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Mechanism of Hydrogenolysis on Ni/SiO$_2$

Machiels and Anderson (*1–3*) have recently made an extensive study of alkane hydrogenolysis over supported metal catalysts. Their reaction mechanism assumes adsorption–desorption equilibrium combined with the rate-controlling carbon–carbon bond-cleavage steps. In some parallel studies which we have made with 2,3-dimethylbutane and 2-methylbutane over nickel/silica catalysts in a chromatographic regime (*4*), we have been able to show that there also exists a distinct surface cleavage route in addition to the cleavage route which takes place via rapid desorption and readsorption.

The basic argument is as follows. If the alkane fragments desorb and adsorb considerably faster than they undergo carbon–carbon bond cleavage, then it would be reasonable to suppose that during the reaction of a C_n alkane the selectivities of the C_{n-x} fragments toward the various lower degradation products would be the same as the parent C_{n-x} gas-phase alkanes, as is postulated by Machiels and Anderson. If, in the other extreme, the primary cleavage products remain tightly bound to the catalyst surface and undergo one or more further carbon–carbon cleavage steps before desorbing (which we shall call the "surface route"), it is possible that the selectivity toward lower products would be different, as suggested by Shephard (*5*).

The distinction between these two cases was clearly illustrated to us by the reaction of 2,3-dimethylbutane over a 2% nickel on silica catalyst at temperatures in the range 80–250°C, hydrogen partial pressures 10–10^3 Torr, and alkane partial pressures 10^{-2}–10^2 Torr using mixed gas streams in a column, the chromatographic properties of which showed that the reaction was free of diffusion control (*4*). In this system the selectivity toward cleavage of the terminal carbon–carbon bond was extremely high ($\geq$98%) so that under low conversions the cleavage product is predominantly 2-methylbutane. At high conversions, considerable secondary cleavage takes place to give *n*-butane and isobutane and hence to lower hydrocarbons. Now if the C_5 intermediate species which is produced on the surface is in rapid equilibrium with the gas or with physisorbed hydrocarbon, its cleavage selectivity toward the two butane isomers would be expected to be identical with that found when 2-methylbutane is used as the primary reactant. If, however, the C_5 intermediate is bound tightly to the surface, its activity toward further cleavage will undoubtedly be different to that of gas-phase 2-methylbutane: in particular it is also probable that its selectivity toward the two butane isomers will be different, especially if attachment is confined to a specific configurational site.

The latter was found to be the case

TABLE 1

Selectivities toward Isobutane at 10^3 Torr Hydrogen Partial Pressure

Temperature (°C)	Proportion (R)[a] of C_4 products as isobutane for reaction of	
	2-Methylbutane	2,3-Dimethylbutane
176	0.52	0.79
197	0.57	0.83
224	0.47	0.63

[a] R = (rate of isobutane formation) (rate of isobutane formation + rate of *n*-butane formation)$^{-1}$.

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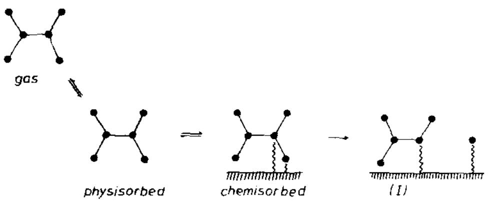

FIG. 1. Primary hydrogenolysis step.

experimentally. Significantly more isobutane was produced during the reaction of 2,3-dimethylbutane than during the reaction of 2-methylbutane under equivalent conditions, as is shown in Table 1. This additional isobutane is thus a measure of the surface cleavage route, which was found to increase in importance with a lowering of the reaction temperature or a lowering of the partial pressure of hydrogen. The results may be expressed more quantitatively in relation to the mechanism if we assume the surface route produces only isobutane. This seems a reasonable hypothesis from the following argument.

The extremely high terminal bond selectivity and the detailed kinetic analysis for hydrogenolysis under our conditions (*6*) suggest strongly that the activated alkane is attached to the metal surface predominantly through the terminal and adjacent carbon atoms (see Fig. 1). The C_5 intermediate (I) formed after the initial cleavage step would consequently itself be attached to the surface in such a way as would lead to isobutane as the only product of further terminal cleavage prior to desorption (see Fig. 2). *n*-Butane will thus only be produced from the C_5 intermediate if the point of attachment is shifted to the other end of the species. This implies detachment or at least limited mobility of the species on the surface. Since reattachment to the surface is then likely to occur at either end of the molecule, the cleavage selectivity toward the two butane isomers by this "detachment route" would be expected to be the same as that for the reaction of 2-methylbutane directly (see Fig. 3).

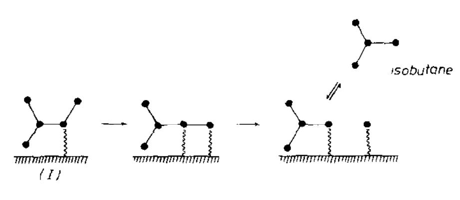

FIG. 2. Secondary hydrogenolysis step—"surface route."

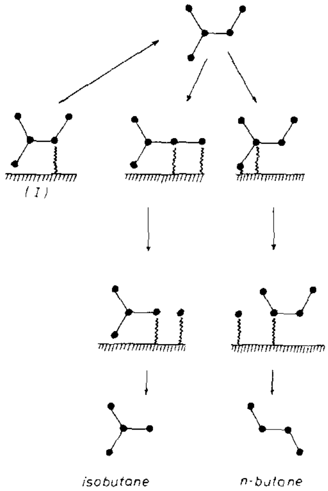

FIG. 3. Secondary hydrogenolysis step—"detachment route."

The ratio of the rate of production of this additional isobutane to that for the rest of the butane and unreacted 2-methylbutane will thus be the ratio ϕ of the rate of surface cleavage to the rate of detachment from the surface of the C_5 intermediate (I) This ratio was calculated as a function of temperature and hydrogen partial pressure to give the differences in the activation energies and entropies and the hydrogen-pressure dependencies of the two processes (*4*). The activation energy for the surface cleavage of the C_5 intermediate was thus found to be only 56 kJ mol^{-1} greater than that for its detachment from the surface. The apparent entropy of activation was 90 J mol^{-1} deg^{-1} greater than that of the detachment route. These kinetic parameters imply that, for example at 200°C and 10^3 Torr partial pressure of hydrogen, the surface cleavage of the C_5 intermediate was 22 times slower than the rate of its detachment from the surface. The hydrogen partial pressure dependence of ϕ was found to be -0.7, so that at 200°C and 10 Torr hydrogen partial pressure the surface rate was only 1.3 times slower than detachment. These kinetics have been interpreted in terms of possible structures of the surface intermediates (*4*, *6*). We hope to publish a fuller account of these experiments shortly.

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