Catalytic Dehydration of Alcohols Studied by Reversed-flow Gas Chromatography

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With the aid of the new technique of reversed-flow gas chromatography (r.f.g.c.), rate constants and activation parameters for the dehydration of propan-1-ol, propan-2-ol and butan-1-ol over 13X molecular sieve and γ -aluminium oxide were determined. These parameters were found to be in agreement with those determined by other techniques. Also, in Vone case the Ciraction of the Hurface which is cally the size was estimated, and was found to coincide with the fractional conversion of reactant into products.

Reversed-flow gas chromatography (r.f.g.c.) is a new technique for studying heterogeneous catalytic reactions and other related phenomena.¹⁻³ This is a differential method used to determine the true rate constants of surface catalysed reactions in the whole range of conversions. In brief, the method uses a gas chromatographic column containing the catalyst, with the reactant introduced as a pulse at a middle position down the column. By repeatedly reversing the direction of flow of the carrier gas, extra peaks are recorded, whose heights and/or areas under the curves have a well defined relation to the time of each flow reversal t_{tot} . The analytic form of this relation depends on the mechanistic scheme for the surface reaction. Note that when the direction of the gas flow is reversed, a sampling is made from the chromatographic column and the product formed in a certain time interval is exhibited as an extra peak.

In our previous papers,^{1, 2} which describe the method in detail, some examples of the applications of the theoretical equations were given. In the present work the agreement between theory and experiment in r.f.g.c. is further exemplified by studying an important class of reaction, namely the catalytic dehydration of alcohols. The success of the theoretical equations in describing the experimental behaviour of the systems studied led to determination of rate constants and activation parameters for the dehydration of various alcohols over two catalysts.

EXPERIMENTAL

MATERIALS

Molecular sieve 13X, 80-100 mesh, and activated aluminium oxide F-1, 80-100 mesh, were used as catalysts. Both were purchased from Applied Science Labs., State College, Pa., U.S.A. The alcohols used were 'uvasol' grade from E. Merck, Darmstadt, G.F.R. Nitrogen from Aga Chropei, Athens, Greece (99.999% purity) was used as carrier gas.

For the experimental identification of the products formed in the dehydration of alcohols the following substances were used. Propene (99.7%), but-1-ene (99.9%), *cis*-but-2-ene (99.9%), *trans*-but-2-ene (99.8%) and 2-methylpropene (99.8%) from Matheson Gas Products, East Rutherford, N.J., U.S.A., and di-isopropyl ether 'puriss' from Fluka A.G., Buchs SG.

APPARATUS AND PROCEDURE

The experimental set-up and the detailed procedure for the application of r.f.g.c. have been reported elsewhere.² The lengths l' and l of the two chromatographic columns (glass, i.d. 4 mm) in which the catalyst was contained are given in table 1.

The conditioning of the columns was carried out *in situ* by holding them at 673 K for 21 h (system 1) or for 24 h (systems 2, 3, 4 and 5) under carrier gas flow $(0.5 \text{ cm}^3 \text{ s}^{-1})$. Following each activation the columns were cooled to the working temperature and, after some preliminary injections, kinetic measurements were conducted in the range 452-568 K, with a gas flow rate of $0.5 \text{ cm}^3 \text{ s}^{-1}$. For each alcohol, 1 mm³ of liquid, using a microsyringe, was injected onto the column length *l* through the injector placed between the two columns and with the carrier gas flowing in direction F.

Plots and other calculations were performed on a Hewlett-Packard 9825A desk-top computer connected to a 9872B plotter.

RESULTS AND DISCUSSION

The main products of the alcohol dehydrations studied, identified experimentally by comparing their retention times with those of pure substances, are given in table 1.

Table	1.—LENGTHS	OF	THE	TWO	SECTIONS	OF	THE	CHROMATOGRAPHIC	COLUMN	MALNOnline
			PRO	DUCT	FORMED IN	N EA	ACH S	YSTEM STUDIED		

system no.	system description	ľ/cm	l/cm	main product
1	propan-1-ol over 13X mol. sieve	3.0	108	propene
2	propan-2-ol over 13X mol. sieve	1.3	45	di-isopropyl ether
3	butan-1-ol over 13X mol. sieve	1.3	45	but-1-ene
4	propan-1-ol over Al ₂ O ₃	1.5	45	propene
5	propan-2-ol over Al_2O_3	1.5	45	propene

The kinetic results obtained with all five alcohol dehydration systems conform to a simple first-order decomposition of the adsorbed reactant to give the adsorbed product(s). Therefore, the area f under the F- and R-peaks (F and R denoting the 'forward' and 'reversed' direction of the gas flow, respectively) is given by the relation² f = meters(ht) there (ht)

$$f = mg \left[\exp \left(kt_{\rm R} \right) - 1 \right] \exp \left(-kt_{\rm tot} \right) \tag{1}$$

where *m* is the mass of alcohol injected, *g* is its fraction on reactive surface sites, *k* is the rate constant for the surface reaction, t_{tot} is the time from the injection of reactant to the last reversal of gas flow, and t_R is the retention time of the product in the opposite direction to the gas flow. According to eqn (1), a plot of $\ln f_R$ or $\ln f_F$ (the subscripts R and F denoting R- and F-peaks, respectively) against t_{tot} should be linear with slope equal to -k. This was confirmed experimentally for the F-peaks, the points from the R-peaks showing a tendency to curve a little, as indicated in the example of fig. 1. This is most probably due to some undetected slow physical process (*e.g.* intraparticle diffusion) owing to the much bigger column length *l* responsible for the R-peaks, as table 1 shows. The deviation from linearity is small, as judged from '*t*-tests' of significance on the coefficients of regression of $\ln f$ on t_{tot} , showing that the probability for the corresponding '*t*'-value being exceeded is < 1% in all cases. Also, table 2, which lists the values of the rate constants determined, shows good agreement between rate constants found from R-peaks (k_R) and from F-peaks (k_F).



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FIG. 1.—Plots of eqn (1) for the dehydration of butan-1-ol to but-1-ene over 13X molecular sieve at 530 K. \bigcirc , R-peaks; \triangle , F-peaks.

as predicted by eqn (1). The last column of table 2 gives the % difference between the two rate constants, defined as $100 (k_{\rm R} - k_{\rm F})/k_{\rm R}$. It also shows that the rate constants for the dehydration reactions increase from a primary to a secondary alcohol, as expected.

Table 3 gives the Arrhenius activation parameters for the dehydration reactions. They were determined from conventional Arrhenius plots. An example is given in fig. 2. It is evident from table 3 that activation parameters determined from R-peaks coincide, within the limits of experimental error, with those found from F-peaks. This, together with the coincidence in the values of rate constants exhibited in table 2, is important, because the lengths l and l' of the chromatographic column responsible for the R- and F-peaks, respectively, differ by a factor of 30 or more (*cf.* table 1). These coincidences indicate that secondary reactions of the detected product or irreversible adsorption of it are negligible.

The activation energies found here are consistent with some literature values. Thus, Gentry and Rudham⁴ determined an activation energy of 110 kJ mol⁻¹ for the dehydration of propan-2-ol to di-isopropyl ether over a 13X molecular sieve surface similar to ours. Lane *et al.*⁵ calculated an activation energy of 134.7 kJ mol⁻¹ for the dehydration of propan-2-ol to propene over γ -Al₂O₃ modified by 10% KCl. Our corresponding values (78 and 81 kJ mol⁻¹) are considerably smaller, and this is explained by the fact that modification of γ -Al₂O₃ with KCl decreased its catalytic activity and hence increased the activation energy for the process studied.

Table 2.—Rate constants for the dehydration of three alcohols over 13X molecular sieve and γ -aluminium oxide, at various temperatures with a volume flow-rate of $0.5\ cm^3\ s^{-1}$

alcohol	T/K	$k_{ m R}/10^{-4}~{ m s}^{-1}$	$k_{\rm F}/10^{-4}~{ m s}^{-1}$	% difference	;
		over 13X molec	ular sieve		
propan-1-ol	492 499	3.5 ± 0.2 5 3 + 0 4	3.2 ± 0.2	+8.6	
	510	3.3 ± 0.4 8 2 ± 0.6	$\frac{4.9 \pm 0.2}{81 \pm 0.4}$	+1.0	
	516	12 ± 1	11.0 ± 0.7	+8.3	
	522	14+2	13+1	+7.1	
	529	18 ± 2	17.6 ± 0.7	+2.2	
propan-2-ol	452	2.5 ± 0.1	2.6 ± 0.1	-4.0	
	458	3.5 ± 0.2	3.7 ± 0.2	-5.7	
	463	5.1 ± 0.4	4.9 ± 0.3	+3.9	
	471	8.3 ± 0.7	8.2 ± 0.4	+1.2	
	478	12 ± 2	11.4 ± 0.4	+5.0	
	485	18 ± 3	18 ± 3	0.0	View Article Onlin
butan-1-ol	522	3.4 ± 0.2	3.6 ± 0.2	- 5.9	
	530	5.8 ± 0.3	6.0 ± 0.1	-3.5	
	538	9.4 ± 0.7	9.9 ± 0.9	-5.3	
	54/	13 ± 1	13 ± 1	0.0	
	220	18 <u>+</u> 2	18.4 ± 0.7	-2.2	
		over γ -alumini	um oxide		
propan-1-ol	506	1.24 ± 0.04	1.19 ± 0.04	+4.0	
	525	2.9 ± 0.1	2.92 ± 0.09	-0.7	
	536	3.9 ± 0.2	3.9 ± 0.3	0.0	
	544	4.8 ± 0.3	5.2 ± 0.3	-8.3	
	553	0.1 ± 0.3	0.1 ± 0.4	0.0	
propan-2-ol	485	7.8 ± 0.3	7.3 ± 0.3	+6.4	
	495	12.3 ± 0.6	11.7 ± 0.5	+4.9	
	508	23 ± 1	22 ± 1	+4.4	
	520 520	30 ± 4 39 ± 6	33 ± 4 37 ± 5	-10.0 + 5.1	
	549	<u> </u>	<u> </u>	T J.1	

The \pm values in the rate constants are standard	ard errors.
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Table 3.—Activation energies (E_a) and frequency factors (A) for the dehydration of three alcohols over 13X molecular sieve and γ -aluminium oxide

	$E_{\rm a}/{ m kJ}$	mol ⁻¹	$\ln\left(A/\mathrm{s}^{-1}\right)$		
alcohol/catalyst	R-peaks	F-peaks	R-peaks	F-peaks	
propan-1-ol/13X	96±4	98±4	16 <u>+</u> 1	16.1±0.9	
propan-2-ol/13X ^a	110.6 ± 0.3	107 ± 3	21.1 ± 0.1	20.1 ± 0.7	
butan-1-ol/13X	118 ± 8	115 ± 8	19 ± 2	19 ± 2	
propan-1-ol/Al ₂ O ₃	78 ± 5	82 ± 6	10 ± 1	10 ± 1	
propan-2-ol/Al ₂ O ₃	78 ± 6	81 ± 7	12 ± 1	13 ± 2	

^a Reported also in ref. (2).



FIG. 2.—Arrhenius plots for the dehydration of propan-l-ol-to propene over 13X molecular sieve. \odot , rate constants determined from R-peaks (lower abscissa); \triangle , rate constants from F-peaks (upper abscissa).

TABLE 4.—RATE CONSTANTS FOR THE DEHYDRATION OF PROPAN-1-OL TO PROPENE OVER 13X MOLECULAR SIEVE AT 491 K AND TWO DIFFERENT FLOW-RATES

$V/\mathrm{cm}^3~\mathrm{s}^{-1}$	$k_{\rm R}/10^{-4}~{ m s}^{-1}$	$k_{\rm F}/10^{-4}~{\rm s}^{-1}$	% difference	
 0.21	3.2 ± 0.2	3.0 ± 0.1	+6.3	
0.50	3.5 ± 0.2	3.3 ± 0.3	+ 5.7	

The effect of two other chromatographic variables on the kinetic parameters was tested. The first variable is the amount of the reactant injected onto the column. To test this the activation energy for the dehydration of propan-1-ol over 13X molecular sieve was determined using 10 mm³ samples of reactant. A value of 96.1 \pm 0.2 kJ mol⁻¹ was found, which agrees well with the values of table 3 determined with 1 mm³ of reactant.

The second variable tested was the volume flow-rate of the carrier gas. This was tested using the same reaction mentioned above with two different flow-rates at one temperature. The results (table 4) show that the flow-rate has no significant effect on the rate constants.

When plotting eqn (1) to find k from the slope, as mentioned before, a relative value for the expression $mg [\exp(kt_R) - 1]$ having the same units as f is obtained. If the response of the detecting system for the product measured can be found, *e.g.* by injecting known amounts of the pure product into an empty column under the same

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experimental conditions, then the absolute value (mol) of the above expression can be calculated. Knowing m and $t_{\rm R}$ from experiment and k from the slope, the fraction of active catalytic surface g can be computed. This was done for system no. 2 (table 1) and the results at various temperatures are collected in table 5. Given the relatively big errors involved in the calculation of g, its value does not seem to change significantly with temperature or from R- to F-peaks.

TABLE 5.—FRACTION (g) OF THE ADSORPTIVE SURFACE WHICH IS CATALYTICALLY ACTIVE FOR THE DEHYDRATION OF PROPAN-2-OL TO DI-ISOPROPYL ETHER OVER 13X MOLECULAR SIEVE

	T/K	active fr	action, g	
		from R-peaks	from F-peaks	
· · · · · · · · · · · · · · · · · · ·	452	0.25	0.26	
	458	0.23	0.28	
	463	0.28	0.32	
	471	0.21	0.28	
	485	0.17	0.26	View Article Onlin

It was pointed out in the previous paper² that the g values determined from the heights h of the R- and F-peaks also give the fractional conversion of the reactant into product. The same applies for the area f under the curve of the peaks. Thus, dividing f by $t_{\rm R}$, an average reaction rate is obtained and then

conversion
$$= \frac{1}{m} \int_{0}^{\infty} \frac{f}{t_{\rm R}} dt_{\rm tot} = \frac{g[\exp(kt_{\rm R}) - 1]}{kt_{\rm R}} \simeq g.$$
 (2)

The last approximation is based on the relation $\exp(x) \simeq 1 + x$ for small values of x. The important point to be noted from the results of table 5 is that the % conversion (=100 g) deviates considerably from 100% in spite of the fact that the reactant is never eluted from the catalytic column. This is most probably due to the active catalytic surface being only a small fraction of the total surface and not to irreversible adsorption of the product on the solid catalyst, since two column lengths (l' and l) containing different amounts of catalyst give virtually the same conversion.

From the results presented in this paper, it is demonstrated that reversed-flow gas chromatography can be used successfully to study heterogeneous dehydration of alcohols with some obvious advantages over other conventional techniques used in heterogeneous catalysis.

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