Final report on grant No. K-128395

The role of the hydrogen atom and electron transfer in the photoreduction of n,π*-carbonyls

The main results achieved in the last five years of the K-128395 project will be discussed in four sections. We conclude the report with a summary of the plans on completing our studies on questions that arose during the project.

1. *Photophysics of 4-dimethylaminopyridine*

In the first part, the influence on the fluorescence of a lesser-known properties of aliphatic alcohols were investigated together with the femtosecond properties of singlet excited 4-dimethylaminopyridine (DMAP). More details were presented in the second year report and in Ref.1. The main novelty of this study is that singlet excited DMAP does not only forms complexes with alcohols, but depending on the acidity of the alcohol, the charge transfer (CT) excited state can produce an excited protonated molecule via a zwitterionic complex. Using two different methods, it has been shown that the basicity of the CT excited state of protonated DMAP reaches an extremely high value, $pK_a = 20.4$. The anomalous solvatochromism of the fluorescence of the DMAP's hydrogen bonded complexes is found to be is caused by this protonation process, which we think is an important observation.

2. *Photochemical removal of pharmaceutical pollutants from wastewater*

We have published two papers in the journal Chemosphere on the possible photochemical reduction-oxidation degradation of pharmaceutical residues in biologically treated wastewater and clean environmental waters. In the first one (Ref. 2, 22 citations in the first two years) we show that in a combined pilot plan - laboratory experiment, the type of the low-pressure mercury lamp emitting in the VUV region (developed by our partner) is very effective in degradation of the pollutants. This is particularly the case if the lamp-cooling air (containing ozone) used for air saturation of the polluted water before irradiation. In the second Chemosphere article (Ref. 3, 7 citations in 1.5 years), we looked at the photodegradation of sitagliptin, a new anti-diabetes drug that is significantly resistant to biological water purification, probably caused by the presence of six fluorine atoms in the molecule. In the first (photochemical) step, two new, relatively stable intermediates of the same molecular weight are formed. Identifying the first was trivial: a hydroxyl group on the aromatic ring substitutes a fluorine atom, but finding out the structure and formation mechanism of the second was challenging. The latter has been shown to be a compound with a seven-membered ring formed via intramolecular cyclization, the critical step in the mechanism being that the leaving fluorine carries away the hydrogen of the entering hydroxyl anion. This mechanism explains the stability of the compound formed and helps one to understand the formation of other minor intermediates in the irradiated system.

3. *The role of hydrogen-bonded complexes in the photoreduction of benzophenone by alcohols*

The main aim of the proposal was to advance our understanding of the kinetics of the historically and educationally important photoreactions, benzophenone photoreduction in various aliphatic alcohols. For this purpose, OTKA funding was essential for the purchase of the wave-plate of the optical parametric oscillator used for the excitation, which allowed the system to be investigated in solvents containing ethanol and methanol. The kinetic results proved to be in agreement with our previous model, although at first it was surprising for us. The key insight was that ketyl radicals are very strong hydrogen-bond donors, as we indicates with quantum chemical calculations, so their reactions are significantly influenced by the strength of the complex they form with certain hydrogen-bond acceptor components of the solvent, such as acetonitrile and alcohols. As the nature and concentration of the latter varies from system to system, significant variations can be observed when the nature of the alcohol is varied. Consistent with our model (by some extension), it is not surprising that the very large variation in the rate of the aliphatic ketyl – benzophenone reaction (a radical conversion step) does not depend very much on the nature of the aliphatic ketyl radicals. However, it is more significantly affected by the nature of the solvent and the concentration as well as hydrogen-bonding properties of the alcohol present. The result is a large decrease of the reaction rate in pure alcohols (especially methanol, less so in ethanol), for which the reduction of the Arrhenius pre-exponential factor is responsible. This is not surprising since the concentration of the complexing alcohol hardly depends on temperature. Moreover, in pure alcohols, not only the ketyl radicals but also benzophenone is significantly complexed (both are unreactive), especially considering that alcohols have many dimers (and higher polymers) that are stronger hydrogen bond donors and acceptors. With regard to the "invisible transient" mentioned in the literature, it has been shown experimentally that it does not form at all. The associated article is in final form (Ref. 4.), but we need a few more weeks for submission, recognizing that the self- and cross-reactions of ketyl radicals are also affected by their complexation with the acceptors present, modifying the activation energy of processes (for aromatic ketyl radical self-combinations this is quite high) otherwise expected to be zero. This year, one half of the oral presentation at the CP2P'23 conference (Mulhouse) and the oral contribution at the 31st International Conference on Photochemistry (Sapporo) were devoted to this topic.

4. *The kinetics of disappearance of triplet benzophenone in the absence of reactants*

The fourth important part of the project was the fate (reactions) of triplet benzophenone in the "inert" acetonitrile solvent. This system became important to us because, contrary to literature and theoretical expectations (the Weller equations as a paradigm), we obtained indications that the electron transfer process takes place not only in triplet-triplet annihilation but also in the self-quenching process, i.e. when the triplet excitation of the molecule is lost in a collision with a ground-state benzophenone. The latter effect contradicts the thermodynamic expectation, so we first proved that the effect is real by alternative experiments. The first surprising observation was a slower than linear increase in the conductivity signal with increasing light intensity (to which the initial triplet concentration changes parallel). If ions were formed only in annihilation, we would expect an initially accelerating and then linear change with triplet concentration. Our new experiments confirmed our previous observations mentioned above. In these we calculated the initial triplet and the maximum of the forming benzophenone anion radical concentration at two very different light intensities using the absolute spectra we measured previously. Applying the full kinetic scheme including the self-quenching step we obtained a good agreement with the experimental data, i.e. about 20% less anion was formed at high light intensity than at very low light intensity. This model was based on the assumption that the disappearance of a triplet benzophenone in the case of self-quenching would result in a radical anion with the same efficiency as two in the case of annihilation. (Of course, if self-quenching did not result in a radical anion, the efficiency of radical anion formation would be higher at high light intensities, because annihilation gradually becomes a dominant triplet consuming step.) Unfortunately, these measurements were only conclusive at the highest benzophenone concentration (0.018 mol/l) that can be used at the 355 nm radiation from our Nd-YAG laser, because below this value, self-extinction makes only a small contribution to the radical anion formation signal, and its effect is reduced by other first-order processes that do not result in radical anions. We intend to repeat these experiments at the 390 nm light from the above mentioned optical parametric oscillator where as high concentration as one mol/l is achievable, so that self-quenching can be the dominant triplet deactivation process. Our theoretical investigations yielded some important results, which have been presented at two conferences this year. Namely, although the triplet energy and electrochemically derived data are correct, the solvation energy for the key intermediate ion pair assumed conventionally is definitely wrong, as is the application of the Coulombic from of interaction (both in the Weller equation). Moreover, we are actually dealing with two different solvated ion pairs: one formed immediately after the electron transfer and the other formed after solvent relaxation. Finally, in the case of our experimental system, in contrast to the Weller model, the reacting benzophenone ions cannot be considered as spherical spheres with a charge in the middle, as long as the negative charge is definitely on the carbonyl oxygen not far from the “surface” of the molecule. We are convinced that these results are important new observations, but due to the paradigmatic nature of the problem, we will publish them only after the electrostatic model has been fully developed and properly applied to our chemical reaction.

We have also studied the photochemistry of 5-(hydroxymethyl)furfural, a compound with rising interest as a platform compound in the utilization of cellulose-containing biomass (Ref. 5). The results show many similarities with the benzophenone photoreactions (indicating that our findings are of more general relevance), but because they are less well measured in this case these results will be published after the studies on benzophenone to be consistent with them.

5. *Future outlook: open questions under study*

During the project some rather interesting questions arose. One of these is the identification of the structure of the notorious light-absorbing transient (LAT) the existence of which is known from extensive experimental investigations. We found that the compound can be identified by NMR spectroscopy after "oxygen-free" HPLC purification, but preparative purification to produce the amount needed for the NMR experiment so far was unsuccessful. Understanding the photoreduction kinetics of benzophenone, we have created a benzophenone derivative that is more reactive than any ever before. We plan to describe this in detail in the near future. I will continue these experiments after the publication of the above-mentioned papers. I am currently a volunteer scientific advisor at the institute, a position that will allow me to carry out the necessary studies in the near future.

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