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Dehydration of Propanols

A Study of the Dehydration of 1- and 2-Propanol over a Molecular Sieve 13X Catalyst

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The kinetics of the vapor phase catalytic dehydration of 1- and 2-propanol over Linde 13X have been compared in a static system at 240 and 270° at propanol pressures up to 10 Torr. The rate of formation of propene from 1- and 2-propanol obeys a first-order rate law with k_s, the reaction rate constant for the surface reaction, given by $3.6 \times 10^6 \exp -(22\,550/RT)$ and $1.7 \times 10^{10} \exp -(28\,400/RT)$ sec^{-1}, respectively, for surface coverages, θ, up to 0.5. Estimates of the heats and entropies of adsorption of these alcohols were deduced from the kinetic measurements.

INTRODUCTION

Several recent studies have been concerned with the dehydration of aliphatic alcohols over zeolite catalysts. The influence of alcohol chain length, pore geometry of the zeolite and catalyst specificity towards olefin or ether formation has been investigated (*1*, *2*) and the mechanism of dehydration of 2-propanol by sodium faujasite has been discussed by Frilette and Munns (*3*). The latter work somewhat contradicts that of Tsitsishvili *et al.* (*4*) who found that synthetic zeolite had considerable catalytic activity for the dehydration of 2-propanol below 300°. A later Russian paper (*5*) confirms the exclusive formation of propene from both 1- and 2-propanol at temperatures as low as 250 and 230°, respectively, over zeolite of structure Y.

A review by Venuto and Landis (*6*) reveals that little work of a detailed kinetic nature has been done and that 1-propanol has been rather neglected in studies of the C_2–C_6 alcohols. Furthermore, comparatively few studies of 1-propanol dehydration appear to have been made even over conventional γ-alumina as catalyst (*7*, *8*). The present paper seeks to remedy some of these omissions and attempts to compare some fundamental parameters associated with the catalytic dehydration of propanols over a well-defined Linde 13X molecular sieve catalyst.

EXPERIMENTAL METHODS

Apparatus

Dehydration was carried out in an electrically heated tubular Pyrex glass reaction vessel (498 ml) provided with a central thermocouple-well and was similar to that previously described (*9*). The change in the composition of gaseous products and reactant in the presence of the catalyst was monitored by automatic scanning of the relevant portion of the mass spectrum using an A.E.I. MS.10 mass spectrometer.

Procedure

The reaction vessel containing the catalyst and the alcohol vapor reservoir were evacuated to 10^{-5} Torr. The reaction vessel was maintained at reaction temperature during this evacuation before each run for 30 min. A greaseless valve connecting the reaction vessel to the remainder of the vacuum system was then closed and alcohol which had previously been frozen in a

CO_2/methanol bath was warmed until the desired alcohol vapor pressure had been achieved in the alcohol reservoir. The greaseless valve connecting this reservoir to the reaction vessel was opened and simultaneously a stop-clock was started. The initial pressure of alcohol vapor in the reaction vessel was recorded by a calibrated manometer. Finally the greaseless valve was closed and the vapor was isolated in the reaction vessel.

(i) 2-Propanol dehydration was followed by scanning the positive ion current response of the $m/\epsilon = 45$ and 41 peaks as a function of time. These peaks represent the most intense peaks of the mass spectrum of 2-propanol (60-CH_3) and propene (42-H), respectively. Corrections have been applied for a contribution to the $m/\epsilon = 41$ through fragmentation of 2-propanol as well as instrument sensitivity for 2-propanol and propene. Peaks at $m/\epsilon = 59$ and 87 were absent at both 240 and 270° indicating that diisopropyl ether (*10*) was not formed.

(ii) 1-Propanol dehydration was followed by scanning $m/\epsilon = 31$ and 41 at known times. The $m/\epsilon = 31$ represents the most intense peak of the mass spectrum of 1-propanol (60-CH_2OH). Corrections have been applied for a contribution to the $m/\epsilon = 41$ through fragmentation of 1-propanol and also instrument sensitivity. At 240° an additional peak at $m/\epsilon = 43$ which was greater than that from fragmentation of 1-propanol could be attributed to the formation of di-*n*-propyl ether (*10*). This effect was discernible at the commencement of a run at initial pressures of 1-propanol greater than about 3 Torr; it has been ignored in the kinetic interpretation of this work.

Materials

BDH 1-Propanol and 2-propanol were distilled twice; the fractions used had boiling points of 97.5° for 1-propanol and 82.5° for 2-propanol.

Linde 13X molecular sieve in powder form, free from binder, was used as catalyst. A convenient quantity 0.004 and 0.063 g for 2-propanol and 1-propanol, respectively, was placed in a fused-silica boat in the reaction vessel adjacent to the thermocouple-well. Thermogravimetric analysis showed that heating the catalyst to 270° caused a 22.5% reduction in weight due to loss of water. This has been taken into account in the calculation of kinetic parameters.

Interpretation of Data

The positive ion currents from both series of experiments were translated into partial pressures of alcohol and olefin. These pressures were expressed as a ratio, designated y_p, and plotted as the function $\log [(1 + y_p)/y_p]$ against time. Experimental values of the reaction rate constant, k_{exp}, have been evaluated from the slopes of the straight lines, characteristic of first-order kinetics, which were obtained.

The relationship between these rate constants, k_{exp}, and the surface rate constants, k_s, for a unimolecular process is given by $k_s C_a A = k_{exp} C_g V$, where A is the area of the catalyst, V is the volume of the gas phase and C_a and C_g are the concentrations of alcohol adsorbed at the surface and in the gas phase. The concentration C_g is given by P/kT, where p is the pressure and k the Boltzmann constant, and C_a by $N_s\theta$ where N_s is the number of catalytic sites per cm^2 and θ is the fraction of the surface covered. Following Eley and Rossington (*11*) substitution of the Langmuir isotherm for θ in the form $\theta = bp/(1 + bp)$, where b is an exponential function of the heat of adsorption of the alcohol and rearranging gives:

$$(k_s A N_s kT/V)(1/k_{exp}) = (1/b) + p. \quad (1)$$

A plot of $1/k_{exp}$ against p should give a straight line if this model is valid. Values of k_s, the surface reaction rate constant and the coefficient b of the Langmuir isotherm may be evaluated from the slope and intercept of the plot provided an estimate of N_s, the number catalytically active sites per cm^2 can be obtained.

Furthermore, a knowledge of k_s and b at different temperatures allows an estimate of the true activation energy of the surface reaction from the former and the heat of adsorption and extent of surface coverage at different pressures from the latter. By referring the entropy of adsorption to a standard state of alcohol vapor of 1 Torr and surface coverage $\theta = 0.5$, the entropy of adsorption has been shown by Kemball (12) to be given by

$$\Delta S^\circ_{\text{ads}} = R \ln b - RTd(\ln b)/dT, \quad (2)$$

$$\text{where} \quad d(\ln b)/dT = \Delta H^\circ_{\text{ads}}/RT^2. \quad (3)$$

Hence $\Delta S^\circ_{\text{ads}}$ and $\Delta H^\circ_{\text{ads}}$ can be deduced from the kinetic data.

RESULTS AND DISCUSSION

In the absence of catalyst no detectable change occurred in the mass spectral pattern of either alcohol when vapor from the reaction vessel was monitored by the mass spectrometer. In the presence of the catalyst dehydration was followed for about 1 hr for each run. Typical first-order plots for 1-propanol and 2-propanol dehydration are shown in Figs. 1 and 2. Good straight lines up to 90 and 60% conversion of 2-propanol at 270 and 240°, respectively, were obtained, Fig. 2. In the case of 1-propanol, Fig. 1, satisfactory straight-line plots were found at 270° up to at least 60% conversion, but at the lower temperature of 240°, departure from a straight-line plot for conversions of less than about 20% at pressures greater than 3 Torr became apparent. The cause of this discrepancy is the formation of di-*n*-propyl ether and since the ratio method employed in the kinetic equations does not take this into account, deviation from the first-order plot occurs.

Thermodynamic data presented by Knözinger and Köhne (13) predicts that the likelihood of ether formation through dehydration of two molecules of alcohol is greater for 1-propanol compared with 2-propanol, $\Delta G^\circ_{550^\circ K}$ being +1.0 and +4.5 kcal/mole, respectively.

Figure 3 shows that the pressure dependence of the reaction rate constant gives a straight-line relationship in accordance with Eq. (1). The values of b and k_s given

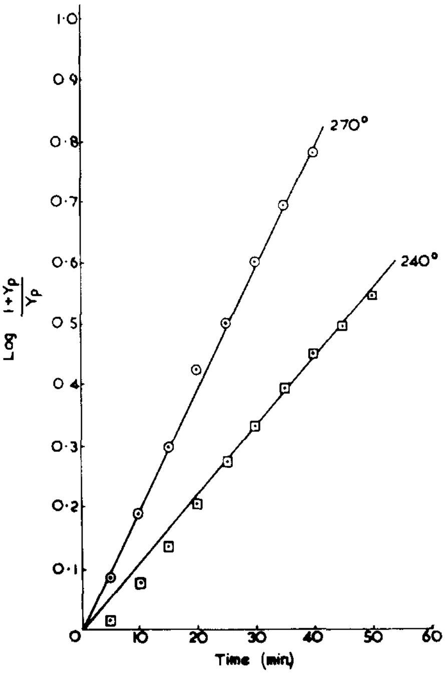

FIG. 1. Typical first-order dehydration of 1-propanol at 240 and 270° at 4 Torr.

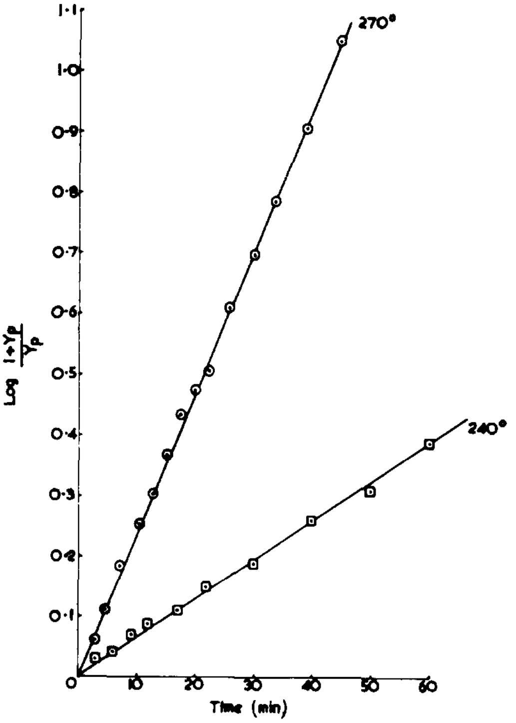

FIG. 2. Typical first-order dehydration of 2-propanol at 240 and 270° at 9 Torr.

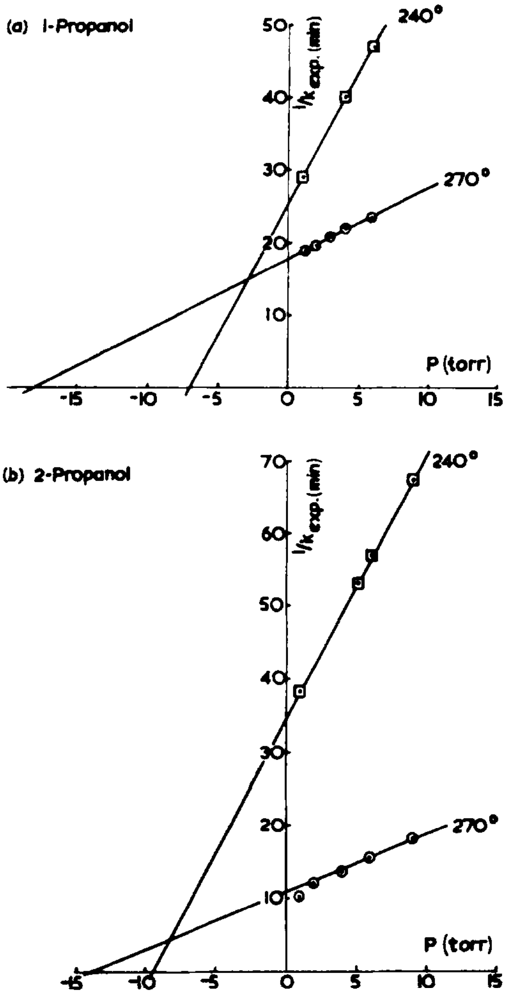

FIG. 3. Reciprocal of experimental first-order rate constants as functions of pressure and temperature. (a) 1-propanol; (b) 2-propanol.

in Table 1 were evaluated from the slope and intercept of these plots. The value of N_s which was used for calculating k_s has been estimated from the value of 10^{21} catalytically active sites/g determined by Turkevich (*14*) and a surface area of 865 m^2/g found by Ward (*15*), on this basis, N_s comes to about 10^{14} sites/cm^2. This value assumes that the internal surfaces of the zeolite is freely available to the alcohol molecules. This is reasonable because the 9 Å port diameter of the molecular sieve is almost twice the size of the alcohol molecules.

Substitution of the b values given in Table 1 into Eq. (3) and solving for $\Delta H^\circ_{\text{ads}}$ gives an estimate of —17.0 kcal/mole for 1-propanol and —8.7 kcal/mole for 2-propanol in the temperature range 240–270°. These values illustrate the difference in alcohol surface interaction. The value for 2-propanol is considerably lower than that for the normal alcohol: it is in reasonable agreement with that found by Wade *et al.* (*16*) for 2-propanol over alumina and lies close to the heat of liquefaction of 2-propanol (*17*). The entropies of adsorption reported in Table 1 were obtained from Eq. (2); again it is apparent that the adsorption process is accompanied by a greater entropy change in the case of 1-propanol than that experienced by 2-propanol.

If the entropies of adsorption given in Table 1 are referred to a standard state of one atmosphere, a factor of R ln 760, i.e., 13.2 gibbs/mole must be subtracted from these experimental values, so that the entropy loss on adsorption becomes 23.9 and 8.2 gibbs/mole for 1-propanol and 2-propanol, respectively. This result may be compared with that calculated for the change in entropy on adsorption due to loss of translational degrees of freedom (*18*). ΔS_{trans}, the total translational entropy in the gas phase at 1 atm pressure for the propanols, molecular weight 60 at 528° is about 41.1 gibbs/mole. For a mobile adsorbate confined to a plane at a standard

TABLE 1

Alcohol	E_t (kcal mole^{-1})	k_0 (sec^{-1})	$\Delta S\ddagger$ (cal deg^{-1} mole^{-1})	b 240°	b 270°	$\Delta H^\circ_{\text{ads}}$ (kcal mole^{-1})	ΔS_{ads} (cal deg^{-1} mole^{-1})
1-Propanol	22.55	3.6 ± 10^6	−27.9	0.139	0.055	−17.0	−37.1
2-Propanol	28.40	1.7×10^{10}	−14.8	0.107	0.07	−8.2	−21.4

concentration of 1 mole/22.5T Å^2, where T is the temperature, ${}_2S_{\text{trans}}$ at 528° is about 19.1 gibbs/mole. The difference, ${}_3S_{\text{trans}} - {}_2S_{\text{trans}} = 22$ gibbs/mole is close to the experimental value found for 1-propanol adsorption. The smaller value of 8.2 gibbs/mole found for 2-propanol must be associated with a type of interaction within the cavities of the zeolite, which is even less restrictive to the 2-propanol molecule. In both cases, these rough calculations are sufficient to show that we are dealing with molecules which have considerable freedom in the proximity of the surface. Indeed, the weakness of the interaction suggests that comparatively mild polarization forces may be responsible, particularly in the case of 2-propanol.

Infrared spectroscopic studies of pyridine adsorbed on zeolites have provided valuable information about the nature of the catalyst surface. It has been established (*15*, *19*, *20*) that Brönsted acid sites are absent and that only Lewis acid sites are present in Na–X zeolite. Furthermore, the alkali cation zeolites do not catalyze carbonium ion reactions, e.g., cumene cracking. Alkaline earth cation zeolites are required for the catalytic cracking reaction where the Brönsted acid sites located at acidic hydroxyl groups are responsible for catalysis (*20*). This shows that proton transfer between catalyst and alcohol molecule resulting in an oxonium or a carbonium ion intermediate is not necessary for the dehydration of the propanols to yield propene. This view correlates with that of Knözinger *et al.* (*21*) who suggested that the ability of alcohols to form ethers, rather than olefins, depends upon the ease of formation of surface alkoxide. The absence of lattice hydroxyl groups in Na–X (*22*) indicates that the propanols cannot be adsorbed by hydrogen bonding to these groups as is believed to occur at an alumina surface (*23*). The scarcity of tri-coordinated aluminium atoms present in Na–X will limit the formation of aluminium propoxide and the only other potentially active sites are the alkali metal lattice cations at the S_{II} and S_{III} sites. Electrostatic polarizing fields in the vicinity of these cation sites would appear to be responsible for the dehydrating activity which has been found.

Another feature of the reaction using the Na–X catalyst is the ease of desorption of the reaction products implied by the first-order disappearance of the propanol. It is known from infrared evidence that although propene adsorption (*24*) is somewhat stronger than ethene adsorption (*25*), it can nevertheless be completely desorbed at 250°. The release of propene from the catalyst surface at the commencement of reaction was evident from the immediate change in mass spectral pattern which was associated with the gain in height of the $m/\epsilon = 41$ peak.

Monitoring the $m/\epsilon = 18$ response showed that release of water from the catalyst surface did not occur so readily. Although reaction was proceeding with the formation of propene, the catalyst was able to tolerate water initially formed as the other product. This water must accumulate, presumably within the cavities of the faujasite, up to an equilibrium level beyond which displacement into the vapor phase will occur. Again, this is in agreement with infrared evidence of Carter *et al.* (*26*) who visualize, on the basis of a broad band at 3400 cm^{-1} and a narrow band at 1655 cm^{-1}, the presence of hydrogen bonded "polymeric water" which is still appreciable at 300° on Na–X.

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