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LETTERS TO THE EDITORS

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

Recently Dautzenberg and Knözinger (*1*) reported that the 1-alkene selectivity from the dehydration of 2-ols with the general formula $RCH_2CHOHCH_3$, where R varied from methyl to *tert*-butyl, fit a linear free energy relationship (LFER) when correlated with Taft's inductive constant, σ^* (*2*). This is an outstanding example of catalysis by a metal oxide since it relates selectivity to a thermodynamic property.

The data in Ref. (*1*) showed that only 29% of the 1-alkene was formed by the dehydration of 2-butanol. Pines and Haag (*3*), on the other hand, have reported that dehydration of 2-butanol yielded 26% 1-butene over alkali-free alumina; as the alkali was increased to 0.38, 1.0, and 1.5% the 1-butene content increased to 38.4, 40.3, and 44.0%, respectively. Substituting the 44% 1-butene obtained by Pines and Haag from 2-butanol dehydration for the 29% plotted in Ref. (*1*) would render the correlation between selectivity and inductive effects less convincing.

We have previously shown that 1-heptene, added to a 2-octanol reactant, does not undergo isomerization during conversion of the alcohol at approximately 1 atm alcohol pressure; hence, the octene products would not undergo isomerization once they desorbed to the gas phase. However, at high conversion and a low alcohol partial pressure, alkene isomerization does become noticeable. Since Dautzenberg and Knözinger apparently carried out their experiments at less than 1 atm alcohol pressure, isomerization may have influenced their results.

We have obtained the alkene selectivities for 2-ol conversion using porous and nonporous γ-alumina and with a preparation based on Nordstrandite alumina. The three aluminas, pretreated with hydrogen at 550°C, produced the same alkene distribution from 2-octanol. The results presented in this communication were obtained with nonporous Alon-C and Nordstrandite aluminas. The experimental procedure and analytic methods have been described (*4*). The selectivities are defined as they were in Ref. (*1*):

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

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

Our selectivities, obtained in the temperature range of 180–200°C, are compared to those reported by Dautzenberg and Knözinger in Table 1. For R = ethyl, *n*-propyl, and i-propyl there is close agreement between both sets of data for both S_{21} and S_{ct}. With 2-butanol we obtained three values of S_{21} for the three reaction conditions. In this study with 2-butanol, alkene selectivities are the average for four samples collected during the course of a run. The greatest deviation from the average for any isomer in any of the three runs was less than $\pm 1.5\%$. The deviation obtained with the other alcohols did not differ appreciably from that of 2-butanol. When 2-butanol was diluted with hydrogen to give approximately 0.3 atm alcohol partial pressure, we obtained a value of

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TABLE 1

Comparison of the Selectivities for the Dehydration of Secondary Alcohols on Alumina from Ref. (*1*) and the Present Study

Substituent R	σ^*	E_s	From Ref. (*1*)		From this study	
			S_{21}	S_{ct}	S_{21}	S_{ct}
Me	0	0	2.4	5.9	2.4	6.3 (0.3 atm alcohol)
					1.8	4.9 (1 atm 2-butanol)
					1.5	5.1 (1 atm mixture of 2-butanol/2-octanol)
Et	−0.1	−0.07	1.5	5.5	1.5	5.2
n-Pr	−0.12	−0.36	1.3	5.2	1.2	6.1
i-Pr	−0.19	−0.47	0.96	4.7	1.1	5.1
t-Bu	−0.30	−1.54	0.64	2.1	0.75	1.7
n-Pe	—	—	—	—	1.1	10

2.4 for S_{21}; this is the same value obtained by Dautzenberg and Knözinger. When we converted pure 2-butanol at 1 atm alcohol pressure S_{21} declined to 1.8; for an equal molar mixture of 2-butanol and 2-octanol with a total alcohol pressure of 1 atm S_{21}

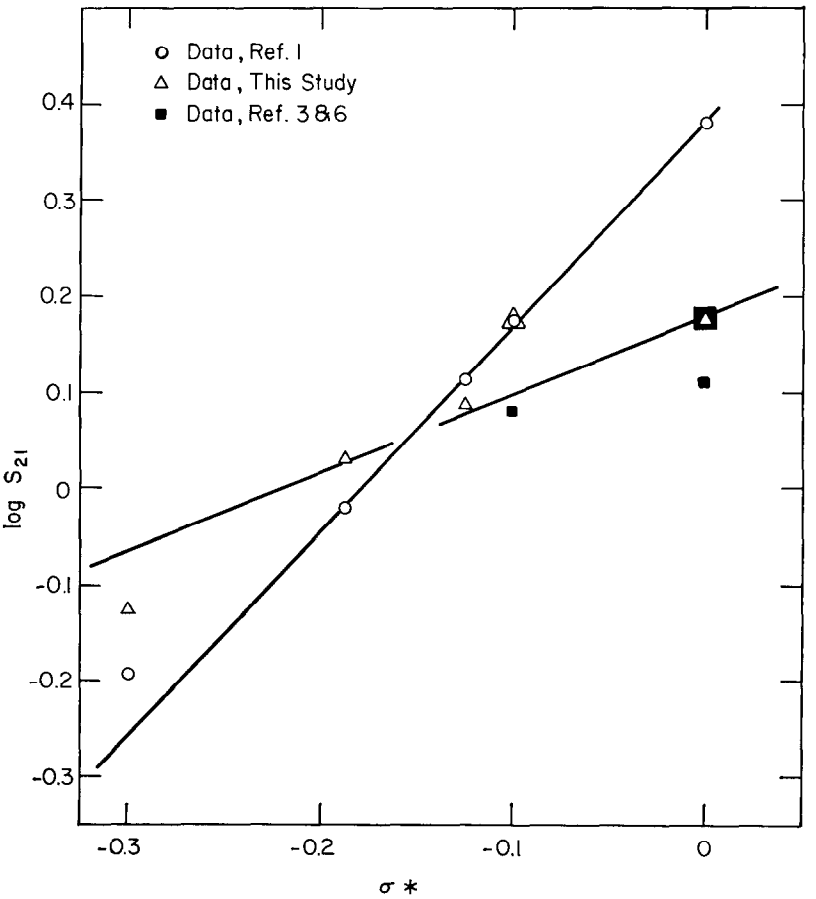

FIG. 1. Correlation of the selectivity S_{21} with Taft's inductive constants.

had the low value of 1.5. S_{21} was 1.1 for the octenes formed during the conversion of the 2-butanol/2-octanol mixture; this is the value we obtained for pure 2-octanol (*4*). Our value of 1.5 for S_{21} from the conversion of 2-butanol in the alcohol mixture is only slightly higher than the value of 1.3 obtained by Pines and Haag (*3*) for alumina containing 1.5% alkali.

At a given temperature, 2-butanol has a considerably higher vapor pressure than does 2-octanol; hence, at a given alcohol pressure 2-butanol will have a much smaller relative pressure (P/P_0), and a lower alumina surface coverage, than 2-octanol. Thus, our results and those of Pines and Haag (*3*) suggest that 2-butanol at 1 atm or less does not provide sufficient alumina surface coverage by alcohol to prevent a secondary isomerization reaction from altering the initial alkene distribution.

Figure 1 is a plot showing the correlation of the selectivity, obtained by Dautzenberg and Knözinger, by Pines and co-workers and in the present study, with Taft's inductive constants. Our results, as well as those of Dautzenberg and Knözinger, give a good correlation. However, our point corresponding to 2-pentanol (R = Et), while agreeing with the one obtained by Dautzenberg and Knözinger, is above our best-fit line. If butenes undergo isomerization due to a low alcohol surface coverage, it would be expected that pentenes would isomerize but to a lesser degree. The data point corresponding to the pentene selectivity obtained by Pines and co-workers (*5*), using pyridine as an acidity poison, does fit our curve. In the present study, the total change in the 1-alkene percentage was about 5 mole% in going through the series from R = methyl to i-propyl. Thus, our correlation, even if valid, does not indicate a strong influence on S_{21} by inductive effects.

Neglecting R = t-butyl, our S_{ct} selectivity is essentially the same for all of the alcohols in Fig. 1. Including the data for 2-octanol, there may be an increase in S_{ct} for normal 2-ols as the alkyl group R increases in carbon number. Thus, S_{ct} will not correlate with either σ^* or Taft's steric constants, E_s. Even in Ref. (*1*), where a linear plot was obtained, E_s for R = Me through i-Pr are so similar that the curve may be dominated by the single point for t-Bu.

In summary, it appears that the low 1-butene content of 29 mole% is caused by an isomerization due to a low relative pressure of 2-butanol. When the isomerization is suppressed by alkali or a higher surface alcohol coverage, the 1-butene selectivity from 2-butanol is only slightly lower than that from the other 2-ols used in the study described in Ref. (*1*). The present data show only a slight dependence of S_{21} on the inductive effect of the alkyl group.

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