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NOTE

Hydrogen Effects as a Possible Cause of Inverse Arrhenius Plots

A recent paper of Somorjai and co-workers seems to supply new, direct evidences that hydrocarbon reactions on single crystals may result in products, selectivities, even reaction rates analogous to those observed over dispersed catalysts (*1*). In addition to several astonishing similarities, no interpretation has been given for such strange phenomena like the inversion of the Arrhenius plot. This means that, upon increasing the temperature one obtains first a constant, then a decreasing reaction rate. This phenomenon was observed to a different extent for various product classes: for example, benzene exhibited a "normal" Arrhenius plot whereas a definite inversion was reported for methylcyclopentane formation from *n*-hexane.

If single crystals and dispersed catalysts are really so analogous, one is tempted to offer an explanation for this phenomenon derived from the behavior of dispersed catalysts. Yields over supported and unsupported platinum have maxima as a function of the hydrogen pressure (*2–4*). The position of the maximum is related to the hydrogen content of the surface intermediate (*5*): reactions requiring more dissociated intermediates like aromatization have their maximum rates at lower hydrogen pressure values than those, e.g., C_5-cyclization whose intermediate is, according to our opinion (*3*), less dissociated. The position of the maxima reflects also the hydrogen content of the catalyst surface: at higher temperature where less chemisorbed hydrogen is on the surface, higher pressures are necessary to reach maximum reaction rates (*3*).

It follows, therefore, that Arrhenius plots obtained *at constant hydrogen pressures* may give misleading results. This is illustrated in Fig. 1 where we compared the yields of toluene and ethylcyclopentane formed from *n*-heptane. It is seen that the maximum rates for C_5-cyclization are, indeed at higher pressures. Any vertical intersection of the bell-shaped curves would result in "normal" Arrhenius plots for toluene formation (Fig. 1b), but the rates of ethylcyclopentane formation are *lower* at higher temperatures in the hydrogen pressure range below the maximum (Fig. 1a). This would result in very similar temperature dependence as reported in Ref. (*1*) for these two classes of products. The curves reported in Ref. (*1*) correspond, indeed to the positive hydrogen order section (i.e., to the range left from the maximum) except for aromatization at the lowest temperature, where a true maximum appears. The reason why the plots in Figs. 1a and b are so different is that C_5-cyclization needs the presence of a certain amount of hydrogen (*3*). Therefore it can be suppressed almost totally at lower surface hydrogen concentrations. Aromatization only needs hydrogen to remove coke precursors.

These results may be considered as additional evidence supporting the analogies between the two types of catalysts in question. This is all the less surprising since the surface of Pt single crystals is covered largely by carbonaceous deposits during hydrocarbon conversions (*6, 7*). XPS studies showed high amounts of carbon on our Pt-black, too (*8*). Thus, the conclusion may be risked that maximum yields of hydrocarbon conversions as a function of the hydrogen pressure may be generally characteristic of carbonized metals; if it is true, the

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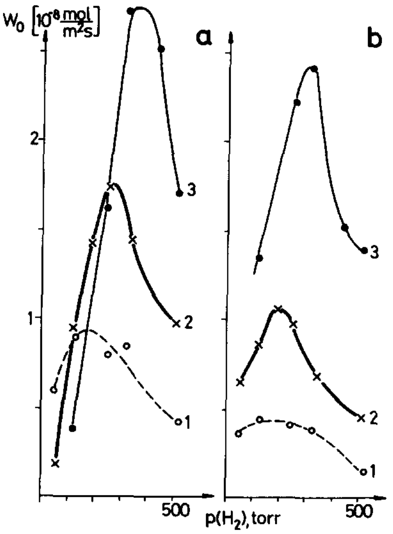

FIG. 1. Yields of ethylcyclopentane (a) and toluene (b) from *n*-heptane over Pt-black, as a function of hydrogen pressure. Catalyst: 0.1 Pt-black-C, static-circulation system, *p* (*n*-Hp) = 9 Torr. (1) 573 K, (2) 603 K, (3) 633 K (*9*).

explanation offered for the inverse Arrhenius behavior should also be correct. Other analogies also would be worth investigating.

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