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The Use of Stopped-Flow Gas Chromatography to Study the Catalytic Dehydration of Alcohols

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The dehydration of alcohols on modified aluminas was studied by using the same material simultaneously as catalyst and as stationary phase in a gas–solid chromatograph. In such a system, periodic stopping of the gas flow through the column leads to the reaction products appearing as sharp chromatographic peaks for each stopped-flow interval, so that the rate of reaction is effectively followed throughout the whole course of the reaction. The reliability of comparative measurements is enhanced by carrying out a standard dehydration (e.g., of *n*-heptanol) together with the dehydration of another alcohol. The results support a *trans*-elimination mechanism and suggest that there are two distinct types of catalytic site. Autocatalysis (by water) and polymerization of olefin products were also investigated and allowance was made for these effects in the kinetic analysis.

In an earlier paper (*1*), we have shown that a number of heterogeneous catalytic reactions may be studied conveniently by using the same surface simultaneously as the catalyst and as a gas-chromatographic column. In this way the products and reactants may be continuously separated from each other. The products form a broad chromatographic band with a sharp head tailing gradually into the peak formed by the reactant, this head being at the start of the chromatogram if the products move through the column more rapidly than the reactant (Fig. 1) (i.e., are less strongly adsorbed on the catalytic surface) and at the end of the chromatogram if products move more slowly than the reactant. Analysis of the chromatogram enables the kinetics of the reaction to be determined.

A generally more-powerful technique involves the periodic stopping and restarting of the carrier-gas flow through the chromatographic/catalytic column so that the products formed in each of the stopped-flow periods themselves form *sharp* peaks superimposed on the broad band of products formed under conditions of continuous gas flow. The resulting chromatogram is illustrated in Fig. 2. Since the areas of these peaks represent the amounts of products formed in a specific small time interval during the course of the reaction (Fig. 3), they give a direct measure of the *rate of reaction* at that time. Since the proportion of reactant on the catalyst may be deduced from the chromatogram, the rate of reaction *on the surface* is also directly determined.

In this study the technique has been applied to the study of the dehydration of alcohols over alumina and alumina modified with 10% KCl. This modification has been shown (*2*) to provide a very satisfactory material for gas–solid chromatography. Furthermore, since alcohols are very tenaciously held by both surfaces while the dehydration products (olefins and water) are relatively weakly adsorbed, it is easy experimentally to produce a large number of sets of stopped-flow peaks, so that a large number of independent rate measurements may be made during one reaction.

The catalytic dehydration of alcohols has been very extensively studied. The review by Winfield (*3*) summarizes studies on a variety of catalysts, while the use of

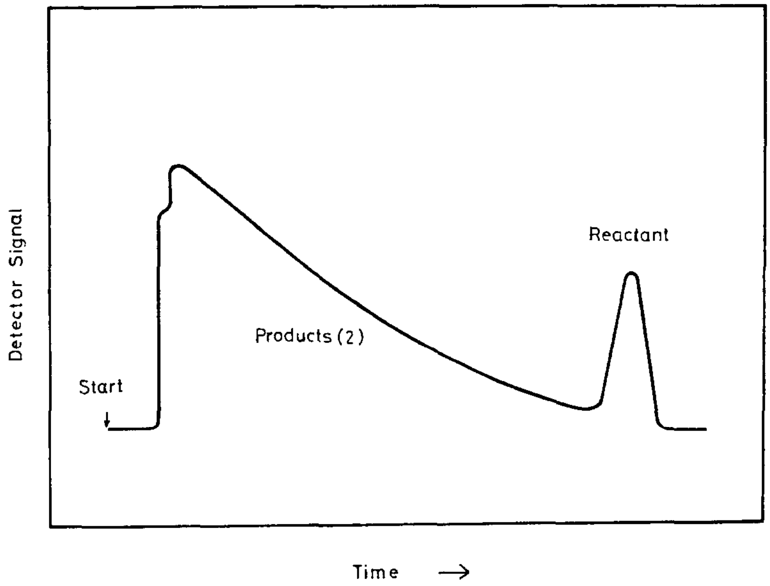

FIG. 1. A reaction chromatogram: The reactant is here more strongly adsorbed than either of the two (detectable) products.

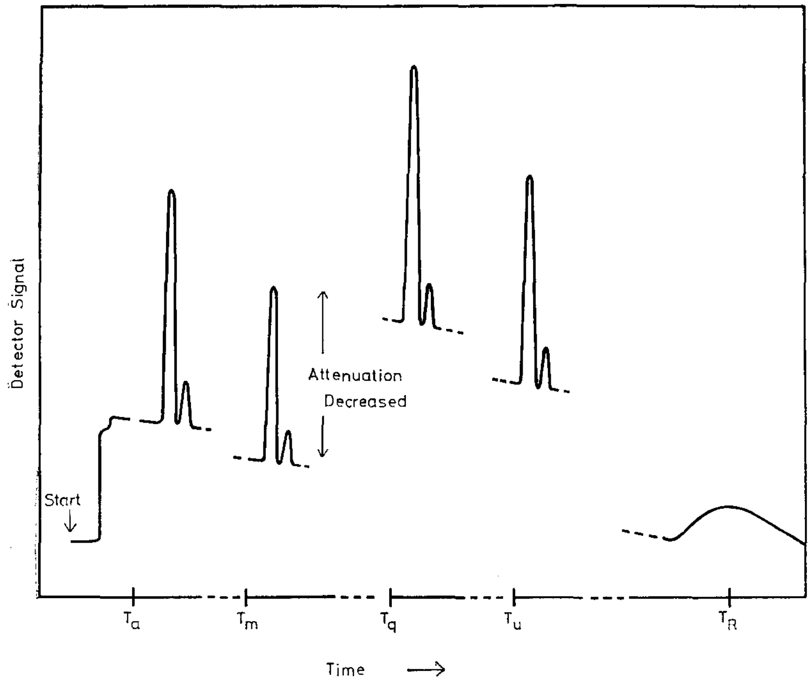

FIG. 2. Sections from a stopped-flow chromatogram: Each pair of peaks corresponds to the (detectable) products generated in the reaction during a stopped-flow interval (e.g., at T_a, T_m, etc.). In this example many stopped-flow intervals are possible because the reactant (emerging at T_R) is much more strongly adsorbed than the products. In the case of alcohols on modified or unmodified Al_2O_3, this adsorption is so strong that no alcohol peak is ever observed; indeed, there is no apparent movement of the alcohol along the column for the stopped-flow peaks emerge at a constant time after the stopped-flow interval. Water is not detected by the flame-ionization detector employed. Note the change of signal attenuation.

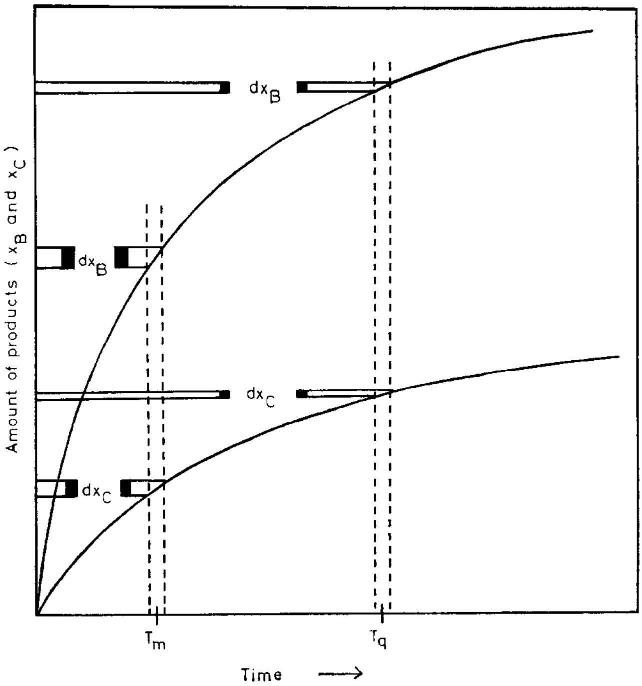

FIG. 3. Plot of amounts of reaction products (B and C) as a function of reaction time: dx_B and dx_C are amounts of products formed in stopped-flow intervals (T_m and T_q, see Fig. 2).

alumina catalysts is discussed particularly in the article by Pines and Manassen (*4*). Alumina is found to give almost entirely dehydration products, with the ratio of ether to olefin rising with reduction of temperature (*5*, *6*) or increasing alcohol pressure (*7*). γ-Alumina appears to cause less isomerization than other aluminas, and small percentages of alkali ions (*8*) further prevent this isomerization. The increasing rate of reaction on changing from primary to secondary to tertiary alcohols is well established, but within and across a series several different apparent orders have been found. We believe that these may arise from the difficulty of making precise comparative measurements by traditional techniques. There appears to be little agreement on the effect of water on catalytic activity, some workers claim that it activates, others that it deactivates the catalyst (*9*, *10*). In our experiments water has clearly been shown to activate the catalyst.

Most measurements have been made with relatively high pressures of alcohol above the catalyst surface (*5*, *11*), so that bimolecular reactions including those between gaseous and adsorbed molecules have been encouraged. In our experiments the vapor pressures of alcohol above the surface have been negligible, so that we have been looking essentially at the direct surface reaction under conditions of low surface coverage.

THEORY OF THE STOPPED-FLOW TECHNIQUE

We shall only consider here the simple case of one reactant decomposing by first-order kinetics to give one or more products which themselves undergo no further reaction. We shall further limit ourselves to those cases where the proportions of different products do not change during the course of the reaction. These limitations correspond to the conditions found in our dehydration experiments.

If x is the amount of product formed; t, the time; k, the velocity constant; f, the fraction of alcohol molecules on the surface (in practice f was 1 *in all our experiments*); and a, the initial amount of reactant; we have

$$dx/dt = kf(a - x),$$

or

$$x = a(1 - e^{-kft}).$$

The amount of product formed in a stopped-flow interval starting at $T - v$ and ending at $T + v$ is then

$$x_{(T+v)} - x_{(T-v)} = 2ae^{-kfT} \sinh(kfv),$$

so that, if S is the area (at constant attenuation of the detector signal) of the chromatographic peak (or peaks) produced,

$$\log_e[S/\sinh(kfv)] = -kfT + \text{const.},$$

which reduces to

$$\log_e(S/kfv) = -kfT + \text{const.},$$

when kfv is sufficiently small. This last equation may be obtained directly by assuming that S/v is a direct measure of the rate at time T; this assumption will of course become justified as v or k is reduced sufficiently.

Experimental Methods

All the experiments were conducted in commercial gas chromatographs (Pye 104) with a flame-ionization detector which gives no response with H_2O. The gas flow was stopped and restarted by means of a tap placed before the start of the column. However, operation of this tap does not lead to an instantaneous stopping and reestablishment of the normal flow conditions because of the pressure drop across the column during normal flow conditions. A correction of about 20 sec was found necessary to reduce the observed stopped-flow time (between turnings of the tap) to the real stopped-flow time. This correction was made by measuring the flow with a soap bubble flow meter, and was confirmed by measuring the differences in retention times of methane (nonretarded) and alkenes with and without a stopped-flow interval. This correction is, of course, insignificant in those experiments where a constant stopped-flow interval is used throughout the run.

A commercial activated alumina (γ-Al_2O_3, Type H, Peter Spence, Widnes, Lancashire, England) was used as the catalyst or catalyst base. Modification was carried out with an aqueous solution of KCl, followed by evaporation drying and sieving. Nitrogen (dried with molecular sieve) was used as carrier gas. Columns were 1.5 m long (except the CaC_2–10% KCl/Al_2O_3 column which was 1.0 m long) and were dried overnight in a stream of nitrogen at 400°C before use.

The alcohols were obtained from commercial sources and their purity was tested by gas–liquid chromatography with a 20% diglycerol/embacel column. Nearly all the alcohols used contained less than 1% total impurities, but a few were found to be grossly impure and had to be purified by preparative gas–liquid chromatography. The impurities were shown to be substances of similar boiling point to the alcohol, generally ketones, esters, and amines, but not halides and not alcohols of the same carbon number or ethers of twice the carbon number. The effects of such impurities should thus be negligible using the chromatographic method. This was demonstrated by making separate measurements on some alcohols of highly varying purity when consistent results were obtained within the experimental error as is shown in Table 1.

TABLE 1
Insensitivity of Rate Measurements to Impurities in Alcohol Sample

Alcohol	Total impurity (%)	Apparent rate of dehydration observed (relative to *n*-heptanol)
n-Pentanol	1.5	0.95
	12.5	1.06
n-Hexanol	0.5	1.02
	45	0.92
4-Methyl-*n*-pentanol	0.5	0.96
	17.5	0.89

The product olefins were identified by their retention times on the alumina or modified alumina columns, using pure olefin samples for comparison. No evidence was found for any movement of alcohol along the column over periods as long as 7 hr, so that the assumption that f is 1 was amply justified.

RESULTS AND DISCUSSION

1. Products

The products of the dehydration reactions were identified as alkenes with the same number of carbon atoms as the alcohol from which they originated. With the 10% KCl/Al_2O_3 columns there was no cracking and no isomerization of any of the alkenes; these observations were also checked by separate injections of the alkenes. As the flame-ionization detector is not sensitive to water vapor, the peaks due to the water were not normally observed, but they were demonstrated by using a special column in which some CaC_2 was placed at the end of the column before the detector. This converted the water into acetylene which gave a signal. The water peaks moved through the column somewhat slower than heptene peaks.

Primary alcohols decomposed readily around 300°C to give only one product, which was shown to be the terminal olefin. Secondary alcohols decomposed readily between 200 and 250°C. Only one product was formed from the cyclic alcohols (e.g., cyclohexene but no methyl cyclopentene from cyclohexanol) and from isopropanol (prop-1-ene); in other cases there was more than one product. Thus *n*-heptan-4-ol gave rise to two stopped-flow peaks corresponding to *cis*- and *trans*-hept-3-ene (see Table 2) as expected from simple dehydration without isomerization. In the series of alkan-2-ols, both *cis*- and *trans*-alk-2-enes were formed with a preponderance of the *cis*-isomer in all cases. The alk-1-ene was also formed but its proportion decreased as the carbon number of the alcohol increased until, at C_6, it could no longer be observed in the stopped-flow chromatogram (in view of the incomplete separation of the three olefins, this corresponds to a maximum of 5%). Tertiary alcohols decomposed very readily about 200°C: 2-methylpropan-2-ol and 2-methyl-*n*-butan-2-ol gave only one product (2-methylprop-1-ene and 2-methylbut-1-ene, respectively) while 2-methylpentan-2-ol gave both possible products (2-methylpent-2-ene and 2-methylpent-1-ene in the ratio of 1:1.5).

TABLE 2

RETENTION TIMES (relative to isobutylene) OF LINEAR C_7 OLEFINS AND OF THE PRODUCTS FROM THE DEHYDRATION OF *n*-HEPTAN-4-OL ON 10% KCl/Al_2O_3 AT 210°C

Olefin	Relative retention time	Relative retention time of products
trans-Hept-3-ene	4.89	4.89 ± 0.05
trans-Hept-2-ene	5.07	
cis-Hept-3-ene	5.43	5.43 ± 0.05
n-Hept-1-ene	5.46	
cis-Hept-2-ene	5.71	

Where more than one olefin was produced, the ratio of products remained constant on one column over a period of several months, but there were slight variations between different columns apparently prepared and treated in the same way. There was no evidence of intermediate ether formation and the first-order kinetics is in agreement with this as is the low surface coverage used. The immobility of the alcohol on the surface suggests surface alkoxide formation, a view supported by various other workers, e.g., Heiba and Landis (*12*). The absence of any skeletal rearrangement points against a carbonium-ion mechanism, and a concerted elimination mechanism seems to be likely as has been proposed by others, particularly Pines and his co-workers (*13–17*). The problem remains whether the elimination is *cis* or *trans* oriented.

To elucidate the mode of elimination the reaction was considered in terms of a mechanism in which the alcohol is bound to the alumina surface (consisting of oxide ions in a plane) as an alkoxide, the oxygen of the alkoxide being in the plane. The retention times for a series of alkenes show that the alumina surface interacts with $-CH_2-$ groups, with a free energy of adsorption at 210°C of approximately —0.55 kcal/mole/$-CH_2-$. One would therefore expect the alkyl groups to lie on the surface. Calvet and Astruc (*18*) have confirmed this by surface area measurements finding that the surface area occupied by alcohols increases by 6 Å^2 per $-CH_2-$ group. However, they find a smaller increase between ethanol and propanol of 4 Å^2 and only a small increase between methanol and ethanol of 3 Å^2, indicating that a methyl or ethyl group attached to the hydroxyl bearing carbon will not lie on the surface under the experimental conditions for dehydration ($T = 500°K$), while longer alkyl chains will lie on the surface.

Similar considerations apply to the transition states for elimination. The proportion of alk-1-ene formed from alkan-2-ol dehydration should therefore decrease rapidly as the alkyl chain length increases. Since the methyl group is off the surface, as soon as the alkyl chain is long enough to lie on the surface in the ground state, little or no alk-1-ene would be expected, i.e., for a C_3 chain (pentan-2-ol) little pent-1-ene is expected, and for C_4 and greater, no alk-1-ene is expected. For the tertiary alcohols studied, one of the methyl groups must lie on the surface, so a considerable proportion of alk-1-ene is always expected.

In this mechanism the transition states for *trans*-elimination have the hydrogen to be eliminated much further from the alumina surface than in the transition states for *cis*-elimination. However, the stereoelectronic path for *trans*-elimination is generally considered to be much more favorable than that for *cis*-elimination. Consequently, no attempt has been made to predict whether *cis*- or *trans*-elimination should occur on the basis of this mechanism, but to see which does occur by comparing the observed products and product ratios with the predictions. The relative energies of the *cis*- or *trans*-olefin formation transition states by either a *cis*- or a *trans*-elimination were estimated from the number of protons lying on the surface for each; e.g., consider *n*-heptan-2-ol; a molecular model shows that the ground state would have the methyl group away from the surface and the alkyl chain lying flat on the surface with 7 hydrogen atoms on the surface. The ground state with the methyl group on the surface is higher in energy. The *trans*-elimination transition state to give the *cis*-olefin has similarly 7 hydrogens resting on the surface, whereas the one giving the *trans*-olefin only 6 hydrogens lie on the surface. Hence for a *trans*-elimination mechanism, a *trans*- to *cis*-olefin ratio less than 1 is predicted. Conversely for a *cis*-elimination mechanism the *cis*-olefin transition state has 5 hydrogens on the surface excluding the one to be eliminated, and the *trans*-olefin transition state has 6 hydrogens; so a *trans*/*cis* ratio greater than 1 is predicted. Using the free energy of interaction of —0.55 kcal/mole/CH_2 as the transition state stabilization per extra hydrogen on the surface, a numerical value to these ratios may be obtained of:

trans-elimination	*trans*/*cis*	0.6,
cis-elimination	*trans*/*cis*	1.8.

The predictions are compared with observations in Table 3.

Several points arise from Table 3; (i) For *n*-heptan-4-ol, both groups lie on the surface so the predicted order is the inverse of the alkan-2-ol case; (ii) the predictions of the amount of alk-1-ene are in fair agreement with the observations. The agreement is good, but the free energy involved in forcing a methyl or ethyl group onto the surface is not known and hence the calculations are only approximate. The widely differing product stabilities between alk-1-ene and alk-2-ene will also affect the transition state energies and this has been neglected. (iii) The agreement between the calculated *trans*/*cis* ratio for a *trans*-elimination mechanism and the observed ratios is extremely good (to some extent this must be fortuitous), but no agreement is obtained with the predictions of a *cis*-elimination mechanism.

Trans-elimination has also been confirmed by other workers (*13–17*) on alicyclic alcohols. Until the predictions of a simple surface mechanism are shown to be incorrect, it seems unnecessary to invoke mechanisms for alcohol dehydration on aluminas involving reactions inside pores or cracks (*19*) or the anchimeric assistance of hydrogens (*4*).

2. Kinetics of n-Heptanol Dehydration

One- to 30-μl liquid samples of *n*-heptanol were injected into 10% KCl/Al_2O_3

TABLE 3

Predicted and Experimental Ratios of Product Olefins

Alcohol	Predicted product ratios				Products observed on Column 2	
	cis-Elimination		*trans*-Elimination			
n-Heptan-4-ol	$\frac{\textit{trans}}{\textit{cis}}$	0.6	$\frac{\textit{trans}}{\textit{cis}}$	1.8	$\frac{\textit{trans}}{\textit{cis}}$	1.86
	Large (50)% *n*-but-1-ene					
n-Butan-2-ol	$\frac{\textit{trans}}{\textit{cis}}$	1.8	$\frac{\textit{trans}}{\textit{cis}}$	0.6		
	i.e., $\frac{\text{1-ene} + \textit{trans}}{\textit{cis}}$	3.2	$\frac{\text{1-ene} + \textit{trans}}{\textit{cis}}$	1.4	$\frac{\text{1-ene} + \textit{trans}}{\textit{cis}}$	1.29
	Small % *n*-pent-1-ene					
n-Pentan-2-ol	$\frac{\textit{trans}}{\textit{cis}}$	1.8	$\frac{\textit{trans}}{\textit{cis}}$	0.6	$\frac{\textit{trans}}{\textit{cis} + \text{1-ene}}$	0.83
	No *n*-hex-1-ene					
n-Hexan-2-ol	$\frac{\textit{trans}}{\textit{cis}}$	1.8	$\frac{\textit{trans}}{\textit{cis}}$	0.6	$\frac{\textit{trans}}{\textit{cis} + \text{1-ene}}$	0.58
	No *n*-oct-1-ene				No *n*-oct-1-ene	
n-Octan-2-ol	$\frac{\textit{trans}}{\textit{cis}}$	1.8	$\frac{\textit{trans}}{\textit{cis}}$	0.6	$\frac{\textit{trans}}{\textit{cis}}$	0.60
2-Methyl-*n*-butan-2-ol	$\frac{\text{alk-1-ene}}{\text{alk-2-ene}}$	3			$\frac{\text{alk-1-ene}}{\text{alk-2-ene}}$	19
2-Methyl-*n*-pentan-2-ol	$\frac{\text{alk-1-ene}}{\text{alk-2-ene}}$	1.5			$\frac{\text{alk-1-ene}}{\text{alk-2-ene}}$	1.53

columns held at 304°C, and the decomposition was studied by means of the stopped-flow technique. Polymerization of the olefin product and autocatalysis of the alcohol decomposition by H_2O were complicating factors: these were studied in more detail (see below). Their effects were eliminated by using short stopped-flow intervals of equal length so that small amounts of products were formed. Polymerization and autocatalysis being bimolecular reactions became negligible at low product concentrations.

If the dehydration were a simple first-order reaction then a plot of $\log_{10} S_n/v_n$ against time should be linear. This was found to be the case for the later stages of the reaction, but in the early part more product was formed than expected. Correction for autocatalysis (see below) did not appreciably affect this observation. The results were, however, consistent with two *and only two* independent first-order reactions in all the experiments on 10% KCl/Al_2O_3. A typical kinetic plot is shown in Fig. 4; as shown, the situation is very similar to the familiar pattern observed in the simultaneous decay of two radioactive isotopes. From most experiments it was possible therefore to extract two velocity constants (k_{fast} and k_{slow}) and by extrapolation the ratio of sites ($a_{\text{fast}}/a_{\text{slow}}$) on which fast and slow reactions were occurring immediately after injection. For extremely small samples (0.5 ml of vapor at room temperature) only the slower reaction was observed. The values of k_{fast} and k_{slow} on a particular column were relatively independent of the amount injected, but the proportion of the fast reaction increased steadily with the amount of alcohol injected up to sample size of 5 μl of liquid, after which the proportion remained fairly constant (Table 4).

These results cannot be explained in terms of a reactive impurity, for this would have to be present in amounts which varied with the quantity injected up to a maxi-

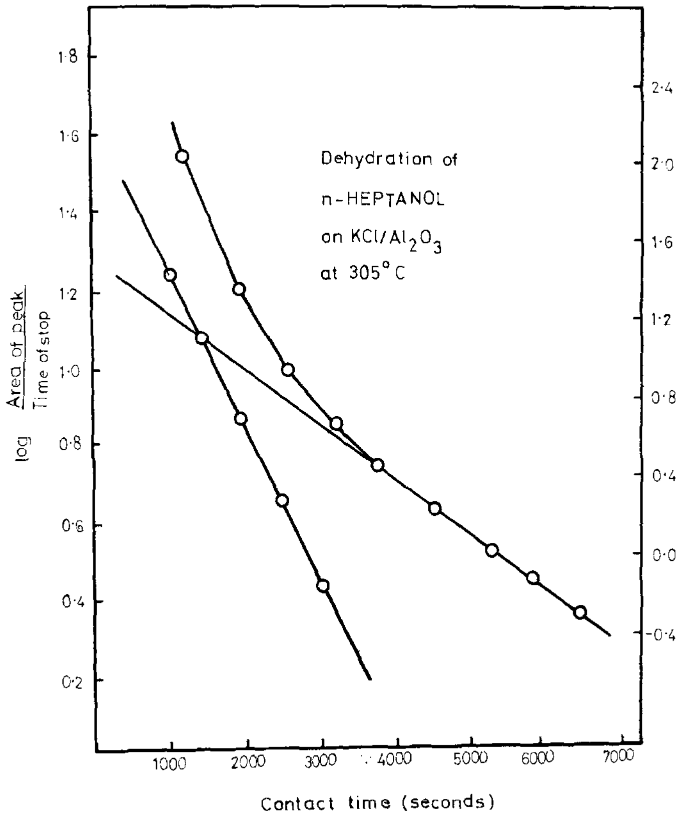

FIG. 4. Kinetics of n-heptanol dehydration suggesting a two-site mechanism: The upper set of points (left-hand scale) are experimental. The lower set (right-hand scale) are obtained from the differences between the straight-line extrapolation (representing the k_{slow} reaction) and the experimental points; they therefore represent the postulated k_{fast} reaction.

mum of 70%! They are however consistent with the occupation by the alcohol of two distinct types of catalytic site.

Values of k_{fast} and k_{slow} do not change significantly with time, nor is there any obvious effect of minor changes in the previous heat treatment of the column. This is brought out by the results given in Table 5. Three other columns of 10% KCl/Al$_2$O$_3$ were also used for the study of the same reaction. They all showed the same pattern of behavior with very consistent values of k_{fast} and k_{slow} and a_{fast}/a_{slow} but somewhat lower than those found on the first column, Table 6. With an unmodified Al$_2$O$_3$ column very similar results were obtained except that small amounts of a still faster reaction became significant (Table 7).

TABLE 4

DEHYDRATION OF n-HEPTANOL ON 10% KCl/Al$_2$O$_3$ AT 304°C

The rate constants have not been corrected for autocatalysis, and so k_{fast} increases with the injected volume.

Run	Alcohol injected (μl of liquid)	$k_{fast} \times 10^4$ (sec^{-1})	$k_{slow} \times 10^4$ (sec^{-1})	a_{fast}/a_{slow}
I	1	13.7	2.39	0.51
II	5	18.7	3.33	2.03
III	3	19.4	3.01	1.26
IV	5	21.0	3.06	2.31
V	1	14.9	2.30	0.38

An estimate of the area of surface per adsorbed heptanol molecule at the start of the reaction was made in the following manner. A 20 μl sample of n-heptanol was injected onto the column under reaction

TABLE 5

Effect of Aging and Heat Treatment of Column on Velocity Constants

Dehydration of *n*-heptanol on 10% KCl/Al_2O_3.

Date of expt.	Temp (°)	$k_{fast} \times 10^4$ (sec⁻¹)	$k_{slow} \times 10^4$ (sec⁻¹)	a_{fast}/a_{slow}	Sample size (μl of liquid)	Purging in nitrogen at		Equilibrating to	
						Temp (°)	Time	Temp (°)	Time
29.11.67	303.5	13.9	1.84	0.64	2	400	1 hr	303.5	Overnight
1.12.67	303.5	13.6	1.85	0.45	2	450	50 min	303.5	2 days
5.12.67	304	15.4	2.16	0.61	2	450	1 hr	304	45 min
7.12.67	303.5	12.2	1.78	0.52	2	400	Overnight	303.5	1.5 days
8.12.67	304	20.1	2.55	1.16	3	450	1 hr	304	40 min
8.12.67	304	14.0	1.64	0.73	2	450	1 hr	304	Overnight
2.2.68	304	13.7	2.39	0.51	1	400	Overnight	304	50 min

TABLE 6

EFFECT OF CHANGE OF COLUMN ON DEHYDRATION OF n-HEPTANOL

All columns were made in the same manner as column 1 used for results given in Tables 1–5. Columns 3 and 4 were packed with 10% KCl/Al_2O_3 from the same batch of prepared material and differed only in that column 4 had a section of CaC_2 at the end to convert H_2O into C_2H_2. All experiments with 30 μl of heptanol.

Column	Temp (°)	$k_{fast} \times 10^4$ (sec^{-1})	$k_{slow} \times 10^4$ (sec^{-1})	a_{fast}/a_{slow}
2	304	4.4	0.61	0.3
3	304.5	4.7	0.81	0.2
4	304	5.3	0.71	0.5

conditions. As soon as the start of the broad heptene band was observed at the end of the column, the column was cooled, a known length of catalyst was removed from the beginning of the column and the column was replaced in the oven. This was repeated until there was a rapid fall to zero in the rate of heptene evolution. Knowing that the surface area of 10% KCl/Al_2O_3 is about 100 m^2/g (*20*), the results of such experiments gave an area of about 125 $Å^2$/molecule immediately after injection. Calvet and Astruc (*18*) have determined the surface area of pure alumina as 50 $Å^2$/molecule of n-heptanol under conditions of complete monolayer coverage.

Of the various possible reaction schemes which would account for the nonobservance of a single first-order reaction, the only one that seems to be consistent with the data is that of two independent first-order reactions occurring on different catalytic sites. The comparative study on unmodified Al_2O_3 suggests that neither of these reactions takes place on the KCl, and that the function of the KCl is to remove the very active dehydration sites. It is therefore likely that the KCl does not coat the surface evenly. Variations in a_{fast}/a_{slow} with the amount of alcohol injected show that the activation energy for *adsorption* of n-heptanol must be less for the slow than for the fast reacting sites, although both activation energies must be very small. Elimination of HCl from cyclopentyl chloride and cyclohexyl chloride has previously been studied in this laboratory by Wormald (*21*) using a similar 10% KCl/Al_2O_3 catalyst; a two-site mechanism had again to be invoked. In this case however the halides were observed to move along the column, but more rapidly from the fast-reacting sites, i.e., the fast-reacting halide was less strongly adsorbed. We have made further measurements confirming these results and a_{fast}/a_{slow} ratios were obtained similar to those found for the alcohols.

TABLE 7

DEHYDRATION OF n-HEPTANOL ON UNMODIFIED Al_2O_3 AT 305.5°C

Alcohol injected (μl of liquid)	$k_3 \times 10^4$ (sec^{-1})	$k_{fast} \times 10^4$ (sec^{-1})	$k_{slow} \times 10^4$ (sec^{-1})	a_{fast}/a_{slow}
3	—	8.45	1.13	1.53
30	20.4	9.31	2.24	0.95
30	33.8	12.0	2.86	2.2

Only two first-order reactions were found with 10% KCl/Al_2O_3. Since alcohol dehydration is thought to proceed via alkoxide formation the results indicate two distinct types of Al ions at the catalytic surface. Now γ-Al_2O_3 contains Al ions in octahedral and tetrahedral sites, with different degrees of ordering between these two sites in the different forms of γ-Al_2O_3. In view of the limiting ratios of a_{fast}/a_{slow} it is of interest to note that the ratio of occupied octahedral to tetrahedral sites in the spinel strucure (γ-Al_2O_3) is 2:1. This would suggest that a possible difference between the two catalytic sites might be the coordination number of the aluminum, and that the alkoxide attached to aluminum in a tetrahedral site is the slower reacting while the alkoxide attached to aluminum in an octahedral site is the faster reacting. It would of course be surprising if such gross variations in site gave rise to such small variations in activity as we have observed, but this could possibly be a further example of the compensation effect whose occurrence in these dehydration reactions we discuss below. If such an explanation were correct then the function of the KCl modifier might well be to cover very active sites such as Al ions exposed on crystal corners or edges.

3. *Kinetics of Dehydration for a Variety of Alcohols*

Measurements with individual alcohols on the 10% KCl/Al_2O_3 columns show that the rate constants for dehydration decrease in the order tertiary > secondary > primary, but that within any series the variations in rate between different alcohols are comparable with the random variation in rate constants observed from experiment to experiment. However, by decomposing two alcohols simultaneously on the same column relative values of k_{slow} could be obtained with greater precision. For any pair of alcohols the ratio of velocity constants was approximately the same on the different columns and for different ovens and for different heat treatments of the column material, and showed little variation with the age of the column: individual rate constants as shown above did however vary from column to column. These general conclusions are illustrated by the results given in Table 8. Injection of the second alcohol after the first had been decomposing for some time produced no effect on the rate of dehydration of the first alcohol showing that the reactions are completely independent.

A set of dehydration rates thus obtained are given in Table 9, for primary alcohols relative to *n*-heptanol and for secondary and tertiary alcohols relative to propan-2-ol. The values quoted are for k_{slow} in each case; where values for k_{fast} were also calculable their relative values were found to be very similar to those for k_{slow}. These results show that in each of the series of straight-chain primary alcohols, acyclic secondary alcohols, and tertiary alcohols, the second member of the series reacts faster than the first and thereafter the reaction rate decreases becoming approximately constant for the longer chain alcohols.

Activation energies for the dehydration reactions were also determined with runs simultaneously involving two alcohols. Because of the large number of stopped-flow measurements possible after a single injection the dehydration reactions could be studied at several temperatures with only one sample injection. It was also possible to do this after the fast reaction was virtually completed so that the slow reaction could be studied separately. The results are given in Table 10. The precision of these measurements (± 1.5 kcal mole^{-1}) did not allow any correlation with differences within a series which would have required a precions of better than ± 0.5 kcal mole^{-1}. However, the difference in activation energy between the primary series and the series of secondary and tertiary alcohols is clearly marked.

Note that the change in the *A* factor acts in the opposite direction to the change in the activation energy, i.e., a *compensation effect* is observed. Such an effect has of

TABLE 8

SOME COMPARATIVE RATE CONSTANTS FOR PAIRS OF ALCOHOLS USING TWO 10% KCl/Al_2O_3 COLUMNS AND TWO DIFFERENT OVENS

Alcohol-1	Alcohol-2	Temp (°)	Oven	Column	$k_1 \times 10^4$ (sec^{-1})	$k_2 \times 10^4$ (sec^{-1})	k_1/k_2
Isobutanol	*n*-Heptanol	277	A	2	1.16	0.63	1.84
	n-Heptanol	278	B	1	3.21	1.94	1.65
Cyclopentanol	Propan-2-ol	212	A	2	1.25	1.41	0.89
	Propan-2-ol	214	B	2	1.18	1.34	0.88
n-Butanol	*n*-Heptanol	311	A	2	0.96	0.71	1.35
	n-Heptanol	304	B	2	0.94	0.65	1.44
	n-Heptanol	304	A	1	3.61	3.00	1.20
	n-Heptanol	304	B	1	2.69	1.85	1.46

TABLE 9

RELATIVE DEHYDRATION RATES FOR DIFFERENT ALCOHOLS ON 10% KCl/Al_2O_3 (values quoted are for k_{slow})

Alcohol-1		Alcohol-2	$k_1 \times 10^4$ (sec^{-1})	$k_2 \times 10^4$ (sec^{-1})	k_1/k_2
	Measurements on Column 1 at 304°				
Ethanol		*n*-Heptanol	1.61	1.16	1.38
n-Propanol		*n*-Heptanol	1.58	0.96	1.64
n-Butanol		*n*-Heptanol	2.69	1.85	1.46
			2.10	1.64	1.28
n-Pentanol		*n*-Heptanol	1.94	1.84	1.06
n-Hexanol		*n*-Heptanol			0.92
	deduced from				
n-Hexanol		Ethanol	1.15	1.72	
	At 278°C, the dehydration of isobutanol being inconviently fast at 304°C				
Isobutanol		*n*-Heptanol	3.21	1.94	1.65
Isopentanol		*n*-Heptanol	2.72	2.35	1.16
Isohexanol		*n*-Heptanol			0.89
	deduced from				
Isohexanol		Ethanol	1.81	2.82	
	Measurements on Column 2 at 212°				
n-Butan-2-ol		Propan-2-ol	0.931	0.648	1.44
n-Pentan-2-ol		Propan-2-ol	0.946	0.648	1.46
n-Hexan-2-ol		Propan-2-ol			1.13
n-Heptan-4-ol		Propan-2-ol			1.08, 1.26
n-Octan-2-ol		Propan-2-ol			0.93
	deduced from				
n-Hexan-2-ol		*n*-Butan-2-ol	0.720	0.915	
n-Heptan-4-ol		*n*-Butan-2-ol	0.689	0.915	
			0.979	1.135	
n-Octan-2-ol		*n*-Pentan-2-ol	0.630	0.986	
Cyclopentanol		Propan-2-ol	1.25	1.41	0.89
	Measurements on Column 2 at 224°				
Cyclohexanol		Propan-2-ol	1.42	1.09	1.30
Cyclopentanol		Propan-2-ol			1.09
	deduced from				
Cyclohexanol		Cyclopentanol	1.76	1.48	
	Measurements on Column 2 at 212°				
2-Methylpropan-2-ol		Propan-2-ol			2.11
2-Methylbutan-2-ol		Propan-2-ol	4.25	1.11	3.83
2-Methylpentan-2-ol		Propan-2-ol			2.95
	deduced from				
2-Methylpropan-2-ol		2-methylbutan-2-ol	1.52	2.76	
2-Methylpentan-2-ol		2-methylbutan-2-ol	2.13	2.76	

course already been observed for a given reaction on a series of catalysts, whereas here a compensation effect is found for a series of related reactions on a single catalyst. Schwab (*22*) has established a general relation between A and E for the former case of

$$\log_{10} A = aE + b$$

where a and b are constants for the given reaction. As shown in Fig. 5, this relationship also holds for our studies with $a = 0.36$ and $b = -2.9$. As this compensation effect also applies to the difference between the values of the fast and slow reactions for one alcohol, it could explain why the difference in reaction rate between the two

TABLE 10

ACTIVATION ENERGIES (E) AND FREQUENCY FACTORS (A) FOR ALCOHOL DEHYDRATION ON 10% KCl/Al_2O_3

Alcohol	E (kcal mole^{-1})	A (sec^{-1})	$\log_{10} A$
Ethanol	45.2	3×10^{12}	12.5
n-Hexanol	42.4	5×10^{11}	11.7
Propan-2-ol	33.2	6×10^{8}	8.7
n-Butan-2-ol	31.5	2×10^{9}	9.3
n-Pentan-2-ol	29.4	2×10^{8}	8.3
	30.4	5×10^{7}	7.7
2-Methyl-propan-2-ol	30.9	2×10^{8}	8.2
Cyclohexanol	24.8	3×10^{5}	5.5
Ethanol (k_{fast})	21.2	1×10^{4}	4.0
n-Hexanol (k_{fast})	17.7	9×10^{2}	3.0

sites is much smaller than would be expected from an explanation involving aluminum ions in two different coordination sites; i.e., an increase in activation energy may be largely balanced by an unfavorable entropy of reaction.

The model for the catalytic reaction proposed earlier can be applied to the order of rate constants in terms of activation energies. Since alcohol dehydration is an endothermic reaction, Hammond's principle leads us to expect that differences in the thermodynamic stability of the product will be dominant in predicting differences of reaction rate:

(i) As the stability of olefins increases the greater the number of alkyl groups attached to the olefinic double bond, increase in dehydration rate should accompany increase in branching at these positions. This seems to be generally observed. Thus rate constants decrease in the orders:

tertiary > secondary > primary alcohol;
n-propanol > ethanol;
n-butan-2-ol > propan-2-ol;
t-pentanol > *t*-butanol;
*iso*butanol > *n*-propanol.

(ii) Chain branching at points more distant from the olefinic bond which is forming in the reaction has a negligible effect on the dehydration rate,

e.g., *n*-butanol ≏ pentan-2-ol
n-pentanol ≏ 4-methyl-*n*-pentanol.

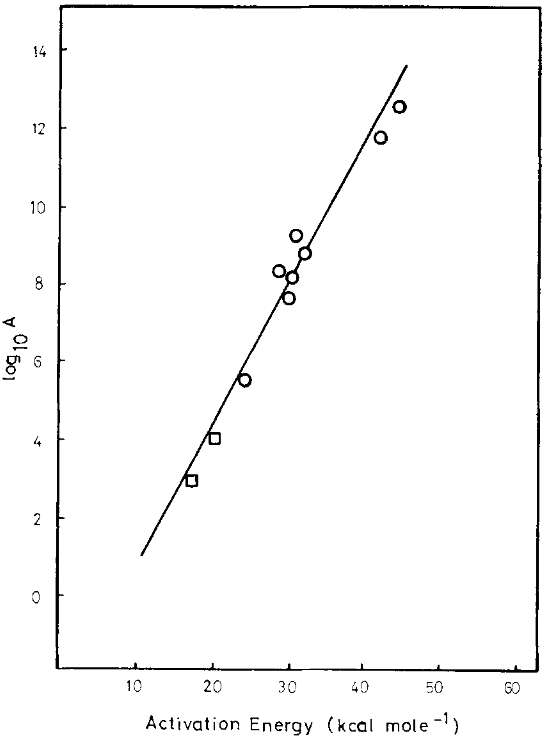

FIG. 5. Compensation effect observed between frequency factor A and activation energy E: ○, experimental points from "slow" reactions; and □, points from "fast" reactions.

(iii) Increasing the length of the carbon chain from the hydroxyl-bearing carbon from C_2 to C_5 reduces the dehydration rate to an approximately constant value. When, in the proposed model, the alcohol is raised from the ground state in which all the alkyl groups possible lie along the surface of the catalyst to the transition state in which the H and O atoms to be eliminated are *trans* to each other, considerable reorganization of the carbon chain is necessary. In particular, for a long carbon chain, only the first few carbon atoms in the chain need to change their positions relative to the catalyst surface. Since these changes must be energetically unfavorable, the activation energy for dehydration will increase with the length of the carbon chain up to about 4 carbon atoms and thereafter remain substantially constant. This could explain the relative rates observed.

Finally for the *n*-alkan-2-ols and the tertiary alcohols, the methyl groups attached to C_2 will, in the model, interact with the surface in the transition state and could well lose their rotational and vibrational freedom. Calculations using transition-state theory show that this effect could account for over 60% of the change in the log *A* factor between primary and acyclic secondary or tertiary alcohols.

4. Autocatalysis

The variation in the amount of olefin produced as a function of the stopped-flow interval was studied with *n*-heptanol on three different columns. It was found that the ratio *S/V*, (olefin produced in unit time), changed when intervals longer than 2 min were used. On column 2, *S/V* increased with interval time, Fig. 6. On column 3, *S/V* increased for intervals up to 12 min and then decreased below the value obtained with short intervals. On unmodified Al_2O_3, *S/V* decreased with interval time. The increases can be explained in terms of autocatalysis by water produced and the decreases by polymerization of the product olefin, with the latter being dominant on unmodified Al_2O_3 and with time on column 3, and the former being dominant on column 2 and at relatively short intervals on column 3. An independent study of the polymerization is described in the following section; here we shall focus attention on the autocatalysis.

Injection of product olefin onto an alcohol while it was being dehydrated had no effect on the reaction rate for short stopped-flow intervals. However, injection of water onto all columns (including the unmodified Al_2O_3) while the dehydration of *n*-heptanol was taking place produced a large increase in the rate of dehydration. The rate returned slowly to normal as the water was carried away from the heptanol by the normal chromatographic process between stopped-flow intervals. The greater the amount of water injected, the greater the increase in the rate of dehydration, see Fig. 7.

If the rate of the autocatalyzed reaction is first order with respect to alcohol *and* first order with respect to water so that

$$\text{Reaction rate} = k[A] + k'[A][H_2O]$$

then it may be shown (*23*) that

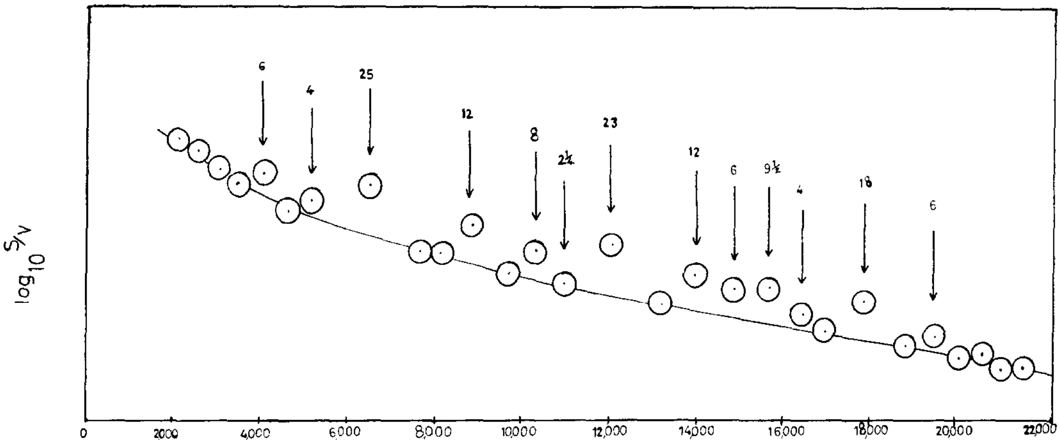

FIG. 6. Autocatalysis: Effect of length of stopped-flow interval (min) on kinetic plot. Points not marked with a number correspond to 2-min intervals.

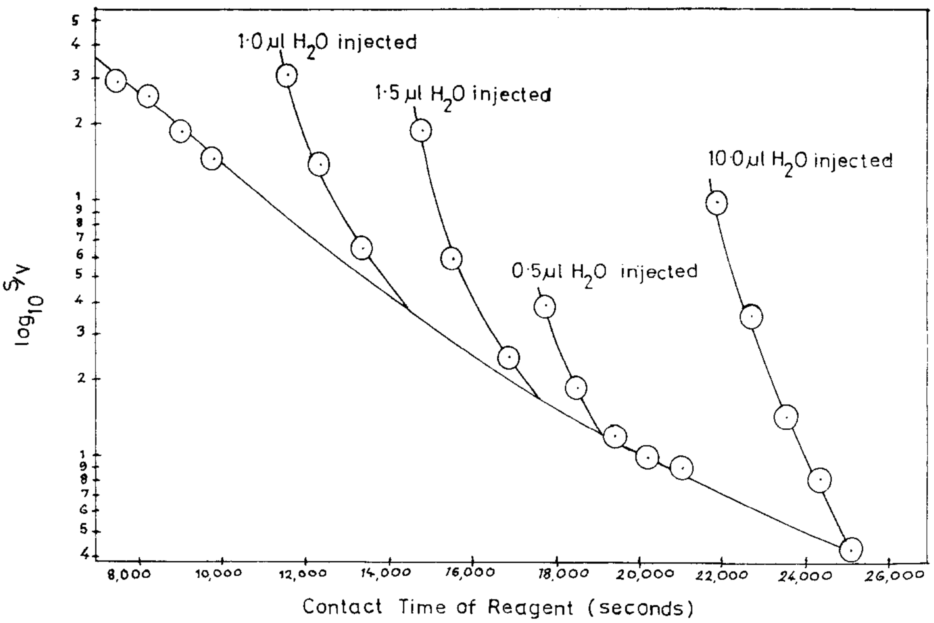

FIG. 7. Catalysis by water: Effect of injecting water on dehydration rate of *n*-heptanol. All stopped-flow intervals were 2 min long.

$$[S_n/V_n - S_2/V_2] = \frac{k'}{kc}(V_n - V_2)\left[\frac{S_nS_2}{V_nV_2}\right]$$

for stopped-flow intervals of n and 2 min. Plots of $[S_n/V_n - S_2/V_2]$ against $[S_nS_2/V_nV_2](V_n - V_2)$ were made and reasonable straight lines were obtained. Results were obtained from the water produced (using column 4) as well as for the olefin produced on column 2. From these plots values of k' were calculated and found to be extremely consistent, Table 11. Using these values of k' it was then possible to correct the original S/V values for long stopped-flow intervals on those columns where extensive polymerization did not occur. The corrected values were found to fit smoothly onto the curves formed by the points for 2-min stopped-flow intervals. Hence the autocatalysis hypothesis is supported qualitatively and quantitatively by the results.

TABLE 11
DEHYDRATION OF 30 μl *n*-HEPTANOL

Column	Product detected	k_{fast} $\times 10^4$ (sec^{-1})	k_{slow} $\times 10^4$ (sec^{-1})	k' $\times 10^9$ (sec^{-1})
2	*n*-Hept-1-ene	4.4	0.60	2.6
2	*n*-Hept-1-ene	4.6	0.64	2.8
4	Water/C_2H_2	5.3	0.71	4.6[a]

[a] Corrected for different detector sensitivities to C_2H_2 and *n*-hept-1-ene.

Thus both the water formed in the reaction and injected water catalyze the dehydration reaction, and in this respect our results agree with those of Topchieva *et al.* (*10*). In other work under conditions of complete saturation of all sites by the alcohol (*8*, *9*), deactivation has been observed; this could arise from competition for sites on the alumina between water and alcohol molecules. Some water moves readily through the column while alcohols are virtually stationary, indicating that the adsorption of the latter is far stronger. We have already suggested that the two catalytically-active sites might possibly be associated with alkoxides formed on aluminum ions in tetrahedral (slow) and octahedral (fast) reaction sites. Since addition of water to γ-alumina will eventually convert it to aluminum hydroxide where all the aluminum ions are in octahedral sites, the expected effect of water would be to convert aluminum ions in tetrahedral sites to ions in sites with a higher coordination number. For those tetrahedral-site alkoxides the effect of water might then be merely to increase the effective coordination number, and thereby increase the rate of reaction.

5. Polymerization

To indicate that polymerization of the product olefin was occurring, a column (column 4) of KCl/Al_2O_3 was constructed with a packing of CaC_2 at the detector end, which converted any water passing through the column into C_2H_2 which could be detected by the flame-ionization detector. In this way the rate of movement of water through the column could also be studied. The amounts of H_2O (as C_2H_2) and *n*-hept-1-ene (from *n*-heptanol) were then studied as the stopped-flow interval was varied. It was found that even for 2-min intervals the number of molecules of hept-1-ene leaving the column were less than the number of water molecules, and this discrepancy increased with increase in the stopped-flow interval.

The polymerization was also studied by direct injections of olefin on to the columns at 305°C either (i) with a variation in the gas-flow rate, or (ii) with a constant flow rate but with a variable stopped-flow interval 1 min after injection. In experiments of type (i) the amount of olefin reaching the detector decreased (approx. exponentially) with increasing retention time as would be expected if the rate of polymerization depended upon the amount of olefin remaining. Experiments of type (ii) showed two classes of behavior:

(a) The polymerization was found to be independent of length of the stopped-flow interval, i.e., no polymerization occurred during the stop.

(b) The amount of polymerization was initially slow (about 1%/min on 10% KCl/Al_2O_3 and 2.5% on Al_2O_3) but increased sharply after a stop of about 10 min (to about 5%/min on both surfaces). With unmodified Al_2O_3, cracking was observed with stopped-flow intervals greater than 15 min, and for longer intervals this became the dominant reaction. This behavior could account for the various trends on the different columns with long stopped-flow times.

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