DOI: 10.1002/anie.200906518

Activation of Methane by Gaseous Metal Ions**

Detlef Schröder*

C–C coupling · C–H activation · gas-phase reactions ·
metal ions · methane

Methane is one of the most ubiquitous feedstocks available in large amounts from petrological as well as biogenic resources. Its economic use for purposes other than mere combustion remains a conceptual problem, however. Steam reforming converts methane into syngas [Eq. (1)] from which methanol can be produced in a second step [Eq. (2)]; the CO:H_2 ratio of the syngas can be adjusted by the water–gas-shift reaction.[1] While the technology of this process is well developed, investment volumes are large and smaller sources of methane cannot be exploited this way.

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \qquad (1)$$

$$CO + 2\,H_2 \rightarrow CH_3OH \qquad (2)$$

Considerable research efforts are devoted to alternative routes and a particularly attractive variant would be the selective partial oxidation of methane according to Equation (3). Methanol as a liquid, easily transportable, and chemically versatile product offers several advantages and it has even been suggested as the basis of future energy economy.[2] While easily written on paper, Equation (3) poses quite a formidable challenge, because methane is the least reactive of all hydrocarbons and hence needs a highly reactive catalyst for activation, whereas methanol can easily be oxidized further, ultimately leading to complete combustion. The selective functionalization of methane has accordingly received quite some attention in condensed-phase research and several promising systems have been developed,[3] though they are still far away from practical applications.[4]

$$CH_4 + {}^1\!/_2\,O_2 \rightarrow CH_3OH \qquad (3)$$

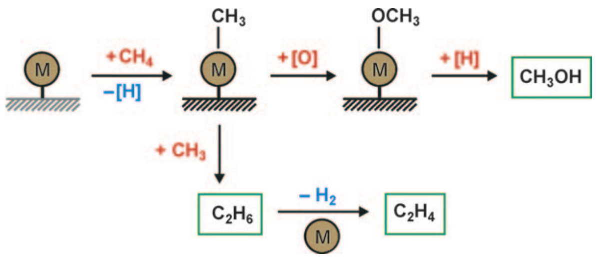
An alternative approach to achieve a fundamental understanding into the requirements for the C–H bond activation of methane are model studies of small reactive fragments in the gas phase.[5,6] In this area, interesting progress has been achieved recently. In 2006 it was reported that methane could be activated by MgO^+, the first main-group metal oxide cation to do this,[7] and by $V_4O_{10}^+$, the first metal oxide cluster.[8] Shortly afterwards $(Al_2O_3)_n^+$ ($n = 3$–5) was reported as the first oxide clusters of a main-group metal to activate methane;[9] also methane activations by non-metallic elements have been found more recently.[10] Most of these reactions are driven by the radicaloid nature of the oxide cations with the spin mostly located on oxygen, which leads to a high preference for hydrogen-atom abstraction from methane to generate methyl radicals. This situation is in contrast to the dehydrogenation of methane by various 5d elements to give metal carbenes MCH_2^+,[6,11] or MCH_2^{2+},[6,12] and to the C–C coupling reactions with methane observed for medium-sized hydrocarbon dications,[13] in which the dehydrogenation takes place with the "CH_2" fragment remaining at the ionic species.

To date, nearly all the bare metal cations M^+ have been screened experimentally with respect to their reactivity towards methane.[6,14] Bare metal cations are, however, an extreme simplification in comparison to real catalysts and in this respect the investigation of gaseous metal clusters is of prime interest.[15] While platinum clusters in various charge states have been shown to activate methane,[16,17] to date, gold clusters, like most other $M_n^{+/-}$ ions, were considered to be unreactive towards methane.[18]

The C–H bond activation of methane is, however, only the first step. The second task is to selectively convert the (free or bound) methyl radical into useful products (Scheme 1), for example, through the C–O coupling with a suitable oxidant to afford methanol [Eq. (3)]. Alternatively, C–C coupling of two methyl entities can lead to ethane which may then be converted into the basic chemical ethene [Eq. (4)].

$$2\,CH_3 \rightarrow C_2H_6 \rightarrow C_2H_4 + H_2 \qquad (4)$$

In this respect, Lang et al. report in this issue that isolated Au_2^+ cluster cations can mediate a C–C coupling of methane



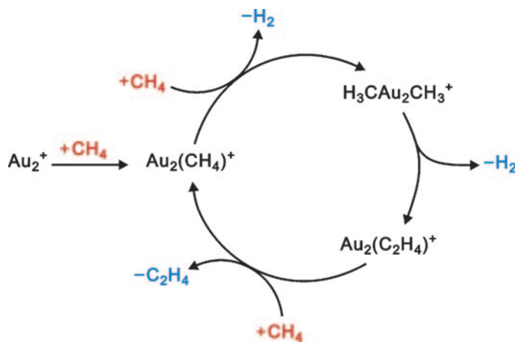
Scheme 1. C–H bond activation of methane and subsequent C–O or C–C coupling.

---

[*] Dr. D. Schröder
Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic
Flemingovo náměstí 2, 16610 Prague 6 (Czech Republic)
E-mail: schroeder@uochb.cas.cz

[**] This work was supported by the Academy of Sciences of the Czech Republic (Z40550506) and the European Research Council (AdG HORIZOMS).

to afford ethene.[19] To this end, they used an ion trap, which—simply put—is the gas-phase chemist's equivalent of a chemical reactor. Specifically, mass-selected Au_2^+ ions (approximately 10^6 ions) were trapped for hundreds of milliseconds in CH_4:He mixtures at pressures of about 1 Pa and temperatures between 200 and 300 K. By careful investigation of the reaction kinetics and the effects of temperature in combination with an exhaustive theoretical study, a catalytic cycle for the dehydrogenative coupling of methane to give ethene could be established (Scheme 2). In addition to the phenomenological description of the processes observed, Lang et al. quantitatively modeled the observed product distribution and thereby derived essential thermodynamic and kinetic parameters.



Scheme 2. Simplified representation of the catalytic cycle for the C–C coupling of methane to ethene realized by Lang et al.[19]

Several aspects of this work are remarkable:

1) Unlike most other gas-phase studies, relatively high pressures are applied, that is, a multicollisional regime is explored which enables the stabilization of reaction intermediates as well as the occurrence of endothermic reactions at increased reaction times.
2) The results illustrate a methane coupling occurring at ambient temperatures, and the analysis of kinetic profiles as a function of temperature provides deep mechanistic insight including the estimation of activation energies.
3) In the multicollisional mechanism, methane plays a crucial role not only as the reactant, but also as a ligand which can replace the product ethene associated to the Au_2^+ species.

These aspects are of particular relevance with regard to the so-called pressure gap,[20] which often hampers the translation of model studies to real catalysis. In their recent work, Lang et al. indeed manage to bridge this gap at least partially. Their study may thus be considered as an important step in basic research towards the understanding of catalytic cycles, which may also bear practical relevance.

Received: November 19, 2009

---

[1] J.-P. Lange, *Catal. Today* **2001**, *64*, 3 – 8.
[2] G. A. Olah, A. Goeppert, G. K. S. Prakash, *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH, Weinheim, **2006**.
[3] a) R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560 – 564; b) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507 – 514; c) M. Lersch, M. Tilset, *Chem. Rev.* **2005**, *105*, 2471 – 2526.
[4] J. A. Labinger, *J. Mol. Catal. A* **2004**, *220*, 27 – 35.
[5] D. K. Böhme, H. Schwarz, *Angew. Chem.* **2005**, *117*, 2388 – 2406; *Angew. Chem. Int. Ed.* **2005**, *44*, 2336 – 2354.
[6] For methane and small alkanes, see: a) D. Schröder, H. Schwarz, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 18114 – 18119; b) M. Schlangen, H. Schwarz, *Dalton Trans.* **2009**, 10155 – 10165; c) J. Roithová, D. Schröder, *Chem. Rev.*, **2010**, *110*, DOI: 10.1021/cr900183p.
[7] a) D. Schröder, J. Roithová, *Angew. Chem.* **2006**, *118*, 5835 – 5838; *Angew. Chem. Int. Ed.* **2006**, *45*, 5705 – 5708. See also: b) A. Bozovic, D. K. Bohme, *Phys. Chem. Chem. Phys.* **2009**, *11*, 5940 – 5951.
[8] S. Feyel, J. Döbler, D. Schröder, J. Sauer, H. Schwarz, *Angew. Chem.* **2006**, *118*, 4797 – 4801; *Angew. Chem. Int. Ed.* **2006**, *45*, 4681 – 4685.
[9] S. Feyel, J. Döbler, R. Hockendorf, M. K. Beyer, J. Sauer, H. Schwarz, *Angew. Chem.* **2008**, *120*, 1972 – 1976; *Angew. Chem. Int. Ed.* **2008**, *47*, 1946 – 1950.
[10] a) BF_2^+: F. Pepi, A. Tata, S. Garzoli, M. Rosi, *Chem. Phys. Lett.* **2008**, *461*, 21 – 27; b) $P_4O_{10}^+$: N. Dietl, M. Engeser, H. Schwarz, *Angew. Chem.* **2009**, *121*, 4955 – 4957; *Angew. Chem. Int. Ed.* **2009**, *48*, 4861 – 4863; c) SO_2^+: G. de Petris, A. Troiani, M. Rosi, G. Angelini, O. Ursini, *Chem. Eur. J.* **2009**, *15*, 4248 – 4252; d) As^+, Se^+: X. Zhang, H. Schwarz, *Chem. Eur. J.* **2009**, *15*, 11559 – 11565.
[11] K. K. Irikura, J. L. Beauchamp, *J. Am. Chem. Soc.* **1991**, *113*, 2769 – 2770.
[12] L. G. Parke, C. S. Hinton, P. B. Armentrout, *J. Phys. Chem. A* **2008**, *112*, 10469 – 10480, and references therein.
[13] a) C. L. Ricketts, D. Schröder, C. Alcaraz, J. Roithová, *Chem. Eur. J.* **2008**, *14*, 4779 – 4783; b) J. Roithová, C. L. Ricketts, D. Schröder, *Int. J. Mass Spectrom.* **2009**, *280*, 32 – 37.
[14] A. Shayesteh, V. V. Lavrov, G. K. Koyanagi, D. K. Bohme, *J. Phys. Chem. A* **2009**, *113*, 5602 – 5611.
[15] a) G. E. Johnson, E. Tyo, A. W. Castleman, Jr., *Proc. Natl. Acad. Sci.* **2008**, *105*, 18108 – 18113; b) G. E. Johnson, R. Mitric, V. Bonačić-Koutecký, A. W. Castleman, Jr., *Chem. Phys. Lett.* **2009**, *475*, 1 – 9.
[16] Pt_n^-: a) U. Achatz, C. Berg, S. Joos, B. S. Fox, M. K. Beyer, G. Niedner-Schatteburg, V. E. Bondybey, *Chem. Phys. Lett.* **2000**, *320*, 53 – 58; b) C. Adlhart, E. Uggerud, *Chem. Commun.* **2006**, 2581 – 2582; Pt_n^0: c) D. J. Trevor, D. M. Cox, A. Kaldor, *J. Am. Chem. Soc.* **1990**, *112*, 3742 – 3749; Pt_n^+: d) T. Hanmura, M. Ichibashi, T. Kondow, *J. Phys. Chem. A* **2002**, *106*, 11465 – 11469; e) K. Koszinowski, D. Schröder, H. Schwarz, *J. Phys. Chem. A* **2003**, *107*, 4999 – 5006; f) G. Kummerlöwe, I. Balteanu, Z. Sun, O. P. Balaj, V. E. Bondybey, M. K. Beyer, *Int. J. Mass Spectrom.* **2006**, *254*, 183 – 188; g) C. Adlhart, E. Uggerud, *Chem. Eur. J.* **2007**, *13*, 6883 – 6890.
[17] a) D. M. Cox, R. Brickman, K. Creegan, A. Kaldor, *Z. Phys. D* **1991**, *19*, 353 – 355; b) K. Koszinowski, D. Schröder, H. Schwarz, *ChemPhysChem* **2003**, *4*, 1233 – 1237; c) S. M. Lang, T. M. Bernhardt, *Eur. Phys. J. D* **2009**, *52*, 139 – 142.
[18] For the spectacular effect of a single argon ligand on the activation of methane by Rh_2^+, see: G. Albert, C. Berg, M. Beyer, U. Achatz, S. Joos, G. Niedner-Schatteburg, V. E. Bondybey, *Chem. Phys. Lett.* **1997**, *268*, 235 – 241.
[19] S. M. Lang, T. M. Bernhardt, R. M. Barnett, U. Landman, *Angew. Chem.* **2010**, *122*, 993 – 996; *Angew. Chem. Int. Ed.* **2010**, *49*, 980 – 983.
[20] R. Imbihl, R. J. Behm, R. Schlögl, *Phys. Chem. Chem. Phys.* **2007**, *9*, 3459.