

## Hydrogenolysis of Hydrocarbons on Iron Catalysts

By R. S. DOWIE, M. C. GRAY, D. A. WHAN, and C. KEMBALL\*

(Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ)

*Summary* The use of a combined g.l.c.-mass spectrometry technique shows that the hydrogenolysis† of ethane, propane, or butane in the presence of deuterium on iron films gives CD<sub>4</sub> as the main product and that the reactions are accompanied by exchange of the hydrocarbons producing mainly the perdeuterio-compounds.

EXCHANGE reactions of alkanes with deuterium<sup>1,2</sup> have provided useful information about the types of adsorbed intermediates formed on metal catalysts in reactions at low or moderate temperatures. At higher temperatures, different adsorbed species may be involved<sup>3</sup> and may be studied by the isomerization or hydrogenolysis of saturated hydrocarbons in the presence of deuterium and by determination of the isotopic composition of reactant and products at low conversions. This can be accomplished by the combination of separation by g.l.c. and of fast-scanning mass spectrometry to determine the isotopic composition of each substance as it emerges from the chromatographic column. The potentialities of this technique, which has not previously been used in catalytic studies, may be evaluated

from our results for ethane, propane, and butane on iron films.

Reactions were carried out in a static system ( $2.44 \times 10^{-4} \text{ m}^3$ ) with hydrocarbon (at  $400 \text{ Nm}^{-2}$ ) over evaporated iron films (*ca.* 10 mg) and a ratio of D<sub>2</sub> to hydrocarbon of 12:1. Samples of the gas were withdrawn and passed into a gas chromatograph linked through a molecular separator directly to a mass spectrometer (A.E.I. M.S. 20 'Rapide'). A mass spectrum could be obtained in less than 1 s and normally *ca.* 20–40 spectra were recorded for each peak. Several scans were needed to obtain adequate analyses of the isotopic content of each hydrocarbon because partial separation of the exchanged hydrocarbons occurred in the chromatograph, the heavier molecules being eluted faster than the lighter ones.

The order of reactivity is clearly butane > propane > ethane (see Table 1) and the ratio of exchange to hydrogenolysis increases with the size of the molecule. The results with butane are characteristic (see Table 2). The major product of hydrogenolysis was methane and only small amounts of propane and ethane were formed; in each

† Hydrogenolysis is used in a generic sense and implies here carbon-carbon fission by either hydrogen or deuterium.

case, the perdeuterio-compound was by far the most abundant isotopic species. The major product of the

TABLE 1  
*Extent of reaction*

Reactant	T/K	t/min	% Reaction	
			hydrogenolysis	exchange
Ethane	504	20	3.6	1.3
Propane	486	15	5.3	2.6
Butane	~461	10	9.3	10.6

TABLE 2

*Isotopic composition of products from the reaction of butane*

Product	Fraction in reacting mixture (%)	Isotopic composition [number of D atoms (%)]	
		D <sub>10</sub> (70), D <sub>9</sub> (20), D <sub>8</sub> or less (10)	D <sub>8</sub> (80), D <sub>7</sub> or less (20)
Exchanged butane	10.6	D <sub>10</sub> (70), D <sub>9</sub> (20), D <sub>8</sub> or less (10)	
Propane .. ..	0.1	D <sub>8</sub> (80), D <sub>7</sub> or less (20)	
Ethane .. ..	0.2	D <sub>8</sub> (85), D <sub>7</sub> or less (15)	
Methane .. ..	9.0	D <sub>4</sub> (82), D <sub>3</sub> (15), D <sub>2</sub> or less (<3)	

exchange reaction was perdeuteriobutane. Propane and ethane behaved similarly; no hydrogenolysis products other than CD<sub>4</sub> were observed. Exchange gave the deuterated propanes C<sub>3</sub>D<sub>8</sub> (70%) and C<sub>3</sub>HD<sub>7</sub> (30%) and the only exchanged ethane detected was C<sub>2</sub>D<sub>6</sub>.

We conclude that desorption of the hydrocarbons from an iron surface is not rapid which accounts for the three principal features of the results. First, the perdeuterio-compound is the main product of exchange because any adsorbed species formed from the reactant and not broken down to lower homologues remains on the surface for a sufficient time for complete replacement of hydrogen by deuterium to take place. The multiple exchange presumably occurs by alternation between two or more types of adsorbed species of different states of hydrogenation, *e.g.* alkyl  $\rightleftharpoons$  alkene. Secondly, species which undergo scission of the carbon-carbon bond mostly end up as C<sub>1</sub>

species leading to methane as the main product of hydrogenolysis. Desorption of intermediate products occurs only to a very small extent with butane and is not observed with propane. Thirdly, the life-time of the C<sub>1</sub> species on the surface is long enough to give CD<sub>4</sub> as the main product. Since all the products from exchange and hydrogenolysis are predominantly perdeuterio-compounds no deductions about the reactive intermediates can be made from the product distributions.

The desorption of methane, being slow, may be the rate-determining reaction but it is not easy to explain why the hydrogenolysis of ethane and propane takes place more slowly than that of butane. A tentative explanation may be the different coverage of the surface by C<sub>1</sub> species in each case. A quantitative study of the virtual pressures<sup>4</sup> of methane to be expected in each reaction might amplify this suggestion.

The predominance of methane as the major product of the hydrogenolysis of butane is greater with iron than with nickel or rhodium.<sup>5</sup> The present evidence for exchange with hydrogenolysis conflicts with a brief report made some years ago of the absence of such exchange with ethane on iron films.<sup>6</sup>

Preliminary experiments with other metals indicate that reversible dissociative adsorption, detectable by exchange techniques, may commonly occur simultaneously with hydrogenolysis.

The technique provides a rapid and sensitive method of following complex processes in heterogeneous catalysis; kinetic data can be obtained readily by analysis of a succession of samples. The high sensitivity is shown by the results for propane in Table 2; the partial pressure of this compound was 0.4 N m<sup>-2</sup> in 5 cm<sup>3</sup> and it would have been difficult to estimate and analyse such a small quantity by conventional trapping and subsequent introduction into a mass spectrometer.

The apparatus was purchased through an S.R.C. grant and one of us (R.S.D.) holds a BP Research Studentship.

(Received, May 19th, 1971; Com. 803.)

<sup>1</sup> C. Kemball, *Adv. Catalysis*, 1959, **11**, 223.

<sup>2</sup> R. L. Burwell, jun., *Accounts Chem. Res.*, 1969, **2**, 289.

<sup>3</sup> C. Kemball, *Catalysis Rev.*, 1971, **5**, 33.

<sup>4</sup> C. Kemball, *Discuss. Faraday Soc.*, 1966, **41**, 190.

<sup>5</sup> J. R. Anderson and B. G. Baker, *Proc. Roy. Soc.*, 1963, *A*, **271**, 402.

<sup>6</sup> J. R. Anderson and C. Kemball, *Proc. Roy. Soc.*, 1954, *A*, **223**, 361.