Journal of Catalysis **185,** 182–191 (1999)
Article ID jcat.1999.2507, available online at http://www.idealibrary.com on IDEAL®

Oxygenates from Light Alkanes Catalyzed by NO_x in the Gas Phase

Kiyoshi Otsuka, Ryo Takahashi, and Ichiro Yamanaka

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

Received December 23, 1998; revised March 27, 1999; accepted March 29, 1999

The partial oxidations of light alkanes (methane, ethane, propane, and *iso*-butane) catalyzed by NO_x in the gas phase have been studied at a pressure of less than 1 bar. For all the alkanes tested, the addition of NO to the mixture of alkanes and O_2 enhanced the selectivities and the yields of oxygenates remarkably. It was suggested that NO_2 generated from NO and O_2 initiated the oxidation of alkanes and would specifically accelerate the C–C bond fission, enhancing the formation of C_1-oxygenates from ethane, propane, and *iso*-butane. NO_2 and NO could be used as a homogeneous catalyst at >600°C because nitroalkanes formed were decomposed completely, releasing the NO_x. The comparison of the product distributions for the decomposition and oxidation of nitroalkanes and alkylnitrites strongly suggested that the oxygenates (HCHO, CH_3CHO, and CH_3COCH_3) were formed from the corresponding alkylnitrites which must be the reaction intermediates during the oxidation of alkanes with an O_2 and NO mixture. © 1999 Academic Press

Key Words: **oxygenates; light alkanes; NO; NO_2; partial oxidation.**

INTRODUCTION

The one-step transformation of alkanes to valuable oxygenates by means of selective oxidation has attracted significant interest in recent years (1–6). Direct routes to useful oxygenates can avoid the energy intensive steam reforming step or thermal cracking step which is required in existing technologies (6, 7).

Whether the desired product is an oxygenate such as alcohol, ketone or aldehyde, the first step in the catalytic partial oxidation of light alkanes must involve the breaking of a C–H bond of the corresponding alkanes on the catalyst surface. The alkyl species thereby formed may undergo reaction with the oxidant on the surface and/or in the gas phase, depending on the nature of catalyst and the reaction conditions. There are some reports demonstrating a high one-pass yield of MeOH (>9%) in the gas phase autooxidation of methane at high pressures of >50 bar (7, 8). However, under a pressure of less than 1 bar, no matter how the reaction proceeds in the gas phase or on the surface, one-pass yields of the sum of useful oxygenates such as MeOH and HCHO from methane or C_2H_5OH, MeCHO, and MeCOOH from ethane could not be greater than 5% (2, 9–11).

Bañares *et al.* recently reported a favorable effect of NO for the selective oxidation of methane to MeOH and HCHO over V_2O_5/SiO_2 catalysts (12). They obtained the highest C_1-oxygenate yield of 7% at atmospheric pressure, suggesting that the presence of NO must alter the equilibria in the gas-phase reactions and in the surface-catalyzed reactions. It has been known since long ago that the oxidation of methane is initiated by NO (13) in the gas phase in the absence of solid catalysts. Lombardo *et al.* (14) and Haruta *et al.* (15) reported the favorable effect of NO and NO_2 on the formation of HCHO for the gas phase oxidation of methane at 1–3 bar. The yield of HCHO was not greater than 4% in these cases. The reaction mechanism and the role of NO_x have to be clarified in more detail for evaluating the favorable effect of NO on the formation of oxygenates from light alkanes in the gas phase.

Recently, we obtained yields higher than 6 and 11% for the oxygenates of methane (HCHO + MeOH) and ethane (HCHO + MeOH + MeCHO), respectively, in the gas-phase oxidation catalyzed by NO (16). In general, it is believed that the role of NO and NO_2 is just to initiate the radical chain oxidation of methane (13, 14). We have suggested that NO_x plays an important role in the formation of oxygenates (16). However, the detailed studies on the NO_x-enhanced oxidation of alkanes, especially by focusing on the formation of oxygenates from ethane, propane, and butanes have not been reported yet. Therefore, the purpose of this work is to show the detailed kinetic results on the formation of oxygenates from these alkanes catalyzed by NO_x and to clarify the role of NO_x in the reaction mechanism.

METHODS

Apparatus and Procedure for Alkane Oxidations

The oxidation of alkanes was performed using a conventional gas flow system with an empty quartz tube reactor (inner diameter 0.8 cm, length 32 cm). The dead volume at the hot zone of the reactor was ca. 6 cm^3. The internal diameter of the reactor at the outlet was reduced to 0.3 cm to remove the products quickly from the hot zone of the reactor. Standard experimental conditions and procedure were as follows. A gas mixture of light alkanes (20 kPa),

0021-9517/99 $30.00

O_2 (10 kPa), and NO (2 kPa) balanced with He to atmospheric pressure was passed through the reactor and kept at a desired temperature (450–650°C) under total gas-flow rate of 120 ml min^{-1}. The temperature indicated in this paper was the temperature in the reaction zone of the reactor. The products were analyzed by on-line gas chromatography (Shimadzu GC-8A TCD and Hitachi 263-30 TCD) with Porapak-Q, Porapak-T, molecular sieve 5A, and VZ-8 columns. Conversions of alkanes, selectivity of products, and product yields were calculated on the basis of the carbon numbers of the alkanes reacted. For example, when the selectivities to HCHO and CH_3COCH_3 are the same, the molar amount of HCHO formed is three times greater than that of CH_3COCH_3.

Reagents

The alkanes, O_2 and NO, used in this study were research grade (purity >99.9%). The nitroalkanes were extra-pure grade obtained from Wako Chemical Company. The reactant gases and nitroalkanes were used without further purification. The alkylnitrites were prepared by the esterification of 1-C_3H_7OH (or 2-C_3H_7OH) with $NaNO_2$ in a sulfuric acid aqueous solution cooled with an ice bath. The formed alkylnitrites were collected and purified by repeated fractional distillation and dried by using Na_2SO_4. The CH_3ONO used was prepared through the transesterification between C_3H_7ONO and CH_3OH. The formed CH_3ONO was collected and purified by fractional distillation.

Reaction Using a FT-IR Cell

The equilibration reaction $2NO + O_2 \rightleftarrows 2NO_2$ was measured using a FT-IR gas cell (dead volume 60 ml) which was connected to a gas flow system. The central part of the cell could be heated to 500°C. A gas mixture of NO and O_2 or NO_2 alone was passed with He as a carrier through the cell at total gas flow rate of 100 ml min^{-1}. After a steady state was reached, the gases inside the cell were isolated by shutting the stopcocks at the entrance and the exit of the cell. The equilibration was followed by measuring the IR bands at 1909 cm^{-1} for NO (N=O stretching) and at 1630 cm^{-1} for NO_2 (O=N=O antisymmetric stretching).

The decomposition of CH_3ONO was also measured using the IR cell described above.

RESULTS

The Effects of NO on Alkane Conversions and Product Selectivities

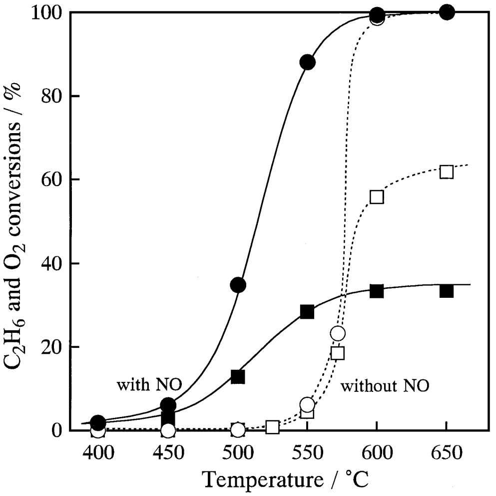


FIG. 1. Effect of NO addition on the conversion of C_2H_6 and O_2. (□) C_2H_6 conversion in the absence of NO; (■) C_2H_6 conversion in the presence of NO; (○) O_2 conversion in the absence of NO; (●) O_2 conversion in the presence of NO. $P(C_2H_6) = 20$ kPa, $P(O_2) = 10$ kPa, $P(NO) = 2$ kPa, flow rate = 120 ml min^{-1}.

Figure 1 shows the effects of the addition of NO on the conversions of C_2H_6 and O_2 under the experimental conditions indicated in the figure caption. In the absence of NO, the oxidation of C_2H_6 requires higher temperatures than 523°C. The addition of NO initiated the reaction at a lower temperature, ca. 400°C. The conversion of C_2H_6 reached a plateau at >600°C because of the complete consumption of O_2 for both cases, i.e., in the absence and presence of NO. The conversion of C_2H_6 at the plateaus is lower for the oxidation in the presence of NO because of the drastic change in the product selectivities by the addition of NO. Figures 2a and 2b show the product distributions as functions of temperature for the oxidation of C_2H_6 without and with addition of NO, respectively. The product distribution in Fig. 2a indicates that the major product is C_2H_4 at all the temperature regions examined in this work. Only a trace of CH_3CHO and HCHO was obtained in the oxidation of C_2H_6 with O_2 in the absence of NO. However, when NO (2 kPa) had been added to a gas mixture of C_2H_6 (20 kPa) and O_2 (10 kPa), the product distribution changed drastically, as can be seen in Fig. 2b. The main product was HCHO at low temperatures (<550°C) and only a trace of C_2H_4 was observed. Although the selectivity to C_2H_4 increased at high temperatures (>550°C), the sum of the selectivities to CO and HCHO at 650°C was about 1.8 times larger than that to C_2H_4. The stoichiometric equations for the oxidative formations of C_2H_4, HCHO, and CO can be written as follows:

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O \qquad [1]$$

$$C_2H_6 + 3/2O_2 \rightarrow 2HCHO + H_2O \qquad [2]$$

$$C_2H_6 + 5/2O_2 \rightarrow 2CO + 3H_2O. \qquad [3]$$

If the selectivities to HCHO and CO on the bases of the C_2H_6 reacted are greater than that to C_2H_4, the conversion of C_2H_6 at complete consumption of O_2 (O_2 conversion 100%) should be less than that in the opposite situation,

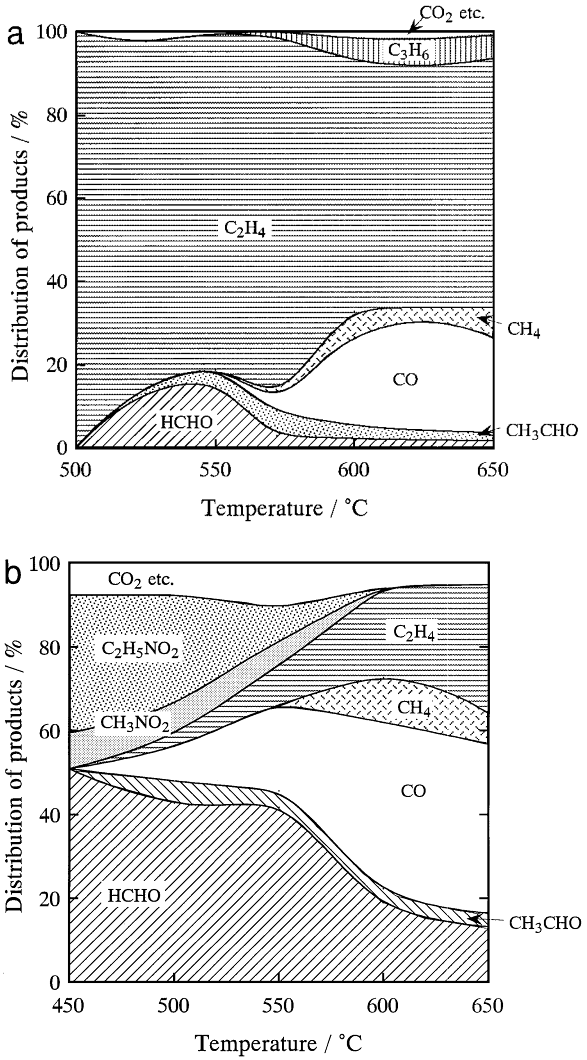


FIG. 2. (a) Effect of temperature on the distribution of products for C_2H_6 oxidation with O_2 (without NO). $P(C_2H_6) = 20$ kPa, $P(O_2) = 10$ kPa, flow rate = 120 ml min^{-1}. (b) Effect of temperature on the distribution of products for C_2H_6 oxidation with O_2 and NO. $P(C_2H_6) = 20$ kPa, $P(O_2) = 10$ kPa, $P(NO) = 2$ kPa, flow rate = 120 ml min^{-1}.

i.e., C_2H_4 selectivity > (HCHO + CO) selectivity. This explains the lower conversion of C_2H_6 at ≥600°C for the oxidation in the presence of NO than the conversion in the absence of NO (Fig. 1). The conversion rates of C_2H_6 at low conversion level (<10%) have been measured at different temperatures for both cases, i.e., in the presence and absence of NO. The plot of the logarithm of the conversion rate as functions of $1/T$ gave good straight lines for both cases. The apparent activation energies calculated from the slopes of the lines were 361 and 138 kJ mol^{-1} for the reaction in the absence and in the presence of NO, respectively. Thus, a dramatic decrease in the activation energy was observed when NO was added to a C_2H_6 and O_2 mixture.

Similar acceleration in the conversion and dramatic change in the product selectivities when NO is cofed have been observed also for CH_4, C_3H_8, and *iso*-C_4H_{10} at the temperature range 300–650°C (16). The apparent activation energies obtained for the conversions of alkanes in the absence of NO under the following experimental conditions were 275(C_3H_8) and 173 kJ mol^{-1} (*iso*-C_4H_{10}): P(alkanes) = 20, $P(O_2) = 10$, $P(He) = 71$ kPa, $T = 300$–550°C. The oxidation of CH_4 under these conditions at ≤650°C did not take place in the absence of NO. However, the oxidation of CH_4 initiated at 450°C with the addition of NO (2 kPa). The apparent activation energies evaluated from the rates of alkane conversions in the presence of NO (2 kPa) were dramatically decreased to 208 (CH_4), 107 (C_3H_8), and 101 kJ mol^{-1} (*iso*-C_4H_{10}).

Examples of the effects of NO on the yields of products and product distributions for oxidations of CH_4, C_2H_6, C_3H_8, and *iso*-C_4H_{10} at 500°C are demonstrated in Fig. 3. Alkenes are the main products for the oxidations of C_2H_6, C_3H_8, and *iso*-C_4H_{10} in the absence of NO, but the addition of NO enhanced the yields of oxygenates (HCHO, CH_3CHO, and CH_3COCH_3) remarkably. The total yields of oxygenates (CH_3OH + HCHO + CH_3CHO + CH_3COCH_3) in the presence and absence of NO are plotted as functions of temperature in Fig. 4a for the oxidations of CH_4 and C_2H_6, and in Fig. 4b for C_3H_8 and *iso*-C_4H_{10} under the reaction conditions indicated in the figure captions. For all the alkanes in Fig. 4, it is clear that the addition of NO to the mixtures of alkanes and O_2 enhances the yields of oxygenates remarkably.

The results in Figs. 3 and 4 indicate that the yields of oxygenates from C_2H_6, C_3H_8, and *iso*-C_4H_{10} increase with a decrease in the C–C bond dissociation energies of the alkanes.

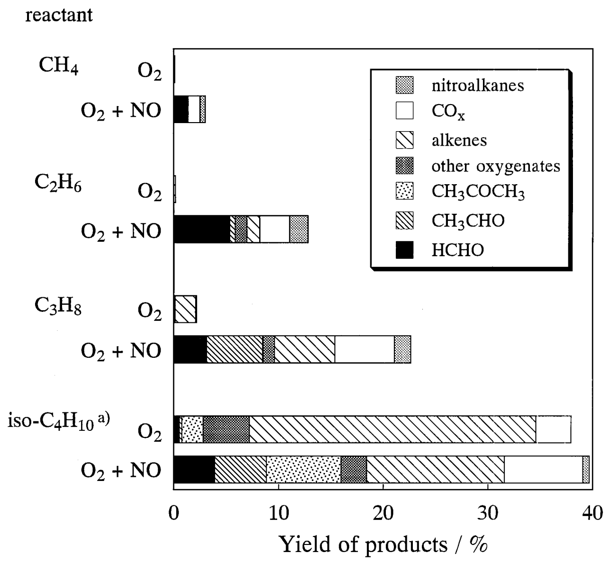


FIG. 3. Effect of NO addition on the yields of products for oxidation of light alkanes with O_2 at 500°C. P(alkane) = 20 kPa, $P(O_2) = 10$ kPa, $P(NO) = 2$ kPa, flow rate = 120 ml min^{-1}. ^{a}P(*iso*-C_4H_{10}) = 10 kPa, $P(O_2) = 5$ kPa, $P(NO) = 1$ kPa, flow rate = 60 ml min^{-1}.

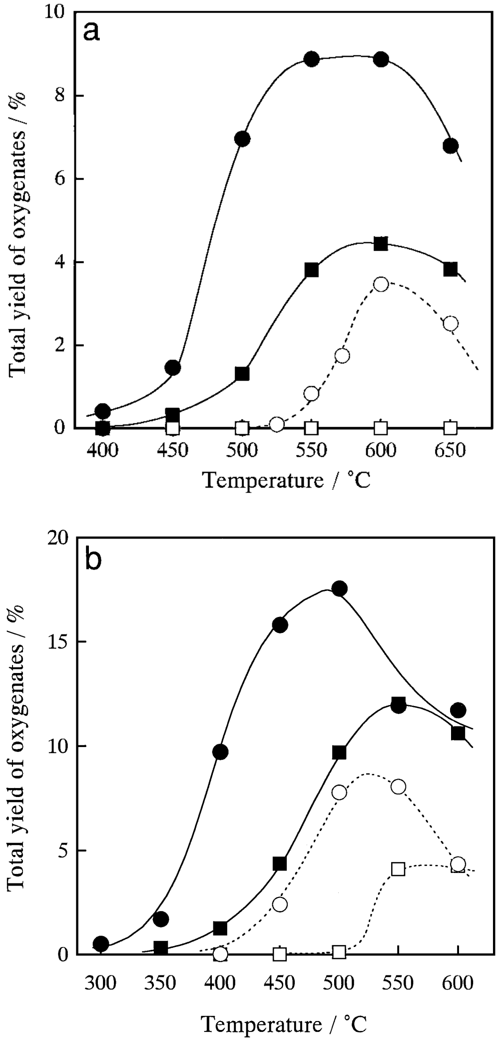


FIG. 4. (a) Effect of NO addition on the yields of oxygenates for CH_4 and C_2H_6 oxidations. (□) Yield of oxygenates from CH_4 in the absence of NO; (■) from CH_4 in the presence of NO; (○) from C_2H_6 in the absence of NO; (●) from C_2H_6 in the presence of NO. $P(\text{alkane}) = 20$ kPa, $P(O_2) = 10$ kPa, $P(NO) = 2$ kPa, flow rate = 120 ml min^{-1}. (b) Effect of NO addition on the yields of oxygenates for C_3H_8 and *iso*-C_4H_{10} oxidations. (□) Yield of oxygenates from C_3H_8 in the absence of NO; (■) from C_3H_8 in the presence of NO; (○) from *iso*-C_4H_{10} in the absence of NO; (●) from *iso*-C_4H_{10} in the presence of NO. C_3H_8 : $P(C_3H_8) = 20$ kPa, $P(O_2) = 10$ kPa, $P(NO) = 2$ kPa, flow rate = 120 ml min^{-1}; *iso*-C_4H_{10}: $P(iso\text{-}C_4H_{10}) = 10$ kPa, $P(O_2) = 5$ kPa, $P(NO) = 1$ kPa, flow rate = 60 ml min^{-1}.

This fact suggests that the formation of oxygenates is accompanied by the dissociation of the C–C bond for each alkane.

Kinetic Studies on Alkane Oxidations in the Presence of NO

The kinetic behaviors for the specific oxidation of light alkanes in the presence of NO were observed in detail for CH_4, C_2H_6, C_3H_8, and *iso*-C_4H_{10}. The changes in the conversion of alkanes and the product selectivities are plotted as functions of gas residence time (V/F) in Figs. 5a and 5b for CH_4 and C_2H_6 and in Figs. 6a and 6b for C_3H_8 and *iso*-C_4H_{10}. For all the alkanes in Figs. 5 and 6, after short induction periods, the conversion of alkanes increased linearly with gas residence time in the low conversion region. In general, the selectivity to aldehyde (HCHO and CH_3CHO) or acetone decreases and in contrast the CO selectivity increases with gas residence time. The effects of the partial pressures of C_2H_6, NO, and O_2 on the rate of conversion of C_2H_6 and on the formation rates of products are demonstrated in Figs. 7–9. The experiments were performed at 440°C at the conversions of C_2H_6 and O_2 less than 10%. The conversion of C_2H_6 depends on each partial pressure by slightly less than first order. Quite similar dependence on the partial pressures of the alkanes, NO and O_2 were also observed for the conversion rates of CH_4 and C_3H_8. The results in Fig. 8 indicate that the oxidation of C_2H_6 with O_2 does not occur in the absence of NO ($P(NO) = 0$) at 440°C under the experimental conditions indicated in the figure caption. Moreover, the results in Fig. 9 indicate that the reaction does not take place with NO alone ($P(O_2) = 0$). Cofeed of NO and O_2 is essential for the oxidation of C_2H_6 at <500°C. These observation were also true for the oxidations of CH_4 and C_3H_8. The NO_2 generated through the following reaction must initiate the oxidation of alkanes as will be discussed later:

$$2NO + O_2 \rightleftarrows 2NO_2. \qquad [4]$$

As described earlier (Fig. 1), the oxidation of C_2H_6 takes place rapidly at 600°C in the absence of NO. The addition of NO rather decreased the conversion of C_2H_6, but enhanced the yield of oxygenates. These tendency are more clearly demonstrated in Table 1. The conversion of C_2H_6 and the yields of products at 600°C are shown as functions of the partial pressure of NO added to the feed gas. The yield of C_2H_4, the major product in the absence of NO, decreased

TABLE 1

Effect of $P(NO)$ on the Yields of C_2H_4 and Oxygenates from C_2H_6 at 600°C

$P(NO)$ (kPa)	Conversion of C_2H_6 (%)	Yield (%)			
		C_2H_4	C_1-oxy[a]	C_2-oxy[b]	Total-oxy
0	55.8	33.7	1.5	2.0	3.5
0.5	38.8	13.0	7.3	1.3	8.5
1.0	36.8	9.8	8.0	1.2	9.2
2.0	34.1	6.2	7.9	1.2	9.1
4.0	33.8	7.1	7.9	1.0	8.9

Note. $P(C_2H_6) = 20$ kPa, $P(O_2) = 10$ kPa, $T = 600$°C; flow rate = 120 ml min^{-1}.

[a] HCHO + CH_3OH.

[b] $CH_3CHO + C_2H_5OH$.

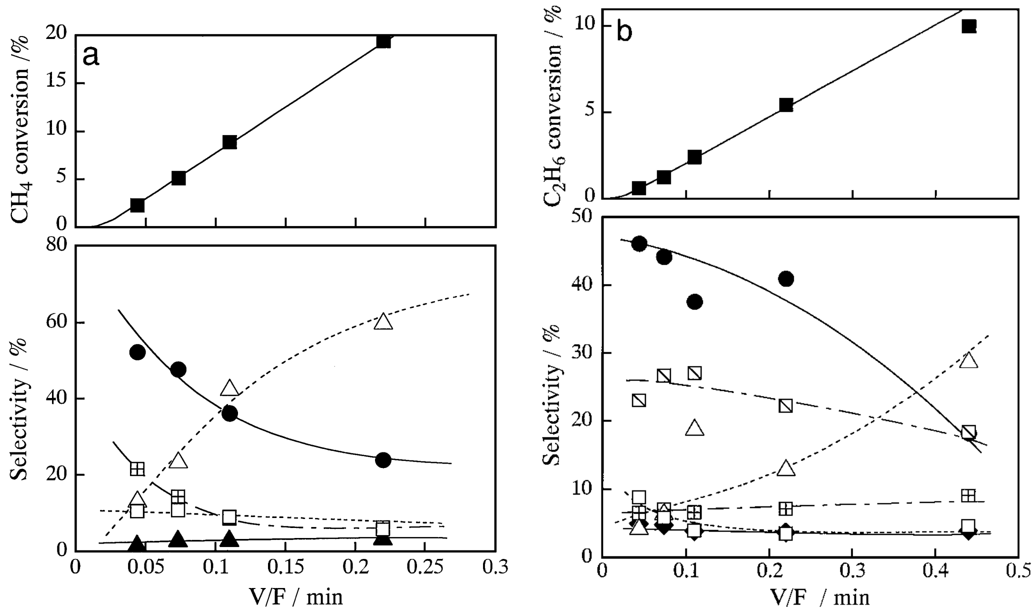


FIG. 5. (a) Effect of V/F on CH_4 oxidation with O_2 and NO. (●) HCHO; (▲) CH_3OH; (⊞) CH_3NO_2; (△) CO; (□) CO_2. $P(CH_4) = 20$ kPa, $P(O_2) = 10$ kPa, $P(NO) = 2$ kPa, $T = 525°C$. (b) Effect of V/F on C_2H_6 oxidation. (●) HCHO; (◆) CH_3CHO; (⊞) CH_3NO_2; (⧅) $C_2H_5NO_2$; (△) CO; (□) CO_2. $P(C_2H_6) = 20$ kPa, $P(O_2) = 10$ kPa, $P(NO) = 2$ kPa, $T = 440°C$.

but the yield of C_1-oxygenates (HCHO and CH_3OH) increased dramatically with a little addition of NO. It should be noted that the yield of CH_3CHO was not increased but decreased with the addition of NO. This fact suggests that NO_2 would specifically accelerate the C–C bond fission, enhancing the formation of C_1-oxygenates. Another point which should be noted in Table 1 was the absence of nitroalkanes in the products.

As can be seen in Fig. 2b, the formation of CH_3NO_2 and $C_2H_5NO_2$ can be neglected at the temperatures higher

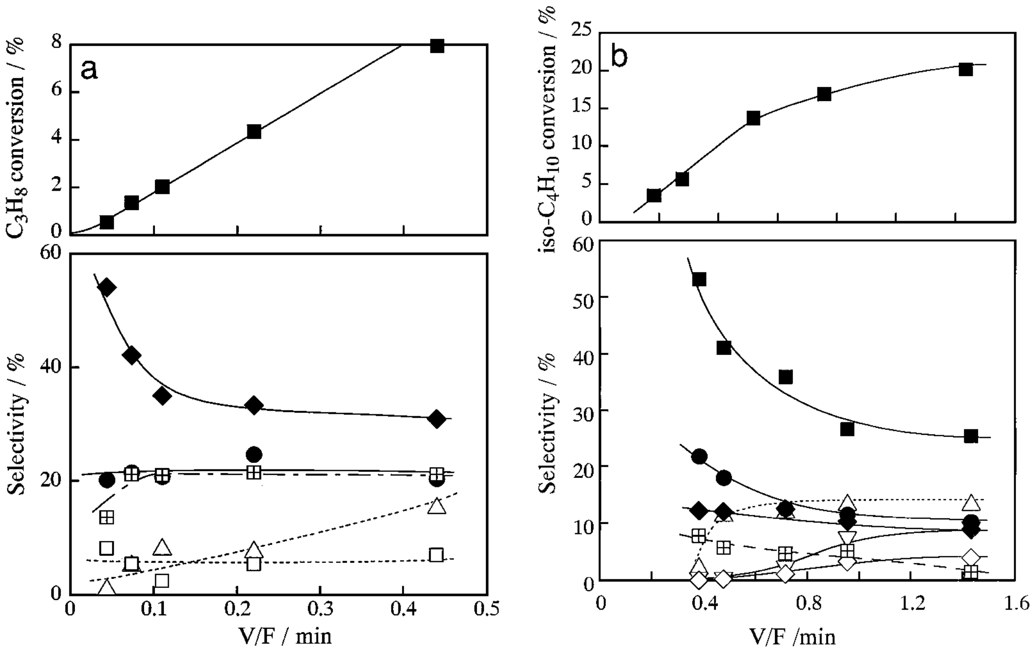


FIG. 6. (a) Effect of V/F on C_3H_8 oxidation. (●) HCHO; (◆) CH_3CHO; (⊞) RNO_2; (△) CO; (□) CO_2. $P(C_2H_6) = 20$ kPa, $P(O_2) = 10$ kPa, $P(NO) = 2$ kPa, $T = 440°C$. (b) Effect of V/F on *iso*-C_4H_{10} oxidation. (●) HCHO; (◆) CH_3CHO; (■) CH_3COCH_3; (⊞) CH_3NO_2; (▽) C_3H_6; (◇) *iso*-C_4H_8; (△) CO. $P(iso\text{-}C_4H_{10}) = 10$ kPa, $P(O_2) = 5$ kPa, $P(NO) = 2$ kPa, $T = 400°C$.

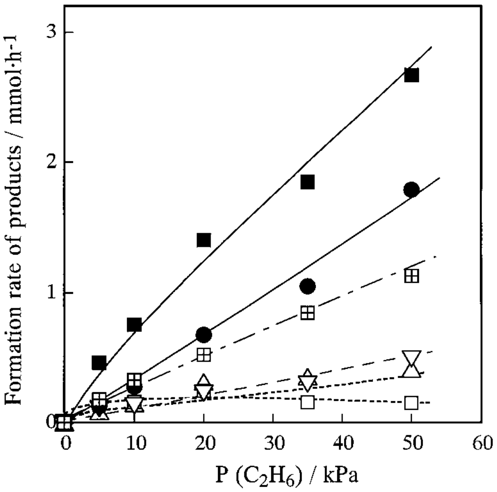


FIG. 7. Effect of $P(C_2H_6)$ on C_2H_6 oxidation with O_2 and NO. (■) Conversion rate of C_2H_6; (●) formation rate of HCHO; (⊞) RNO_2; (▽) C_2H_4; (△) CO; (□) CO_2. $P(O_2) = 10$ kPa, $P(NO) = 2$ kPa, $T = 440°C$, flow rate = 120 ml min^{-1}.

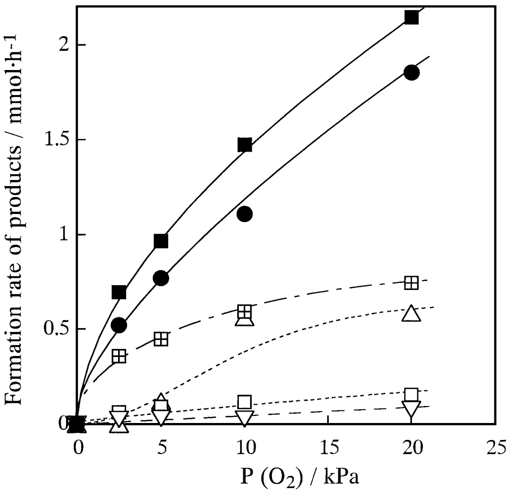


FIG. 9. Effect of $P(O_2)$ on C_2H_6 oxidation promoted by NO. (■) Conversion rate of C_2H_6; (●) formation rate of HCHO; (⊞) RNO_2; (▽) C_2H_4; (△) CO; (□) CO_2. $P(C_2H_6) = 20$ kPa, $P(NO) = 2$ kPa, $T = 440°C$, flow rate = 120 ml min^{-1}.

than 600°C probably due to their decomposition into NO_2 (or $NO + 1/2O_2$) and alkyl radicals. Under these circumstances, NO_2 or NO can be recycled and used as a homogeneous catalyst for the partial oxidation of C_2H_6 into C_1-oxygenates. In fact, all the NO introduced in the feed gas was confirmed to be recovered as NO in the exit gas from the reactor at >600°C when the conversion of O_2 became 100%. The formations of N_2 and N_2O did not occur under the experimental conditions in this work.

The turnover numbers per NO calculated from the conversion of oxygen enhanced by the addition of NO for the oxidations of CH_4 (at 650°C), C_2H_6 (at 550°C), and C_3H_8 (at 500°C) under standard reaction conditions ($P(\text{alkane}) = 20$, $P(O_2) = 10$, $P(NO) = 2$ kPa, flow rate = 120 ml min^{-1}) were 5.0, 4.1, and 4.2, respectively, during the residence time of NO 6 s. These values also suggest that NO or NO_2 would work as a homogeneous catalyst.

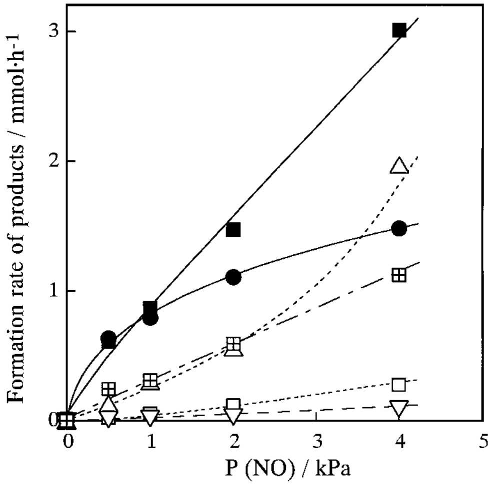


FIG. 8. Effect of $P(NO)$ on C_2H_6 oxidation with O_2 at 440°C. (■) Conversion rate of C_2H_6; (●) formation rate of HCHO; (⊞) RNO_2; (▽) C_2H_4; (△) CO; (□) CO_2. $P(C_2H_6) = 20$ kPa, $P(O_2) = 10$ kPa, $T = 440°C$, flow rate = 120 ml min^{-1}.

Alkane Oxidations with NO_2

It was suggested earlier that the NO_2 generated through reaction [4] would initiate the oxidation of alkanes. In order to get further information about the role of NO and NO_2 in the reaction mechanism, we should consider first the equilibrium of reaction [4]. The equilibrium distributions of NO, NO_2, and O_2 at different temperatures are indicated in Table 2 (17). Under standard reaction conditions, the partial pressures of NO and O_2 in the feed were 2 and 10 kPa, respectively. Therefore, the equilibrium distribution in Table 2 was evaluated on the basis of the following assumption

$$P(NO) + P(NO_2) = 2 \text{ kPa},$$
$$P(O_2) + 1/2P(NO_2) = 10 \text{ kPa}.$$

TABLE 2

Equilibrium Distribution of NO, NO_2, and O_2 at Different Temperatures

Temperature (°C)	Equilibrium distribution (%)			NO/NO_2
	NO	NO_2	O_2	
300	0.3	17.9	81.8	1.58×10^{-2}
400	1.6	16.4	82.0	9.74×10^{-2}
500	4.8	12.9	82.3	3.72×10^{-1}
600	8.9	8.5	82.6	1.04

Note. $P_{\text{initial}}(NO) = 2$ kPa; $P_{\text{initial}}(O_2) = 10$ kPa.

As can be seen in Table 2, the equilibrium at 300°C shifted wholly to NO_2 but the ratio NO_2/NO decreases from 10 : 1 at 400°C to 1 : 1 at 600°C.

The attainment of equilibrium between NO_2 and NO (Eq. [4]) during the alkane oxidation cannot be guaranteed under our experimental conditions because of the following experimental observations. The rate of equilibrium reaction [4] was roughly estimated by measuring the changes in the intensities of the infrared-absorption bands of NO (1909.2 cm^{-1}, N=O stretching) and of NO_2 (1629.6 cm^{-1}, O=N=O anti-symmetric stretching) in an IR gas cell. It took more than 4 min to reach the equilibrium of reaction [4] at 500°C after starting the reaction with the initial mixture of NO (2 kPa) and O_2 (5 kPa). About 8 min was required to reach an equilibrium at 500°C when the reaction started from NO_2 (2 kPa). It should be noted that the gas residence time in a hot zone of the reactor used in the oxidation of alkanes under standard reaction conditions was ca. 6 s. Thus, the equilibrium reaction, $2NO + O_2 \rightleftarrows 2NO_2$, should be far from equilibrium during the stay of the gases in a hot zone of the reactor under the reaction conditions in this work.

By taking into account the results described above, the oxidations of CH_4 and C_3H_8 with NO_2 and with a mixture of NO and O_2 were carried out to determine the active participation of NO_2. Figure 10 shows the product distributions and the conversion of alkanes observed under the conditions noted in the figure caption. The conversions of alkanes were 2 to 5 times greater for the reaction with NO_2 than with the mixture of NO and O_2. This fact strongly supports the idea that NO_2 is an active initiator as well as an oxidant for the oxidation of alkanes. Considerable selectivities to oxygenates (HCHO and CH_3CHO) were observed in the reaction of alkanes with NO_2. Although the product selectivities in Fig. 10 should be compared at similar conversion of alkanes, they are somewhat similar between the oxidations with NO_2 and with the mixture of NO and O_2 for both cases, CH_4 and C_3H_8. These observations are consistent with the idea that NO_2 would initiate and control the partial oxidation of alkanes with the mixture of NO and O_2. The lower conversion of alkanes observed in Fig. 10 in the cases of oxidations using NO and O_2 mixture compared with the conversion using NO_2 can be ascribed to a lower concentration of NO_2 in the former case because the equilibration of the reaction [4] did not attain instantly as noted earlier.

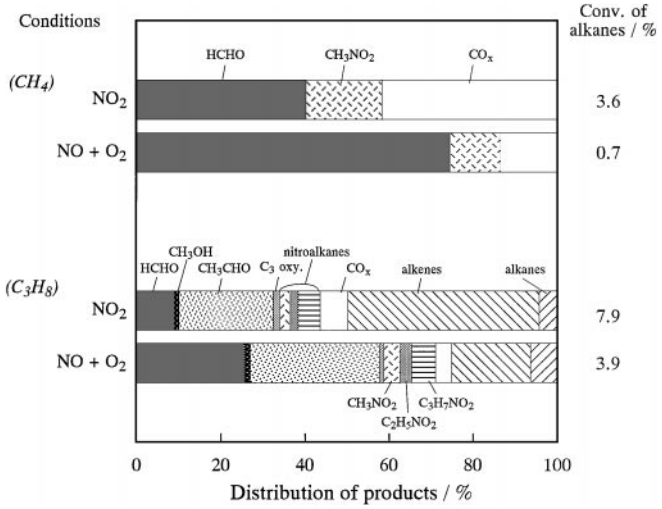


FIG. 10. Distribution of products for the oxidations of CH_4 and C_3H_8 with NO_2 at 500°C. $P(\text{alkane}) = 20$ kPa, $P(NO_2) = 2$ kPa, $P(NO) = 2$ kPa, $P(O_2) = 1$ kPa, $T = 500$°C, flow rate = 120 ml min^{-1}.

DISCUSSION

Reaction Intermediates for Oxygenate Formation

So far, we have suggested the activation of alkanes by NO_2. Thus, the initiation in the oxidation of alkanes (RH) must be started from the abstraction of hydrogen of RH by NO_2,

$$RH + NO_2 \rightarrow R^{\bullet} + HNO_2. \quad [5]$$

The formed $R^{\bullet}$ would react with NO_2 giving alkylnitrite and/or nitroalkane as follows:

$$R^{\bullet} + NO_2 \rightarrow RONO \quad [6]$$

$$R^{\bullet} + NO_2 \rightarrow RNO_2. \quad [7]$$

Of course, we should take into account the addition of O_2 to $R^{\bullet}$:

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}. \quad [8]$$

However, the RO_2 would give alkenes as the main products in the absence of NO, as indicated in Fig. 2a and Ref. (16). Therefore, the oxygenate formation in the presence of NO must be caused by either nitroalkanes (RNO_2) or alkylnitrite (RONO). To examine this assumption, we have measured the conversion of RNO_2 and RONO as well as the product selectivities. The results will be described below.

Product Selectivities for Nitroalkane and Alkylnitrite Reactions

The nitroalkanes tested in this work were CH_3NO_2, $C_2H_5NO_2$, 1-$C_3H_7NO_2$, and 2-$C_3H_7NO_2$. The nitroalkane vapor (1.2 kPa) was passed through the same reactor used for the alkane oxidations at 500°C by helium carrier with and without cofeeding oxygen (5.0 kPa). The results are indicated in Fig. 11. The carbon balance between the nitroalkanes reacted and the sum of the products was better than 95%. The distribution of products were calculated on the bases of the carbon numbers of the nitroalkanes reacted. The decomposition of CH_3NO_2 in the absence of O_2 gave the products in the order of selectivities as $CO_x > HCHO \approx$ alkanes $(CH_4 + C_2H_6) > C_2H_4$.

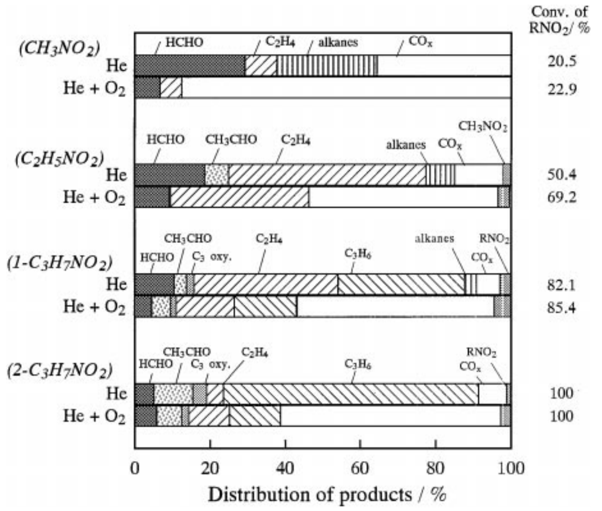


FIG. 11. Conversion of nitroalkanes and product selectivities at 500°C. P(nitroalkane) = 1.2 kPa, $P(O_2) = 5$ kPa, $T = 500$°C, flow rate = 120 ml min^{-1} (balanced with He).

Cofeeding of O_2 with CH_3NO_2 drastically enhanced the formation of CO_x. The selectivity to HCHO decreased to 5%. The decompositions of $C_2H_5NO_2$, 1-$C_3H_7NO_2$, and 2-$C_3H_7NO_2$ in the absence of O_2 gave alkenes (C_2H_4, C_3H_6) as the major products and the selectivities to oxygenates (HCHO + CH_3CHO) were less than 25%. The cofeed of O_2 to these nitroalkanes enhanced the formation of CO_x as the main product and decreased the selectivity of oxygenates to lower than 15%. The selectivity of alkenes ($C_2H_4 + C_3H_6$) was always higher than that of oxygenates in the presence of O_2.

Compared with the results for nitroalkanes described above, the reaction of alkylnitrites showed that the selectivity to aldehydes (HCHO + CH_3CHO) was high and only a trace of alkenes formed. The results for *n*-C_3H_7ONO and *iso*-C_3H_7ONO together with those for *tert*-BuONO(16) are shown in Fig. 12. Under the reaction conditions indicated in the figure caption, the conversion of alkylnitrites was always 100%. Coke formation in the reactor and unidentified oily products were observed on the wall at the exit of the reactor when O_2 had not been cofed with the alkylnitrites. Therefore, mass balance was not confirmed in the absence of O_2. However, the coke and oily products were not observed in the presence of O_2 and a good mass balance was confirmed within an experimental error of ±5%. Figure 12 indicates the distribution of products from the alkylnitrites reacted at 400°C in He, in O_2 diluted with He, and in a mixture of NO and O_2 diluted with He. The product distribution for the decompositions of the alkylnitrites in the absence of O_2 were calculated by excluding the coke and unidentified oily products.

The decomposition of *n*-C_3H_7ONO in He showed quite high selectivity to HCHO. In the case of *iso*-C_3H_7ONO decomposition in He, CH_3CHO was the main product. *Tert*-BuONO gave acetone exclusively. These observations strongly suggest that HCHO, CH_3CHO, and CH_3COCH_3 are formed through the decomposition of the corresponding alkylnitrites as follows:

$$n\text{-}C_3H_7ONO \rightarrow HCHO + C_2H_5^{\bullet} + NO \qquad [9]$$

$$iso\text{-}C_3H_7ONO \rightarrow CH_3CHO + CH_3^{\bullet} + NO \qquad [10]$$

$$tert\text{-}C_4H_9ONO \rightarrow CH_3COCH_3 + CH_3^{\bullet} + NO. \qquad [11]$$

Probably these decompositions occur through the formation of the corresponding alkoxy radicals and NO first, then further decomposition of the alkoxy radicals into alkyl radicals and oxygenates.

In order to confirm the reaction intermediate in methane oxidation, the decomposition of methylnitrite was followed by infrared spectroscopy. When the CH_3ONO vapor in an IR cell was heated up to 215°C, the absorption peaks at 1600 to 1700 cm^{-1} due to O–N=O anti-symmetric stretching vibrations of CH_3ONO started to decrease and the peak at 1745 cm^{-1} due to C=O stretching of HCHO and at 1875 cm^{-1} due to NO increased gradually. These changes occurred rapidly at 250°C and indicated clearly the formation of CO (2115, 2203, 2237 cm^{-1}) as well. These results indicate the formation of HCHO and NO from CH_3ONO:

$$CH_3ONO \rightarrow HCHO + H^{\bullet} + NO. \qquad [12]$$

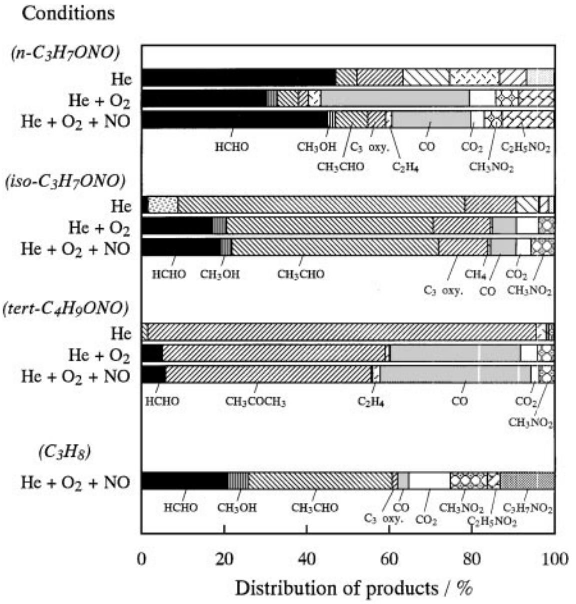


FIG. 12. Distribution of products for the reactions of *n*-, *iso*-C_3H_7ONO, *tert*-C_4H_9ONO, and C_3H_8 at 400°C. $P(RONO) = 1.0$ kPa, $P(O_2) = 5.0$ kPa, $P(NO) = 1.0$ kPa, $T = 400$°C, flow rate = 120 ml min^{-1} (balanced with He). Conversion of the nitrites was always 100%. C_3H_8 oxidation was performed under standard conditions.

CO must be formed through the decomposition of HCHO:

$$HCHO \rightarrow CO + H_2. \quad [13]$$

The results in Fig. 12 for the reaction of *n*-C_3H_7ONO in the presence of O_2 decreased the selectivity to HCHO but increased CO and CO_2 formations. Moreover, nitromethane and nitroethane were produced. These observations suggest that the HCHO formed in Eq. [9] is further oxidized into CO and CO_2:

$$HCHO + O_2 \rightarrow CO \rightarrow CO_2. \quad [14]$$

The NO generated from the decomposition of *n*-C_3H_7ONO is oxidized to NO_2 (Eq. [4]). The NO_2 thus formed reacts with the $C_2H_5^{\bullet}$ generating $C_2H_5NO_2$ and C_2H_5ONO. The nitrite must produce HCHO and $CH_3^{\bullet}$ according to

$$C_2H_5ONO \rightarrow HCHO + CH_3^{\bullet} + NO. \quad [15]$$

The $CH_3^{\bullet}$ thus formed reacts with NO_2, giving CH_3NO_2 and CH_3ONO. The CH_3ONO is converted to HCHO according to reaction [12].

The reaction of *n*-C_3H_7ONO in the presence of both O_2 and NO improved the selectivity to HCHO as can be seen in Fig. 12. The generation of alkylnitrites (CH_3ONO, C_2H_5ONO) and consequently the formation of HCHO through reactions [12] and [15] would be enhanced due to the formation of NO_2 in the presence of both NO and O_2.

The results for *iso*-C_3H_7ONO in Fig. 12 indicate that the presence of O_2 enhanced the formation of HCHO and CH_3NO_2 compared to the results in the absence of O_2. The enhanced HCHO formation can be ascribed to the $CH_3^{\bullet}$ produced in Eq. [10]. The $CH_3^{\bullet}$ must be converted into HCHO through the formation of CH_3ONO (from the $CH_3^{\bullet}$ and NO_2) and its decomposition in Eq. [12]. It should be noted that $C_2H_5NO_2$ was not produced. CH_3NO_2 was the only nitroalkane observed because the decomposition of *iso*-C_3H_7ONO gives only $CH_3^{\bullet}$ as alkyl radical according to reaction [10]. The addition of NO to O_2 and *iso*-C_3H_7ONO mixture increased slightly the selectivity to CH_3NO_2 but did not change much the selectivities for the other products as can be seen in Fig. 12.

The results for *tert*-BuONO in Fig. 12 indicate the remarkable increase in the formation of CO and CO_2 in the presence of O_2 as we expected. The main reason for this CO_x formation must be the oxidation of acetone with O_2. The addition of NO did not change much the product selectivities. It should be noted that acetone and HCHO are the only oxygenates formed. Moreover, CH_3NO_2 was the only nitroalkane obtained. These facts support reaction [11] for the decomposition of *tert*-C_4H_9ONO; i.e., the $CH_3^{\bullet}$ and NO formed in reaction [11] would explain the formations of HCHO and CH_3NO_2 even in the absence of NO in a feed gas of *tert*-C_4H_9ONO and O_2 mixture.

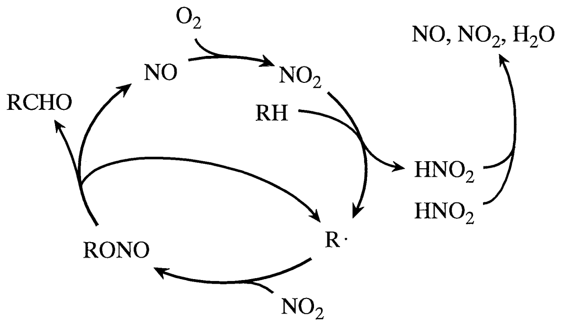
For all the alkylnitrites tested in Fig. 12, alkenes were not formed or only a small C_2H_4 was observed for the reactions of *n*-C_3H_7ONO and *tert*-C_4H_9ONO. This is in striking contrast to the product distributions observed for nitroalkanes in Fig. 11.

The product distribution for the oxidation of C_3H_8 under standard reaction conditions at 400°C is also indicated in Fig. 12 for comparison with the results of *iso*-C_3H_7ONO. Excluding the formations of $C_2H_5NO_2$ and $C_3H_7NO_2$, the product distribution for C_3H_8 oxidation is quite similar to that of *iso*-C_3H_7ONO in the presence of NO and O_2. This fact implies that the oxidation of C_3H_8 in the presence of NO and O_2 occurs mainly via *iso*-C_3H_7ONO (Eq. [10]) as far as the oxygenate formations are concerned.

Reaction Mechanism

As discussed above, the oxidation of light alkanes is initiated through the abstraction of hydrogen by NO_2 generated from NO and O_2. The subsequent addition of NO_2 to the formed alkyl radicals produces both nitroalkanes and alkylnitrites. The alkylnitrites are responsible for the formation of oxygenates through Eqs. [9]–[12] and [15]. The alkyl radicals formed at the same time are further converted into a lower molecular weight oxygenate (HCHO). The NO regenerated is repeatedly used as homogeneous catalyst for the formation of NO_2 which oxidizes alkanes. The reaction mechanism described above is schematically demonstrated in Scheme 1.

The oxidation of light alkanes with O_2 in the absence of NO would proceed through the radical-chain autooxidation mechanism. The reaction proceeds through the formation of alkyl peroxide radical ($RO_2^{\bullet}$) which produces alkenes as the main products. This auto-oxidation mechanism has been studied in detail (18–23) and reviewed by many authors (23–26). We must take into account the contribution of this autooxidation mechanism especially at high temperatures >500°C.



SCHEME 1

REFERENCES

1. Sokolovskii, D., *Catal. Rev. Sci. Eng.* **32**, 1 (1990).
2. Bhasin, M. M., and Slocum, D. W. (Eds.), "Methane and Alkane Conversion Chemistry." Plenum, New York, 1995.
3. Warren, B. K., and Oyama, S. T. (Eds.), "Heterogeneous Hydrocarbon Oxidation," ACS Symposium Series 638. Washington, DC, 1996.
4. Vedrine, J. C., Millet, J. M., and Volta, J. C., *Catal. Today* **32**, 115 (1996).
5. Moro-oka, Y., and Ueda, W., *in* "Catalysis Vol. 11," p. 223. Royal Society of Chemistry, London, 1994.
6. Cavani, F., and Trifirò, F., *Stud. Surf. Sci. Catal.* **110**, 19 (1997).
7. Yarlagadda, P. S., Morton, L. A., Hunter, N. R., and Gesser, H. D., *Ind. Eng. Chem. Res.* **27**, 252 (1988).
8. Gesser, H. D., Hunter, N. R., and Shigapov, A. N., *in* "Methane and Alkane Conversion Chemistry" (M. M. Bhasin and D. W. Slocum, Eds.), p. 271. Plenum, New York, 1995.
9. Pitchai, R., and Klier, K., *Catal. Rev. Sci. Eng.* **28**, 13 (1986).
10. Hall, T. J., Hargreaves, J. S. J., Hutchings, G. J., Joyner, R. W., and Taylor, S. H., *Fuel Proc. Tech.* **42**, 151 (1995).
11. Batiot, C., and Hodnett, B. K., *Appl. Catal. A* **137**, 179 (1996).
12. Bañares, A. M., Cardoso, J. H., Hutchings, G. J., Bueno, J. M. C., and Fierro, J. L. G., *Catal. Lett.* **56**, 149 (1998).
13. Layng, T. E., and Soukop, R., *Ind. Eng. Chem.* **20**, 1052 (1928); McConkey, B. H., and Wilkinson, P. R., *I EC Proc. Design Dev.* **6**, 436 (1967).
14. Irusta, S., Lombardo, E. A., and Miró, E. E., *Catal. Lett.* **29**, 339 (1994).
15. Han, L. B., Tsubota, S., and Haruta, M., *Chem. Lett.* **1995**, 931.
16. Otsuka, K., Takahashi, R., Amakawa, K., and Yamanaka, I., *Catal. Today* **45**, 23 (1998).
17. MALT2, The Japan Society of Calorimetry and Thermodynamic Analysis, Tokyo, 1993.
18. Strausz, O. P., Lown, J. W., and Gunning, H. E., *in* "Comprehensive Chemical Kinetics" (C. H. Bamford and C. F. H. Tipper, Eds.), Vol. 5. Elsevier, Amsterdam, 1972.
19. Pollard, R. T., Hydrocarbons. *in* "Comprehensive Chemical Kinetics" (C. H. Bamford and C. F. H. Tipper, Eds.), Vol. 17. Elsevier, Amsterdam, 1977.
20. Vedneev, V. I., Goldenberg, M. Ya, Gorban, N. I., and Teitelboim, M. A., *Kinet. Catal.* **29**, 1 (1988).
21. Geerts, J. W. M. H., Chen, Q., van Kasteren, J. M. N., and van der Wiele, K., *Catal. Today* **6**, 519 (1990).
22. Zanthoff, H., and Baerns, M., *Ind. Eng. Chem. Res.* **29**, 2 (1990).
23. Foulds, G. A., and Gray, B. F., *Fuel Process. Tech.* **42**, 129 (1995).
24. Mackie, J. C., *Catal. Rev. Sci. Eng.* **33**, 169 (1991).
25. Krylov, O. V., *Catal. Today* **18**, 209 (1993).
26. Lødeng, R., Lindvag, O. A., Søraker, P., Roterud, P. T., and Onsager, O. T., *Ind. Eng. Chem. Res.* **34**, 1044 (1995).