Communications to the Editor

Carbon Monoxide Hydrogenation: Intermediates Derived from Methylene Probes Offering Dual Polymerization Pathways in Fischer−Tropsch Homologation

Ruhksana Quyoum, Valerio Berdini, Michael L. Turner,
Helen C. Long, and Peter M. Maitlis*

Department of Chemistry
The University of Sheffield
Sheffield S3 7HF, U.K.

Received June 6, 1996

In our recent studies on the mechanism of the hydrogenation of carbon monoxide to alkenes (the Fischer−Tropsch reaction) using $^{13}C_2$-labeled probe molecules over rhodium, ruthenium, and cobalt catalysts, we have found that the ^{13}C labels in the products are consistent with a process involving the reactions of surface methylenes with surface *alkenyl* (rather than alkyl) species.[1] We now report, (i) that both diazomethane and nitromethane[2] can be effective C_1 probes and (ii) that while methylenes derived from $^{13}CH_2N_2$ or $^{13}CH_3NO_2$ probes and methylenes formed from ^{12}CO hydrogenation combine randomly over cobalt (giving products containing mixtures of ^{12}C and ^{13}C atoms), quite separate reactions occur over rhodium Fischer−Tropsch catalysts.

In their classic experiments, Brady and Pettit[3] confirmed that methylene was a key intermediate in the hydrocarbon formation and that chain growth occurred by a stepwise oligomerization of surface methylene groups, as originally proposed by Fischer and Tropsch.[4] They analyzed the propylene from a reaction in which an excess of $^{12}CH_2N_2$ had been added to a ^{13}CO hydrogenation over a cobalt catalyst and showed that it contained a distribution of ^{13}C atoms which agreed with that predicted by a mechanism in which surface intermediates, derived from diazomethane, were indistinguishable (apart from their isotopic label) from surface methylene intermediates formed from ^{13}CO and hydrogen.[3] It was proposed that these species could combine (randomly) in a chain growth oligomerization.

We find that addition of small amounts of a diazomethane or a nitromethane probe to a Fischer−Tropsch reaction over three different metal catalysts (rhodium(4%)−ceria−silica,[1,5] ruthenium (4%) on silica, or cobalt (4%) on silica) caused increases in the formation rates of virtually all the hydrocarbon products (Figure 1). The products formed during addition of $^{13}CH_2N_2$ or $^{13}CH_3NO_2$ to the syn gas (H_2-^{12}CO) stream during a Fischer−Tropsch reaction (250 °C, 1 atm, approximate molar ratio of $^{13}CH_2N_2$ or $^{13}CH_3NO_2/H_2/^{12}CO$ = 1:44:22) were analyzed for ^{13}C incorporation as described earlier.[1] Representative mass spectrometric data showing the incorporation of $^{13}C_x$ units into the C_4−C_6 1-alkenes are in Table 1;[6] the results over cobalt show substantial incorporation of $^{13}C_1$ and $^{13}C_2$ into the linear hydrocarbon products and are consistent with a distribution of ^{13}C incorporation based on random mixing of the methylenes derived from syn gas and those from the probe.[7] As expected, only very low levels of products derived exclusively from the probe ($^{13}C_n$) are formed.

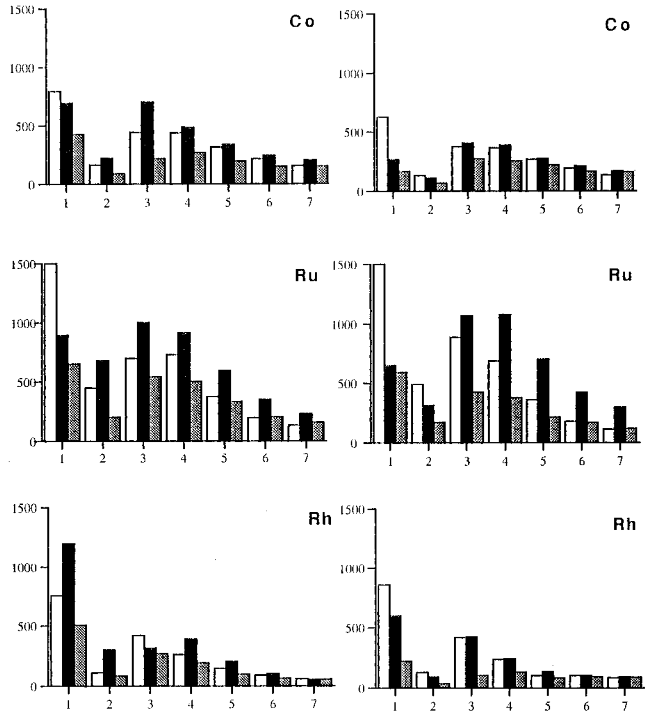

Figure 1. Block diagrams showing product formation rate (*y* axis, μmol of carbon g cat^{-1} h^{-1}) against carbon number (*x* axis) before (white), during (solid), and after (shaded) addition of (a) CH_2N_2 (left) and (b) CH_3NO_2 (right) to syn gas over Co, Ru, and Rh catalysts under Fischer−Tropsch reaction conditions.

In contrast, when a similar reaction is carried out over rhodium, *parallel chain growth reactions occur which each lead to the formation of 1-alkenes*.[6] One is CO hydrogenation, which forms products derived exclusively from ^{12}C, the other is a "homopolymerization" of methylene intermediates derived from the $^{13}CH_2N_2$ or the $^{13}CH_3NO_2$ probe, giving fully ^{13}C-labeled products. Thus, over rhodium, very little crossover occurs between the two chain growth reactions and the primary products are the unlabeled 1-alkenes ($^{12}C_nH_{2n}$ from the CO hydrogenation), containing only ^{13}C at natural abundance, and the fully labeled 1-alkenes ($^{13}C_nH_{2n}$ from the homopolymerization), containing little or no ^{12}C. The same experiments over ruthenium catalysts gave results intermediate between those found for cobalt and rhodium.

To summarize, the hydrocarbon products formed from carbon monoxide hydrogenation over Co have significant incorporation of $^{13}CH_2$ units from either $^{13}CH_3NO_2$ or $^{13}CH_2N_2$ probes showing that there has been random mixing of the two sources of methylene groups, while over Rh there exist two distinct alkene chain growth pathways, one from CO hydrogenation and

---

(1) Turner, M. L.; Long, H. C.; Shenton, A.; Byers, P. K.; Maitlis, P. M. *Chem. Eur. J.* **1995**, *1*, 549. Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z.-Q. *J. Chem. Soc., Chem. Commun.* **1996**, 1. Long, H. C. Ph.D. Thesis, University of Sheffield, 1996. Quyoum, R.; Maitlis, P. M. Unpublished results.

(2) Nitromethane has been reported to act as methylene precursor: Cavalcanti, F. A. P.; Oukaci, R.; Wender, I.; Blackmond, D. G. *J. Catal.* **1990**, *123*, 260.

(3) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181; **1981**, *103*, 1287. Brady, R. C., III Ph.D. Dissertation, University of Texas, 1980.

(4) Fischer, F.; Tropsch, H. *Brennst. Chem.* **1926**, *7*, 97; *Chem. Ber.* **1926**, *59*, 830.

(5) Addition of ceria to rhodium on silica increases the catalyst activity; very similar product and isotope distributions are obtained using Rh/silica with no ceria (see Supporting Information).

(6) 1-Alkenes are the initial products which are isomerised to internal olefins or hydrogenated to alkanes; the precise composition of any C_n fraction depends on the catalyst and the temperature.

(7) We have analyzed the data on the premise that statistical mixing occurs of probe-derived and syn gas derived methylenes, the same approach adopted by Brady and Pettit.[3]

S0002-7863(96)01899-9 CCC: $12.00

Table 1. Percentage Incorporation of $^{13}C_n$ into 1-Butene, 1-Pentene, and 1-Hexene Formed on Addition of $^{13}CH_2N_2$ and $^{13}CH_2NO_2$ Probes to CO Hydrogenations over Co, Rh, and Ru Catalysts under Fischer–Tropsch Reaction Conditions[a]

catalyst	hydrocarbon product	percentage incorporation using													
		$^{13}CH_2N_2$							$^{13}CH_3NO_2$						
		$^{13}C_0$	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	$^{13}C_5$	$^{13}C_6$	$^{13}C_0$	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	$^{13}C_5$	$^{13}C_6$
Co	1-butene	66	18	10	2	4			70	17	6	3	5		
	1-pentene	75	15	7	2	1	0		69	16	6	3	2	4	
	1-hexene	76	18	4	1	0	0	0	62	18	8	4	2	2	3
Ru	1-butene	71	13	5	3	8			77	11	2	2	7		
	1-pentene	77	11	2	2	1	8		76	11	2	1	2	7	
	1-hexene	77	12	2	1	1	1	6	78	12	2	1	1	1	6
Rh	1-butene	69	3	0	1	27			68	10	2	2	19		
	1-pentene	73	4	1	0	1	21		71	9	3	1	2	13	
	1-hexene	72	3	0	0	0	2	22	67	9	2	0	1	3	19

[a] Conditions: 250 °C, 1 atm, approximate molar ratio of $^{13}CH_2N_2$ or $^{13}CH_3NO_2/H_2/^{12}CO$ = 1:44:22; $^{13}CH_2N_2$ prepared from *N*-methyl-^{13}C-*N*-nitroso-*p*-toluenesulfonamide (Aldrich); $^{13}CH_3NO_2$ was purchased from Aldrich.

the other from the polymerization of methylenes derived from the probe molecules.

Since there is now a great deal of evidence favoring surface CH_2 (methylene) as an intermediate in CO hydrogenation,[8] we suggest that the homopolymerization of the probe-derived species may not proceed directly via methylene. Our results indicate that diazomethane and nitromethane react very similarly, presumably via similar surface intermediates (A). The apparent anomaly that A is different from surface methylene formed in the CO hydrogenation can be accommodated if diazomethane and nitromethane undergo a two-step decomposition, giving first A and then surface methylene. If the formation of A is slower than its decomposition to methylene, then A cannot accumulate and the effect will be to generate surface methylene identical to, and interchangeable with, that from CO. This is the situation over cobalt. In contrast, if the formation of A is faster than its decomposition to surface methylene, then A is able to react in another way, for example, by a homopolymerization which is quite separate from the more usual methylene polymerization. This alternative leads to the phenomenon we have observed over rhodium, where *two separate* methylene oligomerization paths leading to hydrocarbons can now be distinguished, one derived from probe molecules and one from CO.

The identity of A is not clear but one possibility is that it could be a surface bound CH_2N; this could also account for the observed formation of some methyl- and ethylamines from nitromethane over the rhodium, but *not* over the cobalt catalyst.[9]

Acknowledgment. We thank the EPSRC, the EU Human Capital and Mobility scheme (Contract no. ERBCH RXCT930147), and the University of Sheffield for support and Dr. Mauro Bassetti for assistance.

Supporting Information Available: Details of the preparation of catalysts, conditions of catalytic reactions, and full product and isotopomer distributions (11 pages). See any current masthead page for ordering and Internet instructions.

JA961899G

---

(8) For example, see: Kaminsky, M. C.; Winograd, N.; Geoffroy, G. L.; Vannice, A. *J. Am. Chem. Soc.* **1986**, *108*, 1315. Anderson, R. B. *The Fischer–Tropsch Reaction*; Academic Press: London, 1984. Roeper, M. *Catalysis in C_1 Chemistry*; Keim, W., Ed.; W. D. Reidel: Dordrecht, The Netherlands, 1983. Biloen, P. *J. R. Neth. Chem. Soc.* **1980**, *99*, 33. Biloen, P.; Sachtler, W. M. H. *Adv. Catal.* **1981**, *30*, 165.

(9) Organometallic models are also known for the N–N fission of coordinated diazoalkanes; for example, on heating the dimethyldiazomethane adduct $[\{\eta^5\text{-}C_5Me_5Mo(CO)_2\}_2(\mu\text{-}\eta^1{:}\eta^2\text{-}NNCMe_2)]$, N–N cleavage occurs with rearrangement to give the cyanato–imino complex $[\{\eta^5\text{-}C_5Me_5Mo\}_2\text{-}(CO)_3(NCO)(\mu\text{-}NCMe_2)]$. Herrmann, W. A.; Bell, L. K. M.; Ziegler, L.; Pfisterer, H.; Pahl, C. *J. Organomet. Chem.* **1983**, *247*, 39. Herrmann, W. A.; Ihl, G. *J. Organomet. Chem.* **1983**, *251*, C1. Also, see: Mizobe, Y.; Ishii, Y.; Hidai, M. *Coord. Chem. Rev.* **1995**, *139*, 308.