Kurze Mitteilungen

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Metals in Organic Syntheses. II. The Effect of Molecular Hydrogen on the Highly Regioselective Hydrocarboxylation of Propene Promoted by a $[PdCl_2(PPh_3)_2]$-PPh_3 Catalyst Precursor *

G. Cavinato and L. Toniolo **
Istituto di Chimica Generale ed Inorganica e di Chimica Inorganica Industriale The University, Padua (Italy)

Abstract

The hydrocarboxylation of propene with MeOH or *n*-BuOH promoted by $[PdCl_2(PPh_3)_2]$ as catalyst precursor in combination with added PPh_3, occurs with high selectivity towards the linear ester, particularly at low P_{CO}. The yield is almost independent of P_{CO} (in the range experienced, 13–95 atm) when using MeOH and decreases on decreasing P_{CO} with *n*-BuOH. With this alcohol the yield can be increased in the presence of molecular hydrogen, while maintaining high the selectivity and without aldehyde formation; this hydrogen effect is observed also with MeOH when using toluene as solvent.

In the course of studying the hydrocarboxylation of propene using the most common primary, secondary, and tertiary alcohols, in the presence of a $[PdCl_2(PPh_3)_2]$-based catalyst, we have recently reported that reaction (I) occurs in high yields within a few hours in every case except with *t*-BuOH, at 90–130 °C, under P_{CO} ranging from ca. 120 to *ca.* 40 atm, with 40–50% selectivity towards the linear isomer [1].

$$CH_3CH{=}CH_2 + CO + ROH \rightarrow \begin{matrix} CH_3CH_2CH_2COOR \\ CH_3CHCOOR \\ \quad | \\ \quad CH_3 \end{matrix} \qquad (I)$$

R = Me, Et, *n*- and *iso*-Pr, *n*-, *iso*-, *s*-, and *t*-Bu

Palladium complexes are widely used as carbonylation catalysts [2]. With simple catalysts such as $PdCl_2$ or $[PdCl_2(PPh_3)_2]$ generally the branched ester predominates [3,4,1]. Knifton has reported that complexes of the type $[MCl_2L_2]$-$M'X_2$ (M = Pd or Pt; L = 5B or 6B donor ligand; X = halogen; M = 4B metal) provide bimetallic catalysts which are highly selective towards the linear isomer [5,6]. Thus, for example, with $[PdCl_2(PPh_3)_2]$-$SnCl_2$ (Pd/Sn = 1/10) and MeOH as hydrogen donor, the *n*-butyrate ester forms with 85% selectivity under P_{CO} = 136 atm, at 70 °C, in methylisobuthylketone as solvent [6]. However, we have found that the yield is unsactisfactory when using the same amount of propene as that used in the study reported here which is greater than that used by Knifton. On increasing the temperature to 90–100 °C the yield cannot be much improved because the catalyst decomposes giving off some PPh_3 which suppresses the reaction.

Here we report that the high selectivity can be achieved using $[PdCl_2(PPh_3)_2]$ as catalyst precursor in combination with added PPh_3, particularly at low carbon monoxide pressure.

Thus, for example, propene is carbonylated under 95 atm of CO yielding the esters in *ca.* 60% yield and *ca.* 70% selectivity towards the linear isomer (see

Table 1: Hydrocarboxylation of Propene Catalyzed by $[PdCl_2(PPh_3)_2]$-PPh_3 [a].

Run No	Alkanol, Solvent	P_{CO}, atm	PH_2 atm	Yield % [b]	Regioselectivity % [c]
1	MeOH	95	–	53	66
2	*n*-BuOH	95	–	61	73
3	MeOH	13	–	50	70
4	*n*-BuOH	13	–	13	86
5	MeOH, T	95	–	100	57
6	*n*-BuOH, T	95	–	100	51
7	MeOH, T	13	–	70	66
8	*n*-BuOH, T	13	–	91	60
9	*n*-BuOH	95	–	55	75
10	MeOH	13	13	50	70
11	*n*-BuOH	13	13	49	81
12	MeOH, T	13	13	100	62

[a] Carbonylations were carried out in a *ca.* 100 ml stainless steel stirred autoclave. Reagents were contained in a pyrex bottle placed in the autoclave to prevent any contamination from other metallic species. The autoclave was "washed" with carbon monoxide at *ca.* 0 °C, charged with propene at 30 °C (10 atm), thermostated at 100 °C, charged with hydrogen (when used), and with carbon monoxide, in this order. (The free volume of the autoclave was reduced to *ca.* 65 ml by the bottle and reagents).

[b] moles of esters pro mole of propene used (except in expts. 5–8 and 12: moles of esters pro mole of alcohol, because propene was in excess).

[c] *n*-butyrate/total esters yield.

T = toluene

Run conditions: 25 mmole of propene; 0.1 mmole of $[PdCl_2(PPh_3)_2]$; 0.2 mmole of PPh_3 except in expt. 9 where 0.25 mmole was used; 0.1 mole of *n*-BuOH (9.3 ml) or 0.23 mole of MeOH (9.3 ml) except in expts. 5–8 and 12 where 0.02 mole of alcohol was used together with toluene (total volume = 9.3 ml); 100 °C, 4 hr (expt. 12 was practically over in 3 hr).

* Received March 29, 1979
** Author to whom correspondence should be addressed

Table, expts. 1 and 2). On lowering the P_{CO} to 13 atm, the selectivity increases; the yield decreases, as it might be expected, only when using *n*-BuOH: rather surprisingly the yield is almost independent of P_{CO}, in the range experienced, when using MeOH (expts. 1–4). The difference in the regioselectivity and in the dependence of the yield with P_{CO} when using MeOH or *n*-BuOH may be due to different mechanisms, in addition to a solvent effect. Note that, when using toluene as solvent, higher yields are obtained under higher P_{CO}, with both alcohols, and that a higher selectivity is achieved with MeOH in respect to *n*-BuOH. The comparison of expts. 1–8 indicates a considerable solvent effect; moreover, it is interesting to observe that a higher selectivity is achieved at the expense of the yield, and viceversa.

The fact that on lowering P_{CO} the regioselectivity increases suggests that the regioselective step is controlled by several intermediates at equilibrium differring from the relative number of PPh_3 or CO ligands coordinated to the metal: under lower P_{CO} the equilibria are shifted towards bulkier catalytic species, thus a higher regioselectivity can be achieved. This suggestion is supported by the fact that a higher regioselectivity is observed when using a larger amount of PPh_3 (compare expt. 2 with 9; only steric factors have here been considered since usually they prevail on the electronic factors when using catalysts having phosphine ligands [6, 7].

It is remarkable that, when using MeOH, the ester forms in relatively good yield even under low P_{CO} (expt. 3): with other alcohols and other palladium-based catalysts a much higher P_{CO} is required [2–4, 6].

With *n*-BuOH under low P_{CO} the yield can be increased, while maintaining a high selectivity, by carrying out the carbonylation in the presence of molecular hydrogen (compare expt. 4 with 11). Under these conditions no aldehyde has been detected in the reaction products. Rather surprisingly, using MeOH in place of *n*-BuOH, under the same conditions, the above beneficial hydrogen effect is not observed (compare expt. 3 with 10). This discrimination may be due to a solvent effect and/or to different reaction mechanisms. Note that using toluene as solvent the beneficial hydrogen effect is observed also with MeOH (compare expt. 7 with 12). The greater hydrocarboxylation rate may be explained both by an enhanced rate in the formation of a Pd-H bond or in the cleavage of a Pd-C bond, in a mechanism occurring *via* insertion of the olefin into a Pd-H bond [8] or to a Pd-COOR bond [9].

No data have been reported in the literature dealing with such a hydrogen effect, though Fenton has found that small partial pressures of hydrogen lead to an increase in yield and also in regioselectivity in the hydrocarboxylation of 1-octene to acids, using water in place of an alcohol as hydrogen donor, $PdCl_2/PPh_3$ = 1/4 as catalyst, and acetic acid as solvent, at 125 °C [9]. Further studies are in progress dealing with the factors controlling the regioselectivity and the hydrogen effect in connection with the reaction mechanism.

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References

1 *G. Cavinato* and *L. Toniolo:* J. Mol. Catal., in the press.
2 *I. Wender* and *P. Pino:* "Organic Syntheses via Metal Carbonyls", Vol. II, *J. Wiley:* New York, London, Sydney, Toronto 1977.
3 *J. Tsuji, M. Morikawa,* and *J. Kiji:* Tetrahedron Lett. (1963) 1437.
4 *K. Bittler, N. v. Kutepow, D. Neubauer,* and *H. Reis:* Angew. Chem., Int. Ed. Engl., *7* (1968) 329.
5 *J. K. Knifton:* J. Org. Chem., *41* (1976) 793.
6 *J. K. Knifton:* J. Org. Chem., *41* (1976) 2885.
7 *C. K. Brown* and *G. Wilkinson:* J. Chem. Soc. A (1970) 2753.
8 *J. Tsuji:* Accounts Chem. Res., *2* (1969) 144.
9a) *D. M. Fenton:* J. Org. Chem., *38* (1973) 3192.
b) *D. M. Fenton:* U.S. Patent 3,641,074 (1972), to Union Oil Company of California.

Collision-induced Mass Analyzed Ion Kinetic Energy (CID/MIKE) Spectra of Isobaric Ions *

D. Stahl ** and J.C. Tabet
Institute of Physical Chemistry, Federal School of Technology, Lausanne, Switzerland

Abstract

Collision-induced mass analyzed ion kinetic energy spectra of isobaric ions requiring a mass separation of 3500 prior to analysis of kinetic energy of fragments has been achieved on a VG-ZAB-2F mass spectrometer. Examples of spectra of a single ionic species obtained under these conditions are given.

* Received June 8, 1979
** Author to whom correspondence should be addressed:
Dr. D. Stahl, Institut de chimie physique, EPFL, Ecublens, CH-1015 Lausanne

Reverse-geometry mass spectrometers for the study of metastable ions and collision-induced dissociation spectra have been described by Beynon and al. [1, 2]. In CID/MIKE spectra the attention is usually focussed on the energy resolution which is obtained by narrowing the slits at the focal points of the electric analyzer. When several ions of different composition are present within a single mass unit, high mass resolution by the magnetic sector is necessary to obtain

the CID/MIKE spectrum of a single ionic species. Maquestiau and al. [3] have mentionned the separation of $C_3H_6^+$ and $C_2H_2O^+$ at m/z = 42 (resolution of about 1200) prior to kinetic energy analysis of collision induced fragments. The present communication describes the possibility of obtaining CID/MIKE spectra of isobaric ions requiring an even higher mass separation by the first sector of the instrument.

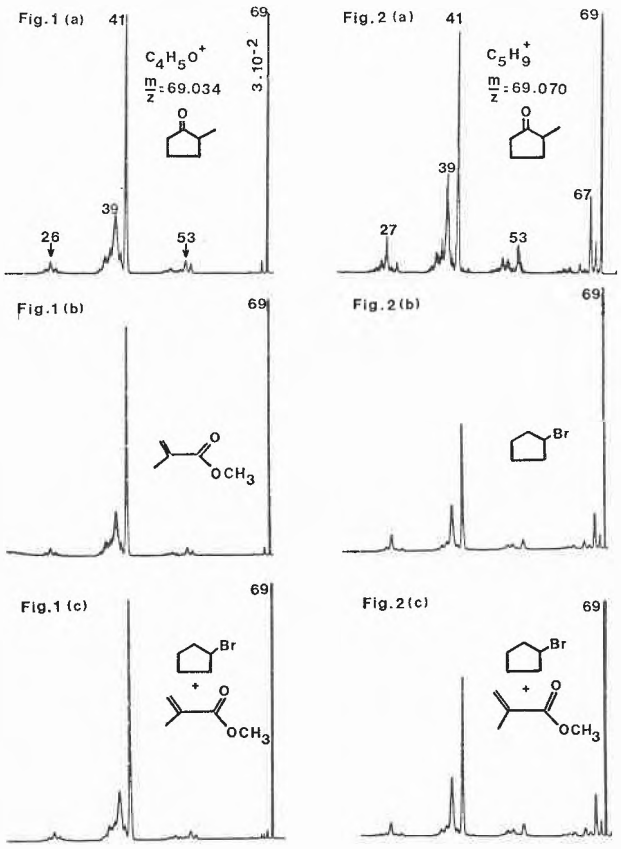

Fig. 1: CID/MIKE spectra of $C_4H_5O^+$ ion
a) separated from $C_5H_9^+$ at m/z = 69 in 2-methylcyclopentanone
b) generated from pure methylmethacrylate
c) separated from $C_5H_9^+$ in a 1/1 mixture of cyclopentylbromide and methylmethacrylate

Fig. 2: CID/MIKE spectra of $C_5H_9^+$ ion
a) separated from $C_4H_5O^+$ in 2-methylcyclopentanone
b) generated from pure cyclopentylbromide
c) separated from $C_4H_5O^+$ in the mixture of methylmethacrylate and cyclopentylbromide

Fig. 1 (a) and Fig. 2 (a) show the CID/MIKE spectra of $C_4H_5O^+$ and $C_5H_9^+$, respectively, obtained by loss of $C_2H_5^\cdot$ and $HCO^\cdot$ from the molecular ion of 2-methylcyclopentanone. As expected $C_4H_5O^+$ and $C_5H_9^+$ have different CID/MIKE spectra. In the group of C_2 fragments, the main peak is at m/z = 26 for $C_4H_5O^+$ while for $C_5H_9^+$ it lies at m/z = 27. The group of fragments containing 3 C atoms looks more similar in both spectra except for the width of peaks at m/z = 39. Other differences are seen on the m/z = 53 and m/z = 67 regions. It was of prime interest to verify that each spectrum does not include a contribution from the other species. The mass spectrum of cyclopentylbromide contains a singlet at m/z = 69 ($C_5H_9^+$ after a loss of $Br^\cdot$ from the molecular ion). Loss of a methoxyradical from the molecular ion of methylmethacrylate also leads to a singlet $C_4H_5O^+$ at m/z = 69. Fig. 1 (b) and Fig. 2 (b) represent the CID/MIKE spectra of $C_4H_5O^+$ from $C_5H_8O_2$ and of $C_5H_9^+$ from C_5H_9Br, respectively. Each compound was introduced separately into the ion source. Fig. 1 (c) and Fig. 2 (c) show the spectra of the same ions when a mixture 1/1 of cyclopentylbromide and methylmethacrylate is used. Spectra (a), (b) and (c) of Fig. 1 are exactly the same. This is also true for (a), (b) and (c) of Fig. 2. This demonstrates that the CID/MIKE spectrum of $C_5H_9^+$ at m/z = 69,070 does not contain any contribution from the ion $C_4H_5O^+$ at m/z = 69,034 and vice-versa. Furthermore the analogy between spectra (a) and (b) of Fig. 1 reveals that the $C_4H_5O^+$ ions from 2-methylcyclopentanone and from methylmethacrylate have the same CID/MIKE spectrum. This indicates that either they have the same structure, or that the same mixture of different structures is present. The same holds for the two $C_5H_9^+$ ions from 2-methyl-cyclopentanone and from cyclopentylbromide. Discussion of the structure of ions obtained in the mass spectroscopy of cycloalkanones will be published later.

Experimental

The spectrometer used is the ZAB-2F manufactured by VG-Micromass Ltd [2]. Measurements were made at 8 kV accelerating voltage and 100 μA trap current with 70 eV electrons. The resolution of the magnetic

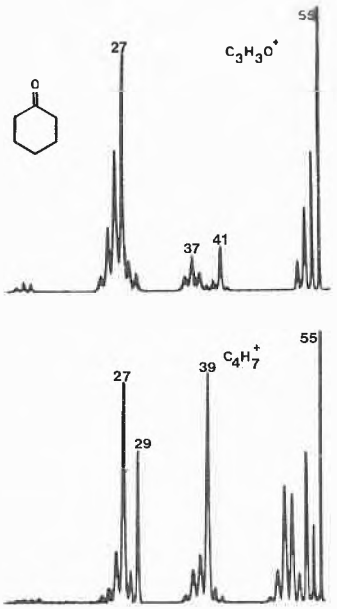

Fig. 3: CID/MIKE spectra of $C_3H_3O^+$ and $C_4H_7^+$ at m/z = 55 from cyclohexanone.

sector was set at 3300 (much higher than the required resolution to separate $C_5H_9^+$ from $C_4H_5O^+$ at m/z = 69; $M/\Delta M$ = 1900). At this resolution it is of the greatest importance that, during the electric sector scan, both magnet field and accelerating voltage remain as constant as possible. Possible drifts in the magnetic field are corrected by use of a beam-lock circuit [2,4]. The energy resolution was fixed at 1200 for the spectra given here. It was then raised to 4000 by reducing the width of the collector slit without much of a loss in sensitivity.

In conclusion it has been shown that the CID/MIKE spectra of two ions could be resolved in a experiment requiring a resolution of about 3500 for mass separation before kinetic energy analysis of the fragments. This type of experiment is extremely important in the following cases:

a) the measurement of the translational energy T released in the fragmentation of ions.
b) determination of ion kinetic energy loss Q as given by the peak position.
c) in the analysis of single compounds or complex mixtures which can lead to ion fragments of nearly equivalent m/z. The former case is clearly demonstrated by the different spectra in Fig. 3.

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References

1 *J. H. Beynon, R. G. Cooks, J. W. Amy, W. E. Baitinger* and *T. Y. Ridley:* Anal. Chem., *45* (1973) 1023 A.
2 *R. P. Morgan, J. H. Beynon, R. H. Bateman* and *B. N. Green:* Int. J. Mass Spectrom. Ion Phys., *28* (1978) 171.
3 *A. Maquestiau, Y. Van Haverbeke, R. Flamang, C. De Meyer* and *A. Mann:* Org. Mass Spectrom., *12* (1977) 709.
4 *P. D. Bolzon, G. W. Trott, A. G. Brenton* and *J. H. Beynon:* Int. J. Mass Spectrom. Ion Phys., *29* (1979) 179.

Ruthenium Oxide, a Suitable Redox Catalyst to Mediate Oxygen Production from Water *

J. Kiwi and M. Grätzel **
Institut de Chimie Physique, Ecole Polytechnique Fédérale, Lausanne, Suisse

Abstract

RuO_2 dispersions were found to catalyze in aqueous solution the one electron reduction of Ce^{4+} and $Ru(bipy)_3^{3+}$ ions under simultaneous evolution of oxygen from water. The reaction is first order with respect to the concentration of oxidants and in the case of Ce^{4+} the specific rate is 0.3 h^{-1} at ambient temperature and 2 h^{-1} at 50 °C. The rate is drastically augmented when colloidal Ru dispersions are employed.

Dispersions of noble metal oxides, such as PtO_2, in aqueous solution have recently shown [1] to be capable of mediating oxygen evolution from water via

$$4D^+ + 2H_2O \rightarrow 4D + 4H^+ + O_2 \quad (1)$$

where D^+/D stands for a redox couple whose standard potential is more positive than $E^\circ(O_2/2H_2O)$. The importance of these redox catalysts lies in the fact that they may be used in artificial light energy conversion systems as a substitute for their biological counterpart, i.e. the defect electron storage system in photosystem II. In our search for catalytic materials that are more stable and efficient than PtO_2 we have discovered unique, and from the standpoint of photoinduced water splitting, highly desirable properties of RuO_2 on which we wish to report in the present communication.

As an electrode material RuO_2 distinguishes itself by a low overvoltage for O_2 release from water [2]. Also in the domain of potentials and *p*H relevant for oxygen production it displays extremely high stability [3]. Finally, in water it forms a macrodispersion which can readily be brought in or removed from contact with the aqueous environment.

In order to explore the efficacy of RuO_2 as a mediator in reaction (1), we used a test system consisting of a Ce^{4+} solution in 1 N aqueous H_2SO_4. Under these conditions the Ce^{4+} ion is stable although from its redox potential, $E^\circ(Ce^{4+}/Ce^{2+}) = +1.44$ V, it should spontaneously liberate oxygen from water:

$$4Ce^{4+} + 2H_2O \rightarrow 4Ce^{3+} + 4H^+ + O_2 \quad (2)$$

In the absence of redox catalyst, this reaction fails to occur as it has to proceed through high energy intermediates, e.g. OH radicals.

Cerium (IV) sulfate (*Merck*, p.a.) and RuO_2 (*Alfa*, hydrated) were used as supplied. Ruthenium tris-bipyridinium (II), (99.9 %) was obtained from Strem. Deionized water was distilled from a MnO_4-solution, and subsequently twice from a quartz still. All solutions were deaerated prior to use by flushing with Ar or N_2. The quantitative analysis of the oxygen produced via reaction (2) was carried out with an "end-O-mess" model D instrument (Friedrichsfeld GmbH, Mannheim, West Germany). An inert carrier gas (N_2) removes the oxygen from the reaction vessel and leads it directly into the detection system. The calibration was performed by injecting varying amounts of O_2 in the degassed Ce^{4+}- and catalyst-free solution. With this method, the reproducibility of the data was shown to be better than 95 % and the lower detection limit of the technique 10^{-7} M. During the experiments the reaction mixture was stirred with the catalyst at a constant speed of 300 r.p.m. The stirring was interrupted

* Received June 21, 1979
** Prof. Dr. M. Grätzel, Institut de Chimie physique, EPFL-Ecublens, CH-1015 Lausanne

periodically to allow for removal of O_2 and spectroscopic analysis of the solution.

Results obtained are presented in Fig. 1 which shows the decrease in Ce^{4+}-concentration and the formation of O_2 as a function of time. At 20 °C the initial Ce^{4+} reduction rate is 16.3×10^{-3} M/ltr/h which is about 16 times higher than that observed with PtO_2 under identical conditions. The rate decreases as the conversion to Ce^{3+} proceeds, the time law being first order with respect to Ce^{4+} concentration over almost the total reaction time. From a semilogarithmic plot, we obtain a rate constant of 3 h^{-1}. Also in Fig. 1 is illustrated the influence of temperature on the catalytic activity of RuO_2. At 50 °C the Ce^{4+} reduction rate is drastically increased, the rate constant being here 12 h^{-1}. This result is particularly interesting as similar temperatures may prevail in solar energy devices.

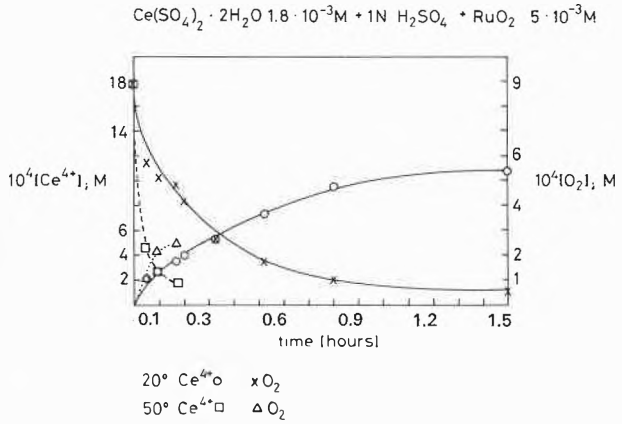

Fig. 1: Rate of oxygen evolution in Ceric sulfate IV dissolved in 1 N H_2SO_4 as a function of time.
- O oxygen evolution in a 5×10^{-3} M RuO_2 catalyzed solution stirred at 300 RPM and 20 °C
- × Ce^{4+} ion decrease in the same solution 300 RPM, 20 °C
- Δ oxygen evolution at 50 °C, same solution, no stirring
- □ Ce^{4+} ion decrease in the same solution at 50 °C, no stirring.

An augmentation of the reaction rate is also observed when the concentration of RuO_2 in the solution is increased. This effect is illustrated in Fig. 2 where spectral data obtained with solutions of 1.2×10^{-2} M RuO_2 are presented. Within a time interval of only 10 min., the Ce^{4+} absorption has disappeared and is replaced by the Ce^{3+} spectrum. Evidently, the increase in RuO_2 concentration improves the area of contact of the catalyst with the aqueous solution resulting in a higher efficacy. Extraordinary high O_2 evolution rates were obtained when colloidal dispersions of RuO_2 were employed as a redox catalyst. These effects will be described in a forthcoming publication.

The analysis of the gas evolved during the stirring process showed that O_2 is produced from the Ce^{4+} reaction with water. In fact from Fig. 1 it is seen that the oxygen formation occurs concomitantly with the conversion of Ce^{4+} into Ce^{3+}. The concentration ratio $r = \frac{-\,d\,(Ce^{4+})}{d\,(O_2)}$ should be 4 if reaction (2) proceeded quantitatively.

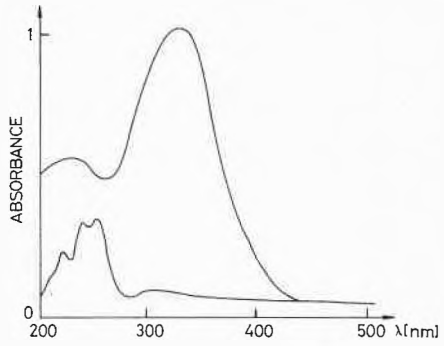

Fig. 2: Upper curve: spectrum of a 1.8×10^{-3} M Ce^{4+} solution in 1 N H_2SO_4.
Lower curve: same solution as above, stirred 30 min. at 300 RPM with 1.2×10^{-2} M RuO_2 at 20 °C.

In most of the experiments we found initially a higher r-value, i.e. around 6, that decreased to 4 during the course of the Ce^{4+} reduction process. The slight O_2-deficiency found at the onset of the reaction can be attributed to chemisorption of O_2 on RuO_2 [4]. Taking this into account, it may be concluded that the oxidation of water is quantitative in the presence of redox catalyst. In order to ascertain the correctness of this interpretation, a series of blanc experiments was performed. First, a Ce^{4+} solution in 1 N H_2SO_4 was stirred over a 24-hour period in the absence of catalyst. Practically, no depletion of Ce^{4+} and absolutely no O_2 formation was observed. Also, no O_2 could be detected after prolonged stirring of the catalyst in 1 N H_2SO_4 in the absence of Ce^{4+}. From these observations, it is inferred that the presence of both Ce^{4+} and RuO_2 is required in order that oxygen formation from water can take place. The role of the RuO_2 particles may be envisaged to be that of a defect electron storage system: through electron transfer from the catalyst to Ce^{4+} ions an anodic potential is imposed on these microelectrodes which is sufficiently positive to induce water oxidation. Under standard conditions, the free energy available to drive reaction (2) is -200 mV. Apparently, the very low over-voltage for O_2-evolution on RuO_2 allows the redox process to occur quantitatively and at high speed. In the course of this investigation, it was found that water oxidation can also be achieved by oxidants other than Ce^{4+}. For example, the trivalent tri-bipyridine complex of ruthenium, $Ru(bipy)_3^{3+}$, in an aqueous solution of *p*H 2 in the presence of RuO_2 is reduced to the bivalent form, $Ru(bipy)_3^{2+}$, with simultaneous liberation of oxygen. This result is significant with regards to the eventual use of $Ru(bipy)_3^{2+}$ as the photoactive electron donor in a light energy conversion system. The excited state of this species can reduce certain electron acceptors [5], which in turn have the chemical potential to produce hydrogen from water:

$$Ru(bipy)_3^{2+} + A \rightarrow Ru(bipy)_3^{3+} + A^- \quad (3)$$

$$2A^- + H_2O \rightarrow H_2 + 2A + 2OH^- \quad (4)$$

Though the hydrogen formation usually does not

occur spontaneously, it may also be mediated by redox catalysts such as PtO_2 [6,7], colloidal platinum [6,8,9] and gold [9]. Hence, through a combination of selective redox catalysts, cyclic water splitting may become feasible.

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Literature References

1 *J. Kiwi* and *M. Grätzel:* Angew. Chem., Int. Ed. Engl., *17* (1978) 860.
2 *H. H. Miles:* J. Electroanal. and Interf. Electrochem., *60* (1975) 84.
3 *M. Pourbaix:* Atlas d'Equilibres Electrochimiques, Gauthier-Villars, Paris 1963.
4 *J. T. Sommerfeld* and *G. Parravano:* J. Phys. Chem., *69* (1965) 102.
5 *H. D. Gafney* and *A. W. Adamson:* J. Amer. Chem. Soc., *94* (1972) 8238.
R. C. Young, T. J. Meyer and *D. G. Whitten:* ibid., *98* (1976) 286.
6 *B. V. Koryakin, T. S. Dzhabier* and *A. E. Shilov:* Dokl. Akad. Nauk. SRRR, *238* (1977) 620.
7 *J. Kiwi* and *M. Grätzel:* Helv. Chim. Acta, *61* (1978) 2720.
8 *J. M. Lehn* and *J. P. Sauvage:* Nouveau J. Chim., *1* (1977) 449.
9 *A. Morapour, E. Amouyal, P. Keller* and *H. Kagan:* Nouveau J. Chim., *2* (1978) 547.