Oxidative Couplings of Methane, Ethane, and Propane with Sodium Peroxide at Low Temperatures

KIYOSHI OTSUKA,[1] YASUSHI MURAKAMI, YUJI WADA, A. A. SAID,[2] AND AKIRA MORIKAWA

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

Partial oxidations of CH_4, C_2H_6, and C_3H_8 proceeded over sodium peroxide at low temperatures (600–650 K). The only partial oxidation product from CH_4 was ethane, a coupling product. The quantity of its formation depended on the second order of the methane pressure. The products from C_2H_6 were ethylene and butane. The formation rate of ethylene depended on the first order but that of butane depended on the second order of the ethane pressure. In the case of C_3H_8, the products were C_6 alkanes, C_4 alkanes, ethylene, and traces of propylene. The formation rates of C_6 and C_4 alkanes depended on the second order but those of ethylene and propylene depended on the first order of the propane pressure. The activation energies for the conversions of CH_4 (127 kJ mol^{-1}) were considerably larger than those of C_2H_6 (83) and C_3H_8 (89). The transition state of CH_4 in its activation is suggested to be different from those of C_2H_6 and C_3H_8. The presence of gaseous oxygen decreased the selectivities to the coupling products and to the dehydrogenation products, although the rates of conversion of alkanes were not affected by gaseous oxygen. These observations suggest that the activation of alkanes is caused only by peroxide anions, but the selectivities to further reactions of the surface alkyl groups formed are affected strongly by the presence of gaseous oxygen. © 1990 Academic Press, Inc.

INTRODUCTION

The activation and functionalization of methane, ethane, and propane have attracted much attention from chemists and chemical engineers who wish to convert natural gas into transportable chemicals such as higher order hydrocarbons or C_1-, C_2-, and C_3-oxygenates. However, the activation of light alkanes at temperatures lower than 773 K is not easy, and still more difficult is their conversion into functionalized products.

Among many trials in converting methane into functionalized products, oxidative coupling of methane into ethane and ethylene is so far the most successful and promising reaction (*1–9*). In general, basic oxides such as rare earth oxides, alkaline earth oxides, and especially alkali metal-doped metal oxides are active and selective catalysts in oxidative coupling of methane (*5*). However, only a few fundamental studies have been reported concerning the oxygen species responsible for the catalytic activation of methane over basic metal oxides (*6–8*). Moreover, the reaction mechanisms proposed so far are not quite in agreement (*9*).

Recently, kinetic work in our laboratory has suggested that the activation of methane is initiated by diatomic oxygen species such as O_2^-, O_2^{2-}, or O_2 chemically adsorbed on the surface (*10*). Sinev *et al.* first reported the formation of ethane through the reduction of barium peroxide with methane at temperatures above 723 K (*11*). We have demonstrated that methane can be activated and converted to C_2 compounds at temperatures lower than 673 K with alkali

[1] To whom correspondence and reprint requests should be addressed.

[2] Present address: Chemistry Department, Faculty of Science, United Arab Emirates University, Al-Ain, P.O. Box 15551, United Arab Emirates.

or alkaline earth metal peroxides such as Na_2O_2, BaO_2, and SrO_2 (12). Therefore, we suggested that O_2^{2-} peroxide anions could be responsible for abstraction of H from CH_4 over rare earth oxides (10, 12).

In this work, we describe in more detail the reactions of methane as well as ethane and propane with Na_2O_2 in order to understand the general features of activation of light alkanes by peroxide anions. This study may contribute to progress in defining the reaction mechanism of catalytic, oxidative coupling of light alkanes into higher hydrocarbons over basic metal oxides.

EXPERIMENTAL

The Na_2O_2 powder used was obtained from Wako Pure Chemical Co. The purity of the metal (Na) in the sample was >99%. The purity of alkanes used was above 99.9%. The experiments were carried out applying a conventional microcatalytic method using a gas-flow system with helium carrier. Prior to each run of reaction of alkanes with Na_2O_2, the peroxide was treated in a stream of helium for 2 h at the reaction temperatures of 600–650 K. Evolution of oxygen from the sample oxides

due to the decomposition of the impurity NaO_2 in the sample was observed during this pretreatment (12), but it ceased within the first 30 min of the treatment. A pulse of alkanes diluted with helium (total 2.7 ml STP) was introduced into a helium stream (30 ml min⁻¹ flow rate) upstream from a fixed bed of Na_2O_2 (0.50 g). The effluent gases from the Na_2O_2 were analyzed directly by TCD-GC using a Gaschropack 54 column. The conversions of alkanes were calculated on the basis of C_1, C_2, or C_3 for the CH_4, C_2H_6, and C_3H_8 reacted, respectively. All the kinetic studies described later were carried out at an alkane conversion of less than 18%.

RESULTS

Product Distribution and Reactivities of Light Alkanes

The reactivities of methane, ethane, and propane and the yields of products from each alkane have been examined under the following reaction conditions: T = 648 K, pressure of alkanes = 15.5 kPa ((17.4 ± 0.1) × 10⁻⁶ mol), weight of Na_2O_2 = 0.50 g. The results are shown in Table 1. The only
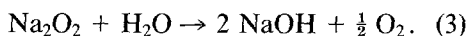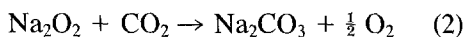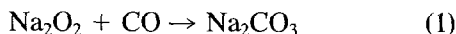
TABLE 1

Partial Oxidation of Alkanes over Na_2O_2

Pulse No.	Reactant	Conversion (%)	Yield (%)[a]
1	CH_4	13.0	C_2H_6 0.88
2	CH_4	13.7	C_2H_6 0.97
3	CH_4	13.9	C_2H_6 1.11
4	CH_4	14.1	C_2H_6 1.50
5	CH_4	14.0	C_2H_6 1.55
6	CH_4	13.2	C_2H_6 1.69
7	CH_4	13.6	C_2H_6 1.61
8	C_2H_6	13.1	n-C_4H_{10} 1.58, C_2H_4 1.88[b]
9	C_2H_6	12.2	n-C_4H_{10} 1.76, C_2H_4 1.76[b]
10	C_2H_6	11.0	n-C_4H_{10} 1.68, C_2H_4 1.71[b]
11	C_3H_8	17.9	C_6H_{14} 0.80, C_4H_{10} 0.65, C_2H_4 0.55[c]
12	C_3H_8	14.9	C_6H_{14} 1.03, C_4H_{10} 0.52, C_2H_4 0.49[c]

[a] The yields of C_2H_6, C_4H_{10}, and C_6H_{14} were calculated on the basis of C_1, C_2, or C_3 for the CH_4, C_2H_6, and C_3H_8 reacted, respectively.

[b] With a trace of acetaldehyde.

[c] With a trace of propylene.

product observed for the reaction of methane was ethane. The other possible products, CO, CO_2, and H_2O, were trapped in the peroxides. In fact, separate experiments showed that, CO, CO_2, and H_2O were irreversibly captured by Na_2O_2 at 573 K, probably due to the reactions

$$Na_2O_2 + CO \rightarrow Na_2CO_3 \qquad (1)$$

$$Na_2O_2 + CO_2 \rightarrow Na_2CO_3 + \tfrac{1}{2} O_2 \qquad (2)$$

$$Na_2O_2 + H_2O \rightarrow 2\,NaOH + \tfrac{1}{2} O_2. \qquad (3)$$

The products from ethane in the effluent gas were butane, ethylene, and a trace of acetaldehyde. The products in the reaction of propane with Na_2O_2 were C_6 alkanes (isomers were not separated), C_4 alkanes (n- and isobutanes), ethylene, and trace of propylene. The conversion of methane was constant within experimental error of ±0.5% for pulses 1 to 7, but yield of ethane increased from 0.88 to 1.50% with the number of methane pulses and became constant at 1.62 ± 0.07% for pulses 5 to 7. The conversions of ethane and propane were constant within ±0.6 and 1.5%, respectively, with the number of pulses. The conversions and the yields listed in Table 1 show that the selectivities to the coupling products are 11 ± 1 (pulses 5–7), 13 ± 1 (pulses 8 and 9), and 5.5 ± 1.5% (pulses 11 and 12) for the reactants of CH_4, C_2H_6, and C_3H_8, respectively. The selectivities increased with increased temperature because the apparent activation energy of the coupling reaction was considerably greater than that of the conversion of each alkane, as will be described later.

The total amount of alkanes converted after pulse 12 in Table 1 was 2.9×10^{-5} mol. The Na_2O_2 in the sample (0.50 g) used in Table 1 was 6.4 ± 10^{-3} mol. The surface area of the Na_2O_2 sample measured by the BET method using N_2 adsorption was 0.70 ± 0.05 $m^2\,g^{-1}$. Assuming that the number of Na_2O_2 units on the surface is roughly $3 \times 10^{18}\,m^{-2}$ on the basis of the lattice parameters of the oxide, the number of surface Na_2O_2 units in the sample (0.50 g) used in

Table 1 was 1.1×10^{18} (1.8×10^{-6} mol). Therefore, the total amount of alkanes converted in Table 1 was 16 times greater than the surface Na_2O_2 molecules. It is surprising that the reactivity of the oxides does not decrease with the number of pulses, as can be seen in Table 1. This observation suggests that the migration of O_2^{2-} anions from the bulk to the surface is quite rapid at 648 K or that the Na_2CO_3 and NaOH formed aggregate locally on the surface, which always preserves the exposure of the reactive Na_2O_2 on the surface.

Effects of Alkane Pressures on the Quantities of Products

1. Methane. Figure 1 shows the quantity of the ethane formed plotted against the partial pressure of methane in the pulse of methane diluted with helium. The data in Fig. 1 were plotted against the square of the methane pressure in Fig. 2. The straight line in Fig. 2 indicates that the rate of coupling reaction depends on the second order of the methane pressure.

2. Ethane. The effect of ethane pressure on the quantity of products is shown in Fig. 3. The quantity of ethylene is proportional to the pressure of ethane. On the other hand, the quantity of n-butane depends on the square of the ethane pressure (Fig. 4). These results show that the formation rate
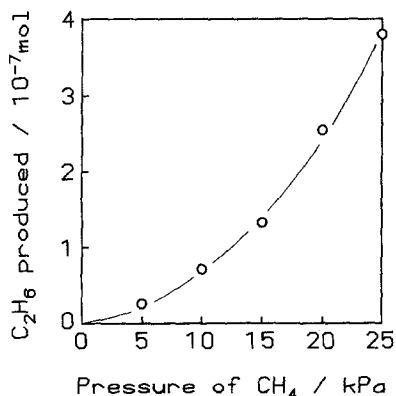

FIG. 1. Effect of methane pressure on the amount of ethane formed at 648 K over Na_2O_2 (0.5 g).
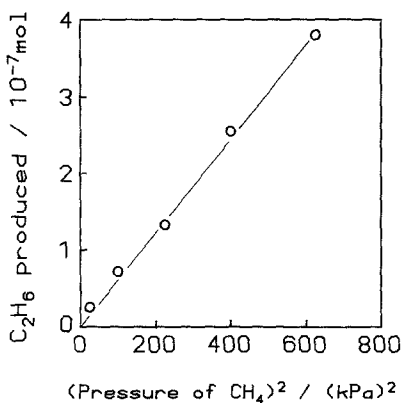
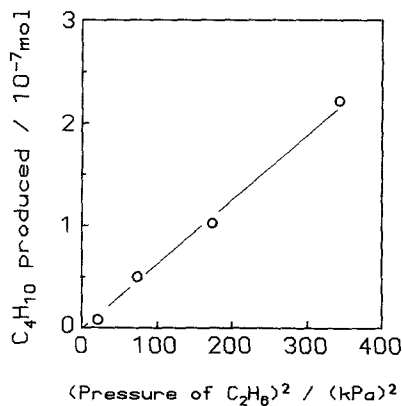FIG. 2. Plots of the amount of ethane formed against $P^2_{CH_4}$.

FIG. 4. Plots of the amount of n-butane formed against $P^2_{CH_4}$.

of ethylene depends on the first order but that of butane depends on the second order of the ethane pressure.

3. Propane. In the case of the propane oxidation, the formation rates of ethylene and propylene depend on the first order of the propane pressure, as can be seen in Fig. 5. However, the formation rates of C$_6$-alkanes and C$_4$-alkanes depend on the second order of the pressure of propane (Fig. 6).

Temperature Effects

Temperature effects on the conversion and the amounts of products from methane, ethane, and propane are shown in Figs. 7, 8, and 9, respectively. The logarithm of the amounts of starting alkanes reacted (R_c) and the logarithm of the amounts of each product (R_f) are plotted against the inverse of temperature in Figs. 7, 8, and 9.

Comparison of the apparent activation energies (E_a) shown in Figs. 7, 8, and 9 indicates that (1) the activation energies for the conversion of alkanes are in the order CH$_4$ > C$_2$H$_6$ ≃ C$_3$H$_8$, and (2) the activation energies for the formations of coupling products are in the order C$_2$H$_6$ (from CH$_4$) > C$_4$H$_{10}$ (from C$_2$H$_6$) ≃ C$_6$H$_{14}$ (from C$_3$H$_8$). It must
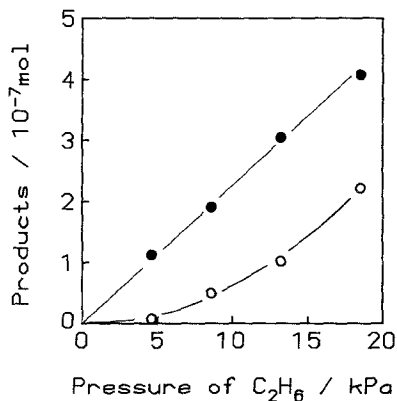

FIG. 3. Effect of ethane pressure on the amounts of n-butane (○), and ethylene (●) formed at 648 K over Na$_2$O$_2$ (0.5 g).
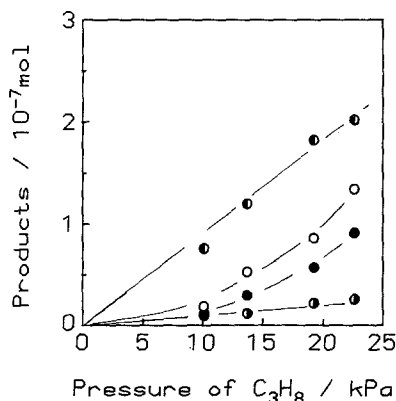

FIG. 5. Effect of propane pressure on the amounts of hexanes (○), butanes (●), propylene (◗), and ethylene (◖) formed at 648 K over Na$_2$O$_2$ (0.5 g).
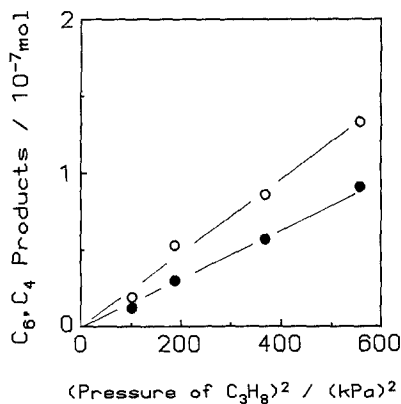
FIG. 6. Plots of the amounts of hexanes (O), and butanes (●) formed against $P_{C_3H_8}^2$.

FIG. 8. Effect of reaction temperature on the amounts of ethane converted (●; $E_a = 83$ kJ mol^{-1}) and of n-butane (O; $E_a = 134$ kJ mol^{-1}) and ethylene formed (◑; $E_a = 61$ kJ mol^{-1}) at $P_{C_2H_6} = 15$ kPa over Na_2O_2 (0.5 g).

be noted that the activation energy of the coupling reaction for each alkane is considerably larger than that of conversion of the corresponding alkane. In the case of reaction of C_2H_6 with Na_2O_2, the activation energy in the formation of C_2H_4 is the smallest, as can be seen in Fig. 8. These results will later be discussed on the basis of the proposed mechanism.

Effect of Gaseous Oxygen

All the experiments described above have been carried out in the absence of gaseous oxygen to determine the direct reac-
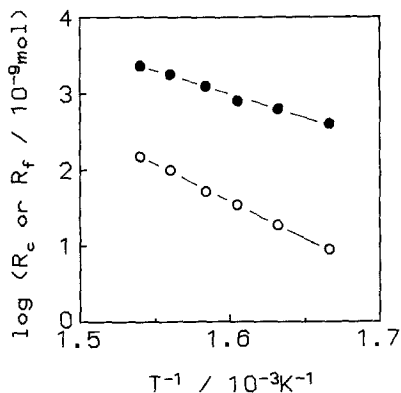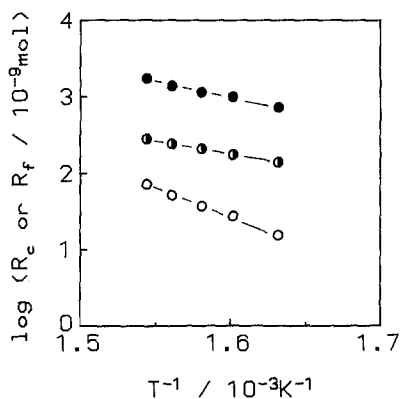
tion of CH_4 with the O_2^{2-} anions in the solid. Under the usual catalytic oxidative coupling of methane, the experiments are carried out with cofeeding CH_4 and O_2. Thus, it is interesting to examine the effect of gaseous oxygen on the reactions described earlier. The experiments were carried out under a constant pressure of alkanes (15 kPa, $(17.3 \pm 0.1) \times 10^{-6}$ mol in the pulse) with various partial pressures of oxygen added.

FIG. 7. Effect of reaction temperature on the amounts of methane converted (●; $E_a = 127$ kJ mol^{-1}) and of ethane formed (O; $E_a = 192$ kJ mol^{-1}) at $P_{CH_4} = 15$ kPa over Na_2O_2 (0.5 g).
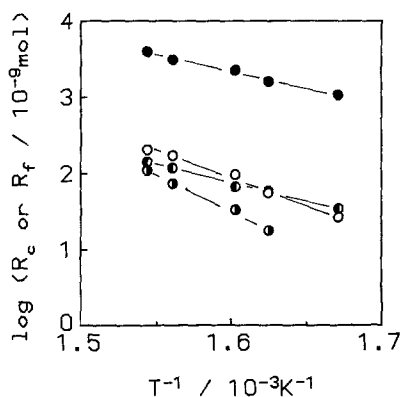

FIG. 9. Effects of reaction temperature on the amounts of propane converted (●; $E_a = 89$ kJ mol^{-1}) and of hexanes (O; $E_a = 137$ kJ mol^{-1}), butanes (◑; $E_a = 177$ kJ mol^{-1}) and ethylene formed (◐; $E_a = 94$ kJ mol^{-1}) at $P_{C_3H_8} = 15$ kPa over Na_2O_2 (0.5 g).

TABLE 2

Partial Oxidation of CH_4 over Na_2O_2 in the Presence of Gaseous O_2

P_{O_2}/kPa	Conversion of CH_4 (%)	C_2H_6 Selectivity (%)
0	12.6	10.9
5	14.1	4.7
10	13.3	1.8
15	13.8	0.6

Note. Weight of Na_2O_2 = 0.50 g, P_{CH_4} = 15 kPa.

The effects of gaseous oxygen on the conversion of CH_4 and on the selectivity to C_2H_6 are shown in Table 2. The conversion of CH_4 was not affected at all by gaseous oxygen within experimental error, but the selectivity to C_2H_6 was decreased appreciably in the presence of gaseous oxygen.

Similar results were observed in the case of oxidation of C_2H_6 as shown in Table 3. The conversion of C_2H_6 did not change in the presence and absence of gaseous oxygen. However, the selectivities to C_2H_4 and C_4H_{10} decreased with increasing partial pressure of oxygen.
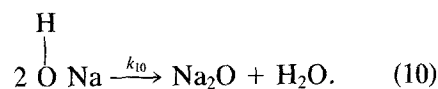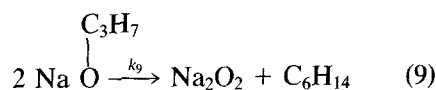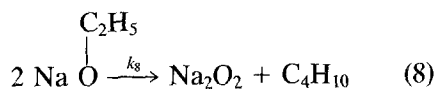
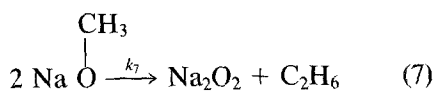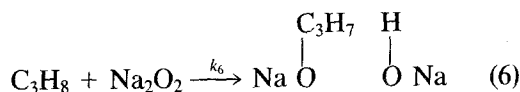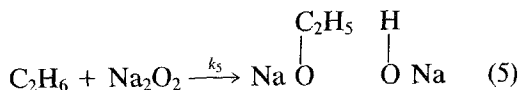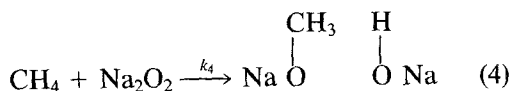## DISCUSSION

Activation of Alkanes by Na_2O_2

In general, oxidative coupling of methane occurs at a temperature higher than ~873K (*9, 13*). The partial oxidations of ethane and propane by oxygen do not require such high temperatures, but the main reactions are oxidative dehydrogenation of the alkanes giving ethylene and propylene, respectively (*14*). Recently, we have demonstrated the direct formations of C_2- and C_3-oxygenates from ethane (*15*) and propane (*16*), respectively, but there were no coupling products at all. As far as we know, no one has ever reported oxidative dimerization of ethane and propane.

As described in this work, although the reactions were not catalytic, methane, ethane, and propane were partially oxidized by Na_2O_2 giving ethane, butane, and hexane, respectively, as the main reaction products

at temperatures <650 K. The results in Figs. 2, 4, and 6 show that the formation rate of each coupling product depends on the square of the partial pressure of the corresponding starting alkane. These observations can be explained by assuming the following activation of alkanes and subsequent coupling of the produced alkyl groups on the surface:

$$CH_4 + Na_2O_2 \xrightarrow{k_4} Na \overset{CH_3}{\underset{|}{O}} \quad \overset{H}{\underset{|}{O}} Na \quad (4)$$

$$C_2H_6 + Na_2O_2 \xrightarrow{k_5} Na \overset{C_2H_5}{\underset{|}{O}} \quad \overset{H}{\underset{|}{O}} Na \quad (5)$$

$$C_3H_8 + Na_2O_2 \xrightarrow{k_6} Na \overset{C_3H_7}{\underset{|}{O}} \quad \overset{H}{\underset{|}{O}} Na \quad (6)$$

$$2 \, Na \overset{CH_3}{\underset{|}{O}} \xrightarrow{k_7} Na_2O_2 + C_2H_6 \quad (7)$$

$$2 \, Na \overset{C_2H_5}{\underset{|}{O}} \xrightarrow{k_8} Na_2O_2 + C_4H_{10} \quad (8)$$

$$2 \, Na \overset{C_3H_7}{\underset{|}{O}} \xrightarrow{k_9} Na_2O_2 + C_6H_{14} \quad (9)$$

$$2 \, \overset{H}{\underset{|}{O}} Na \xrightarrow{k_{10}} Na_2O + H_2O. \quad (10)$$

Further oxidation of the adsorbed alkyl groups by Na_2O_2 gives deep oxidation prod-

TABLE 3

Partial Oxidation of C_2H_6 over Na_2O_2 in the Presence of Gaseous O_2

P_{O_2}/kPa	Conversion of C_2H_6 (%)	Selectivity (%)	
		C_2H_4	C_4H_{10}
0	13.2	14.5	12.1
5	12.8	10.7	8.4
10	12.9	8.3	5.2
15	13.6	6.2	2.3

Note. Weight of Na_2O_2 = 0.50 g, $P_{C_2H_6}$ = 15 kPa.

ucts, CO and CO_2. For example, in the case of deep oxidation of methane, the deep oxidation may be written as

$$\begin{array}{c} CH_3 \\ | \\ Na\ O \end{array} \quad + \ Na_2O_2 \xrightarrow{k_{11}} \xrightarrow{+Na_2O_2}$$

$$CO, CO_2, H_2O. \quad (11)$$
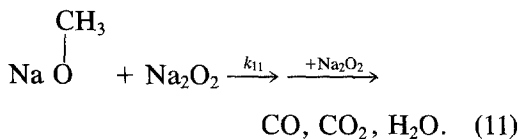
Steady-state approximation for the concentration of the surface methyl groups, for example, can be expressed as

$$\frac{d[CH_3\text{-}]}{dt} = k_4 P_{CH_4}[Na_2O_2] - k_7[CH_3\text{-}]^2$$

$$- k_{11}[CH_3\text{-}][Na_2O_2] = 0. \quad (12)$$

Since the selectivity to the coupling reaction was less than 11% under the conditions of this work, the concentration of methyl groups can be written as

$$[CH_3\text{-}] \approx \frac{k_4}{k_{11}} P_{CH_4}. \quad (13)$$

Thus, the formation rate of ethane from methane can be written as

$$R_f(C_2H_6) = k_7[CH_3\text{-}]^2$$

$$= k_7 \left(\frac{k_4}{k_{11}}\right)^2 P_{CH_4}^2. \quad (14)$$

This second-order dependence of the formation rate of ethane on the pressure of methane explains well the observation in Fig. 4. The conversion rate of methane, $R_c(CH_4)$, is simply expressed by

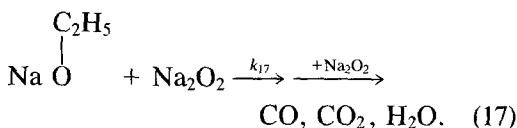$$R_c(CH_4) = k_4 P_{CH_4}[Na_2O_2]. \quad (15)$$

The larger activation energy observed for the conversion of CH_4 than that for the formation of C_2H_6 in Fig. 7 can be explained by the rate equations 14 and 15 as follows: assuming that the initiation step (Eq. 4) and the coupling of methyl groups on the surface (Eq. 7) have higher activation energies than that of deep oxidation (Eq. 11), the apparent activation energy in the formation of C_2H_6 ($= E_4 + (E_4 - E_{11}) + (E_7 - E_{11})$) should be greater than the activation energy for the conversion of methane ($= E_4$).

In the case of reaction of ethane, the

ethyl groups formed in Eq. 5 can couple forming n-butane in Eq. 8 or release hydrogen producing ethylene as follows:

$$\begin{array}{c} C_2H_5 \\ | \\ Na\ O \end{array} \quad \xrightarrow{k_{16}} NaOH + C_2H_4. \quad (16)$$

However, the total selectivities to those products were less than 30%. The fate of surface ethyl groups is mostly to be oxidized deeply into CO and CO_2:

$$\begin{array}{c} C_2H_5 \\ | \\ Na\ O \end{array} \quad + \ Na_2O_2 \xrightarrow{k_{17}} \xrightarrow{+Na_2O_2}$$

$$CO, CO_2, H_2O. \quad (17)$$

Thus, a treatment for the steady-state concentration of the ethyl groups similar to that for the methyl groups described above shows that the formation rates of ethylene, $R_f(C_2H_4)$, and of butane, $R_f(C_4H_{10})$, can be expressed as

$$R_f(C_2H_4) = k_{16} \frac{k_5}{k_{17}} P_{C_2H_6} \quad (18)$$

$$R_f(C_4H_{10}) = k_8 \left(\frac{k_5}{k_{17}}\right)^2 P_{C_2H_6}^2. \quad (19)$$

These rate equations explain the first- and second-order dependences of the formation rates of ethylene and butane, respectively, on the partial pressure of ethane as shown in Figs. 3 and 4. The absolute formation rate of ethylene was much greater than that of butane (Figs. 3 and 8). The apparent activation energy for the former was about half that of the latter reaction (Fig. 8). These observations suggest that the release of hydrogen from ethyl groups (Eq. 16) is easier than coupling reaction (Eq. 8) under the reaction conditions applied in this work.

In the case of partial oxidation of propane, we can expect the formations of both normal- and isopropyl intermediates by the oxidative dehydrogenation of propane in Eq. 6. Coupling of these propyl groups produces n-hexane, 2-methyl pentane, and 2,3-dimethyl butane. Since we cannot estimate the relative formation rates of the different

propyl groups at the moment, the results in Figs. 5, 6, and 9 can be explained only qualitatively as follows: The second-order dependence of the total formation rate of C$_6$-alkanes on the pressure of propane observed in Fig. 6 can be explained in terms of the similar discussion described earlier for the coupling products from methane and ethane providing that the rates of coupling reactions between each propyl intermediate (n-propyl + n-propyl, n-propyl + isopropyl, and isopropyl + isopropyl) are similar. Unimolecular decomposition of the propyl groups produces ethylene or propylene,

$$C_3H_7 \rightarrow C_2H_4 + CH_3 \qquad (20)$$

$$C_3H_7 \rightarrow C_3H_6 + H, \qquad (21)$$
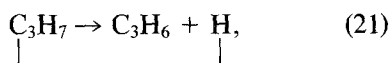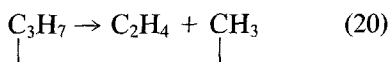
explaining the first-order dependence of their formation rates on the pressure of propane (Fig. 5). The apparent second-order dependence of the formation rate of butanes (n- + isobutanes) demonstrated in Fig. 6 may be ascribed to the coupling of propyl groups with methyl groups formed in Eq. 20. The speculations described above must be verified by detailed studies in the future.

The activation energies for the conversions of the three alkanes (Eqs. 4, 5, and 6) were in the order of CH$_4$ (127) > C$_2$H$_6$ (83) $\simeq$ C$_3$H$_8$ (89 kJ mol^{-1}). These observations show that the activation of CH$_4$ is difficult compared to those of C$_2$H$_6$ or C$_3$H$_8$. The large difference in the activation energies between CH$_4$ and C$_2$H$_6$ (or C$_3$H$_8$) cannot simply be ascribed to the difference in the dissociation energies of C–H bonds for CH$_4$ and C$_2$H$_6$ (or C$_3$H$_8$). For C$_2$H$_6$ and C$_3$H$_8$, a collision of the molecules whose C–C or C–C–C configuration is parallel to the surface might reduce the potential energy barrier for their C–H bond cleavage compared to the rigid collision of CH$_4$. Another possible explanation is that the stabilities of the alkoxy intermediates are different between CH$_3$–O and C$_2$H$_5$–O (or C$_3$H$_7$–O). CH$_3$–O is much less stable than C$_2$H$_5$–O and C$_3$H$_7$–O because of localization of charge density on CH$_3$ groups.

Effect of Gaseous Oxygen

The results in Tables 2 and 3 showed that the presence of gaseous oxygen decreased the selectivities to the coupling products from methane and ethane and to the dehydrogenation product (C$_2$H$_4$) from ethane. However, the rates of conversion of alkanes were not affected by gaseous oxygen. These observations suggest that the activation of methane is caused only by peroxide anions, but further reactions of the formed surface alkyl groups are affected strongly by gaseous oxygen. The alkyl groups would react with the adsorbed oxygen or directly with gaseous oxygen (Rideal type), promoting deep oxidation into CO and CO$_2$. This idea may explain the general observation that the oxidative coupling of light alkanes cannot be observed at low temperatures (<873 K) in the presence of gaseous oxygen (alkane and oxygen cofeed conditions).

Although there are many active catalysts for the C–H cleavage of the alkanes at low temperatures, such as transition metals or their oxides, the subsequent reaction of the formed alkyl groups on the surface goes exclusively to deep oxidation in the presence of gaseous oxygen and never produces coupling products. We would suggest that the one way to avoid deep oxidation of the alkyl intermediates is to desorb them into the gas phase before being oxidized to CO and CO$_2$ on the surface. The desorption of the alkyl intermediates, however, must have a high activation energy, thus requiring high temperatures to obtain coupling products with high selectivity. In the case of oxidative coupling of methane, it appears that many catalysts generate gas-phase methyl radicals which undergo subsequent coupling, forming ethane (17). In fact, most of the catalysts selective to the oxidative coupling of methane required temperatures higher than 973 K (5, 9, 13).

If the deep oxidation of alkyl groups is

caused by adsorbed oxygen (L-H mechanism), the desorption of oxygen with increasing temperature may diminish the deep oxidation. In such cases, we can expect the selective coupling of the alkyl groups on the surface. This hypothesis may be an alternative explanation for the observations that the selective synthesis of coupling products is possible only at high temperatures (>973 K).

REFERENCES

1. Keller, G. E., and Bhasin, M. M., *J. Catal.* **73,** 9 (1982).
2. Hinsen, W., Bytyn, W., and Baerns, M., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 3, p. 581. Dechema, Frankfurt-am-Main, 1984.
3. Ito, T., and Lunsford, J. H., *Nature (London)* **311,** 721 (1985).
4. Otsuka, K., Jinno, K., and Morikawa, A., *Chem. Lett.,* 499 (1985).
5. Otsuka, K., *Sekiyu Gakkaishi* **30,** 6 (1987), and references therein.
6. Ito, T., Wang, J.-X., Lin, C.-H., and Lunsford, J. H., *J. Amer. Chem. Soc.* **107,** 5062 (1985).
7. Lin, C.-H., Campbell, K. D., Wang, J.-X., and Lunsford, J. H., *J. Phys. Chem.* **90,** 534 (1986).
8. Wang, J.-X., and Lunsford, J. H., *J. Phys. Chem.* **90,** 3890 (1986).
9. For example, *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Terman, Eds.), Vol. 2, pp. 883–990. Chem. Institute of Canada, Ottawa, 1988; and *Catal. Today* **4**(3–4), 271–494 (1989).
10. Otsuka, K., and Jinno, K., *Inorg. Chim. Acta* **121,** 237 (1986).
11. Sinev, M. Yu., Korchak, V. N., and Krylov, O. V., *Kinet. Katal.* **27,** 1274 (1986).
12. Otsuka, K., Said, A. A., Jinno, K., and Komatsu, T., *Chem. Lett.,* 77 (1987).
13. Otsuka, K., Komatsu, T., Jinno, K., Uragami, Y., and Morikawa, A., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Terman, Eds.), Vol. 2, p. 915. Chem. Institute of Canada, Ottawa, 1988.
14. Thorsteinson, E. M., Wilson, T. P., Young, F. G., and Kasai, P. H., *J. Catal.* **52,** 116 (1978); Fox, D. B., and Lee, E. H., *CHEMTECH,* March, 186 (1973); and Matsuda, T., Hasegawa, H., Tsukuda, H., Hamada, F., and Tanaka, H., *Kougyo Kagaku* **73,** 2546 (1970).
15. Murakami, Y., Otsuka, K., Wada, Y., and Morikawa, A., *Chem. Lett.,* 535 (1989).
16. Komatsu, K., Uragami, Y., and Otsuka, K., *Chem. Lett.,* 1903 (1988).
17. Driscoll, D. J., Mastir, W., Wang, J.-X., and Lunsford, J. H., *J. Amer. Chem. Soc.* **107,** 58 (1985); Campbell, K. D., Zhang, H., and Lunsford, J. H., *J. Phys. Chem.* **92,** 750 (1988); Campbell, K. D., and Lunsford, J. H., *J. Phys. Chem.* **92,** 5792 (1988).