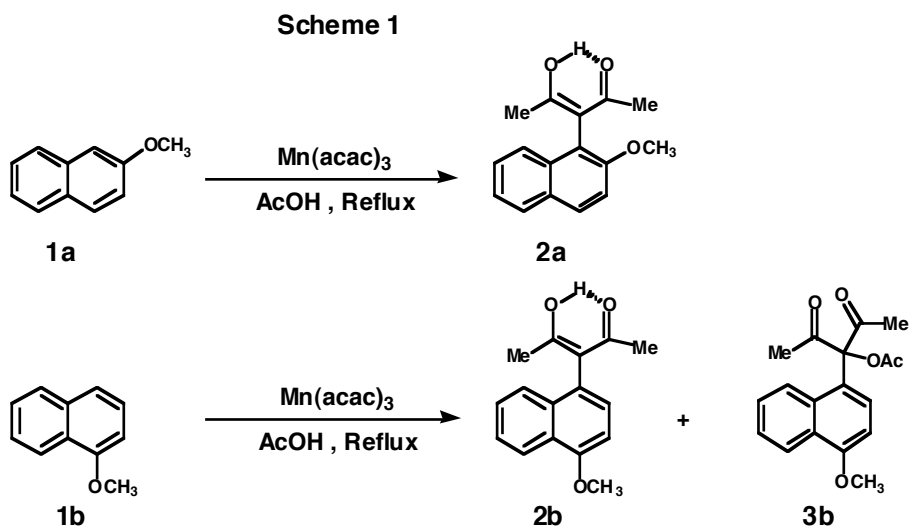


Pressure Effect of Manganese(III)-Based Oxidative Free-Radical Substitution of Aromatic Compounds

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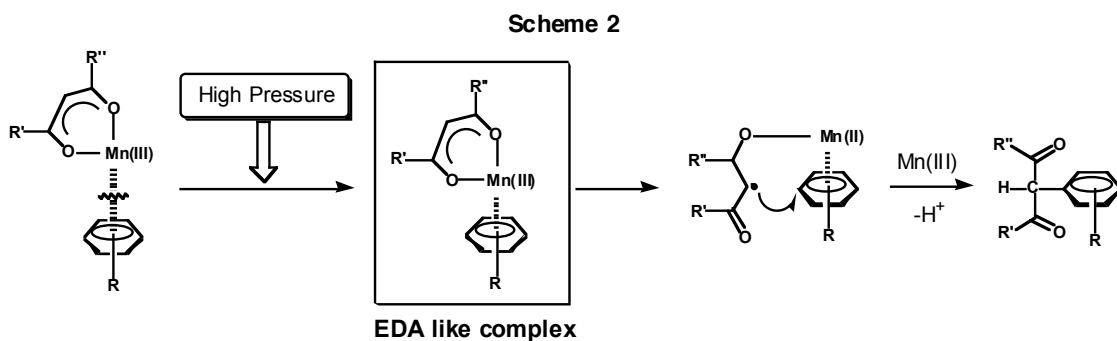
Md. Taifur Rahman and Hiroshi Nishino*

Oxidation of aromatic hydrocarbons mediated by trivalent manganese complexes has been studied extensively in the last 60's¹ and 80's² and the entire investigation was carried out only under the atmospheric pressure. The objective of the present study is to investigate the effect of the pressure increase on the product yield percentage of the reactions between 2-methoxynaphthalene (**1a**) or 1-methoxynaphthalene (**1b**) with trivalent manganese complexes e.g., manganese(III) acetate, [Mn(OAc)₃] and tris(2,4-pentanedionato)manganese (III), [Mn(acac)₃] (Scheme 1).³

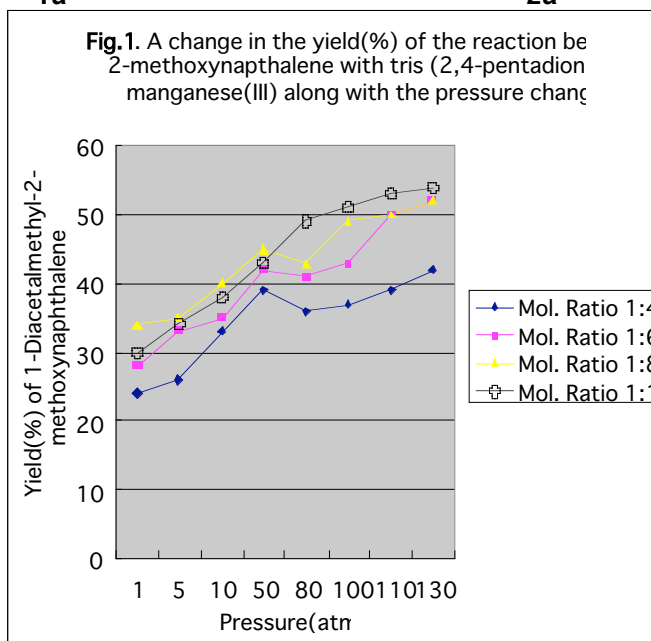
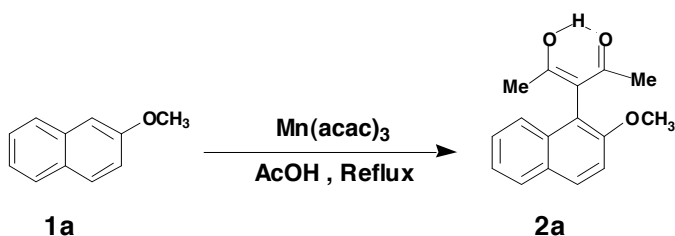


Both these reactions involve electron donor-acceptor like complexes (EDA complexes). Electron donor-acceptor like complex formation occurs (i) between the Mn(III) complex and the solvent and (ii) between the Mn(III) complex and the aromatic π -electron system, and these complex formations are very important factors for the oxidation of the aromatic compounds (Scheme 2).⁴⁻⁶ In this study, we established the hypothesis of the formation of electron donor-acceptor (EDA) like complex, and investigated the role of high pressure on the facile formation of EDA like complex between the aromatic

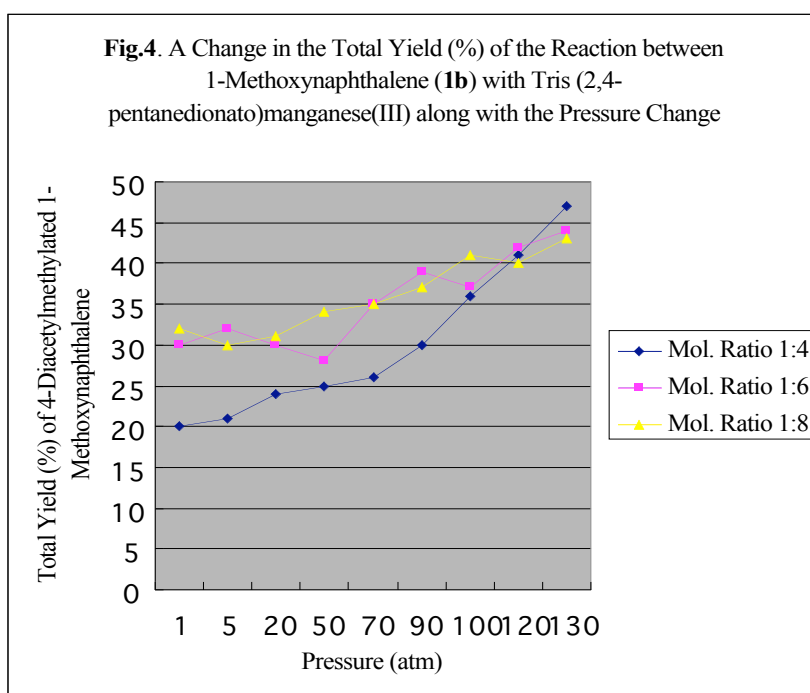
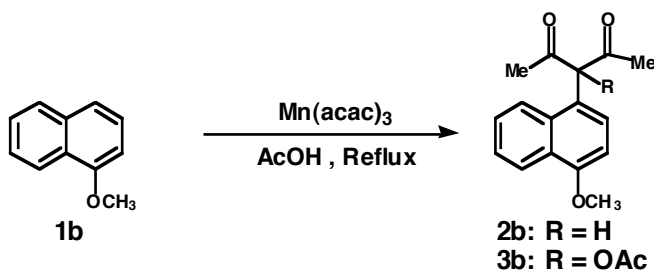
compounds and Mn(III) complexes. In addition, we also studied on the electrostatic interaction between the aromatic ring and Mn(III) complexes under high pressure.



Here we show one example of the reaction of 2-methoxynaphthalene (**1a**) with $Mn(acac)_3$ under argon pressure (1-130 atm) and the result of the pressure effect on the yield (%) (Fig. 1).



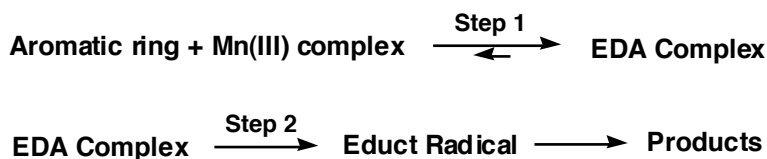
We show another example of the reaction of 1-methoxynaphthalene (**1b**) with $\text{Mn}(\text{acac})_3$ under argon pressure (1-130 atm) and the result of the pressure effect on the total yield (%) (Fig. 2).



It was found that the pressure exerted very important effects on the formation of EDA like complex by the following possible ways:

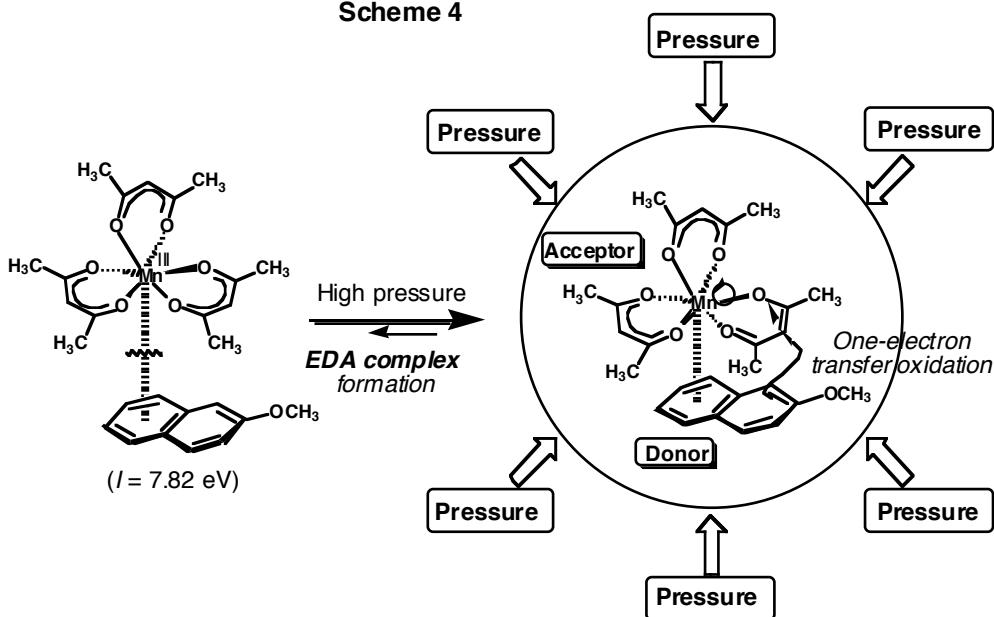
1. High pressure could compensate for the loss of entropy associated with the formation of EDA like complex.
2. The partial molar volume of EDA like complex is believed to be smaller than the added partial molar volume of the substrates. So from the general law of thermodynamics it could be assumed that the equilibrium (Step 1) would be favorably shifted towards the right direction, i.e., formation of EDA like complex, as the pressure increased (Scheme 3).

Scheme 3



3. High pressure could make the approach of the Mn(III) complex to the aromatic molecule facile and allows more electrostatic interaction between the *d*-orbital of the Mn(III) complex and the aromatic electronic system (Scheme 4).

Scheme 4



We have concluded based on our experimental results as follows:

1. The product yield (total yield %) usually increased along with the pressure.
2. Increasing trend in the products yield (%) remained more or less consistent over the wide range of molar ratios of the substrates, i.e., aromatic compounds : Mn(III) complexes, along with the pressure increase.
3. This increasing trend in the product yield (%) resulting from the pressure gradient provided some support for the hypothesis of facile EDA like complex formation between the aromatic ring and manganese(III) complex under higher pressures.

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