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Study of Highly Reactive Inorganic Intermediates Using a Fast Coulostatic Technique

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Highly reactive inorganic intermediates can be produced by fast perturbation techniques such as irradiation of a system by short pulses of ionizing radiation. Recently convenient and reliable information on transient species has been obtained by combining electrochemical techniques with radiation chemical methods. In the present work are reported experimental results and the physical-chemical properties of the primary radicals of water dissociation, H and OH, obtained by a fast coulostatic technique after irradiation of the system with 30 ns X-ray pulses.

Introduction

In the last 15 years a variety of electrochemical methods have been used to study the reactions involving highly reactive inorganic intermediates, produced by the energy transferred to the system from short pulses of radiation. The best known of these are methods involving studies of transient changes in electrical conductivity [1–13]. Simple conductivity methods were introduced by Henglein and co-workers [1], and give much novel information. Subsequently, this experimental approach was developed further and in its more advanced form yielded quantitative information about the physical and chemical properties of primary radiation chemical products observed for aqueous and alcoholic media [8–11]. Another less obvious electrochemical approach involves the study of photocurrents observed during the irradiation of electrodes with light, these currents being initiated by the light-induced deposition of hydrated electrons in solution [14, 15]. A further method of considerable interest is the study, using polarographic techniques, of currents at mercury electrodes caused by electrochemical reactions involving species formed by pulses of ionizing radiation employing either electron pulses from a Linac or X-ray pulses from a pulsed Van der Graff generator or a Febetron electron accelerator [16–19]. This galvanostatic method was first employed successfully by Henglein and co-workers [16] and recently a more involved variant, requiring measurements under so-called quasi-coulostatic conditions has been developed at Bologna* [19].

In the present paper attention is focused mainly on the quasi-coulostatic method for the polarographic study of radiation-produced intermediates.

Coulostatic Study of Current Associated with Electrochemical Reactions Involving Species Formed by Pulse Radiolysis

A major problem in the detection and measurement of electrical signals connected with the reduc-

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*The term 'galvanostatic' here implies current measurement at supposedly constant potential. 'Coulostatic' implies no flow of charge from the external circuit(s), *i.e.* a virtually open circuited cell.

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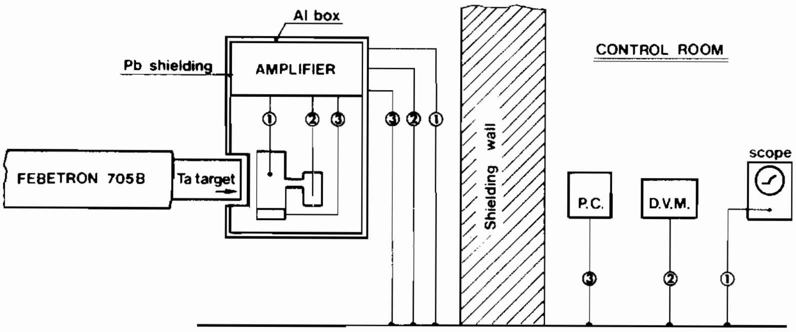

Fig. 1. Schematic layout of the quasi-coulostatic system: DME, ①, dropping mercury electrode; SCE, ②, saturated calomel electrode; CE, ③, counter electrode; PC, potential control; DVM, digital voltmeter.

tion or oxidation of transient species using a reliable electrode, such as the conventional dropping mercury electrode (DME) used in polarography, is the avoidance of complications in the analysis of experimental data caused by the reaction of intermediates in pairs, at the same time obtaining an adequate signal: noise ratio.

The most promising solution to these difficulties is to study, instead of the electrode current at supposedly constant potential, the small gradual (coulostatic) change in electrode potential with elapsed time produced by the same current when there is virtually no short-term control of potential.

The coulostatic change in the interfacial potential produced by the faradaic current across the double layer at the working electrode is given by

$$\Delta E = \frac{1}{C_{dl}} \cdot \int_0^t \Sigma_{x=A,B,C} i_x dt \qquad (1)$$

where t is the elapsed time, i_x is the contribution of the species X to the total faradaic current density at the electrode surface and C_{dl} is the specific differential capacity. If only one species reacts at the electrode, the process being virtually diffusion-controlled, and there is no loss of the intermediate in question by reaction in pairs, or by reaction with any other intermediate, the change in interfacial potential is proportional to $t^{1/2}$ and is given by

$$\Delta E = \frac{1}{C_{dl}} \cdot \frac{2nF}{\pi^{1/2}} \cdot D_x^{1/2} C_x t^{1/2} \qquad (2)$$

where n is the number of electrons involved in the faradaic reaction of the electroactive species and D_x and C_x are its diffusion coefficient and concentration respectively, and F is the faraday.

Employing this experimental approach the double layer capacity of the test electrode in effect becomes a current integrating capacity.

Experimental

In Fig. 1 is shown schematically the apparatus that has been used [1] in conjunction with a 2 MeV Febetron electron accelerator, the thin tantalum X-ray target of the latter providing an intense X-ray pulse of 30 ns duration. This pulse originates close to the dropping mercury electrode, DME, of the 3-electrode polarographic cell but, as indicated in the figure, the X-ray target lies just outside a large thick-wall aluminium screening box containing (a) the cell and (b) a lead-screened preamplifier. Experimental data in the coordinates voltage–elapsed time are processed using a Hewlett-Packard desk calculator, and are first subjected to deconvolution to remove slight distortion caused by the finite time constant (order of 0.5 ms) of the combination of drop double layer capacity and cell resistance plus amplifier input resistance. Subsequently the corrected data are processed for the simultaneous occurrence of more than one electrochemical reaction and also for effects such as those caused by the reaction of intermediates in pairs, Fig. 2.

Dosimetry

The yields of the species produced by energy transfer from ionizing radiation are measured as G-values, defined by

$$G(X) = \frac{n(X)}{\text{Dose (eV)}} \times 100 \qquad (3)$$

where n(X) is the number of molecules produced, destroyed or changed per each 100 eV of energy absorbed by the system.

A convenient system for the determination of the dose absorbed, using coulostatic and galvanostatic techniques, is 10^{-3} *M* $K_4Fe(CN)_6$ solution saturated with N_2O. The ferricyanide formed by reaction 4:

$$Fe(CN)_6^{-4} + OH \longrightarrow Fe(CN)_6^{-3} + OH^- \qquad (4)$$

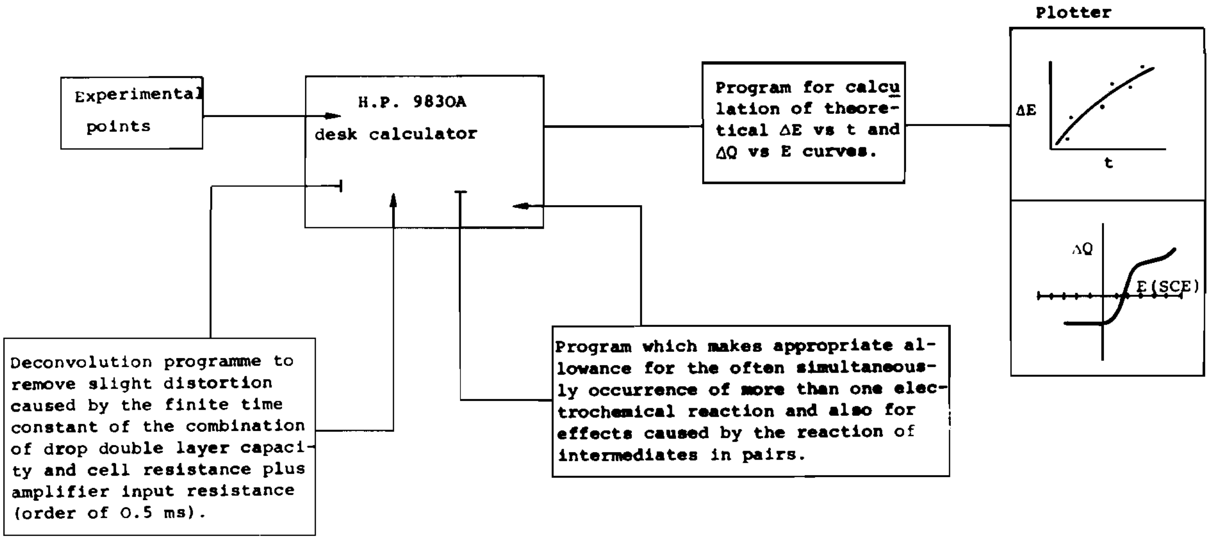

Fig. 2. Data analysis scheme for the experimental results obtained by the quasi-coulostatic system.

is reduced at the electode in the negative potential range by a diffusion-controlled process and its electrochemical properties are known. Therefore the dose can be calculated from the value of [Fe-$(CN)_6^{-3}$] obtained by means of eqn. 2, the relevant value of D_x being known.

In the present work the dose was such as to produce initial concentrations of primary radicals in the range 5×10^{-7} *M* to 5×10^{-6} *M*.

Results and Discussion

The primary chemical changes produced by the absorption of high energy radiation in water can be schematically represented by the expression:

$$H_2O \rightsquigarrow H, OH, e_{aq}^-, H_2, H_2O_2 \qquad (5)$$

and the yields of the primary products are $G(H) = 0.6$, $G(OH) = 2.7$, $G(e_{aq}^-) = 2.7$, $G(H_2) = 0.45$, $G(H_2O_2) = 0.7$.

In the absence of reactive solutes the primary radicals react to yield the final stable products of water radiolysis:

$$H_3O^+ + e_{aq}^- \longrightarrow H + H_2O \qquad (6)$$

$$H + H \longrightarrow H_2 \qquad (7)$$

$$H + OH \longrightarrow H_2O \qquad (8)$$

$$OH + OH \longrightarrow H_2O_2 \qquad (9)$$

The radicals H and e_{aq}^- have high reducing properties and the OH radical has high oxidizing properties.

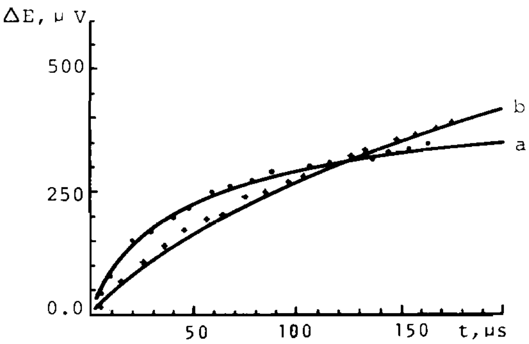

Fig. 3. Observed and calculated changes in interfacial potential with time for 0.5 *M* Na_2SO_4 saturated with pure N_2O. a) before, b) after making the solution 10^{-3} *M* in $K_4Fe(CN)_6$.

When a solute is added to the system the reaction with the primary radicals of the water radiolysis can in turn produce highly reactive intermediates.

In irradiated 0.5 *M* Na_2SO_4 solution saturated with N_2O, the hydrated electron, e_{aq}^-, is rapidly converted to OH by reaction with N_2O:

$$N_2O + e_{aq}^- \xrightarrow{H_2O} N_2 + OH + OH^- \qquad (10)$$

$$k_{10} = 8.9 \times 10^9 \ M^{-1} \ s^{-1}$$

and thus it can be assumed that the only radical present is OH due to the low yield, under these conditions, of the H radical.

The observed potential change, under quasi-coulostatic conditions, is caused by the reaction of OH radicals at the electrode, where they are reduced to OH^-.

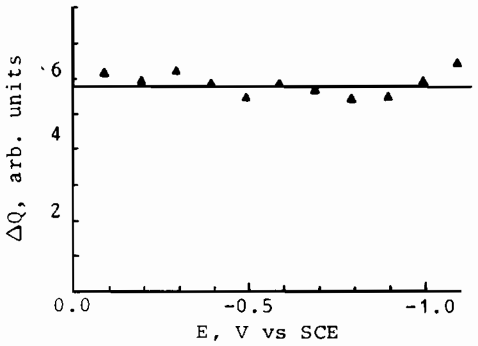

Fig. 4. Change in double-layer charge *vs.* potential, 50 μs elapsed time, for 0.5 *M* in Na_2SO_4 saturated with pure N_2O. Data only corrected for signal decay caused by finite input impedence of preamplifier.

The diffusion coefficient of OH radical, D_{OH}, was determined (Fig. 3) by comparing the waveform obtained with N_2O saturated solution in the absence and presence of $Fe(CN)_6^{4-}$ where stoichiometric conversion of OH radical to the stable $Fe(CN)_6^{3-}$ ion occurs, reaction 4. Allowance was made in the calculation for OH combination in pairs, reaction 9, and a value $D_{OH} = 2.0 \pm 0.2 \times 10^{-5}$ $cm^2\ s^{-1}$ was obtained, which does not differ much from an early photoelectrochemical value [21], though it is markedly larger than a recent photoelectrochemical value of $1.0 \pm 0.3\ 10^{-5}\ cm^2\ s^{-1}$ [21]. The larger value currently appears more credible, with regard to the fact that the OH radical is not large and, as it is uncharged, has no charge-induced hydration sheath. The computed value of the rate constant k_9, Fig. 3, which gives the best fit to experimental data was $2k = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}$, in good agreement with the low ionic strength value given in the literature [22].

Figure 4 shows the dependence of the change of the double layer charge on potential for OH radical. The results indicate that the reduction of OH radicals at a mercury electrode is diffusion-controlled throughout the accessible potential range.

Earlier experimental work, using the galvanostatic method [18], seems to indicate that the reduction of OH radical becomes diffusion controlled at potentials more negative than ~−0.8 V *vs.* SCE. We believe that the results of reference 18 are strongly influenced by the high rise time of the set up and by the difficulties to control, at low values of elapsed time, the electrode potential applied.

In acid solutions the hydrated electrons are rapidly converted by reaction 6 to H atoms. Much has been learnt about the electrochemical reactivity of this radiation product in the last decade, using various photoelectrochemical methods based on light-induced electron emission at potentials more negative than *ca.* −0.5 V *vs.* SCE [15]. It is known that at more positive potentials H atoms are largely oxidised at the surface of mercury.

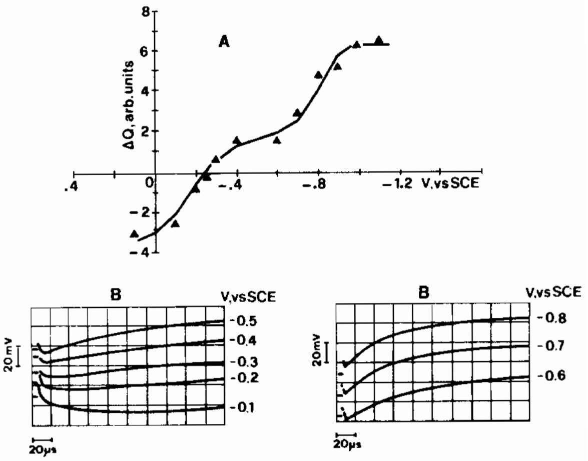

Fig. 5. Coulostatic charge density change *vs.* potential, A, for 0.5 *M* Na_2SO_4 solutions containing H_2SO_4 at pH = 1, at 50 μs elapsed time, and coulostatic changes in electrode potential with elapsed time, B.

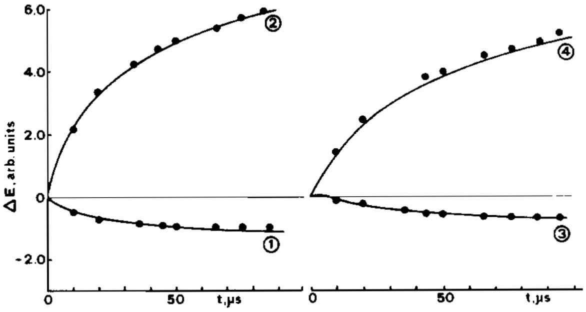

Fig. 6. Observed and calculated changes in interfacial potential with time at different applied potentials for 0.5 *M* Na_2SO_4 solution containing H_2SO_4 at pH = 1; ① + 0.1 V; ② −1.0 V; ③ −0.2 V; ④ −0.8 V.

The study of physicochemical properties of H atoms produced by pulses of ionizing radiation is complicated by the multiplicity of primary intermediates, of which the OH radical is the most troublesome. Henglein and co-workers [23] have tried to overcome the latter problem by working with solutions saturated with hydrogen at high pressure so as to destroy OH homogeneously [24]. Their approach permitted the study of H atoms formed at high alkalinity directly from e_{aq}^-, but as their findings for the range of potential in which unambiguous conclusions can be drawn from the results of 'clean' photoelectrochemical results for acidified solutions differ considerably from the latter, [15], it seems likely that, despite the presence of hydrogen at high concentration, their observations were affected by the presence of H_2O_2 formed in the spurs, the doses used being of the order of 10 krad.

To clarify the situation we have recently studied the behaviour of deoxygenated 0.5 *M* Na_2SO_4 solutions containing sulphuric acid of pH = 1–3 (see Fig. 5). Knowing the dose absorbed by the system, G_H, $G_{e_{aq}^-}$ and G_{OH}, and also D_{OH}, it was possible to correct the composite coulostatic charge density changes for charge connected with the reduction of OH radicals, and also to allow for effects due to the homogeneous loss of H atoms by (a) reaction with OH, and (b), reaction in pairs (using literature rate constant values). This was done assuming various values for (a) the diffusion coefficient of the H atom, and (b), the kinetic parameters of the two main processes involved in the heterogeneous destruction of adsorbed H atoms on mercury, namely

$$H_{ad} \longrightarrow H^+ + e^- \qquad (11)$$

$$H_{ad} + H_2O(H^+) + e^- \longrightarrow H_2 + OH^- \qquad (12)$$

It has been reported that hydrogen atoms enter into electrode reactions only in the absorbed state, [20, 25]. Good agreement between theory and experiments for the H charge *vs.* potential curves, was obtained taking $D_{OH} = 2.1 \times 10^{-5}$ cm^2 s^{-1} and $D_H = 8 \times 10^{-5}$ cm^2 s^{-1} (Fig. 6). Knowing, from electrophotochemical studies, that the sum of the transfer coefficients for eqns. 13 and 14 is very close to 0.5 for low pH and knowing also the potential at which the rate constants of eqns. 13 and 14 are equal, it was possible to assign tentative absolute values to these kinetic parameters. Figure 7 shows the good agreement between theory and corrected experimental data for two values of elapsed time and the potential range 0.1 to –1.1 V *vs.* SCE for solutions of pH = 1.0. These results of Figs. 6 and 7 suggest that at the point at which the rates of reactions 11 and 12 are equal, their rate constants are $k_{11} = k_{12} \cong 5.0 \times 10^3$ s^{-1}, treating both reactions as first order processes:

$$k_{11} = k^\circ \exp\left(\alpha \cdot \varphi \cdot \frac{nF}{RT}\right) \qquad (13)$$

$$k_{12} = k^\circ \exp\left(-\beta \cdot \varphi \cdot \frac{nF}{RT}\right) \qquad (14)$$

where α and β are the electron transfer coefficients, $\varphi = E - E^\circ$, where E° is the potential at which $k_{11} = k_{12} = k^\circ$ and E is the potential applied to the cell.

The transfer coefficient for reaction (12) employed in the calculations was 0.36, while that for reaction 11 was 0.2. The interesting features of these results are firstly that at the potential at which the net faradaic current is zero, (*ca.* –0.6 V *vs.* SCE), the half-life of an absorbed H atom is quite long, and secondly that the oxidation of adsorbed H only slowly becomes diffusion controlled as the potential becomes more positive. The approach to diffusion control for reaction 11 also is slower than expected. For higher pH (*e.g.* pH = 3) the null point for the current moves to a more negative potential (–0.7 V *vs.* SCE for pH = 3) but otherwise the kinetic parameters are, within the experimental accuracy, the same as for pH = 1.

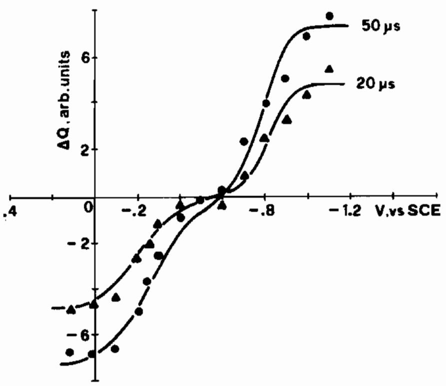

Fig. 7. Coulostatic charge density changes *vs.* potential and theoretical curve (see text) for 0.5 *M* Na_2SO_4 containing H_2SO_4 at pH = 1. The charge density changes were corrected for the contribution of OH radicals and refer to 20 μs elapsed time, ▲, and 50 μs elapsed time, ●.

Recently the ionization rate constant value of hydrogen atoms adsorbed on mercury has been reported using the method of photocurrent induced by laser pulses [25].

The rate constant reported for the potential corresponding to zero net current for the charge transfer steps involving H_{ads} seems smaller by about one order of magnitude for 0.1 *M* H_3O^+ in 0.5 *M* Na_2SO_4 solution, than the corresponding value for k_{12} for a variety of acidified solutions (*e.g.* 0.1 *M* HCl in 1 *M* KCl solution) reported recently by Benderskii and co-workers, [25], though it would seem that the present results indicate values for k_{12} at negative potential agreeing rather better with the earlier results of Benderskii *et al.*, [21], for the same hydrogen ion concentration (the medium seems not to be specified unambiguously).

There also are differences between the transfer coefficients assumed in the present work and those reported in ref. [25]. We do not intend to discuss quantitatively the causes of these discrepancies which, although important from an electrochemical viewpoint, do not prevent us from concluding that H atoms formed homogeneously by pulse X-radiolysis at the surface of a mercury electrode behave in much the same way as H atoms formed within a very thin reaction layer by the capture of hydrated photoelectrons by proton-donating species such as the hydrogen ion.

That the results obtained by the pulse X-radiolysis method should differ somewhat from those obtained by the photoemission method using pulsed laser light sources is not particularly surprising. There are many potential causes of error when these quite sophisticated perturbation methods are employed, which have to be borne in mind when comparing data obtained by the two methods. In this connection it is important to note that while in the pulse radiolysis case one is studying, at moderately large values of elapsed time the motion to the electrode of electrochemically-active intermediates (H, OH, H_2O_2) is at a quite low concentration, in the photoemission experiments using laser light one is dealing with reactions in a very thin reaction layer at the electrode surface. In the latter case the surface concentration of H_{ads} rises to values exceeding by several orders of magnitude those occurring when the system is subjected to pulse X-radiolysis.

Currently it is not possible to discuss sources of error associated with the two methods quantitatively, and below we merely indicate sources which have, to our knowledge, not been discussed adequately (or have gone unmentioned) in the literature.

In the case of the coulostatic pulse X-radiolysis method thought should be given to the following points:

(I) Errors (hopefully of minor importance) clearly could arise in the analysis of charge–time data due to the use of inaccurate kinetic data for side reactions such as the homogeneous reactions of primary intermediates of similar or dissimilar type (*e.g.* OH + OH, H + H, H + OH).

(II) Due allowance must be made for ion association at the surface and in the bulk of the solution (important is the formation of HSO_4^- in acidified solutions of high SO_4^{2-} concentration). Also, media containing halide ions should be avoided to evade complications due to the reaction of the OH radicals with halide ions other than F^- (the use of which is ruled out by other considerations).

(III) Strict allowance should be made for effects due to heating by radiation pulse of the solution and of the mercury drop. In the present work no allowance has been made for heating of the double layer, largely because the magnitude of the effects is difficult to calculate with accuracy. It is thought, however, that neglect of this correction is not the cause of the discrepancies mentioned earlier.

(IV) It is crucial that a dropping mercury electrode be employed to avoid errors of possibly serious magnitude, connected with contamination of the mercury surface by the diffusion to the surface of surface-active impurities and by migration from the solid surfaces (glass or plastic) which make contact with the Hg surface.

When the photoemission approach is employed one must not lose sight of several of the above points, and in addition one must remember:

(V) that using a high concentration for the electron acceptor (to enhance the measured signal) an appreciable fraction of the electron adduct (H, H_3O *etc.*) may arrive by diffusion at the electrode surface while the electrode is being irradiated and the resulting excitation of the mercury ions and electrons may accelerate reactions involving the adsorbed adduct (H_{ads}, H_3O_{ads} (??)).

(VI) that if (V) is an irrelevant point there remain possible errors connected with the reaction in pairs of the adsorbed adduct which, although stabilized somewhat by adsorption, may nevertheless decay quite rapidly close to the potential at which k_{11} equals k_{12} by the non-faradaic step

$$H_{ads} + H_{ads} \longrightarrow H_2 \qquad (15)$$

As far as one can judge there is no evidence to show that this reaction is unimportant when light of quantum energy of about 4.5 eV is employed and the energy deposition is of the order of 40 kW cm^{-2}, as shown in the extensive and ambitious work of Benderskii [25]. Light of such intensity and energy might induce photolysis of solvent molecules at the mercury surface. Clearly some studies of the influence of light intensity on the observed kinetic parameters are needed.

Finally it should be mentioned that the work described in [25], although perhaps slightly suspect as regards accuracy, endorses completely the view that the H atoms are rapidly adsorbed on a mercury surface at potentials close to the potential at which reactions 11 and 12 are important, a point which has not found universal acceptance in the literature.

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