

Twentieth century developments in photochemistry. Brief historical sketches*

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Abstract: In the 20th century, photochemistry blossomed from a poorly defined to a highly sophisticated science. Early breakthroughs in exploratory photochemistry and the underlying physical principles led to new diverse, yet inter-related areas of research. The alluring goal of asymmetric synthesis with circularly polarized light proved elusive. The discovery of the electron brought a gradual awakening to the idea of electron transfer. Time-resolved spectroscopy developed from ms to fs resolution. The field of photosynthesis progressed from an interest in function and structure of photosynthetic pigments to the isolation and structure elucidation of photosynthetic reaction centers (*rhodobacter sphaeroides*), to the detailed kinetics of sequential electron-transfer steps in natural and synthetic light-harvesting systems.

INTRODUCTION

At the turn of the 20th century, photochemistry was barely developed as a science. Although many photoreactions were known due to accidental or intentional exposure of substrates to (sun) light [1], the underlying principles were poorly understood. The “first law of photochemistry” had been recognized by Grotthus (1817) and Draper (1843), but the quantum nature of light and its consequences for photochemistry were yet to be discovered.

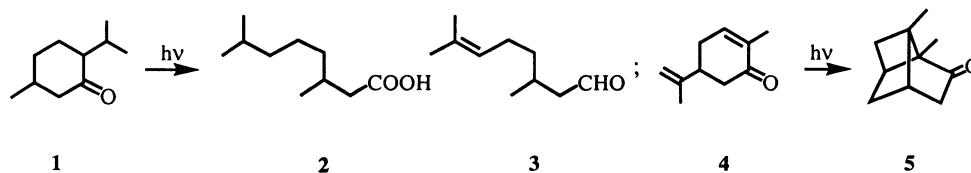
EXPLORATORY AND SYNTHETIC STUDIES

The first breakthrough of the new century came in exploratory photochemistry. Ciamician and Silber studied “azioni chimiche della luce” (“Chemische Lichtwirkungen”), culminating in Ciamician’s prophetic *Science* article [2]. Ciamician and Silber’s investigation of photochemical reactions surpassed any previous effort and established photochemistry as a significant branch of chemistry. They studied photoreactions of carbonyl compounds and observed photoreductions, photopinacolization, intramolecular cycloaddition, and α - and β -cleavage. These systems later revealed fundamental principles such as the concepts of excited singlet and triplet as well as n,π^* and π,π^* states. Two products, **2**, **3**, resulting from α -cleavage of “menthone”, **1**, are shown, as formulated by the authors (Scheme 1) [3]. The intramolecular cyclization of carvone, **4**, to carvone camphor, **5**, was recognized as an intramolecular cycloaddition [4], as was the intramolecular redox reaction of *o*-nitrobenzaldehyde, **6** (Scheme 2) [5]. The collaboration between Ciamician and Silber truly was a “profitable partnership” [6].

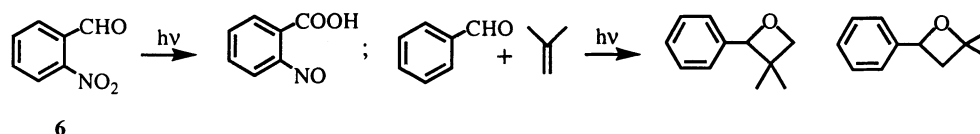
A second Italian research group studied synthetic reactions (“sintesi per mezzo della luce”). Paternó and Chieffi observed the first cycloadditions of carbonyl compounds onto alkenes, the Paternó-Büchi reaction [7–9]. World War I brought the work of the Italian groups to a premature end. Because

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neither group left an “heir”, who would continue their work, their contributions were forgotten and had to be rediscovered by later generations.



Scheme 1



Scheme 2

PHYSICAL PRINCIPLES AND SPECTROSCOPIC METHODS

In physics, the early decades of the new century brought a wealth of fundamental discoveries relevant to photochemistry and molecular spectroscopy. The developments are summarized by Nobel laureates, with (shortened) citations: Röntgen, “discovery of the remarkable rays” (1901); Lorentz and Zeeman, “research into the influence of magnetism upon radiation phenomena” (1902); Michelson, “for his optical precision instruments and spectroscopic investigations” (1907); Wien, “for his discoveries regarding the laws governing the radiation of heat (1911); Planck, “discovery of energy quanta” (1918); Stark, “discovery of the Doppler effect ...and the splitting of spectral lines in electric fields” (1919); Einstein, “discovery of the law of the photoelectric effect” (1921); Millikan, “for his work on the elementary charge of electricity and on the photoelectric effect” (1923); De Broglie, “discovery of the wave nature of electrons” (1929). Some findings had immediate impact on photochemistry. In 1901, Planck’s work on the emission of black bodies led to the concept of radiation quanta of discrete energies [10].

$$E = h\nu = h \times c / \lambda \quad (1)$$

Four years later, Einstein explained the “photoelectric effect” discovered by Hertz in terms of Planck’s theory, suggesting that quanta of light absorbed by metals cause ejection of electrons [11]. Stark and later Einstein formulated the “quantum equivalence law” (“second law”) for photochemistry, which might be paraphrased as “each absorbed quantum of radiation causes one equivalent of a chemical reaction”. Stark and Bodenstein later recognized that this postulate should apply only to *primary* photochemical processes. The second law is valid for systems with short-lived excited states and low-intensity irradiation.

ASYMMETRIC SYNTHESIS WITH CIRCULARLY POLARIZED LIGHT?

The synthesis of optically active compounds or the resolution of racemic mixtures by circularly polarized light (cpl) was an alluring early target of photochemistry. The potential of this method, recognized by van’t Hoff and LeBel, was given a sound basis with the detection of circular dichroism [12]. After many futile attempts, W. Kuhn had modest success in the irradiation of α -bromopropionic esters [13] or α -azidopropionic dimethylamide ($\Delta\epsilon_{290}$ 2%). After 40% decomposition, the remaining azide showed a rotation of $\sim 1^\circ$, an enrichment of $\sim 0.5\%$ [14]. Davis and Heggie claimed “a total asymmetric synthesis” (adding Br_2 to 2,4,6-trinitrostilbene in cpl; $\lambda = 430\text{--}589$ nm) [15]. In 1965, Hammond and Cole achieved an asymmetric induction of 7% using an optically active sensitizer [16]. This work stimulat-

ed new interest in asymmetric photochemistry as judged by the number of references in a 1983 review (71) [17] and one nine years later (327) [18].

GAS-PHASE PHOTOCHEMISTRY AND SPECTROSCOPY

The new century saw major advances in gas-phase photochemistry, beginning with (seemingly) simple inorganic compounds. The steady-state assumption, introduced by Bodenstein [19] allowed the derivation of rate laws and their interpretation in terms of mechanisms, e.g., for the photochemical reaction between Br_2 and H_2 [20]. Some reactions initiated via bond dissociation were found to have long free-radical chains ($\sim 4 \times 10^6$ events, photolysis of Cl_2 in the presence of H_2). In general, photoinduced free-radical reactions in the gas phase were fairly well understood, albeit ambiguous in details. Newly developed experimental tools allowed deeper insights. Thus, the photochemical synthesis of HCl from the elements in the presence of O_2 presented major problems due to “invasive” methods of following the reaction [21,22]. The problems were overcome by probing the quantity of Cl_2 spectroscopically [23]. Decades later, J. C. Polanyi studied the infrared chemiluminescence of HCl formed by reaction of $\text{H}\cdot$ with Cl_2 [24]. He shared the 1986 Nobel Prize in chemistry “for contributions concerning the dynamics of chemical elementary processes”. Photochlorination was applied also to organic substrates, including olefins; thus, a simple mechanism and a simple rate law were derived for the chlorination of ethylene [25]. The photolysis of halocarbons in the stratosphere poses a serious threat to the ozone layer. The study of the underlying free-radical chain reactions (see, e.g., ref. 26) earned P. Crutzen, M. Molina, and F. S. Rowland the 1995 Nobel Prize in chemistry.

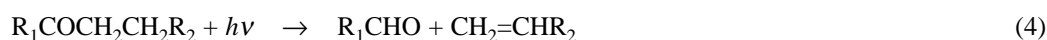
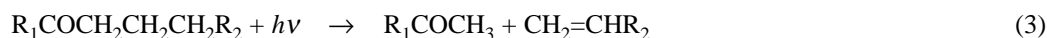
A related area of research deals with free-radical emission spectra obtained from discharges. These spectra provide detailed information about electronic structure, geometry, and stability of many diatomics and some larger species. Early milestones include Franck’s correlation of spectrum type with dissociation [27] and the recognition of predissociation [28]. G. Herzberg is acknowledged as a major contributor to this field (1971 Nobel Prize in chemistry, “for contributions to the knowledge of electronic structure and geometry of molecules, particularly free radicals”). Among many elegant studies, two triatomics, formyl radical, $\text{HCO}\cdot$, and triplet methylene, $\text{CH}_2\cdot\cdot$, were especially challenging [29].

Organic compounds also were photolyzed in the gas phase. In 1910, Berthelot and Gaudechon found equal volumes of CO and ethane upon UV photolysis of acetone [30]. Carbonyl compounds continued to be of interest in the 1920s and 1930s [31] and (at least) two groups observed an emission from (excited-state) acetone [32,33]. Carbonyl photoreactions were formulated initially as extrusions of CO; however, the product mixture from methyl ethyl ketone (ethane, propane, butane, CO) [34] suggested a free-radical mechanism [35]. This was confirmed [36] using the Paneth–Hofeditz technique of dissolving metal mirrors [37]. In the 1930s, Leighton and Blacet began to study aldehyde photolyses, mostly in the gas phase, measuring product and quantum yields. They noted significant differences between saturated and unsaturated substrates [38,39].

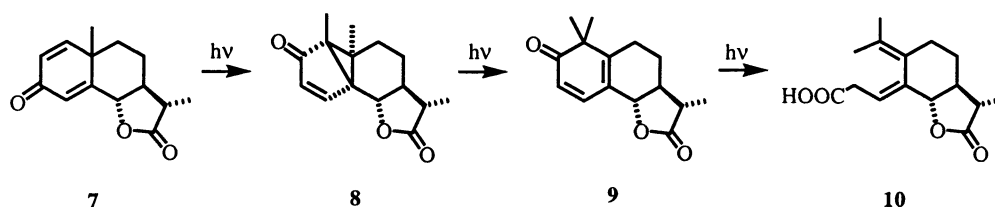
PROGRESS IN SOLUTION PHOTOCHEMISTRY

During the early decades of the new century, various laboratories studied photoreactions, however, mostly as isolated cases. In the mid-1930s, Norrish and coworkers began a systematic study, extending their work on aldehyde and ketones to the liquid phase [40,41]. The results suggested three different types of decompositions. The first reaction (eq. 2) is the familiar dissociation of ketones into radicals. Formulated originally as a two-bond cleavage, a step-wise cleavage was adopted when products such as biacetyl were found in acetone photolysis [42]. The second process (eq. 3) is a general reaction for ketones with H atoms on one γ -carbon; a third reaction, (eq. 4) less common (and less fully substantiated), was observed for some ketones with H atoms on one β -carbon. It became customary to refer to these reactions as Type I, II, III, or Norrish Type I, II, III reactions.

In paraffin solutions, Type I reactions were “suppressed” and the products modified by reaction with the solvent (hydrogen abstraction), resulting in unsaturated solvent-derived products. Type II reactions, on the other hand, had similar quantum yields in the gas phase and in solution, leading to the conclusion that the reaction occurred by an intramolecular step. Studies of cyclic ketones yielded equivalent results [43]. The photodegradation of polymers, viz., poly(methylvinylketone), also was ascribed to the Type II process [44]. The suggested (or implied) mechanisms were also studied in North America, where several groups invoked “internal hydrogen bonding” as aiding the formation of cyclic transition states for the Type II and III reactions [45–48]. The formation of pentenal as well as cyclobutane from cyclopentanone confirmed the involvement of two consecutive biradicals [49].



In the 1950s, a longstanding photochemical puzzle dating back to the 1860s was solved when the photoproducts of santonin, **7**, were elucidated [50–54]. Lumisantonin, **8**, its isomer **9**, and photosantoninic acid, **10**, clearly showed that unsaturated ketones reacted by pathways different from those of saturated ones (Scheme 3). This insight and other reactions of unsaturated ketones led to “a new approach to mechanistic organic photochemistry” [55].



Scheme 3

PHOSPHORESCENT OR TRIPLET STATE

So far, reactivities were discussed without reference to the (electronic) nature of the excited species causing the reaction. Bäckström noted a connection between electronic nature and reactivity; he called the excited benzophenone abstracting H a “biradical” [56]. Significant insights were gained in luminescence studies. In 1895, a long-lived luminescent “afterglow” was noted after irradiation of dyes in gelatin [57], clearly different from the longer-lived “Nachfarben” (radical ion *absorption* spectra) [58,59]. Decades later, F. Perrin suggested a “metastable” state below the excited singlet [60], which Jablonski considered the source of the phosphorescence [61]. Lewis and coworkers measured an absorption spectrum of a phosphorescent (“P”) state and considered it an “electromer” of the ground state [62], while Terenin derived the triplet nature of metastable states of aromatics [63]. Phosphorescence data for a range of substrates established the generality of this emission and led Lewis and Kasha to recognize the “metastable” state as the lowest triplet state [64]. Lewis and Calvin unequivocally identified a phosphorescent state as a triplet when they observed its paramagnetic susceptibility [65]; Evans found that phosphorescence and magnetism decayed exponentially with identical lifetimes [66]. The deeper understanding of the phosphorescent state brought the realization that this state was involved in many photoreactions. This insight stimulated new directions in photochemistry, such as work on triplet energy transfer [67] and accurate triplet energies for a range of molecules [68].

PHOTOINDUCED ELECTRON TRANSFER

The 1920s and 1930s brought a gradual awakening to the idea of electron transfer (ET), in fields such as fluorescence quenching, photosensitization, inhibition of light and dark reactions [69,70], including chain reactions [71], and photosynthesis (*vide infra*). The electron was recognized as an elementary particle only in the 20th century. Electron beams were known as *cathode rays* (since 1876); their *corpuscular* nature was recognized in 1897 [72]. The term *electron* was used for the fundamental unit of electricity (the charge of a hydrogen ion) [73]. The term was applied to the *corpuscles* and generally accepted only with Millikan's determination of the electronic charge [74]. As early as 1923, Weigert invoked ET (from chlorophyll to oxygen) as the primary process in photosynthesis [75]. Baur called fluorescence quenching a "molecular electrolysis" [76] and Weiss recognized ET as an important step in deactivating excited states [77]. Interestingly, he designated the reactants as *donor* and *acceptor*, albeit in a manner different from today's usage [78].

The role of ET in fluorescence quenching was confirmed by the absorption spectrum of perylene anion during the quenching of perylene fluorescence by *N,N*-dialkylanilines [79]. Concurrently, an interest developed in such intermediates as excimers [80–82], "heteroexcimers" (exciplexes) [79], or radical ion pairs, in the many chemical reactions initiated by ET [83], and in radical ion structures [84]. The understanding of photoinduced ET has been advanced significantly by modern spectroscopic methods.

R. A. Marcus made major contributions to ET theory. He formulated ET rates as a function of two parameters, the driving force, ΔG^0 , and a "solvent reorganization energy", λ_s , leading to the striking prediction that ET rates increase with increasing ΔG^0 to a maximum, at $\lambda_s = \Delta G^0$, but decrease upon further increases [85]. The essential predictions were reproduced by various additional theoretical approaches [86].

$$k_{\text{ET}} = A' \exp[-(\Delta G^0 + \lambda_s)^2 (4 \lambda_s k_{\text{B}} T)^{-1}] \quad (5)$$

It took nearly 30 years before the prediction was confirmed by experiment. ET can occur as charge separation, charge recombination, or electron exchange between charged and neutral species; only charge separation is a primary photoreaction. The ΔG^0 dependence of fluorescence quenching rates for organic or organometallic donor–acceptor pairs showed essentially diffusion-limited maximum ET rates, without an "inverted" region [87–89].

The first published data supporting the Marcus inverted region were ET rates between radical anions and aromatic hydrocarbons in frozen solutions ($0.01 < -\Delta G^0 < 2.75$ eV) [86]. Assuming a random distance distribution between donor and acceptor (which cannot be probed readily), the ET rates decreased at high exothermicities [86]. Subsequently, intramolecular ET was studied in a series of molecules, A-Sp-A', containing two acceptors linked by the rigid 5 α -androstane unit. The ET rates interconverting the monoanions, A-Sp-A'•⁻ and A•⁻-Sp-A', unambiguously confirmed ET theories descending from the original idea of Marcus [90].

The Marcus inverted region for *charge recombination* was observed and elaborated [91,92]. Marcus behavior was invoked also for *charge separation* in radical pairs, X-Np-CH₂••O-(C=O)-CH₂Ph, generated by photolysis of naphthylmethyl phenylacetates [93].

In special cases, *charge recombination* may give rise to molecular triplet states [94,95]. This interesting phenomenon is explained as arising from hyperfine-induced intersystem crossing in radical ion pairs, a mechanism first proposed by G. N. Taylor [96].

FLASH PHOTOLYSIS/TIME-RESOLVED SPECTROSCOPY

The 1967 and 1999 Nobel Prizes in chemistry highlight the beginning of a new era in photochemistry and the breathtaking development in the new field. In 1949, R. G. W. Norrish and G. Porter introduced "flash photolysis" [97,98]. This highly significant breakthrough forever changed photochemistry.

Norrish and Porter shared the 1967 Prize with M. Eigen “for their studies of *extremely fast* chemical reactions”. Before flash photolysis, reactions were studied under (steady-state) conditions where intermediates could not be detected. A modest degree of time resolution was achieved by the rotating sector method [99,100]. The 1999 Prize was awarded to A. Zewail “for studies of the transition states of chemical reactions using femtosecond spectroscopy” [101]. In 50 years, flash photolysis/time-resolved spectroscopy developed from ms resolution to the current state of the art, where laser spectroscopy with ns or even ps resolution is almost routine, and fs resolution is no longer uncommon. The development of fs resolution began in the 1970s with a “sub”-ps laser (0.3 ps); it had its crucial breakthrough in the colliding-pulse mode-locked dye laser [102].

PHOTOSYNTHESIS

The most important photoreaction on this planet, the photosynthesis in green plants or organisms, has been studied in detail. The macroscopic changes associated with photo-synthesis were established in the 19th century by de Saussure: when exposed to light, plants consume water and carbon dioxide and generate oxygen [103]. The crucial role of ET was only recognized well into the 20th century, despite the efforts of leading scientists such as Liebig [104], Baeyer [105], or Willstätter, recipient of the 1915 Nobel Prize in chemistry [106]. In 1923, Weigert postulated ET (from chlorophyll to oxygen) as the primary photochemical process in photosynthesis [107]. Later, Rabinowitch and Weiss found that ethyl chlorophyllide was reversibly oxidized in light, while FeCl₃ was reduced [108]. Deeper insights into the “carbon dioxide assimilation in plants” earned M. Calvin the 1961 Nobel Prize in chemistry. More recent advances include the landmark isolation of photosynthetic reaction centers (purple bacterium *rhodospirillum rubrum*, Deisenhofer, Huber, Michel, Nobel Prize in chemistry, 1988) [109], the detailed kinetics of the primary and sequential ET steps [110], and progress in synthetic light-harvesting systems [111].

CONCLUDING REMARKS

The selection of developments in 20th century photochemistry offered here is incomplete, and all topics are treated too briefly; some references reflect a compromise between the available space and the need to convey content. A more comprehensive and detailed treatment of this fascinating topic is in preparation. Financial support for part of this work by the National Science Foundation (CHE-9714850) is gratefully acknowledged. I also thank A. M. Trozzolo (Notre Dame) and E. Castner (Rutgers) for helpful discussions and comments.

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