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The ozone sensitized oxidative conversion of methane to methanol and ethane to ethanol

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The reaction of O_2, O_3, and CH_4 or C_2H_6 of 7.76, 0.24 and 92% of the hydrocarbon respectively (residence time of 8.8 min) at 1 atm, and 400°C for CH_4 and 300°C for C_2H_6 gave CO, CO_2, H_2O, CH_2O and CH_3OH from CH_4 and in addition CH_4, C_2H_4, CH_3CHO and C_2H_5OH from C_2H_6. No reaction occurred when O_3 was absent indicating that the partial oxidation was sensitized (initiated) by the oxygen atoms formed by the decomposition of ozone.

Keywords: Methane; ethane; methanol; ethanol; ozone; oxygen atom; oxidation; sensitization

1. Introduction

We have demonstrated that it is possible to sensitize the oxidation of alkanes by converting a portion of the oxygen in an homogeneous oxidative system to ozone. In the reactor itself the ozone decomposes thermally to produce molecular oxygen and oxygen atoms which then initiate the chain reaction. Methanol selectivity from methane has been estimated to be about 20% with methane conversions of about 2%. A similar reaction with ethane produces ethanol as well as acetaldehyde, methanol and formaldehyde.

It has previously been shown [1] that the homogeneous oxidation of methane to methanol at high pressure can be sensitized by a variety of substances. The formation of the free radicals involved in the oxidative chain process can be facilitated by the presence of other free radicals or by the introduction of compounds which have an easily abstractable hydrogen. The high levels of sensitizers required and their net consumption make such a sensitized process impractical.

The initiation reaction for the homogeneous oxidative process [2]

$$CH_4 + O_2 \rightarrow CH_3 + HO_2$$

is still a major energy hurdle ($E_a = 55$ kcal/mol) which must be overcome or by-passed if any improved efficiency is to be achieved. We believe that the conversion of part of the oxygen used in the reaction into ozone and the subsequent thermal conversion of the ozone into molecular oxygen and atomic oxygen is a process which can achieve that goal. The half-life of ozone depends on its concentration and, at 2 wt% in O_2, it decreases from 100 s at 150°C to about 0.1 s at 250°C [3]. It was shown by Kleimenov et al. [4] that the oxidation of methane at low temperatures was sensitized by O-atoms formed in the thermal decomposition of ozone. Other work from Nalbandyan's laboratory [5–7] included the oxidation of propane and the identification of CH_3OOH, HCHO, and CH_3OH as products of the reaction. Recent mass spectrometer studies have confirmed these products as well as H_2O_2 [8]. A low pressure kinetic and chemiluminescence study of the reaction has been performed by Toby and Toby [9]. No plug-flow studies have been reported with the view of initiating the partial oxidation of methane to methanol or ethane to ethanol.

2. Experimental

An apparatus with dual-flow lines and mass flow controllers for hydrocarbon and for oxygen was used. The oxygen passed through an ozonizer which could be switched on or off. The reactor was a pyrex tube 22 mm i.d. (heated volume = 110 ml) with a thermocouple well to monitor temperature. The products were analyzed by gas chromatography on a Poropak Q column and on a 13x sieve column for O_2, CO, N_2 and CH_4, which were not well separated on the Poropak column. The concentration of ozone was determined by the oxidation of iodide to iodine which was measured by absorption at 350 nm.

3. Results and discussion

With 8% O_2 in the reaction mixture it was possible to obtain 3% O_3 (by volume) in the O_2 flow corresponding to 0.24% in the CH_4/O_2 mixture flowing at 12.5 ml/min.

Some results at 1 atm pressure are shown in fig. 1 for CH_4 and fig. 2 for C_2H_6. In both cases the temperature of the reactor was maintained at the point where no oxidation took place with just oxygen and methane (or ethane) in the feedstock stream. When the oxygen was passed through a silent discharge to form about 3 mol% ozone in the oxygen, oxidation was initiated and normal oxidation products were obtained. Methane produced CO, CO_2, H_2O, HCHO, and CH_3OH. From C_2H_6 the same products were observed as well as CH_4, C_2H_4, CH_3CHO and C_2H_5OH.

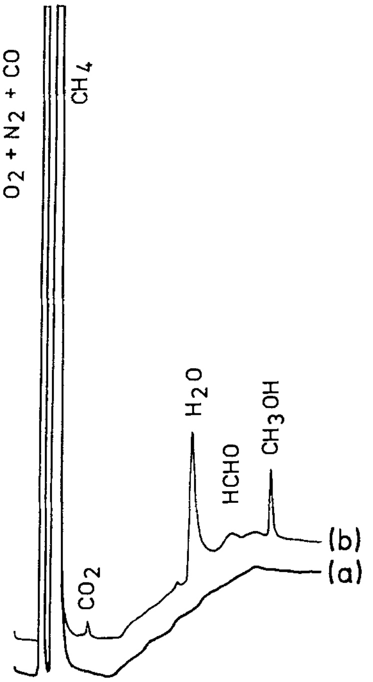

Fig. 1. (a) Lower GC. $CH_4 + 8\%\ O_2$, 400°C 1 atm, 12 ml/min. Reactor vol = 110 ml. (b) Upper displaced GC as in (a) except for conversion of 3% of the O_2 to O_3.

An estimate of the CH_3OH selectivity based on carbon products is about 20% from CH_4 and about 30% from C_2H_6 where the C_2H_5OH/CH_3OH ratio was 0.2. We believe the following reactions are occurring:

for ozone: $O_3 \rightarrow O_2 + O$;

for methane:
$$O + CH_4 \rightarrow CH_3 + OH \ (E_a \approx 8 \text{ kcal/mol}),$$
$$OH + CH_4 \rightarrow CH_3 + H_2O,$$
$$CH_3 + O_2 \rightarrow CH_3O_2, \quad \text{etc.};$$

for ethane:
$$O + C_2H_6 \rightarrow C_2H_5 + OH,$$
$$OH + C_2H_6 \rightarrow C_2H_5 + H_2O,$$
$$C_2H_5 + O_2 \rightarrow C_2H_5O_2, \quad \text{etc.}$$

The homogeneous high pressure oxidation reactions for CH_4 [2] and C_2H_6 [10] have been described and presumably follow the above reaction sequence.

Conversion of the hydrocarbon was about 2% for CH_4 and about 4% for C_2H_6. When nitrogen was substituted for the hydrocarbon, it was shown that the ozone was fully decomposed in the reactor at temperature above 260°C.

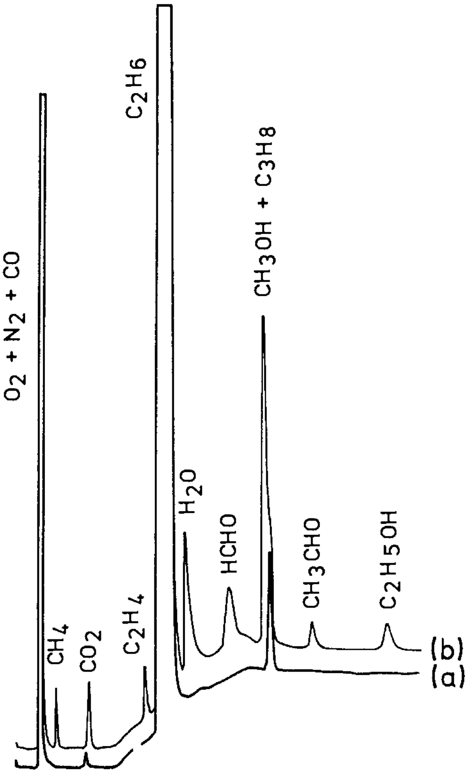

Fig. 2. (a) Lower GC. $C_2H_6 + 8\%\ O_2$, 300°C 1 atm 12.5 ml/min. Reactor vol = 110 ml. (b) Upper displaced GC as in (a) except for conversion of 3% of the O_2 to O_3.

When the O_3/O_2 reaction with methane or ethane was allowed to proceed at room temperature, no products were observed. This result indicates that the direct reaction of O_3 with the hydrocarbon does not occur.

A detailed study of alcohol formation under various reaction conditions is presently in progress.

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