

Activities of photochemistry in Egypt

S E MORSI¹ and M S A ABDEL-MOTTALEB^{2*}

¹Supreme Council of Universities, Cairo University, Giza, Egypt

²Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt

Abstract. Several research activities in the different topics of photochemistry, photophysics and photobiology are being conducted. Trends of research in Egyptian institutions include –

(A) Preparative organic photochemistry. Studies on the photolysis of different organic compounds have been carried out. Moreover, research work is aimed at investigating the utilization of solar energy in the photooxidation of inexpensive organic compounds to produce precious ones of pharmaceutical interest.

(B) Research work is performed in different areas related to fluorescence spectrometry and laser dyes. The first field involves studies on the essential photophysical properties of some groups of electron–donor–acceptor (EDA) molecules like the styrylcyanine type and coumarins. Currently, research is pursued along the following lines: (1) Solvatochromism and photochromism of these dyes with special reference to *cis-trans* quantum yield determination. (2) Molecular aggregation of functionalized surfactant cyanines and their fluorescence quenching. (3) The analytical use of these dyes and others as fluorescent probes for various systems of biological and industrial importance. Another important field of research is the field of photochemical and emission characteristics of new laser dyes of the diolefinic type and pyrazinyl Schiff-base derivatives.

Research work also includes photochemical studies on some polymeric materials and photoconductivity.

Keywords. Activities of photochemistry; Schiff-base derivatives; polymeric materials.

Historical introduction

The history of photochemistry in Egypt, closely related to that of Egypt itself, begins with the establishment of the worship of the Sun god *Aton* by Akhenaton (18th Dynasty, 1550–1306 BC). *Aton*, “Lord of the Sun”, became god of the sun in the theology of Heliopolis. The sun was symbolized by the solar disc, whose rays shone down to the earth, ending in open hands or in the Egyptian sign meaning life. The Sun God created all life. He also gave life to the important gods, such as Isis, Osiris etc.

Representations of the sun can be found everywhere in Egypt: in tombs, in the *mastabas*, in the pyramids. It is just as if the departed souls wanted to take with them into the Other World the light and heat of which they had need. It was commonplace to put in tombs, boats known as “sun barges”. Clearly if the Egyptians attached such importance to the sun, it must have been due to those esoteric elements, its heat and light. Ancient Egyptians also considered the Sun as complementary to the River Nile which brought life. Neither one without the other could bring life to the Earth.

* For correspondence

These and many other examples show the importance and place of the Sun in Egyptian culture. Moreover there are many other showing the importance of the sun in Egyptian science. Many centuries ago, the Egyptians used the powdered seeds of a plant which grew in the Nile Delta to cure leukoderma (a skin disease). The depigmented areas of the skin were treated by exposure to the sun light after the patient had eaten the powdered seeds. The areas thus illuminated showed blistering followed by pigmentation. Then it gradually assumed the colour of the surrounding skin. This was one of the first examples of the application of photochemistry in medicine (Nada 1983).

Recently (in 1937) the hours of sunshine available in Egypt (ca. 3500 hours/year) attracted Professor A Schoenberg, who came to Egypt as Professor of Organic Chemistry in the Faculty of Science, Cairo University. He used sunlight to initiate chemical reactions. This signalled the start of research in the field of preparative photochemistry.

The great interest of Professor Schoenberg in his work and the enthusiasm of young Egyptian graduates at that time led to the establishment of an extensive research program in applied, pharmaceutical and medical chemistry. Members of his group took their places in chemistry departments in Egyptian Universities (now 15 in number) and in the National Research Centre in Cairo.

After the departure of Professor Schoenberg to Berlin in 1957, the late Professor Ahmed Mustafa became the head of the photochemistry group.

During this period (1937–1957) an extensive number of publications in preparative organic photochemistry came out of Egypt. One of the fundamental reactions discovered by the group was the photoinduced (4 + 2) cyclo-addition of *o*-quinones to olefinic double bonds giving 1,4-dioxene derivatives.

Furthermore, the first edition of *Preparative Organische Photochemie* (Schoenberg 1958), one of the first comprehensive books on photochemistry of organic molecules, was written in Cairo by Professor Schoenberg with the assistance of Professor A Mustafa. It was published in 1958. The second edition (in English) appeared in 1968.

As a continuation of the Schoenberg period, Egyptians scientists carried on research in photochemistry using mainly solar energy (Mostafa 1964). Some Egyptian scientists have had the chance to carry on advanced research work in photochemistry in laboratories in Europe, Canada and USA where modern instrumentation is available. Although photochemistry was one of the fields recommended in 1976 by the Egyptian Academy of Science as a potential joint research project with developed countries, no significant advances have been achieved. However, some research teams in physical, inorganic and organic photochemistry have already started work in some Egyptian Universities and in some research centers.

Current research activities

Several research activities in the different topics of photochemistry, photophysics and photobiology are being conducted. Trends of research in Egyptian institutions include the following:

(A) *Preparative (synthetic) organic photochemistry*

Studies on the photolysis of different organic compounds, e.g. phenylhydroxylamine, N-hydroxyphthalimide, mono-, di- and tri-alkylamines and the photocarbylamine reactions have been carried out (Sidky 1977; Badr *et al* 1983, 1985; Nada and Aly 1985; Raphael *et al* 1989). Direct UV irradiation of these organic compounds in different solvents gives rise to different products, suggesting a free radical mechanism. Also, photocatalytic production of methanol and some aldehydes are the main topics of the research currently being carried on in photochemistry labs. Interest is focused also on utilization of semiconductors (titania pigments) coated with metal-phthalocyanine dyes (Fe(II) or Co(II)) to produce methanol by heterogeneous photoreduction of sodium carbonate (Raphael *et al* 1989).

Several novel ring systems are synthesized via photoaddition of enamionitrile and enaminoesters to electron-poor olefins.

Moreover, research work is aimed at investigating the utilization of solar energy in the photooxidation of furfuryl alcohol. This compound undergoes a sensitized photooxidation process to yield 5-hydroxy-2(5H)-furanone as the main product, with other side products, when aluminum phthalocyaninetetrasulfonate is used as a sensitizer. Furfuryl alcohol is considered an inexpensive chemical compound that can be prepared from biomass – sawdust, straw, corn cobs etc. On the other hand, 5-hydroxy-2(5H)-furanone is considered an expensive and very fine chemical compound which is used extensively in pharmaceutical preparations.

(B) *Photophysical properties of EDA dyes*

Research work is being carried out in different areas related to fluorescence spectrometry, photophysics and laser dyes (Abdel-Mottaleb *et al* 1983, 1986, 1989, 1990; El-Zeiny *et al* 1983, 1986, 1988; Abdel-Halim 1986; Abdel-Kader *et al* 1986; Abdel-Halim *et al* 1988; Ebeid *et al* 1988).

The first field involves studies on the essential photophysical properties of some groups of electron-donor-acceptor (EDA) molecules.

Styrylcyanine type (I): These stilbazolium salts constitute an important class of compounds with possible potential application as saturable absorbers for dye lasers, in fluorescence probe techniques, in photovoltage production, in solar energy conversion and in nonlinear optical devices. Currently research is pursued along the following lines.

- (1) Solvatochromism and photochromism of these dyes with special reference to *cis-trans* quantum yield determination. Some of these dyes (merocyanines) constitute a molecular reaction cycle which serves as a chemical model for the storage of information and subsequent regeneration of the information carrier. The model provides insight into vision processes and a cycle related to the molecular mechanism of the light-driven proton pump of *Halobacterium halobium*.
- (2) Molecular aggregation of functionalized surfactant cyanines and their fluorescence quenching (Abdel-Halim 1986; Abdel-Halim *et al* 1988; El-Zeiny *et al* 1988).

(3) The analytical use of these dyes and others as fluorescent probes to monitor solubilization sites in micelles and reversed micelles and to follow up polymerization processes. The fluorescent probe technique has been also used in the field of photobiology (El-Komashy *et al* 1983; El-Sebe *et al* 1983; El-Raey and Helmi 1983; Hasan 1983; Hasan *et al* 1983) to study conformational transitions in chloroplast coupling factor 1 and to investigate the mechanism of enzyme-catalyzed photophosphorylation in chloroplasts. Moreover, the inhibition of photosynthetic energy coupling adenosine triphosphatase activity of chloroplasts by different herbicides from different chemical groups has been investigated.

Another important field of research is the field of photochemical and emission characteristics of new laser dyes of the diolefinic type (El-Zeiny *et al* 1983, 1986, 1988) (e.g. 1,4-bis (beta-pyridyl-2-vinyl)-benzene "P2VB") in different media including microemulsion media. Another class of compounds which have been investigated belongs to pyrazinyl Schiff-base derivatives. Moreover, studies on the luminescence of some Schiff bases are of interest. Most of the biochemical reactions catalyzed by pyridoxal were inhibited by many hydrazine derivatives such as methylhydrazine, semi- and thio semicarbazides as well as other acylhydrazines.

The observed inhibition action of pyridoxal-catalyzed enzymes by aroylhydrazine and the activation of other enzymes as well as a mobilization agent of iron from reticulocytes and other biological tissues, prompt the interest in pyridoxalaroyl hydrazones. Such a study may throw some light on the nature of pyridoxalaroyl hydrazones in solution and may assist in the understanding of their role within the biological system (El-Komashy *et al* 1983; El-Sebe *et al* 1983; Hasan 1983; Hasan *et al* 1983)

Coumarin laser dyes (II): These classes of intramolecular charge transfer (ICT) molecules have received attention because of their possible profitable applications in industry, e.g. optical recording media, laser switching devices, xerographic photoreceptors, solar energy concentrators, photobiological energy transfer processes, fluorescent probe techniques etc.

The studies involve a research program on fluorescence quenching by inorganic complexes and the heavy atom effect.

Work is now focused on fluorescence measurements of structurally related coumarin laser dyes of electron donor-acceptor (EDA) type. Fluorescence quenching of aqueous and micellar solutions of these dyes by some redox systems, e.g. hexacyano complexes of Fe(II) and Fe(III) show different sensitivities related to electronic factors. Stern-Volmer rate constants were determined at different temperatures and the activation energies for the deexcitation of the singlet-excited state of the dyes were obtained. The results have direct bearings on energy and electron-transfer mechanisms for the bimolecular quenching process.

The objective was to investigate, in a general way, the influence of various medium properties (e.g. solvent properties of macro- and microscopic nature, pH effect, rigidity and viscosity, . . . , etc.) on the essential photophysical properties (fluorescence quantum yield, Stokes shift, . . . , etc.) of these classes of dyes, with particular focus on the interplay of dye structure and specific solvent-solute interactions that govern the competition between radiative and non-radiative decay (Abdel-Mottaleb 1983, 1986, 1989, 1990; Abdel-Kader *et al* 1986).

Furthermore, the studies are complemented by application of the CNDO and PPP-SCF-CI-MO quantum chemical methods to calculate the electron structure for a better understanding of the effect of light absorption on the electron distributions and dipole moments of these dyes (Abdel-Mottaleb 1983, 1986, 1989, 1990; Abdel-Kader *et al* 1986).

Some work has been done to demonstrate the utility of some of these dyes as sensors for some systems of technological and biological importance. Fluorescence probes are especially well-suited to provide answers to questions of dynamics, conformation and morphology in polymer systems.

Dynamical changes upon light excitation of flexible fluorescent dye molecules of the EDA type with twisted ICT state molecules (such as rotation about single bonds and geometrical isomerization about double bonds) are sensitive to and provide information on the local environment (e.g. the effective polarity and rigidity) of the surrounding medium of interest.

In the light of these considerations, our group (jointly with the group of R Loutfy, Xerox, Canada, and the group of K Schaffner, MPI/Muelheim, Germany) has recently synthesized and studied the photophysical properties of a novel styrylcoumarin (SC) dye of flexible bichromophoric EDA type for use as a medium with properties of a fluorescence sensor. They have extended the work to follow up the changes induced in the fluorescence behaviour of SC during the free-radical polymerization of methyl methacrylate (MMA) to explore the potential of this new dye as a fluorescence probe for polymerization.

The fundamental information gleaned about the photophysical properties of these groups of dyes reveal a number of interesting features. The weak fluorescence intensity and shortening of the fluorescence lifetime (acceleration of fluorescence decay) observed for most flexible coumarins, particularly in protic solvents, have been explained in terms of a non-radiative relaxation process of the planar ICT state involving exciplex formation with polar solvents and producing a twisted ICT state (called TICT) via possible internal rotation and geometrical isomerization channels.

Specific hydrogen-bonding interactions between dye molecules and protic solvents like ethanol or water have a marked influence on the photophysical properties and fluorescence sensitization or quenching of the coumarins studied due to excited state complex formation.

The results are discussed on the basis of the electronic structure of these dyes obtained by application of the well-known quantum chemical PPP-SCF-CI MO method. This gives us an insight into the singlet excited state properties and hydrogen-bonding complexation of these dyes and the dynamics and mechanism of solute-solvent relaxations. Moreover, rotational relaxation behaviour, as reflected in the fluorescence polarisation of highly fluorescent dyes, is correlated with solvent viscosity/free volume. Through measurements of the temperature/viscosity dependence of the fluorescence depolarization ($1/P$) in glycerol, they are able to establish an Arrhenius-like relationship linking ($1/P$) to free-volume fraction of the medium. Furthermore, depolarization data fit the Perrin equation with a slope proportional to the sensitivity of molecular structure towards medium fluidity. The results imply the promising utility of these highly fluorescent dyes as bifunctional fluorescent probes for local fluidity and polarity of the surrounding medium of interest. Moreover, they demonstrate possible analytical application of the commercially available coumarin-6

as a promising fluorescent probe for medium properties (e.g. fluidity, polarity and for following micellization in solutions of some ionic surfactants).

The same technique of fluorescence depolarization provides important molecular level information in the case of a number of flexible dyes of electron donor–acceptor (EDA) type; 1-methyl-4-(4'-R-styryl)pyridinium and -quinolinium iodide (R = H, OCH₃ for N(CH₃)₂). The response of fluorescence quantum yield (ϕ_f) or rotational relaxation time to viscosity/temperature changes ($n(T)$ function) was a sensitive function of stilbazolium dye structure. Analysis of ϕ_f data within the framework of the free-volume (FV) hypothesis showed that the size of dye molecule is a sensitive function of $(n/T)^x$ or (x'/f) function of the glycerol (where x or x' is a fraction reflecting the degree of flexibility or the size of a dye molecule and f is the FV fraction of the solvent). Moreover, probe rotational relaxation dynamics were accurately described in terms of the FV hypothesis. This information has been combined with the results of SCF-PPP-CI MO calculations in an attempt to develop an intriguing gauge of the interplay between average medium microviscosity/free-volume and some molecular properties such as donor–acceptor character, molecular size and flexibility (Abdel-Mottaleb 1983, 1986, 1989, 1990; Abdel-Kader *et al* 1986).

(C) Photochemical studies on some polymeric materials

(1) Polymers with pendant cinnamoyl groups find wide application in the manufacture of microelectronic components, miniature and integrated circuits, photo-engraving and precision-milling (William *et al* 1987; Kandil and Morsi 1990). The work in this area is devoted to studying both the absorption and the emission properties of cinnamic acid, ethylcinnamate and polyvinylcinnamate and many other compounds and their excimer fluorescence. The effect of irradiation on these compounds has been also studied in order to gain some information concerning the mechanism of photodimerization and photocrosslinking either as solid or in solution. Irradiation of heated polyvinylcinnamate film at 320 nm causes a pronounced decrease in both molecular and excimeric emissions due to the formation of cyclobutane crosslinked polymer. Irradiation of the heated polyvinylcinnamate film at 365 nm gives a state quite similar to the freshly prepared film.

(2) Another research activity aims at preparing new polymers derived from polymethacrylic acid hydrazide having different pendant groups with potential photochemical properties including photochromic, proton transfer, photoisomerization and photodimerization. The properties may show up in the solid state or in solution, Research work includes –

(a) Preparation of some polymeric compounds derived from polymethacrylic acid and its related monomers.

(b) Characterization of these polymers and the monomers by the following methods: elemental analysis, IR spectroscopy, thermal analysis (DTA) and ¹H NMR spectra of the monomers.

(D) Photoconductivity

Finally, research work is being carried on (Abdel-Ati and Tauefik 1987) in the field of photodissolution of silver in arsenic selenide-based chalcogenide films. The

photodoping of silver through semiconducting films is followed by electrical resistivity measurements. The kinetics of the photodissolution process are investigated.

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