cursor for **14** is supposed to be acylrhodium(III) pent-4′-enyl complex 13, attempts to characterize this complex failed: addition of pyridine-d_5 in $CDCl_3$ 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 Br_2 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 Br_2. Rearrangement of 12 to 13 is the key step in this work. Some ring opening reactions of strained ring molecules, especially cyclobutylcarbinyl group, were reported[12]. Since a vacant coodination site as well as a ring strain of the cyclobutyl group is generated in 12, a 16-electron Rh(III) species formed by hydride-insertion into a coodinated olefin in 11, C-C bond activation becomes very facile[13].

In an attempt to trace the aldehyde-proton in 3, the reaction was carried out by using 3-d_1[14] as a substrate for C-H bond activation giving 14-d_1. The deuterium resides only in the 4-position in 4-pentenyl group. None has been incorporated into the aliphatic CH_2 or the terminal CH_2 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[12a].

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

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Permanganate Colorimetric Rapid Method for Chemical Oxygen Demand in Seawater

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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[1,2] However, no one has ever made such an attempt to eliminate that tedious and insensitive detection procedure for the alkaline-permanganate method[3] which is superior to dichromate reflux method in which chloride interference is largely prevented by complexing method.[4]

Herein we report a rapid and sensitive method that is consistent with the official procedure[3] for the determination of COD in seawater, a typical sample of low COD. In this experiment, the COD in a 5-m*l* sample was determined by measuring the excess permanganate spectrophotometrically at 535nm after digestion in alkaline medium. Since we expect

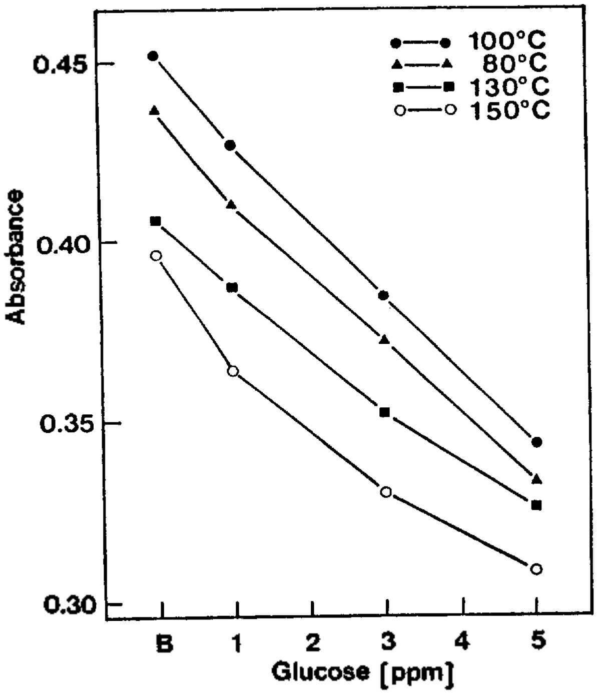

Figure 1. Effect of digestion temperature on A-COD graph, measured after allowing suspensions to settle down. Digestion time was 10 min in a temperature-controlled heating mantle, with 0.001N $KMnO_4$; 0.2% NaOH.

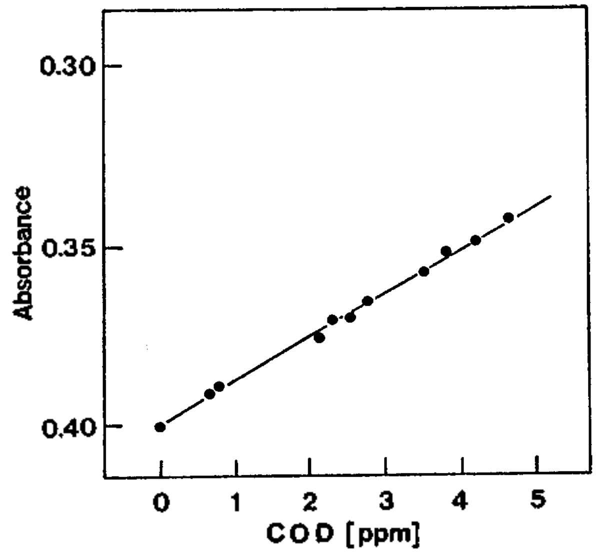

Figure 2. A calibration graph prepared by successive diluting the accurately known seawater sample with artificial seawater.

an absorbance(A) to be decreasing as the COD increases, a graph of A versus ppm-COD will have a negative slope starting from a reagent blank value when distilled water is employed as the reference, 100%T. The experiment was conducted to find out the best conditions which will give the maximum linearity and slope of the graph. Experimental conditions which have been determined are sample size, concentrations of permanganate and sodium hydroxide, and the digestion temperature and time, all those influence one another.

Figure 1 shows a representative behavior of **A** *vs* ppm-COD curves with varying the digestion temperature. A ppm-glucose(theoretical) equivalents to 0.93 mg glucose in a liter of artificial seawater. One of the major problems encountered in this procedure is the formation of hydroxide precipitates during digestion in alkaline solution, suspended particles, which interfer seriously the photometric measurement. It takes more than 50 min for the suspension to settle down completely by which the advantage of the attained rapidity is offset. We found that dissolution of the suspension by addition of ammonium molybdate, $(NH_4)_6Mo_7O_{24}$, has given the best result.

As a conclusion, the best conditions are as follows: 1.0 m*l* of 2% sodium hydroxide, 1.0m*l* of 0.0075N permanganate for sample size of 5m*l*, and digestion time of 10 min in boiling water bath. After dissolving the suspension by adding 1 m*l* of 0.1M ammonium molybdate, the volume was adjusted to 10.00m*l*. Reading absorbance by emplying 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.

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