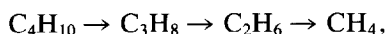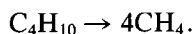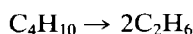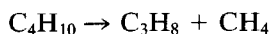# LETTER TO THE EDITORS

The Mechanism of Alkane Hydrogenolysis

It is still a matter for discussion (*1*) as to whether the hydrogenolysis of alkanes proceeds sequentially by a series process, e.g.,

$$C_4H_{10} \rightarrow C_3H_8 \rightarrow C_2H_6 \rightarrow CH_4,$$

or by simultaneous parallel processes, e.g.,

$$C_4H_{10} \rightarrow C_3H_8 + CH_4$$
$$C_4H_{10} \rightarrow 2C_2H_6$$
$$C_4H_{10} \rightarrow 4CH_4.$$

To imply that these are alternatives is however to create a false antithesis. To begin with, such reaction statements do not carry any mechanistic information; they do not allude to possible adsorbed intermediates; they are not even balanced chemical equations. The question which must be asked is the following, Is C_2H_6 formed *only* from C_4H_{10} or *only* from C_3H_8 or are *both* routes possible? There is no doubt that on many metal catalysts the direct route is possible, since C_2H_6 is observed as a significant product at low conversions. If the series process were operative, C_3H_8 and CH_4 in equal amounts would be the *only* initial products. However, any increase in C_2H_6 selectivity with time (in a static system) or with contact time (in a flow system) is more likely to be due to the sequential reaction of C_3H_8 by its readsorption. The observation (*1*) of CH_4 at low conversion in amounts exceeding that of C_3H_8 must in principle mean its direct formation from C_4H_{10}; but the simultaneous breaking of three C–C bonds is implausible, and it is more likely that CH_4 will arise through the sequential breaking of C–C bonds in adsorbed C_3 and C_2 species. The real distinction between the series and the parallel formulations is thus whether *gaseous* C_3H_8 is or is not a necessary interme-

diate in the formation of C_2H_6, and whether *gaseous* C_3H_8 and C_2H_6 are or are not necessary intermediates in forming CH_4. Clearly they are not when (as is usually the case) C_2H_6 and excess CH_4 are seen at low conversion: the series process is therefore incorrect (or at least incomplete and uninformative), but it is incorrect only because it has been written in a way that fails to reveal what happens in practice.

These apparent contradictions are readily resolved by a comprehensive reaction scheme due originally to Kempling and Anderson (*2*). This is a "rake" scheme and is written for C_4H_{10} as
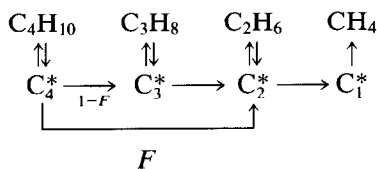
Suitable selection of relative values for the rate constants of the constituent steps allows for any possibility, e.g., selective formation of $C_3H_8 + CH_4$ (as is sometimes found on Pt catalysts at low conversion) or the selective formation of C_2H_6, or of CH_4, or of course of any blend of products. A steady-state analysis of this scheme is available (*2*), and a critique of its utility has been published (*3*). Accurate estimation of the relative rate constants requires the following of the reaction over a wide range of conversion (*2*), but an alternative approach is to apply results obtained with C_3H_8 as reactant to provide the information that is missing if the C_4H_{10} reaction is not taken to high conversion. This method has been applied successfully to the reaction of n-C_4H_{10} on Ru/TiO_2 catalysts (*4*).

It is of interest to note that the differences in the activities for n-C_4H_{10} hydrogenolysis of Rh/SiO$_2$ after low- and high-temperature reduction (LTR and HTR), as recently reported by Gao and Schmidt (1), closely resemble those we have found (4–7) for Ru supported on TiO$_2$, Al$_2$O$_3$, and SiO$_2$. Such variations do not however occur with Pt/SiO$_2$ (3). Even more surprisingly, the changes they observe in their product distributions mirror those we have found with supported Ru catalysts; i.e., oxidation followed by LTR usually affords higher CH$_4$ yields than are found after HTR.

It is of further interest to apply the Kempling–Anderson analysis to the results obtained by Gao and Schmidt (1) in order to identify more precisely the effects of pretreatment conditions on reaction mechanism. Since they have reported results for both C$_3$H$_8$ and n-C$_4$H$_{10}$ under identical conditions, it is possible to analyze their results in some detail. The three parameters derived from this method of analysis are (i) the splitting factor F (defined as shown in the scheme above), (ii) T_2, and (iii) T_3, where T_i represents the fraction of the species having i C atoms that appears in the gas phase as C_iH_{2i+2} in the steady state. Now all three parameters cannot be derived from

TABLE 1

Product Selectivities for the Hydrogenolysis of C$_3$H$_8$ and of C$_4$H$_{10}$ over Rh/SiO$_2$ (1)

Alkane	Catalyst	i	(A) $S_i^c = r_i/\Sigma r_i$	(B) $S_i^m = r_i/\Sigma(r_i/i)$	(C) S_i^m	(D) S_i^{KA}
C$_3$H$_8$	Annealed	1	0.3	0.5	0.54	1.11
		2	0.6	0.5	0.46	0.95
C$_3$H$_8$	Oxidized	1	0.38	0.55	0.56	1.17
		2	0.62	0.45	0.44	0.92
C$_4$H$_{10}$	Annealed	1	0.20	0.36	0.32	0.79
		2	0.47	0.43	0.54	0.95
		3	0.33	0.21	0.14	0.44
C$_4$H$_{10}$	Oxidized	1	0.32	0.52	0.54	1.37
		2	0.41	0.33	0.36	0.94
		3	0.27	0.15	0.10	0.25

Note. Column A, "carbon-based" selectivities from rates at 230°C. Column B, "molecule-based" selectivities from rates at 230°C. Column C, molecule-based selectivities from Figs. 7 and 8 of Ref. (1) at 235°C. Column D, Kempling–Anderson selectivities derived as explained in the text.

the n-C_4H_{10} product selectivities, as there are only two that are independently variable. However, by assuming that S_2 for C$_3$H$_8$ is the value of T_2 for n-C_4H_{10} (4), firm values for T_3 and F can then be obtained. In order to do this, the selectivity values given by Gao and Schmidt in Figs. 7 and 8 of their paper (1) must first be converted to a "carbon basis," since notwithstanding the statement made on p. 213 they are clearly expressed on a "molecule basis" and are not derived by their Eq. (2). This is readily shown by considering their results for C$_3$H$_8$ on the annealed Rh/SiO$_2$ catalyst: from Fig. 7, $S_1^m \simeq S_2^m \simeq 0.5$, while from Table 2, S_1^c ı $r_1/(r_1 f r_2)$ ı 0.33 if Eq. (2) is used, where the rates are expressed on a carbon basis. The superscripts c and m stand respectively for carbon and molecule. The values shown in the figures are therefore derived from the quoted rates by the equation

$$S_i^m = r_j/\Sigma(r_j/j).$$

Table 1 shows the selectivities calculated both ways from the rates at 230°C for the reactions of C$_3$H$_8$ and of C$_4$H$_{10}$ on both the oxidized and the annealed Rh/SiO$_2$ catalysts, and the values obtained are compared with those given in the figures for 235°C at zero conversion. This comparison leaves no doubt that the latter are indeed "molecular" values. To obtain selectivities in the form from which the Kempling–Anderson parameters can be derived, the following equation must be applied,

$$S_i^{KA} = nc_i \Big/ \sum_{i=1}^{i=n-1} ic_i,$$

where n is the number of carbon atoms in the reactant alkane and c_i is the mole fraction of product having i carbons, i.e., S_i^m. It follows then that

$$\sum_{i=1}^{i=n-1} iS_i^{KA} = n.$$

Table 1 also shows the selectivities calculated in this way, and Table 2 the associated

TABLE 2

Kempling–Anderson Parameters

Alkane	Catalyst	T_2	F	T_3
C_3H_8	Annealed	0.95	—	—
C_3H_8	Oxidized	0.92	—	—
C_4H_{10}	Annealed	(0.95)	0.43	0.78
C_4H_{10}	Oxidized	(0.92)	0.28	0.34

Kempling–Anderson parameters. The effect on C_4H_{10} hydrogenolysis of annealing an "oxidized" catalyst is chiefly to increase T_3 more than twofold, thus encouraging the desorption of the intermediate C_3^* species as C_3H_8, so that the C_3H_8 yield is increased and that of CH_4 decreased. There is a lesser effect on F, with the annealed catalyst showing a 50% greater probability of central-bond fission than the oxidized catalyst. The structure changes effected by annealing therefore alter both the bond-breaking chances and the reactivity of the adsorbed intermediates.

REFERENCES

1. Gao, S., and Schmidt, L. D., *J. Catal.* **111,** 210 (1988).
2. Kempling, J. C., and Anderson, R. B., *Ind. Eng. Chem. Process Des. Dev.* **11,** 146 (1972).
3. Bond, G. C., and Xu Yide, *J. Chem. Soc. Faraday Trans. 1* **80,** 969 (1984).
4. Bond, G. C., Rajaram, R. R., and Burch, R., *J. Phys. Chem.* **90,** 4877 (1986).
5. Burch, R., Bond, G. C., and Rajaram, R. R., *J. Chem. Soc. Faraday Trans. 1* **82,** 1985 (1986).
6. Bond, G. C., Rajaram, R. R., and Burch, R., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 4, p. 1130. Chemical Institute of Canada, Ottawa, 1988.
7. Bond, G. C., Rajaram, R. R., Flamerz, S., and Yahya, R., unpublished work.

GEOFFREY BOND

Department of Chemistry
Brunel University
Uxbridge UB8 3PH, United Kingdom