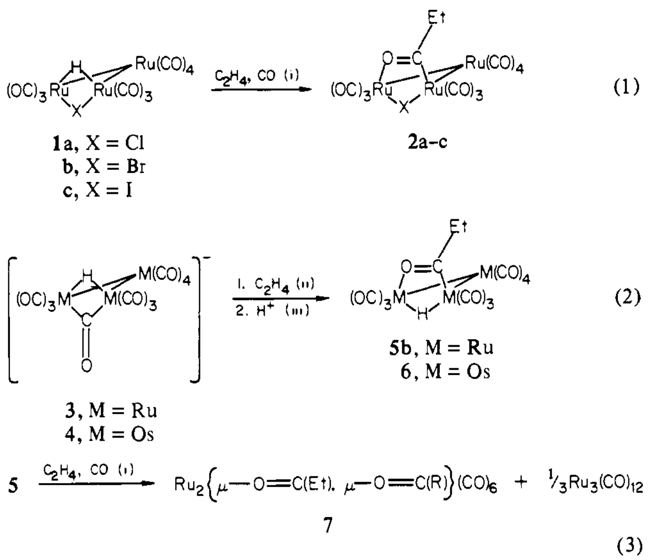
Scheme I[a]



1a, X = Cl
b, X = Br
c, X = I

2a-c

3, M = Ru
4, M = Os

5b, M = Ru
6, M = Os

7

5 or 7	a	b	c	d
R =	Me	Et	Ph	N(Me)$_2$

[a] (i) C_2H_4, 3 atm; CO, 1 atm; 26 °C in hexane. (ii) C_2H_4, 3 atm; 26 °C in THF. (iii) $HBF_4 \cdot 2Et_2O$.

even less than by) other routes,[6] but important in demonstrating this reaction path.

Further reaction of ethylene with any of the acyl- or amido-bridged trinuclear hydride complexes **5a-d** gives the result represented in eq 3 of Scheme I. Mass balance is achieved nearly quantitatively (95–100%). $Ru_3(CO)_{12}$ is crystallized out at −20 °C; when the solution is warmed back to room temperature, half the solvent removed under vacuum, and the solution again cooled to −20 °C, complexes **7a–d** (respectively) are now crystallized out. These compounds can be separated on silica gel columns with 50/50 petroleum ether/CH_2Cl_2.[4b] By ^{13}C NMR[7] and similarity of their IR absorptions to the complex $(OC)_3Fe\{O{=}C(Ph)\}_2Fe(OC)_3$[8] we believe them to be dimers as indicated in Scheme I.

The bridging acyl groups are three-electron donors, and the presence of two of these along one edge of a trimer would require loss of the metal–metal bond between the ruthenium atoms thus bridged.[9] *Instead*, we observe loss of an $Ru(CO)_4$ group giving $Ru_3(CO)_{12}$ and a metal–metal-bonded dimer. The instability of the trinuclear unit with the two bridging μ-acyl groups is an important observation of relevance to the question of the stability of cluster complexes under catalytic conditions.[10]

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-79-08406) and an SERC Fellowship to N.M.B.

Registry No. 1a, 85220-73-1; **1b**, 85220-74-2; **1c**, 85220-75-3; **2a**, 85220-76-4; **2b**, 85220-77-5; **2c**, 85220-78-6; **3**, 85220-79-7; **4**, 85220-80-0; **5a**, 85220-81-1; **5b**, 85220-82-2; **5c**, 85220-83-3; **5d**, 85220-83-3; **6**, 85220-85-5; **7a**, 85220-86-6; **7b**, 85220-87-7; **7c**, 85220-88-8; **7d**, 85220-89-9; $Ru_3(CO)_{12}$, 15243-33-1; $Ru_3(\mu\text{-Br},\mu\text{-O}{=}C(n\text{-}C_3H_7))(CO)_{10}$, 85220-90-2; $Ru_3(\mu\text{-Br},\mu\text{-O}{=}(iso\text{-}C_3H_7))(CO)_{10}$, 85220-91-3; C_2H_4, 74-85-1; propene, 115-07-1.

---

(6) Azam, A. K.; Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1982**, 91–98.

(7) (a) $^{13}C\{^1H\}$ NMR for **7d** (relative to Me_4Si at 26 °C in $CDCl_3$) δ 287.1 ($O{=}C$(Et)), six maxima 206.5 to 195.0, 180.4 ($O{=}CN(CH_3)_2$), 55.5 (CH_2 of Et), 40.3, 34.8 (CH_3 of $O{=}CNMe_2$), 8.19 (CH_3 of Et). (b) IR absorptions in the carbonyl region (in hexane, cm^{-1}). **7a**: 2089 w, 2053 vs, 2019 s, 2012 sh, 1983 m. **7b**: 2086 m, 2052 vs, 2018 s, 2012 sh, 1982 m. **7c**: 2088 m, 2053 vs, 2019 s, 2012 sh, 1983 m. **7d**: 2085 m, 2049 vs, 2012 s, 2008 sh, 1975 m.

(8) (a) Fischer, E. O.; Kiener, V.; Bunbury, D. Dt. P.; Frank, E.; Lindley, P. F.; Mills, O. S. *Chem. Commun.* **1968**, 1378. (b) Lindley, P. F.; Mills, O. S. *J. Chem. Soc. A* **1969**, 1279–1285.

(9) The presence of two three-electron donor groups on the edge of a trinuclear complex results in *loss* of metal–metal bond order along that edge: cf.: (a) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *104*, 297–307. (b) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl. L. F. *Ibid.* **1974**, *70*, 413–420. (c) Mason, R.; Mingos, D. M. P. *Ibid.* **1973**, *50*, 53–61.

(10) (a) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 193. (b) Pittman, C. U., Jr.; Ryan, R. C. *Chem. Technol.* **1978**, 170–175.

Dihydrogen Evolution from Aqueous Vanadium(II)–Cysteine Solutions at pH 6.0–9.5

G. Kalatzis, J. Konstantatos, E. Vrachnou-Astra,* and D. Katakis

Greek Atomic Energy Commission
Nuclear Research Center "Demokritos"
Chemistry Department
Aghia Paraskevi Attikis, Athens, Greece
Inorganic Chemistry Laboratory, University of Athens
Navarinou 13A, Athens, Greece

Received July 27, 1982

Few homogeneous metal ion systems[1] have been reported that are capable of reducing water thermally under mild conditions in alkaline media, and to the best of our knowledge none in neutral solutions. These systems are based on polyamine[2] and pyrochatechol ligands.[3]

We report here on another system based on a sulfur ligand. When excess cysteine is added to a V^{II} solution, substitution occurs, followed by electron transfer to electron acceptors present in the solution and to water in their absence, leading eventually to dihydrogen evolution. These reactions were investigated in the pH range 6.0–9.5 and can be represented by eq 1 and 2. The first

$$V^{II} + \text{cys} \rightarrow V^{II}\text{–cys} \qquad (1)$$

$$V^{II}\text{–cys} + H_2O \rightarrow V^{III}\text{–cys} + HO^- + {}^1/{}_2H_2 \qquad (2)$$

reaction is fast and is monitored by stopped flow. Before mixing, the vanadium(II) solution is acidic. Dihydrogen release is slow—it takes several minutes. During the reaction pH remains within experimental error constant; the system is a fairly good buffer. The data in Table B (supplementary material) show that the stoichiometry of the redox reaction corresponds to eq 2. Stoichiometry measurements were made in the pH range 7.5–8.5, at temperatures between 20 and 62 °C, and with initial concentrations $[V^{II}]_0 = 0.2\text{–}0.1$ M and $[\text{cys}]_0 = 0.62\text{–}1.47$ M, and $[\text{cys}]_0$ to $[V^{II}]_0$ ratios of 6.6–38.

In the pH range investigated precipitation of hydrolyzed vanadium species is avoided by using a large excess of cysteine (always larger than 20-fold). Under these conditions even small amounts of impurities in cysteine may cause extensive oxidation and lead to faulty results. It is, therefore, important to recrystallize the organic reagent (purchased from Riedel-de Haën AG) carefully, under an inert atmosphere.

V^{II}–cys is formed with a rate law first order in V^{II} and in cysteine. The kinetic data were collected in the temperature range 24–54 °C with $[V^{II}]_0 = 3 \times 10^{-4}$ M and $[\text{cys}]_0 = 0.10\text{–}0.64$ M (Table A and Figure A_1, supplementary material). The second-order rate constant depends upon pH and at 24 °C reaches a maximum value $k_2 = 1.00 \pm 0.05\ \text{mol}^{-1}\ \text{L}\ \text{s}^{-1}$ at pH 8.25 (Figure 1). The points in this figure are averages of many measurements. The Arrhenius activation energy (Figure A_2, supplementary material) is $10.0 \pm 1.0\ \text{kcal mol}^{-1}$, in agreement with the value

---

*Address correspondence to this author at the Greek Atomic Energy Commission.

(1) Excluding metal hydrides.

(2) Kopple, K. D.; Svatos, G. F.; Taube, H. *Nature (London)* **1961**, 393.

(3) (a) Nikonova, L. A.; Isaeva, S. A.; Perskowa, N. I.; Shilov, A. E. *J. Mol. Cata.* **1975**, *1*, 367. (b) Schrauzer, G. N.; Palmer, M. L. *J. Am. Chem. Soc.* **1981**, *103*, 2659.

0002-7863/83/1505-2897$01.50/0 © 1983 American Chemical Society

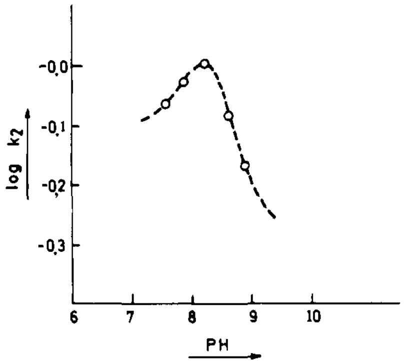


Figure 1. pH dependence of the second-order rate constant of the reaction between V^{2+}(aq) and cysteine. The reaction was followed by stopped flow at 400 nm; $[V^{2+}] = 3 \times 10^{-4}$ M, [cys] = 10^{-1} M; room temperature.

for substitution on $V(H_2O)_6^{2+}$.[4] The preexponential factor is 2.1 × 10^6.

The formation of dihydrogen follows linear first-order kinetics with respect to V^{II}–cys. The value of the rate constant at 21 °C is 2.3×10^{-3} s^{-1}. The estimation was based on dihydrogen and the known stoichiometry (1:0.5). The rate of this stage is independent of the concentrations of cysteine and of pH (in the range 7.5–8.5; Table B, supplementary material). The Arrhenius energy of activation is 12.9 ± 0.4 kcal mol^{-1} (Figure B_1, supplementary material). The preexponential factor is 5 × 10^6.

Products of oxidation and/or reduction of cysteine itself were not detected.

The lack of dependence of the rate of the redox reaction on hydrogen and/or hydroxide ion concentration (10-fold change around pH 8) forces us to rule out separate implication of these ions in the rate-determining step and to suggest that both are involved simultaneously or that neutral water is the reactant. One way both H^+ and HO^- could be implicated is to assume that the form of the complex participating in the rate-determining step of the redox process is hydrolyzed and that this step is catalyzed by acid.

Addition of V^{IV} or cystine, after V^{II}–cys is formed, supresses dihydrogen formation, the product in this case being only V^{III}–cys.

Both V^{II}–cys and V^{III}–cys are intensely yellow. In Figure 2 we compare their spectra with those of $V(H_2O)_6^{2+}$ and $V(H_2O)_6^{3+}$. The main feature is the appearance of two new charge-transfer bands in the UV region, one of which (ca. 280 nm) can be assigned to ligand-to-metal charge transfer. Similar assignments have been made[5] for a variety of other complexes containing metal-to-sulfur bonds. The other band (ca. 390 nm) is tentatively assigned to a metal-to-ligand charge transfer and indicates strong back-bonding. In fact, with mercaptoacetate this back-bonding is so strong that it leads to a net electron transfer from V^{II} to the ligand and to a break of the C–S bond.[6]

The increase in absorptivities and the broadening and the small shifts of the d–d transitions are consistent with the postulate of strong interaction between sulfur and the metal ions.

Spectra of the V^{II}–cys complex could not be taken under conditions of fast hydrogen production (because V^{II}–cys changes quickly to V^{III}–cys and H_2 bubbles form). The V^{III}–cys spectrum, however, did not change appreciably for pH values in the range 7.0–8.5 and for all ratios [cys]/[V^{III}] tried down to the value of 20.

Thus, it seems that the extra electron in the V^{II}–cys system remains delocalized over V^{II} and cysteine, until it is transferred to an oxidant such as V^{IV} or cystine or, by a slower process, to a water molecule. In the absence of oxidants and/or water the electron can presumably be "stored" indefinitely.

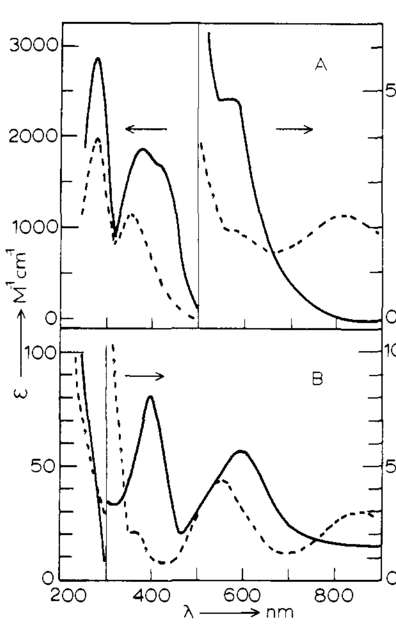


Figure 2. (A) Spectra of V^{II}–cys (---) and V^{III}–cys (—) complexes at pH 8, room temperature; [V^{II}] = [V^{III}] = 9×10^{-4} M, [cys] = 9.4×10^{-2} M. (B) The corresponding spectra for $V(H_2O)_6^{2+}$ and $V(H_2O)_6^{3+}$. The spectra in A were taken with cysteine in the reference compartment.

Registry No. Vanadium, 7440-62-2; L-cysteine, 52-90-4; water, 7732-18-5.

Supplementary Material Available: Tables A and B, containing experimental data for the rate law of the substitution reaction and experimental data for the stoichiometry and the rate law of the redox step, Figures A_1 and A_2, showing kinetic and Arrhenius plots, respectively, for the substitution reaction, and Figure B_1, showing the Arrhenius plot for the redox reaction (4 pages). Ordering information is given on any current masthead page.

---

[4] (a) Price, H. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1. (b) Sutin, N. *Acc. Chem. Res.* **1968**, *1*, 225. (c) R. G. Livick, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, 303.

[5] (a) Schmidtke, H. H. *Ber. Bunsenges. Phys. Chem.* **1967**, *71*, 1138. (b) Jorgensen, C. K. *Inorg. Chim. Acta Rev.* **1968**, *2*, 65. (c) Weschler, C. J.; Deutch, E. *Inorg. Chem.* **1973**, *12*, 2683. (d) Lane, R. H.; Sedor, F. A.; Girloy, M. J.; Eisenhart, P. F.; Bennett, J. P., Jr.; Ewall, R. X.; Bennett, L. E. *Ibid.* **1977**, *16*, 93. (e) Balahura, R. J.; Lewis, N. A. *Ibid.* **1977**, *16*, 2213.

[6] Konstantatos, J.; Kalatzis, G.; Vrachnou-Astra, E.; Katakis, D., busmitted for publication.

Phenomenon of Slowing Down in the Autocatalytic Trypsinogen to Trypsin Conversion in a Continuous-Flow Stirred-Tank Reactor

H. Lachmann and F. W. Schneider*

Institute of Physical Chemistry, University of Wuerzburg
D-8700 Wuerzburg, GFR

Received October 22, 1982

The phenomenon of critical slowing down is an important feature of open nonlinear chemical reactions near points of instability.[1-4] It signifies that the approach to a steady state is very slow near these points. Critical slowing down was predicted theoretically by Schlögl[5] for certain open autocatalytic systems. In recent theoretical work we showed that critical slowing down may occur when a simple autocatalytic reaction A + B → 2B is carried out in a continuous-flow stirred tank reactor (CSTR).[6] Slowing down effects in a CSTR were also calculated by us in computer simulations of a cyclic mechanism of enzymatic poly

---

[1] H. Haken, "Synergetics. An Introduction", Springer, Berlin, 1977.

[2] F. Jähnig and P. H. Richter, *J. Chem. Phys.*, **64**, 4645 (1976).

[3] C. Vidal and A. Pacault, Eds., "Nonlinear Phenomena in Chemical Dynamics", Springer, Berlin, 1981, part IV.

[4] M. Suzuki, K. Kaneko, and S. Takesue, *Prog. Theor. Phys.*, **67**, 1756 (1982).

[5] F. Schlögl, *Z. Phys.*, **248**, 446 (1971); **253**, 147 (1972); *Ber. Bunsenges. Phys. Chem.*, **84**, 351 (1980).

[6] M. Heinrichs and F. W. Schneider, *Ber. Bunsenges. Phys. Chem.*, **84**, 857 (1980); *J. Phys. Chem.*, **85**, 2112 (1981).

0002-7863/83/1505-2898$01.50/0