Hydroxylation of benzophenone with ammonium phosphomolybdate in the solid state *via* UV photoactivation†

Mrinmoyee Basu,[a] Suresh Sarkar,[a] Surojit Pande,[a] Subhra Jana,[a] Arun Kumar Sinha,[a] Sougata Sarkar,[a] Mukul Pradhan,[a] Anjali Pal[b] and Tarasankar Pal*[a]

Received (in Cambridge, UK) 23rd March 2009, Accepted 1st October 2009
First published as an Advance Article on the web 15th October 2009
DOI: 10.1039/b905718h

UV photoactivation of a mixture of benzophenone and ammonium phosphomolybdate (APM) in the solid state splits adsorbed moisture, resulting in selectively hydroxylated benzophenone and leaving an electron trapped in green (reduced) solid APM.

The term polyoxometalates (POMs)[1] is applied to an extremely large group of generally anionic clusters with frameworks built from transition metal oxo anions linked by shared oxide ions. The POMs have recently gained significant interest owing to their versatile architecture, facile synthesis, material properties, and especially their catalytic activity and redox properties,[2–4] and most of the elements in the periodic table can be incorporated into the structural framework of these compounds.[1] Among the first POMs to be structurally characterized were the Keggin ions, for example the insoluble phosphomolybdate ion employed here. The Keggin core has a special ability to accept one or several electrons, which remain delocalized within the Keggin structure without causing any structural change.[5] As a result, after electron trapping the Keggin ion can act as a reducing agent, or before reduction it can serve as an oxidizing agent. The reduced Keggin species frequently posses a deep blue color, which justifies their name "heteropoly blues".

Keeping this background in mind, we have successfully photoactivated an intimate mixture of benzophenone and ammonium phosphomolybdate (APM) in the solid state, whereby benzophenone is oxidized by the phosphomolybdate ion with the introduction of a hydroxyl group into the 2- or 3-position of the aromatic moiety. As a consequence APM becomes green and contains trapped electrons. Hydroxylation of benzophenone has been reported previously in the presence of reagents or supports containing hydroxyl groups,[6] but in this study, the source of the hydroxyl groups is simply available moisture. The present report is new and full of promise. Further, to the best of our knowledge, this is the first example of selective photoconversion of benzophenone to 2- and 3-hydroxybenzophenone as a consequence of decomposition of available water molecules.

In a typical experiment, 0.25 g of benzophenone, 1 ml of ethanol and 0.5 g of as-prepared APM were mixed together. The slurry in a Petri dish was dried in air and the dry mass was kept under UV light of wavelength 365 nm, 15 W (at a distance of 3 cm from the light source) for 12 h for photoactivation (~30 °C) (high-power UV light removed the adsorbed moisture and hence water splitting was not observed and no hydroxylation of benzophenone took place). Visually we observed that the yellow mass changed color to green. For maximum yield, the exposed mixture was again treated with an alcoholic suspension of 0.5 g of APM and was air dried as before. The mixture was again irradiated with the same UV light source for 8 h. The photoproduct was separated from the green solid with 5 ml ethanol by centrifugation. The residue was washed and dried and then treated with dilute nitric acid for reuse. Similar photoactivation experiments were carried out in different alcohols, dichloromethane and also in diethyl ether. Every time, 2- and 3-hydroxybenzophenone were identified by thin layer chromatography as the oxidation products, and subsequently these two isomers were separated by column chromatography using a solvent mixture of petroleum ether–ethyl acetate (20 : 1). Finally, the separated products were characterized by UV-visible spectroscopy, NMR, FTIR and GC-MS studies. Quantification of the product yield was obtained from HPLC.

Benzophenone is a prototypical aromatic carbonyl compound that has been extensively studied to better understand its photophysics and photochemistry.[7] During photoactivation, an excited state of the ketone extracts a hydrogen atom from a hydrogen donor and the ultimate reaction products are formed through coupling and disproportionation reactions from the as-obtained radicals. In the case of benzophenone the lowest singlet (S_1 nπ*) and triplet (T_2 ππ*) states are separated by a small energy gap and are strongly coupled *via* a spin–orbit interaction.[8] Due to this small energy gap and the strong spin-orbit coupling, upon irradiation, state T_1 is produced with a large yield close to unity. The T_1 state is typically responsible for all the major photochemical reactions of benzophenone. Benzopinacol is the product of the photolysis of benzophenone alone under oxygen-free condition, while in aerated conditions, hydroxylated benzophenones are produced with a very low quantum yield.[6]

It was not previously known that APM, a very simple and low cost compound, a waste product of the undergraduate laboratory, can show such a clean and effective process of hydroxylation of benzophenone in the presence of UV-light (365 nm) and moisture (Fig. 1). Also of interest here is that the

---

[a] *Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, India. E-mail: tpal@chem.iitkgp.ernet.in*
[b] *Department of Civil Engineering, Indian Institute of Technology, Kharagpur-721302, India*

† Electronic supplementary information (ESI) available: 1: Schematic representation of the photochemical reaction pathway, 2: FTIR spectra of benzophenone and 2- and 3-hydroxybenzophenone, 3: GC-MS spectra of 2- and 3-hydroxybenzophenone and 4: EDS analysis of (a) yellow and (b) green APM *i.e.*, before and after UV light irradiation. See DOI: 10.1039/b905718h

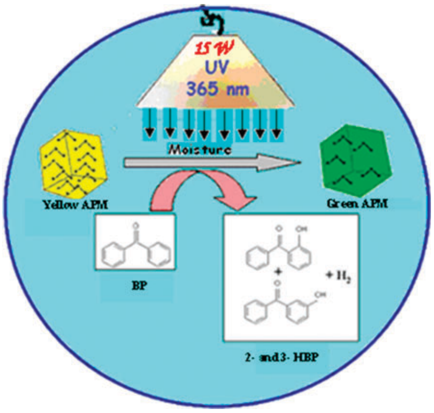

Fig. 1 Schematic representation of the overall reaction.

catalyst APM can be recovered after the reaction due to its high molecular weight and insoluble nature, and can be reused repetitively (ESI 1†). Hydroxylation is thus carried out by multi-step addition of APM since the reaction takes place in the upper surface of the mixture just like in a solid state photochemical reaction.

The photochemistry of benzophenone on surfaces is in fact wavelength dependent. The photoproducts of benzophenone can be explained by considering three main reaction pathways. Upon excitation with 266 nm, α-cleavage of benzophenone predominates, and a variety of photoproducts has been identified.[9] In contrast, 365 nm light irradiation produces benzophenone (BZP) ketyl radical only. Photohydrolysis takes place on a silica surface *via* the formation of diphenylketyl radical. Otherwise if the photoexcited benzophenone ketyl radical receives a hydrogen radical, it gives rise to the product, diphenylcarbinol.[10]

Initially the photoproducts from benzophenone were examined by UV visible spectroscopy. Benzophenone shows an absorption peak at 253 nm in ethanol before the reaction, and after the reaction a new peak appeared at $\lambda_{\max} > 300$ nm. Explicitly, 2-hydroxybenzophenone shows absorbance maxima at 337 and 260 nm whereas 3-hydroxybenzophenone shows peaks at 315 and at 252 nm (Fig. 2). These wavelengths are in good agreement with the absorption maxima of authentic 2- and 3-hydroxybenzophenone, and thus from the UV-visible absorption spectra we can conclude that these are the two isomeric products.

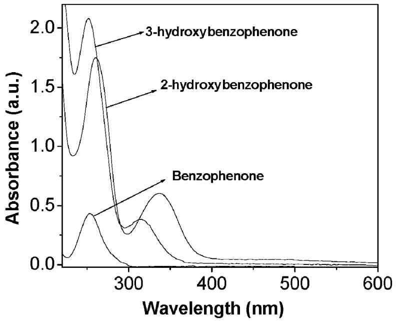

Fig. 2 UV-visible spectra of benzophenone and hydroxylated benzophenones.

Both the products, obtained from the phosphomolybdate induced photoreaction of benzophenone, were also characterized by FTIR (ESI 2†) ^{1}H and ^{13}C NMR spectra and also GC-MS analysis. For 2-hydroxybenzophenone the GC-MS spectrum shows the M$^+$ peak at 197 whereas for 3-hydroxybenzophenone the M$^+$ peak is at 198 (ESI 3†).

The optimal yield of both the hydroxybenzophenone isomers is calculated from HPLC studies. The yield increases considerably up to 20 h and reached 44% for 2-hydroxybenzophenone and 42% for 3-hydroxybenzophenone.

The products 2- and 3-hydroxybenzophenone can easily be separated from aqueous alcoholic solution by using the selective chelating ability of 2-hydroxybenzophenone with Fe(III) chloride at pH ~8.0. A stable six-membered red chelate complex is produced with 2-hydroxybenzophenone only, as an insoluble suspension, whereas 3-hydroxybenzophenone can not give any metal chelate complex, due to steric constraints, and it remains in solution.

The formation of the two products helps to justify the reaction pathway (ESI 1†). First, benzophenone (**A**) is excited by 365 nm light and then in the presence of APM the excited benzophenone (**B**) gives rise to the BZP radical cation (**C**) through electron elimination. This radical cation is then transformed into BZP$^\bullet$OH (**D**) by abstracting –OH functionality from adsorbed moisture. From this BZP$^\bullet$OH, two isomers of hydroxybenzophenone (**E**, **F**) are formed as the two end products. In presence of UV light, APM abstracts an electron from the benzophenone moiety and becomes green. The electron abstraction in turn helps the formation of the BZP radical cation intermediate. Thus APM is reduced and simultaneously BZP is oxidized. It is known that reduced green APM can be prepared if photoirradiated alone[11] but if this green mass is mixed with BZP hydroxylation does not take place. Further, the BZP radical cation can not abstract any hydrogen radicals while APM is present and thus we obtain only the two isomers of hydroxybenzophenone. The same reaction was carried out in different solvents (ethanol, methanol and butanol) and in all these cases we observe the same product. Interestingly, deliberate change in water content in the different alcohols changes the product yield of hydroxylated benzophenone. If we carry out the reaction in a solvent devoid of OH functionalities, the same product is obtained. However when photoactivation is carried out under strictly moisture-free condition no product is detected. From this result we presume that the OH radical comes from the adsorbed moisture as a result of the dissociation of water molecules. Importantly the organic solvent aids dispersion of benzophenone onto the APM microcrystals. If the reaction is carried out in aqueous suspension or without APM no product is obtained from benzophenone.

Several interesting BZP hydroxylation reactions have been reported very recently.[9,12] A general consensus is that an electron injection process occurs from the excited benzophenone to the solid matrix as in the present case. However, yellow unexposed APM, unlike the reported solid supports does not bear any OH functionality. Thus the reaction is driven by BZP radical cation formation as in the earlier reports. However, as mentioned above, under strictly moisture free conditions no product is obtained in the

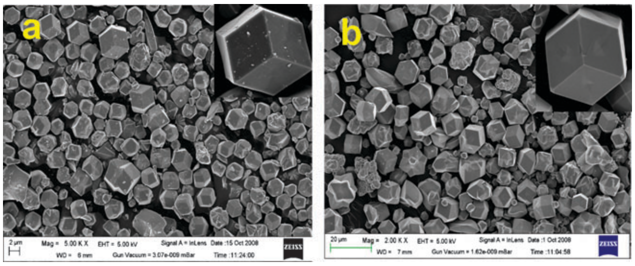

Fig. 3 FESEM images of yellow (a) and green (b) APM *i.e.*, before and after UV light irradiation.

present scenario, so clearly adsorbed water and the BZP radical cation are instrumental in the hydroxylation reaction, and thus some water molecules must be present to allow this reaction to occur.

The compounds benzil, diphenylamine, naphthalene, anthracene, anthraquinone and acetophenone individually can not furnish hydroxylated products. It is also observed that addition of benzoyl peroxide to the reaction mixture dramatically enhanced the product yield while, on the other hand, hydroquinone does not support any product formation. This phenomenon supports a free radical mechanism for the proposed photoactivation process. During the course of reaction solid APM abstracts electrons but its shape, morphology and composition remain unchanged as authenticated from FESEM images (Fig. 3(a) and (b)) and EDS studies (ESI 4†). The present photoactivation with solid APM should lead to new possibilities for different redox reactions.

In conclusion, a novel property of APM, hitherto unknown, is discovered which has been exploited for formation of 2- and 3-hydroxybenzophenone in the presence of adsorbed water. Further the probable mechanism for the formation of these two products has been proposed and the reusability of APM for this reaction reported.

The authors are thankful to the UGC, CSIR & DST in New Delhi and Indian Institute of Technology, Kharagpur, India.

Notes and references

1 C. L. Hill (ed.), *Chem. Rev.*, 1998, **98**, 1.
2 C. Martin, C. Lamonier, M. Fournier, O. Mentre, V. Harle, D. Guillaume and E. Payen, *Inorg. Chem.*, 2004, **43**, 4636.
3 M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, 1983.
4 Y. Seki, J. Min, S. Misono and M. Mizuno, *J. Phys. Chem. B*, 2000, **104**, 5940.
5 J. M. Maestre, X. Lopez, C. Bo, J. M. Poblet and N. Casañ-Pastor, *J. Am. Chem. Soc.*, 2001, **123**, 3749.
6 J. P. Da Silva, I. F. Machado, J. P. Lourenço and L. F. Vieira Ferreira, *Microporous Mesoporous Mater.*, 2006, **89**, 143.
7 W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.*, 1961, **83**, 2789.
8 B. K. Shah and D. C. Neckers, *J. Am. Chem. Soc.*, 2004, **126**, 1830.
9 J. P. Da Silva, I. F. Machado, J. P. Lourenço and L. F. Vieira Ferreira, *Microporous Mesoporous Mater.*, 2005, **84**, 1.
10 L. F. V. Ferreira, I. F. Machado, J. P. Da Silva and T. J. F. Branco, *Photochem. Photobiol. Sci.*, 2006, **5**, 665.
11 N. V. Sidgwick, *The Chemical Elements and their Compounds*, Oxford University Press, Oxford, 1950.
12 S. Baral-Tosh, S. K. Chattopadhyay and P. K. Das, *J. Phys. Chem.*, 1984, **88**, 1404.