Energy Resources through Photochemistry and Catalysis

Edited by

Michael Grätzel

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Preface

The development of new energy resources constitutes a very active and challenging area of modern-day research. Confronted with dwindling supplies of fossil reserves, scientists face the task of conceiving alternative ways of energy conversion. New energy carriers need to be generated for use in future economic systems. This requires a vast research effort covering such diverse fields as solid-state physics, chemistry, and biology. Such an interdisciplinary venture has to be undertaken now when there appears to be still plentiful coal and petrol, in order to acquire the fundamental scientific knowledge on which mankind can rely and build once the conventional resources are exhausted.

While research in the area of new energy-conversion devices has been carried out for a relatively short time only, there has been an explosion of information on this subject. To cover all the significant discoveries in this field would be beyond the scope of a single book. Therefore, we decided to concentrate on topics of general importance where rapid progress has been achieved over the past few years and where a comprehensive documentation of the state of the art is needed. Thus, catalysis intervenes in most chemical transformations where energy is converted or needs to be saved. Catalysis of redox reactions and their application to the photocleavage of water, reduction of carbon dioxide, and fixation of nitrogen therefore constitute the central themes of the present book.

In photochemical or photoelectrochemical conversion systems, these catalytic events are linked to light-energy-harvesting and charge-separation processes. Including a discussion of some fundamental aspects of these phenomena appeared to us as being useful, in particular since many concepts that helped in the design of these devices and the understanding of their operation were developed only recently. This concerns, for example, light-induced redox reactions, reaction dynamics in organized assemblies such as micelles, colloidal

metals, or semiconductors, and strategies for molecular engineering of artificial photosynthetic devices. Furthermore, the principles of electrochemical conversion of light energy via semiconductor electrodes or semiconducting particles are treated.

To deal with all these points in an encyclopedic manner would be a tantalizing experience for a single author. Fortunately, outstanding scientists from all over the world agreed to participate in this effort and address the important issues in individual contributions. Their expertise, acquired through extensive and excellent research in the particular areas of the field covered by the book, is thus made available to a wide readership. I am most grateful to these authors for their enthusiastic participation in the work which has made this venture successful.

Contents

1 Light-Induced and Thermal Electron-Transfer Reactions

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I. Introduction

In principle, conversion of solar energy into chemical energy can be obtained by means of any thermodynamically uphill reaction produced by visible-light excitation (*1–4*). In practice, however, the conversion and storage of solar energy into a real energy resource requires the transformation of an abundant and low-cost raw material into a fuel (i.e., into a highly energetic chemical species that can be stored and transported). Simple economical, ecological, and energetic considerations show that water, carbon dioxide, and nitrogen are the most attractive raw materials that can be used as feedstocks of solar reactors, and that hydrogen, methane, methanol, and ammonia are among the most valuable fuels that one would like to obtain (*5*, *6*). Thus it is not surprising that most of the current activity in the field of solar photochemistry is devoted to the four processes shown in Table I. Such processes, as well as the natural photosynthetic processes (*7*) are based on electron-transfer reactions. The elucidation of the factors that govern electron-transfer reactions (*8–16*) is fundamental for any progress in the field of photochemical conversion of solar energy.

A photochemical conversion system based on a redox process must involve a light-induced electron-transfer reaction. As we shall better see in Section VI,C, when a molecule absorbs a photon of suitable energy an electronically excited state is obtained that is a better oxidant and reductant than the ground state. An electron-transfer reaction between such an excited state and a suitable reaction partner may convert a fraction of the

TABLE I

Some Fuel-Forming Reactions Starting from Abundant and Low-Cost Materials[a]

	ΔG (kJ mol^{-1})[b]	n[c]	E(V)[d]
$H_2O(l) \xrightarrow{h\nu} H_2(g) + \frac{1}{2}O_2(g)$	237	2	1.23
$CO_2(g) + 2H_2O(l) \xrightarrow{h\nu} CH_3OH(l) + \frac{3}{2}O_2(g)$	703	6	1.21
$CO_2(g) + 2H_2O(l) \xrightarrow{h\nu} CH_4(g) + 2O_2(g)$	818	8	1.06
$N_2(g) + 3H_2O(l) \xrightarrow{h\nu} 2NH_3(g) + \frac{3}{2}O_2(g)$	678	6	1.17

[a] From Bolton and Hall (*6*).
[b] Free-energy change.
[c] Number of electrons transferred.
[d] Potential energy stored per electron transferred.

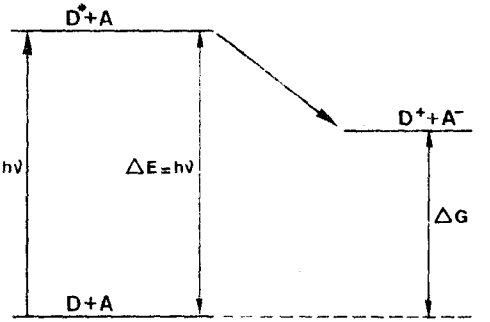

Fig. 1. Schematic energy diagram showing the conversion of light energy into chemical energy. D, Donor; A, acceptor.

absorbed light into chemical energy (Fig. 1). Usually, the raw material that we would like to convert into fuel (Table I) cannot be electronically excited by solar radiation. A typical example is that of water, the electronic absorption spectrum of which does not overlap the emission spectrum of the sun. In such a case the process must be mediated by a suitable chemical species called a *photosensitizer* (P) (*17*) (Fig. 2). Electron-transfer reactions converting raw materials into fuels are usually very slow because they involve the transfer of more than one electron (Table I). It follows that the excited state of the photosensitizer would usually undergo deactivation before reacting with the raw material. Therefore, a *relay* (R) species is usually needed that must first undergo a fast electron-transfer reaction with the excited state of the photosensitizer and then induce a thermal electron-transfer process that transforms the raw material into fuel (*18, 19*). The latter process is again slow because of its multielectron nature, whereas the competing back electron-transfer reac-

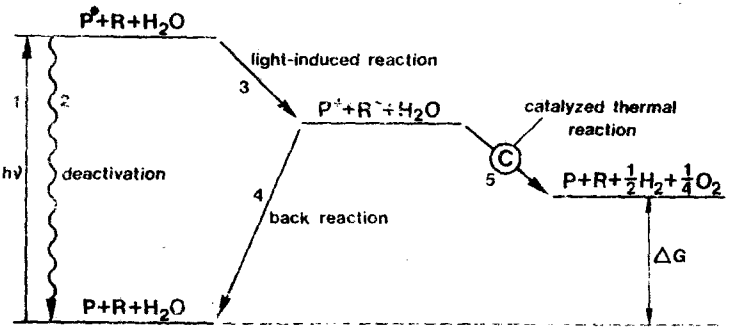

Fig. 2. Schematic energy diagram showing the photochemical conversion of a raw material (exemplified by H_2O) into fuel mediated by a photosensitizer (P) and a relay (R).

tion is very fast (Fig. 2). Thus a homogeneous or heterogeneous catalyst (C) is usually needed to speed up the thermal reaction leading to fuel (*18, 19*).

In conclusion, any artificial system for photochemical conversion and storage of solar energy consists of a light-induced electron-transfer reaction, which is followed by a sequence of thermal electron-transfer reactions that may involve homogeneous and/or heterogeneous catalysts. The efficiency of the system will depend on the relative rates of the various electron-transfer steps. In this chapter, the state of the art of the theories of electron-transfer reactions will be presented, and the role played by the various factors in governing the reaction rates will be discussed. We shall deal explicitly with homogeneous reactions, but many concepts that will be illustrated can also be applied to heterogeneous processes, such as those involving electrodes or heterogeneous catalysts.

II. Kinetic Formulation

A bimolecular electron-transfer reaction originating from a weak interaction[1] between a donor and an acceptor [Eq. (1)] can be discussed in terms of elementary steps as shown in the scheme

$$D + A \xrightarrow{k_{exp}} D^+ + A^- \tag{1}$$

$$D + A \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} D\cdots A \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} D^+\cdots A^- \xrightarrow{k'_{-d}} D^+ + A^- \tag{2}$$

where the electronic states of D and A are left unspecified; k_d, k_{-d}, and k'_{-d} are diffusion or dissociation rate constants; and k_e and k_{-e} the (unimolecular) rate constants for the forward and back electron transfer in the encounter. In the inorganic literature $D\cdots A$ and $D^+\cdots A^-$ are often called precursor and successor complex, respectively (*12, 20*). Note that the $D^+\cdots A^-$ successor complex in some systems can disappear via additional channels not shown in Eq. (2); in such cases the following kinetic treatment retains its validity, provided that k'_{-d} is substituted by the sum of the rate constants of the various channels. One such channel may be the rapid dissociation of D^+ and/or A^- into fragments. For excited-state electron-transfer reactions an important way for the disappearance of

[1] Classical cases of weak-interaction electron-transfer processes are outer-sphere electron-transfer reactions of transition-metal complexes (*10*). The problem of the magnitude of the interaction in electron-transfer processes will be discussed in later sections.