OSCILLATORY GAS EVOLUTION DURING THE VISIBLE-LIGHT-INDUCED CLEAVAGE OF WATER IN PLATINUM-FREE CLAY–HYDROXIDE SUSPENSIONS[†]

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Summary

The visible light irradiation of a mixed colloidal system prepared from sepiolite–$Ru(bpy)_3^{2+}$–RuO_2 (bpy $\equiv$ 2,2'-bipyridine) composite particles and $Al_x Eu_{1-x}(OH)_3$ gels leads to the oscillatory evolution of hydrogen and oxygen. With respect to the previously reported results obtained with $Al_x Eu_{1-x}(OH)_3$–Pt, the following differences were obtained: (i) the amplitude of the oscillations and the total amount of gas are much smaller; (ii) the descending part of the oscillations is more gradual; (iii) the oscillations are no longer damped. All these features are related to the catalytic properties of platinum. The origin of the oscillations (either physical or chemical) is briefly discussed.

The variety of photochemical systems leading to the generation of temporal, spatiotemporal or spatial structures is now considerable (see for example ref. 1). Recently [2], we reported the occurrence of photochemical oscillations in a system characterized by the following combination of physicochemical features: (i) visible light is the energy source; (ii) the oscillatory behaviour affects the evolution of gases; (iii) the reactions take place at a solid–solid or a solid–solution interface in a mixed colloidal dispersion. The process that we were studying was the photodecomposition of water into hydrogen and oxygen according to a classical reaction scheme based on a light-induced electron transfer from a sensitizer S to an acceptor A, followed by two catalytic reactions in parallel:

$$S + A \xrightarrow{\quad h\nu \quad} S_{ox} + A_{red} \tag{1}$$

$$S_{ox} + OH^- \xrightarrow{\text{Cat}_{ox}} S + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \tag{2}$$

$$A_{red} + H^+ \xrightarrow{\text{Cat}_{red}} A + \tfrac{1}{2}H_2 \tag{3}$$

In our original system, S was the $Ru(bpy)_3{}^{2+}$ ion (bpy $\equiv$ 2,2′-bipyridine), A was europium(III), Cat_{ox} was RuO_2 and Cat_{red} was platinum. To minimize all the possible "short-circuits" of such a reaction scheme (the most important being $S_{ox} + A_{red} \rightarrow S + A$), the actual system was designed in such a way as to couple, as closely as possible, S_{ox} with Cat_{ox} and A_{red} with Cat_{red}. This was achieved by compartmentalizing the system into two subsystems at a microscopic level: the sensitizer and the catalyst for oxygen evolution were deposited onto negatively charged colloidal clay particles, whereas the catalyst for hydrogen evolution was deposited onto positively charged aluminium hydroxide particles in which the acceptor ions (Eu^{3+}) were embedded. When both solids are dispersed together in water, spontaneous association by electrostatic interaction takes place [3], allowing efficient electron transfer from the excited sensitizer to the acceptor [4] while still keeping the oxygen and the hydrogen generation sites well separated from each other. This system was found to yield a mixture of hydrogen and oxygen on illumination with visible light in a closed stirred static (no gas circulation) reactor, but, as pointed out above, the gas evolution displayed an oscillatory behaviour in the majority of cases [2]. Puffs of gases, separated by periods during which the pressure in the reactor decreased steadily, were observed. The periodicity of the oscillations was reasonably constant (20 - 40 min), but their amplitude decreased; the production of gas did not last for longer than a few hours. The truly catalytic nature of the process was not clear since the maximum turnover number for the $Eu^{3+}|Eu^{2+}$ electron relay was only 5.

One obvious conclusion of our previous work was that recombination of hydrogen and oxygen took place in our closed reactor. This is not surprising since platinum is known to be an excellent catalyst for hydrogen–oxygen recombination. We report here the behaviour that we observed on removal of platinum from the system. *A priori*, the removal of platinum may be expected to limit the loss of hydrogen and oxygen, but it may also be expected to decrease the rate of hydrogen formation by the reduced europium ions. We have already shown that under sacrificial conditions, *i.e.* with a secondary electron donor such as ethylenediaminetetraacetic acid which is oxidized instead of OH^-, the rate of photoreduction of H^+ is considerably smaller when no platinum is deposited onto the hydroxide particles containing the europium ions [4].

The reaction was studied as previously in a cylindrical closed static reactor with a total volume of 100 ml. Irradiation was performed from below with a blower-cooled 1000 W tungsten–halogen lamp (Osram SLV 1000; Superphot) through a 10 cm water filter. The reactor was filled with 50 ml of aqueous clay–hydroxide suspension, and the same volume was thus

left for the gas phase. The lower part of the reactor, containing the suspension, was thermostatted at 25 ± 0.5 °C. The mixture was continuously stirred from the side with a magnetic stirrer at 200 rev min^{-1}. The pressure in the gas phase was measured with a Bell and Howell 4100-01 transducer. The reactor was connected to a classical vacuum line and gas-handling system, which was used to degas the suspension before irradiation and which allowed for direct injection of the evolved gases into a gas chromatograph.

The fibrous clay was sepiolite, as in our previous work, with a nitrogen Brunauer–Emmett–Teller surface area of 330 m^2 g^{-1}. It was first loaded with 2 wt.% RuO$_2$, by decomposition of RuO$_4$, and activated at 300 °C overnight. It was then loaded with 10 mmol Ru(bpy)$_3^{2+}$ per gram of clay, as described previously. The mixed Al–Eu hydroxide was prepared by adding 1 N NaOH to a solution of the nitrates, up to pH 10. The precipitate was centrifuged and freezedried. No platinum was added. The aluminium:europium molar ratio was 0.7:0.3. The reaction mixtures were prepared by dispersing the clay and the hydroxide colloids in phthalate buffer at pH 4.2, which is below the isoelectric point of the hydroxide (about 6.0 determined potentiometrically).

As shown in Fig. 1(a), the oscillatory behaviour observed in this study, in the absence of a platinum catalyst, is drastically different from the damped oscillatory behaviour previously observed when the hydroxide colloid was loaded with platinum metal [2]. The oscillations are no longer damped. On the contrary, their amplitude increases as the reaction proceeds but, simultaneously, the time interval between successive pressure rises becomes longer. Finally, no more gas evolution is observed.
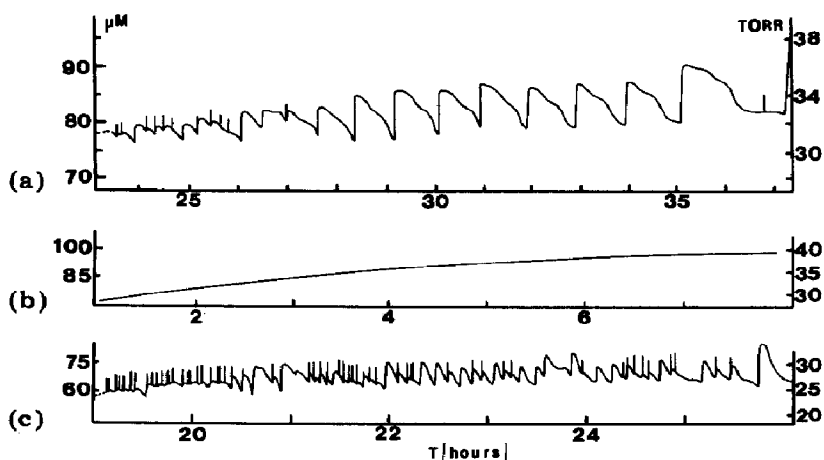

Fig. 1. Typical parts of pressure recordings during the photolysis of water in a closed static photoreactor as described in the text. Two different runs are illustrated: (a) first run, a stable oscillating regime which shows the gathering character of the oscillations; (b) second run, the non-oscillating region which was observed at the beginning of the experiment; (c) second run, the unstable regime which settled in after the gas phase had been sampled for analysis. After the unstable regime of (c) an oscillating regime very similar to that shown in (a) was observed.

Notwithstanding this "crescendo" behaviour (up to the final catastrophe) the amplitude of the oscillations remains much lower than in platinum-containing systems. The largest oscillations correspond to a turnover of about 0.1 electron per europium ion, compared with about 1.0 for the very first (*i.e.* the largest) oscillation with the platinum—hydroxide colloid [2]. The rate of recombination, in the decreasing part of the oscillations, is also slower than with platinum. Both features may be quite easily understood in terms of the catalytic properties of platinum which, as already pointed out above, catalyses both the hydrogen evolution reaction from europium(II) and hydrogen—oxygen recombination.

Figures 1(b) and 1(c) show an interesting phenomenon which may provide a clue for understanding the instabilities of our system. The reaction run which is shown first followed a continuous oscillation-free regime for more than 16 h (Fig. 1(b)). The gas phase was then expanded in the gas-handling system for chromatographic analysis. This lowered the pressure in the reactor from 40 to 20 Torr. From there on, growing instabilities were observed, which turned into an oscillatory regime very similar to that illustrated in Fig. 1(a), for more than 20 h.

It is also noteworthy that, in spite of the stirring of the suspension, gas bubbles were observed in our reactor. They gave rise to almost instantaneous pressure peaks, which appear as spikes in the pressure recordings (Fig. 1). They can in no way be confused with the oscillations, which are characterized by a much longer time scale. However, the gas evolution in the rising part of the oscillations is so rapid that a gas bubble very often forms at this point.

Several non-photochemical gas evolution oscillators have been reported in the literature [5 - 8]. The oscillatory evolution of carbon monoxide during the decomposition of formic acid in concentrated sulphuric acid (the Morgan reaction [5]) has been particularly well investigated, both experimentally and theoretically. Noyes and coworkers [9, 10] showed clearly that a smooth non-oscillatory input of carbon monoxide coupled with nucleation and growth of gas bubbles can lead to oscillatory gas pulses, even with "gentle" or "moderate" stirring. This type of purely physical mechanism, relying on the repetitive release of supersaturation by homogeneous nucleation, has certainly to be considered seriously in our case, especially in view of the triggering effect that we observed on sampling the gas phase (hence modifying the gas—solution equilibrium). However, against it, we have to point out that neither the photoreduction nor the photo-oxidation of water under sacrificial conditions exhibits oscillatory gas evolution in the same experimental system [4].

A detailed kinetics analysis of the cyclic photochemical cleavage of water by a mechanism identical with that considered here (reactions (1) - (3) plus the "back" electron transfer reaction from A_{red} to S_{ox}) has already been presented by Dung and Kozak in this journal [11] and elsewhere [12]. The time evolution of the system and the asymptotic stability of the photo-stationary state were analysed by kinetics and thermodynamic methods. The

main conclusion was that, although the asymptotic stability of the single photostationary state is guaranteed, small perturbations of the system away from this steady state could be rectified by an oscillatory return to the steady state. Interestingly, the possibility of "overshoots" in the concentrations of intermediates such as A_{red} was also established by time evolution studies, especially in regimes of suppressed catalytic activity. Dung and Kozak [11] suggested that, in order to take advantage of such overshoots (the production of hydrogen for instance is obviously coupled to the concentration of A_{red}), it may be desirable to run the system away from the steady state, by opening it to mass transfer for instance. The development of oscillations in our closed reactor, after removal of the gas phase for chromatographic analysis, might well be related to such overshoots.

Although we are still far from a detailed understanding, in kinetics terms, of the complex colloidal system we are dealing with, it is encouraging to see that the type of behaviour that we observe is not unexpected on a theoretical basis. It is clear, however, that several side-reactions have to be taken into account if we want to improve our insight into the system. Some of these side-reactions may be included in reaction loops. This is the case for the hydrogen—oxygen recombination reaction which takes place as well in the presence as in the absence (although more slowly) of a platinum catalyst. Oxidation and reduction reactions of the surface of the catalyst particles also fall into this category. Other side-reactions may have an irreversible character. This would be the case for the structural modifications of the Al—Eu hydroxide, which may be involved in the irreversible poisoning of the system. Side-reactions involving dissolved oxygen and the reduced acceptor may also seriously reduce the efficiency of hydrogen production, as shown by recent numerical simulations [13]. These various considerations suggest that one way of approaching, in a stationary regime, the optimal conditions which seem to be currently realized only transiently in the rising part of the oscillations would be to run the reaction in a continuous flow photochemical reactor. Attempts in this direction are in progress (with considerable experimental difficulties related to the very small gas volumes which are produced). The results will also help in deciding whether physical or chemical processes are responsible for the oscillatory behaviour.

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