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Hydrogenolysis of Isopentane on Iron

In the hydrogenolysis of paraffinic hydrocarbons, iron catalysts differ widely from those of other group VIII metals. Iron produces principally methane and only traces of intermediate hydrocarbons. Dowie *et al.* (*1*) found that hydrogenolysis on iron using deuterium led to rapid splitting of C–C bonds and extensive exchange. They suggested that the rate of desorption of products was slower than the breaking of C–C bonds. Sinfelt (*2*) and Matsumoto *et al.* (*3*) also made qualitative statements that desorption must be slower than splitting on iron. For metals other than Fe and possibly Re, however, mechanisms and rate equations for hydrogenolysis are usually based on the assumption that the breaking of the C–C bond is the rate determining step and that the rate of adsorption and desorption are very rapid compared to the slow step (*2*). In the present note, data are presented for the hydrogenolysis of isopentane on iron. The reaction network analysis developed in this laboratory (*4–6*), which assumes no rate determining step, is applied to these data to yield a quantitative estimate of the ratios of rates of splitting to desorption.

The experimental work was performed with reduced iron ammonia synthesis catalyst, D3001, fused magnetite containing K_2O, MgO, SiO_2, and Cr_2O_3 as promoters.

The catalyst was reduced in a high flow of H_2 at 450°C for 45 hr. The surface area of the reduced catalyst was about 10 m^2/g and the average pore diameter 350 Å. A 0.75-cm-i.d. stainless steel tube was used as the reactor. The catalytic bed was about 1 cm^3 and the particles were in the 14–25 mesh range. The products were recycled to achieve differential reactor conditions. The feed ratio, H_2/isopentane, was 7.0. Pressure was maintained at about 125 kPa and reaction temperature at 355°C. Two gas chromatographs analyzed the exit gases for hydrocarbons and hydrogen. A liquid nitrogen trap was used to collect adequate amounts of intermediate hydrocarbons, butanes, propane, and ethane for analysis. Overnight, hydrogen was passed over the catalyst bed at the reaction temperature. The activity of the catalyst was constant throughout the experiment.

Figure 1 presents a plot of selectivities as a function of conversion of isopentane. Methane accounted for 99% of the products. Less than 0.02 mole of each intermediate hydrocarbons was formed per mole of isopentane converted. The selectivities were relatively constant over the range of conversions studied, although relatively scattered for the intermediate hydrocarbons due to small quantities involved.

The complete derivation of selectivity equations for the reaction network applied to isopentane hydrogenolysis is described in a recent paper (*6*). Parameters of these equations were obtained by nonlinear regression of the experimental data and are given in Table 1. The ratio k''_h/k''_{i5} compares the overall rate of hydrogenolysis of a given product *h* with that of isopentane. Table 1 shows that *n*-butane reacts 2.5 times faster than isopentane, and is also more reactive than any other intermediate; isobutane has the lowest reactivity.

The splitting factors or probabilities for breaking a given C–C bond could not be obtained from the regression analysis, because the selectivities are relatively independent of conversion and they have very low values. Therefore, reasonable assumptions were made, based on the cracking patterns observed on nickel and ruthenium

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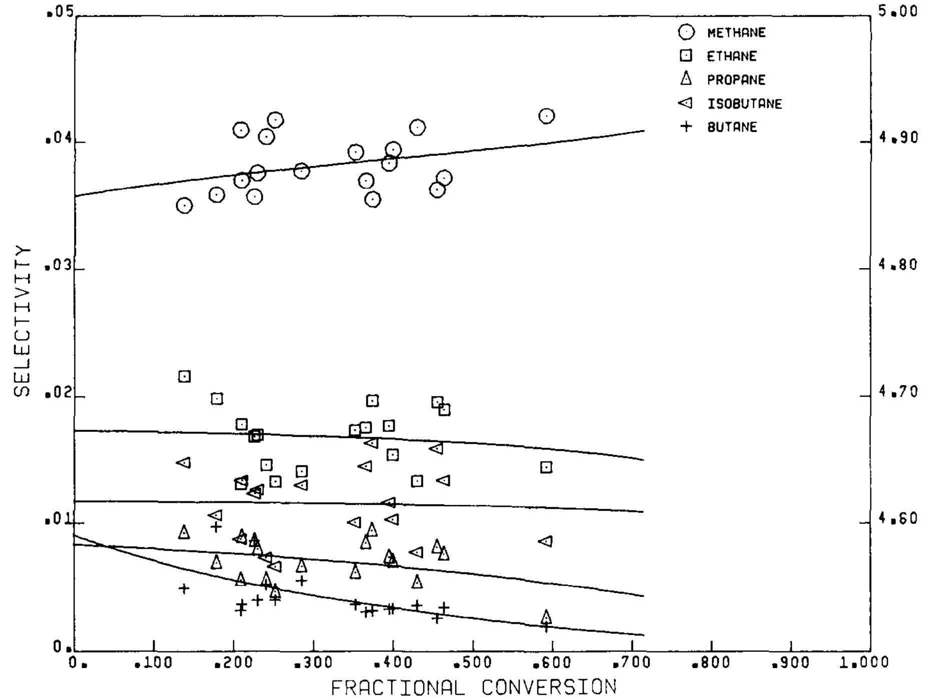

FIG. 1. Product selectivity curves for the hydrogenolysis of isopentane over reduced Fe at 355°C.

which may be regarded as two limiting cases. The reaction mechanism on Ni involves demethylation, while on Ru random splitting of the C–C bonds is observed. Nickel (*7*) forms about twice as much n-C_4H_{10} as i-C_4H_{10}. Splitting factors f and f' are, therefore, equal to $\frac{1}{3}$ and $\frac{2}{3}$, respectively. Since Ni removes only the terminal C atoms from straight chain paraffins, F is set equal to 0.0. On the other hand, ruthenium attacks with difficulty C–C bonds involving a ternary C atom (*4*). Therefore, isopentane is mostly broken into i-C_4H_{10} and CH_4. Probabilities f and f' are then equal to 0.82 and 0.08, respectively. Random splitting of n-C_4H_{10} sets F equal to $\frac{1}{3}$. Table 1 gives values of k_h^*/k_h' for the intermediate hydrocarbons, the ratio of the rate of breaking of C–C bonds to the rate of desorption of the adsorbed species. Even with the widely different assumptions for the splitting factors, the k_h^*/k_h' values are quite similar and large. By assuming equal values of k_h^*/k_h' for all intermediate hydrocarbons, the splitting factors may be eliminated from the selectivity equations. This approximation gave an average splitting–desorption ratio of 64. Also given in Table 1 are values of k_h^*/k_h' obtained from hydrogenolysis on Ni and Ru (*4*, *7*); these numbers are less than 0.45. Therefore, product desorption is the rate determining step in the hydrogenolysis reactions on iron. Hydrocarbon species ad-

TABLE 1

Parameters for the Hydrogenolysis of Isopentane over Fe at 355°C and 7.0 Feed Ratio

h	k_h''/k_{i5}''	k_h^*/k_h' for Fe		Observed k_h^*/k_h'	
		Pattern A[a]	Pattern B[b]	Ni	Ru
n-C_4H_{10}	2.516	73	8	0.45	0.11
i-C_4H_{10}	0.033	27	69	0.33	
C_3H_8	0.382	119	115		0.18
C_2H_6	0.067	57	65		

[a] Same splitting pattern as nickel.

[b] Same splitting pattern as ruthenium.

sorbed on the surface of the catalyst are largely completely hydrocracked to CH_4 before they desorb. Our results confirm the conclusions of Dowie *et al.* (*1*).

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REFERENCES

1. Dowie, R. S., Kemball, C., and Whan, D. A., *J. Phys. Chem.* **80,** 26 (1976).
2. Sinfelt, J. H., "Advances in Catal." Vol. 23, p. 91. Academic Press, New York, 1973.
3. Matsumoto, H., Saito, Y., and Yoneda, Y., *J. Catal.* **22,** 182 (1971).
4. Kempling, J. C., and Anderson, R. B., "Catalysis" (J. W. Hightower, Ed.), Vol. 2, p. 1099. Elsevier, Amsterdam, 1973.
5. Machiels, C. J., and Anderson, R. B., *J. Catal.* **58,** 253, 260, 268 (1979).
6. Monnier, J., and Anderson, R. B., *J. Catal.* **78,** 419 (1982).
7. Machiels, C. J., and Anderson, R. B., *J. Catal.* **60,** 339 (1979).

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