

SYNTHESIS AND PHOTOCHEMICAL PROPERTIES OF POLYOXOMETALATES CONTAINING *para* – NITROBENZENE PHOSPHOROUS ACID FRAGMENT

Dmitry V. Katin, Sergei V. Zelentsov

Nizhnii Novgorod State University,
Gagarin Ave., 23, Nizhnii Novgorod, 603950, Russia

Phone: +7(8314)659912

E-mail: zelentsov@chem.unn.ru

Summary. We synthesized a new hybrid organo-inorganic polyoxometalate from Na_2WO_4 and di-sodium salt of *para*-nitrophenyl ester of phosphoric acid, $\text{Na}_2\text{C}_6\text{H}_4\text{NO}_2@[\text{PW}_{12}\text{O}_{40}]$. Photochemical activity of the compound towards mandelic acid and isopropyl alcohol was studied. It was shown that the polyoxometalate synthesized behaves itself as a powerful photooxidizing agent and/or a catalyst of the photochemical oxidation of the said H-atom donors by nitrocompound in the presence of oxygen.

Keywords: hybrid polyoxometalate, synthesis, *para*-nitrophenyl ester of phosphoric acid, photochemical oxidation, catalytic activity

Hybrid organo-inorganic compounds have gained a great piece of interest recently [1]. The interest is reasoned by the unique collection of different chemical properties in the case of hybrid polyoxometalates (HPOM) [2]. HPOM has a real nanomolecular nature that gives a possibility to obtain a combination of controllable properties such as size, shape, charge, redox potentials, solubility and so on [3] in the same material.

Our aim was to synthesize HPOM containing both $[\text{PW}_{12}\text{O}_{40}]$ and nitro aromatic fragments using hydrothermal procedure.

Method of the HPOM synthesis

1.35 g of $\text{Na}_2\text{WO}_4 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 ml of distilled water. 67.5 mg of *para*-nitrophenyl ester of phosphoric acid (RNO_2) was added to the solution. The reaction mixture was stirred up to dissolution of solids. After that 10 ml of concentrated H_2SO_4 was added drop wise into the constantly stirring reaction mixture. After some time a precipitate began to form. The reaction mixture was heated up to 50 °C for 3 min. The precipitate began to form more intensively.

The solution was kept in dark for 3 days at room temperature. The precipitate became dense and its amount increased. Its color became grey-green. The precipitate was filtered and dried in dark at room temperature for a day. After that the product was purified with crystallization from ethyl alcohol. The alcohol was evaporated, and the newly formed precipitate was washed with water and dried. Recrystallization procedure was repeated some times. There

were some problem with purification of other hybrid organo-inorganic compounds (the same situation was observed during phenylimido functionalization of α -[PW₁₂O₄₀]³⁻[9]).

IR identification of the synthesized HPOM

IR- Spectra of the synthesized HPOM in the KBr matrices were measured (see Fig.1). UV-spectrophotometer (Prestige 21, Shimadzu) was used. Table 1 contains some results of our interpretation of the obtained data.

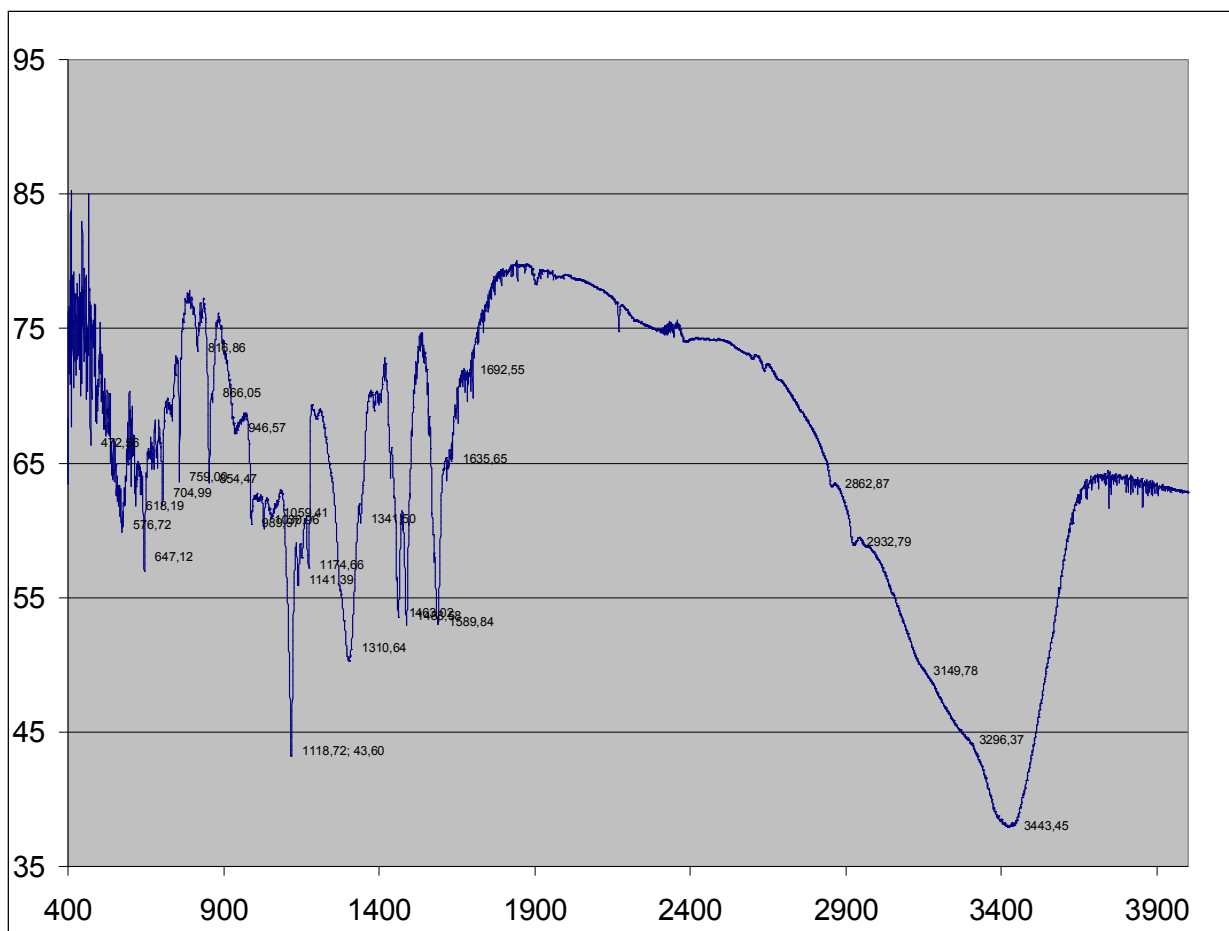


Fig.1 IR- Spectrum of the synthesized HPOM in the KBr matrices

Table 1 IR- Spectra of the synthesized HPOM in the KBr matrices

Wave number, cm ⁻¹	Intensity ¹⁾	Interpretation ²⁾	Literature/ comparison with the starting compounds
3443.45	S., B.	$\nu_{as}(\text{OH})$	3444.89 in RNO ₂ 3440.55 in Na ₂ WO ₄ *6H ₂ O
2932.79	M.	$\nu_{as}(\text{CH})$	[7]/ 2939.06 in RNO ₂
2862.87	M.	$\nu_{as}(\text{CH})$	[7]/ 2939.06 in RNO ₂
1635.65	M.	Vibrations of aromatic	1627.93 in RNO ₂

		ring	
1589.84	S.	Vibrations of aromatic ring	1562.35 in RNO ₂
1489.09	S.	$v_{as}(NO_2)$	1523.29 in RNO ₂
1463.03	S., Shp.		
1340.50	S.	$v_s(NO_2)$	1343.43 in RNO ₂
1310.64	S.		
1174.66	M.		1176.59 in RNO ₂
1141.38	M.		1132.22 in Na ₂ WO ₄ *6H ₂ O
1118.72	S.		
1059.81	S.	$v_{as}(PO)$, KS	[5]
989.97	M.	Stretching, WO, KS	[5], [6]
990.45	M.	$v_{as}(WO)$, KS	[5]
964.57	M.	$v_{as}(WO)$, KS	[5]
932.78	M.	$v_{as}(WO)$, KS	[6]
816.34	M.	Stretching, WO, KS	[5]
758.99	S.		752.73 in Na ₂ WO ₄ *6H ₂ O
704.99	S.		
618.19	S.		
576.72	S.	Stretching, WO, KS	[5]
573.34	M.		
522.76	M.	Stretching, WO, KS	[5]
472.16	M.	Stretching, WO, KS	[5]

¹⁾ S. – Strong, B. – Broadened, M. – Mediate, Shp. – Sharp

²⁾ as – asymmetrical stretching vibration; KS – Keggin structure.

To make the interpretation easier we have measured IR-spectra of the starting materials (see Fig. 2 and 3).

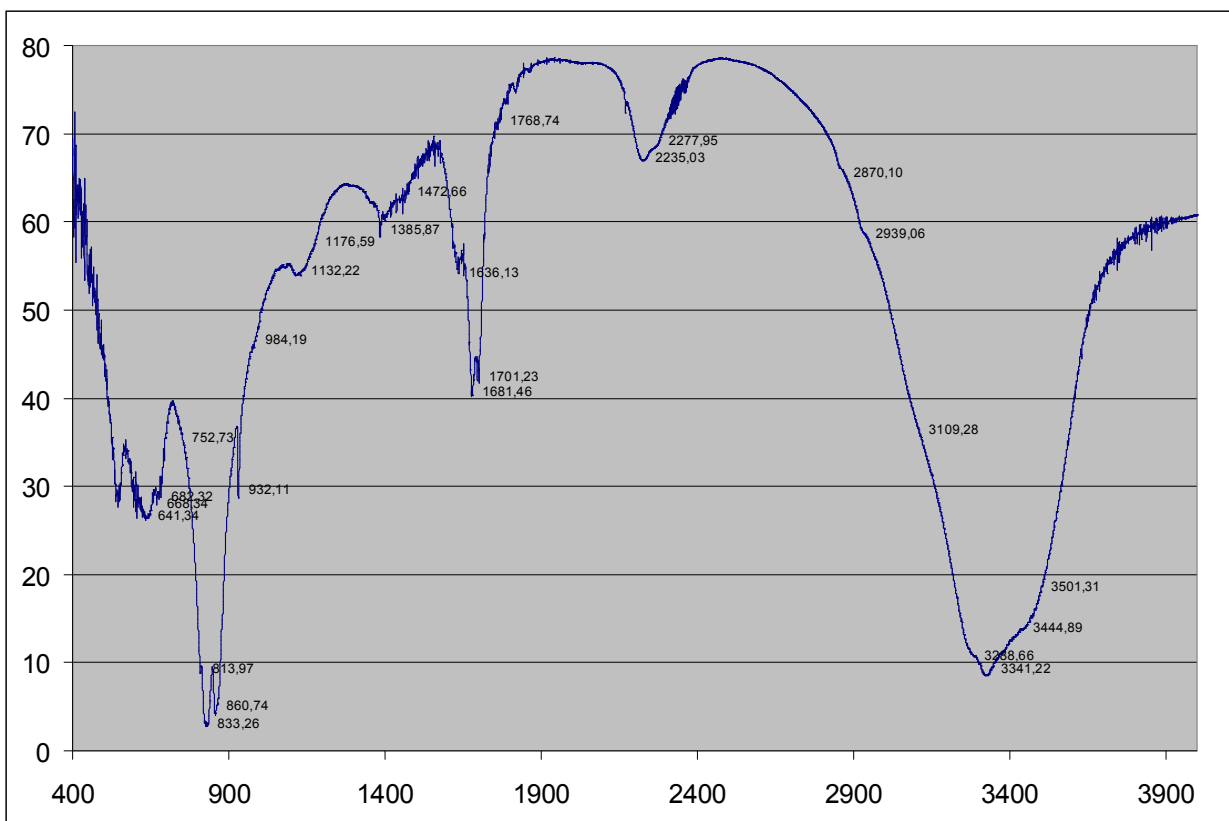


Fig.2 IR- Spectrum of $\text{Na}_2\text{WO}_4 \cdot 6\text{H}_2\text{O}$ in the KBr matrices.

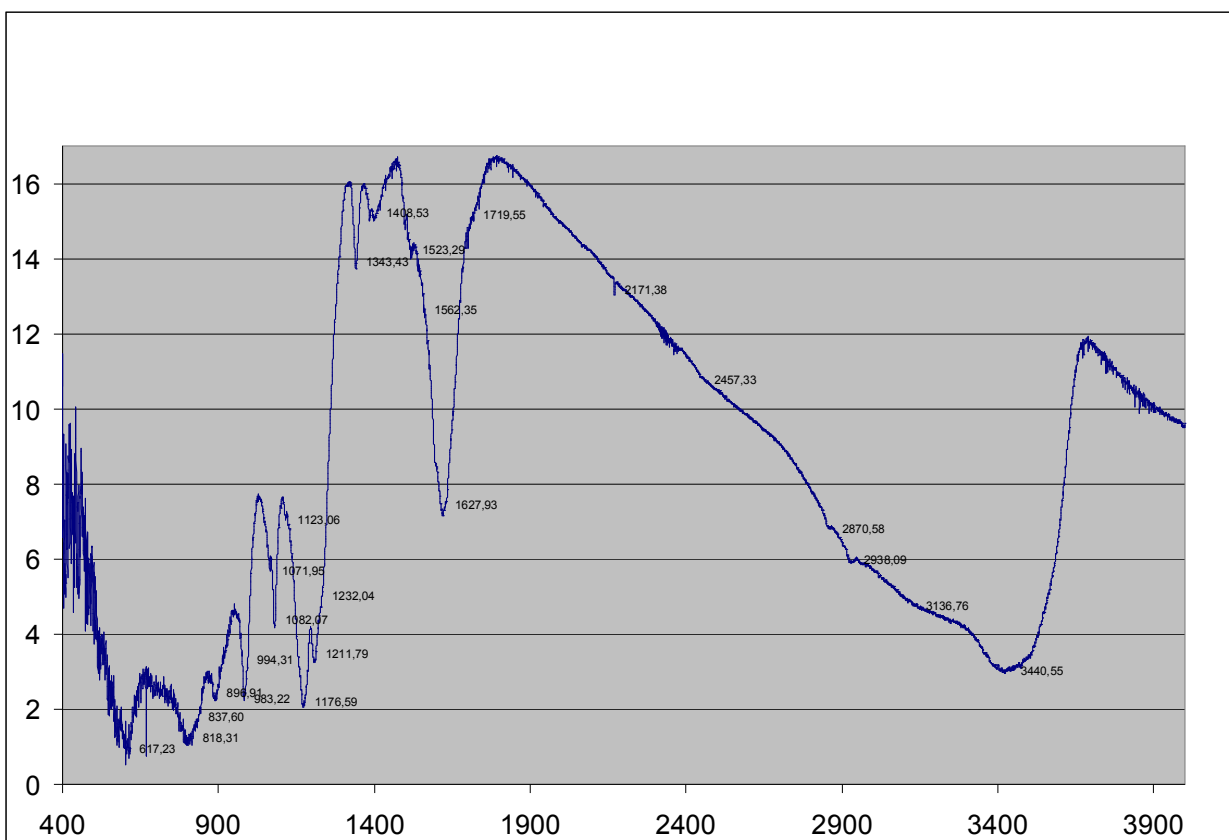


Fig.3 IR- Spectrum of *para*- nitrophenylic ester of phosphoric acid in the KBr matrices.

It is worth to note that there are vibrations at 1059.81 (stretching vibration of P-O bond), 989.97, 990.45, 964.57, 932.78, 816.34, 576.72, 522.76 and 472.16 cm^{-1} being valence vibrations of the W-O bonds (in different crystallographic positions the vibrations differ) that are characteristic for the Keggin-type structure of $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ fragments. In addition, one can observe some vibrations at 1059.81 cm^{-1} that are typical for P-O bonds. They are identified as the PO_4^{3-} tetrahedral vibrations. The aromatic C-H bond vibrations at 2932.79 and 2862.87 cm^{-1} and the aromatic ring vibrations at 1589.84 cm^{-1} can be also found. And at last it is useful to note two vibrations at 1489.09 and 1340.50 cm^{-1} . They could be attributed to asymmetrical and symmetrical vibrations of the nitro groups.

Thus, it should be note that the obtained HPOM contains vibrations of bonds from fragments of its main components and the IR spectra observed give us a possibility to assign the HPOM to the Keggin type compound.

To enforce the statement we used X-ray fluorescence analysis (ERD-900 X-ray fluorescence spectrometer from Shimadzu) to determine amounts of main atoms containing in the product. The product contained 8.95 % of P and 64.03 % of W.

Photochemical reactions of the HPOM

To demonstrate oxidative potential of the HPOM we have used it to produce photochemical oxidation of compounds containing active hydrogen atoms such as isopropyl alcohol and mandelic acid.

Fig 4 shows changes in UV spectra of the reaction mixture consisting of HPOM (1 mmole/l) and *i*-PrOH under UV irradiation (with intensity of 22.5 mW/cm^2) in the presence of air.

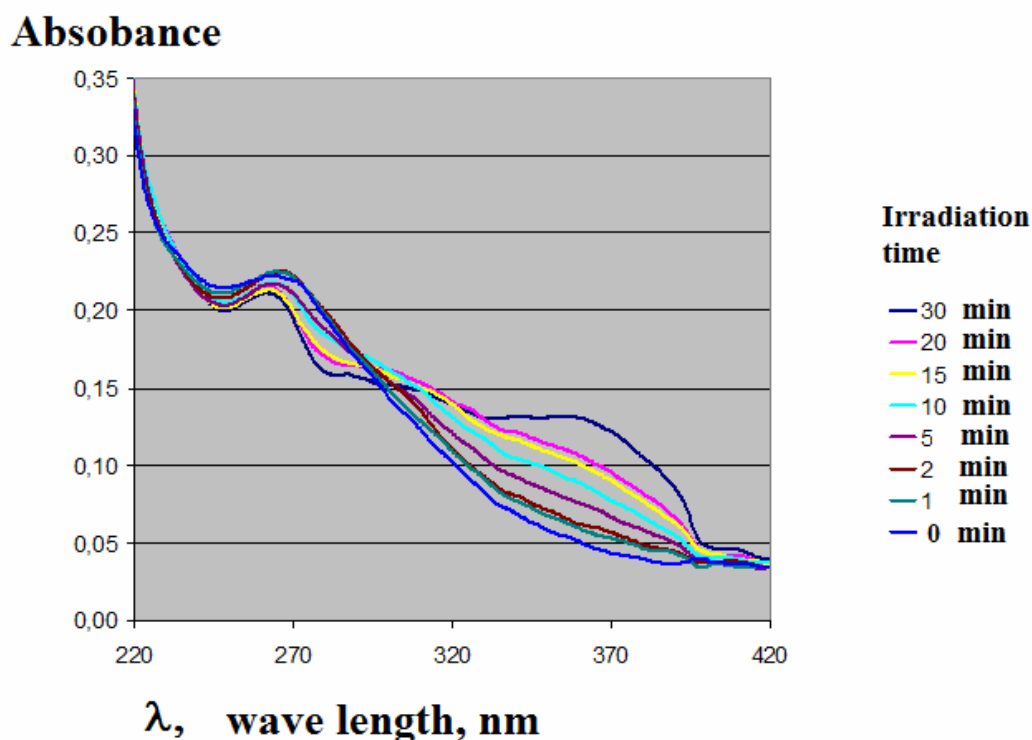


Fig. 4 Changes in UV spectra of the reaction mixture consisting of HPOM (1 mmole/l) and *i*-PrOH under UV irradiation (with intensity of 22.5 mW/cm²) in the presence of air.

Much more pronounced effect was observed in the course of the UV irradiation of mandelic acid under UV irradiation (with intensity of 22.5 mW/cm²) in the presence of air (Fig.5).

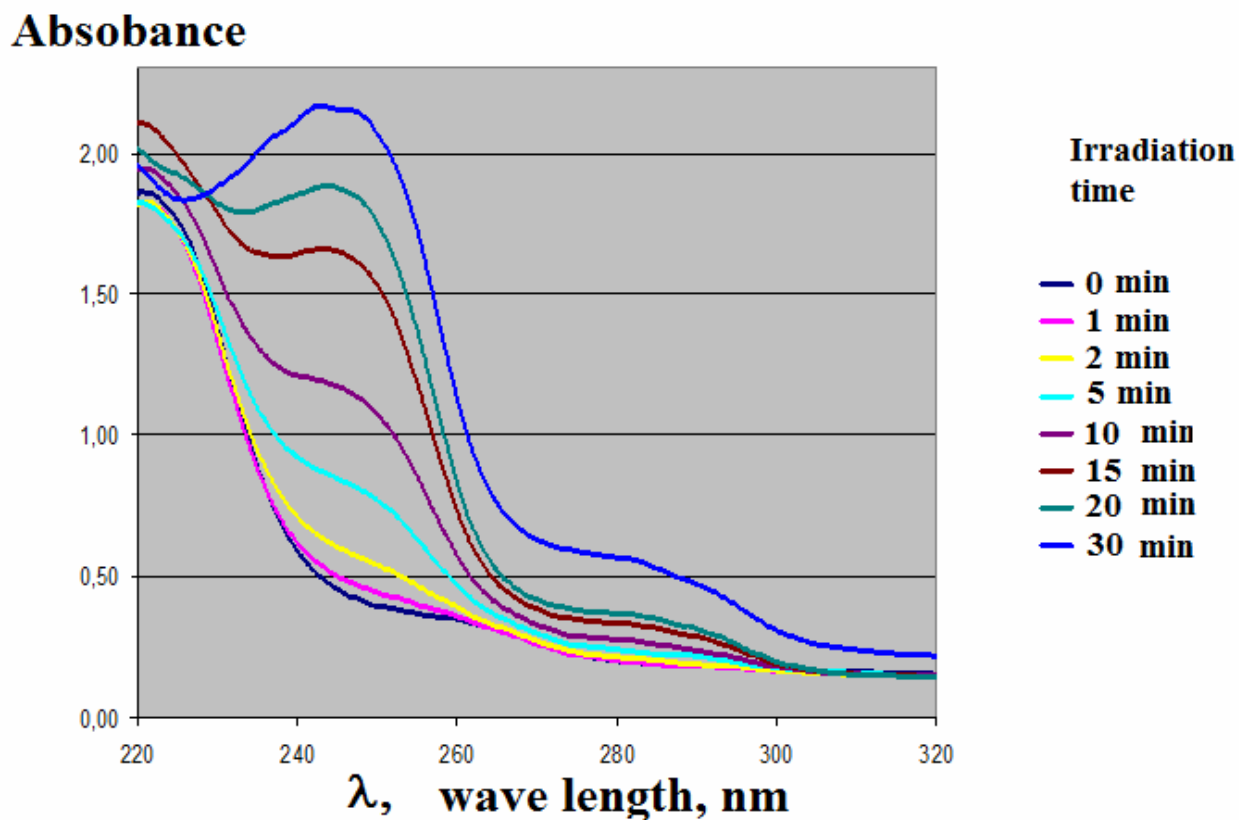
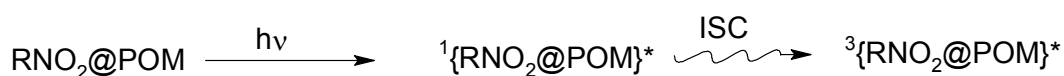


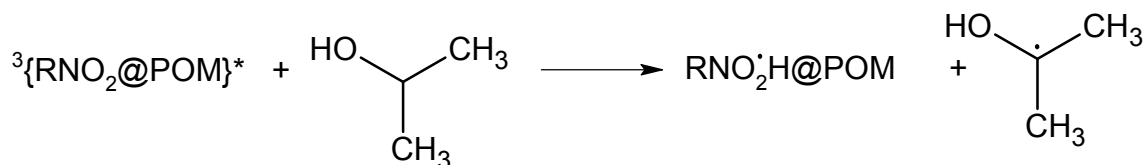
Fig. 5 Changes in UV spectra of the reaction mixture consisting of HPOM (1 mmole/l) and mandelic sodium (1 mmole/l) in acetonitrile under UV irradiation (with intensity of 22.5 mW/cm²) in the presence of air.

Discussion

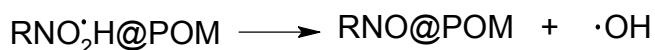
Nitro aromatic compounds transfer into the excited singlet state under UV irradiation. The excited singlet state turns into the triplet state due to intersystem crossing (*isc*) [10]. The transformation is catalyzed, as rule, with compounds containing heavy atoms [13]. The role of the atoms can successfully play heavy atoms contained in HPOM.



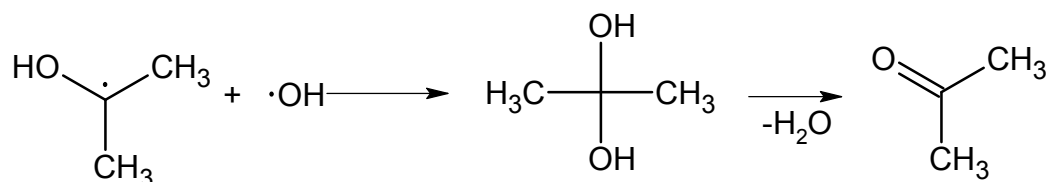
The triplet HPOM containing nitro groups are very active and could easily abstract hydrogen atom from isopropyl alcohol giving two radical products: the C-centered radical formed from isopropyl alcohol and the radical derived from HPOM having added hydrogen atom at oxygen atom of the nitro aromatic moieties.



Afterwards the radical from HPOM decomposes to nitroso compound and hydroxyl radical.



Hydroxyl radicals could recombine with the C-centered radical that at the end should give acetone[11]. It was a final product that was detected in the corresponding experiments. Hydroxyl radical oxidation of alcohols is widely known [11].

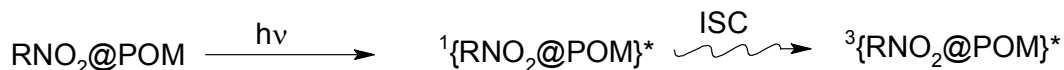


It should be noted that HPOM containing nitroso group could in its turn be oxidized into nitro aromatics due to possible activation of molecular oxygen with polyoxometalate fragment.

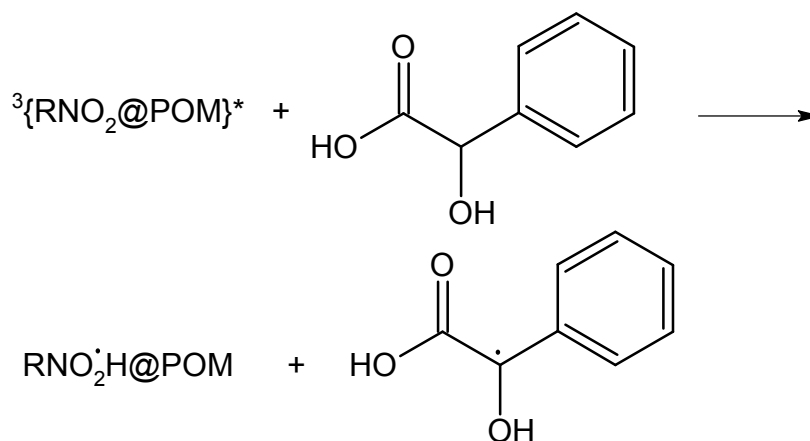


The last reaction occurs because of the POM ability to undergo redox reactions [1,3].

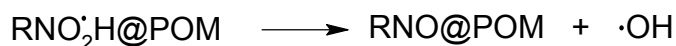
Photochemical oxidative decarboxylation of mandelic acid and its derivatives in the presence of HPOM proceeds in the same manner as in the case of the isopropyl alcohol – HPOM system.



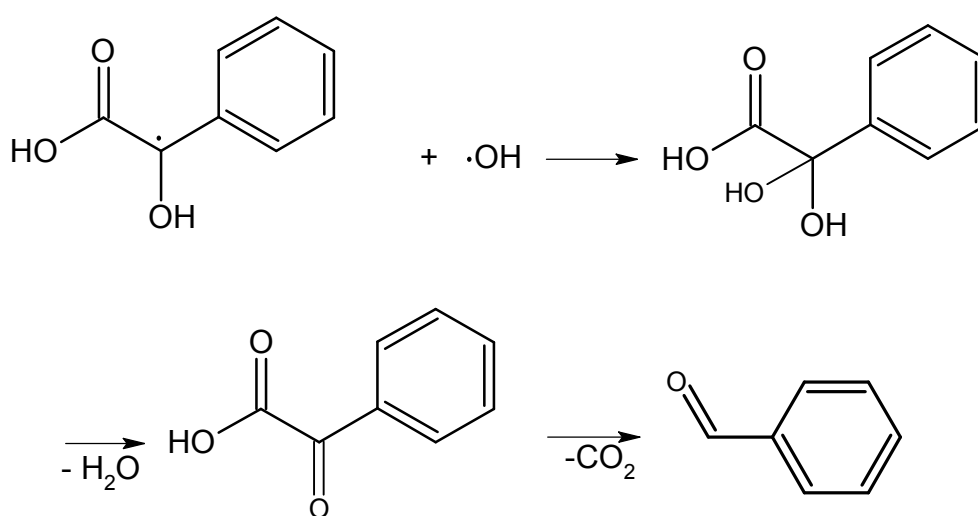
HPOM in the triplet state abstracts mobile hydrogen atoms from the alcoholic carbon atom from the mandelic acid molecule to give the C-centered radical and an adduct of hydrogen atom with nitro aromatic fragment of HPOM.



The hydrated HPOM could eliminate hydroxyl radicals to turn into nitroso-containing POM



The C-centered radical in its turn could recombine with hydroxyl radical, eliminate water molecule and transforms into phenylglyoxalic acid. The said acid eliminates CO₂ giving benzaldehyde as the main product. The analogous mechanism was proposed in [12].



In the presence of molecular oxygen HPOM containing nitroso compound could oxidized into nitro compound.



The reaction schemes proposed give us a possibility to rationalize our observations.

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