

Unusual Deuterium Isotope Effect in the Oxidative Coupling Reaction of Methane over a Samarium Oxide Catalyst

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The oxidative coupling reaction of methane over various metal oxide catalysts has attracted much interest and speculation on plausible reaction mechanisms.¹ We have recently shown² that the addition of small amounts of C₂H₆ to the reactants using Sm₂O₃ catalysts at 700 °C resulted in no significant change in the total CO_x formation, but in a substantial reduction in the net CH₄ conversion. Use of ¹³C₂H₆ also showed that under these conditions a large part of the total CO_x formed was derived from the added ¹³C₂H₆.

We now report that the replacement of ¹³C₂H₆ by ¹²C₂D₆ in similar experiments results in an unusually large effect on the net CH₄ conversion and on the products formed from the CH₄ and the additives. The data confirm the conclusions reached in our previous work,² illustrate the dramatic effect that small disturbances in reaction rates have on the product distribution, and suggest that the interpretation of isotope effects in these systems may be more complex than previously thought.

An isotope switching apparatus similar to that described previously² was used. However, for these experiments a GC/MS system was employed to permit the quantitative analysis of exit gas as well as the isotopic composition (i.e., ¹³C and D content) of the reaction products CO, CO₂, C₂H₆, and C₂H₄. For a typical experiment, CH₄ (3800 μmol s⁻¹ g⁻¹), O₂ (590 μmol s⁻¹ g⁻¹), and ¹²C₂H₆ (75–300 μmol s⁻¹ g⁻¹) were passed over Sm₂O₃ catalyst at 700 °C. The ¹²C₂H₆ was then replaced by a 30–120-s pulse of either ¹³C₂H₆ or ¹²C₂D₆. A full exit gas analysis was performed halfway during the pulse. For experiments with C₂D₆, ¹³CH₄ was used to allow tracing the origin of carbon oxides. The ¹²C₂H₆ in the inlet stream was subsequently replaced with an equivalent flow of He to obtain the reference reading. Under the reaction conditions employed, both the empty reactor effect and ¹³C/¹²C isotope effect were found to be negligible.

The addition of ethane to the feed reduced the CH₄ conversion³ as found earlier,² but a much larger effect was observed on addition of ¹²C₂D₆ to ¹³CH₄ (Figure 1). The addition of He under these conditions resulted, as expected, in only a minor decrease in CH₄ conversion due to the dilution of the reactants.

A comparison of the effects of ¹³C₂H₆ and ¹²C₂D₆ on the reaction products shows (Table I) large ¹²C₂D₆/¹³C₂H₆ effects on (i) the C₂H₆ and C₂H₄ formation from CH₄, (ii) the conversion of the added ¹²C₂D₆ and ¹³C₂H₆ to ethylene and CO_x, and (iii) the CH₄ and O₂ consumption. An interesting aspect of the results is that the total CO_x formation, i.e., the sum of that derived from the CH₄ and the additive, is virtually constant for all experiments, the addition of the additives resulting only in a change in the origin of the CO_x products. This observation again suggests that the

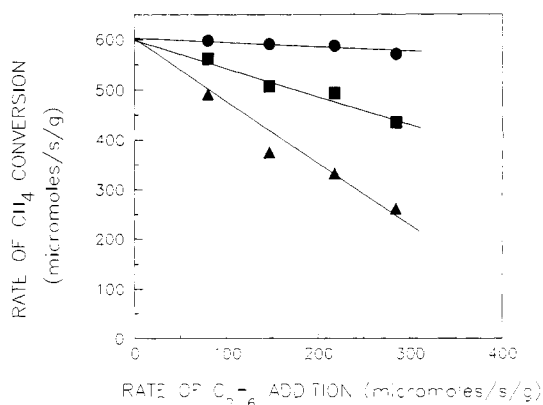


Figure 1. Effect of added He and C₂H₆ on the total CH₄ conversion: ●, ¹²CH₄/He; ■, ¹²CH₄/¹³C₂H₆; ▲, ¹³CH₄/¹²C₂D₆.

Table I. Comparison of the Effects of the Addition of He, ¹³C₂H₆, and ¹²C₂D₆ on the Oxidative Coupling Reaction^a

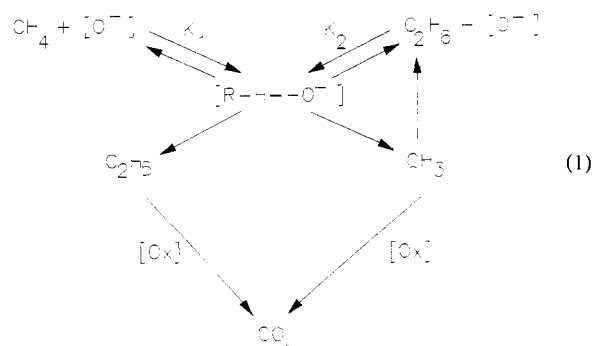
compd	rate of formation or consumption, μmol s ⁻¹ g ⁻¹ catalyst				
	A1 ¹² CH ₄	B1 ¹² CH ₄	B2 ¹³ C ₂ H ₆	C1 ¹³ CH ₄	C2 ¹² C ₂ D ₆
CO	87	64	45	38	14
CO ₂	118	66	45	162	18
CO _x	205	130	96	201	35
C ₂ H ₄	81	59	89	6	21
C ₂ H ₆	101	93		24	
-CH ₄	571	435		261	
-C ₂ H ₆			138		40

^a Column A1 summarizes the rates of formation of products derived from the CH₄ in the presence of He as the additive. Columns B1 and C1 contain the rates of the products formed from the CH₄ in the presence of added ¹³C₂H₆ and ¹²C₂D₆, while B2 and C2 contain the appropriate rates of the formation of products derived from these additives. Conditions: Sm₂O₃ catalyst, 700 °C, 13.8 vol % O₂, 6.5 vol % (285 μmol s⁻¹ g⁻¹) He, ¹³C₂H₆ or ¹³C₂D₆ addition.

formation of CO_x is determined by the availability of the oxidant, not the reductant.²

The above are clearly not just simple *primary* isotope effects and are probably better interpreted as a reflection on a system of delicately balanced reaction rates whose minor disturbance results in disproportionately large effects in the final products.⁴ This is clearly suggested by the observation that while the overall D/H isotope effect on the slopes of the appropriate data in Figure 1 is 2.3, the corresponding ratio in the C₂H₄ formation from CH₄ is almost 10, but only 4 for the ratio of C₂H₄ derived from the additive.

While the interpretation of these results is complicated by the necessity of obtaining the data under integral reactor conditions, they appear to be consistent with a reaction mechanism similar to mechanism 1, in which Ox is an oxidizing species, either in the



(4) For example, since the C₂H₆ from the CH₄ is formed by the gas-phase dimerization of the primary CH₃, its formation rate may change according to the square of the CH₃ radical concentration. See also: Thibbin, A.; Ahlberg, P. *Chem. Soc. Rev.* 1989, 18, 209.

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(3) The CH₄ conversion was calculated as [CO_x + 2(C₂H₆ + C₂H₄)] having the same carbon isotopic composition as the feed CH₄.

gas phase or on the catalyst surface, which is not molecular oxygen.² This mechanism requires (i) an equilibrium of $[O^-]$ with simple alkanes to form the surface species $[R-H-O^-]$, (ii) the value of the appropriate equilibrium constants to be in the order $C_2D_6 > C_2H_6 > CH_4$, (iii) that the CH_3 or C_2H_5 radicals formed by the $[O^-]$ site are the precursors of CO_x , and (iv) that the direct oxidation of CH_4 , C_2H_6 , C_2H_5 , or CH_3 by molecular gas-phase O_2 is not kinetically important under the chosen reaction conditions. In this mechanism, the reduction in the CH_4 conversion on addition of the C_2H_6 , and the switch in the origin of the CO_x from the CH_4 to the additive, are initiated by the competition in ii above.

A full analysis of these and other similar results will be presented elsewhere. It appears, however, that the above results could complicate the analysis of isotope replacement experiments which have been interpreted⁵ as showing that the rate-determining step of the oxidative coupling reaction was the rupture of the C-H bond of the CH_4 molecule. This conclusion was in contrast to other evidence,² which suggested that the rate of lattice oxygen exchange (and hence the formation of the active species $[O^-]$) was rate determining.

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Water-Free Self-Assembly of Phospholipid Tubules

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The rationale for synthetic modification of biological lipids, such as lecithins, to include polymerizable groups such as diacetylenes,¹⁻⁵ methacrylates, vinyl groups, and thiols⁵ is to design and create inherently stable, polymerizable, self-assembling microstructures. The polymerization of these moieties has been shown to alter functional properties of these microstructures including changes in permeability and to enhance stability to extremes in temperature or hydration.⁶ The synthetic modification of lecithins has also been found to result in the formation of microstructures with unique morphologies and functional properties.^{2,8} One such assembly is the formation of hollow cylinders (or tubules) from the diacetylenic phosphatidylcholines.⁷ Tubules are typically 5–150 μ m in length, with a 0.5- μ m core surrounded by two to seven bilayers.

The sequestering of nonpolar moieties of biological amphiphiles from water is thought to be an important driving force for self-assembly into supramolecular structures.⁹ We have discovered

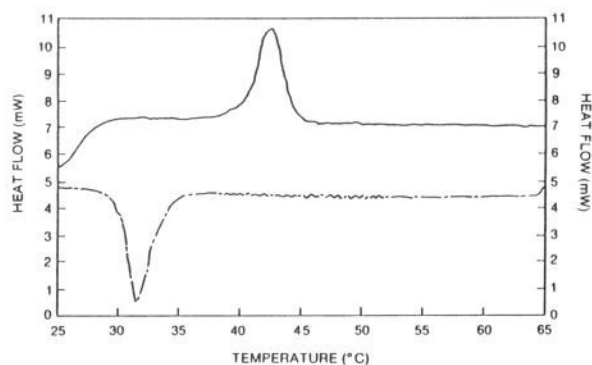


Figure 1. Calorimetric trace of heating and cooling of the diacetylenic phosphatidylcholine, 1,2-di-10,12-tricosadiynoyl-*sn*-glycero-3-phosphocholine in acetonitrile. The transition temperature on heating was observed at 42.5 °C upon heating with an enthalpy of 17.8 kcal/mol. Cooling revealed an exothermic event at 31.5 °C with an enthalpy of 18.9 kcal/mol. All experiments were performed at a scan rate of 1 °C/min and sample weights determined by gravimetric analysis before and after loading of a pan with the solution of lipid and acetonitrile in a glove box purged with dry nitrogen.

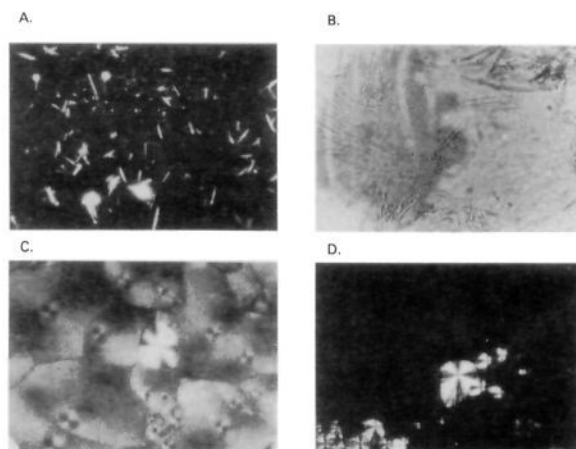


Figure 2. (a) Dark-field optical micrograph of tubules formed in acetonitrile taken from the DSC pan. Note the pieces of incompletely formed tubules and material that appears nontubular. Magnification = 125 \times . (B) Light-field optical micrograph of longer tubules (30–50 μ m) formed on the thermal stage in acetonitrile. Magnification = 125 \times . (C) Light-field optical micrograph under cross polarization of spherulites and focal domains of $DC_{8,9}PC$ in dry acetonitrile. (d) Dark-field micrograph of spherulites formed in the DSC pan. Magnification = 125 \times . In these experiments, dry lipid was dissolved in dry acetonitrile at 50 °C and vortexed. An aliquot of this solution was then pipetted onto a glass slide and sealed with a glass coverslip.

that the self-assembly of tubules does not depend on the presence of bulk water. The inherent self-assembly of this lipid into lamellar structures in the absence of bulk water is also manifest by the observation of spherulitic structures (with uniaxial symmetry). The observation that self-assembly of this lecithin will occur in the absence of water may have important technological implications in the development of these microstructures for use in organic solvents and under controlled environmental conditions.

The polymerizable phosphatidylcholine we have studied, 1,2-di-10,12-tricosadiynoyl-*sn*-glycero-3-phosphocholine, has two diacetylenic groups at the C10 and C12 positions along the fatty acyl chains.³ The diacetylenes will polymerize when exposed to UV light, resulting in a polymer with variable conjugation length.³ Previous spectroscopic and calorimetric studies led us to believe that bulk water may not be required for the formation of tubules.^{7,11-13} We therefore chose acetonitrile for these studies, an

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