

enone system. The tertiary alcohol of 14 was readily converted to the corresponding TMS ether 17. The potassium dienolate of 17 was generated with potassium *bis*(trimethylsilyl)amide and subsequently treated with the Davis oxaziridine<sup>16</sup> to give diol 18 after aqueous workup.<sup>17</sup> Formally, C-4 of 18 can be viewed as corresponding in stereochemistry to C-2 of 1. However, the preservation of this stereogenicity throughout the steps leading to 1 could

prove to be particularly challenging.

We are currently attempting to extend the findings, described herein, in programs directed toward the total syntheses of taxol and potentially useful analogs thereof.

**Acknowledgment.** We thank V. Parmakovich and B. Sporer from the Department of Chemistry of Columbia University for mass spectral analyses.

**Supplementary Material Available:** Procedures and spectral data (<sup>1</sup>H and <sup>13</sup>C NMR, IR, HRMS) for compounds 4-18 (47 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(16) (a) Davis, F. A.; Vishwakarma, L. C.; Billmers, J. M.; Finn, J. J. *Org. Chem.* 1984, 49, 3241. (b) Vishwakarma, L. C.; Stringer, O. D.; Davis, F. A. *Org. Synth.* 1987, 66, 203.

(17) Aqueous workup readily removes the TMS ether. Flash chromatography using a 20-40% EtOAc in CH<sub>2</sub>Cl<sub>2</sub> gradient elution was needed to remove the *N*-phenylsulfonamide byproduct.

## Autocatalysis during the Reduction of Tetra-*n*-propylammonium Perruthenate by 2-Propanol

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Received January 2, 1992

**Summary:** A kinetic study has revealed that the reaction between tetra-*n*-propylammonium perruthenate and 2-propanol in methylene chloride solutions is strongly autocatalytic.

Tetraalkylammonium perruthenates are particularly good oxidants for the conversion of primary alcohols to aldehydes or secondary alcohols to ketones under nonaqueous conditions. Griffith and Ley<sup>1</sup> have demonstrated that excellent yields are obtained in most cases, that a variety of functional groups (double bonds, amines, ethers, etc.) may be present during the reaction, and that the reactions are particularly facile. In this paper, we wish to report on kinetic experiments that reveal why these reactions are so rapid.

Under appropriate conditions the rates of the reactions may be followed visually by noting the appearance of a dark green/black product or determined precisely by monitoring spectral changes associated with the reduction of perruthenate. Although the product has the appearance and general spectroscopic properties of a colloid<sup>2</sup> its final absorbance conforms to Beer's Law.<sup>3</sup> The colloidal nature of the product is also consistent with the observation that a fine, black solid precipitates from the solution after about 72 h.

From a consideration of the spectra of the reactant, tetra-*n*-propylammonium perruthenate, and the product of the reaction, presumably ruthenium dioxide, it can be seen (Figure 1) that the largest spectral change occurs at approximately 270 nm. At this wavelength the extinction coefficient for tetra-*n*-propylammonium perruthenate is  $1080 \pm 10 \text{ cm}^{-1} \text{ M}^{-1}$  while that for the product is  $3680 \pm 160 \text{ cm}^{-1} \text{ M}^{-1}$ . When the absorbance at 270 nm is plotted against time as in Figure 2, a sigmoidal curve typical of autocatalytic reactions results.<sup>4</sup> A plot of  $dA/dt$  against

time (Figure 3) is typical of other autocatalytic reactions such as the oxidation of glycine and other reductants by permanganate.<sup>5,6</sup> The rate, initially slow, accelerates sharply as the concentration of the product builds up and then decreases near the end of the reaction because of a reduction in the concentration of the reactants giving what is commonly referred to as a "bell-shaped curve". The sharpness of the curve in Figure 3 indicates that the reaction under consideration is strongly autocatalytic.

Similar results were obtained with other primary and secondary alcohols such as 2-butanol, 1-methoxy-2-propanol and 2-phenylethanol.

The catalytic nature of the product of this reaction was further demonstrated in an experiment where additional tetra-*n*-propylammonium perruthenate was added after all of the oxidant originally present had been reduced by excess 2-propanol. As shown by the curve reproduced in Figure 4, the reaction immediately resumed at an accelerated rate. However, after 72 h a product precipitated giving a transparent solution that no longer exhibited catalysis in the initial stages of the reaction.

In analogy with autocatalytic permanganate oxidations, where the catalyst is known to be colloidal manganese dioxide,<sup>7</sup> it seems reasonable to expect that the product responsible for the autocatalytic nature of these reactions is colloidal ruthenium dioxide which is known to be the product formed when perruthenate is reduced by organic reductants.<sup>8</sup> Partial confirmation of this possibility was obtained from the observation that RuO<sub>2</sub> produced by the reduction of RuO<sub>4</sub> with an excess of 2-propanol in methylene chloride<sup>9</sup> also caused the rate of reaction between tetra-*n*-propylammonium perruthenate and 2-propanol to

(4) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; p 26.

(5) Perez-Benito, J. F.; Mata-Perez, F.; Brillas, E. *Can. J. Chem.* 1987, 65, 2329.

(6) Stewart, R. In *Oxidation in Organic Chemistry*; Wiberg, K. B., Ed.; Academic Press: New York, 1965; Part A, pp 6, 20.

(7) Lee, D. G.; Perez-Benito, J. F. *J. Org. Chem.* 1988, 53, 5725.

(8) Lee, D. G.; Congson, L. N. *Can. J. Chem.* 1990, 68, 1774.

(9) Lee, D. G.; van den Engh, M. In *Oxidation in Organic Chemistry*; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; Part B, pp 177-227.

(1) Griffith, W. P.; Ley, S. V. *Aldrichimica Acta* 1990, 23, 13.

(2) Between 300 and 500 nm the absorbance of the solution is inversely proportional to  $\lambda^4$  as required by the Rayleigh Law for light scattering by a colloid. See: Moore, W. J. *Physical Chemistry*, 4th ed.; Prentice-Hall: Englewood Cliffs, 1972; p 934.

(3) Skoog, D. A.; West, D. M. *Fundamentals of Analytical Chemistry*, 2nd ed.; Holt, Rinehart and Winston: New York, 1963; p 646.

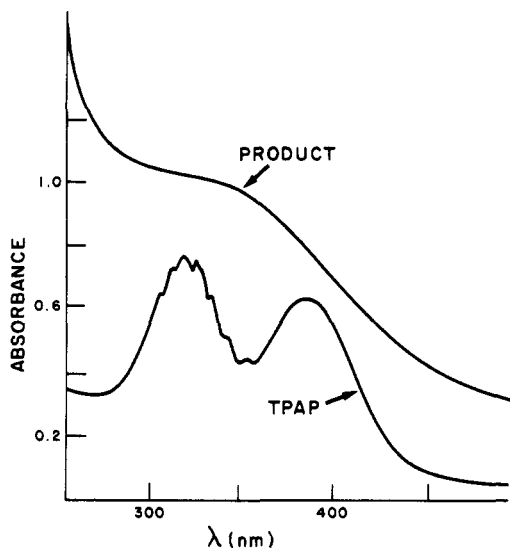


Figure 1. Spectra of tetrapropylammonium perruthenate (TPAP) and the product of the reaction ( $\text{RuO}_2$ ).

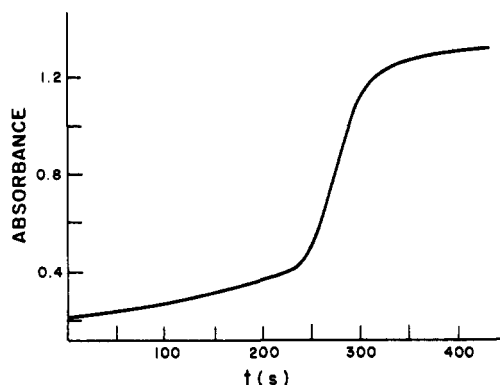


Figure 2. Plot of absorbance (270 nm) vs time for the oxidation of 2-propanol ( $1.2 \times 10^{-2}$  M) by tetrapropylammonium perruthenate ( $3.8 \times 10^{-4}$  M) in methylene chloride at 25 °C.

proceed at an accelerated rate without an induction period.

Although the precise nature of the catalytic reaction (for both permanganate oxidations and the reaction that is the subject of this report) is not exactly defined, the available experimental evidence<sup>8</sup> suggests that it results from coordination with colloidal particles of the product ( $\text{MnO}_2$  or  $\text{RuO}_2$ ) as depicted in eq 1.



It is known that the presence of small amounts of water reduces autocatalysis in permanganate oxidations<sup>8</sup> and the fact that a similar effect is observed for the reduction of perruthenate by 2-propanol emphasizes the similarity of these two processes. It is likely that water reduces the catalytic nature of  $\text{RuO}_2$  by occupying sites of possible coordination on the colloidal particles.<sup>7</sup>

Experimentally, sufficient tetra-*n*-propylammonium perruthenate, obtained commercially (Aldrich), was dis-

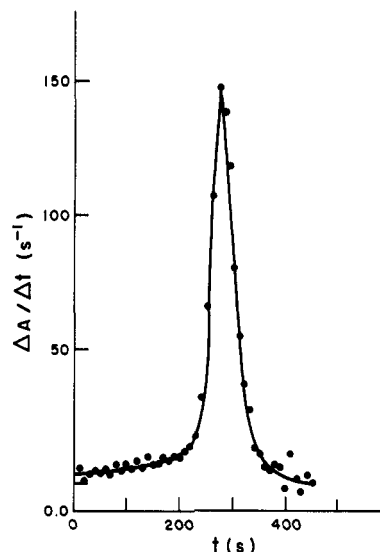


Figure 3. Plot of rate vs time for the oxidation of 2-propanol ( $1.2 \times 10^{-2}$  M) by tetrapropylammonium perruthenate ( $3.8 \times 10^{-4}$  M) in methylene chloride at 25 °C.

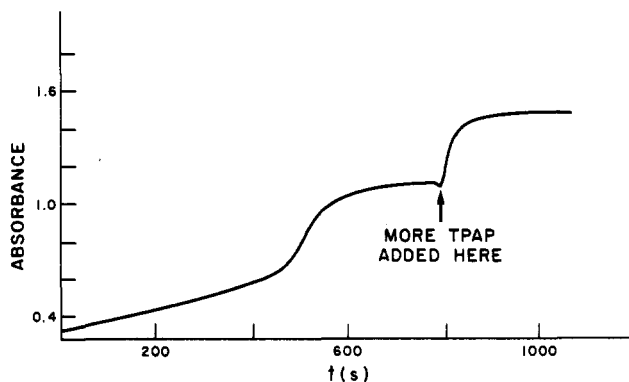


Figure 4. The effect of adding more tetrapropylammonium perruthenate to a solution of product ( $\text{RuO}_2$ ) and excess 2-propanol.

solved in 10.0 mL of methylene chloride (previously purified by successive distillations from calcium hydride and tetrabutylammonium permanganate) to give a concentration of approximately  $3 \times 10^{-4}$  M. This solution was thermostated in a water bath before 2.0 mL was transferred to a cuvette in the thermostated cell compartment of an HP 8450A spectrophotometer. A known excess of 2-propanol was then added from a microliter syringe, the solution stirred to achieve homogeneity, and the reaction rate determined by monitoring absorbance changes at 270 nm. Reaction rates,  $dA/dt$ , were obtained by measuring the changes in absorbance for fixed time intervals.

**Acknowledgment.** The authors are grateful for financial support from the Natural Sciences and Engineering Research Council of Canada.