

Organic reactions in inorganic matrices—Oxidation of hydroquinone to *p*-benzoquinone on solid MoO₃ surfaces

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MS received 11 December 1980; revised 12 March 1981

Abstract. Hydroquinone can be complexed on MoO₃ surfaces and is converted to *p*-benzoquinone in a mild solid phase redox reaction while MoO₃ is reduced to Mo(V) and Mo(III) species.

Keywords. Redox; solid state; MoO₃; hydroquinone.

1. Introduction

Solid state transformations of organic molecules under very mild conditions have been achieved when the molecular environments have been made very specific for reaction through the formation of complexes and intercalates in inorganic-layered compounds. For instance diprotonated 4, 4'-diamino-*trans*-stilbene that has been intercalated within montmorillonoid sheet silicates is converted to aniline while triphenylamine that is complexed on the surface of a similar solid matrix is converted to N,N,N'N'-tetraphenylbenzidine, both these transformations occurring under mild conditions (Tennakoon *et al* 1974; Tricker *et al* 1975). In this paper we report the interaction of hydroquinone (1, 4-dihydroxybenzene) with molybdenum trioxide, MoO₃. This latter compound has a layered structure consisting of double sheets of edge and corner shared MoO₆ octahedra (Kihlberg 1963). Since it is also a mild oxidizing agent (Forzatti *et al* 1974; Volta and Moraweck 1980) and quite inert in non-basic organic solvents it seemed to be a good choice as a solid substrate for complexation or intercalation of organic molecules from solution and for their subsequent oxidation in the solid state.

2. Results and discussion

Molybdenum trioxide was prepared by heating ammonium heptamolybdate. The very pale yellow solid that was obtained gave no ESR signal. When MoO₃ thus obtained was refluxed in an acetone solution of hydroquinone for 5-6 hr

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and the solid material well washed the result was a light grey material that contained 1-2% of its weight of hydroquinone. This solid gave an ESR spectrum (figure 1). X-ray powder diffraction patterns of the MoO_3 before and after interaction with hydroquinone were identical thus demonstrating that the hydroquinone was not intercalated under the preparative conditions used.

When the MoO_3 -hydroquinone complex was heated *in vacuo* at temperatures greater than 160°C the colour of the solid turned dark grey and *p*-benzoquinone was produced as indicated by its IR spectrum. The sublimate also contained a small amount of unoxidized hydroquinone and quinhydrone. The residue obtained on heating the complex also gave an ESR spectrum (figure 2).

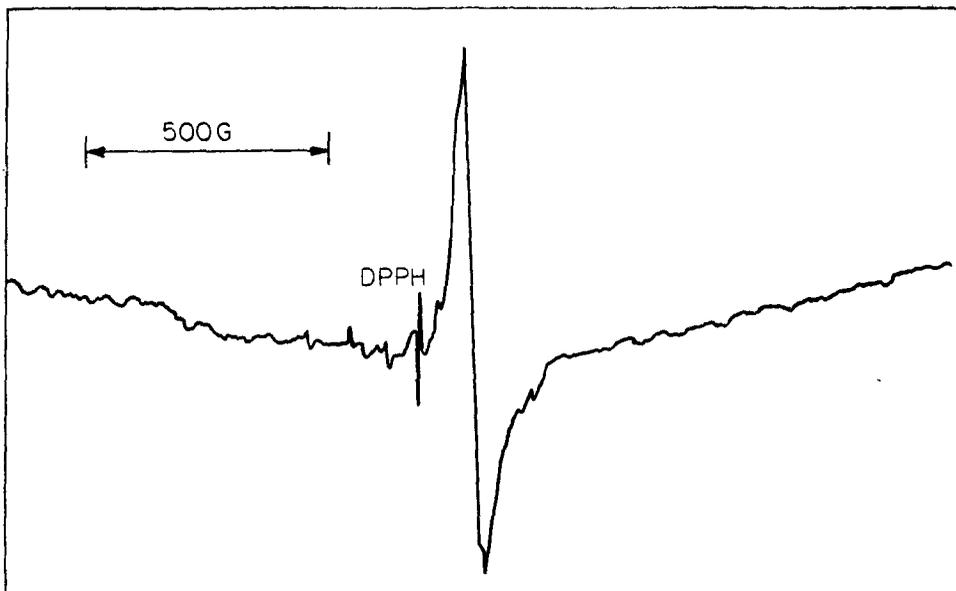


Figure 1. ESR spectrum (at -146°C) of the MoO_3 -hydroquinone complex.

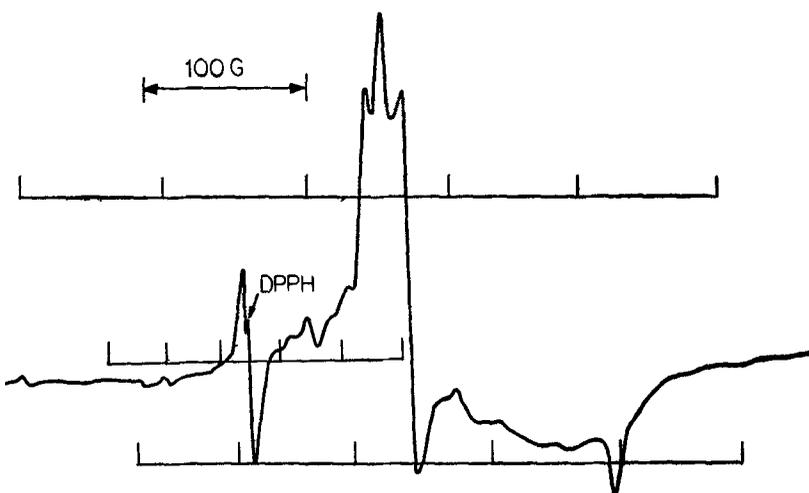


Figure 2. ESR spectrum (at -146°C) of the residue obtained on heating the MoO_3 -hydroquinone complex at 160°C .

The fact that the MoO_3 -hydroquinone complex gives an ESR signal is a clear indication that the hydroquinone has interacted chemically with the MoO_3 surfaces. An examination of the crystal structure of MoO_3 (figure 3) (Kihlborg 1963) shows that one of the six oxygen atoms in the MoO_6 octahedron is unique. Not only is it the sole oxygen atom that is bound to a single metal atom (the others being shared between two or three metal atoms as required by corner or edge sharing) but its distance to the metal atom is significantly shorter than those of the other five oxygen atoms (1.7 Å vs 1.8–2.3 Å). This oxygen atom also protrudes into the interlayer space and is in a location that is relatively accessible to the hydroquinone molecules. All these observations tend to suggest that hydroquinone molecules can interact with the MoO_3 surfaces through hydrogen bonding to the 'unique' oxygen atoms of the MoO_6 octahedra. The ESR signal at $g = 1.934$ suggests that Mo(V) is implicated. This could be produced through a partial redox reaction between the hydroquinone and the Mo(VI) species at the solid surface.

Although partial electron transfer may have taken place in the solid complex, any significant oxidation of the hydroquinone probably occurs only after the solid complex is heated. Not only is there a colour change on heating but the ESR spectrum of the residue is quite different from that of the original complex. The spectrum of the residue (figure 2) shows many features that have been previously reported for reduced MoO_3 samples (Mann and Khulbe 1975). For instance there is a signal at around $g = 2.000$ with its six hyperfine lines at approximately equal spacings (around 36G). The hyperfine lines arise from ^{95}Mo and ^{97}Mo (total abundance 25%). This signal has been ascribed to an Mo(III) species. The rest of the spectrum is due to the Mo(V) ion. The darkening of colour on heating is another indication of the formation of an Mo(V) species since the visual absorption arises from the intervalence charge transfer transition $\text{Mo(V)} \rightarrow \text{Mo(VI)}$ (So and Pope 1972). Thus it may be concluded that oxidation of hydroquinone in the solid MoO_3 matrix occurs because of a favourable topochemistry. A facile thermal transfer of hydrogen atoms from the hydroquinone

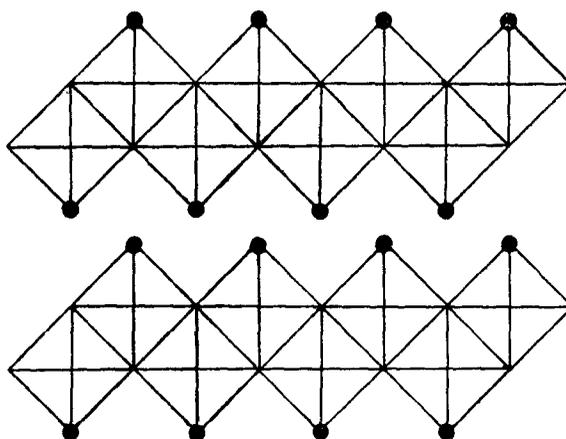


Figure 3. Schematic representation of the MoO_3 structure showing the layer arrangement. The 'unique' oxygen atoms are heavily shaded.

to the MoO_6 octahedra in the solid state gives Mo(V) and Mo(III) ions and *p*-benzoquinone as reaction products. The presence of unoxidized hydroquinone in the condensate is probably because sublimation of hydroquinone is a competing process at elevated temperatures.

3. Experimental

ESR spectra were recorded on a JEOL JESFE3X spectrometer. Molybdenum trioxide was obtained by heating a sample of recrystallized ammonium heptamolybdate (E. Merck), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{42}\cdot 4\text{H}_2\text{O}$ at 600°C in a muffle furnace. It may be noted that unless the molybdate was recrystallized grey coloured solids were obtained on heating. These gave ESR signals and were discarded. Hydroquinone was sublimed before use.

In a typical preparation of the MoO_3 -hydroquinone complex 5 g of MoO_3 were refluxed for 6 hr in a solution of 1 g of hydroquinone in about 200 ml of acetone. The solid was well washed with acetone and then dichloromethane. Gravimetric experiments over several runs showed that the solid contained between 1-2% by weight of hydroquinone. Small amounts (*ca* 500 mg) of the MoO_3 -quinol complex were used for the redox reactions. Infrared spectroscopy showed that the organic sublimate was almost entirely *p*-benzoquinone with a small amount (est. 10%) of hydroquinone. Extraction of the solid residue with methanol showed that no organic materials remained in the residue after the heating was complete.

4. Conclusions

That a substance like hydroquinone can be complexed on solid surfaces such as MoO_3 is significant. The subsequent redox reaction is yet another example where a specific interaction between molecules in the solid state can be exploited to achieve controlled reactivity. The prospects of 'tailoring' the structure of an oxidizable organic molecule to form an intercalate within the MoO_3 layers can only increase the scope of such a reaction and are being investigated currently.

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