^7$ | 6 |
| $LCu^+(aq) + {}^{\bullet}CH_3 \longrightarrow (LCu^{II}–CH_3)^+$ | $1.2 \times 10^8$ | 6 |

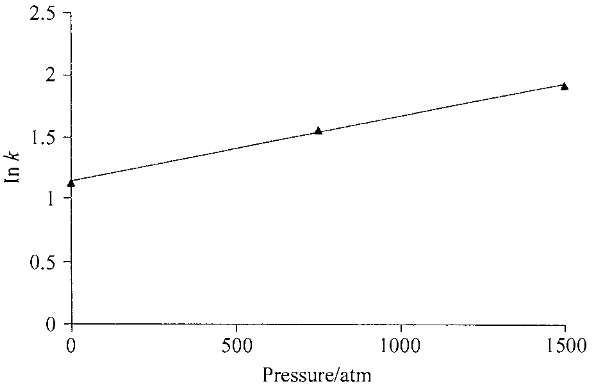
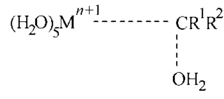


**Fig. 2** Dependence of the decomposition rate constants of the complex $[(H_2O)_5Cu^{III}–CH_3CO_2^-]^+$ on pressure. Solution composition: $1 \times 10^{-3}$ M $Cu^{2+}_{aq}$ and 0.1 M Acetate, $N_2O$ saturation, pH 5.1. 10 pulses delivered.

The kinetics of formation and decomposition of transient complexes with copper–carbon σ bonds were studied before[5,6] and the results obtained in this study are in agreement with these as shown in Tables 1 and 2.

The dependence of the rate constant of the decomposition reaction of the complexes on pressure was measured and the volumes of activation were calculated from the slope $(= -\Delta V^{\ddagger}/RT)$ of a plot of ln *k* *vs.* pressure (see a typical example in Fig. 2). The volumes of activation for heterolysis of the $Cu^{III}–C$ σ bonds of the complexes $[Cu^{III}–CH_2CO_2^-]^+$ and $[Cu^{III}–CHCl_2]^{2+}$ are significantly different, *viz.* −12.4 ± 0.5 and +10.0 ± 0.7 cm$^3$ mol$^{-1}$, respectively, although the observed rate constants are rather similar. The volume of activation for heterolysis of the $Cu^{III}–C$ σ bond of the complex $[LCu^{II}–CH_2CO_2^-]$ is +5.0 ± 1.0 cm$^3$ mol$^{-1}$. These very different values point to important differences in the heterolysis mechanisms and require a more detailed discussion.

Reductive heterolysis of the complexes $[Cu^{III}–CH_2CO_2^-]^+$ and $[Cu^{III}–CHCl_2]^{2+}$ proceeds according to reaction (2). The significantly negative volume of activation found for the heterolysis of $[Cu^{III}–CH_2CO_2^-]^+$ could indicate the direct participation of a solvent water molecule, either binding to the complex in the transition state or undergoing partial ionization to $OH^-$ and $H^+$. Ionization of a water molecule is accompanied by a volume collapse of 22 cm$^3$ mol$^{-1}$ as a result of an increase in electrostriction due to charge creation.[9] If the dissociation of the solvent molecule plays an important role in the rate-determining step then the reaction rate should slow down significantly in $D_2O$. This was checked by repeating the experiments in $D_2O$ as solvent, and no kinetic isotope effect was observed. Thus the latter explanation can be rejected. Bond formation with a solvent molecule in reductive heterolysis will give a transition state of the following type, *i.e.* the water molecule binds to the carbon atom and shifts the M–C σ bond electrons towards the metal center, thus causing its reduction.



$$(H_2O)_5M^{n+1}\text{--------}\underset{\substack{\vdots\\ OH_2}}{CR^1R^2R^3}$$

**Table 2** Summary of observed rate constants

| $10^3[Cu^{2+}]$/M | $10^3[Cu^+]$/M | $10^3$[L]/M | Solute | [Solute]/M | $\lambda^a$/nm | $k_d{}^b/s^{-1}$ | $\Delta V^{\ddagger c}/cm^3\ mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1.0 | — | — | $CH_3CO_2H$ | 0.1 | 390 | 2.8 | −12.4 |
| 0.3 | — | — | $CHCl_3$ | 0.1 | 360 | 0.9 | +10.0 |
| — | 1.0 | 2.0 | $CH_3CO_2H$ | 0.1 | 405 | 11.8 | +5.0 |
| — | 1.0 | 2.0 | DMSO | 0.1 | 380 | $8.6 \times 10^6\ M^{-1}\ s^{-1\,d}$ | −5.0 |

[a] Where the kinetics were measured. [b] Rate constant for the decomposition reaction. [c] Error limit ±1.0 $cm^3\ mol^{-1}$. [d] This is a second order reaction.

Ionization of the water molecule obviously does not play a significant role in the transition state of the process, such that the overall process can be visualized as a water-induced heterolysis reaction. Furthermore, eqn. (4) points out that

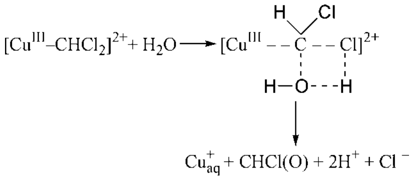
$$[Cu^{III}–CH_2CO_2^-]^+ + H_2O \longrightarrow Cu^+(aq) + CH_2(OH)CO_2^- + H_3O^+ \quad (4)$$

charge is formed in the overall process, which might also partially contribute towards the negative volume of activation.[10]

The significantly positive value found for heterolysis of the $[Cu^{III}–CHCl_2]^{2+}$ complex clearly demonstrates that additional factors contribute to the transition state in this reaction. Two plausible explanations can be offered to account for this observation. (a) The reaction observed is as in eqn. (5a), *i.e.* a process

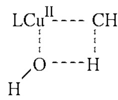
$$[Cu^{III}–CHCl_2]^{2+} + H_2O \longrightarrow Cu^+(aq) + HOCHCl_2 + H^+ \quad (5a)$$

that involves charge dilution that will be accompanied by a decrease in electrostriction and a positive volume of activation. At this point, however, it remains difficult to decide whether the electrostriction contribution can solely account for the large difference in activation volumes (*ca.* 22 $cm^3\ mol^{-1}$) found for reactions (4) and (5a).[10] (b) Alternatively, it could be proposed that the binding of the water molecule to the carbon is accompanied also by induction of cleavage of a C–Cl bond. Thus it is proposed that the reaction observed is as summarized in eqn. (5b). If the transition state is a late one, *i.e.* considerable M–C and C–Cl bond cleavage has already occurred, then these positive volume contributions will compensate for the volume collapse associated with C–O bond formation and result in the overall positive volume of activation observed. (Since $CHCl_2$(OH) is unstable in solution and hydrolyses into HCl and formate, one cannot determine experimentally at which stage the C–Cl bond is broken.) However, the simultaneous cleavage of two bonds may energetically be unfavourable.



(5b)

The small positive volume of activation of +5 $cm^3\ mol^{-1}$ found for the oxidative heterolysis of $[LCu^{II}–CH_2CO_2^-]$ can neither be due to partial co-ordination of a solvent molecule, nor partial ionization of water. It is tempting to suggest as a first approximation that the heterolysis proceeds according to a regular aquation mechanism in which $–CH_2CO_2^-$ is displaced by a water molecule. Such ligand substitution reactions on octahedral copper(II) complexes generally follow a dissociative interchange ($I_d$) mechanism characterized by a small positive volume of activation.[11] However, this suggestion is oversimplified and it is more reasonable that the heterolysis reaction proceeds *via* a similar mechanism to that discussed for the $Cr^{III}$–C σ bond heterolysis in the introduction, and therefore a similar transition state is suggested.

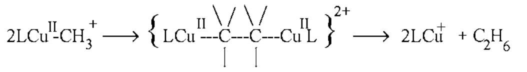


## Decomposition mechanism of the $[LCu^{II}–CH_3]^+$ complex

$N_2O$/Ar-saturated solutions containing $1.0 \times 10^{-3}$ M $LCu^+$, where L = 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane (the concentration of L was always twice that of $Cu^I$), 0.1 M DMSO, and pH 7.5 to 8.0, were irradiated by a short electron pulse from the linear accelerator. The reaction of aquated $Cu^I$ with $^\bullet CH_3$ radicals was studied previously.[6] The results obtained under the present experimental conditions are in accord with the previous ones, see Tables 1 and 2. The decomposition of the transient complex $[LCu^{II}–CH_3]^+$ obeys a second-order rate law and the measured volume of activation is $-5 \pm 1\ cm^3\ mol^{-1}$. The decomposition reaction proceeds *via* reaction (6).[6]

$$2[LCu^{II}–CH_3]^+(aq) \longrightarrow 2LCu^+(aq) + C_2H_6 \quad 2k_6 = 8.6 \times 10^6\ M^{-1}\ s^{-1} \quad (6)$$

Three different routes were suggested for the decomposition mechanism, two being ruled out. That proposed, which fits the previous results, is described in Scheme 2. For the above mechanism it is suggested that the formation of the transition state involves a coherent partial C–C bond formation process, which will be associated with a volume collapse and a stretching of the Cu–C bonds. The latter will be associated with a volume increase that will partially offset the volume collapse. Most likely for the decomposition reaction studied here, the C–C bond formation process is the dominant factor in determining the sign of $\Delta V^\ddagger$. Therefore, the small negative volume of activation that was found supports the suggested mechanism.[6]



**Scheme 2** The suggested decomposition mechanism of the complex $[LCu^{II}–CH_3]^+$.

## Conclusion

The results obtained in this study are in accord with the different roles of the solvent (water) in oxidative and reductive heterolysis of metal–carbon σ bonds in complexes of the investigated type. In oxidative heterolysis reactions the water oxygen binds to the central metal cation and one of its hydrogens bridges to the carbon atom, which gives a concerted four-center transition state. On the other hand, in reductive heterolysis of metal–carbon σ bonds the water oxygen binds to the carbon, thus inducing a shift of the σ bond electrons to the metal. It follows that the specific role of the solvent (water) in inducing an heterolysis reaction differs quite significantly for oxidative and reductive heterolysis reactions.

## Acknowledgements

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## References

1 M. J. Sisley, W. Rinderman, R. van Eldik and T. W. Swaddle, *J. Am. Chem. Soc.*, 1984, **106**, 7432.

2 H. Cohen, R. van Eldik, W. Gaede, A. Gerhard, S. Goldstein, G. Czapski and D. Meyerstein, *Inorg. Chim. Acta*, 1994, **227**, 57.

3 J. H. Espenson, *Adv. Inorg. Bioinorg. Mech.*, 1982, **1**, 1 and references therein.

4 H. Cohen, W. Gaede, A. Gerhard, D. Meyerstein and R. van Eldik, *Inorg. Chem.*, 1992, **31**, 3805; W. Gaede, R. van Eldik, H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1993, **32**, 1997.

5 M. Freiberg and D. Meyerstein, *J. Chem. Soc.*, *Faraday Trans. 1*, 1980, **76**, 1825.

6 N. Navon, G. Golub, H. Cohen and D. Meyerstein, *Organometallics*, 1995, **14**, 5670.

7 S. Goldstein, G. Czapski, R. van Eldik, H. Cohen and D. Meyerstein, *J. Phys. Chem.*, 1991, **95**, 1282; J. F. Wishart and R. van Eldik, *Rev. Sci. Instrum.*, 1992, **63**, 3224.

8 R. van Eldik and D. Meyerstein, *Acc. Chem. Res.*, 2000, **33**, 207.

9 Y. Kitamura and T. Itoh, *J. Solution Chem.*, 1987, **16**, 715.

10 A. Drljaca, C. D. Hubard, R. van Eldik, T. Asano, M. V. Basilevsky and W. J. le Noble, *Chem. Rev.*, 1998, **98**, 2167; G. Stochel and R. van Eldik, *Coord. Chem. Rev.*, 1999, **187**, 329; J. J. Sachinidis, R. D. Shalders and P. A. Tregloan, *Inorg. Chem.*, 1996, **35**, 2497.

11 D. H. Powell, P. Furrer, P. A. Pettit and A. E. Merbach, *J. Phys. Chem.*, 1995, **99**, 16622.