Homogeneous Catalysis in Liquefied Gas. Complex-Catalyzed Selective and Direct Conversion of Propane to Butanal at Room Temperature

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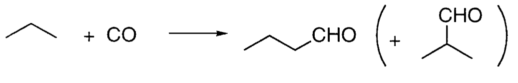
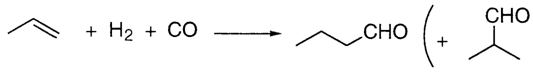
Homogeneous catalysis in liquefied gas proves to be a promising approach to functionalize gaseous alkanes selectively; upon illumination, $RhCl(CO)(PMe_3)_2$ catalyzes carbonylation of liquefied propane at room temperature to produce butanal with high regioselectivity.

Current petrochemical industry basically depends on olefins produced through thermal decomposition (cracking) of alkanes at high temperature, typically in the range of 800 - 900 °C.[1] In place of this energy consuming and non-selective procedure, development of a more efficient new chemical process based on selective and direct conversion of alkanes at low temperature has been long and strongly sought after.[2] Particularly, utilization of gaseous alkanes (e.g. methane and propane) has been of great interest to chemists since these gases are quite abundant, but underutilized as chemical resources. For example, annual world LPG (liquid petroleum gas) supply is nearly 200 million tons, most of which is being consumed merely as fuel. We report here the successful conversion of a gaseous alkane (propane; bp - 42 °C) to an industrially very useful compound (butanal) near room temperature by homogeneous catalysis in liquefied gas. It is a recent trend to develop new reaction media for homogeneous catalysis, like supercritical fluids, water, and so on. This work demonstrates the possibility of new alkane conversion processes in liquefied gases.

Compared with heterogeneous catalysis, functionalization of alkanes by homogeneous systems has been less developed: some relatively well known processes with limited application are i) radical reaction typically represented by chlorination, ii) electrophilic substitution promoted by strong acids or metal complexes, and iii) oxygenation catalyzed by enzyme models such as porphyrin or other complexes.[2] Some of the recent examples of catalytic alkane transformation by homogeneous systems are oxidative carbonylation using excess oxygen gas or $K_2S_2O_8$ in the presence of group 8, 9, or 10 metal-complexes,[3,4] addition of alkyl radicals to SO_3 initiated by $K_2S_2O_8$ in fuming sulfuric acid,[5] photo-assisted radical sulfination or carbonylation sensitized by mercury metal[6] or polyoxotungstate,[7] reaction with concentrated sulfuric acid mediated by mercury salts,[8] and oxygenation in the presence of transition metal complexes.[9]

When it is not necessary to consider the generation of regio-isomers, as in the case of transformation of methane, ethane, cyclohexane, etc., various hetero- or homogeneous reactions are applicable.[1-9] However, for the reactions of linear alkanes with more than three carbons (e.g. propane), regioselective reaction, especially selective activation of methyl groups, is difficult to realize except when using a sophisticated biological system (enzyme). From the industrial point of view, one of the most attractive but difficult alkane transformations is the regioselective production of butanal from propane (eq 1). The importance of this reaction is made quite obvious by observing that (i) about four million tons of C_4-aldehydes are produced annually by hydroformylation of propene (eq 2),[10] (ii) scientific reports concerning hydroformylation number over 4000,[11] and (iii) selective conversion of gaseous alkanes is currently a challenging pursuit for synthetic chemists as stated above.


(1)


(2)

We have already reported the photo-assisted carbonylation of hydrocarbons catalyzed by $RhCl(CO)(PMe_3)_2$.[12] Although many reports on the mechanistic aspects of hydrocarbon carbonylation by our catalytic system have been described by other groups using various techniques such as flash photolysis,[13] kinetics,[14] identification of intermediates,[15] and computational chemistry,[16] carbonylation of gaseous alkanes by this system was never reported. This is because the carbonylation reaction is usually conducted using the liquid hydrocarbon itself as a solvent. For example, our previous work of pentane carbonylation was carried out in neat pentane.[12] On the other hand, although some solvents are necessary to perform homogeneous catalysis of gaseous alkanes, there is no suitable solvent for such purpose; normal solvents react under the alkane-activation conditions.

Several substances have been proposed so far as solvent for C-H bond activation by metal-complexes; liquid xenon,[17] perfluorohydrocarbons,[18] perfluorocarboxylic acids,[19] concentrated sulfuric acid,[8] water,[3] and so on. However, each solvent has drawbacks such as high cost and/or low solubility of metal-complexes and substrates. Although we previously proposed bulky hydrocarbons with t-butyl groups as solvent for alkane dehydrogenation by the $RhCl(CO)(PMe_3)_2$-hν system,[20] those hydrocarbons are rather expensive and, as a more significant problem, are not tolerant of the benzene photo-carbonylation conditions.[21] Therefore, we need another way to functionalize gaseous alkanes by homogeneous catalysis. The methodology we tried was to utilize liquefied propane itself as solvent of the $RhCl(CO)(PMe_3)_2$-hν system in order to produce butanal.

A typical reaction procedure was as follows: In a stainless-steel autoclave (inner volume 30 cm^3) equipped with a quartz window (20 mm ϕ) (details of the reactor will be reported elsewhere), propane (60 atm: 1 atm = 1.01×10^5 Pa) was added to a mixture of $RhCl(CO)(PMe_3)_2$ (10 mg, 0.031 mmol) and CO (3 atm) at room temperature. Propane was completely liquefied under these conditions and made a pale-yellow homogeneous solution. Then the solution was irradiated from the outside by a high-pressure mercury lamp (Ushio, USH-500D) through the window. The autoclave was kept in a thermostat at 35 °C or 15 °C. After the reaction, C_4-aldehydes were trapped by bubbling the reaction mixture through cold toluene and analyzed by GC and GC-MS. The results are summarized in eq 3 and Table 1.

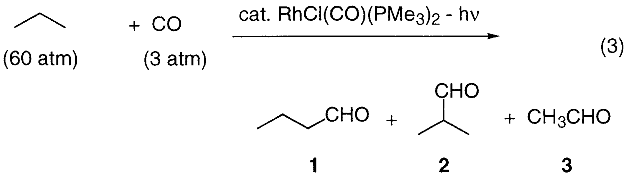


Table 1. Carbonylation of Liquefied Propane

Temp / °C	Time / h	Turnover		
		1	**2**	**3**
35	24	6.1	0.13	> 0.2
35	48	11.5	0.58	> 0.2
15	48	20.3	0.36	> 0.2

The major product was butanal (**1**) accompanied by a small amount of the branched regioisomer (**2**). The most important problem in hydroformylation of propene (eq 2) is how to improve the n-/iso- ratio.[22] In this regard, our system showed excellent regioselectivity to produce the n-aldehyde predominantly; n-/iso- ratio was 98/2 after 48 h at 15 °C. This high regioselectivity for the methyl group is the striking feature of our system compared with other C-H bond activation reactions.[1,2,4,5,6,7,9] The secondary photoreaction of butanal to acetaldehyde (**3**) (Norrish type II reaction) was negligible under the reaction conditions.[12] It was also noteworthy that the aldehyde yield after 48 h at 35 °C was almost the double that after 24 h, indicating no appreciable catalyst deactivation occurred in this time range. The lower reaction temperature (15 °C) was substantially preferable to achieve higher reaction rate.[12,14] The rather slow reaction observed here should be primarily due to the reactor design. It was already reported that our carbonylation system was promoted dramatically by raising the light intensity, suggesting a multi-photon catalytic cycle.[23,14b] Hence, turnover rate will presumably be improved to a great extent by increasing the relative irradiation intensity.

To summarize, we have exhibited the promising properties of liquefied gases as a reaction media of homogeneous catalysis. We will continue to study various homogeneous catalysis using liquefied gases or supercritical fluids.[24]

References and Notes

1 "Thermal Hydrocarbon Chemistry," ed by A. G. Oblad, H. G. Davis and R. T. Eddinger, Adv. Chem. Ser. 183, American Chemical Society, Washington, D. C. (1979).

2 R. H. Crabtree, *Chem. Rev.*, **85**, 245 (1985); "Activation and Functionalization of Alkanes," ed by C. L. Hill, John Wiley & Sons, New York (1989).

3 M. Lin and A. Sen, *Nature*, **368**, 613 (1994).

4 Y. Fujiwara, K. Takaki, and Y. Taniguchi, *Synlett.*, **1996**, 591; K. Nakata, Y. Yamaoka, T. Miyata, Y. Taniguchi, K. Takaki, and Y. Fujiwara, *J. Organomet. Chem.*, **473**, 329 (1994); K. Nakata, T. Miyata, Y. Taniguchi, K. Takaki, and Y. Fujiwara, *J. Organomet. Chem.*, **489**, 71 (1995).

5 N. Basickes, T. E. Hogan, and A. Sen, *J. Am. Chem. Soc.*, **118**, 13111 (1996).

6 R. R. Ferguson and R. H. Crabtree, *J. Org. Chem.*, **56**, 5503 (1991).

7 B. S. Jaynes and C. L. Hill, *J. Am. Chem. Soc.*, **117**, 4704 (1995).

8 R. A. Periana, D. J. Taube, E. R. Evitt, D. G. Löffler, P. R. Wentrcek, G. Voss, and T. Masuda, *Science* , **259**, 340 (1993).

9 N. Komiya, T. Naota, and S.-I. Murahashi, *Tetrahedron Lett.*, **37**, 1633 (1996); S.-I. Murahashi, Y. Oda, T. Naota, and T. Kuwabara, *Tetrahedron Lett.*, **34**, 1299 (1993); D. H. R. Barton and D. Doller, *Acc. Chem. Res.*, **25**, 504 (1992).

10 "Ullmann's Encyclopedia of Industrial Chemistry ," ed by W. Gerhartz, VCH, Weinheim (1985), vol. A4, pp447-453.

11 "Chemical Abstracts" on line search by the key word "hydroformylation," 1967-1997.

12 T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada, and M. Tanaka, *J. Am. Chem. Soc.*, **112**, 7221 (1990); T. Sakakura and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1987**, 758.

13 P. C. Ford, T. L. Netzel, C. T. Spillett, and D. B. Pourreau, *Pure & Appl. Chem.*, **62**, 1091 (1990).

14 a) G. P. Rosini, W. T. Boese and A. S. Goldman, *J. Am. Chem. Soc.*, **116**, 9498 (1994); b) G. P. Rosini, K. Zhu, and A. S. Goldman, *J. Organomet. Chem.*, **504**, 115 (1995).

15 S. E. Boyd, L. D. Field, and M. G. Partridge, *J. Am. Chem. Soc.*, **116**, 9492 (1994).

16 N. Koga and K. Morokuma, *J. Phys. Chem.*, **94**, 5454 (1990); P. Margl, T. Ziegler, and P. E. Blöchl, *J. Am. Chem. Soc.*, **118**, 5412 (1996).

17 M. B. Sponsler, B. H. Weiller, P. O. Stoutland, and R. G. Bergman, *J. Am. Chem. Soc.*, **111**, 6841 (1989).

18 J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, **105**, 7190 (1983).

19 M. Lin, T. E. Hogan and A. Sen, *J. Am. Chem. Soc.*, **118**, 4574 (1996); Y. Fujiwara, K. Takaki, J. Watanabe, Y. Uchida, and H. Taniguchi, *Chem. Lett.*, **1989**, 1687.

20 T. Sakakura, K. Ishida, and M. Tanaka, *Chem. Lett.*, **1990**, 585.

21 T. Sakakura, unpublished results.

22 I. Tkatchenko, in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone and E. W. Abel., Pergamon Press, Oxford (1982), vol. 8, p.101.

23 H. Moriyama, T. Sakakura, A. Yabe, and M. Tanaka, *J. Mol. Catal.*, **60**, L9 (1990).

24 We have already succeeded in C-H activation (benzene carbonylation) by the $RhCl(CO)(PMe_3)_2$-hv system using supercritical CO_2 as an inert solvent. The result will be reported separately.