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Inductive Effects and Product Distributions in the Dehydration of Secondary Alcohols on Alumina

Reply to the Comments by B. H. Davis

We have recently shown (*1*) that inductive and steric effects influence the product distribution in the dehydration of secondary alcohols on γ-Al_2O_3. The logarithm of the selectivity,

$$S_{21} = \frac{\text{concn of product 2-olefins}}{\text{concn of product 1-olefin}},$$

could be linearly correlated with Taft's inductive constant σ^*, while the logarithm of the selectivity,

$$S_{ct} = \frac{\text{concn of } cis\text{-2-olefin}}{\text{concn of } trans\text{-2-olefin}},$$

was a linear function of the steric constant E_s. Davis (*2*) has questioned these correlations with the argument that secondary isomerization of the product olefins may have occurred under the conditions of our experiments. He correctly states that secondary isomerizations may occur at high conversions and low alcohol partial pressures. However, we had definitely excluded secondary isomerization reactions in our experiments. We had explicitly stated in our paper: "Transport phenomena did not affect the conversions and product distributions. Experimental conditions were always chosen such that conversions were less than 15% (usually between 1 and 10%) and secondary reactions did not influence the primary product distribution." Thus, high conversions obviously did not occur under our experimental conditions. Moreover, Davis' argument that the partial pressure of 2-butanol was too low in our experiments to prevent secondary isomerization reactions certainly does not hold, since the dehydration reaction was zero order in all cases, as mentioned in (*1*). A kinetic order zero obviously indicates monolayer coverage of the active dehydration sites. Even in the case of 2-butanol the relative pressure was high enough to accomplish these conditions. Moreover [these results had not been mentioned in (*1*)], the product distributions were independent of W/F (W = weight of catalyst used, F = flow rate) and addition of a terminal olefin to the reaction mixture under dehydration conditions did not cause any detectable isomerization of the added olefin.

Davis argues that Pines and Haag (*3*) yielded 26% 1-butene over alkali-free alumina, which compares well with the value of 29% reported in our own paper. An alumina containing 1.5% alkali increased the 1-butene yield to 44% (*3*). From these data, Davis concluded that the data reported by us were influenced by secondary isomerization reactions. This argument must then also imply that the value of 26% 1-butene reported by Pines and Haag did not represent the true composition of primary products. However, this value was obtained by extrapolation to zero contact time and must therefore definitely correspond to the kinetically

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controlled product distribution. The increased 1-butene yield with increased alkali content is therefore due to the different surface properties of the aluminas which are reflected in the elimination mechanism. It must, moreover, be emphasized that our data and those of Pines and Haag (*3*) are not strictly comparable since not only were different aluminas used but also the reaction temperature was 210°C in our case, while Pines and Haag worked at 350°C.

Davis included the value of 44% 1-butene (*3*) into our set of data and demonstrates that a linear correlation between selectivity and Taft's inductive constant is no longer valid. This result is not surprising, but must be expected and does by no means demonstrate that our correlation is invalid. As mentioned above, the data reported by Pines and Haag (*3*) refer to a catalyst of different surface properties and to largely different reaction temperatures. The elimination mechanism is temperature dependent (*4*). We believe, moreover, that a quantitative correlation of selectivity data obtained on different catalysts is not reasonable. Linear free energy relationships (LFER) should only be made from sets of data obtained on the same catalyst. Davis himself shows that the data he obtained on his catalyst do fit a LFER, although the slope of his straight line is smaller than that reported by us. One should, however, keep in mind that the slope ρ^* as defined by Taft's equation,

$$\log k_{\mathrm{rel}} = \rho^*\sigma^*,$$

is sensitive to the mechanism of the reaction which also determines primary product distributions. Since Davis used different aluminas than we did, the dehydration mechanisms may well have differed in the corresponding experiments.

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DIRK DAUTZENBERG
HELMUT KNÖZINGER

Institute of Physical Chemistry
University of Munich
Sophienstrasse 11, 8000 München 2,
West Germany

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