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Processes at the Metal—Solution Interface Induced by Light*

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Various processes are discussed which take place under the effect of light at pure metallic surfaces in solutions not absorbing light. Particular attention is paid to the most thoroughly studied of these processes, the photoemission of electrons into aqueous solutions of electrolytes. Besides, the mechanism of heterogeneous photochemical charge transfer between metal and solution is outlined and illustrated on examples where photoemission cannot occur.

INTRODUCTION

The specific properties of a boundary between phases in general become prominent under the effect of light. With light falling at an interface the well studied physical phenomena of reflection and refraction take place. Besides, when passing from one phase to another, the light is absorbed to a different extent in either of the phases and, possibly, also in the interfacial layer. The absorption of light can represent an initial step of a process which continues by transfer of energy or charge across the interface and ends by a chemical reaction characteristic for the given composition of phases.

The elementary processes of the light absorption and of the interfacial energy transfer are conveniently studied by spectroscopic techniques.

For investigation of the light-induced transfer of charge across an interface a particularly useful method appears to be the measurement of photocurrent generated by irradiation by UV and visible light of a polarizable metallic electrode in an electrolytic solution. However specialized this system may seem, the main results it brings are of general interest.

The purity of the metal surface is of great importance in these measurements: surface compounds of semiconductor character like oxides, sulphides, halides, *etc.* on irradiation give rise to electron-hole conduction which can completely mask the photoeffect on pure metal. For this reason the majority of fundamental measurements were carried out with the dropping mercury electrode. As source of light various lamps were used giving steady, intermittent or pulse irradiation, as well as lasers. As a rule, care was taken to avoid homogeneous photoreactions in the solution by appropriate choice of optical filters which would transmit only light not absorbed by the solvent or solute. The photocurrents were measured by more or less modified d.c.-, a.c.-, square-wave-, and pulse-polarographic or by coulostatic techniques.

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The experimental results gathered in the past 10 years lead to the conclusion that the elementary transfer of charge caused by light between a pure metal and a liquid phase can occur, according to the conditions, either by photoemission of electrons from the metal to the liquid or by phototransfer of an electron between the metal and a species from the liquid phase which is in contact with the metal and acts as electron donor or acceptor. It seems that under quite broadly varied conditions both mechanisms can operate simultaneously in parallel reactions.

While the mechanism of the transfer of charge by emission of electrons has been conclusively proved experimentally, the mechanism of phototransfer of an electron between the metal and the donor or acceptor, though very probable, remains still in the hypothetical stage.

Photoemission of Electrons

The mechanism of photoemission of electrons from metals into non-polar media does not differ essentially from the photoemission into vacuum, only the net quantum efficiency of the photocurrent is lower by 2—3 orders of magnitude[1]. The dependence of the current of emission i_e on the energy of light $h\nu$ is given by the formula[2]

$$i_e = K\,(h\nu - h\nu_0)^2 \tag{1}$$

where K is a constant and $h\nu_0$ is the work function characteristic of each metal (Fig. 1).

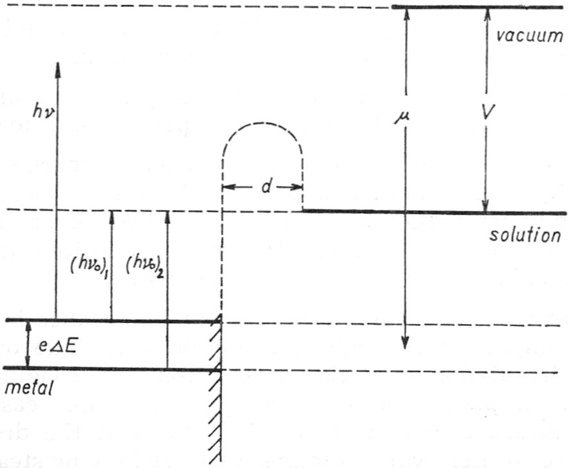


Fig. 1. Schematic representation of the energy levels of electrons for the photoemission from metals into the solution or into vacuum. $h\nu$-energy of an electron emitted from the metal into the solution, $(h\nu_0)_1$ and $(h\nu_0)_2$ — electrochemical work functions differing by $e\Delta E$ (ΔE = difference in electrode potential), d — thickness of the surface potential barrier (= action distance of surface forces, equal to the thickness of the electric double layer in this case), μ — chemical potential of electron in the metal, V — potential of electron in the solution. According to[6].

The situation is different with the photoemission into polar liquids, particularly into electrolytic solutions[3–6]. Here on leaving the metallic surface the electron is electrically screened by the surrounding polar medium and is therefore not affected by the image forces. In consequence, the current of photoemission follows a different expression:

$$i_e = A\,(h\nu - h\nu_0)^{5/2} \tag{2}$$

where A is a constant. The term $h\nu_0$, this time the electrochemical work function, depends on the solvent[7] and changes linearly with the metal/solution potential E measured from some arbitrary reference potential (Fig. 1):

$$i_e = A\,(h\nu - /h\nu_0/_{E=0} - eE)^{5/2} \tag{2a}$$

With the metal/solution potential held constant the electrochemical work function, contrary to the »classical« work function, is the same for all metals[7,8]. At the potential of —0.20 V *versus* normal hydrogen electrode (potential of zero charge of mercury) the energy necessary for emission of electrons from different metals into aqueous solutions is 3.3 eV. (Ref. 3, *cf.* also 9).

The envisaged fate of the emitted electron is generally as follows[10,11] (Fig. 2): after losing excess energy on its trajectory through the solution it becomes thermalized and eventually gets solvated at a distance of the order of tens of Ångström units from the metal depending on the energy of the initial light quantum. The solvated electrons diffuse in the solution according to their concentration gradient and since they are readily discharged at the metallic surface, most of them return back to the metal. In presence of electron scavengers

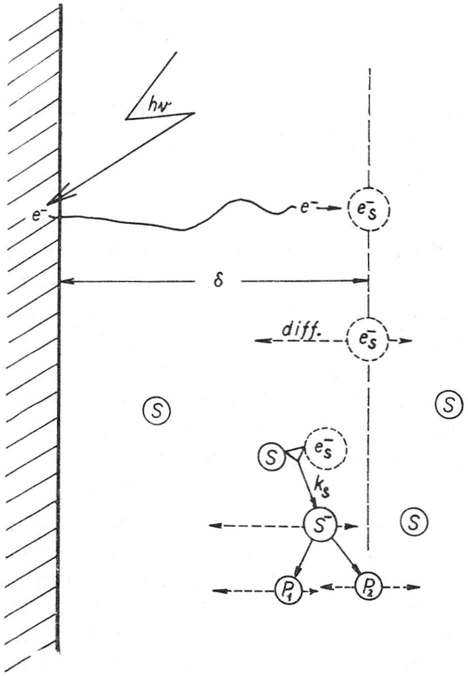


Fig. 2. Fate of the electron after emission into a polar solution (see text), $h\nu$ — quantum of energy sufficient for emitting electron e^-, e_s^- — solvated electron, δ — average distance of formation of solvated electrons from the metal surface, S — electron scavenger, S^- — primary product of the reaction of scavenger with electron, k_s — rate constant of scavenging reaction, P_1, P_2 — secondary products of scavenging reactions. Dotted lines with arrows indicate direction and magnitude of diffusion flux.

(species reacting at a high rate with solvated electrons, like N_2O, H_3O^+, acrylonitrile *etc.*) the solvated electrons are removed from the solution by chemical reaction. The products of such reactions, as a rule partly chemically unstable, can in their turn increase or diminish the electric charge of the metal by entering into an electrode reaction. The experimentally measured photocurrent i_p consists then of several components: the emission current i_e, the current due to solvated electrons returning back to the electrode — i_b, and the elementary contribution by the electroactive product of the scavenging reaction, $\pm i_s$:

$$i_p = i_e - i_b \pm i_s \tag{3}$$

In agreement with the above model the small photocurrents ($i_p \ll i_e$) show a linear dependence on the square root of the scavenger concentration c_s according to the approximate relation[10]

$$i_p = F c_e^{\delta} \sqrt{k_s \cdot c_s \cdot D_e} \tag{4}$$

where F is the charge of 1 Faraday, c_e^{δ} the concentration of solvated electrons at the mean distance δ of their formation from the metal surface in the solution, k_s the rate constant of the scavenging reaction and D_e the diffusion coefficient of the solvated electron. Eq. (4) serves for comparative measurements of the rate constants k_s[11]. At sufficiently high scavenger concentration all the emitted electrons are trapped ($i_b = 0$) and, with an appropriate choice of scavenger (like N_2O, for example), the product of scavenging reaction takes up another electron from the metal ($i_e = +i_s$). In those conditions

$$i_p = 2\, i_e \tag{5}$$

and equation (2a) can be experimentally tested and applied for further studies. These include fundamental problems of electrode kinetics and chemical and physico-chemical properties of unstable ions and radicals[12–15].

A crucial experimental proof of correctness of the theory of photoemission of electrons into the solution was provided[16,12] by producing photocurrent by means of polarized light and following its response to the change of the angle between the incident plane of the polarized light and the metal surface. The effect was the same as for photoemission in vacuum, in agreement with theory[5].

The photoemission is the only way in which hydrated electrons can be produced in the system electrode-aqueous solution, obviously because they are actually formed only at a certain distance from the electrode. The suggestion that hydrated electrons arise during »dark« electrode reactions[17] has been disproved both theoretically[18,19] and experimentally[20].

From Eq. (2a) it follows that for a given energy of light quantum $h\nu$ a metal needs a definite minimum negative »red limit« potential in order to emit electrons. *Vice versa,* with a metal at a given electrochemical potential light of a definite »red limit« energy is necessary for the emission of the electrons into the solution. The relation between the critical values of energy of light and of electrochemical potential is represented in Fig. 3. The straight line represents the red limit of photoemission: under experimental conditions corresponding to the plane below that line photo-electrons cannot be emitted from metals into the solution. However, cathodic photocurrents corresponding to the transfer of electrons in the direction from the metal to the solution were observed under such conditions, for example (Fig. 3) at the potential of

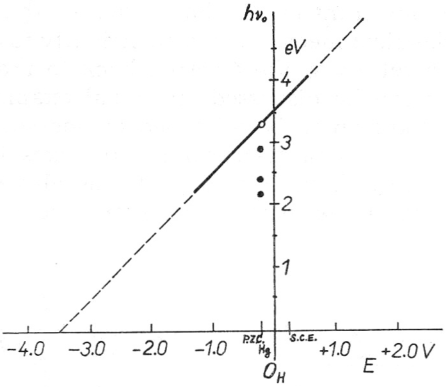


Fig. 3. Dependence of the energy of light quantum on the electrode potential for the red limit of photoemission of electrons from metals into aqueous solutions. Obtained by extrapolating Eq. (2a) to zero current for light of various wavelengths. Black points denote conditions under which the red limit of photocurrent was obtained experimentally in some cases which shows that the mechanism in question was different from photoemissoin (see text).

zero charge of mercury in solutions of potassium tellurate with the light quantum of 2.9 eV ($\lambda = 427$ nm), in solutions containing NO with light of the energy of 2.4 eV ($\lambda = 517$ nm), in solutions of bromates or iodates with energy as small as 2.15 eV ($\lambda = 576$ nm). Further, with certain organic compounds anodic photocurrents can be obtained. Here the transfer of charge has the direction opposite to that of emission of electrons from the metal. For such cases obviously a different mechanism had to be postulated.[38]

The Heterogeneous Photochemical Electron Transfer

The absorption of a light quantum by chemical species results in raising an outer electron to a higher orbital whereby the electron remains within the sphere of the species. In case the system exposed to light contains species of the nature of an electron donor by the side of species capable of reactions like an electron acceptor and if the two species can come into contact so that the lowest unoccupied orbital of the acceptor overlaps with the highest occupied orbital of the donor, then the absorption of a light quantum can lead to the transfer of electron from one species (donor) to the other (acceptor). This is the principle of the electron transfer in the excited state of electron donor-acceptor complexes[21]. The transfer of the electron is accomplished irrespective of whether the actual light-absorbing species is the donor, the acceptor or the complex as such with its characteristic charge-transfer absorption band[22].

The charge-transfer interaction is believed to be a possible component of forces in adsorption on metals[23–26]. The metals can play both roles, either that of electron donor or that of acceptor. In adsorption on mercury of unsaturated organic compounds from solutions the flat orientation of molecules is explained by π-electron interaction in which the molecule is electron donor and the electrode is electron acceptor[27]. When the metal in contact with electron donor or acceptor is exposed to light, an electron transfer is presumably accomplished, like in the case of homogeneous charge-transfer complexes. However, the life-time of the »charge-transfer exciplex« with the electron transferred from the donor to the acceptor (of which one or the other is the metal) will be of the order of the time charge relaxation in metal, *i. e.* no longer than 10^{-14} sec[28].

This means that if a net transfer of charge across the interface has to be realized by the photochemical mechanism, a sufficiently fast irreversible process must compete with the return of the electron back to the donor. The possible kind of such a process can be discussed on actual examples.

Nitric oxide NO is known to be adsorbed on mercury[29] and other adsorbents[30] and in homogeneous charge-transfer complexes to figure as electron acceptor in its dimeric form[31]. In this form it was also found to undergo its electroreduction[32]. In Fig. 4 the generation of an elementary cathodic photocurrent by the mechanism of heterogeneous photochemical charge transfer is shown schematically, and demonstrated on the hypothetical course of the reaction of nitric oxide. The acceptor's lowest unoccupied orbital overlaps with the electronic levels of the metal. As the result of light absorption an electron is transferred to the acceptor from where it either returns back to the metal or by an irreversible reaction it completes its transfer to the solution. In nitric oxide which enters into charge-transfer interaction as a dimer with one of the $N = O$ bonds polarized as indicated, the irreversible step seems to consist in breaking of the N—N bond.

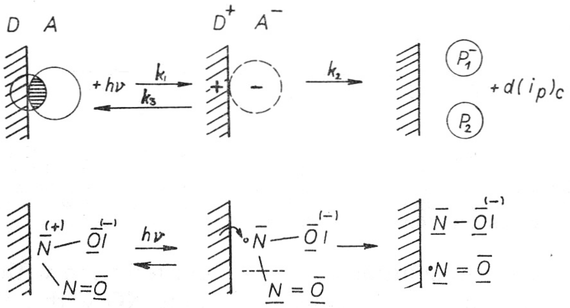
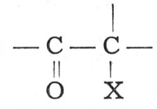


Fig. 4. Schematic representation of the mechanism of cathodic photocurrent through heterogeneous photochemical electron transfer with its illustration on the example of nitric oxide (see text).

The quantum efficiency fo the photocurrent is approximately of the order of 10^{-4}. If we assume, in a rough estimate, that one of ten absorbed light quanta leads to a charge transfer excitation, then the actual quantum efficiency of the complete charge transfer, $10^{-4} \times 10 = 10^{-3}$, is given by the ratio $k_2/(k_2 + k_3)$ (Fig. 3). From here with k_3 of the order of 10^{14} (see above) the rate constant k_2 should be 10^{11}. This result would be in harmony with the assumption that the rupture of the N—N bond takes place if the charge transfer occurs at the time of maximum amplitude of the bond vibration, the period of vibration being of the order of 10^{-11} sec.

An analogous mechanism can explain the anodic photocurrent[33]. This current is observed with solutions containing organic compounds of the structure



$$—\underset{\underset{\displaystyle O}{\|}}{C}—\overset{|}{\underset{\underset{\displaystyle X}{|}}{C}}—$$

where X stands for a negative substituent. To the active compounds belong oxalic acid and its derivatives, α-diketones, α—OH—, α—NH_2— and α-halogeno-ketones, -acids and others. The organic compound in contact with metal enters presumably into charge-transfer interaction as electron donor with both oxygen and the negative group directed towards the metallic surface. From homogeneous photochemistry it is known that complex oxalates of heavy metals which contain a strong charge-transfer band in their absorption spectrum[34], undergo photolytic decomposition starting by transfer of electron from the ligand to the cation[35]. The C—C bond in the complex oxalates is known to be weakened by coordination and to break easily[36]. Moreover, the mechanism of oxidation of several of the above compounds (*e. g.* ref. 37) is known to proceed through formation with the oxidant of a cyclic intermediate which eventually splits in the C—C bond. These facts seem to justify the reaction scheme proposed in Fig. 5. The reaction proceeds either like in the case of nitric oxide: phototransfer of the first electron followed up by the fission of the bond, and the products reacting at the electrode in a »dark« electrode reaction, or it is also possible that after the photochemical transfer of the first electron, the second electron is taken up by the electrode in a following fast »dark« electrochemical step still within one period of stretching vibration of the C—C bond which consequently breaks.

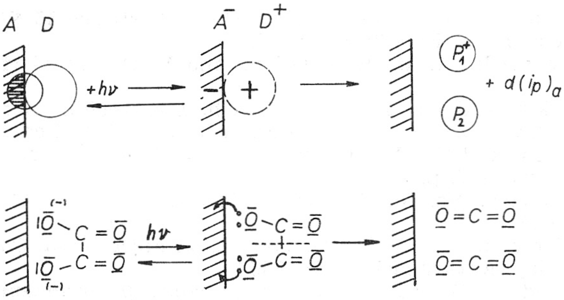


Fig. 5. Schematic representation of the mechanism of anodic photocurrent through heterogeneous photochemical electron transfer with its illustration on the example of oxalate anion (see text).

For the photocurrents due to photochemical heterogeneous charge-transfer besides the difference in energy parameters[38] the effect of polarized light can serve as indication: they do not give the dependence typical for photoemission[16].

A study of photocurrents based on charge-transfer interaction with the metal seems to be more prospective than study of photoemission, as far as the chemistry of the interface metal-solution is concerned.

Other Processes

Several authors[39-42] expressed the opinion that the transfer of electron in electrode reaction is generally accelerated by light. To this question, unfortunately, no systematic experimental research has been done.* This task does not seem to be an easy one: the increase of current will certainly not be too great — therefore a particularly careful elimination of heating effects will have to be provided, and besides, the danger of competition of photocurrents due to other mechanisms will have to be constantly borne in mind.

At high intensities of flash irradiation of the metal, especially by light of longer wavelengths, the solution near to metal warms up and the density

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* The works of Durst and Taylor [*J. Res. Bur. Stand.* **69A** (1965) 517.] and of Crow and Ling [*J. Chem. Soc Dalton* (1972) 698.] represent attempts in this direction.

of the ions in the electric double layer, and with it the double layer capacity, decreases. This is accompanied by a non-faradaic current[11,43] which is anodic at negative potentials, cathodic at positive potentials and zero at the potential of zero charge. This effect provides a method for determining the point of zero charge of different metals[44].

The occurrence of the effect of photodesorption known from the metal-gas interface[45] has not been experimentally unambiguously confirmed at the boundary between metal and solution.

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IZVOD

Procesi na granici faza metal-otopina koji su inducirani svjetlošću

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Prikazani su neki procesi koji nastaju kao posljedica utjecaja svjetlosti na površinu čistih metala u otopinama koje ne adsorbiraju svjetlost. Posebna pažnja posvećena je problemu fotoemisije elektrona u otopinu. Obrađeni su i mehanizmi heterogenog prijenosa elektrona između metala i otopine, a navedeni su i primjeri gdje ne može doći do fotoemisije.

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