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Evidence for Adsorption as the First Step in the Solid-state Oxidation of **Benzenehexol with Active Manganese Dioxide**

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Oxidation of benzenehexol on the surface of amorphous, precipitated (' active ') manganese dioxide proceeds by a concerted mechanism, involving ionic and free-radical pathways, to give a croconic acid derivative. This manganese dioxide has a polycrystalline chain structure, in contrast to the crystalline oxidant prepared in deuterium oxide.

DISCOVERY¹ of the mild oxidizing character of precipitated (' active ')² manganese dioxide * toward vitamin A was followed by contributions 3-11 that firmly established the unique character of this reagent for the oxidation of a series of organic compounds in neutral solvents.^{2,12-15a} As pointed out,² the mechanism of these oxidations has

* The oxidizing properties of precipitated manganese dioxide were known to German organic chemists over a hundred years ago (see works by Liebig, Hoffmann, Nietzki, and Wallach).

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not yet been elucidated; the *a priori* triphasic reactionpathway postulated ¹ (adsorption of the substrate on the surface of the manganese dioxide followed by oxidation, and desorption of product) has some validity. However, there is strong evidence that, alternatively, the oxidation involves a radical intermediate 8,11,16-21 and. in certain cases, formation of a complex.⁹

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This report presents evidence for an unusual adsorption on the surface of manganese dioxide, as the first step in the solid-state oxidation of benzenehexol (1) to give the croconic acid derivative (4) (see Scheme); it also discusses a possible pathway in the conversion of (1)into (4), and suggests a structure for the solid oxidant.



Possible Structure of the Precipitated Manganese Dioxide.—The adsorptive ability of manganese dioxide

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has been thoroughly studied: e.g., its adsorption of water or benzene vapours,22 hydrogen,23 organic substrates from solution,²⁴ and inorganic cations (Ba²⁺, Mn²⁺, or Na⁺); ²⁵ here we describe an example of adsorption of an organic solid on a solid.

The mechanism of the oxidations with manganese dioxide undoubtedly involves a process typical of heterogeneous reactions,¹² and the difficulties encountered in the study of these reactions may involve the structure of the oxidant, particularly the relationship of its surface-active sites toward a substrate (quadrupole-dipole electrostatic interaction).²⁶ The amorphous character of the precipitated ⁴ manganese dioxide, shown in the X-ray diffraction spectra A-1 and B-1 (Figure 1), is in accordance with earlier observations.^{2,27} However, the oxidant prepared in deuterium oxide instead of water $[MnSO_4 + KMnO_4 + D_2O]$ (acidic, 80 °C) \longrightarrow MnO₂] was a dark, crystalline product with the pattern shown in C-1 and D-1 (Figure 1). The structure of this compound resembled that ^{28,29} of γ -MnO₂ as shown by comparison of their interplanar spacings and intensities (Table 1 for C-1). In order to

TABLE 1

X-Ray powder diffraction spectra of manganese oxides and related compounds

| Compound γ-MnO ₂ (for C-1, Figure 1) | Interplanar spacings in Å with intensities in parentheses 4.10 (90); 3.22 (30); 2.67 (30); 2.45 (100); 2.25 (40); 2.14 (60); 1.64 (100): and 1.44 (30) |
|--|--|
| γ-MnO ₂ (ref. 29, strongest peaks) | 3.96 (90); 2.60 (40); 2.42 (100); 2.32 (50); 2.12 (60); 2.05 (20) |
| MnO _{1.88} (from active manganese dioxide) | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ |
| MnO _{1.88} (ref. 31, strongest peaks) | 3.13 (80); 2.39 (100); 2.15 (60) |
| Manganese oxalate (strongest peaks) | 5.12 (85); 4.97 (70); 3.10 (80); $2.72(100); 1.85 (85)$ |

elucidate its structure,³⁰ a sample of active manganese dioxide ^{4,5} (300 mg) was decomposed by stirring it with aqueous hydrochloric acid (3M, 20 ml) at room temperature for 24 h in a hood. Chlorine was evolved and the dark residue (50-60 mg) that resisted decompositon was crystalline. The isolated oxide contained manganese of the lower valency, and its interplanar spacings resembled ³¹ those of MnO_{1.88} (see Table 1). Moreover, its i.r. spectrum showed little or no absorption in the region of hydroxyl bands, in comparison to that of the initial manganese dioxide which was prepared in water (OH band at 3380, water of hydration at 1625 cm⁻¹) or the manganese dioxide prepared in deuterium oxide

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(1)



PLATE Electron-diffraction pattern of the manganese dioxide complex (D, Figure 3) lying on a carbon film

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(OD band at 3350, deuterium oxide of 'hydration' at 1535 cm⁻¹). A crystalline oxide containing manganese of lower valency was also obtained on partial decomposition of the active manganese dioxide with aqueous hydrogen peroxide at room temperature. On the basis of this evidence and the e.s.r. spectrum of the oxidant, discussed below, precipitated manganese dioxide may rate of disappearance of the hexol (1) was monitored by use of an X-ray powder diffractometer. Figure 3 shows the background spectrum A (amorphous manganese dioxide); the decrease in the concentration of (1) with time is seen in spectrum B [30 s, structure shown is primarily due to (1)] and in spectrum C [50 min, ca. 45%of (1) adsorbed]; in spectrum D, at 100 min, ca 97\% of



FIGURE 1 X-Ray powder diffraction pattern of manganese dioxides (Cu- K_{α} radiation): A-1, precipitated manganese dioxide (ref. 4), dried *in vacuo* at room temperature; B-1, sample A-1 dried in an oven at 125 °C; C-1, manganese dioxide prepared in deuterium oxide as described in the text (dried *in vacuo* at 100 °C); D-1, sample C-1 exposed to air for 3 months

contain a locked, water-associated chain (Figure 2); this structure provides important active sites of low electron-density on the surface of the solid oxidant ^{9,26} and potentially labile hydroxy-groups.



FIGURE 2 Proposed locked, water-associated chain structure for precipitated (amorphous) manganese dioxide

Adsorption of Benzenehexol (1) by Manganese Dioxide.—A 1:6 (w/w) mixture of finely ground ³² benzenehexol and manganese dioxide was mechanically shaken at room temperature in air (or under nitrogen) and the

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(1) is adsorbed. The high affinity of manganese dioxide for (1), which seems to be an example of an irreversible adsorption [none of (1) could be extracted from the complex] is typical of a chemisorption; ^{33,34} also, the adsorption can be explained partially as being due to the formation of a π -complex between (1) and the oxidant.³⁵ The formation of an ionic bond (-O-Mn-O-) is, however, evident from the isolation of (4).

The amorphous pattern shown in spectrum D (Figure 3) was almost identical with that of manganese dioxide (spectrum A); however, an electron-diffraction probe of the complex at this stage showed, indeed, a crystalline pattern (see Plate), thus proving that adsorption of (1) by the oxidant is a surface-interaction process exclusively.

Extraction of this complex with water, and gradual

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concentration of the extract, yielded, first, a small quantity of white crystals, identified as manganese oxalate ³¹ by X-ray diffraction (see Table 1), and then greenish crystals of manganese croconate (4) (E. Figure 3). The yield of (4), isolated as soluble (with difficulty) barium croconate,³⁶ is increased by increase in pH of the

for the deuteriated oxidant is expected.³⁷ The above peaks are different from the considerably narrower peaks derived from possible oxidation intermediates, namely, manganese salts of 2,3,5,6-tetrahydroxy-p-benzoquinone (2),³⁸ rhodizonic acid (3),³⁶ and croconic acid (4).³⁸ In general, the shape and magnetic parameters of the e.s.r.



FIGURE 3 X-Ray powder diffraction pattern. (Cr- K_{α} radiation) of aliquots, on mixing of 1:6 (w/w) benzenehexol (1) and manganese dioxide. (The 1:6 ratio is for substrate to oxidant.) A, precipitated (amorphous) manganese dioxide; B, 30 s, structure shown is primarily due to (1); C, 50 min, ca. 45% of (1) adsorbed; D, 100 min, ca. 97% of (1) adsorbed, complex D; and E, manganese croconate trihydrate, purified product extracted from D

solution; the yield was 3-5% when prepared in the dry state, 8-12% on refluxing with water, and up to 75-80% on refluxing in 0.8M-sodium hydroxide.³⁶

The e.s.r. measurements (see Table 2) of the oxidant (A, Figure 3) and of the complex (D, Figure 3) showed, for each, a broad, one-line peak which can be explained as being due to a dipole-dipole interaction between polycrystalline manganese dioxide aggregates. Alternatively, the line broadening observed may be due to interaction of an unpaired electron with a proton of a neighbouring water molecule, as has been reported ³⁷ for certain co-ordination complexes, in this case, precipitated manganese dioxide. The situation is comparable to the change in structure of the oxidant from amorphous to crystalline when hydrogen is replaced by deuterium (see Figure 1), and lessening in the line width 36 A. J. Fatiadi, H. S. Isbell, and W. F. Sager, J. Res. Nat.

TABLE 2

Magnetic parameters ^a (ΔH width and g values) for manganese dioxide and related manganese compounds

| Compound | Temp. | $\Delta H/\mathrm{gauss}$ | g |
|---|---------------|---|--|
| Manganese dioxide ^ø | 77 K 25 °C | $\begin{array}{r} 5200 \pm 500 \\ 3520 \pm 300 \end{array}$ | ${}^{1\cdot78} \pm 0{\cdot}15 \\ {}^{2\cdot33} \pm 0{\cdot}10$ |
| Manganese dioxide complex ¢ | 25 °C | 2900 ± 200 | $2{\cdot}47\pm0{\cdot}10$ |
| 2,3,5,6-Tetrahydroxy- p-benzoquinonato- manganese (2) | 25 °C | 220 ± 2 | $2 \cdot 005 \pm 0 \cdot 003$ |
| Manganese rhodizonate (3) | 25 °C | 277 ± 5 | $2{\cdot}011\pm0{\cdot}002$ |
| Manganese croconate (4) ^d | 25 °C | $327~{\pm}~5$ | 2.036 ± 0.018 |
| e | 25 °C | 361 ± 10 | 2.027 ± 0.003 |
| f | 25 °C | $295 ~{\pm}~ 15$ | 2.010 ± 0.002 |

^a Indicated limits of error for the width (ΔH) and g values are the maximum estimated errors. ^b Prepared according to ref. 4. • Manganese complex D (Figure 3). ⁴ Authentic sample of manganese croconate trihydrate, ref. 36. • Manganese croconate prepared on refluxing (1) with the oxidant in water. ⁷ Manganese croconate extracted from complex D (Figure 3).

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spectra of the oxidant (Mn^{4+}) and the Mn^{2+} salts (2), (3), and (4) (see Table 2) are different from 39,40 the six-line e.s.r. spectra characteristic of Mn²⁺ ions.

The measurements of magnetic susceptibility of the 1:6 (w/w) mechanical mixture of (1) and manganese dioxide at room temperature showed little appreciable change (from 2254 to 2262×10^{-6} cm³ mol⁻¹) after 5, 30, 60, 100, and 1000 min; the final value observed is comparable to that reported 41 for precipitated manganese dioxide (2280 $\times 10^{-6} \text{ cm}^3 \text{ mol}^{-1})$.

Reaction Mechanisms Involved in Oxidation of Benzenehexol (1) to Croconic acid (4) by Manganese Dioxide. Possible chemical transformations of (1) into (4) are shown in the Scheme; this conversion may involve the manganese ester intermediate (5), an oxidation process to give intermediates (6) and (7), and benzilic acid-type rearrangements 42,43 of intermediates (8) and (9), to give, via carbonium ion (10), product (4). Whereas conversion of (7) into (4) requires participation of a strong nucleophile (hydroxyl ions) 43 [see also, the correlation of the increase in the yield of (4) in alkaline media], the steps from (1) to (7) and the presence of manganese oxalate in the product [probably arising from carbon-carbon cleavage of (1)] can only be reconciled by invoking radical participation.

Heating under reflux (60 min) of a mixture of benzenehexol (1 g), manganese dioxide 5,36 (12 g), and dry benzene (200 ml, Dean-Stark trap 16) gave 0.25-0.40 ml of water. Crude (4) (250 mg) was obtained by extraction of the reaction mixture with water. After the reaction, analysis of the benzene (by g.l.c.) revealed the presence of a trace of phenol,* which could have been formed by collision of hydroxyl radicals (derived from manganese dioxide) with the solvent; also, the trapped water indicated the participation of hydroxyl radicals.16,17

A striking example of the participation of hydroxyl radicals apparently derived from active manganese dioxide is the following. Treatment of pyrene (in chloroform) with manganese dioxide gave a mixture of 1,6- and 1,8-pyrenequinones (mainly the 1,6-isomer) in low yield; the formation of these products can be envisaged as an attack by hydroxyl radicals on the hydrocarbon at the positions having the highest unpairedelectron densities⁴⁴ or unpaired-spin densities,⁴⁵ to give a dihydroxy-derivative that, on further oxidation, yields quinones; the apparent two-fold character of the oxidant may be noted. No coupling product, namely, bipyrene, could be isolated from the oxidation mixture; however, the yield of quinones was lower when a small proportion of a radical quencher (benzene-1,4-diol or acrylonitrile) was initially added to the reaction mixture. Also, a sample of pyrene-1,6-diol was readily converted by manganese dioxide into the 1,6-quinone in a yield of over 80%. In contrast, treatment of pyrene with manganese dioxide in warm glacial acetic acid gave 1,6diacetoxypyrene as the major component.

Assuming that our hypothesis is correct, consumption of one equivalent of active oxygen present in manganese dioxide corresponds to two hydroxyl radicals, as shown for a certain hydrated form of it [MnO(OH), ---- $2OH^{\bullet} \rightarrow 2O^{*} + H_2O + Mn^{2+}$; and this pathway would provide species that could either abstract hydrogen atoms or donate hydroxyl radicals. This mechanistic approach is analogous to that proposed for the oxidation of alcohols by nickel peroxide,46 with the difference that any paramagnetic species formed on the surface of manganese dioxide is probably consumed immediately, as, otherwise, any species having free spins would have been detected by the balance used in magnetic-susceptibility measurements. In this alternative aspect, trapping of free radicals in solution 47 may furnish additional evidence to clarify the mechanism of the oxidation.

Thus, conversion of (1) into (4) by manganese dioxide probably proceeds by a concerted mechanism involving ionic and free-radical pathways.

EXPERIMENTAL

Materials .--- The manganese dioxide used in this study was prepared according to refs. 4, 5, and 36; analysis showed hydrogen 0.5 (ref. 4) and 0.04% (ref. 5); active oxygen (iodometric) 12.8 (ref. 4) and 14.1% (ref. 5); total oxygen (vacuum-fusion analysis, Balzar Exhalograph-EA2, temperature of nickel capsule and bath 1675 °C, collection period 3 min; carbon monoxide determined by use of calibrated i.r. absorption spectrum) 25.4% (ref. 5), 25.8% (ref. 36), 23.5% (ref. 4); manganese dioxide residue by hydrochloric acid treatment for 24 h at 25 °C, 20.2%; for 4 h at 85 °C, 17.2%.

Magnetic Parameters .--- For the e.s.r. calculations, the following equations were employed, where g_{cal} is the g value calculated from the spectrum, $\nu_k = klystron$ frequency, and $v_p = proton$ frequency; $g_{cal} = 3041.9 v_k/v_p$; Δ (gauss) = $(v_p - v_{p'}) \times 2.3486 \times 10^{-4}$. For e.s.r. spectra of manganese dioxide and manganese dioxide complex (Table 2), for which broad lines were usually observed, calculation of the g values involved a certain degree of estimation.

'Self-conditioning' of Active Manganese Dioxide .--- A thoroughly dried (110°/0.01 torr, 4 h) and cooled (25 °C) sample of active MnO₂ was exposed to the atmosphere; it showed an apparent 'conditioning,' as evidenced by its

^{*} A trace of phenol has also been observed in an aqueous extract following decomposition of complex D (9) with water.

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gain in weight [the sample (400 mg) gained ca. 12 mg in 30 min].

Attempted Oxidation of Benzene-1,2-, -1,3-, or -1,4-diols or Benzene-1,3,5-triol with Manganese Dioxide.-Oxidation of polyhydroxybenzene derivatives with manganese dioxide in organic solvents has been little studied.^{2,11} Generally, oxidations were conducted by stirring at room temperature (or as indicated) with a 1:6 ratio (w/w) of substrate to oxidant for the first run followed by repetition of the run with a 1:12 ratio (w/w). The following are some results: hydroquinone in tetrahydrofuran (THF) gave quinhydrone (30-40% yield), but, in chloroform or benzene, the reaction product was p-benzoquinone (60-62% yield). Pyrocatechol in THF gave a complex which yielded the parent compound on extraction with water (an example of reversible adsorption); however, oxidation in chloroform (50 °C, 45 min) gave a complex mixture from which o-benzoquinone was isolated in 25% yield by column chromatography [silica gel, 3:1 (v/v) or 2:1 (v/v) heptane-ethyl acetate]. Resorcinol in THF gave traces of an unknown quinone and polymeric products; benzene-1,3,5-triol in THF was recovered unchanged.

Oxidation of Benzenehexol (1) with Manganese Dioxide.— Stirring of (1) in 1,2-dimethoxyethane (or THF) with manganese dioxide rapidly gave complex D (9), as evidenced by the disappearance of a benzenoid absorption at 260-266nm; (9) has also been obtained from tetrahydroxy-*p*benzoquinone (in THF, but not in acetone) and from rhodizonic acid in THF. When complex (9) was slowly heated (95 °C), carbon dioxide was liberated; extraction of the residue with water gave (4), with an increase of 25%in the yield as compared to that from unheated complex. This indicates that decarboxylation of (9) is one of the thermodynamic factors partaking in the conversion of (1) into (4).

Oxidation of Pyrene with Manganese Dioxide.—(a) A suspension of pyrene (2 g) in chloroform (100 ml) and manganese dioxide (12 g) was boiled under reflux for 1 h (or stirred for 24 h at room temperature), cooled (40°), and filtered. The orange-red filtrate was evaporated, to give a solid which, on separation by column chromatography ⁴⁸

* Certain commercial instruments are mentioned in this paper; this does not imply recommendation or endorsement by the National Bureau of Standards.

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[1:4 (v/v) chloroform-acetic acid], gave yellow-orange 1,6-pyrenequinone (70 mg, 3% yield), m.p. $320-322^{\circ}$, and red 1,8-pyrenequinone (12 mg, 0.5% yield), m.p. $270-272^{\circ}$, each identical with an authentic sample of the respective compound.⁴⁸

(b) To a solution of pyrene (5 g) in glacial acetic acid containing 2% of acetic anhydride (150 ml) was gradually added manganese dioxide (15 g); the mixture was stirred at 85-90° for 15 min, and at 105-110° for 10 min, cooled (60°), and filtered. The dark-brown filtrate was concentrated to 10 ml, diluted with warm water (50 ml), and stirred, and the suspension was filtered; the brown solid was fractionated by column chromatography with successive elution with 4:1 (v/v) pentane-glacial acetic acid, 1:4(v/v) glacial acetic acid-pentane, and glacial acetic acid. The first fractions gave unreacted pyrene (strong, blue fluorescence); these were followed by a dark-brown fraction (green fluorescence), and then an orange-red fraction (very weak fluorescence). Concentration of the dark-brown eluate gave a solid which, on trituration with 1:1 (v/v) benzene-pentane (30 ml), left crude 1,6-diacetoxypyrene (510 mg, 6.5% yield). A sample recrystallized from glacial acetic acid (carbon), gave light-yellow crystals (green fluorescence), m.p. 222-224°, identical with authentic 1,6-diacetoxypyrene.49

Concentration of the orange-yellow fraction gave 1,6pyrenequinone, and some of the 1,8-isomer.

X-Ray powder diffraction spectra were measured with a Philips X-ray diffractometer * (LiF monochromator, Cu- K_{α} radiation, $\lambda = 1,54056$ Å and Cr- K_{α} radiation, $\lambda = 2.28962$ Å); e.s.r. spectra were recorded with a Varian Model 4500 spectrometer; the magnetic susceptibility was measured by the Gouy and the Thorpe-Senftle method; ⁵⁰ the electron-diffraction pattern was obtained with a JEM 6A Electron Microscope.

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