



COMMUNICATION

The production of hydrogen peroxide from dioxygen using hydroxylamine as substrate catalysed by Mn^{2+} -exchanged montmorillonite clay

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(Received 24 May 1996; accepted 6 August 1996)

Abstract— Mn^{2+} -exchanged montmorillonite clay, in milligramme quantities, efficiently catalyses the production of hydrogen peroxide from dioxygen (or air) and hydroxylamine at pH 8.0 in aqueous solution; concentrations of hydrogen peroxide $> 0.40 \text{ mol dm}^{-3}$ ($\sim 1.5\% \text{ w/v H}_2\text{O}_2$, $\sim 86\%$ based on hydroxylamine) in 50 min and turnover numbers $[\text{H}_2\text{O}_2]/[\text{Mn}^{2+}] > 10^5$ were obtained. The mechanism for hydrogen peroxide production in this system is discussed together with the possibilities of developing a dual system to use the *in situ* generated hydrogen peroxide to effect some organic oxidation transformations. Copyright © 1997 Elsevier Science Ltd

Keywords: hydrogen peroxide; dioxygen; manganese; clay; catalysis; hydroxylamine.

Hydrogen peroxide is seen as the ideal oxidant from an environmental point of view, producing only water as a byproduct. It has been estimated [1] that of the 900,000 tonne per annum production of hydrogen peroxide, only 10% is used in the synthetic organic industry, mostly for epoxidation reactions and the paucity of practical applications contrasts with the clear environmental advantages. Solutions to the problems of the activation of hydrogen peroxide which results in this under-use are being found [2] and it is envisaged that the use of hydrogen peroxide will increase markedly in the coming decade.

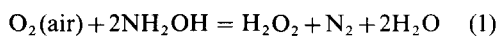
The oxidation of organic molecules usually requires the use of fairly concentrated solutions of hydrogen peroxide or organic peroxides (30%), but recently dilute solutions of hydrogen peroxide ($\sim 2\%$) have been used to epoxidise alkyl-substituted alkenes [3]. Other important potential applications in the gen-

eration of dilute solutions of hydrogen peroxide from air or dioxygen in aqueous solution include the formulation of liquid laundry detergents and the disinfection of process waters and water used for air-conditioning etc. The *in situ* generation of hydrogen peroxide has additional environmental advantages in terms of the transport, storage and handling problems associated with hydrogen peroxide.

There has been a number of reports of the production of hydrogen peroxide by reaction of dioxygen and transition metal ions or complexes, although in the majority of these systems the peroxide rapidly disappears by further reaction or catalytic decomposition. In the presence of a reducing substrate, catalytic production of hydrogen peroxide is possible. Thus, it has been shown by one of us that manganese(II)/4,5-dihydroxybenzene-1,3-disulfonate (Tiron) provides an efficient homogeneous catalyst for the reduction of dioxygen to hydrogen peroxide with hydroxylamine in the pH range 7.5–8.6 [4]. Peroxide concentrations greater than 0.20 mol dm^{-3} and

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turnover numbers $[\text{H}_2\text{O}_2]/[\text{Mn}^{2+}] > 10^4$ were obtained. Unpublished data suggest that the overall process can be represented as follows:



Preparation of modified clay

Sodium bentonite (MPS-1), a montmorillonite supplied by Volclay, was dried for several hours at 105°C and then cooled in a desiccator. A 5% (w/v) suspension of the clay (20 g) in a 0.1 M aqueous solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was stirred overnight, the supernatant liquid discarded and the clay washed several times with distilled water. The clay was isolated by centrifugation and again washed with distilled water until all the excess MnCl_2 had been removed (tested with AgNO_3). The Mn^{2+} -exchanged clay was dried (as before) and then crushed and powdered and sieved through a 500 micron mesh. Analysis of both Mn^{2+} -exchanged clay and sodium bentonite for manganese content was achieved by ICP with XRD being used to provide basal spacings data.

Hydrogen peroxide production and analysis

Accurately weighed portions of the clay were added to a Dreschel bottle (in a water bath) containing de-ionized water (100.0 cm³) containing ACS grade $\text{NH}_2\text{OH} \cdot \text{HCl}$ (0.5 or 1.0 mol dm⁻³) and Tiron (6×10^{-4} mol dm⁻³), buffered using 4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid (EPPS, 0.1 mol dm⁻³) to pH 8.0 using semiconductor grade, carbonate-free aqueous NaOH. A good supply of dioxygen from a cylinder or air *via* a vacuum created by a water pump were supplied to the stirred solution. Aliquots of the solution were removed at defined periods and analysed for hydrogen peroxide concentration using the colorimetric method based on titanium (IV) sulfate [5,6]. A Philips UV-vis spectrophotometer PU 8720 was used for colorimetric measurements.

The results are shown in Fig. 1. The yields of H_2O_2 produced with Mn^{2+} -clay, ~ 0.23 mol dm⁻³ ($\sim 90\%$ based on NH_2OH) were consistent with earlier results using homogeneous catalysis [4], but the rate of production of hydrogen peroxide, $[\text{H}_2\text{O}_2]_{\text{max}}$ in ~ 30 min, was found to be a marked improvement. With NH_2OH (1.0 mol dm⁻³) and using Mn^{2+} -clay (0.0074 g), remarkable concentrations of H_2O_2 of ~ 0.43 mol dm⁻³ ($\sim 1.5\%$ w/v H_2O_2 , $\sim 86\%$ based on NH_2OH) could be obtained in only *ca* 50 min.

In the absence of added clay (Fig. 1) only slow formation of H_2O_2 was observed which can probably be attributed to catalysis by adventitious traces of Mn^{2+} [7]. With sodium bentonite, there is also a slow (but slightly higher) formation of H_2O_2 , which presumably results from catalysis by small quantities of manganese present within the clay, measured by ICP

to be 0.15 mmol of total manganese per 100 g of clay. The Mn^{2+} -exchanged clay is catalytic in milligramme quantities with "saturation" being observed at weights of exchanged clay of 5 mg (per 100 cm³ of reaction solution). The amount of Mn^{2+} exchanged in the clay was determined by ICP to be 33.95 mmol per 100 g of clay, corresponding to a cation exchange capacity (CEC) of the clay of 67.6 meq (mmol) per 100 g, giving turnovers of $[\text{H}_2\text{O}_2]/[\text{Mn}^{2+}] \sim 10^5$.

Previously "saturation" was achieved at levels of 1×10^{-4} mol dm⁻³ when using aqueous MnCl_2 [4], corresponding to a weight of manganese(II) of *ca* 50 mg. This clearly shows the greater efficiency of Mn^{2+} within the clay support to catalyse the process. This result can be either explained by the effect of the restricted two-dimensional space within a layered clay structure, thus allowing a greater probability for reactants to meet [8], or the effect of the reactants proximity adsorbed on the outer surface of the modified clay.

X-ray powder diffraction (XRD) analysis of sodium bentonite (undried) and Mn^{2+} -clay both produced sharp peaks implying an interlayer structure with basal spacings (d_{001}) of 1263 and 1281 pm, respectively. These results would give an interlayer (interlamellar) spacing of approximately 300 pm and 320 pm for the Na^+ - and Mn^{2+} -clay, respectively [9]. In the aqueous reaction medium used, it would be expected that the Mn^{2+} -clay would fully hydrate, increasing the interlayer space to approximately 800 pm and this space would be important in especially enabling the intercalation and binding of the ligand (Tiron), and also the substrate (hydroxylamine) and dioxygen.

The rate of formation of hydrogen peroxide in air using Mn^{2+} -exchanged clay was approximately 1/5 that in pure dioxygen, indicating that dioxygen is involved in the rate-determining step. A mechanism for the homogeneous process has been proposed [4], whereby both dioxygen and hydroxylamine become bound to a square-planar assembly of manganese(II) and catecholate ligand with the resulting complex acting as an "electron sink" for the transfer of electron density from the bound substrate to dioxygen. The faster rates of hydrogen peroxide production with this partial heterogeneous system imply that the presence of manganese(II) adsorbed either onto the surface or within the interlamellar space of the clay facilitates this process.

Recently Uemura and *et al.* have reported the use of Mn^{2+} -clay to catalyse the oxidation of alkanes with *tert*-butyl hydroperoxide [10]. With the system described here, there is the possibility of developing a dual process which cannot only generate hydrogen peroxide *in situ*, but also catalyse important organic oxidation processes. Work is also continuing to search for alternative substrates to hydroxylamine to make this process more economically viable and for which some success has been achieved. This system is also of

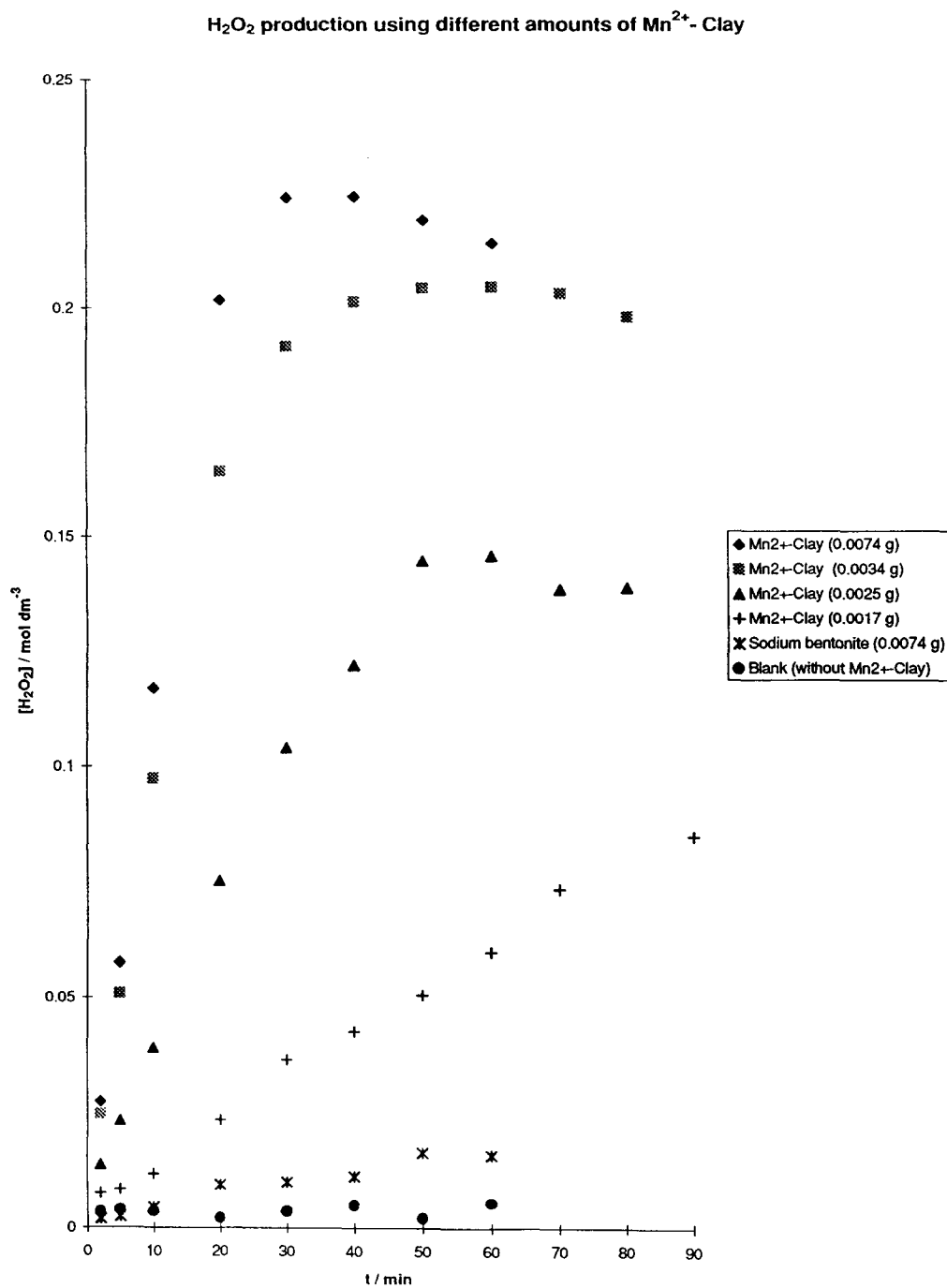


Fig. 1. The production of H₂O₂ in the Mn²⁺-clay/Tiron/NH₂OH system in the presence of O₂ at 25 ± 0.5°C and different weights of Mn²⁺-clay. In all runs, the [Tiron] was 6 × 10⁻⁴ mol dm⁻³, the initial [NH₂OH] was 0.5 mol dm⁻³ and the pH was 8.0 [0.1 mol dm⁻³, 4-(2-hydroxyethyl)-1-piperazinepropanesulfonate (EPPS) buffer].

interest in modelling natural systems such as galactose oxidase [11].

Acknowledgements—B.H. would like to thank The Nuffield Foundation for the provision of a research bursary (NUF-URB95); J.R. would like to thank the Society of Chemical Industry for the provision of a maintenance grant under the Messel Fund. A gifted supply of sodium bentonite MPS-1 from Volclay Ltd is acknowledged with gratitude.

REFERENCES

1. Buchner, W., Schliebs, R., Winter, G. and Bucher, K. H., *Industrial Inorganic Chemistry*. VCH, Weinheim, 1989, p. 21.
2. Strukel, G., *Catalytic Oxidations With Hydrogen Peroxide As Oxidant*. Kluwer Academic Publishers, Dordrecht, 1992; Wilson, S. L., *Performance Chemicals*, October/November, 1993, 39.
3. Al-Ajlouni, A. M. and Espenson, J. H., *J. Org. Chem.* 1996, **61**, 3969.
4. Sheriff, T. S., *J. Chem. Soc., Dalton Trans.* 1992, 1051.
5. Egerton, A. C., Everett, A. J., Minkoff, G. J., Rudrakanchana, S. and Salooja, K. C., *Anal. Chim. Acta*, 1954, **10**, 422.
6. Clapp, P. A., Evans, D. F. and Sheriff, T. S., *Anal. Chim. Acta*, 1989, **218**, 332.
7. Ottoway, J. M. and Hale, D. J., *Pure Appl. Chem.* 1986, **58**, 1308; Gretzinger, K., Kotz, L., Tols, G. and Tschopel, P., *Talanta*, 1982, **29**, 1011.
8. Laszlo, P., *Acc. Chem. Res.* 1986, **19**, 121.
9. Clark, J. H., Kybett, A. P. and Macquarrie, D. J., *Supported Reagents: Preparation, Analysis and Applications*. VCH Publishers, New York, 1992, p. 51.
10. Tateiwa, J., Horiuchi, H. and Uemura, S., *J. Chem. Soc., Chem. Commun.* 1994, 2567.
11. Malmstrom, G., *Annu. Rev. Biochem.* 1982, **51**, 42.