

Photosensitized oxidation of bromide to bromine catalyzed by niobium pentachloride in methanol solution Formation and crystal structure of the tetraphenylphosphonium tribromide

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Abstract

This article examines the photoproduction of bromine by UV–vis light irradiation in the presence of niobium pentachloride in methanol media, under aerobic conditions. The reaction of tetraphenylphosphonium bromide with niobium pentachloride in methanol, thus, produced the corresponding tribromide. X-ray studies were performed on the tribromide compound to confirm the oxidation reaction. To our knowledge, the homogeneous photocatalytic oxidation of halogen ions when niobium pentachloride is photosensitized is the first example of the photocatalytic properties of this reagent. The photo-oxidation of the halogen ions was carried out under several conditions. The nearly linear oxo-bridges seem to favour this photocatalytic action.

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1. Introduction

In our previous publication, we have reported that the reaction of NbCl_5 with methanol occurred with partial substitution of chloride ions by alkoxide units resulting in the formation of polyoxoalkoxy complexes $\text{NbCl}_{5-x}(\text{OMe})_x$ [1]. Transition metal polyoxoalkoxide complexes (in their high oxidation states) have been studied extensively as versatile molecular precursors of oxides and polyoxometalates (POM) [2,3]. Metal alkoxides are of interest both as examples of soluble metal oxide coordination compounds and as molecular species which provide a bridge between the oligomeric metal alkoxides $[\text{M}(\text{OR})_n]_x$ and the macromolecular metal oxides. Metal oxides including Nb_2O_5 are the heterogeneous photocatalysts that are extensively used for the degradation of dyes and mineralization of organic compounds [4–10] as well as for the photocatalytic water splitting

[11] and the photochemical oxidation of halide ions [12]. In addition, many POM systems have found widespread application in homogeneous photocatalysis [13–16]. The photoredox chemistry of POM is based on the change of their redox properties in the excited state, compared to the ground state. Excitation renders these systems powerful oxidizing reagents, able to oxidize a great variety of organic compounds [17]. Similarities between polyoxometalates ($\text{PW}_{12}\text{O}_{40}$) as a homogeneous photocatalyst and semiconductor oxide (TiO_2) as a heterogeneous photocatalyst have been identified and their ability to oxidize organic compounds has been demonstrated [18]. Thus, metal polyoxoalkoxides are of great interest as molecular species, which exhibit photocatalytic activity analogous to those aforementioned [19]. But there has yet no report about the effects of the metal polyoxoalkoxides on the photocatalytic oxidation of halides.

The photo-induced and photocatalyzed oxidation reactions of halide ions have received special attention [20–22]. Reichman et al. reported the photoproduction of halogen molecules in oxygen saturated aqueous solution. The photosensitized oxidation

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of bromide, for example, has been reported in water using colloidal or powdered forms of TiO_2 as photoactive semiconductor surface [12,23,24]. The oxidation of quaternary ammonium and phosphonium bromide produces the corresponding tribromides which can act as clean and selective brominating agents for a variety of organic substrates and also are more suitable than molecular halogens [25,26]. Bromination of organic substrates, particularly aromatics, has garnered a lot of attention in recent years due to the commercial importance of such compounds as potent antitumor, antibacterial, antifungal, antineoplastic, antiviral and antioxidizing agents and also as industrial intermediates for manufacture of speciality chemicals, pharmaceuticals and agrochemicals [27].

In this study, we report the photo-induced and photocatalytic oxidation of bromide in niobium pentachloride and methanol oxygenated conditions. The molecular constitution of the methanol solutions and the effect of the methanolysis of NbCl_5 on the photocatalytic activity were also studied. The oxidized bromide species (tetraphenylphosphonium tribromide) crystallize in the monoclinic space group $P2_1/n$ and the Br–Br–Br is totally symmetrical according to the X-ray analysis.

2. Experimental

2.1. Materials and methods

Niobium pentachloride obtained from Fluka, tetraphenylphosphonium bromide and potassium bromide obtained from Aldrich were used without further purification. Methanol obtained from Merck and de-ionized and distilled water was used throughout this study. Deuterated solvents for use in the NMR, $\text{MeOD-}d_1$, $\text{DMSO-}d_6$ and CDCl_3 were purchased from Merck. The photocatalytic activity experiments were performed at room temperature. The UV source was a 1000 W mercury lamp equipped with a cool water circulating filter to absorb the near IR radiation. Light passed through a UV cut-off filter ($\lambda > 250 \text{ nm}$) and then the filtered light was focused onto a 1 cm cell from quartz. The UV–vis absorption spectra in the range 900–200 nm were recorded using a Cary 3E spectrophotometer. Cyclic voltammograms were recorded on an AFCBP1 Biopotentiostat (Pine Instrument Company) and a standard three-electrode

assembly (working: platinum electrode, auxiliary: platinum wire, reference: Ag/AgCl , supporting electrolyte: LiCl (0.1 M), scan rate: 100 mV s^{-1}). ^1H NMR spectra were recorded on a Varian UNITYplus operating at 300 MHz spectrometer using the solvent peak as an internal reference. Diffraction measurements were made on a Bruker Smart Apex CCD diffractometer using graphite monochromated $\text{Mo K}\alpha$ radiation. The structure was solved by direct methods and refined in full-matrix least-squares procedure on F^2 with DIRDIF. Crystallographic data for the structural analysis of tetraphenylphosphonium tribromide have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 609927. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

2.2. General procedures (photolysis and analyses)

A methanol solution (10 ml) of niobium pentachloride (2.57 mmol) was added to a methanol solution (10 ml) of tetraphenylphosphonium bromide (0.31 mmol) resulting a colorless mixture under aerated conditions. We used excess niobium catalyst (129 mM) compared to bromide concentration (15.5 mM) with the ratio catalyst/bromide = 8.32. One aliquot of the solution was kept in the dark and a second one was kept under light conditions. After 5 days the color of the solution stored in the light became yellow whereas the solution maintained in darkness remained colorless. The yellow solution gave after 6 days yellow crystals suitable for X-ray analysis. The composition and structure of this compound have been determined by X-ray crystallography, showing it to be $[\text{PPh}_4]\text{Br}_3$. The same procedure was followed in order to prepare the solution for the photolysis experiment. The solution was allowed to stand at room temperature. Upon irradiation for 3 h the color of the solution turned to yellow. During irradiation a blue color detected on the cell attributed to the intervalence electron transfer between adjacent metal ions as has been mentioned earlier from Hiskia et al. for reduced POM [15].

In order to investigate the effect of the concentration of either Br^- or Nb^{5+} ions in the oxidation reaction, a methanol solution containing equimolar amounts of niobium (64.3 mM) and bro-

Table 1
The effect of the concentration of niobium pentachloride and bromide ions in the photochemical production of bromine

	$[\text{Br}^-]$ (mM) ^a	$[\text{NbCl}_5]$ in MeOH (mM) ^a	$[\text{NbCl}_5]$ in MeOH/ H_2O (M) ^a	$[\text{NbCl}_5]/[\text{Br}^-]$	Irradiation time (h)	Product ^b	Oxidation potential/ V^c
1	15.5 ^d	129 ^d		8.32	3	Br_3^-	0.985
2	15.5 ^e	129 ^e		8.32	3	No product	
3	15.5		129	8.32	3	No product	
4	64.3	64.3		1	1.30	Br_3^-	1.040
5	64.3		64.3	1	3	No product	
6	15.5	1.94		1/7.99	3	Br_3^-	1.103
7	50.0	0.100		1/500	3	No product	

^a Final concentrations.

^b The photochemical production of bromine was followed by the color change of the solution.

^c Supporting electrolyte: LiCl (0.1 M) and scan rate: 100 mV s^{-1} .

^d Solution after storage of 10 days in darkness.

^e Freshly prepared solution.

mide ions (64.3 mM) and a methanol solution containing a small excess of Br^- (15.5 mM) over Nb^{5+} (1.94 mM) were prepared by the same procedure but using potassium bromide instead of tetraphenylphosphonium bromide. Photolysis experiments were performed under the same conditions. The color of the solution containing equimolar ratio of catalyst (Nb^{5+}) and substrate (Br^-) in concentration 64.3 mM turned to yellow upon irradiation for less than 3 h while the color of the solution containing the ratio of catalyst/bromide = 1/7.99 turned to yellow after 3 h irradiation. A raise of bromide concentration resulted to an increase of the reaction rate whereas when the niobium concentration decreases the reaction rate lowers down (Table 1).

Another experiment was carried out in order to investigate the effect of water addition in the oxidation of bromide. To this goal, a methanol solution of Nb^{5+} (64.3 mM) was added to an aqueous solution containing equimolar amount of KBr (64.3 mM). The resulting mixture of $\text{MeOH}/\text{H}_2\text{O}$ (50%, v/v) was irradiated for 3 h. The absence of any yellow color ensures that no reaction takes place. The addition of water causes the hydrolysis of all of the chloro-methoxide niobium complexes and the formation of a white precipitate due to the non-soluble niobium oxides.

3. Results and discussion

3.1. Characterization of the photocatalytic system (solvolysis of NbCl_5 by methanol)

Within 1–3 h of irradiation of the bromide solutions containing the NbCl_5 catalyst, the solutions became colored with the bromine color (light yellow for the solutions 1, 4 and 6). The light yellow color and the UV–vis spectrum of the solution from which crystal of tetraphenylphosphonium tribromide was isolated revealed that amounts of bromine were produced under the same conditions when the cells contained different equimolar ratio of catalyst (Nb^{5+}) and substrate (Br^-). Some of the results are summarized in Table 1. Based on the experiments upon the photooxidation of bromide ion several points should be noted for the oxidation reaction and the photocatalytic system. The photocatalytic reaction is carried out in a solution containing niobium polyoxomethoxide complexes formed during the solvolysis of NbCl_5 in methanol. The photocatalytic activity of the polyoxomethoxoniobate species depends on their electronic and structural properties and is related to the $\text{Nb}-\text{O}-\text{Nb}$ bond angles [11].

^1H NMR spectroscopy has been used to determine over time the molecular constitution of the methanol solution and identifies the more reactive complexes towards the oxidation of bromide ion. In a typical experiment, a solution containing 60.0 mM NbCl_5 in MeOD was prepared and monitored by ^1H NMR spectroscopy over time. The ^1H NMR spectrum of the freshly prepared solution of NbCl_5 in methanol (Fig. 1, curve I) shows peaks in the region 4.2–3.6 ppm that are assigned to the bridging-MeO and terminal-MeO group. It is confirmed that the formation of the methoxo complexes of niobium is immediate and polymeric species of the general formula $[\text{NbCl}_{5-x}(\text{OMe})_x]_n$ are present, but such a solution upon irradiation causes no reaction with the bromide ion. When the solution of NbCl_5 was allowed

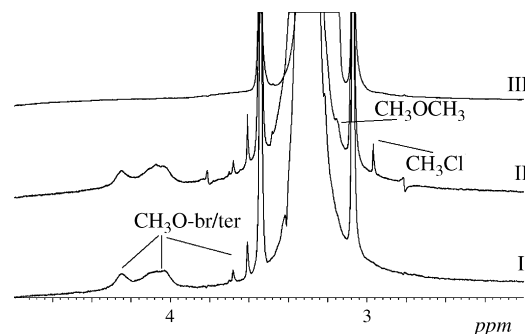


Fig. 1. ^1H NMR spectra of NbCl_5 solution in MeOD freshly prepared, after 3 days and after addition of water (curves I–III, respectively).

to stand for 3 days the methyl groups from the more strongly bound MeO-bridge groups bind to the neighbouring coordinated Cl^- and MeO-terminal group to form organic products such as MeCl and Me_2O (Fig. 1, curve II), as it is stated in our previous work [11]. This means that upon storage methoxide complexes are converted into oxo-complexes (which are more stable). It is obvious that the conversion of methoxo and chloro-bridges into oxo-bridges leads to the formation of polyoxomethoxoniobate complexes, which are photosensitive in solution whereas the photoredox reaction proceeds effectively in the presence of bromide ions. Thus, the increased photosensitivity of polyoxomethoxoniobate compounds is attributed to the existence of $\text{Nb}-\text{O}$ moieties. Resonance Raman and UV–vis spectroscopy showed that a nearly linear $\text{Nb}-\text{O}-\text{Nb}$ bridge moiety causes the photochemical activation because this is followed by a perfect orbital-mixing delocalization of d^1 electron in the reduced polyoxomethoxo species.

In another NMR experiment, a solution of NbCl_5 in a mixture of $\text{MeOD}/\text{D}_2\text{O}$ (50%, v/v) was prepared. In the ^1H NMR spectrum (Fig. 1, curve III) no peaks attributed to MeO are observed reflecting the conversion of methoxide bridges to oxo-bridges upon the addition of water. Such a solution containing oxo-complexes of niobium with a different structure and a resultant different $\text{M}-\text{O}-\text{M}$ bond angle causes no reaction with the bromide ion. Since no bromine was detected during the irradiation of the solution containing equimolar amounts of Nb^{V} and Br^- in $\text{MeOD}/\text{D}_2\text{O}$ 1:1 we suggest that this solution contains no photoactive species.

These results confirm our hypothesis that the reactive complexes are those with oxo-groups, which are essential to keep a suitable $\text{Nb}-\text{O}-\text{Nb}$ bond angle. The closer the bond angle $\text{Nb}-\text{O}-\text{Nb}$ is to the ideal 180° , the more easily the electron–hole pairs move. The photocatalytic action which is initiated by the reduction of polyoxoniobate is related to the extent of delocalization of the d^1 electron and the $d\pi-\text{p}\pi-d\pi$ orbital-mixing resulting in a $\text{Nb}-\text{O}-\text{Nb}$ bond angle of about 180° as it has been demonstrated for the photoactivation of polyoxotungstate system [17].

3.2. UV–vis studies

The spectroscopic data obtained help us to interpret the findings in the bromide reaction and the intermediates gen-

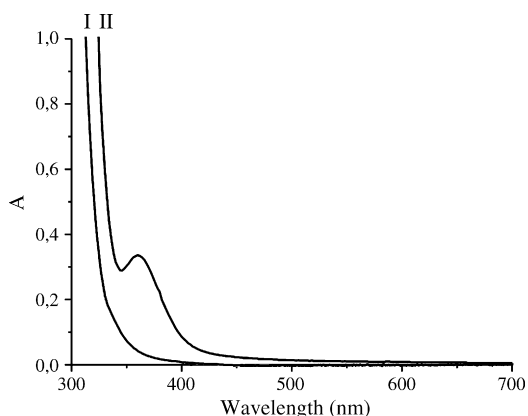


Fig. 2. UV-vis spectrum of the methanol solution containing $[\text{Nb}^{\text{V}}]/[\text{Br}^-] = 8.32$ before and after irradiation (curves I and II, respectively).

erated in the process of oxygen activation at metal centers. For the oxidation reaction of bromide ions in the presence of excited polyoxomethoxoniobate (POMN) complexes, the participation of O_2 is necessary. The role of O_2 is very important in the photoreactions by acting as an electron acceptor and forming reactive oxygen radical species such as $\text{O}_2^{\bullet-}$.

Upon mixing of a methanol solution of potassium bromide with a methanol solution of niobium pentachloride with ratio 1/8, the UV-vis spectrum shows a band assigned to $\text{MeO} \rightarrow \text{Nb}^{\text{V}}$ (243 nm). No band is observed at a wavelength of $>300\text{ nm}$ (Fig. 2, curve I). After irradiation in the UV range, the absorbance at 266 nm due to Br_3^- [21] is covered by the more intense bands assigned to $\text{MeO} \rightarrow \text{Nb}^{\text{V}}$ (243 nm) and $\text{Cl}_{\pi^-} \rightarrow \text{T}_{2g}$ charge transfer [1]. Another characteristic absorption band is observed at 360 nm (Fig. 2, curve II) attributed to either NbOO^{3+} produced by the inserting of the superoxide radical anion in the metal coordination sphere or to $\text{Br}_2^{\bullet-}$ [21] produced by the reaction between the peroxy intermediate and the bromide ions. $\text{Br}_2^{\bullet-}$ can also be produced by the combination of bromine atom with another bromide ion [21b]. The reactivity and the lifetimes of such intermediates increase with increasing acidity [17,20]. All the experiments were carried out in acidic methanol solutions.

3.3. Cyclic voltammetry

The electrochemical oxidation of bromide in the presence of niobium pentachloride under oxygenated conditions has been studied using cyclic voltammetry. The potential scan is initiated at 0.00 V in the anodic direction. A CV blank experiment of dissolved KBr (15.5 mM) in methanol solution using 0.1 M LiCl as supporting electrolyte (scan rate: 100 mV/s), show anodic and cathodic peaks at 1.182 and 0.696 V, respectively, which correspond to the two electron transformation of bromide to bromine and vice versa (Fig. 3a) [28]. Fig. 3, curve b, shows the cyclic voltammogram obtained for 15.5 mM solution of KBr in the presence of 1.94 mM NbCl_5 (solution 6 of Table 1)

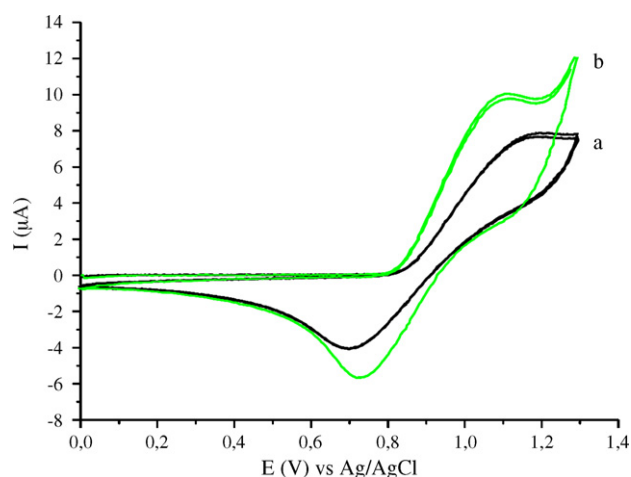
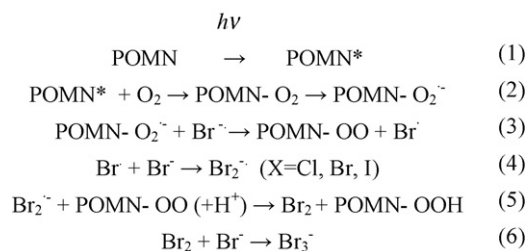


Fig. 3. Cyclic voltammograms of (a) 15.5 mM KBr and (b) in the presence of 1.94 mM NbCl_5 with the ratio $\text{Nb}^{5+}/\text{Br}^- = 1/7.99$ (supporting electrolyte: LiCl (0.1 M), scan rate: 100 mV s^{-1}).

which exhibits an anodic peak at 1.103 V and a cathodic one at 0.722 V. Thus, the presence of niobium compound has an effect on the oxidation of bromide. In addition, using niobium pentachloride solution in different concentration ratios, bromide ions can be more easily oxidized (Supplementary 1). From the electrochemical study of the solutions 1–7 (Table 1), the oxidation potential shift to higher values with the increase of Br^- concentration, and to lower values with the increase of NbCl_5 concentration. The minimum value of 0.985 V corresponds to solution 1, while the maximum one (1.103 V) to solution 6.

3.4. Proposed reaction pathway

For the oxidation of bromide ions in polyoxoalkoxide niobate (POMN) system under UV irradiation, the proposed pathway involves $\text{O}_2^{\bullet-}$, Br^{\bullet} and $\text{Br}_2^{\bullet-}$ radicals. By considering that the photoreaction was slower in de-aerated conditions, we infer that $\text{O}_2^{\bullet-}$ plays an important role in the oxidation of bromide. Coordination between the excited polyoxoalkoxide niobate (Eq. (1)) and O_2 could form a peroxy intermediate that reacts with bromide to produce Br^{\bullet} radicals (Eqs. (2–4)). The reactions depicted in Scheme 1 explain the oxidation process and the formation of



Scheme 1. The reaction pathway for the photocatalytic oxidation of bromide ion, showing, also, the participation of dioxygen.

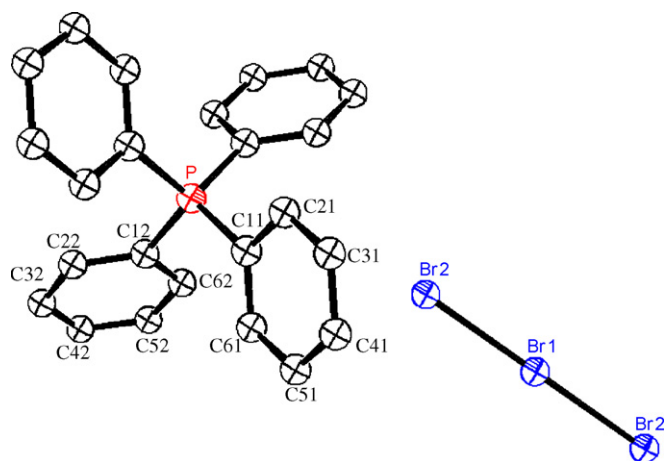


Fig. 4. ORTEP drawing of tetraphenylphosphonium tribromide with atomic numbering.

the tribromide ion. The excited state for POMN can be described as POMN^* .

3.5. Characterization of the tribromide oxidation product

3.5.1. X-ray studies

The X-ray structure of tetraphenylphosphonium tribromide which is formed from the corresponding bromide in the presence of niobium pentachloride in methanol shows that the compound crystallizes in the monoclinic space group and the Br–Br–Br is

Table 2
Crystallographic data summaries for $[\text{PPh}_4]\text{Br}_3$

Empirical formula	$\text{C}_{24}\text{H}_{20}\text{Br}_3\text{P}$
Formula weight	579.10
Crystal size	$0.20 \times 0.30 \times 0.80$
T (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	10.1373(2)
<i>b</i> (Å)	7.52530(10)
<i>c</i> (Å)	14.5868(2)
α (°)	90
β (°)	92.5370(10)
γ (°)	90
<i>V</i> (Å ³)	1111.68(3)
<i>Z</i>	2
<i>D</i> _{calc} (mg/m ³)	1.730
μ (Mo K α) (mm ⁻¹)	5.523
<i>F</i> (0 0 0)	568
Reflections collected	16192
Independent reflections (<i>R</i> _{int})	3372(0.0331)
Goodness-of-fit (on <i>F</i> ²)	1.015
<i>R</i> ^a	0.0326 ^c
<i>Rw</i> ^b	0.0904 ^c

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b Rw = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2]^{1/2}.$$

^c For 2686 reflections with $I > 2\sigma(I)$.

Table 3
Selected atomic distances (Å) and bond angles (°) for $[\text{PPh}_4]\text{Br}_3$

Distances			
Br(1)-Br(2)#1	2.5470(3)	P(1)-C(11) #2	1.791(2)
Br(1)-Br(2)	2.5470(3)	P(1)-C(11)	1.791(2)
		P(1)-C(12) #2	1.791(2)
		P(1)-C(12)	1.791(2)
C(11)-C(61)	1.391(3)	C(12)-C(22)	1.392(3)
C(11)-C(21)	1.407(3)	C(12)-C(62)	1.398(3)
C(21)-C(31)	1.382(3)	C(22)-C(32)	1.390(3)
C(31)-C(41)	1.389(3)	C(32)-C(42)	1.380(4)
C(41)-C(51)	1.380(4)	C(42)-C(52)	1.383(4)
C(51)-C(61)	1.392(3)	C(52)-C(62)	1.395(3)
Angles			
Br(2) #1-Br(1)- Br(2)	177.52(2)	C(11) #2-P(1)-C(11)	105.27(14)
		C(11) #2-P(1)-C(12) #2	111.09(9)
		C(11)-P(1)-C(12) #2	111.72(9)
		C(11) #2-P(1)-C(12)	111.72(9)
		C(11)-P(1)-C(12)	111.09(9)
		C(12) #2-P(1)-C(12)	106.05(14)
		C(22)-C(12)-C(62)	120.4(2)
C(61)-C(11)-C(21)	120.3(2)	C(22)-C(12)-P(1)	121.25(17)
C(61)-C(11)-P(1)	122.08(17)	C(62)-C(12)-P(1)	118.31(16)
C(21)-C(11)-P(1)	117.52(15)	C(32)-C(22)-C(12)	119.2(2)
C(31)-C(21)-C(11)	119.6(2)	C(42)-C(32)-C(22)	120.6(2)
C(21)-C(31)-C(41)	120.0(2)	C(32)-C(42)-C(52)	120.5(2)
C(51)-C(41)-C(31)	120.4(2)	C(42)-C(52)-C(62)	119.9(2)
C(41)-C(51)-C(61)	120.5(2)	C(52)-C(62)-C(12)	119.5(2)
C(11)-C(61)-C(51)	119.2(2)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, y, -z + 3/2$ #2 $-x + 1/2, y, -z + 1/2$.

totally symmetrical (Fig. 4). The $C_{24}H_{20}P^+$ cations form stacks along the y -axis, while the Br_3^- anions are arranged between the stacks (Fig. 5). The two Br–Br distances in the anion are identical (2.5470(3) Å) and the bond angle Br(2)#1–Br(1)–Br(2) is 177.52(2)°. The crystal data for the compound are listed in Table 2 and the bond lengths and the bond angles in the molecule are given in Table 3.

3.5.2. 1H NMR studies

The 1H NMR spectrum of tetraphenylphosphonium tribromide in deuteriochloroform revealed three signals at 7.68 m (4H), 7.80 m (8H) and 7.92 m (8H) ppm similar with those observed in the spectrum of the analogous diiodobromide [29]. The ^{31}P NMR spectrum of the tribromide compound in CD_3Cl gave one peak at 19 ppm. The reactivity of tribromide anions was determined by NMR experiments monitoring their reaction with dimethylsulphoxide (DMSO). The spectrum (Fig. 6) shows a peak at 3.16 ppm assigned to the methyl protons of dimethylsulphoxide ($DMSO_2$). From the reaction of the tribromide ion with dimethylsulphoxide indicates that the only oxidation product is the dimethylsulphone as it was found earlier to be the main product of the reaction between DMSO and BrO [30]. This suggests a complex mechanism, possibly involving formation of BrO radicals.

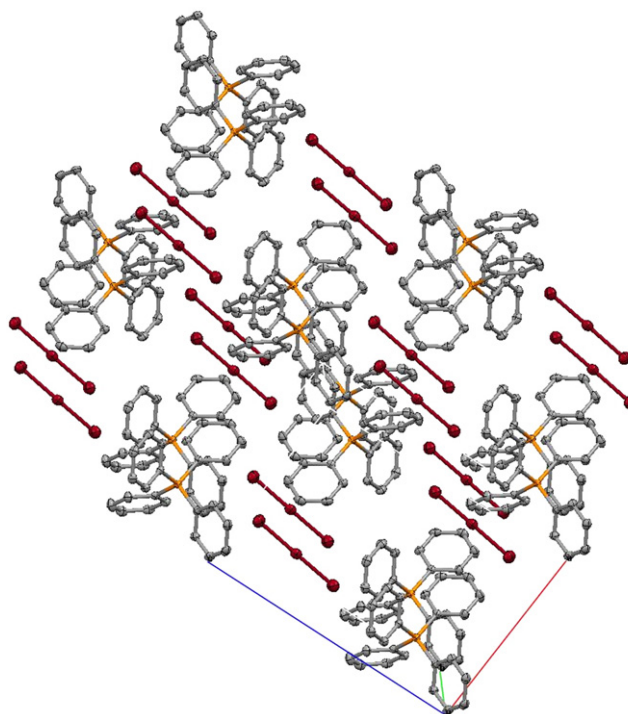


Fig. 5. Fragment of crystal structure of tetraphenylphosphonium tribromide.

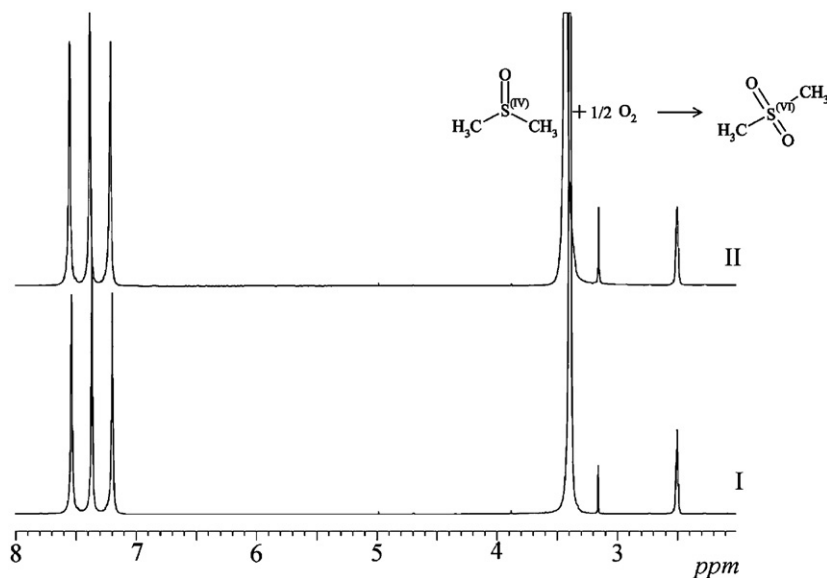
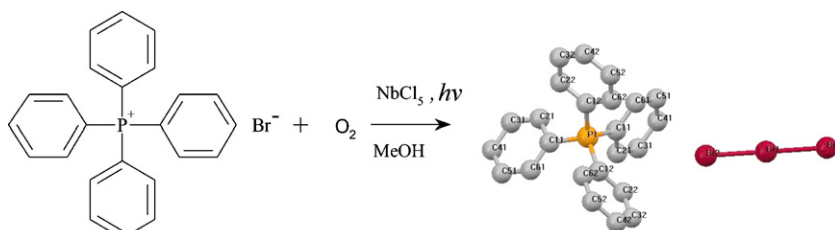


Fig. 6. 1H NMR spectrum of the freshly prepared solution of the crystal of tribromide ion in DMSO and the same solution after 1 day of the dissolution (curves I and II, respectively).



Graphic 1.

4. Conclusions

The photoproduction of bromine from the respective halide methanol solutions in the presence of NbCl₅ was demonstrated. Our X-ray work of tetraphenylphosphonium tribromide fully confirms our proposal. The species sensitized the oxidation of bromide ions in the presence of oxygen and light are polyoxomethoxoniobate complexes. The photocatalytic activity of this system is connected to methanolysis and oxo-bridges existence. For activation of the catalytic system and photoreaction to occur, it is required the formation of POMN with a specific structure and a linear Nb–O–Nb bond angle. The reaction of the excited catalyst with bromide ion occurs through the formation of the peroxoniobate intermediate. The superoxide radical anion produced from the reduction of O₂, which plays an important role in the oxidation of bromide, inserts in the metal coordination sphere. Finally, we reported the crystal structure of the isolated tetraphenylphosphonium tribromide (**Graphic 1**).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2007.02.032.

References

- [1] A. Karaliota, M. Kamariotaki, D. Hatzipanayioti, *Transit. Met. Chem.* 22 (1997) 411.
- [2] W. Clegg, M.R.J. Elsegood, R.J. Errington, J. Havelock, *J. Chem. Soc. Dalton Trans.* (1996) 681.
- [3] J. Zubieta, *J. Mol. Eng.* 3 (1993) 93.
- [4] A.G.S. Prado, E.A. Faria, J.R. Souza, J.D. Torres, *J. Mol. Catal. A: Chem.* 237 (2005) 115.
- [5] M.K. Silva, R.G. Marques, N. Machado, O.A.A. Santos, *Braz. J. Chem. Eng.* 19 (2002) 359.
- [6] H. Kominami, K. Oki, M. Kohno, S. Onoue, Y. Kera, B. Ohtani, *J. Mater. Chem.* 11 (2001) 604.
- [7] J.C. Zhao, C.C. Chen, W.H. Ma, *Top. Catal.* 35 (2005) 269.
- [8] S.P. Vijayalakshmi, G. Madras, *J. Appl. Polym. Sci.* 100 (2006) 3997.
- [9] A. Akyol, M. Bayramoglu, *J. Hazard. Mater.* 124 (2005) 241.
- [10] K. Sayama, H. Arakawa, *J. Phys. Chem.* 97 (1993) 531.
- [11] Z.G. Zou, H. Arakawa, *J. Photochem. Photobiol. A: Chem.* 158 (2003) 145–162.
- [12] R. Dabestani, X.L. Wang, A.J. Bard, A. Campion, M.A. Fox, S.E. Webber, J.M. White, *J. Phys. Chem.* 90 (1986) 2729.
- [13] E. Papaconstantinou, A. Ioannidis, A. Hiskia, P. Argitis, D. Dimotikali, S. Korres, *Mol. Eng.* 3 (1993) 231.
- [14] C.C. Chen, W. Zhao, P.X. Lei, J.C. Zhao, N. Serponer, *Chem.-Eur. J.* 10 (2004) 1956.
- [15] A. Hiskia, A. Mylonas, E. Papaconstantinou, *Chem. Soc. Rev.* 30 (2001) 62.
- [16] A. Hiskia, A. Troupis, S. Antonarakis, E. Gkika, P.K. Papaconstantinou, *Int. J. Environ. Anal. Chem.* 86 (2006) 233.
- [17] T. Yamase, *Catal. Surv. Asia* 7 (2003) 203.
- [18] S. Kim, H. Park, W. Choi, *J. Phys. Chem. B* 108 (2004) 6402.
- [19] H. Ueda, *Polym. J.* 25 (1993) 825.
- [20] A. Bakac, *Coord. Chem. Rev.* 250 (2006) 2046.
- [21] (a) M.L. Hung, A. Bakac, *Inorg. Chem.* 44 (2005) 9293;
(b) M. Gratzel, M. Halmann, *Solar Energy Mater.* 20 (1990) 117.
- [22] A. Bakac, C. Shi, O. Pestovsky, *Inorg. Chem.* 43 (2004) 5416.
- [23] B. Reichman, C.E. Byvic, W. Choi, *J. Phys. Chem.* 85 (1981) 2255.
- [24] M.A. Fox, T.L. Petit, *J. Org. Chem.* 85 (1985) 5013.
- [25] U. Bora, M.K. Chaudhuri, D. Dey, S.S. Dhar, *Pure Appl. Chem.* 73 (2001) 93.
- [26] M. Baghmar, P.K. Sharma, *Proc. Indian Acad. Sci. (Chem. Sci.)* 113 (2001) 139.
- [27] U. Bora, G. Bose, M.K. Chaudhuri, S.S. Dhar, R. Gopinath, A.T. Khan, B.K. Patel, *Org. Lett.* 2 (2000) 247.
- [28] D. Nematollahi, N. Akaberi, *Molecules* 6 (2001) 639.
- [29] O.N. Kazheva, G.G. Aleksandrov, O.A. D'Yachenko, M.S. Chernov'yants, S.S. Simonyan, E.O. Lykova, *Russ. J. Coord. Chem.* 30 (2004) 739.
- [30] B. Ballesteros, N.R. Jensen, J. Hjorth, *J. Atmos. Chem.* 43 (2002) 135.