

# Oxidative Dimerization of Methane over a Lithium-Promoted Magnesium Oxide Catalyst

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**Abstract:** Lithium-promoted magnesium oxide was used as a catalyst for the partial oxidation of methane by molecular oxygen in a conventional flow reactor. Ethane and ethylene (C<sub>2</sub> compounds) were obtained with 50% selectivity at a 38% conversion of CH<sub>4</sub> over 4 g of 7 wt % Li-promoted MgO at 720 °C. The initial reactant mixture had a CH<sub>4</sub> to O<sub>2</sub> ratio of ca. two. The other products were CO and CO<sub>2</sub>. In this reaction system both the C<sub>2</sub> selectivity and the CH<sub>4</sub> conversion increased with an increase in reaction temperature up to ca. 700 °C. All catalysts doped with 1 to 26 wt % Li were effective in the C<sub>2</sub> production, while undoped and 0.2 wt % Li-promoted MgO caused nonselective oxidation. EPR spectroscopy revealed that [Li<sup>+</sup>O<sup>-</sup>] centers probably were the active sites responsible for initiating the reaction by abstracting a hydrogen atom from CH<sub>4</sub>. The [Li<sup>+</sup>O<sup>-</sup>] centers exist in an equilibrium state only at high temperatures in the presence of oxygen. Based on kinetic analyses a mechanism has been proposed in which most of the products, including CO and CO<sub>2</sub>, are produced via CH<sub>3</sub>·; the coupling of two CH<sub>3</sub>· leads to C<sub>2</sub>H<sub>6</sub>, which is partly oxidized to C<sub>2</sub>H<sub>4</sub>. Below 700 °C CO and CO<sub>2</sub> are produced by reactions of CH<sub>3</sub>· with either surface O<sup>2-</sup> ions or gaseous O<sub>2</sub>. The latter reaction leads to chain reactions in which additional methyl radicals are generated. The Li-promoted MgO contains no transition metals; thus it is a new type of oxidation catalyst on which thermally generated O<sup>-</sup> ions activate methane.

Methane, which is abundant as the main component of natural gas, also may be produced by the hydrogenation of carbon, carbon monoxide, or carbon dioxide. High molecular stability, however, makes it difficult to convert CH<sub>4</sub> into other useful chemicals. The partial oxidation of methane into more reactive chemicals such as methanol, ethylene, and other aliphatics is a current problem of great significance in heterogeneous catalysis. In general, it has not been possible to achieve both high conversions of CH<sub>4</sub> and good selectivities for the partial oxidation products.<sup>2-7</sup>

Work in our laboratory has demonstrated that on MgO surfaces O<sup>-</sup> ions, formed from N<sub>2</sub>O, react readily with simple alkanes by abstracting a hydrogen atom at room temperature.<sup>8,9</sup> These results parallel those of gas-phase studies involving O<sup>-</sup> and alkanes.<sup>10</sup> On the surface the resulting alkyl radicals react with surface O<sup>2-</sup> ions to produce further oxidized products. Although these reactions were carried out in a stoichiometric rather than a catalytic manner, we may expect that O<sup>-</sup> is an important intermediate in the partial oxidation of alkanes. Using molybdenum supported on silica, Lipatkina et al.<sup>11</sup> also investigated the stoichiometric reaction of O<sup>-</sup> with CH<sub>4</sub> and confirmed the formation of CH<sub>3</sub>· radicals.

Recent results from our laboratory<sup>12-15</sup> have demonstrated that alkyl radicals, formed by the reaction between surface O<sup>-</sup> ions and alkanes over Mo/SiO<sub>2</sub> catalyst, are part of a catalytic cycle

Table I. Influence of Lithium Concentration on Catalytic Activity<sup>a</sup>

Li conc (wt %)	0	0.2	1	3	7	14	26	
surface area (m <sup>2</sup> g <sup>-1</sup> )	60	37	8.0		8.9		5.7	
conversion (%)	1.0	3.0	4.4	3.9	2.6	2.3	2.2	
C <sub>2</sub> selectivity (%)	0.0	17.7	54.7	50.8	72.5	69.9	67.1	
Product	CO <sub>2</sub>	1.40	3.22	4.62	4.56	2.21	2.03	2.17
pressure (torr)	CO	1.68	4.72	1.86	1.67	0.12	0.24	0.21
	C <sub>2</sub> H <sub>4</sub>	0.00	0.10	0.81	0.63	0.55	0.42	0.33
	C <sub>2</sub> H <sub>6</sub>	0.00	0.75	3.02	2.55	2.50	2.17	2.07

<sup>a</sup> A reactant mixture containing 320 torr of CH<sub>4</sub> and 15 torr of O<sub>2</sub> was fed over 0.5 g of catalyst at 650 °C and at a flow rate of 0.83 mL s<sup>-1</sup>.

in the partial oxidation of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. During the oxidation of CH<sub>4</sub>, formaldehyde and methanol were the main partial oxidation products, although the selectivity was high only at relatively low conversions.<sup>14,15</sup> Ethylene and acetaldehyde were the principal products during the partial oxidation of ethane.<sup>12,13</sup> These catalytic systems, however, have limited utility since the results were achieved with N<sub>2</sub>O as the oxidant.

In the present paper we report on the selective conversion of methane to ethylene and ethane at relatively high conversions, using O<sub>2</sub> as the oxidant. The C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are produced by the formation and coupling of methyl radicals over a Li-promoted MgO catalyst. Kinetic and spectroscopic data provide evidence for the role of [Li<sup>+</sup>O<sup>-</sup>] centers in the generation of methyl radicals.

## Experimental Section

**Catalytic Experiments** The Li-promoted MgO catalysts (Li/MgO) were prepared by adding Aldrich MgO (Gold Label, >99.999%) and Fisher Li<sub>2</sub>CO<sub>3</sub> (Certified ACS, >99.0%) to deionized water and evaporating the water, while stirring, until only a thick paste remained. The paste was dried at 140 °C for more than 5 h. The Li<sub>2</sub>CO<sub>3</sub>/Mg(OH)<sub>2</sub> (see below) was then converted to the Li-promoted MgO at 465 °C (thus below). By this method six catalysts promoted with 0.2, 1, 3, 7, 14, and 26 wt % Li were prepared (the weight percentage is defined as ratio of Li to sum of Li plus MgO). An unpromoted MgO catalyst was prepared in the same manner, except for the addition of Li<sub>2</sub>CO<sub>3</sub>. Catalysts of 20-40 mesh and having an apparent density of ca. 0.4 g mL<sup>-1</sup> were used to obtain the kinetic data. In other experiments an unsieved powder was used. The methane (>99.97%), oxygen (>99.6%), nitrous oxide (>99.0%), and ethane (>99.0%) were obtained from Matheson Gas. No further purification was attempted.

The catalytic experiments were carried out in a fixed-bed reactor operated at 1 atm.<sup>15</sup> The samples were treated in the reactor at 465 °C for 1 h under an oxygen flow of 0.83 mL s<sup>-1</sup>. After the oxygen treatment a reacting gas mixture (usually methane and oxygen) was introduced, and the catalyst was raised to the desired temperature. A typical flow rate of the reactant gas mixture was 0.83 mL s<sup>-1</sup>. Helium (Airco, >99.995%)

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**Table II.** Conversion and Selectivity during Methane Oxidation<sup>a</sup>

run no.		3% Li/MgO <sup>b</sup>				7% Li/MgO <sup>c</sup>			
		1	2	3	4	5	6	7	8
reactant	He	678	651	599	300	672	666	642	425
pressure	CH <sub>4</sub>	55	85	85	303	59	58	89	218
(torr)	O <sub>2</sub>	27	24	76	157	29	36	29	117
product	CO <sub>2</sub>	10.04	8.39	28.75	75.20	11.29	13.69	11.11	51.15
pressure	CO	0.21	0.00	1.09	3.90	0.00	0.16	0.00	1.48
(torr)	C <sub>2</sub> H <sub>4</sub>	3.14	3.93	5.58	20.20	3.53	3.68	4.64	15.44
	C <sub>2</sub> H <sub>6</sub>	1.94	2.87	2.64	9.66	2.19	2.08	3.06	7.44
conversion (%)		37.0	25.6	51.4	38.2	37.8	42.8	29.1	37.5
C <sub>2</sub> selectivity (%)		49.8	61.8	35.5	43.0	50.3	45.4	58.1	46.5
C <sub>2</sub> yield <sup>d</sup> (%)		18.4	15.8	18.3	16.4	19.0	19.4	16.9	17.4

<sup>a</sup> Over 4 g of catalyst at 720 °C and at a reactant flow rate of 0.83 mL s<sup>-1</sup>; both catalysts had been exposed to reactants at 770 °C. <sup>b</sup> SA = 1 m<sup>2</sup>/g. <sup>c</sup> SA = 2 m<sup>2</sup>/g. <sup>d</sup> C<sub>2</sub> yield is defined as the product of conversion and C<sub>2</sub> selectivity.

was used as a diluent to achieve a total pressure of 1 atm. For the first run on a fresh catalyst the activity was measured after 3 h of reaction. All of the gases except HCHO were analyzed by gas chromatography; the method has been described in detail elsewhere.<sup>15</sup> Typically a 98% carbon mass balance was achieved by this method.

The surface area of the used catalysts was measured by a volumetric method with krypton at -196 °C. The cross-sectional area of a krypton molecule was assumed to be 19.5 × 10<sup>-20</sup> m<sup>2</sup>.<sup>16</sup>

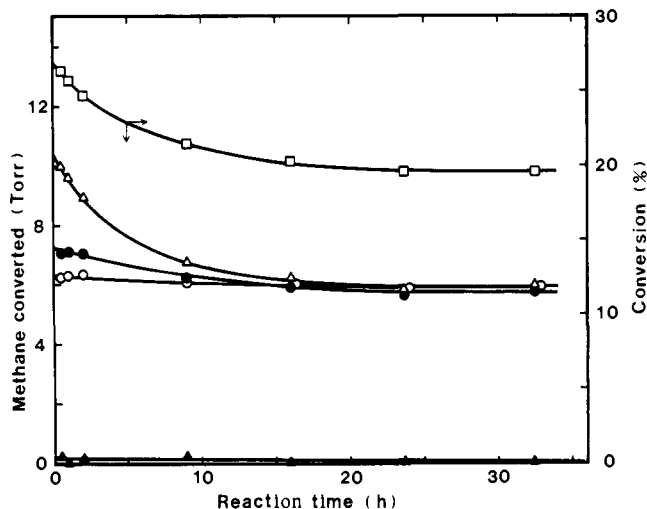
**EPR Measurements.** The EPR spectra of [Li<sup>+</sup>O<sup>-</sup>] centers (see below) in the catalysts were measured at ~196 °C using a Varian E-6S EPR spectrometer. A new type of reactor was constructed in which the samples were heated under the presence of O<sub>2</sub> (or an O<sub>2</sub>/Ar mixture) and then were dropped into liquid oxygen (or solid argon) at -196 °C.<sup>17</sup> This quenching technique was necessary to observe the [Li<sup>+</sup>O<sup>-</sup>] centers because these are transient centers which exist in an equilibrium state only at elevated temperatures.<sup>18</sup> The catalyst was subsequently transferred to a fused quartz EPR side arm. The EPR spectra were recorded after the gases were evacuated at -196 °C. The *g* values are reported relative to a phosphorus-doped silicon standard with *g* = 1.9987. In this paper only the relative concentration of the [Li<sup>+</sup>O<sup>-</sup>] centers is reported. This was obtained by measuring the signal height in the EPR spectra. It should be noted that the shape of the signal was independent of the amplitude.

## Results

**Effect of the Lithium Concentration.** To examine the effects of the lithium, catalytic runs were carried out at 620 °C over 0.5-g catalysts promoted with various concentrations of Li<sup>+</sup>. The results are summarized in Table I. In the absence of a catalyst no reaction occurred under these experimental conditions.

Table I shows that the Li/MgO catalysts resulted in the formation of C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> (C<sub>2</sub> compounds) in addition to CO and CO<sub>2</sub>, while the unpromoted oxide produced no C<sub>2</sub> compounds. Among this set of catalysts the maximum conversion of CH<sub>4</sub> was achieved over 1% Li/MgO with 54.7% selectivity for C<sub>2</sub>. Better selectivities for C<sub>2</sub> (ca. 70%) were achieved over the catalysts promoted with 7% or more Li<sup>+</sup>. The amounts of CH<sub>4</sub> converted over Li/MgO were higher than over the pure oxide by factors of 2 to 4. The surface area measured after the catalytic runs was considerably lower for Li/MgO; thus the conversions based on an equivalent surface area were 20–30-fold greater over Li/MgO than over pure MgO. In a separate experiment the effect of MgO surface area on selectivity was evaluated by comparing high surface area (34 m<sup>2</sup>/g) and low surface area (8 m<sup>2</sup>/g) MgO catalysts. At comparable conversion (16%) the C<sub>2</sub> selectivities were 5 and 29%, respectively.

**Maximum Yields for the C<sub>2</sub> Compounds.** In order to obtain the maximum C<sub>2</sub> yields over Li/MgO, with high selectivities, catalytic runs were carried out using 4 g of 3 and 7% Li/MgO. Table II summarizes results obtained at 720 °C; higher and lower temperatures gave lower yields for C<sub>2</sub>.<sup>19</sup> Methanol and formaldehyde



**Figure 1.** Change in catalytic activity with reaction time when a reactant mixture containing 90 torr of CH<sub>4</sub> and 30 torr of O<sub>2</sub> was fed over 1 g of 7% Li/MgO at 700 °C at a flow rate of 0.83 mL s<sup>-1</sup>: □, conversion of CH<sub>4</sub>; Methane converted: ○, to C<sub>2</sub>H<sub>6</sub>; ●, to C<sub>2</sub>H<sub>4</sub>; ▲, to CO; △, to CO<sub>2</sub>.

were also detected, but only in trace amounts. In the absence of the catalyst, conversion of CH<sub>4</sub> was only 0.2% under the same experimental conditions.

When a reactant gas mixture contained about twice as much CH<sub>4</sub> as O<sub>2</sub>, both the C<sub>2</sub> selectivity and the CH<sub>4</sub> conversion were generally very good; about 50% selectivity was achieved at a 38% conversion level (runs no. 1 and 5). Approximately 85% of O<sub>2</sub> in the reactant mixture was consumed in these runs. Good results were also obtained for the reactant mixtures containing higher partial pressures of CH<sub>4</sub> and O<sub>2</sub> if the ratio of the two gases was kept at nearly two (runs no. 4 and 8). Note that the ratio of He to O<sub>2</sub> in the reactant mixture of run no. 8 is close to that of N<sub>2</sub> to O<sub>2</sub> in air. A larger CH<sub>4</sub> to O<sub>2</sub> ratio led to a higher C<sub>2</sub> selectivity but to a lower conversion (runs no. 2 and 7), while a lower CH<sub>4</sub> to O<sub>2</sub> ratio resulted in a higher conversion but in lower C<sub>2</sub> selectivity (runs no. 3 and 6). The catalyst used in runs no. 5 through 8 had a very low surface area, ca. 2 m<sup>2</sup> g<sup>-1</sup>, after the reaction. A very high C<sub>2</sub> selectivity of 80% was obtained when the same reactant mixture as used in Table I was fed over 2.9 g of 7% Li/MgO at 670 °C, but the conversion dropped to 9.5%. The results presented in Table II are considerably better than literature values reported recently.<sup>3,6,7</sup> The maximum C<sub>2</sub> yields were no more than 5% in these earlier studies.

The decrease in catalytic activity during the reaction was examined over 1 g of 7% Li/MgO at 700 °C, and the results are shown in Figure 1. In these experiments the reactant mixture was introduced over a catalyst which had been heated at 700 °C for 2 h in a helium flow. This pretreatment led to the evolution of CO<sub>2</sub> from any carbonates which might be decomposed under these conditions (see below). The conversion dropped from 27.0

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to 20.3% in the first 15 h, but after this period very little change in activity was observed. This initial deactivation was mainly due to a decrease in the rate of  $\text{CO}_2$  formation which resulted in an increase in  $\text{C}_2$  selectivity. The decrease in  $\text{C}_2$  yield was only 1.5% (from 14.9 to 13.4%) after 15 h. The surface area of this catalyst measured after a long period of reaction was ca.  $2 \text{ m}^2 \text{ g}^{-1}$ .

At  $720^\circ\text{C}$   $\text{C}_2\text{H}_4$  was the main  $\text{C}_2$  compound, but  $\text{C}_2\text{H}_6$  was also produced in considerable amounts (Table II). The former is considered to be a more valuable chemical than the latter; thus it is desirable to convert  $\text{C}_2\text{H}_6$  into  $\text{C}_2\text{H}_4$ . This conversion proceeds rather easily over several catalysts.<sup>20</sup>

X-ray powder diffraction of the 7% Li/MgO catalyst used at 700 and  $770^\circ\text{C}$  indicated that two phases were present, MgO and  $\text{Li}_2\text{CO}_3$ . The carbonate is not extensively decomposed at these temperatures (the decomposition pressure reaches 760 torr at  $1310^\circ\text{C}$ <sup>21</sup>), although some  $\text{Li}_2\text{O}$  is probably present. The solubility of lithium ions in a MgO lattice is also small. The actual concentration of lithium in single crystals of MgO, which were grown by an arc-fusion technique using MgO powder doped with  $\text{Li}_2\text{CO}_3$  to a concentration of about 5% by weight, was only 0.03 to 0.05 atom %.<sup>18</sup>

In view of the relatively large mole fraction of Li in these samples, the catalytic properties of the  $\text{Li}_2\text{O}/\text{Li}_2\text{CO}_3$  phase must be considered. A 0.22-g sample of the carbonate (surface area (SA) =  $0.6 \text{ m}^2 \text{ g}^{-1}$ ) was tested and found to be less active by a factor of 10 at  $700^\circ\text{C}$  than a 7% Li/MgO catalyst which contained an equivalent amount of  $\text{Li}^+$ . A 5.5-g sample of  $\text{Li}_2\text{CO}_3$  (SA =  $0.4 \text{ m}^2 \text{ g}^{-1}$ ) catalyzed at  $675^\circ\text{C}$  a 5% conversion of  $\text{CH}_4$  ( $\text{CH}_4:\text{O}_2 = 2:1$ ) with a  $\text{C}_2$  selectivity of 70%. Thus, if the  $\text{Li}_2\text{CO}_3$  remained undispersed its contribution to the overall activity would be negligible. If, however, the  $\text{Li}_2\text{CO}_3$  spread uniformly over the MgO, its contribution would be dominant. In order to explore this possibility XPS experiments were carried out to determine the remaining exposed  $\text{Mg}^{2+}$  in the used catalysts. By measuring the Mg/O area ratios in the XPS spectra it is estimated that for the used 3 and 7% Li/MgO catalysts of Table II the remaining exposed  $\text{Mg}^{2+}$  was 70 and 45%, respectively. Runs no. 1 and 5 show that the activities and selectivities for the two catalysts were very similar; however, if the reaction were catalyzed mainly by  $\text{LiO}/\text{Li}_2\text{CO}_3$ , one would expect that the sample with the larger amount of  $\text{Li}_2\text{CO}_3$  would exhibit the greater activity. It is also possible to estimate the contribution of the dispersed  $\text{Li}_2\text{CO}_3$  to the total activity. At  $670^\circ\text{C}$  the  $\text{Li}_2\text{CO}_3$  promoted about 2.3% conversion/ $\text{m}^2 \text{ Li}_2\text{CO}_3$ . From the XPS data 30% of the 3% Li/MgO catalyst (SA =  $1 \text{ m}^2 \text{ g}^{-1}$ ) is  $\text{Li}_2\text{CO}_3$ . The expected conversion from  $\text{Li}_2\text{CO}_3$  on 4 g of this material is 2.8%. The total conversion on the 3% Li/MgO catalyst at  $670^\circ\text{C}$  was 21%; thus up to 13% of the total activity may have been derived from the  $\text{Li}_2\text{CO}_3$  phase. The latter percentage, which is an upper limit, probably increases with an increasing amount of  $\text{Li}_2\text{CO}_3$ . The mode of addition of the lithium does not seem to be critical, as a sample prepared from an aqueous solution of  $\text{LiNO}_3$  and  $\text{Mg}(\text{NO}_3)_2$  by adding  $\text{NH}_4\text{OH}$  had a catalytic activity at  $700^\circ\text{C}$  comparable to that exhibited by the Li/MgO catalyst prepared from  $\text{Li}_2\text{CO}_3$ .

The identification of the active component currently is being addressed from another standpoint. The model for selective conversion of  $\text{CH}_4$  described below requires that the alkali metal ion be able to substitute for the alkaline earth ion. Although  $\text{Na}_2\text{CO}_3$  has activity similar to that of  $\text{Li}_2\text{CO}_3$ , a  $\text{Na}_2\text{CO}_3/\text{MgO}$  catalyst exhibits poor activity and selectivity.<sup>22</sup> By contrast  $\text{Na}_2\text{CO}_3/\text{CaO}$  is an active and selective catalyst, comparable to  $\text{Li}_2\text{CO}_3/\text{MgO}$ . The most obvious explanation for these phenomena is that  $\text{Na}^+$  ions are too large to substitute for  $\text{Mg}^{2+}$  ions, but they

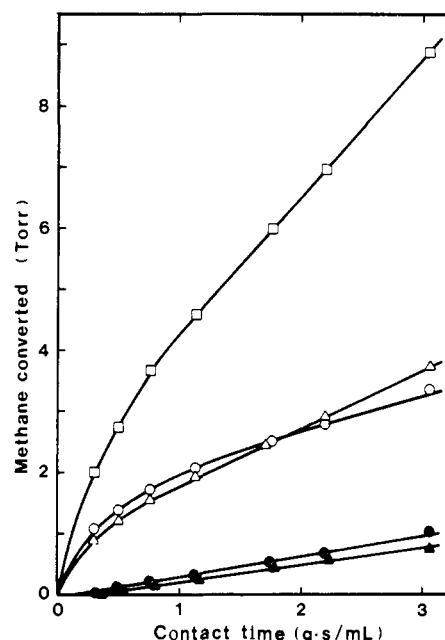


Figure 2. Change in amount of  $\text{CH}_4$  converted with pseudo-contact time,  $W/F$ , when a reactant mixture containing 300 torr of  $\text{CH}_4$  and 60 torr of  $\text{O}_2$  was fed over 1 g of 7% Li/MgO at  $620^\circ\text{C}$ :  $\square$ , total;  $\circ$ , to  $\text{C}_2\text{H}_6$ ;  $\bullet$ , to  $\text{C}_2\text{H}_4$ ;  $\blacktriangle$ , to CO;  $\triangle$ , to  $\text{CO}_2$ .

may easily substitute for  $\text{Ca}^{2+}$  ions. Moreover, these observations support the conclusion made here that the major part of the activity results from the substitution of a monovalent cation into a divalent site, and not simply from the enhanced dispersion of the alkali carbonate.

**Kinetic Measurements.** After the long-term experiment depicted in Figure 1, kinetic experiments described in this section were carried out using the same catalyst (7% Li/MgO, 1 g) because of its stable activity. In order to obtain kinetic parameters at low conversions, all reactions were carried out at  $620^\circ\text{C}$ , except when the temperature effect was determined. Conversions were always kept at less than 6% for  $\text{CH}_4$ , but in a few cases 10 to 18% of the  $\text{O}_2$  was consumed during the reaction.

The partial pressure of  $\text{CH}_4$  converted into each product is depicted in Figure 2 as a function of the pseudo-contact time,  $W/F$ , where  $W$  is the weight of catalyst and  $F$  is the flow rate of the reactant mixture. The sum of the partial pressure of all the products, as well as the partial pressure of each component, changed linearly with  $W/F$  values above  $0.8 \text{ g s mL}^{-1}$ . Moreover, in a separate experiment it was observed that the conversion was proportional to the amount of catalyst present.

The lines in Figure 2, however, do not pass through the origin. A similar phenomenon was also observed in a  $W/F$  region of 0 to  $18 \text{ g s mL}^{-1}$  when 4 g of 7% Li/MgO was used. The reason for this unusual phenomenon is not obvious. It is unlikely that a diffusion process is operative because the linear relation holds over a wide range of  $W/F$  values. The absence of diffusion limitations is also supported by the fact that the surface area of the catalyst was low ( $2 \text{ m}^2 \text{ g}^{-1}$ ), which suggests the absence of micropores. As described later a chain mechanism is operative to some degree, and this may explain the abnormal relation between the contact time and the partial pressure.

The apparent activation energy for this reaction was determined to be  $55.2 \pm 1.6 \text{ kcal mol}^{-1}$  over the temperature range from 560 to  $660^\circ\text{C}$ . The temperature dependence of each product is shown in Figure 3. The partial pressure of  $\text{CH}_4$  converted into each product rapidly increased with the reaction temperature, except for CO which did not increase appreciably above  $640^\circ\text{C}$ . It should be emphasized that the  $\text{C}_2$  selectivity was greater at the higher temperatures; the observed  $\text{C}_2$  selectivities were, e.g., 0.0, 29.4, 52.8, and 66.6% at 560, 580, 620, and  $660^\circ\text{C}$ , respectively. This means that the  $\text{C}_2$  compounds can be produced in much greater yields at higher temperatures because both the  $\text{CH}_4$  conversion

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(22) At  $700^\circ\text{C}$ ,  $P_{\text{CH}_4} = 100 \text{ torr}$ , and  $P_{\text{O}_2} = 40 \text{ torr}$ , the conversion and selectivity over 15% Na/CaO (1 g) were 22 and 52%, respectively. Under the same conditions, the conversion and selectivity over 20% Na/MgO (1 g) were only 12 and 18%, respectively. The sodium levels correspond to a constant mol %.

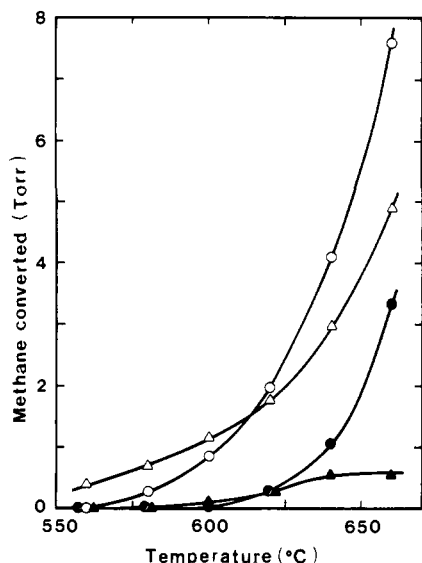


Figure 3. Change in amount of CH<sub>4</sub> converted with respect to an increase in reaction temperature when a reactant mixture containing 300 torr of CH<sub>4</sub> and 60 torr of O<sub>2</sub> was fed over 1 g of 7% Li/MgO at a flow rate of 0.83 mL s<sup>-1</sup>: ○, to C<sub>2</sub>H<sub>6</sub>; ●, to C<sub>2</sub>H<sub>4</sub>; ▲, to CO; △, to CO<sub>2</sub>.

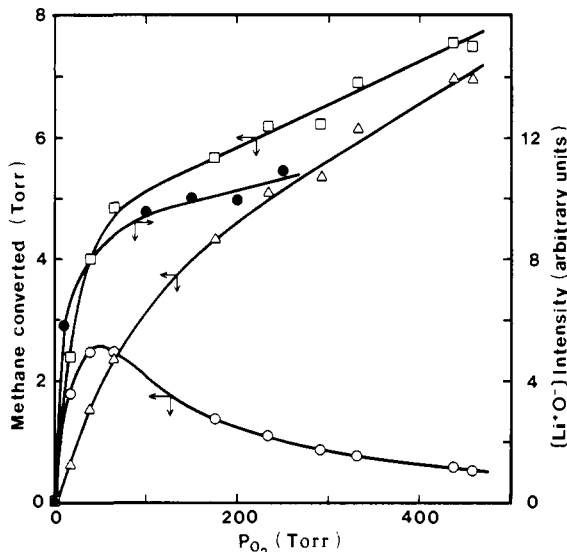


Figure 4. Changes in amount of CH<sub>4</sub> converted and concentration of [Li<sup>+</sup>O<sup>-</sup>] centers with respect to an increase in O<sub>2</sub> pressure. A reactant mixture containing 300 torr of CH<sub>4</sub> was fed over 1 g of 7% Li/MgO at 620 °C and at a flow rate of 0.83 mL s<sup>-1</sup>: □, total; ○, to C<sub>2</sub>H<sub>6</sub> plus C<sub>2</sub>H<sub>4</sub>; △, to CO plus CO<sub>2</sub>.

and the C<sub>2</sub> selectivity are improved. This was no longer valid above ca. 700 °C as the C<sub>2</sub> selectivity tended to decrease.<sup>19</sup>

In order to understand the reaction mechanism more fully, the partial pressure of CH<sub>4</sub> converted into products was determined as a function of the pressure of each reactant. The effect of O<sub>2</sub> pressure is shown in Figure 4, where the C<sub>1</sub> (CO plus CO<sub>2</sub>) and the C<sub>2</sub> (C<sub>2</sub>H<sub>6</sub> plus C<sub>2</sub>H<sub>4</sub>) pressures are illustrated. As shown below, C<sub>2</sub>H<sub>4</sub> was produced mainly by the further oxidation of C<sub>2</sub>H<sub>6</sub>. In fact, the dependence on O<sub>2</sub> pressure was similar for C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>, though the former was produced in higher concentrations than the latter by factors of 7 to 10 at these levels of conversion. The CO<sub>2</sub> to CO ratio in the product mixture was 4 to 6.

The presence of two regions in the dependence of total CH<sub>4</sub> conversion on the O<sub>2</sub> pressure is apparent in Figure 4. The amount of CH<sub>4</sub> converted increased steeply with the increase in O<sub>2</sub> pressure below 50 torr, but above this pressure the increase was much slower though it was still approximately linear. Below 50 torr the increase resulted mainly from the C<sub>2</sub> products. On the other hand, only

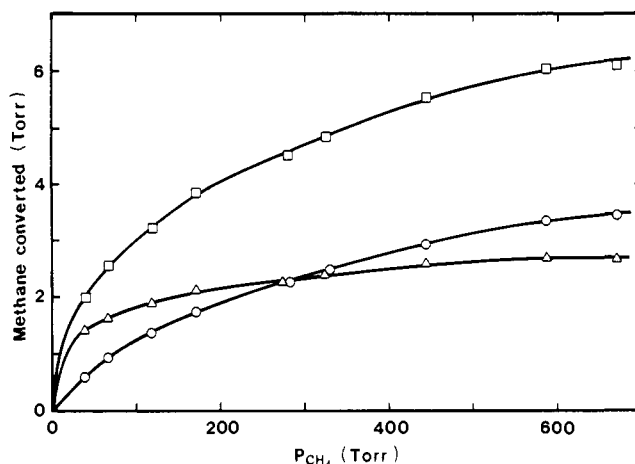


Figure 5. Change in amount of CH<sub>4</sub> converted with respect to an increase in CH<sub>4</sub> pressure when a reactant mixture containing 60 torr of O<sub>2</sub> was fed over 1 g of 7% Li/MgO at 620 °C and at a flow rate of 0.83 mL s<sup>-1</sup>: □, total; ○, to C<sub>2</sub>H<sub>6</sub> plus C<sub>2</sub>H<sub>4</sub>; △, to CO plus CO<sub>2</sub>.

Table III. Reactivity of Methane and Ethane<sup>a</sup>

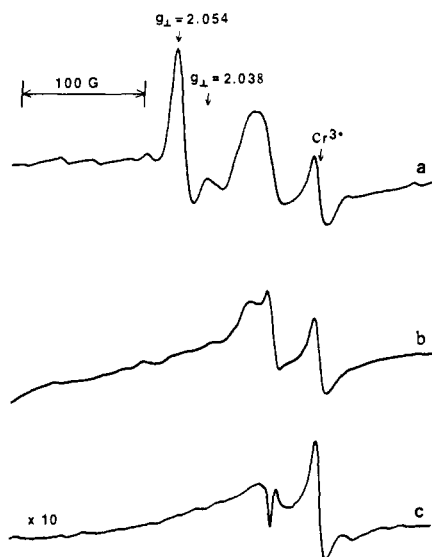
run no.		1	2	3
reactant pressure (torr)	CH <sub>4</sub>	279.47	0.00	286.16
	C <sub>2</sub> H <sub>6</sub>	0.00	2.93	3.37
	O <sub>2</sub>	62.79	62.07	61.14
product pressure (torr)	CO <sub>2</sub>	1.89	0.49	1.75
	CO	0.40	0.14	0.45
	CH <sub>4</sub>	(278.65)	0.00	(281.82)
	C <sub>2</sub> H <sub>4</sub>	0.15	0.82	0.57
	C <sub>2</sub> H <sub>6</sub>	1.01	(1.67)	(3.67)

<sup>a</sup>Reactant mixture was fed over 1 g of 7% Li/MgO at 620 °C at a flow rate of 0.83 mL s<sup>-1</sup>. Values in parentheses show partial pressure, in the product mixture, of the component which is fed as a reactant.

CO and CO<sub>2</sub> increased above 50 torr; the C<sub>2</sub> formation decreased with increasing O<sub>2</sub> pressure.

Figure 5 illustrates the effect of the CH<sub>4</sub> pressure. In this case the conversion of CH<sub>4</sub> increased gradually over the entire pressure range. A log-log plot showed that this increase was approximately proportional to the 0.4 power of the CH<sub>4</sub> pressure. In the very low pressure region, less than 40 torr, CO and CO<sub>2</sub> increased steeply, while above 40 torr the increase in conversion was mainly due to C<sub>2</sub> (especially to C<sub>2</sub>H<sub>6</sub>). Ratios of C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub> to CO in the products were approximately 6 and 4, respectively.

In determining a mechanism it is important to know whether the CO and CO<sub>2</sub> came from the C<sub>2</sub> compounds or from CH<sub>4</sub> via another pathway. This was examined at 620 °C by feeding either CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub> as the reactant, and the results are summarized in Table III. In run no. 1 an ordinary reactant of CH<sub>4</sub> was fed, while C<sub>2</sub>H<sub>6</sub> was used in run no. 2. The partial pressure of C<sub>2</sub>H<sub>6</sub> in the reactant mixture was chosen to be approximately equal to the sum (3.45 torr) of the partial pressures of all the products in the former run. The total amount of CO and CO<sub>2</sub> produced from CH<sub>4</sub> was larger than that from C<sub>2</sub>H<sub>6</sub> by a factor of 3.6. In addition, it is important to note that C<sub>2</sub>H<sub>6</sub> can easily react with surface O<sup>-</sup> ions to produce C<sub>2</sub>H<sub>4</sub>, CO, and CO<sub>2</sub>.<sup>8,9,23</sup> This strongly suggests that active sites for the conversion of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are the same. These centers competitively react with CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> if both the reactants coexist. This situation is actually reflected in run no. 3 where both the reactants were present. For example, the amount of C<sub>2</sub>H<sub>4</sub> produced in this run was less than that in run no. 2 where only C<sub>2</sub>H<sub>6</sub> was present. Based on these considerations we conclude that at 620 °C and low CH<sub>4</sub> conversions the dominant route to produce CO and CO<sub>2</sub> is not the further oxidation of C<sub>2</sub>H<sub>6</sub>. By comparing runs no. 1 and 2 similar arguments can be used to show that CO and CO<sub>2</sub> are not derived primarily from C<sub>2</sub>H<sub>4</sub>.



**Figure 6.** EPR spectra of the samples heated at 650 °C for 1 h followed by rapid cooling to  $-196$  °C: a, 7% Li/MgO used in Table II was heated in 170 torr of  $O_2$ ; (b) the same sample was heated in 270 torr of Ar; (c) pure MgO (a fresh sample) was heated in 190 torr of  $O_2$ .

**Oxidation by  $N_2O$ .** Nitrous oxide is an effective oxidant for the partial oxidation of alkanes provided electrons are available for the formation of  $O^-$  via the reaction  $N_2O + e^- \rightarrow N_2 + O^-$ .<sup>9,12-15,24</sup> By contrast,  $N_2O$  is not as effective as  $O_2$  in the generation of  $CH_3\cdot$  from  $CH_4$  over pure MgO.<sup>25</sup> Preliminary experiments were carried out at 620 °C over several Li/MgO catalysts using  $N_2O$  as the oxidant. At low Li loadings (<1%) the total  $CH_4$  conversion was comparable to that found with  $O_2$  as the oxidant, but at greater Li loadings the conversions were much less with  $N_2O$ . Moreover, for Li loadings >1%, the yield for  $C_2$  products was substantially greater with  $O_2$ . For example, under the experimental conditions of Table I and at 7% Li, with  $N_2O$  as the oxidant, the  $C_2$  yield was 0.16% compared to 1.92% with  $O_2$  as the oxidant.

**EPR Spectra.** The 7% Li/MgO catalyst used in the runs listed in Table II was examined by EPR spectroscopy, and the spectra obtained are illustrated in Figure 6. When this sample was heated at high temperatures in the presence of  $O_2$  and then quenched to  $-196$  °C, a clear signal was observed at  $g_{\perp} = 2.054$  (spectrum a). This signal is in excellent agreement with the published value of  $g_{\perp} = 2.0545$  for  $[Li^+O^-]$  centers in MgO single crystals.<sup>18</sup> The  $g_{\parallel}$  component at 2.0049 was not resolved, presumably because of overlap with strong signals of impurity ions such as  $Fe^{3+}$ . In a related study, however, the  $g_{\parallel}$  component was clearly seen following UV irradiation of the catalyst at  $-196$  °C.<sup>17</sup> An additional signal appeared in this spectrum at  $g_{\perp} = 2.038$  with a much weaker intensity. This  $g_{\perp}$  component is consistent with that of  $O^-$  or  $V^-$  centers in MgO.<sup>23</sup> Only a trace amount of  $[Li^+O^-]$  was evident when the catalyst was slowly cooled from high temperatures. Neither  $[Li^+O^-]$  centers nor  $V^-$  centers were detected when the same sample was heated in a pure argon atmosphere (spectrum b); i.e., the presence of  $O_2$  during the heat treatment is essential for the creation of both the centers. These observations are consistent with the formation of  $[Li^+O^-]$  in MgO single crystals.<sup>18</sup>

Fresh samples, which had not been used in catalytic runs, behaved in a very similar manner as the used catalysts although the signal intensity was greater in the used catalysts. In an unpromoted MgO sample  $[Li^+O^-]$  centers and  $V^-$  centers were not observed, even after heating in  $O_2$  followed by quenching (spectrum c).

The solid points in Figure 4 illustrate the effect of oxygen partial pressure on the signal intensity of  $[Li^+O^-]$  centers. The samples

were heated in an  $O_2$  or  $O_2/Ar$  atmosphere prior to quenching. The signal intensity was a strong function of the  $O_2$  pressure up to 50 torr, but above this pressure the increase was less dramatic.

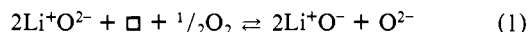
## Discussion

**Active Centers for the Formation of Methyl Radicals.** The presence of ethane as a major product suggests the formation and coupling of methyl radicals; thus the ensuing discussion will focus on the active site for the formation of these radicals and their subsequent reactions, both on the surface and in the gas phase. It is convenient to divide the reaction into two steps: (1) the formation of  $[Li^+O^-]$  centers and the generation of  $CH_3\cdot$  on them, and (2) the formation of the stable products from  $CH_3\cdot$ .

The  $[Li^+O^-]$  centers have been studied in detail by Abraham and co-workers using single crystals of MgO and CaO doped with Li.<sup>18,26-29</sup> The  $[Li^+O^-]$  centers could be produced thermally by heating their samples above 1000 °C in the presence of  $O_2$  and then rapidly quenching them. According to their mechanism thermally generated  $[Li^+O^-]$  centers in MgO are the result of the diffusion of  $Li^+$  ions from regions of  $Li_2O$  precipitates to substitutional  $Mg^{2+}$  sites; the rapid cooling from high temperatures prevents the  $Li^+$  ions from reaggregation which leads to the disappearance of the  $[Li^+O^-]$  centers.<sup>29</sup> It is also possible that quenching prevents the  $[Li^+O^-]$  centers from releasing their trapped holes, which results in the desorption of  $O_2$ .<sup>17</sup>

The mechanism for the  $[Li^+O^-]$  formation in the powder samples used in this study is analogous to that described above except that the substitutional  $Li^+$  ions are generated from  $Li_2CO_3$  precipitates instead of  $Li_2O$ .<sup>25,30</sup> For every two  $Li^+$  ions leaving carbonate phases, only one  $Mg^{2+}$  enters to form  $MgCO_3$ .<sup>27</sup> From stoichiometric considerations, this excess of cations in the MgO matrix suggests the formation of oxygen vacancies which may exist on the surface. Gaseous oxygen molecules, however, immediately react with the vacancies at high temperatures, resulting in  $O^{2-}$  ions and holes. The  $[Li^+O^-]$  centers are produced by these holes being trapped at  $O^{2-}$  ions which are adjacent to  $Li^+$  ions.<sup>29</sup>

This process may be expressed as follows:



where  $\square$  denotes an oxygen vacancy. Although reaction 1 is not necessarily a *true* equilibrium state, the number of  $[Li^+O^-]$  centers are mainly determined by the temperature and the oxygen pressure. The mechanism for the formation of  $[Li^+O^-]$  centers in these catalysts will be treated in detail elsewhere.<sup>17</sup>

The  $[Li^+O^-]$  centers also probably exist in the  $Li_2O/Li_2CO_3$  phase and are responsible for the activity of this material. An attempt is currently being made to detect  $[Li^+O^-]$  centers in quenched  $Li_2CO_3$ . At considerably higher temperatures (1527 °C) LiO has been detected in the vapor phase over  $Li_2O$ , and the molecules may best be described by a completely ionic model, i.e.,  $Li^+O^-$ .<sup>31</sup>

In a series of related experiments it has been demonstrated that methyl radicals were produced when methane and oxygen were passed over similar Li-promoted MgO catalysts at 500 °C. The methyl radicals formed at the surface were released into the gas phase and trapped downstream in a solid argon matrix, where they were analyzed by EPR spectroscopy.<sup>25,30</sup> It is significant that the rate of radical formation and the concentration of  $[Li^+O^-]$  centers behaved in a parallel manner with respect to Li loading. Thus,

(26) Chen, Y.; Tohver, H. T.; Narayán, J.; Abraham, M. M. *Phys. Rev. B* **1977**, *16*, 5535-5542.

(27) Lacy, J. B.; Abraham, M. M.; Boldu, O. J. L.; Chen, Y.; Narayan, J.; Tohver, H. T. *Phys. Rev. B* **1978**, *18*, 4136-4142.

(28) Boldu, O. J. L.; Abraham, M. M.; Chen, Y. *Phys. Rev. B* **1979**, *19*, 4421-4426.

(29) Olson, D. N.; Orera, V. M.; Chen, Y.; Abraham, M. M. *Phys. Rev. B* **1980**, *21*, 1258-1263.

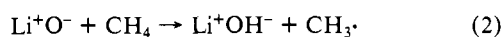
(30) Driscoll, D. J.; Martir, W.; Wang, J.-X.; Lunsford, J. H. "Proceedings of the Symposium on Adsorption and Catalysis on Oxide Surfaces", Brunel University, 1984.

(31) Freund, S. M.; Herbst, E.; Mariella, R. P.; Klemperer, W. *J. Chem. Phys.* **1972**, *56*, 1467-1476.

(24) Iwamoto, M.; Taga, T.; Kagawa, S. *Chem. Lett.* **1982**, 1469-1472.

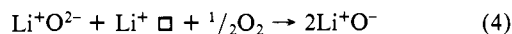
(25) Driscoll, D. J.; Martir, W.; Wang, J.-X.; Lunsford, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 58-63.

it was concluded that  $\text{CH}_3\cdot$  was produced by a reaction between  $\text{CH}_4$  and  $\text{O}^-$  of  $[\text{Li}^+\text{O}^-]$  centers:



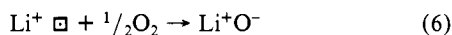
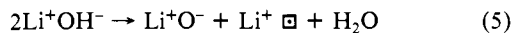
Under the experimental conditions employed in this study,  $\text{CH}_3\cdot$  is believed to be formed in a similar manner.

The regeneration of  $[\text{Li}^+\text{O}^-]$  centers after reaction 2 was proposed to occur by the following scheme:<sup>25</sup>



The  $[\text{Li}^+\text{O}^-]$  centers produced in reaction 4 again react with  $\text{CH}_4$  by reaction 2. The latter does not appear to be an activated process because most of the  $\text{O}^-$  ions on  $\text{Mo/SiO}_2$ , for example, reacted with  $\text{CH}_4$  even at 77 K.<sup>9</sup> Reaction 3 is a typical dehydroxylation process which requires high temperatures. Reaction 4 may also require high temperatures because it includes the dissociation of the O-O bond, and perhaps the migration of  $\text{Li}^+$  ions. Either reaction 3 or 4 is the rate-determining step in the catalytic production of  $\text{CH}_3\cdot$ .

An alternate pathway may be possible for the regeneration process of reactions 3 and 4. In the  $\text{MgO}$  matrix  $\text{Li}^+$  would be stabilized more by a nearby monovalent negative charge than by divalent or neutral one. In such a case the regeneration process is expressed as follows:



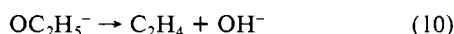
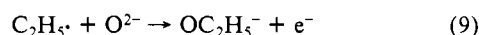
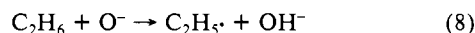
where  $\square$  denotes an electron trapped at an oxygen ion vacancy.

Both the intensity of  $[\text{Li}^+\text{O}^-]$  centers and the total amount of  $\text{CH}_4$  converted showed very similar  $\text{O}_2$ -pressure dependence (Figure 4). Thus, the number of  $[\text{Li}^+\text{O}^-]$  centers available during the catalytic reaction is believed to be proportional to that observed by EPR. The latter amount was present in the equilibrium state which was controlled by reaction 1.

**Production of Stable Products from Methyl Radicals.** A coupling of two  $\text{CH}_3\cdot$  radicals, probably in the gas phase but near the surface, produces  $\text{C}_2\text{H}_6$ .<sup>3,32</sup>



which further reacts with surface  $\text{O}^-$  ions to produce ethylene.<sup>3,8,9</sup>

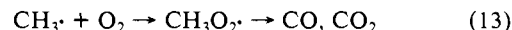
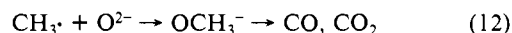
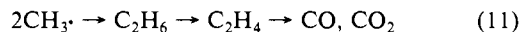


In the temperature range below 700 °C both the  $\text{CH}_4$  conversion and the  $\text{C}_2$  selectivity were greater at higher temperatures (Figure 3). According to reaction 7 the formation of the  $\text{C}_2$  compounds should be proportional to the square of the  $\text{CH}_3\cdot$  concentration, while the amount of  $\text{CO}$  plus  $\text{CO}_2$  is expected to follow some lower order with respect to  $\text{CH}_3\cdot$  concentration (see below). Higher temperatures produce more methyl radicals which are favorable for the  $\text{C}_2$  formation. This situation can be realized only when further oxidation of  $\text{C}_2$  to  $\text{CO}$  and  $\text{CO}_2$  is relatively small. Above 700 °C further oxidation becomes appreciable, leading to the observed decrease in  $\text{C}_2$  selectivity.<sup>19</sup>

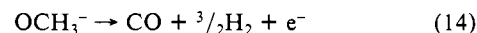
At the lower temperatures carbon monoxide and carbon dioxide also were produced mainly through  $\text{CH}_3\cdot$ . This may be demonstrated by considering the following data. The concentration of  $[\text{Li}^+\text{O}^-]$  centers increased slowly with increasing pressure of  $\text{O}_2$  above 50 torr (Figure 4); therefore, the rate of methyl radical formation by reaction 2 also is expected to increase gradually. In this pressure range, however, the amount of  $\text{C}_2$  decreased considerably, while the amount of  $\text{CO}$  plus  $\text{CO}_2$  increased. Since only a small part of the  $\text{CO}$  and  $\text{CO}_2$  was derived from further oxidation of  $\text{C}_2$  compounds (Table III), the observed decrease in

$\text{C}_2$  formation must be compensated by the formation of additional  $\text{CO}$  and  $\text{CO}_2$  from  $\text{CH}_3\cdot$ .

There are three possible pathways to form  $\text{CO}$  and  $\text{CO}_2$  from  $\text{CH}_3\cdot$ :



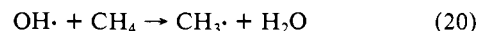
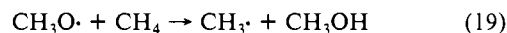
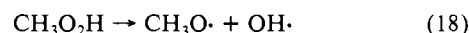
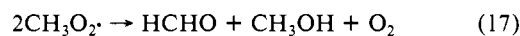
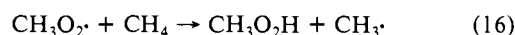
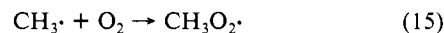
In pathway 11,  $\text{CO}$  and  $\text{CO}_2$  are produced from  $\text{C}_2$  compounds.<sup>6,9,13,24</sup> As discussed previously, this was not a major route to  $\text{CO}$  and  $\text{CO}_2$  at the reaction temperature of 620 °C in the presence of  $\text{CH}_4$  (Table III). In pathway 12 the reaction of  $\text{CH}_3\cdot$  with surface  $\text{O}^{2-}$  ions results in methoxy ions, which subsequently decompose.<sup>8,9</sup> The formation of  $\text{CO}$  and  $\text{CO}_2$  via this reaction should be related to the surface area of the catalysts. In the experiments discussed here the reaction temperature was sufficiently high to decompose surface  $\text{OCH}_3^-$  ions according to<sup>8</sup>



The decrease in  $\text{CO}$  and  $\text{CO}_2$  production as a function of the time on stream (Figure 1) may result from a decrease in surface area due to sintering of the catalyst. The direct relationship between  $\text{C}_1$  selectivity and surface area, described above, supports this hypothesis.

Pathway 13 is a gas-phase reaction between  $\text{CH}_3\cdot$  and  $\text{O}_2$  to produce  $\text{CH}_3\text{O}_2\cdot$  radicals.<sup>32-34</sup> In this case the amount of  $\text{CO}$  and  $\text{CO}_2$  should depend on the  $\text{O}_2$  pressure. Below 50 torr of oxygen pressure the total amount of  $\text{CH}_4$  converted, shown in Figure 4, increased significantly with the  $\text{O}_2$  pressure. This increase is mainly due to a similar increase in  $[\text{Li}^+\text{O}^-]$  concentration (Figure 4). In this pressure range, the  $\text{C}_2$  compounds increased more than the  $\text{CO}$  plus  $\text{CO}_2$ . Above 50 torr the total amount of  $\text{CH}_4$  converted continued to increase, but with a more gentle slope. The concentration of  $[\text{Li}^+\text{O}^-]$  centers also increased although its increment was less than that of  $\text{CH}_4$  converted. It should be noted that, in this pressure range, the amount of  $\text{C}_2$  decreased while the amount of  $\text{CO}$  plus  $\text{CO}_2$  increased. In order to explain this phenomenon, reaction 13 also must be included as one of the main routes for complete oxidation.

Methylperoxy radicals, which were observed over  $\text{Li/MgO}$  together with  $\text{CH}_3\cdot$ ,<sup>25</sup> are known to be involved in chain reactions.<sup>32-34</sup> One such chain reaction is:<sup>33-36</sup>



Since  $\text{CH}_3\text{OH}$  and  $\text{HCHO}$  were detected only in trace amounts, it is likely that these products were further oxidized at the elevated temperatures. Reaction 15 is actually reversible, and a ratio of  $[\text{CH}_3\text{O}_2\cdot]/[\text{CH}_3\cdot] = 0.056$  at 60 torr of  $\text{O}_2$  and 620 °C has been estimated.<sup>36</sup> In view of the high  $\text{C}_2$  selectivities which could be obtained in these experiments, the chain reaction described by reactions 15 to 20 probably was not significant over the  $\text{Li/MgO}$  catalysts except when larger partial pressures of  $\text{O}_2$  were used.

## Conclusions

Ethane and ethylene are produced in high yields with good selectivities when  $\text{CH}_4$  and  $\text{O}_2$  are passed over  $\text{Li/MgO}$  catalysts at high temperatures. These  $\text{C}_2$  compounds are formed via the

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coupling of the gas-phase methyl radicals, which are produced mainly by the reaction of  $\text{CH}_4$  with active  $[\text{Li}^+\text{O}^-]$  centers on  $\text{MgO}$ . One cannot exclude the additional formation of methyl radicals through branching gas-phase chain reactions. An unusual feature of this reaction system is that both the  $\text{C}_2$  selectivity and the  $\text{CH}_4$  conversion increase with increasing temperatures up to ca.  $700^\circ\text{C}$ . One of the dominant pathways which leads to un-

desirable products of  $\text{CO}$  and  $\text{CO}_2$  is the reaction of  $\text{CH}_3\cdot$  with surface  $\text{O}^{2-}$  ions; therefore, low surface areas favor high  $\text{C}_2$  selectivities. The  $\text{Li/MgO}$  system is a new type of oxidation catalyst which does not contain metal ions having a variable oxidation state.

**Acknowledgment.** This work was supported by the National Science Foundation under Grant No. CHE-8405191.

## Infrared Photochemistry of Tetramethyldioxetane. 2. The Nature of Electronically Excited Products

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*Received December 28, 1984*

**Abstract:** The decomposition of tetramethyldioxetane (TMD) following either overtone excitation or infrared multiple photon excitation (IRMPE) under low-pressure conditions is discussed and compared to recent results obtained upon UV photoexcitation of acetone vapor. It is shown that the results are consistent with a mechanism by which IR excitation of TMD results in producing electronically excited acetone, which may be considered as a mixed state containing contributions from both the singlet and the triplet states.

The chemiluminescent decomposition of tetramethyldioxetane (TMD) has been studied extensively in liquid solutions<sup>1-4</sup> and to a somewhat lesser extent in the gas phase. The reaction seems to be well characterized kinetically and in thermal systems an Arrhenius expression of the type  $k(T) = A_0 \exp(-E_a/RT)$  fits the unimolecular decay rates reasonably well, with  $A_0 = 10^{13} \text{ s}^{-1}$  and  $E_a$  in the range of 24–26 kcal/mol. Low-pressure vapor-phase measurements, using overtone excitation (OTE)<sup>5</sup> and infrared multiphoton excitation (IRMPE),<sup>6,7</sup> can be interpreted by using a statistical model with  $k(E)$ , the energy-dependent decomposition rate constant, calculable from the RRKM theory.<sup>8,9</sup> Since the reaction results in electronically excited products, it has been argued<sup>10</sup> that it does not lead to the statistically most probable products. This fact is not in conflict with applying RRKM theory to the process as rapid energy redistribution in the vibrationally excited parent molecule, prior to the reaction, is the only basic requirement. We have recently proposed<sup>7,11</sup> that if vibrational energy is indeed rapidly scrambled, the energy distributions of molecules excited by IRMPE can be estimated by comparison with OTE results.

In this paper we discuss another aspect of the reaction, the nature of the electronically excited product. Most early work on

TMD was performed in liquid solutions under conditions where vibrational relaxation is much faster than the reaction rate or the decay of electronically excited states. On the basis of fluorescence sensitization experiments<sup>12</sup> and on chemical titration methods<sup>13</sup> it has been concluded that the major product is acetone triplet in its vibrationally relaxed state ( $T_1^{\text{VR}}$ ). The quantum yield has been estimated to range between 30 and 50%,<sup>4</sup> namely almost quantitative. On energetic grounds, only one of the two product acetone molecules can be electronically excited. Some vibrationally relaxed singlet acetone ( $S_1^{\text{VR}}$ ) is also formed. Its yield is low with estimates ranging between  $10^{-5}$  to  $10^{-3}$ .<sup>4</sup>

Low-pressure vapor-phase work, based on rapid excitation by laser sources,<sup>6</sup> appeared at first to be at variance with these results. Under these conditions, the time evolution of the system can be studied with  $10^{-8}$  s time resolution. The amount of internal energy in the reacting molecules can be controlled by varying the laser's wavelength (in OTE experiments) or fluence (in IRMPE work). Thus, the rate of the reaction can be varied, as well as the internal energy in the product molecules. Furthermore, the resulting kinetics and emission spectra can be studied in real time.

A complicated kinetic pattern is revealed<sup>5</sup> with the emission decay being distinctly nonexponential. Overtone results could be approximately reproduced by fitting the observed chemiluminescence (CL) signal intensity,  $I_{\text{CL}}$ , to the following empirical relation

$$I_{\text{CL}}(t) = -A \exp(-kt) + B \exp(-k_2t) + C \exp(-k_3t) \quad (1)$$

The first term relates to the reaction rate and is strongly dependent on the internal energy in the excited TMD molecules. The second and third terms are due to the decay of two kinetically distinct species, termed by Cannon and Crim<sup>5</sup> (CC) the fast and slow components. The slow component can be identified with  $T^{\text{VR}}$ , based on its decay time and emission spectrum. The fast one is clearly not the singlet observed in liquid solution or previous

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