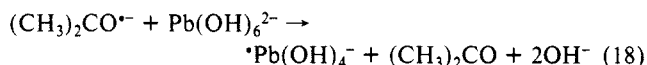
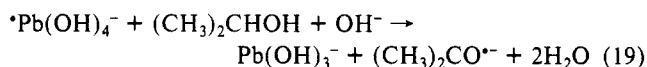


reduction being  $\text{Pb(OH)}_4^-$ . The efficiency of the various organic radicals to reduce  $\text{Pb(OH)}_6^{2-}$  is quite different.

The reduction became a chain reaction in solutions containing propanol-2 or methanol, i.e., in which strongly reducing 1-hydroxyalkyl radicals were produced. These radicals are protolytically dissociated at pH = 13.<sup>5</sup> The first step in the reduction of  $\text{Pb(OH)}_6^{2-}$  is formulated as an electron transfer from the radical to the solute, such as



In order to carry on the chain reaction, a reaction of the  $\text{Pb}^{\text{III}}$  species formed with the alcohol has to be postulated, where the 1-hydroxyalkyl radical is re-formed:



The fact that the rate of the chain reaction increases linearly with alcohol concentration (Figure 9) shows that reaction 19 is the rate-determining step of chain growth. Furthermore, as the chain length increases linearly with the reciprocal square root of intensity (inset of Figure 9) one can say that the chains are terminated by the mutual deactivation of the reactive intermediate of reaction 19. This reaction, eq 9, occurs with  $2k = 4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The standard stationary-state treatment gives the following expression for the rate of  $\text{Pb}^{2+}$  formation:

$$\frac{d[\text{Pb}^{2+}]}{dt} = \frac{k_{19}}{(2k_9)^{1/2}} [\text{ROH}] I^{1/2} + I \quad (20)$$

where the intensity  $I$  is expressed as rate of radical formation and the  $k$ 's are the rate constants of the corresponding reactions ( $\text{ROH}$  = alcohol). The mean chain length is obtained by dividing this expression by the intensity:

$$l = \frac{k_{19}}{(2k_9)^{1/2}} [\text{ROH}] I^{1/2} + 1 \quad (21)$$

(5) Asmus, K.-D.; Henglein, A.; Beck, G. *Ber. Bunsen-Ges. Phys. Chem.* **1966**, *70*, 756.

From the slope of the straight line in Figure 9 and using the above value for  $2k_9$  one obtained  $k_{19} = 1.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . The rate constant of reaction 18 was determined pulse radiolytically by following the build up of the absorption of the  $\text{Pb}^{\text{III}}$  species in a solution of  $\text{Pb(OH)}_6^{2-}$  in which  $(\text{CH}_3)_2\text{CO}^\bullet$  radicals were generated. To avoid a chain reaction, the solution did not contain propanol-2 but 0.1 M acetone as  $e_{\text{aq}}^-$  scavenger; it is well-known that the reaction of  $e_{\text{aq}}^-$  with acetone also yields  $(\text{CH}_3)_2\text{CO}^\bullet$ .  $k_{18} = 1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was found.

In the case of *tert*-butyl alcohol, no chain reaction occurs. The yield of 2.7/100 eV of  $\text{Pb}^{2+}$  formation is exactly the yield of formation of hydrated electrons. An equal amount of the non-reducing  $\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$  radical, which has little reducing power,<sup>6</sup> is also formed in this solution. The irradiation experiment in presence of  $\text{N}_2\text{O}$ , in which only  $\text{CH}_2(\text{CH}_3)_2\text{COH}$  radicals were generated, gave a reduction yield of almost zero, which shows that this radical is not able to reduce  $\text{Pb(OH)}_6^{2-}$ . However, as two electrons are required to reduce the  $\text{Pb}^{\text{IV}}$  species to the bivalent state, one must conclude that the second electron must somehow have been delivered by the alcoholic component. The pulse radiolysis experiments showed that the intermediate  $\text{Pb}^{\text{III}}$  state, i.e.  $\text{Pb(OH)}_4^-$ , from reaction 15 is able to react with *tert*-butyl alcohol. As this reaction does not lead to a radical of high reduction power (as in the case of primary or secondary alcohols) a chain reaction cannot develop. We tentatively propose that the electron transferred from an alcohol to  $\text{Pb(OH)}_4^-$  stems from a nonbonding orbital of the alcoholic oxygen atom. It has previously been pointed out that this transfer can occur in the oxidation of ethyl alcohol and acetone by a species having an oxidation potential of 2.0 V (on the standard electrochemical scale).<sup>7</sup> The transfer is accompanied by the loss of a proton from the alcohol, creating the corresponding free radical.

**Registry No.**  $\text{Pb}^{2+}$ , 14280-50-3;  $\text{Pb(ClO}_4)_2$ , 13637-76-8;  $\text{Pb(OH)}_2^+$ , 3352-57-6;  $\text{OH}^\bullet$ , 125474-93-3;  $\text{Pb(OH)}_3^+$ , 125474-94-4;  $\text{Pb(OH)}^\bullet$ , 12168-64-8;  $\text{PbO}_2$ , 1309-60-0;  $\text{Pb(OH)}_3^-$ , 18155-37-8;  $\text{Pb(OH)}_6^{2-}$ , 125474-75-1;  $(\text{PbO}_2)_2$ , 125474-11-7;  $\text{Pb}^{3+}$ , 18466-73-4; *tert*-butyl alcohol, 75-65-0; propanol-2, 67-63-0; methanol, 67-56-1.

(6) Henglein, A. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1976; Vol. 9, p 163.

(7) Frank, A. J.; Grätzel, M.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1976**, *80*, 593.

## ADDITIONS AND CORRECTIONS

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**Victoria M. Knepp and Richard H. Guy\***: Transport of Steroids at Model Biomembrane and across Organic Liquid-Aqueous Phase Interfaces.

Page 6818. The first reference to Figure 1 should be omitted.

Page 6819. The first reference to Figure 2 should be to Figure 1, and the first reference to Figure 3 should be to Figure 2B.