Permanganate Colorimetric Rapid Method for Chemical Oxygen Demand in Seawater

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cursor for 14 is supposed to be acylrhodium(III) pent-4'-enyl complex 13, attempts to characterize this complex failed: addition of pyridine-d₅ in CDCl₃, in order to solubilize a chlorine-bridged dimer complex gave complicated ¹H NMR spectrum. The IR band of the carbonyl in 3 at 1690 cm⁻¹ moved to 1640 cm⁻¹ in 13 similar to 7a (7b). Addition of Br₂ to the metal complex generated 1,2,5-tribromopentane, which was confirmed by comparison with the authentic specimen obtained by the reaction of 5-bromopentene and Br₂. Rearrangement of 12 to 13 is the key step in this work.

The use of the cyclobutylcarbinyl group, as reported 12, was described by hydride-insertion into a coodinated olefin in 11, C-C coordination site as well as a ring strain of the cyclobutyl group. From this result, ring-opening reaction can be explained by p-alkyl elimination of the cyclobutylcarbinyl group. Relative low isolated yields of 9a and 9b compared with that of 14 may come from little amount of formation of 2a and 2b respectively since bulky alkyl groups seem to retard facile coordination of the exocyclic olefin to Rh rather than small size cyclobutyl group 12.

In an attempt to trace the aldehyde-proton in 3, the reaction was carried out by using 3-d₁₄ as a substrate for C-H bond activation giving 14-d₁. The deuterium resides only in the 4-position in 4-pentenyl group. None has been incorporated into the aliphatic CH₂ or the terminal CH₂ group. From this result, ring-opening reaction can be explained by β-alkyl elimination of the cyclobutylcarbinyl system 15. Most of the numerous studies devoted to ring opening reactions have been concerned with cycloalkylcarbinyl radicals 16. Although the mechanism is not clear, some evidences previously showed that the bond homolysis for this kind of Rh-alkyl complexes produced alkyl radicals 17. Relative low isolated yields of 9a and 9b compared with that of 14 may come from little amount of formation of 2a and 2b respectively since bulky alkyl groups seem to retard facile coordination of the exocyclic olefin to Rh rather than small size cyclobutyl group 12.

Detailed kinetic and other mechanistic investigations of C-H bond and C-C bond activations are under way.

References


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Recently, there has been considerable interest in simplifying the rather tedious standard chemical oxygen demand(COD) procedure for the dichromate reflux method which has limitations for the samples of low to moderate COD with chloride concentrations approaching that of seawater. However, no one has ever made such an attempt to eliminate that tedious and insensitive detection procedure for the alkaline-permanganate method which is superior to dichromate reflux method in which chloride interference is largely prevented by complexing method.

Herein we report a rapid and sensitive method that is consistent with the official procedure for the determination of COD in seawater, a typical sample of low COD. In this experiment, the COD in a 5-ml sample was determined by measuring the excess permanganate spectrophotometrically at 535 nm after digestion in alkaline medium. Since we expect...
Figure 1. Effect of digestion temperature on A–COD graph, measured after allowing suspensions to settle down. Digestion time was 10 min in a temperature-controlled heating mantle, with 0.001 N KMnO₄, 0.2% NaOH.

Figure 2. A calibration graph prepared by successive diluting the accurately known seawater sample with artificial seawater.

As a conclusion, the best conditions are as follows: 1.0 ml of 2% sodium hydroxide, 1.0 ml of 0.0075N permanganate for sample size of 5ml, and digestion time of 10 min in boiling water bath. After dissolving the suspension by adding 1 ml of 0.1M ammonium molybdate, the volume was adjusted to 10.00ml. Reading absorbance by employing the reagent blank as the 0.4 A reference, rather than distilled water as the 100%T reference, completes the measurement. For quantitation, then, compare to calibration curve in Figure 2 which has been prepared by successive diluting a known solution of seawater by artificial seawater.

To determine the comparability of data, five seawater samples were analyzed by both the official and the colorimetric COD methods, duplicating for each sample 10 times. Applying t-tests indicates (t = 1.52 for four degree of freedom) that the two methods are not significantly different.

In conclusion, adequate sensitivity and linearity of 535 nm are achieved by using a 1 cm cell to measure COD values in the range of 0–5 mg/l in seawater. An overall running time was less than 15 min.

References