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# OXYGEN ATOM REACTIONS WITH METALLOCENES

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We investigated the products of atomic oxygen reaction with ferrocene and nickelocene, comparing them with those of oxygen atom reaction with 1,3-cyclopentadiene. In the case of cyclopentadiene, important products were $C_4H_6$ isomers and in the case of metallocenes, vinylacetylene.

Several works on the reactions of metallic species with atoms[1,2] have been reported, but little has been done on the fate of ligands of the metallic species. We have been interested in the reaction of metallocenes with oxygen atoms and tried to clarify the products of the reaction.

The stream of oxygen atoms (mainly $O(^3P)$) was obtained by a micro-wave discharge of the stream of oxygen gas or of the mixture of nitrous oxide and argon (the concentration of oxygen atoms in the reaction system could not be determined exactly, because it changed during the proceeding of the reaction as described later, but the dissociation percent of molecular oxygen was found to be about 10 % by nitrogen dioxide titration[3]). Ferrocene or nickelocene, sublimed at about 60°C, was added to the stream of oxygen atoms. The gaseous reaction products were trapped about 1 sec after the addition of the reactant at the temperature of liquid nitrogen or of dry-ice.

As soon as ferrocene or nickelocene was added to the stream of oxygen atoms, brown colored metallic species began to precipitate on the reactor wall, which caused the interruption of the reaction through decreasing catalytically the concentration of oxygen atoms. The wall could be cleaned by washing with nitric acid and sulfuric acid; therefore, by repeating the reaction run several times, we could collect enough amount of low boiling organic products to analyse. The reaction was considered to be characterized in the distribution of the low boiling products (Table), though there were found some kinds of unidentified high boiling products containing polymeric species.

The products were relatively similar to those of the reaction of 1,3-cyclopentadiene with oxygen atoms, which were studied in the same reactor. In the case of cyclopentadiene, the $C_4H_6$ isomers were found to be main low boiling products. In parallel, some trials were made by using a flow reactor attached directly to a time of flight type mass-spectrometer (the apparatus was described in the lit.[4]). Under similar conditions, as one example, the reaction proceeded approximately at the time of 7.7 msec as follows; 1 $C_5H_6$ (in the discharged oxygen) $\longrightarrow$ 0.8 $C_4H_6$ + 0.8 CO + other minor products. This reaction is considered to proceed through an

oxygen adduct ($C_5H_6O^*$) as a hot intermediate which decomposes partly to $C_4H_6$ and CO, in the light of the results of the reaction of olefins with oxygen atoms.[5] It is known that 3-cyclopenten-1-one photolytically decomposes almost completely to 1,3-butadiene and CO,[6] and it seems interesting to clarify the $C_5H_6O^*$ species involved in these two reactions.

Though some of the reaction products from the metallocenes may be produced through successive reactions of primarily produced cyclopentadiene, vinylacetylene was considered to be a specific product of the reaction of the metallocenes. In fact, no amount of vinylacetylene could be found in the reaction of cyclopentadiene. The difficulties of carrying out the reaction under uniform conditions as already stated, and the probable complexities of the reaction do not allow us confidently to draw a detailed mechanistic scheme. But it may be safely stated that the vinylacetylene should be made from the reaction of oxygen atoms with cyclopentadienyl (a free radical or as a ligand), considering that no route seems to exist to yield the $C_4H_4$ species in the decomposition reactions of metallocenes investigated till now (for example, thermal decompositions to yield cyclopentadienyl and others,[7,8] and mass-spectrometrically studied electron impact decompositions.[9]).

Table Relative Yields of the Trapped Low Boiling Products

| species | condition | products | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | I | II | III | IV | V | VI | VII | VIII | IX |
| ferrocene | A | 39 | 29 | 12 | 89 | 100 | ~0 | 25 | 12 | 45 |
| | B | 18 | 11 | 3 | 81 | 100 | ~0 | 28 | 21 | 4 |
| nickelocene | A | 370 | 72 | 32 | 90 | 100 | 12 | 120 | 110 | 260 |
| cyclopentadiene | A | 18 | 84 | 6 | ~0 | 100 | 11 | 370 | 0 | 4500*1 |
| | B | 54 | 110 | 40 | ~0 | 100 | 16 | 630 | 0 | 4700*1 |

Products: I, acetylene; II, propylene; III, allene; IV, propyne; V, 1,3-butadiene (standard); VI, 1,2-butadiene(*2); VII, 1-butyne(*2); VIII, vinylacetylene; IX, cyclopentadiene: *1 : containing the unreacted cyclopentadiene, *2 : $C_4H_6$ isomers were assumed to have the same gaschromatographic sensitivity as 1,3-butadiene
Reaction Conditions: A; oxygen gas discharge system, total pressure (0.24 torr), oxygen ($5.5 \times 10^{-6}$ mol/sec), metallocene ($1.4 \times 10^{-6}$ mol/sec), cyclopentadiene ($0.2 \times 10^{-6}$ mol/sec); B; nitrous oxide-argon discharge system, total pressure (0.51 torr), nitrous oxide ($3.1 \times 10^{-6}$ mol/sec), argon ($7.9 \times 10^{-6}$ mol/sec), the flow rate of the reactant is the same as that of the condition A

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