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OXIDATIVE DIMERIZATION OF CH_4/CD_4 MIXTURES: EVIDENCE FOR METHYL INTERMEDIATE

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Isotope tracer experiments prove the role of methyl in the oxidative coupling of methane and disprove a recently proposed mechanism involving methylene. The ethane product from oxidative coupling of CH_4/CD_4 mixtures over a Li/MgO catalyst consists of C_2H_6, C_2D_6 and CH_3CD_3 thus proving that ethane is formed by combination of methyl intermediates. The co-reaction of labelled CH_4 (D and ^{13}C) with C_2H_4 produces propylene labelled predominantly at the methyl (3) position, thus proving C_3 formation by terminal addition of methyl to ethylene rather than via a cyclic intermediate as has been proposed.

Many solid oxides are capable of catalyzing the oxidative coupling of methane to produce moderate yields of C_2 and small amounts of C_3+ hydrocarbons at high temperatures (> 650° C) [1–19]. Much mechanistic work supports the heterogeneous/homogeneous mechanism [1,3,5,7,10] of the reaction wherein a surface oxygen intermediate serves to abstract a hydrogen atom from methane,

$$\underline{O} + CH_4 \rightarrow \underline{OH} + CH_3 \tag{1}$$

and the primary product, ethane, is produced by condensation of two gas phase methyl radicals.

$$2CH_3 \rightarrow C_2H_6. \tag{2}$$

Gas phase radical chemistry appears to control the formation of ethylene and other higher hydrocarbon products [1,5,7,11]. Another mechanism has been recently proposed which claims that ethane is formed by reaction of CH_2 radicals with CH_4 [12].

$$CH_2 + CH_4 \rightarrow C_2H_6. \tag{3}$$

This conclusion is based on scavenging experiments with ethylene in which cyclopropane has been reported to form via the following reaction:

$$CH_2 + C_2H_4 \rightarrow \text{cyclo-}C_3H_6. \tag{4}$$

Many of the earlier mechanistic studies implicating methyl radicals, while convincing, were either obtained at conditions very different from those of the steady state reaction [10] or did not provide enough information (i.e. *in situ* CH_3 concentrations) [5] to prove the relationship between the ethane product and radical generation. Two recent studies have put the methyl mechanism of C_2 formation on firm ground. Campbell et al. have demonstrated agreement (to within a factor of 2) between methyl concentration profiles in the post-catalyst region and the C_2 formation rate [13]. Nelson et al. have recently published the results of the oxidative coupling of CH_4-CD_4 mixtures which found CH_3CD_3 to be the predominant isotopically mixed product [14]. This agrees with the methyl radical path since the direct methylene pathway predicts $C_2D_4H_2$ and $C_2D_2H_4$ to be the isotopically mixed products.

We have investigated the role of methyl in C_2 and C_3 hydrocarbon production during methane oxidative coupling by steady state isotopic tracing. In addition to a competitive CH_4-CD_4 experiment using detailed mass spectra in GCMS which corroborates the results in ref. [14] we demonstrate the role of methyl in C_3 formation co-reaction of labelled methane ($^{13}CH_4$ or CD_4) with C_2H_4. Propylene labelled at the methyl position should result if the reaction proceeds by methyl addition to ethylene. If cyclopropane is formed as reported in ref. [12], the labels will be isotropically distributed.

For this study we used a lithium-magnesia catalyst prepared according to the recipe given by Lunsford [7]. The catalyst contained 7% Li by weight ($Li/Mg = 0.4$). The calcined powder was pelletized, crushed and sieved to yield 80–120 μm particles. The reactor was a small (6 mm od) quartz tube reactor which tapered to a small (1 mm) bore after the catalyst bed to minimize post-bed gas residence time [11]. The behavior of the catalyst was equivalent to that reported by other workers [7]. The products were examined at low conversion to minimize scrambling and secondary reactions.

ETHANE FORMATION

We used two CH_4/CD_4 ratios in these experiments. The conditions and productivities are given in table 1. The catalyst in Experiment A had been in the reactor for several weeks and the C_2 selectivity had degraded from an initial value near 60% to the 29% value shown. Experiment B was performed with a catalyst which had been under reaction conditions only 5 hours. The rates and selectivities also depend on the isotopic composition of the gas as has been reported by Cant et al. [15]. Samples of the product gas from these experiments were trapped and analyzed by GCMS. Mass spectra were obtained with 40 eV electrons except for investigation of the C_1 ions from methane, where the energy was decreased to 25 eV. The CD_4 was purchased from MSR Research and contained 2.6% CD_3H. The methane at the reactor exit contained approximately this same amount of CD_3H, showing that isotopic scrambling in the methane reactant is negligible during the experiments.

Table 1
Conditions for CH_4-CD_4 experiments

	Experiment	
	A	B
$CH_4/(CD_4+CH_4)$	0.61	0.33
Temperature, °C	715	730
Methane/O_2/Ar	2:1:5	2:1:6
Catalyst wt, g	0.18	0.24
Total flow, Std cm^3/min	90	80
Methane conversion	0.058	0.054
Selectivity		
CO	0.06	0.05
CO_2	0.65	0.34
C_2H_4	0.04	0.09
C_2H_6	0.25	0.52

The concentrations of $C_2D_xH_{6-x}$ in the ethane product determined by GCMS are shown in fig. 1. GCMS removes interference from the mass spectra of the other products. The data show the dominant products to be C_2H_6, CH_3CD_3, and C_2D_6. Good fits to the ethane C_2 ion distribution for both experimental conditions were obtained with ethane isotopomer distributions shown in the first panel [16]. The concentrations of $C_2D_xH_{6-x}$ ($x = 6$, 5, 4 and 3) are quite well determined because little interference arises from the predominant ethylene ions of the more highly deuterated products. It is also possible to identify the 1, 1, 1 D_3 ethane as the trideuterated product over the 1, 1, 2 isotopomer since the predominant 1, 2 hydrogen loss feature to form the ethylene ion produces quite different 30^+ and 31^+ intensities for the two molecules [17–19]. The concentrations of $x = 2$, 1, 0 are less certain because of the accumulated uncertainties associated with the ethylene ions from the more highly deuterated products and rough upper limits on $x = 1$, 2 concentrations consistent with the mass spectral data are indicated in the figure. However, since the amounts of D_4 and D_5 ethanes are very small (the small yield of D_5 ethane is approximately that expected from the CD_3H impurity) it is unlikely that more than 2–3% of the product consists of D_1 and D_2 ethanes.

This product distribution is verified by the ethane-derived C_1 ion spectrum shown in fig. 1b. At the electron energy used to obtain this spectrum (25 eV) the C_1 ions are exclusively methyl ($CH_2^+/CH_3^+ < 0.005$ in C_2H_6). These methyl ions contain information about the composition of the methyl groups in the original molecules [16,17] with CD_3^+ and CH_3^+ dominating the methyl spectrum from CH_3CD_3. Smaller, energy invariant yields of mixed methyl ions arise from intramolecular rearrangements during ionization [19]. The methyl ion spectrum predicted from the ethane distribution in fig. 1a is in excellent agreement with the data and is shown in 1b [20]. Any mixed methyl groups in the ethane would

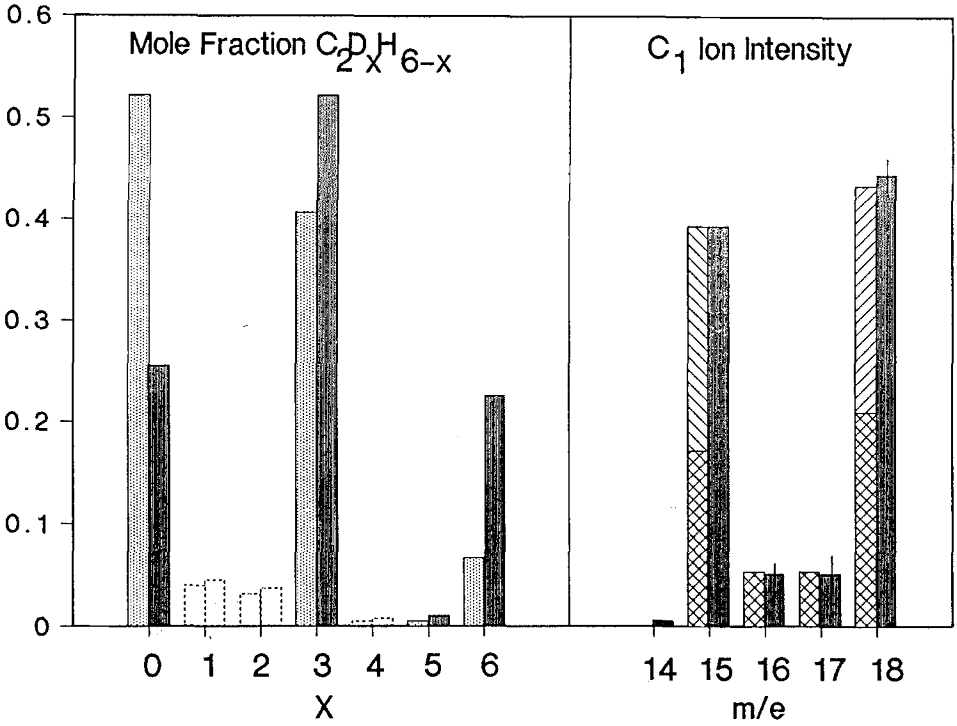

Fig. 1. Mass spectral results showing the isotopic composition of ethane from the coupling of CH_4/CD_4 mixtures. *Panel a*. Distribution of isotopomers determined from mass spectral results at two CH_4/CD_4 ratios. Expt A, $CH_4/CD_4 = 1.56$; Expt B, $CH_4/CD_4 = 0.50$. Dashed bars represent maximum concentrations consistent with the data. *Panel b*. C_1 ion spectrum of ethane produced from expt B. ion intensities measured at 25 eV; Second set of bars are a simulation using the distribution in panel a and measured fragmentation patterns. contribution from C_2H_6, contribution from C_2D_6, contribution from CH_3CD_3. Vertical lines on the data bars represent experimental uncertainties (one standard deviation).

produce significantly higher intensities at mass 16 and 17. Thus the ethane product consists of at least 95% CH_3 and CD_3 groups, in agreement with the methyl radical mechanism and in contradiction to the methylene mechanism. Clearly the data are consistent with recombination of surface methyl groups as well [4].

The isotope effect previously reported [15] for methane activation is evident in our results. Table 2 compares the CH_3/CD_3 ratios in the products to the CH_4/CD_4 ratios in the reactants and shows CH_3 to be enriched by a factor of approximately 1.75 in the ethane product in this competitive experiment. These values are in excellent agreement with the value of 1.75 obtained by comparing the relative rates *of hydrocarbon formation* in isotopically pure methanes [15]. The measured isotope effect reflects not only the probability of formation of the two methyl isotopomers, but also their relative success in forming C_2 products and

Table 2
Isotope effect

Expt [a]	CH_4/CD_4	CH_3/CD_3	Isotope effect
A	0.61/0.39	0.73/0.27	1.73+0.15
B	0.33/0.67	0.47/0.53	1.77+0.15

[a] Experimental conditions in table 1.

can be influenced by relative rates to form other products and thus to experimental conditions. In this competitive experiment exchange processes such as

$$CH_3 + CD_4 \rightarrow CD_3 + CH_3D \tag{4}$$

and

$$CD_3 + CH_4 \rightarrow CD_3H + CH_3 \tag{5}$$

would be expected to further enrich CH_3 because of an isotope effect favoring reaction [5]. Preliminary calculations using literature rate constants for these gas phase reactions indicate that they are not fast enough under our conditions to significantly affect the methyl isotope distribution. The agreement between the competitive experiment here and the results in ref. [15] implies little alteration of the nascent CH_3/CD_3 by reactions (4) and (5). However there is some disagreement between our isotope effect and the value of 1.4 derived from the IR results in ref. [14] for their competitive experiment. The origin of the discrepancy between the two studies is unclear. We note that different CH_4/O_2 ratios and somewhat different temperatures were used in the two studies so that different reaction conditions could be responsible for the difference in measured values. Despite our use of standards and the internal consistency of our C_1 and C_2 ion results, there is still an estimated +10% uncertainty in our measurements, due in part to the absence of partly deuterated standards. We also note some uncertainty in the results of ref. [14], however, in that the CH_3CD_3 concentrations in the IR experiment were obtained by difference. Furthermore, although these authors acknowledge uncertainty in their MS results, their $C_2H_3D_3/C_2D_6$ ratio derived by MS is 50% higher than that derived from IR. The finer details of kinetic isotope effects in this reaction obviously require further study. The concentrations in fig. 1a agree to within experimental error with the binomial distributions predicted by random combinations of the CH_3 and CD_3 groups, showing that the distribution has not been significantly altered by secondary reactions with kinetic isotope effects (e.g. further oxidation of ethane).

PROPYLENE FORMATION

Ethylene addition to a methane-oxygen mixture under reaction conditions results in an increase in C_3+ hydrocarbon production. The conditions for our

Table 3
Conditions for $*CH_4$-C_2H_4 experiment

Experiment	Base	Ethylene addition
Temperature °C	702	–
Catalyst wt, g	0.26	–
Reactant flow rates, μmol/sec		
CH_4	13.5	13.5
O_2	6.7	6.7
Ar	33.7	33.7
C_2H_4	0.00	5.5
Product flow rates, μmol/sec		
CO	0.044	0.22
CO_2	0.099	0.25
C_2H_4	0.014	5.5
C_2H_6	0.12	0.11
C_3	0.0009	0.047

experiment are shown in table 3. The addition of 8% ethylene in the reactant gas produces approximately a 50-fold increase in C_3 production so that the product arising from the added ethylene dominates that produced from methane alone. In the tracer experiment labelled methane ($^{13}CH_4$ or CD_4) is introduced and the resulting product is trapped and separated into carbon number fractions by GC. The isotope distribution in these labelled fractions is determined by NMR in a manner similar to that previously used in isotope transient studies of hydrocarbon synthesis [21].

The results for the C_3 fraction are summarized in table 4. The significant results are the following:

(1) The product consists solely of propene (86%) and propane (14%) – no cyclopropane was detected (< 1% of the C_3 product).

(2) The distribution of ^{13}C in the product is highly asymmetric with none detected at the 2-position of either propene and propane. This result rules out a cyclic intermediate in which all carbons are identical.

Table 4
C_3 Isotopic compositions in $*CH_4$-C_2H_4 experiment

	Intramolecular position				
	Propylene			Propane	
	$CH_2=$	$CH-$	CH_3	$(CH_3)_2-$	CH_2
^{13}C Fraction [a]	0.13	0.00	0.81	0.49	0.01
$^2D_1$ Fraction [b]	0.08	0.00	0.76	0.44	0.00

[a] Ethylene addition conditions in table 3 with $^{13}C(99+\%)$ methane, corrected for natural abundance. Values +0.02.

[b] Ethylene addition conditions in table 3 with D-4(99+%) methane. Values +0.05.

(3) Methane is the predominant source of the carbon in the propene methyl group, a fact consistent with the methyl + ethylene pathway. The correspondingly small amount of ^{13}C at the 1-position is explained by a 1, 3 hydrogen shift in the nascent propyl radical prior to beta-elimination of hydrogen to form propylene.

$$\begin{tikzcd}
{*CH_3 + C_2H_4} \arrow[r] & {*CH_3CH_2CH_2} \arrow[r, "-H"] \arrow[d, "1,3"'] & {*CH_3CH{=}CH_2} \\
 & {*CH_2CH_2CH_3} \arrow[r, "-H"] & {*CH_2{=}CHCH_3}
\end{tikzcd} \qquad (6)$$

A similar hydrogen tracing experiment in which CD_4 and C_2H_4 are reacted at these conditions shows that the hydrogen from methane is also retained predominantly at the 3-position. The proton NMR intensities show the methyl group to be 75–80% deuterated and the 1-position is 10–15% deuterated. Thus the retention of hydrogen at the methyl position is very similar to that observed in the carbon tracing experiment, indicating little disruption of the original C-H(D) bonds in the methyl fragment except for the 1,3 shift noted above.

A minor, but experimentally significant, mismatch between the isotopic contents at the 1- and 3-positions is evident in the data from both the hydrogen and carbon tracer experiments. There is more methane-derived hydrogen and carbon at the 1-position than is missing from the 3-position: a balance between these is required by the 1,3 hydrogen shift mechanism. Several sources of this effect are plausible and include selective hydrogen exchange at the methyl position or, more likely, a minor indirect pathway for C_3 production. A more detailed report of the tracing of secondary reactions in methane oxidative coupling will be published separately.

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