

## Measurements of Kinetic Isotope Effects and Hydrogen/Deuterium Distributions over Methane Oxidative Coupling Catalysts

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The kinetic isotope effect for  $\text{CH}_4$  compared to that for  $\text{CD}_4$  has been measured for the oxidative coupling reaction of methane over  $\text{Li/MgO}$ ,  $\text{SrCO}_3$ , and  $\text{Sm}_2\text{O}_3$  catalysts in a flow reactor. Each catalyst gave results consistent with C-H bond breaking being the slow step. For temperatures between 680–780°C over  $\text{Li/MgO}$ ,  $k_{\text{H}}/k_{\text{D}}$  decreased slightly with temperature. The isotope effect for ethane production was more sensitive to the level of conversion and declined from 1.8 at low conversion to near unity under conditions where the ethylene to ethane ratio was high (~1). Selectivities to hydrocarbons were lower with  $\text{CD}_4$  and did not change with decreased flow rates, implying that either  $\text{CO}_x$  and  $\text{C}_2$  products arise by totally separate slow steps or, if a common step with  $\text{CH}_3$  radicals is involved, then  $\text{CO}_x$  formation occurs on the catalyst. Experiments with  $\text{CH}_4/\text{CD}_4$  mixtures showed that  $\text{CH}_3\text{CD}_3$  and  $\text{CH}_2\text{CD}_2$  were the dominant mixed products. The distribution of the ethanes always reflected the relative concentrations of  $\text{CH}_3$  and  $\text{CD}_3$  determined by the kinetic isotope effect. At low ethylene to total  $\text{C}_2$  ratios (~0.2) this was also true for ethylene; but at higher ratios substantial exchange to produce ethylenes other than  $\text{C}_2\text{H}_4$ ,  $\text{CH}_2\text{CD}_2$ , and  $\text{C}_2\text{D}_4$  occurred. The concentration of the exchanged methanes correlated with total methane conversion but was dependent on the surface. Exchange in the ethylenes also correlated with exchange in the methanes and purely gas phase processes appear at least partially responsible.  $\text{H}_2$ :HD:D<sub>2</sub> ratios are always at equilibrium and exchange also occurs between  $\text{CD}_4$  and  $\text{H}_2$ . © 1989 Academic Press, Inc.

### INTRODUCTION

The conversion of methane, the major constituent of natural gas, to transportation fuels and petrochemical feedstocks has long been the subject of catalytic research. Currently, commercial processes achieve this conversion by the initial production of synthesis gas from steam reforming or partial oxidation. An alternative technology, based on the direct oxidation coupling of methane to  $\text{C}_2$  hydrocarbons, is attractive from energetic considerations and recently a number of catalytic systems which give methane conversions and  $\text{C}_2$  hydrocarbon selectivities of practical significance have been reported (1–12).

The mechanism of oxidative coupling involves the initial formation of methyl ( $\text{CH}_3$ ) radicals which combine to form  $\text{C}_2\text{H}_6$ . Evidence for the formation of  $\text{CH}_3$  has been obtained by a matrix isolation electron spin

resonance (MIESR) technique (13–15), by the Paneth lead mirror test (10), and by isotopic studies using  $\text{CH}_4/\text{CD}_4$  mixtures (16). Ethylene, the commercially desirable product, is formed by secondary reactions of  $\text{C}_2\text{H}_6$  over Li-promoted  $\text{MgO}$  ( $\text{Li/MgO}$ ) catalysts (16, 17), although direct formation of  $\text{C}_2\text{H}_4$  may be important for other catalysts. The relative importance of heterogeneous and purely homogeneous processes in the formation of  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$  has also received considerable attention. Lunsford and co-workers (14, 15) have shown, using the MIESR technique, that gas phase  $\text{CH}_3$  radicals are present under reaction conditions and can account for at least 30–40% of the  $\text{C}_2$  hydrocarbons produced. The lack of any H/D exchange in the ethanes produced from  $\text{CH}_4/\text{CD}_4$  mixtures (16) also suggests a predominantly homogeneous process.

The rate-controlling step in the reaction over  $\text{Li/MgO}$  was originally proposed (4) to

be reoxidation of the catalyst. However, the measurement of a kinetic isotope effect (for CH<sub>4</sub> versus CD<sub>4</sub>) of 1.5 at 750°C (18) shows that the rate-controlling step at this temperature is C–H bond breaking. An interesting observation in this experiment was that selectivities were also affected, with CD<sub>4</sub> producing more carbon oxides.

In fact major mechanistic uncertainty still exists for the formation of carbon oxides in oxidative coupling reactions. The methylperoxy radical (CH<sub>3</sub>O<sub>2</sub>) has been invoked to explain the formation of carbon oxides (4) but no definitive evidence for its importance under reaction conditions has been obtained. Secondary oxidation of the C<sub>2</sub> hydrocarbons is undoubtedly responsible for some carbon oxide production particularly at high conversion (17), but the source of primary CO<sub>x</sub> production remains uncertain.

In this work we report further measurements of kinetic isotope effects over a number of oxidative coupling catalysts. The measurements of the kinetic isotope effects were designed to investigate the reasons for the selectivity differences observed with CD<sub>4</sub> (18) and to establish the influence of reaction conditions and different catalysts. Hydrogen–deuterium distributions from CH<sub>4</sub>/CD<sub>4</sub> mixtures are also reported. The compositions of the ethanes, ethylenes, and hydrogens provide mechanistic information about the formation of these products over a range of temperatures and surfaces.

#### EXPERIMENTAL

The Li/MgO catalyst was similar to that used previously (17). Samarium oxide was pelleted and crushed, and the –1.2 + 0.6-mm fraction separated for use. Strontium carbonate (BDH, 99.0% min) was slurried in boiling water, heated to a thick paste, dried at 200°C for 2 h, left to stand at 250°C overnight, and then heated in flowing air for 5½ h at 950°C. The catalyst was crushed and the –1.2 + 0.6-mm fraction separated for use.

Experiments were performed under atmospheric pressure using a flow system and a reactor constructed from fused alumina tubing (4 mm i.d., Alsint 99.7) which was mounted vertically and heated by a tube furnace. The catalyst bed was supported on a bed of crushed alumina which was held in place by the tip of an alumina thermocouple sheath, inserted into the bottom of the reactor. A second thermocouple, also sheathed in alumina, was located just above the catalyst bed. Bed sizes were 0.100 g for Li/MgO, 0.094 g for Sm<sub>2</sub>O<sub>3</sub>, and 0.153 g for SrCO<sub>3</sub>.

Pretreatment comprised heating the sample to reaction temperature in flowing helium over a period of 1 h. The reaction mixture, with preset composition and flow rate, was then introduced and the system run until stable activity was reached (2 to 5 h). The catalyst remained usable for a further 10 to 30 h before a steep increase in carbon monoxide production and loss of hydrocarbon selectivity occurred due to depletion of lithium by volatilization. Catalytic activity was calculated as the methane conversion rate defined as

$$\text{CH}_4 \text{ conversion rate} = F \sum n C_i / W.$$

Here,  $F$  is the molar flow of the gas stream passing from reactor to gas chromatograph,  $C_i$  is the volume percent of each hydrocarbon product in that stream,  $n$  is the carbon number of the particular product, and  $W$  the catalyst weight. Accurate measurements of the kinetic isotope effect were made at low conversion (in methane <10%, in oxygen <7%) in which situation the reactor approaches differential operation and conversion rate accurately reflects true rate. In some cases it was of interest to study the reaction at oxygen conversions up to 40%. The conversion rate then underestimates the true rate quite substantially, especially as carbon dioxide is a significant catalyst inhibitor (15). Even so, conversion rate is a convenient measure of relative activity.

Ultrahigh-purity  $\text{CH}_4$  (99.9% minimum), high-purity  $\text{N}_2$  (99.99%), and industrial  $\text{O}_2$  (99.5% minimum) were used without further purification.  $\text{CD}_4$  (99.4 at.% D),  $\text{CH}_3\text{CD}_3$  (99.2 at.% D), and  $\text{CH}_2\text{CD}_2$  were supplied by MSD isotopes.

To facilitate flow of the two  $\text{C}_2$  compounds small amounts (20 to 50  $\text{cm}^3$ ) (STP) were transferred to 75- $\text{cm}^3$  stainless-steel cylinders and pressurized with methane to 1000 to 2000 kPa. Flows of all gases were controlled by separate electronic mass flow controllers (Brooks Division, Emerson Electric Co.). The valving of the gas supply to the reactor allowed rapid partial or complete substitution of  $\text{CH}_4$  flow by  $\text{CD}_4$  or mixtures of the deuterium-labeled  $\text{C}_2$  compounds in  $\text{CH}_4$ .

Feed and product gas were analyzed by gas chromatography (GC) using a Chromosorb 102 column coupled to thermal conductivity (TCD) and flame ionization detectors (FID) in series. The system was calibrated against standard gas mixtures (CIG Ltd., Australia) of similar composition to the product mixture. Analyses of  $\text{CH}_4$  and  $\text{CD}_4$  at equal concentrations showed no significant differences in response to the FID and identical responses were also assumed for  $\text{C}_2\text{H}_6$  and deuterated ethanes and for  $\text{C}_2\text{H}_4$  and deuterated ethylenes. The effluent from the reactor was connected to the inlet system of a quadrupole mass spectrometer (VG SX-200) operated in the multiple ion monitoring mode. This was used to determine the H/D distributions of ethanes, ethylenes, and hydrogens. It was not possible to measure H/D distributions in water because of the facile exchange reactions of  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixtures with surfaces.

Samples of feed and product gas were also collected in an infrared gas cell (10-cm path length) and gas-phase FTIR spectra were obtained using Digilab FTS 20/80 and 15/80 spectrometers. The spectra were recorded at 0.25  $\text{cm}^{-1}$  resolution by the coaddition of 256 scans.

## RESULTS AND DISCUSSION

### *Kinetic Isotope Effects*

Our previous measurement (18) of the relative rates of oxidation of  $\text{CH}_4$  versus  $\text{CD}_4$  over Li/MgO at 750°C showed an overall kinetic isotope effect (rate ( $\text{CH}_4$ )/rate ( $\text{CD}_4$ )) of 1.48 to all products. However, the value determined for hydrocarbon formation was significantly greater than that for formation of carbon oxides. In consequence hydrocarbon selectivity was lower with  $\text{CD}_4$  (51%) than with  $\text{CH}_4$  (59%). Two possible causes may be considered. One is that the two classes of product arise from entirely different pathways with quite different isotope effects. Alternatively, one might envisage that a gas-phase methyl species is common to both paths and undergoes either coupling, according to second-order kinetics or oxidation by first-order kinetics. Hydrocarbon selectivity is then expected to fall if the concentration of the gas-phase species is reduced. The isotope effect is expected to induce this when  $\text{CH}_4$  is substituted by  $\text{CD}_4$  as methane conversion is reduced under conditions of constant flow as used previously (18).

In theory the two possibilities can be distinguished by carrying out the  $\text{CD}_4$  experiment with a flow reduced so as to compensate for the lower conversion. If the second explanation is true, one expects that the concentration of methyl radicals will be increased and that identical selectivities will be observed for  $\text{CH}_4$  and  $\text{CD}_4$ . If the first explanation holds, the apparent isotope effect and selectivity should be unaffected. There is a complication to this proposal since changing the flow may cause a variation in the transport of species away from the catalyst particle. This will be considered in more detail below.

A test of these hypotheses was carried out over Li/MgO using a mixture with identical composition (10% methane, 7% oxygen, balance nitrogen) to that employed previously (18). The results are shown in

TABLE 1

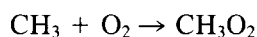
Test for Effect of Flow Rate on Reaction of CD<sub>4</sub> versus CH<sub>4</sub> over Li/MgO at 750°C<sup>a</sup>

Reactant	Total flow (cm <sup>3</sup> min <sup>-1</sup> ) (STP)	Methane conversion	Oxygen conversion	Conversion rates (μmol g <sup>-1</sup> min <sup>-1</sup> )				
				Overall	Ethylene	Ethane	CO	CO <sub>2</sub>
CH <sub>4</sub>	92	5.4	~7	221	19	113	8	81
CH <sub>4</sub>	92	5.5	~7	224	19	115	8	82
CD <sub>4</sub>	92	3.5	~5	143	8	65	6	63
CH <sub>4</sub>	92	5.5	~7	223	19	116	8	80
CD <sub>4</sub>	64	4.6	~7	131	6	60	5	60
CD <sub>4</sub>	64	4.6	~7	133	8	60	5	60
CH <sub>4</sub>	92	5.6	~7	230	20	116	8	86
CH <sub>4</sub>	92	5.6	~8	230	20	116	9	86
Average rate (CH <sub>4</sub> )/rate (CD <sub>4</sub> )				1.6 ± 0.1	2.6 ± 0.5	1.8 ± 0.1	1.5 ± 0.3	1.33 ± 0.1
Average selectivity (%)								
CH <sub>4</sub>					9	51	4	36
CD <sub>4</sub>					5	46	4	45

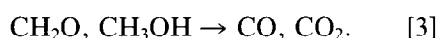
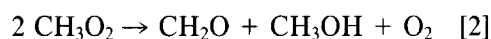
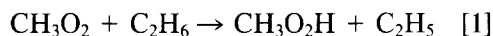
<sup>a</sup> Over 100 mg catalyst with inlet composition 10% methane, 7% oxygen throughout.

Table 1. The measurements with CD<sub>4</sub> were carried out with interleaving CH<sub>4</sub> runs and these showed no evidence of deactivation (see rows 1, 2, 4, 7, and 8). The data show little difference in rate to any product when using CD<sub>4</sub> in a mixture with flow of 92 cm<sup>3</sup> (STP) min<sup>-1</sup> (row 3) compared to 64 cm<sup>3</sup> (STP) min<sup>-1</sup> (rows 5 and 6). Despite the much increased oxygen and methane conversions with the lower CD<sub>4</sub> flow rate, there was no tendency for hydrocarbon production rate to increase relative to that for carbon oxides. If anything, the absolute values for both are reduced, possibly due to the increased reactant depletion at the lower flow. Thus the change in selectivity on substitution of CD<sub>4</sub> for CH<sub>4</sub> cannot be explained on the basis of a gas-phase methyl radical being common to production of both hydrocarbons and carbon oxides by different kinetics.

This result implies that formation of carbon oxides by homogeneous reactions of the methylperoxy radical, CH<sub>3</sub>O<sub>2</sub>, is unlikely. This radical is produced by an addition reaction:



and was invoked by Lunsford and co-workers to explain carbon oxide formation over Li/MgO (4) and Na/CaO (19) catalysts. In this scheme carbon oxides were produced by subsequent reactions of CH<sub>3</sub>O<sub>2</sub>:

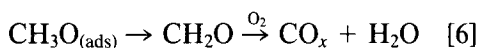
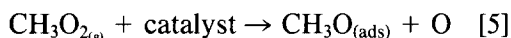
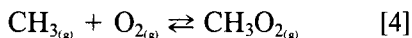


A possible interpretation of our results, therefore, is that C<sub>2</sub> hydrocarbons and carbon oxides arise from separate slow steps with quite different isotope effects. A transition state for carbon oxide formation, involving removal of two hydrogens, is possible, but it would not be predicted to have a very different isotope effect (20).

However, as foreshadowed above, there is an alternate explanation. Under differential conditions and in the absence of mass transfer limitations, the flux of CD<sub>4</sub> (or CH<sub>4</sub>) to the surface will be independent of flow rate of the external stream. Thus the CD<sub>3</sub> (or CH<sub>3</sub>) generation rate will also be independent of flow rate if the generation step is rate controlling and the CD<sub>3</sub> concen-

tration in any truly stagnant layer will be near constant. If dimerization of methyl to form ethane and reactions of  $\text{CH}_3\text{O}_2$  with the surface which form carbon oxides proceed entirely in a stagnant, boundary layer, then changes to the flow rate will not change selectivity (in accord with our observations).

If, however, the chemistry proceeds only partially in the boundary layer then flow-rate changes can have an effect. At higher flow rates the thickness of the boundary layer is reduced and a greater fraction of the methyl radicals will reach the bulk gas stream. The selectivity is then expected to increase. As this was not observed we conclude that either the products form by separate, slow steps or that the carbon oxides are produced on the catalyst surface. If this is the case a role for  $\text{CH}_3\text{O}_2$  could be invoked by a scheme such as:



This would only be possible if the equilibrium constant for [4] was high enough at  $750^\circ\text{C}$  to produce significant quantities of  $\text{CH}_3\text{O}_2$ . In fact recent measurements of the equilibrium constant (21, 22) show that significant amounts of  $\text{CH}_3\text{O}_2$  will be present under our experimental conditions of temperature and oxygen partial pressure ( $[\text{CH}_3\text{O}_2]/[\text{CH}_3] \sim 0.2$  for  $T = 750^\circ\text{C}$  and 10%  $\text{O}_2$ ).

The participation of  $\text{CH}_3\text{O}_2$  is an attractive idea since it explains why selectivity declines with increasing  $\text{O}_2$  pressure (more  $\text{CH}_3\text{O}_2$  formed) and decreasing temperature (longer  $\text{CH}_3\text{O}_{2(\text{g})}$  lifetime). However, direct reaction of  $\text{CH}_3$  with the surface is another possible route to carbon oxides.

Average values for the kinetic isotope effects to each product and selectivities using  $\text{CH}_4$  and  $\text{CD}_4$  are shown at the bottom of Table 1. The latter agree very well with those reported earlier (18). The kinetic iso-

tope effects are all slightly larger, reflecting the slightly reduced rates with  $\text{CD}_4$  in the lower flow experiment.

The measurements of Table 1 correspond to differential conditions (less than 10% conversion of either reactant). Further determinations of the kinetic isotope effect were carried out under other conditions as detailed in Table 2. The measurements used mixtures containing 20% methane and 10% oxygen and spanned a range of total flows ( $W/F$  values). However, the same  $W/F$  was used with  $\text{CH}_4$  and  $\text{CD}_4$  in any one test. Apparent kinetic isotope effects are listed in Table 3. The apparent isotope effects on both hydrocarbons decline steeply with oxygen conversion as may be seen from Fig. 1. The trend is particularly pronounced for ethane. Under the most severe conditions with Li/MgO ( $775^\circ\text{C}$ , 40% oxygen conversion, ethylene-ethane ratio near unity) the rate ratio,  $\text{C}_2\text{H}_6/\text{C}_2\text{D}_6$ , is only 1.08.

This behavior can be interpreted in terms of sequential reactions in a plug flow reactor. The concentration of ethane leaving the reactor will increase with oxygen conversion at low conversions but eventually pass through a maximum as some of it is converted further to other products. If, under certain conditions, the oxygen conversion with  $\text{CH}_4$  is beyond the point of maximum  $\text{C}_2\text{H}_6$  yield, then the lower oxygen conversion with  $\text{CD}_4$  under the same conditions may place the  $\text{C}_2\text{D}_6$  yield closer to its maxi-

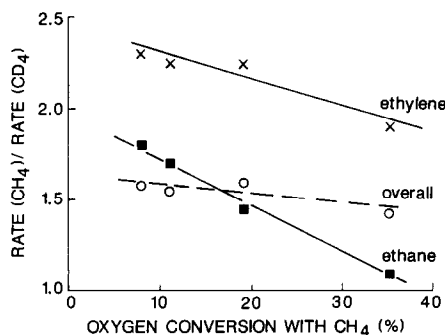


FIG. 1. Apparent kinetic isotope effect versus oxygen conversion.

TABLE 2

Comparison of Overall Conversion Rate and Product Selectivity with CH<sub>4</sub> and CD<sub>4</sub> (in Parentheses) during Methane Coupling under Various Conditions with Several Catalysts<sup>a</sup>

Catalyst	Temp. (°C)	W/F (g cm <sup>-3</sup> s)	Oxygen conversion	Overall rate <sup>b</sup>	Selectivity (%)			
					Ethylene	Ethane	CO	CO <sub>2</sub>
Li/MgO	680°	0.096	7 (6.5)	55 (35)	6.5 (4)	46 (39)	4.9 (6)	42 (51)
Li/MgO <sup>c</sup>	750°	0.0176	11 (10)	372 (229)	7.3 (4.2)	46 (40)	6.7 (7.8)	40 (48)
Li/MgO	750°	0.088	19 (15)	208 (130)	21 (13)	46 (50)	2.5 (2.7)	28 (33)
Li/MgO	774°	0.085	35 (27)	363 (255)	33 (23)	31 (41)	3.5 (2.2)	30 (31)
SrCO <sub>3</sub>	800°	0.061	23 (20)	181 (154)	18 (11)	37 (42)	14 (15)	30 (31)

<sup>a</sup> All tests done with inlet composition 20% methane, 10% oxygen, balance N<sub>2</sub> except where noted.

<sup>b</sup> In units of μmol (methane) g<sup>-1</sup> min<sup>-1</sup>.

<sup>c</sup> Inlet composition 10% methane, 7% oxygen, balance N<sub>2</sub>.

mum. The apparent isotope effect in ethane production will be much reduced. The effect could be exaggerated if an isotope effect was present in the ethane to ethylene conversion. By contrast the apparent isotope effect for ethylene will be much less affected since it is derived from ethane and will be much below its maximum yield for both CH<sub>4</sub> and CD<sub>4</sub> under such conditions.

As may be seen from Fig. 1 the overall isotope effect declines slightly with oxygen conversion. This may be due to the greater oxygen depletion when using CH<sub>4</sub> compared to CD<sub>4</sub> and additional departure from

the differential reactor approximation used to estimate rates. However, the higher temperatures used to achieve higher conversions may also be a factor since kinetic isotope effects decline with increasing temperature (20). The single measurement with SrCO<sub>3</sub> shows somewhat lower isotope effect than Li/MgO at equivalent oxygen conversions. The higher temperature used with SrCO<sub>3</sub> may be contributing but a somewhat lower intrinsic isotope effect seems likely.

Table 3 includes determinations of H<sub>2</sub> versus D<sub>2</sub> yields under several conditions. For Li/MgO, the rate difference is much

TABLE 3

Apparent Deuterium Kinetic Isotope Effects for Methane Conversion over Different Catalysts from Experiments of Table 2

Catalyst	Temp. (°C)	W/F (g cm <sup>-3</sup> s)	Rate (CH <sub>4</sub> )/rate (CD <sub>4</sub> )					
			Overall	Ethylene	Ethane	CO	CO <sub>2</sub>	H <sub>2</sub> (D <sub>2</sub> )
Li/MgO	680	0.096	1.59	2.6	1.8	1.5	1.33	—
Li/MgO	750	0.0176	1.55	2.5	1.7	1.4	1.38	1.4
Li/MgO	750	0.088	1.60	2.5	1.45	1.5	1.39	1.6
Li/MgO	774	0.085	1.43	2.0	1.09	2.2	1.42	2.3
SrCO <sub>3</sub>	800	0.061	1.24	2.0	1.08	1.27	1.17	1.2

TABLE 4

Conditions for Reaction of Equimolar Mixtures of CH<sub>4</sub> and CD<sub>4</sub> over Various Catalysts<sup>a</sup>

Catalyst	Temp. (°C)	W/F (g cm <sup>-3</sup> s)	Methane conversion (%)	Oxygen conversion (%)	Selectivity (%)	
					Ethylene	Ethane
Li/MgO	680	0.090	1.5	15	7	58
Li/MgO	750	0.090	7.2	43	21	54
	(+780) <sup>b</sup>	(0.090) <sup>b</sup>	(7.3) <sup>b</sup>	(47) <sup>b</sup>	(31) <sup>b</sup>	(40) <sup>b</sup>
Li/MgO	775	0.090	11.5	70	35	41
SrCO <sub>3</sub>	800	0.070	3.1	21	15	47
Sm <sub>2</sub> O <sub>3</sub>	600	0.043	10	94	8	31

<sup>a</sup> The input composition for all runs was 45% CH<sub>4</sub>, 45% CD<sub>4</sub>, and 10% O<sub>2</sub>.<sup>b</sup> Product from catalyst at 750°C passed through empty reactor at 780°C.

more pronounced when the ethylene-ethane ratio is high, suggesting that hydrogen is being derived by ethane dehydrogenation. However, that trend does not carry over to SrCO<sub>3</sub>, so such a suggestion is not universally true.

#### Reactions of Equimolar CH<sub>4</sub> plus CD<sub>4</sub> Mixtures

(1) *Isotopic composition of ethane and ethylene.* Previously (16) we have shown that for a CH<sub>4</sub>/CD<sub>4</sub>/O<sub>2</sub> mixture over Li/MgO no significant hydrogen exchange occurred between CH<sub>4</sub> and CD<sub>4</sub>. C<sub>2</sub>H<sub>6</sub>, CD<sub>3</sub>CH<sub>3</sub>, and C<sub>2</sub>D<sub>6</sub> were the only ethanes detected and C<sub>2</sub>H<sub>4</sub>, CD<sub>2</sub>CH<sub>2</sub>, and C<sub>2</sub>D<sub>4</sub> the

only ethylenes. The relative concentrations of the ethanes and ethylenes reflected the concentrations of CH<sub>3</sub> and CD<sub>3</sub> determined by the kinetic isotope effect. To investigate the generality of these results further measurements were performed with Li/MgO under different conditions and with SrCO<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub>. Measurements with these mixtures were carried out with streams containing nominally 45% CH<sub>4</sub>, 45% CD<sub>4</sub>, and 10% oxygen. The conditions used are listed in Table 4 and the deuterium distribution in the product ethanes in Table 5. For one experiment over Li/MgO the product gas from the catalytic reactor at 750°C was passed through a second, empty reactor at

TABLE 5

Distribution of Deuterium in Ethanes from Reaction of CH<sub>4</sub> and CD<sub>4</sub> over Various Catalysts (Conditions as per Table 4)

Catalyst	Temp. (°C)	Mass spectrometry			FTIR			f(%) <sup>a</sup>
		C <sub>2</sub> H <sub>3</sub> D <sub>3</sub>	C <sub>2</sub> HD <sub>5</sub>	C <sub>2</sub> D <sub>6</sub>	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> CD <sub>3</sub>	C <sub>2</sub> D <sub>6</sub>	
Li/MgO	680	3.1	0.02	1.00	nd	3.3	1.0	nd
Li/MgO	750	3.3	0.07	1.00	2.1	3.1	1.0	103
	+780 <sup>b</sup>	3.2	0.06	1.00	1.7	3.2	1.0	106
Li/MgO	775	3.2	0.09	1.00	1.9	3.1	1.0	105
SrCO <sub>3</sub>	800	3.6	0.05	1.00	nd	nd	nd	nd
Sm <sub>2</sub> O <sub>3</sub>	600	3.4	0.09	1.00	1.7	3.0	1.0	101

<sup>a</sup> f is the ratio of the sum of the concentrations of C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>CD<sub>3</sub>, and C<sub>2</sub>D<sub>6</sub> (determined by FTIR) to the total ethane concentration (determined by GC) expressed as a percentage.<sup>b</sup> Empty reactor experiment.

780°C to investigate the effect of secondary gas-phase reactions. The mass spectral data gives the relative amounts of  $C_2H_3D_3$ ,  $C_2HD_5$ , and  $C_2D_6$  with the latter set equal to unity. Fragmentation from these ethanes and overlap with ethylene and oxygen signals prevented determination of the amounts of ethanes containing 0, 1, and 2 deuteriums. The signal at  $m/e = 34$  corresponding to the parent ion of  $C_2H_2D_4$  did not differ significantly from that expected by fragmentation of  $C_2D_6$  using the determinations of Amenomiya and Pottie (23). Hence the quantity of  $C_2H_2D_4$  is not significant. As demonstrated previously (16) the FTIR measurements prove that  $CH_3CD_3$  is the species containing three deuteriums.

The ratio  $C_2H_3D_3/C_2D_6$ , as determined by mass spectrometry, lies in the range  $3.3 \pm 0.3$  for all five runs of Table 5. The expected value is 3.0 for coupling of  $CH_3$  and  $CD_3$  species produced from a mixture of  $CH_4$  and  $CD_4$  (of 1 : 1 ratio) with a kinetic isotope effect in methyl radical formation of 1.5. The values of Table 5 indicate a slightly higher isotope effect that this in accord with the values found for production of the  $C_2$  hydrocarbons in comparative experiments and listed in Tables 1 and 3. It is significant to note that the  $CH_3CD_3/C_2D_6$  ratio with  $Sm_2O_3$  is similar to that of the other systems even though the  $Sm_2O_3$  catalyst is so active at 600°C that oxygen is almost completely consumed. Thus a kinetic isotope effect in the reaction of  $CH_4$  versus  $CD_4$  can be inferred from the mixed experiment under conditions when comparative measurements using  $CH_4$  against  $CD_4$  would be fruitless.

The FTIR measurements for the ethanes are also shown in Table 5. These are a considerable improvement on those reported previously (16) because the concentrations of  $CH_3CD_3$  and  $CH_2CD_2$  have been determined by calibrations obtained using pure compounds, not by difference. The ratios  $C_2H_6/C_2D_6$  and  $CH_3CD_3/C_2D_6$  are given together with a factor,  $f$ , which is the ratio of the sum of the concentrations of  $C_2H_6$ ,

$CH_3CD_3$ , and  $C_2D_6$  (determined by FTIR) to the total ethane concentration (determined by GC) expressed as a percentage. The ratio  $CH_3CD_3/C_2D_6$  agrees very well with that determined by MS. The factor,  $f$ , is  $103 \pm 3\%$  for all runs and shows that for both Li/MgO and  $Sm_2O_3$  and all conditions tested essentially all the ethanes produced can be accounted for by the products  $C_2H_6$ ,  $CH_3CD_3$ , and  $C_2D_6$ . Measurements made on  $SrCO_3$  under conditions somewhat different from those shown in Table 5 show that this is also true for this catalyst. Thus the ethanes formed under a wide range of conditions and over three separate catalysts can be accounted for by coupling of  $CH_3$  and  $CD_3$  alone. A purely homogeneous process is indicated.

The low ratios of  $C_2HD_5$  to  $C_2D_6$  in the mass spectral data of Table 5 also show the lack of substantial exchange. There is however some variation between runs. The  $CHD_3/CD_4$  ratio was 0.023 in the original deuteromethane leading to an expected minimum  $C_2HD_5/C_2D_6$  ratio of 0.016 allowing for the isotope effect. Values above this indicate some exchange in either methanes prior to reaction or ethanes after their formation. Exchange between methanes could be readily monitored by FTIR since both  $CH_3D$  and  $CHD_3$  exhibit characteristic bands of high extinction coefficient at 1156 and  $1036\text{ cm}^{-1}$  (24), respectively. As can be seen from Fig. 2, plots of the absorbance of these bands versus methane conversion to chemical products are linear for Li/MgO. However, the points for  $SrCO_3$  and  $Sm_2O_3$  fall respectively above and below these lines.

Similar conclusions may be reached from the mass spectral data of Table 6. This lists the increase in  $CHD_3$  concentration above that in the feed relative to the sum of the  $CHD_3$  and  $CD_4$  concentrations. This is based on measurements at  $m/e = 19$  and 20 with allowance for the different sensitivities of the mass spectrometer to the two methanes. Since, unlike the FTIR results, the results are absolute, the number of methane



TABLE 6

Methane Exchange Rates and Methane Conversion Rates during Reaction of Equimolar Mixtures of CH<sub>4</sub> and CD<sub>4</sub> over Various Catalysts (Conditions as per Table 4)

Catalyst	Temp. (°C)	$\Delta\text{CHD}_3$ CHD <sub>3</sub> + CD <sub>4</sub>	Methane <sup>a</sup> exchange rate	Methane <sup>a</sup> conversion rate	Exchange Conversion
Li/MgO	680	0.008	56	109	0.51
Li/MgO	750	0.035	253	527	0.48
	+780 <sup>b</sup>	0.056	400	531	0.75
Li/MgO	775	0.068	480	824 <sup>c</sup>	0.58
SrCO <sub>3</sub>	800	0.047	440	345	1.28
Sm <sub>2</sub> O <sub>3</sub>	600	0.032	550	1757 <sup>c</sup>	0.31

<sup>a</sup> In  $\mu\text{mol (methane) g}^{-1} \text{min}^{-1}$ .

<sup>b</sup> Empty reactor experiment.

<sup>c</sup> Limited by O<sub>2</sub> consumption (see Table 4 for values).

molecules exchanged can be calculated assuming CH<sub>3</sub>D and CHD<sub>3</sub> are produced in equal amounts. This is given in column 3 of Table 6 and compared with the chemical conversion rate to all products (column 4). The ratio of exchange rate to conversion rate is about 0.5 for the three runs with Li/MgO but higher with SrCO<sub>3</sub> and lower with Sm<sub>2</sub>O<sub>3</sub> in accord with the FTIR data plotted in Fig. 2. This indicates some dependence of the exchange rate on catalyst properties. With the exception of Sm<sub>2</sub>O<sub>3</sub> there is a rough correlation between exchange in ethane (Table 5) and that in methane (Table 6).

The experiment with the second empty reactor at 780°C did not reveal any significant differences in the distribution of the ethanes either by MS or FTIR. However, some additional exchange in the methanes was observed suggesting that gas-phase processes could be responsible for some exchange. As previously noted (16) the gas-phase reactions



could possibly make a significant contribution to the overall exchange based on data for CH<sub>3</sub> concentrations over Li/MgO catalysts (14) and the rate constant for the overall exchange reactions (25, 26). There is

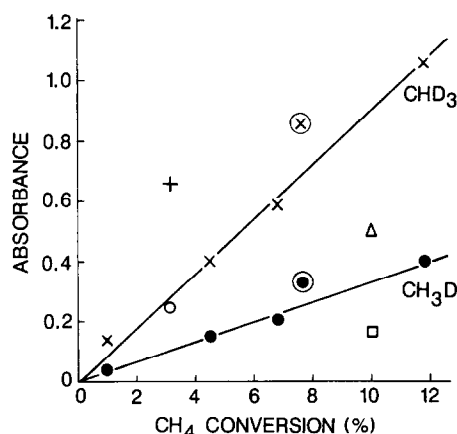


FIG. 2. Relationship between absorbance of exchanged methanes and methane conversion. CH<sub>3</sub>D: (●) Li/MgO; (○) SrCO<sub>3</sub>; (□) Sm<sub>2</sub>O<sub>3</sub>. CHD<sub>3</sub>: (×) Li/MgO; (+) SrCO<sub>3</sub>; Δ = Sm<sub>2</sub>O<sub>3</sub>. Circled points refer to experiment with second empty reactor.

also the possibility that the additional exchange occurs on the walls of the empty reactor.

Results for the distribution of the ethylenes in these experiments are given in Table 7. FTIR alone was used for these determinations as the MS signals for the relevant masses were overlapped by fragmentation peaks of the lighter ethanes and by CO. In the case of ethylene it is clear that although the relative distributions of C<sub>2</sub>H<sub>4</sub>, CH<sub>2</sub>CD<sub>2</sub>, and C<sub>2</sub>D<sub>4</sub> does not change significantly in these experiments, a substantial proportion of the ethylenes exchange to produce species other than the above. These species

TABLE 7

Distribution of Deuterium in Ethylenes from Reaction of Equimolar CH<sub>4</sub> and CD<sub>4</sub> over Various Catalysts (Conditions as per Table 4)

Catalyst	Temp. (°C)	C <sub>2</sub> H <sub>4</sub>	CH <sub>2</sub> CD <sub>2</sub>	C <sub>2</sub> D <sub>4</sub>	f(%) <sup>a</sup>	ethylene total C <sub>2</sub>
Li/MgO	750	2.3	4.0	1.0	68	0.28
	+780 <sup>b</sup>	2.3	4.0	1.0	63	0.42
Li/MgO	775	2.3	3.9	1.0	57	0.46
Sm <sub>2</sub> O <sub>3</sub>	600	nd	4.0	1.0	—	0.21

<sup>a</sup> *f* is the ratio of the sum of the concentrations of C<sub>2</sub>H<sub>4</sub>, CH<sub>2</sub>CD<sub>2</sub>, and C<sub>2</sub>D<sub>4</sub> (determined by FTIR) to the total ethylene concentration.

<sup>b</sup> Empty reactor experiment.

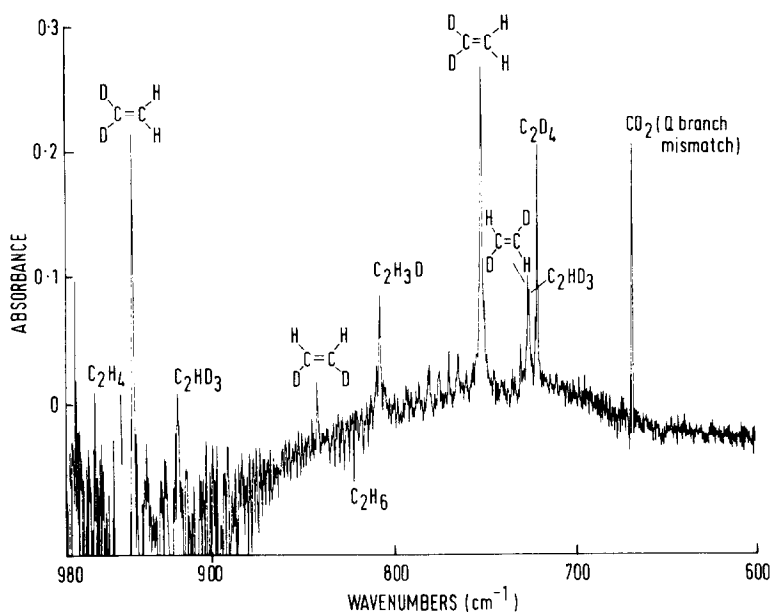


FIG. 3. FTIR difference spectrum: product gas from  $\text{CH}_4/\text{CD}_4/\text{O}_2$  mixture over Li/MgO at  $775^\circ\text{C}$  minus  $\text{CD}_4$  and  $\text{CO}_2$ .

have been identified on the basis of published studies of the IR spectra of deuterated ethylenes (24) and are shown in Fig. 3 for Li/MgO at  $775^\circ\text{C}$  where only 57% of the ethylenes could be accounted for by  $\text{C}_2\text{H}_4$ ,  $\text{CH}_2\text{CD}_2$ , and  $\text{C}_2\text{D}_4$ .

Previously we reported (16) that exchange in the ethylenes was also low and that the distribution of the ethanes and ethylenes was indistinguishable. This previous result was recalculated using the calibration for  $\text{CH}_2\text{CD}_2$  to show that 94% of the ethylenes could be accounted for by  $\text{C}_2\text{H}_4$ ,  $\text{CH}_2\text{CD}_2$ , and  $\text{C}_2\text{D}_4$ . The distribution of the ethylenes is clearly very close to that of the ethanes. However, under these conditions the ethylene to total  $\text{C}_2$  ratio was low (0.22). In the present experiments the ethylene to total  $\text{C}_2$  ratio is higher (0.28–0.46) and a much larger proportion of the ethylenes have exchanged.

In Fig. 4 the total concentrations of the ethylenes other than  $\text{C}_2\text{H}_4$ ,  $\text{CH}_2\text{CD}_2$ , and  $\text{C}_2\text{D}_4$  are plotted against the absorbance of  $\text{CH}_3\text{D}$  ( $1156\text{ cm}^{-1}$ ) and  $\text{CHD}_3$  ( $1036\text{ cm}^{-1}$ ) for experiments over Li/MgO. As these ex-

periments were all performed with 45%  $\text{CH}_4$  and 45%  $\text{CD}_4$  these absorbances are a direct measure of the concentration of the exchanged methane species. This plot in-

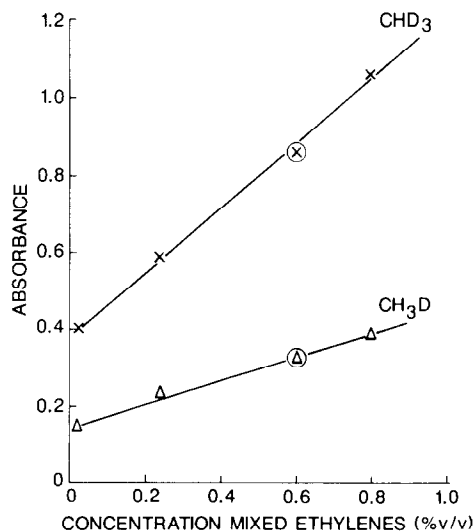


FIG. 4. Relationship between absorbance of exchanged methanes and concentration of exchanged ethylenes. (x)  $\text{CHD}_3$ ; ( $\Delta$ )  $\text{CH}_3\text{D}$ . Circled point refers to experiment with second empty reactor.

cludes the recalculated result reported previously (16) and the experiment with the second empty reactor. It is clear that there is a very close correlation between exchange in the methanes and the ethylenes and that this appears to be independent of the catalyst as the empty reactor data also fit. The relationship has a nonzero intercept implying that exchange is possible in the methanes unrelated to any exchange in the ethylenes. The fact that the correlation holds for the experiment with the second empty tube reactor suggests a purely gas-phase process. A possible candidate is



and analogous reactions with deuterium-containing compounds. If this equilibrates, the exchange in the methanes will correlate with exchange in the ethylenes.

Tests as to whether the exchange could proceed in the gas phase were carried out by feeding both  $\text{CH}_4/\text{CH}_3\text{CD}_3/\text{O}_2$  and  $\text{CH}_4/\text{CH}_2\text{CD}_2/\text{O}_2$  mixtures separately over Li/MgO and down empty alumina tubing. In all experiments with  $\text{CH}_3\text{CD}_3$ ,  $\text{C}_2\text{H}_6$  derived

from the  $\text{CH}_4$  was the only other ethane detected by FTIR and the concentration of  $\text{CH}_3\text{CD}_3 + \text{C}_2\text{H}_6$  accounted for  $100 \pm 5\%$  of the total ethane detected by GC. However, significant exchange occurred in the ethylenes, and in the empty tube experiment 18% of the ethylenes were exchanged. Figure 5 shows the FTIR difference spectrum for this empty reactor experiment analogous to Fig. 3 which was obtained over Li/MgO. The same exchanged ethylenes are evident. Significant quantities of  $\text{CH}_3\text{D}$  but no  $\text{CHD}_3$  were detected in these experiments. This is consistent with the postulated exchange reaction and shows that the exchanged methanes are not derived from  $\text{CH}_3$  (or  $\text{CD}_3$ ) from  $\text{CH}_3\text{CD}_3$  since  $\text{CHD}_3$  would then be observed. The experiments with  $\text{CH}_4/\text{CH}_2\text{CD}_2/\text{O}_2$  mixtures showed 14% exchanged ethylenes and  $\text{CH}_3\text{D}$  but no  $\text{CHD}_3$ . No deuterium-labeled products were detected in the ethanes.

Although these results are consistent with a purely gas-phase mechanism of exchange, they do not preclude the involvement of the surface. In particular, the de-

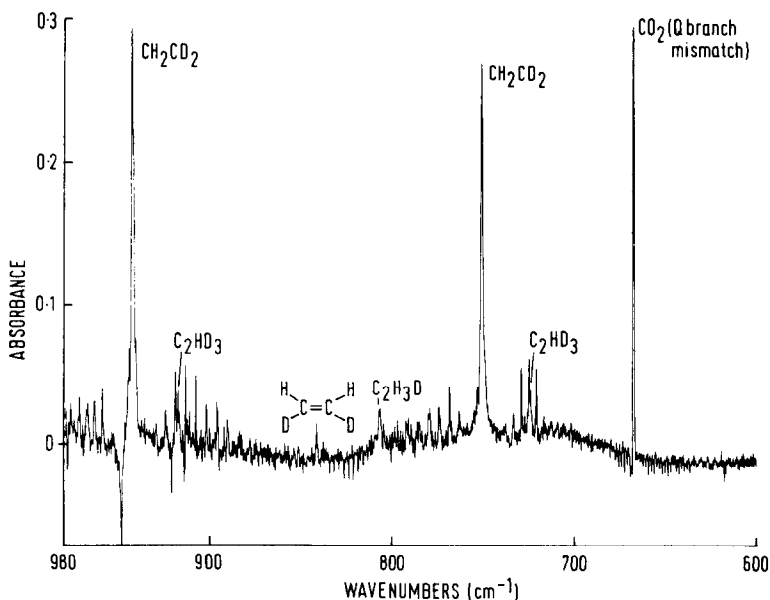


FIG. 5. FTIR difference spectrum: product gas from  $\text{CH}_4/\text{CH}_3\text{CD}_3/\text{O}_2$  mixture down empty alumina tube at  $780^\circ\text{C}$  minus  $\text{CO}_2$ .

tection of *cis*- and *trans*-CHDCHD in the products would require a hydrogen shift to occur and this, while possible in the gas phase, may be more facile on a surface. Nevertheless, the results do show unequivocally that ethane or the ethyl radical are not significantly involved since exchange is never observed in the ethanes.

(2) *Isotopic composition of the hydrogen.* The isotopic composition of the hydrogen was also determined in these experiments by mass spectrometry. The distribution should approach equilibrium if the mechanism of methyl radical formation and ethane to ethylene conversion is as described above. However, in isotopic transient experiments over a  $\text{Sm}_2\text{O}_3$  catalyst, the  $\text{D}_2$  formation rate was claimed to be substantially higher than that of HD and a molecular formation of hydrogen was postulated (27, 28).

The relative amounts of  $\text{H}_2$ , HD, and  $\text{D}_2$  produced in the experiments with the equimolar mixtures of  $\text{CH}_4$  and  $\text{CD}_4$  are given in Table 8. In each case the H/D ratio is in the range 1.5 to 2.0. This is consistent with either direct production of hydrogen (deuterium) from methane with an isotope effect or dehydrogenation of ethane. In the latter case no isotope effect need be assumed since the H:D ratio in the ethanes as a whole exceeds 1.5 due to the isotope effect in their production. The data indicate that HD is at equilibrium with  $\text{H}_2$  and  $\text{D}_2$  in each run although the accuracy of the on-line

TABLE 8

Distribution between  $\text{H}_2$ , HD, and  $\text{D}_2$  when Reacting Equimolar  $\text{CH}_4$  and  $\text{CD}_4$  over Various Catalysts (Conditions as per Table 4)

Catalyst	Temp. (°C)	Fraction of total			H/D	$\frac{[\text{HD}]^2}{[\text{H}_2][\text{D}_2]}$
		$\text{H}_2$	HD	$\text{D}_2$		
Li/MgO	680	0.39	0.48	0.13	1.7	$4.5 \pm 1.5$
Li/MgO	750	0.47	0.43	0.10	2.1	$4.1 \pm 1.5$
	+780 <sup>a</sup>	0.42	0.49	0.09	2.0	$6.2 \pm 2$
Li/MgO	775	0.44	0.45	0.11	2.0	$4.2 \pm 1.5$
SrCO <sub>3</sub>	800	0.37	0.51	0.12	1.7	$5.8 \pm 2$
$\text{Sm}_2\text{O}_3$	600	0.37	0.51	0.12	1.7	$5.8 \pm 2$

<sup>a</sup> Empty reactor experiment.

TABLE 9

Hydrogen-Deuterium Distribution in Products from Reaction of  $\text{CD}_4/\text{H}_2$  and  $\text{CH}_4/\text{CD}_4$  Mixtures over  $\text{SrCO}_3$  at 800°C

Reactant mixture <sup>a</sup>	Quantity in product stream (%)			$\frac{[\text{HD}]^2}{[\text{H}_2][\text{D}_2]}$	$\frac{\Delta\text{CHD}_3}{\text{CHD}_3 + \text{CD}_4}$
	$\text{H}_2$	HD	$\text{D}_2$		
$\text{CH}_4/\text{O}_2/\text{diluent}$	1.31	—	—	—	—
$\text{CH}_4/\text{O}_2/\text{H}_2/\text{diluent}$	3.91	—	—	—	—
$\text{CD}_4/\text{O}_2/\text{N}_2$	—	—	1.1 <sup>b</sup>	—	—
$\text{CD}_4/\text{O}_2/\text{H}_2/\text{diluent}$	0.78	1.85	1.47	3.0	0.028
$\text{CH}_4/\text{CD}_4/\text{O}_2/\text{N}_2$	0.59	0.50	0.13	3.3	0.050

<sup>a</sup> All with total methane ~56%,  $\text{O}_2$  ~ 11.5% plus either balance Ar or  $\text{N}_2$  or 3.8%  $\text{H}_2$  balance Ar or  $\text{N}_2$ . The distribution between chemical products was similar to the entry for  $\text{SrCO}_3$  in Table 4.

<sup>b</sup> Estimated from measurements under slightly different conditions.

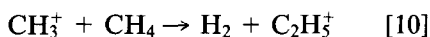
mass spectral analyses ( $\pm 10\%$  for each species) does not allow this to be established very accurately. The expected value for  $[\text{HD}]^2/[\text{H}_2][\text{D}_2]$  at 750°C is 4.2 by standard calculation using data from the tables of Burcat (29). The experimental values are not distinguishable from this.

If H (and D) are detached one at a time from  $\text{CH}_4$  (and  $\text{CD}_4$ ) one expects equilibrium on initial desorption. Alternatively equilibrium could arise by repeated exchange between initially nonequilibrated species (although it is difficult to see how the latter might arise). A test for the speed of hydrogen-deuterium exchange under reaction conditions was carried out over  $\text{SrCO}_3$  (the least active conversion catalyst studied here). This was done by including 3.8%  $\text{H}_2$  in a reacting mixture of  $\text{CD}_4$  and oxygen. The results are given in Table 9 together with those of a variety of control experiments and an experiment employing equal flows of  $\text{CH}_4$  and  $\text{CD}_4$  with the same total methane pressure. The  $[\text{HD}]^2/[\text{H}_2][\text{D}_2]$  ratio for the product of the latter is very close to that for the oxidation of the  $\text{CD}_4/\text{H}_2$  mixture. (The relative precision, but not the absolute accuracy, of these ratios is considerably better than for those of Table 7 since the runs were made one after the other using the same mass spectrometer calibra-

tion.) Thus it is certain that D<sub>2</sub> produced from CD<sub>4</sub> exchanges very rapidly with H<sub>2</sub>.

This result is not surprising since it has previously (30) been shown that SrO exhibits significant activity for CH<sub>4</sub>/D<sub>2</sub> exchange at 300°C. It was suggested that the exchange was initiated by the abstraction of an H<sup>+</sup> by basic sites on the catalyst.

The reason for the significantly different results obtained in this study compared to those reported previously (27, 28) for Sm<sub>2</sub>O<sub>3</sub> is probably due to the relatively large signal produced for *m/e* = 2 (or 4) with high concentrations of CH<sub>4</sub> (or CD<sub>4</sub>) in the mass spectrometer. The source of these signals is the well-known ion-molecule reaction



utilized in chemical ionization mass spectrometry. In support of this, relatively large signals were also observed for *m/e* = 29 (for C<sub>2</sub>H<sub>5</sub><sup>+</sup> when feeding CH<sub>4</sub>) and *m/e* = 34 (for C<sub>2</sub>D<sub>5</sub><sup>+</sup> when feeding CD<sub>4</sub>). Thus the signals at *m/e* = 2 and 4 must be corrected to obtain true H<sub>2</sub> and D<sub>2</sub> concentrations.

The data of Table 9 shows one additional feature which is at first sight rather curious. For each of the experiments in which no H<sub>2</sub> was added the combined amount of H<sub>2</sub>, HD, and D<sub>2</sub> produced is a little over 1% (1.3% with CH<sub>4</sub>, 1.1% with CD<sub>4</sub>, and 1.2% for CH<sub>4</sub> + CD<sub>4</sub>). However, the amount of deuterium derived from CD<sub>4</sub> in the experiment with added H<sub>2</sub> is equivalent to 2.3% D<sub>2</sub> which is much greater. The reason is H<sub>2</sub>/CD<sub>4</sub> exchange. As may be seen from the last column of Table 9, reaction was accompanied by an increase of 0.028 in the fraction of CHD<sub>3</sub> relative to CD<sub>4</sub> + CHD<sub>3</sub>. For 56% CD<sub>4</sub> in the feed this is equivalent to the formation of 1.6% HD or 0.8% D<sub>2</sub> which accounts for most of the additional amount noted above.

Two other points may be made concerning the data of Table 9. First, methane exchange as measured by the fractional increase in CHD<sub>3</sub> relative to CD<sub>4</sub> is much higher for the CH<sub>4</sub>/CD<sub>4</sub> mixture (0.050 with

both CH<sub>3</sub>D and CHD<sub>3</sub>) than with the CD<sub>4</sub>/H<sub>2</sub> mixture (0.028 with only CHD<sub>3</sub> formed). Given that the amounts of hydrogen/deuterium present are much less in the former experiment it is clear that these substances are not the dominant pool for exchange into methane. Some other source must be sought to explain the exchange data of Fig. 2 and Table 6. Secondly, it is clear that some of the H<sub>2</sub> introduced in some of the tests of Table 9 was itself reacted. In each case 3.8% was added and the expected yield from methane based on the controls was ~1.2%. The actual yields were less than the sum of these (3.9% for CH<sub>4</sub>/H<sub>2</sub> and 4.1% for CD<sub>4</sub>/H<sub>2</sub>). The difference is probably converted to water, some of which reacts further by the water-gas shift reaction with carbon monoxide, since the yield of the latter was somewhat reduced in those runs in which H<sub>2</sub> was added.

#### CONCLUSIONS

From experiments involving deuterium labeling of methane the following conclusions about the mechanism of oxidative coupling over Li/MgO catalysts may be made:

(i) *Kinetic isotope effects.* The overall kinetic isotope effect for CD<sub>4</sub> in place of CH<sub>4</sub> declines slightly with increase in temperature over the range 680 to 780°C. The kinetic isotope effect for the formation of ethane falls quite sharply to not much above unity once the ethylene to ethane ratio exceeds 1. The results confirm that C-H bond breaking is the rate-determining step over a wide temperature range.

(ii) *Selectivity differences with CD<sub>4</sub> in place of CH<sub>4</sub>.* Selectivities to hydrocarbons are lower with CD<sub>4</sub> than with CH<sub>4</sub> even when the flow rate with CD<sub>4</sub> is reduced to compensate for the higher rate with CH<sub>4</sub>. This implies that either CO<sub>x</sub> and C<sub>2</sub> products arise by totally separate slow steps or, if a common step with CH<sub>3</sub> is involved, then CO<sub>x</sub> formation occurs on the catalyst. Surface reactions of CH<sub>3</sub>O<sub>2</sub> radicals are a

possibility for the latter. A purely homogeneous chain reaction involving  $\text{CH}_3\text{O}_2$  is unlikely.

(iii) *Exchange with  $\text{CH}_4/\text{CD}_4$  mixtures.*

The dominant mixed products are always  $\text{CH}_3\text{CD}_3$  and  $\text{CH}_2\text{CD}_2$ . The distribution of the ethanes always reflects the relative concentrations of  $\text{CH}_3$  and  $\text{CD}_3$  determined by the isotope effect. Higher conversions produce more exchange into ethylene but not into ethane. The coupling of methyl radicals, therefore, is probably a purely homogeneous process. There is always some exchange between methanes (i.e.,  $\text{CH}_3\text{D}$  and  $\text{CHD}_3$  formation) at about the same rate as methane conversion, but from the results of experiments with  $\text{SrCO}_3$  and  $\text{Sm}_2\text{O}_3$  this is surface-dependent. Exchange in the ethylenes correlates with exchange in the methanes even in an empty reactor; thus gas-phase processes seem to contribute. The participation of homogeneous reaction is supported by the observation of exchanged ethylenes from reactions of  $\text{CH}_4/\text{CH}_3\text{CD}_3/\text{O}_2$  and  $\text{CH}_4/\text{CH}_2\text{CD}_2/\text{O}_2$  mixtures in empty reactors.

(iv) *Hydrogen-deuterium exchange.* The  $\text{H}_2$ :HD:D<sub>2</sub> ratios in the product stream using  $\text{CH}_4/\text{CD}_4$  mixtures are always at equilibrium. There is a large excess of H over D as expected from the kinetic isotope effect.

(v)  *$\text{CD}_4/\text{H}_2$  exchange.* H/D exchange also occurs when oxidizing  $\text{CD}_4/\text{H}_2$  mixtures; HD was produced in equilibrium amounts by exchange between the  $\text{H}_2$  and  $\text{D}_2$  derived from  $\text{CD}_4$  over a  $\text{SrCO}_3$  catalyst.

Results with  $\text{SrCO}_3$  and  $\text{Sm}_2\text{O}_3$  were more limited. They show that  $\text{SrCO}_3$  behaved similarly to Li/MgO although the kinetic isotope effect was less. The very high activity of  $\text{Sm}_2\text{O}_3$  prevented a measurement of the kinetic isotope effect by rate comparisons using  $\text{CD}_4$  in place of  $\text{CH}_4$ . However, it can be calculated from the  $\text{CH}_3\text{CD}_3/\text{C}_2\text{D}_6$  ratio from the experiment using 1:1  $\text{CH}_4/\text{CD}_4$  mixtures. For reaction at 600°C the kinetic isotope effect was similar to that for Li/MgO at 750°C. Even though oxygen

conversion was near total, little ethane or ethylene exchange took place.

#### ACKNOWLEDGMENTS

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