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The Master and the Slave. A glance at the social life of molecules

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Abstract. Low energy interactions induce the formation of molecular assemblies that can display a large variety of sizes and shapes such as dimers, oligomers, colloids, gels, helices, cylinders, etc. These grouping modes mimic human relationships, as people generally flock together according to their affinities. Moreover, chemical reactions, undergone under strong energy interactions, that result in bond breaking and formation of new compounds, can also be compared to human behaviour.
The fables usually involve animals but rarely molecules to play the role of human beings. In this article, we report a molecular tale where two different 9-substituted anthracene derivatives compete in a photochemical reaction, simulating the behaviour of a master and a slave, respectively.

Keywords. Molecular sociology, photochemistry, aromatic endoperoxides, singlet oxygen, graduate education.

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INTRODUCTION

Oil and water are known to repel each other. Despite shaking a mixture of the two in a bottle, they quickly form two distinct layers. The substances soluble in oil are called lipophilic (vitamines A, D, E...) whereas those soluble in water are said to be hydrophilic (sugars, amino-acids...). Fats cannot be eliminated with pure water, but require the use of surfactants to bring them into solution. These substances have affinity both to oil and water and contribute to form a single macroscopic phase.[1]

Such behaviour results from low-energy intermolecular interactions as compared to much stronger ones governing molecular bonds. Non-covalent intermolecular associations are wide-spread in abiotic as well as in biological systems and are fundamental for the formation of molecular assemblies. These can be very diverse: dimers, oligomers, cylinders, helices, colloids, liquid crystals, cellular membranes, to cite but a few. They form the basis of "supramolecular chemistry".[2]

The affinities between molecules mimic human relationships. An interesting example was reported by Green *et al*. in the form of *sergeants* and *soldiers*.[3] Alkylisocyanates copolymers are known to adopt a rigid helical con-

formation in solution. The authors observed that, in solutions of copolymers formed from chiral and achiral monomers, even a small proportion (ca 1%) of chiral monomers induced a high enantiomeric excess; thus, a small number of chiral motifs (playing the role of sergeants) can trigger the movements of a large number of achiral motifs (the soldiers).

Apart from the above soft interactions, chemical reactions transform starting materials into products, through bonds breaking and bond formation. *This activity may also be compared to human behaviour.* For example, in his third novel "the elective affinities",[4] Goethe compared acid-base reactions to love affairs between human couples. Amongst other reactions, one of them inspired Cohen *et al.*[5] who compared molecules to *wolfs* and *lambs*, like in story tales. Here, two molecules, reacting fiercely with one another in solution and leading to a mixture of products, become mutually inactive when tightly linked to two different polymers (Merrifield resins); a third reactant, in solution, reacts successively with one of them (the wolf) then with the second (the lamb), to generate a single product with high yield.

In this article, we describe a particularly relevant reaction where two different molecules (M and E) compete in an addition reaction to a special reactant produced *in situ* through light irradiation. The reaction, which is reminiscent of human behaviour, is briefly described below.

MATERIALS AND METHODS

Formation of endoperoxides

9,10-Endoperoxides "AO_2" (Figure 1) are formed by a hetero Diels-Alder addition of singlet oxygen ($^1O_2$) to anthracenes "A".[6,7,8] Singlet oxygen can be generated by several processes. One of them, photosensitization,[9,10,11,12] involves energy transfer from an organic compound in its excited triplet state (T_1). Anthracene derivatives can be good singlet oxygen producers when they have high yields of triplet formation.[8] The energy transfer from the triplet state and dioxygen leads to singlet oxygen $^1O_2$ which can participate in the addition reaction as shown in Figure 1.

The two anthracene derivatives considered here are 9-isopropyl (E) and 9-tertiobutyl (M) anthracene. Although E was found to readily generate $^1O_2$, M was shown to be unable to do so.[8] The primarily reached photochemical state is deactivated much too fast and no triplet state can be formed; therefore M cannot act as a sensitizer.[13,14] Thus, irradiation of E in solution in the presence of dioxygen generates the endoperoxide

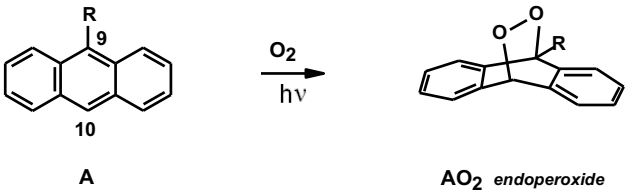

Figure 1. Addition of singlet oxygen to 9-alkylanthracenes (hetero Diels-Alder reaction).

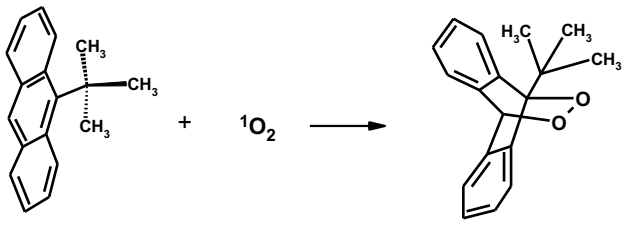

Figure 2. Developed formulae of M and MO_2 respectively, suggesting the steric overcrowding due to the tertiobutyl substituent.

"EO_2" in high yield. Under the same experimental conditions, M is not transformed into "MO_2" and remains unchanged.

Competition reaction

The irradiation through Pyrex of an equimolecular mixture of E and M in solution in dioxygen-saturated ether, at room temperature initially leads to the exclusive formation of the endoperoxide of M (MO_2), Figure 2. Then, after the complete transformation of M, the reaction of E with singlet oxygen begins, leading entirely to the formation of EO_2.[8] The sequence is illustrated in the following sketches: (1), (2) and (3) of Figure 3.

One observes that M, the most crowded molecule, is considerably more reactive with $^1O_2$ than E. This is called a steric acceleration, due to a relief of strain in the activated complex that is product-like. The same phenomenon was also noted for other anthracene derivatives.[15] The thermal and photochemical stability of the two adducts during the reaction attests to its irreversibility. [8,16]

CONCLUSIONS

Master and Slave

The above molecular behaviour is suggestive of human attitudes. Singlet oxygen might be compared to food, produced only by E, the slave. As soon as the food is available,

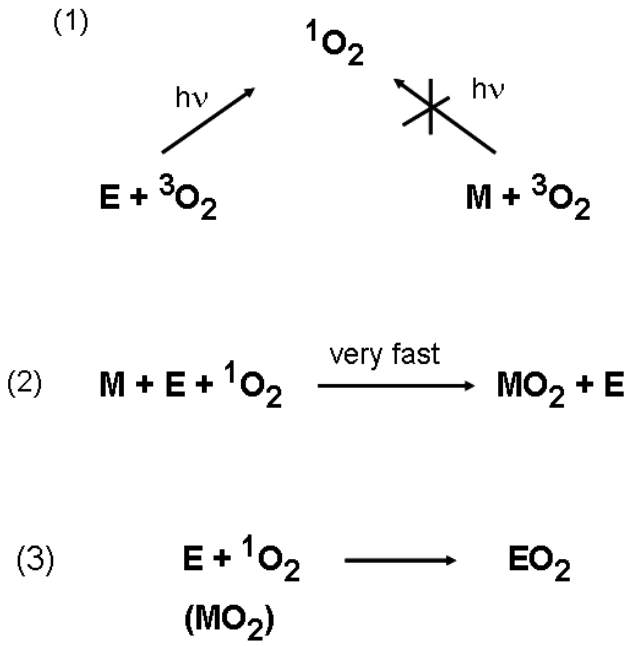

Figure 3. (1) A solution of M and E in equal amounts is irradiated under dioxygen bubbling; E produces singlet oxygen (the food) in contrast to M, which is unable to do so. (2) M swallows and consumes all the food available. (3) M being entirely transformed into MO_2, E can in turn eat the food and generate EO_2.

M (the master) rushes at it in a gluttonous manner until he has eaten his fill. When he has gorged himself, then the poor slave is allowed to eat. The story stops there because after the meal, both master and slave are in a peaceful longstanding state. The nasty master is not punished, in contrast to what generally happens in fairy tales.

One could imagine other scenarios:

1) instead of an equal number of E and M, an excess of M would lead to an accumulation of MO_2; thus a single slave would work for many masters. This would delay the meal time of E.

2) if the irradiation is stopped after M's hunger is satisfied, then in the dark, E would no longer produce the food and be doomed to be starving for ever.

Today, slavery has been abolished on earth. However, it seems that some inactive people are prompt to eat what others have strained to produce. This observation might be extended to relationships between countries.

It could be argued that human beings have common ancestors in the Mendeleev table, especially carbon, hydrogen, oxygen, etc., and that their reptilian brain keeps traces of their molecular constitution; this might partly explain their shocking deeds. However, the extreme complexity of human behaviours cannot be traced back to simple chemical reactions.

Let this short tale contribute to inspire to everybody with a humble attitude.

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