Photosciences: a look into the future

DOI: 10.1039/c0pp90028a

It is often mentioned in lecture courses and textbooks that the Italian scientist Giacomo Ciamician may be considered the father of photochemistry. Indeed, he studied in depth a number of photochemical reactions and recognized a sizeable fraction of the key photoprocesses well in advance of the actual start of mechanistic photochemistry several decades later. His photochemical papers were mainly published between 1900 and 1910, with a couple more in the following years. As fate would chose, a few other scientists were also active in the same field in these years and by 1910 photochemistry seemed well established as one of the most promising fields of chemistry, so it can be concluded that this discipline reached maturity a century ago.[1]

It may be worthwhile to look at this flourishing period in the frame of what was chemistry at that time. Browsing through the chemical literature of those years evidences a very characteristic attitude among scientists. It was felt that chemistry had reached a turning point by finally demonstrating that it could produce the same compounds as nature did, even on an industrial scale. Then, however, it became important to obtain the same products in a better way, and again nature set the standard.

This concept was perhaps most clearly expressed by another Italian scientist, E. Paternò, who, when addressing the 7th International Symposium on Applied Chemistry (the precursor of the IUPAC series) in 1909 in London, declared that initially chemists had taken into consideration only the target, not the means. However, the target had been reached and it was apparent that now they should concentrate on obtaining the same results, indeed better ones, through a shorter, easier and cheaper path.† What was required to reach this goal was a full understanding of the transformations carried out by light, micro-organisms, enzymes and catalysts (it should be noted that at that meeting the section on photochemistry was one of the best attended).[3]

Likewise, Ciamician pointed out in a talk before the French Chemical Society in 1908 in Paris that chemists had to arrive at the best results under mild conditions and avoid the 'show of brute force' usual in the chemical lab.‡ This was possible, he thought, by using either of two means: enzymes or solar irradiation.

Thus, it was thought that photochemistry had a central role in the future of chemistry. The contribution of this discipline would be of the greatest importance in two fields: synthesis and energy. As for the first subject, what was expected was a shift toward what we now call green chemistry. In the view of these scientists and of other colleagues (see below), photochemistry could offer a perfectly viable solution, judging from the number of surprising chemical transformations that avoided the use of heat or of aggressive chemicals that had been discovered in the preceding years.

For his part, Ciamician continued his talk[4] by presenting the photoreactions he had himself found, including H-abstraction and α-cleavage of ketones, 2+2 cycloaddition of enones, reduction to various degrees of nitro compounds, isomerization of X═Y bonds, various oxidations and other processes. Paternò, in the talk quoted above,[2] similarly advocated the development of photochemistry and went on by illustrating the 2+2 carbonyl + alkene addition and several further examples of what he had found.

Likewise, the German chemist H. Stobbe devoted his presentation before the Bunsen Society (physical chemistry) in 1908 in Vienna[5] to a review of the photochemical reactions recently discovered (including the photochromic fulgides on which he was working) and expressed the belief that photochemistry had great synthetic potential,§ provided that a sufficient number of chemists was active in the field.

As for energy, at the General Meeting of the German Chemical Society in 1910 in Munich, K. Schaump pointed out the importance of photochemistry in two respects:¶[6] on the practical side because it supplied an amount of energy sufficient for the development of mankind, and with regard to education because it was easily changed to other forms of energy, thus offering an excellent way of teaching chemistry.

Ciamician had already expressed his view about the sun as a source of clean energy in the 1908 talk, but expanded it more fully in the celebrated and often quoted talk at the 8th Applied Chemistry Symposium in 1912 in New York.[7] He explained his integrated plan for obtaining energy from the sun, through agriculture on suitable land and through the artificial conversion of simple chemicals into high-energy compounds (planting 'a forest of glass tubes') where this was not possible. This would have given mankind a free and boundless energy source in the place of

† "*E però, se nel primo periodo i chimici senza preoccuparsi dei mezzi hanno mirato soltanto al fine, ora che la meta è stata conseguita, è evidente che debbano rivolgere i loro sforzi ad ottenere i medesimi risultati, anzi risultati maggiori, per una strada più breve, con maggior comodità, con una più grande economia. Per rendere più diretta, più rapida, più vicina alle condizioni in cui avviene in natura, la sintesi delle sostanze organiche è necessaria la conoscenza completa delle trasformazioni che sono operate dalla luce, dai microrganismi, dagli enzimi, dai catalizzatori*" (ref. 2).

‡ "*Au grand victoires de la chimie organique moderne on a souvent reproché d'être des victoires acquises avec trop d'appareilles de force. Et, pour être juste, il faut convenir que de telles objections ne sont pas sans fondement; l'intervéntion des réactifs les plus énergiques et des températures les plus élevées est presque toutjour inévitable dans les synthèses organiques de laboratoire .... L'étude de ces moyens dont se servent les organismes dans les actions chimiques ... en premier lieu les ferments ou enzymes ... et la lumière*" (ref. 4).

§ "*Habe ich nun konstatiert, daß die photochemische Tatsache der organischen Chemie ... weit zahlreicher sind, als man bisher in allgemeinen geglaubt hat*" (ref. 5).

¶ "*Ist es um den Unterricht in der Photochemie, die die Beziehungen der chemischen Energie zu strahelnden untersucht – von wenigen Hochschulen abgelesen ... photochemische Grundsetze und Methoden bereits für Wissensschaft un Technik von größter Bedeutung geworden sind, un ganz besonders weil die bedeutungsvollsten Problemen, von deren glücklicher Lösung das Wohl der gesamten Menschheit abhängt, aller Wahrscheintlichkeit nach ihre Bearbeitung auf dem Boden der Photochemie finden müssen*" (ref. 6).

the non-renewable coal, and open a new, peaceful and clean era after the dirty and nervous era of coal.

The outbreak of war put an end to such hopes, provided that they had grounds. However, even later photochemistry has been in demand in moments of change, where handling energy in large amounts appeared particularly appealing, *e.g.* in the fuel crisis in the Seventies or in the present concern for the greenhouse effect and pollution. Therefore, it appeared advisable to celebrate the centennial of photochemistry by making a new bet and to try and think of which directions photochemistry may take in the future, attempting, whether seriously or as a joke, to recover the prophetic spirit of early-day photochemists.

What came out from this idea was an intense day in Ferrara (and a really hot one, July 17, 2010, in the Aula Magna of the University), where different aspects of photochemistry were confronted. Some had been the key issues from the start, *viz*. synthesis (M. García-Garibay) and energy (D. Nocera), now at a highly sophisticated level and promising effective applications. The conversion of light into mechanical energy had been considered by Schaum, but nowadays the photon can be converted in a predicted movement of molecules for monitoring or directing events (V. Balzani *et al.*) or, on a larger scale, by making crystals bend and lift weights (M. Irie). Some of the topics were new, outside even the dreams a century ago. These included the rationalization and prediction of photochemical reactions by using a computer (M. Olivucci), applications in biology, such as the use of singlet oxygen luminescence for exploring the cell structure (P. Ogilby), and in medicine, where large tumors can be eradicated avoiding the risk of damaging healthy tissues (D. Phillips).

The list of the topics (which are only some of the possible choices, others would have been possible with equal right) gives an idea of the diversity of applications. The high energy of photons, which can be precisely delivered to a small area, and the selection of wavelength, time and temperature give photophysical and photochemical processes an unparalleled versatility that plays an ever increasing role in today's (and tomorrow's) high-technology world.

This themed issue gathers the communications presented in Ferrara (two will appear in later issues). Furthermore, the participants (about 80) presented their own view of the future of photochemistry; these were likewise collected and will be published in the EPA Bulletin.

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