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## Homogeneous catalysis studied by reversed-flow gas chromatography

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### ABSTRACT

The reversed-flow gas chromatography technique was used to study the kinetics of dehydration of 2-butanol in phosphoric acid solution. A combination of the mathematical analysis developed in heterogeneous catalysis, mass transfer across gas–liquid boundaries, and diffusion of gases in liquids was employed to find the relevant equations pertaining to the present problem of homogeneous catalysis in a liquid phase. The equation describing the diffusion band of the reaction product(s) was derived for both a stirred solution and a quiescent one. These equations were then used to analyze the experimental data, from which the rate constants for the first-order reaction and for transporting the products away from the solution were determined. From the latter rate constant, the overall mass transfer coefficient of butenes in the liquid phase was found. This increases with temperature, showing that mass transfer across the gas–liquid boundary is activated, with an activation energy of  $60.9 \text{ kJ mol}^{-1}$ . The diffusion coefficient of butenes in the reaction mixture, and their partition coefficient between the gas and the liquid phase, were also determined. The activation energy of the first-order reaction was found to be equal to  $34.1 \text{ kJ mol}^{-1}$ .

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### INTRODUCTION

The application of the reversed-flow gas chromatography (RF-GC) technique to heterogeneous catalysis is described in detail in a recently published book [1] and some newer publications [2–6]. The same technique has been used to study mass transfer of gases across gas–liquid boundaries [7] and diffusion of gases in liquids [8], both combined with partition coefficient determination in the gas–liquid interfaces. A combination of the mathematical analysis developed in the above three cases, namely catalysis, mass transfer, and diffusion in liquids, can be employed for finding the relevant equations pertaining to homogeneous catalysis in a liquid phase. This is the subject of the present work using as a probe reaction the dehydration of 2-butanol to butenes in phosphoric acid solution. The experimental arrangement was the same as that previously reported [7,8]. It is repeated schematically in Fig. 1 for the purposes of the theoretical analysis.

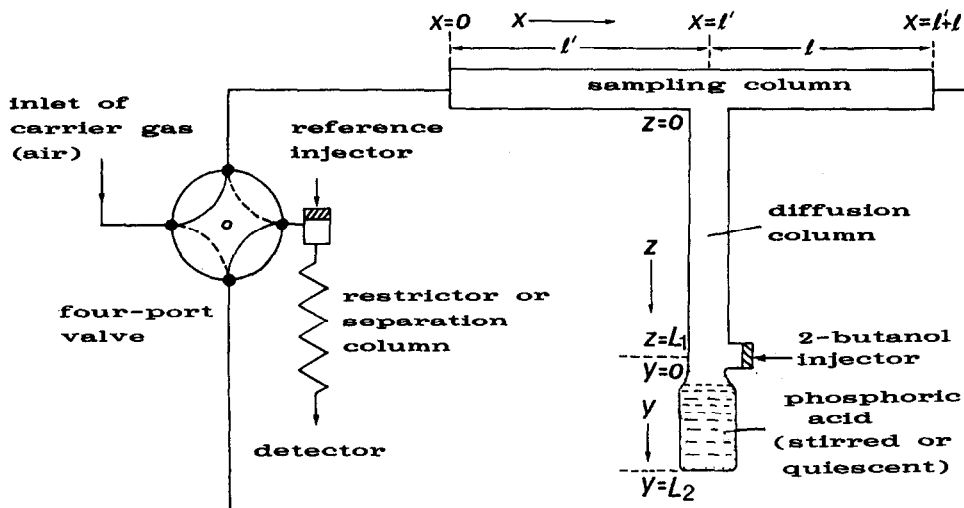


Fig. 1. Schematic representation of columns and gas connections in the reversed-flow gas chromatography technique.

## THEORETICAL

The equation giving the diffusion band (plot of the logarithm of the sample peak height,  $\ln h$ , vs. time of flow reversal,  $t_0$ ) when a chemical reaction takes place inside vessel  $y$  will be derived for two cases: a stirred solution and a quiescent one.

### *Stirred solution*

In gaseous region  $z$  the diffusion equation of a reaction product is:

$$\partial c_z / \partial t_0 = D_G \partial^2 c_z / \partial z^2 \quad (1)$$

where  $c_z = c_z(z, t_0)$ , and  $D_G$  is the diffusion coefficient of that product into the gaseous phase filling column  $z$  (see Fig. 1). The initial condition is  $c_z(z, 0) = 0$ , and the boundary conditions at the junction of the sampling and the diffusion columns, *i.e.* at  $x = l'$  and  $z = 0$ , are given by the relations:

$$c_z(0, t_0) = c(l', t_0) \quad (2)$$

$$D_G (\partial c_z / \partial z)_{z=0} = v c(l', t_0)$$

where  $c(l', t_0)$  is the concentration of the solute (product) in the sampling column and  $v$  is the linear velocity of the carrier gas in that same column.

The solution of eqn. 1, subject to the boundary conditions (eqn. 2), is obtained in an analogous way as before [7,8] (the initial condition is now different), the result, in the form of Laplace transform with respect to time, being:

$$C_z = C(l', p_0) \cosh q_1 z + (v/D_G q_1) C(l', p_0) \sinh q_1 z \quad (3)$$

where:

$$q_1^2 = p_0/D_G \quad (4)$$

with  $p_0$  denoting the time transform parameter. The capital letters  $C_z$  and  $C$  represent the  $t_0$  Laplace-transformed functions  $c_z$  and  $c$ , respectively.

Going now to the other boundary of the diffusion column at  $z = L_1$  and  $y = 0$ , the condition in this boundary is:

$$D_G a_G (\partial c_z / \partial z)_{z=L_1} = K_L a_L (c_L - c_L^*) \quad (5)$$

where  $a_G$  is the cross-sectional area in the columns  $z$  and  $x$ ,  $a_L$  the free surface area of the liquid,  $c_L$  the concentration of the solute in the bulk liquid phase,  $c_L^*$  the solute concentration in a fictitious liquid in equilibrium with the real bulk gas phase, and  $K_L$  the overall mass transfer coefficient of the solute in the liquid.

The rate of change of the dissolved product is given by the relation:

$$\frac{\partial c_L}{\partial t_0} = r - \frac{K_L a_L}{V_L} (c_L - c_L^*) \quad (6)$$

where  $r$  is the rate of its formation by the chemical reaction in the liquid phase and  $V_L$  the volume of the liquid.

If one takes the  $t_0$  Laplace transforms of all terms of eqns. 5 and 6, with initial condition  $c_L(0) = 0$  (*i.e.* no solute dissolved in the liquid initially), and then combines the transformed equations to eliminate  $C_L$ , there results:

$$D_G \left( \frac{dC_z}{dz} \right)_{z=L_1} = \frac{K_L a_L}{a_G} \cdot \frac{R}{p_0 + k_{-1}} - \frac{K_G a_L}{a_G} \cdot \frac{p_0 C_z(L_1)}{p_0 + k_{-1}} \quad (7)$$

where  $R$  is the  $t_0$ -transformed reaction rate  $r$ ,  $k_{-1}$  is given by the relation

$$k_{-1} = K_L a_L / V_L \quad (8)$$

and  $K_G$  is the overall mass transfer coefficient of the solute in the gas phase, related to the partition coefficient  $K$  of the solute between the two phases by the equation

$$K = c_L^* / c_z(L_1) = K_G / K_L \quad (9)$$

according to the two-film theory previously employed [7].

Finally, eqn. 3 is used to calculate both  $(dC_z/dz)_{z=L_1}$  and  $C_z(L_1)$  of eqn. 7, with the result, after rearrangement:

$$C(I', p_0) = \frac{K_L a_L}{D_G q_1 a_G} \cdot \frac{R}{p_0 + k_{-1}} \left[ \sinh q_1 L_1 + \frac{v}{D_G q_1} \cosh q_1 L_1 + \frac{K_G a_L}{D_G q_1 a_G} \cdot \frac{p_0}{p_0 + k_{-1}} \left( \cosh q_1 L_1 + \frac{v}{D_G q_1} \sinh q_1 L_1 \right) \right]^{-1} \quad (10)$$

To facilitate the inversion of this equation, we employ the same approximations as before [7,8], viz. omission of  $\sinh q_1 L_1$  compared with  $(v/D_G q_1) \cosh q_1 L_1$ , and also omission of  $\cosh q_1 L_1$  compared with  $(v/D_G q_1) \sinh q_1 L_1$ . Then, eqn. 10 becomes:

$$C(l', p_0) = \frac{K_L a_L}{\bar{V}} \cdot \frac{R}{p_0 + k_{-1}} \left( \cosh q_1 L_1 + \frac{K_G a_L}{D_G q_1 a_G} \cdot \frac{p_0}{p_0 + k_{-1}} \sinh q_1 L_1 \right)^{-1} \quad (11)$$

where  $\bar{V} = a_G v$  is the volumetric flow-rate of the carrier gas.

A further simplification of eqn. 11 is based on the approximations:

$$\cosh q_1 L_1 \approx 1 \quad \text{and} \quad \sinh q_1 L_1 \approx q_1 L_1$$

provided  $L_1$  is small enough. Substituting these into eqn. 11, one obtains

$$C(l', p_0) = \frac{K_L a_L R}{\bar{V}(1 + K_G L_1 a_L / D_G a_G)} \left( p_0 + \frac{k_{-1}}{1 + K_G L_1 a_L / D_G a_G} \right)^{-1} \quad (12)$$

Finally, the inversion of this transformed function depends on the form of the rate equation describing the formation of the product(s). In the simplest case of a first-order reaction, the rate equation is  $r = k_2 c_R$ , where  $c_R$  is the concentration of the reactant in solution and  $k_2$  is the rate constant of the reaction. The integrated rate equation is the well-known expression:

$$r = k_2 c_R = k_2 c_0 \exp(-k_2 t_0) \quad (13)$$

$c_0$  denoting the initial reactant concentration. The Laplace transform of this is

$$R = \frac{k_2 c_0}{p_0 + k_2} \quad (14)$$

and the substitution of the right-hand side for  $R$  in eqn. 12 gives

$$C(l', p_0) = N_3 [(p_0 + k_2)(p_0 + k_3)]^{-1} \quad (15)$$

where

$$N_3 = \frac{K_L a_L k_2 c_0}{\bar{V}(1 + K_G L_1 a_L / D_G a_G)} \quad (16)$$

and

$$k_3 = \frac{k_{-1}}{1 + K_G L_1 a_L / D_G a_G} \quad (17)$$

Taking now the inverse Laplace transform with respect to  $p_0$  of eqn. 15, one finds the function describing the height  $h$  of the sample peaks:

$$h = 2c(l', t_0) = \frac{2N_3}{k_3 - k_2} [\exp(-k_2 t_0) - \exp(-k_3 t_0)] \quad (18)$$

This equation describes a diffusion band which depends on the competition of two phenomena: a chemical reaction forming the solute under investigation with a rate constant  $k_2$  and its expulsion from the solution with a rate constant  $k_3$  (cf. eqn. 17) depending on  $a_G$  and  $a_L$ , on  $K_G$ ,  $D_G$  and  $K_L$  (cf. also eqn. 8), and on  $L_1$  and  $V_L$ . By changing the length of the diffusion column  $L_1$  and/or the volume of the liquid  $V_L$ , we can change the value of  $k_3$ , and in favorable cases decide which of the two phenomena above becomes rate-controlling.

### Quiescent solution

In this case the diffusion of the product from the bulk liquid phase to the surface of the liquid must be taken into account. In the liquid region  $y$  (see Fig. 1) the diffusion equation reads:

$$\partial c_y / \partial t_0 = D_L \partial^2 c_y / \partial y^2 + r \quad (19)$$

which is similar to eqn. 7 of ref. 8, differing only in the term  $r$  due to the chemical reaction. This equation is solved in exactly the same way as before [8], the result being:

$$C_y(0) = \left[ \frac{R}{D_L q_2} - C_y(0) q_2 \right] \tanh q_2 L_2 \quad (20)$$

where  $C_y'(0) = (dC_y/dy)_{y=0}$ ,  $C_y(0)$  is the value of the transformed function  $C_y$  at  $y = 0$ ,  $D_L$  is the diffusion coefficient of the product in the liquid phase, and  $q_2$  is given by a relation analogous to eqn. 4:

$$q_2^2 = p_0 / D_L \quad (21)$$

Now, eqn. 20 holding in region  $y$  is linked with eqn. 3 valid in region  $z$ , using the boundary conditions at  $z = L_1$  and  $y = 0$ :

$$K = C_y(0) / C_z(L_1) \quad (22)$$

$$a_G D_G (\partial C_z / \partial z)_{z=L_1} = a_L D_L (\partial C_y / \partial y)_{y=0} \quad (23)$$

where the equilibrium 22 is assumed to be rapidly established. Calculation of  $C_z(L_1)$  and  $(\partial C_z / \partial z)_{z=L_1}$  from eqn. 3 and substitution into eqns. 22 and 23, using also eqn. 20, gives:

$$C(l', p_0) = \frac{a_L R \tanh q_2 L_2}{a_G D_G q_1 q_2} \left[ \sinh q_1 L_1 + \frac{v}{D_G q_1} \cosh q_1 L_1 + \right. \\ \left. + K \frac{a_L D_L q_2}{a_G D_G q_1} \tanh q_2 L_2 \left( \cosh q_1 L_1 + \frac{v}{D_G q_1} \sinh q_1 L_1 \right) \right]^{-1} \quad (24)$$

This is similar to eqn. 15 of ref. 8.

Using the same approximations as in the case of the stirred solution applied to eqn. 10, and in addition the approximation employed earlier for diffusion in liquids [8], *viz.*:

$$\frac{\coth q_2 L_2}{D_L q_2} \approx \frac{1}{L_2} \left( \frac{1}{p_0} + \frac{\pi^2}{3\beta} \right) \quad (25)$$

where:

$$\beta = \pi^2 D_L / L_2^2 \quad (26)$$

we obtain from eqn. 24 the simpler expression:

$$C(l', p_0) = \frac{a_L R}{\check{V}(L_2/3D_L + KL_1 a_L / D_G a_G)} \left[ p_0 + \frac{1}{L_2(L_2/3D_L + KL_1 a_L / D_G a_G)} \right]^{-1} \quad (27)$$

As before, the inversion of this transformed function depends on the form of the rate equation for the formation of the product(s). If this is  $r = k_2 c_R$ , *i.e.* a simple first-order reaction, the integrated rate equation is eqn. 13, and its Laplace transform eqn. 14. When the latter is substituted for  $R$  in eqn. 27, it gives:

$$C(l', p_0) = N_4 [(p_0 + k_2)(p_0 + k_4)]^{-1} \quad (28)$$

where:

$$N_4 = \frac{a_L k_2 c_0}{\check{V}(L_2/3D_L + KL_1 a_L / D_G a_G)} \quad (29)$$

and:

$$k_4 = \frac{1}{L_2(L_2/3D_L + KL_1 a_L / D_G a_G)} \quad (30)$$

Eqns. 28, 29 and 30 are analogous to eqns. 15, 16 and 17, respectively, applied to a stirred solution. Taking now the inverse Laplace transform with respect to  $p_0$  of eqn. 28, the function is obtained describing the diffusion band from a quiescent solution in which a first-order reaction takes place:

$$h = 2c(l', t_0) = \frac{2N_4}{k_4 - k_2} [\exp(-k_2 t_0) - \exp(-k_4 t_0)] \quad (31)$$

This has exactly the same form as eqn. 18 for a stirred solution. The diffusion band depends again on two phenomena: a chemical reaction with a rate constant  $k_2$  and the transport of the product(s) away from the solution, described by the rate coefficient  $k_4$ , depending on the same parameters as  $k_3$  (see eqn. 17) except for the replacement of  $K_L$

by  $3D_L/L_2$ . This is easily seen by substituting eqn. 8 for  $k_{-1}$  in eqn. 17 and dividing both terms of the fraction by  $K_L a_L/V_L = K_L a_L/a_L L_2 = K_L/L_2$ . The result (taking also into account eqn. 9) is:

$$k_3 = \frac{1}{L_2(1/K_L + KL_1 a_L/D_G a_G)} \quad (32)$$

Division of both terms of eqn. 16 by  $K_L$  gives:

$$N_3 = \frac{a_L k_2 c_0}{\bar{V}(1/K_L + KL_1 a_L/D_G a_G)} \quad (33)$$

A comparison of eqns. 32 and 33 with 30 and 29, respectively, indicates that stirring of the solution results in an overall mass transfer coefficient  $K_L$  equivalent to a diffusion through a liquid layer of thickness  $L_2/3$ , *i.e.* one-third of the total liquid height.

Summarizing the theoretical predictions, one concludes that the diffusion band must depend on three rate processes: a chemical reaction, the diffusion in the liquid, and the diffusion in the gas phase. The last-mentioned effect can be minimized by using a gas diffusion length  $L_1$  that is as short as possible. Then, the rate constants  $k_3$  and  $k_4$  depend only on liquid diffusion. It is easy to distinguish whether a slope extracted from the diffusion band is  $-k_2$  or  $-k_3$  and  $-k_4$ , by increasing the height of the liquid layer  $L_2$ . If this causes a decrease in the slope, it is  $-k_3$  and  $-k_4$  which is measured. If, on the other hand, the slope remains unaffected by  $L_2$ , it is equal to  $-k_2$ .

In conclusion, various possibilities arise when the RF-GC technique is applied to homogeneous catalysis in a liquid phase, either stirred or quiescent, with or without a diffusion column. Some of these possibilities are demonstrated in the Results and discussion section.

## EXPERIMENTAL

### Materials

2-Butanol was obtained from BDH, and orthophosphoric acid was an 85% RPE-ACS product of Carlo Erba.

The carrier gas was nitrogen of 99.99% purity from Linde (Athens, Greece).

### Apparatus

The experimental set-up is outlined in Fig. 1. The sections  $l$ ,  $l'$  and  $L_1$  of the sampling cell were  $1/4$ -in. stainless-steel tubes with lengths  $l = l' = 50$  cm and  $L_1 = 35$ – $50$  cm. The reacting liquid consisted of  $0.25$ – $1.5$  cm<sup>3</sup> of phosphoric acid, into which  $0.5$ – $15$   $\mu$ l of 2-butanol were dissolved. The liquid was placed in a glass vessel of 17.5 mm I.D. at its lower part and of 4 mm I.D. at its upper part, which was connected to the stainless-steel column  $L_1$  with a  $1/4$ -in. Swagelok union. The gaseous volume between the liquid's surface and column  $z$  was  $1.67$ – $5.80$  cm<sup>3</sup>, while the height of the liquid phase  $L_2$  was  $0.41$ – $0.85$  cm.

An additional separation column for butenes at  $48$ – $87^\circ\text{C}$  was used, and this was a  $2.4$  m  $\times$   $1/8$  in. Chromosil 310 column purchased from Supelco SA. The pressure drop along this column was 44 cmHg, while that along column  $l' + l$  was negligible (less than 1 mmHg).

### Procedure

After placing the solution of 2-butanol in phosphoric acid in its position (see Fig. 1) and waiting for the steadily rising concentration-time curve to appear in the detector signal, the chromatographic sampling procedure was started by reversing the direction of the carrier gas flow for 6–10 s, which is a shorter time period than the gas hold-up time in both column sections  $l$  and  $l'$ . Examples of sample peaks created by the flow reversals have been given many times elsewhere [1,2,4–8].

With the additional separation column in place, two or three sample peaks were obtained after each flow reversal, whereas a single sample peak appeared without the separation column. In all cases the sample peaks were due to product butenes. No peak of 2-butanol was detected owing to its low vapour pressure at the working temperatures.

In each experimental run a long series of sample peaks was obtained. By then plotting the logarithm of the height of the peaks vs. the time of the respective flow reversals, the diffusion band for each run was constructed. The appearance of these bands was similar to those previously published [1,4–9].

### RESULTS AND DISCUSSION

A typical diffusion band obtained in the present work is shown in Fig. 2. All bands had the same shape, as predicted by both eqn. 18 applied to a stirred solution and eqn. 31 pertaining to a quiescent liquid. From each diffusion band the two exponential coefficients  $k_2$  and  $k_3$  (or  $k_4$ ) can be determined by means of a suitable computer program or, if these two coefficients are sufficiently different, by applying a method similar to that described elsewhere [7], *viz.* by finding first the slope  $-b_1$  and the intercept  $\ln h_0$  of the descending linear part of the  $\ln h$  vs.  $t_0$  plot (after

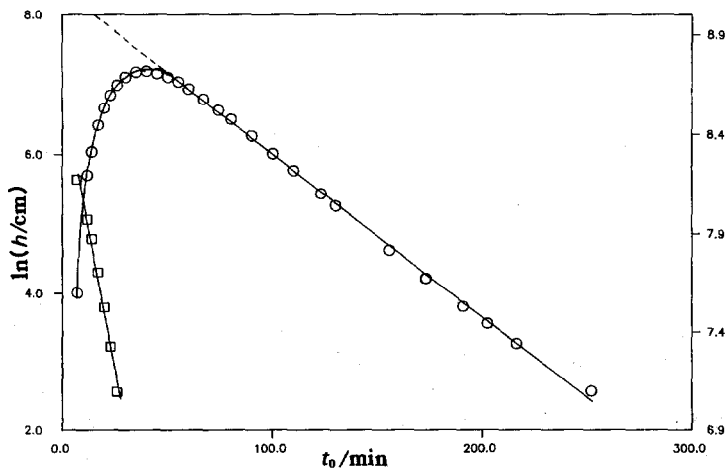


Fig. 2. A diffusion band obtained with a quiescent solution of  $0.5 \mu\text{l}$  2-butanol in  $0.25 \text{ cm}^3$  of 85% phosphoric acid, at 408.2 K. A diffusion column  $L_1$  of 35 cm was used and the experimental points (O) represent a mixture of all butenes (left ordinate). Points  $\square$  (right ordinate) were obtained by subtracting the experimental points before the maximum from the extrapolated (dashed line) linear descending part of the band.



the maximum), and then replotting the initial data (before the maximum) as  $\ln[h_0 \exp(-b_1 t_0) - h]$  vs.  $t_0$ . An example is given in Fig. 2. The slope  $-b_2$  of the new straight line thus obtained refers to the ascending part of the diffusion band. In experiments without a diffusion column  $L_1$  (see Fig. 1), it was difficult to determine the slope  $-b_2$  because the ascending part was very fast. When an additional separation column was employed (see Experimental section and Fig. 1) various isomeric butenes were recorded, each giving separate sample peaks and diffusion bands.

#### *Experiments with a stirred solution*

The slopes  $-b_1$  (descending) and  $-b_2$  (ascending) calculated from the diffusion bands, obtained with a stirred solution of 1–15  $\mu\text{l}$  2-butanol in 0.5 or 1.5  $\text{cm}^3$  85% phosphoric acid, and with a 50-cm diffusion column  $L_1$  or without such a column, are collected in Table I. The following conclusions can be drawn from the data of this table, in conjunction with eqn. 17 or 32.

(1) Changing the flow-rate of the carrier gas from 30 to 13.3  $\text{cm}^3 \text{min}^{-1}$  at the same temperature (see experiments 22 and 26) has only a small effect on the slope.

(2) The descending slopes measured must represent the rate constant  $k_3$  for transporting the products away from the solution. This is indicated by the fact that removal of the diffusion column ( $L_1 = 0$ ) increase this slope considerably, as predicted by eqn. 17 or 32. Moreover, eqn. 32, for  $L_1 = 0$ , gives  $k_3 = K_L/L_2$ , and, since  $L_2$  is the known height of the liquid layer,  $K_L$  is easily calculated by simply multiplying the descending slope of Table I by  $L_2$ . For example, in experiment 22 (when 0.5  $\text{cm}^3$  of solution was used)  $L_2$  was 0.52 cm and thus  $K_L = 16.08 \cdot 10^{-4} \times 0.52 \cdot 10^{-2} = 8.36 \mu\text{m s}^{-1}$ . In experiment 27 (with 1.5  $\text{cm}^3$  of solution)  $L_2$  was 0.85 cm and  $K_L = 8.21 \mu\text{m s}^{-1}$ . These overall mass transfer coefficients of butenes in the liquid phase are of the same order of magnitude as those of butane in hexadecane measured earlier [7], being 2.18–2.93  $\mu\text{m s}^{-1}$  at much lower temperatures (326–327 K).

(3) The increase in  $K_L$  with temperature (experiments 21–27) shows that mass transfer across the gas–liquid boundary is activated. From a plot of  $\ln K_L$  vs.  $1/T$  an activation energy of 60.9  $\text{kJ mol}^{-1}$  is calculated. This is too high a value for a physical mass transfer phenomenon. For the transfer of propene across a gas– $\gamma\text{Al}_2\text{O}_3$  surface, an activation energy of 13.8  $\text{kJ mol}^{-1}$  was found [10]. The value of 60.9  $\text{kJ mol}^{-1}$  determined here probably indicates that the removal of butenes from the reaction mixture is not a simple expulsion of them from the solution but involves some chemical process.

(4) The ascending slopes in Table I must represent the reaction rate constant  $k_2$ .

#### *Experiments with a quiescent solution*

The results from such experiments are listed in Table II. The slopes  $-b_1$  (descending) and  $-b_2$  (ascending) of the diffusion bands were determined here with five different flow-rates of the carrier gas, three lengths  $L_1$  of the diffusion column, three different heights  $L_2$  of the liquid solution, and at various temperatures. According to eqn. 31, these slopes give either  $k_2$  or  $k_4$ . It remains to be decided which is which. This and other conclusions drawn from Table II are mainly based on the physical content of the rate constant  $k_4$  as that described by eqn. 30. They are the following:

(1) Changing the flow-rate  $\dot{V}$  at the same temperature (experiments 2, 9, 10) has a small effect on the slopes.

(2) Removing the diffusion column  $L_1$  at 433.2 K (compare experiments 12 and 25) causes a big increase in the descending slope, an indication that this slope measures  $k_4$ . From eqn. 30, by setting  $L_1 = 0$ , we obtain  $k_4 = 3D_L/L_2^2$ , and from the slope  $26.06 \cdot 10^{-4} \text{ s}^{-1}$  and  $L_2 = 0.52 \text{ cm}$  of experiment 25, one finds  $3D_L/L_2 = 13.6 \mu\text{m s}^{-1}$ , in acceptable agreement with  $K_L = 17.2 \mu\text{m s}^{-1}$  calculated at the same temperature from the slope of a stirred solution (see experiment 24 in Table I). Furthermore,  $D_L$  is calculated as  $2.35 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$  at 433.2 K.

(3) Increasing the height of the liquid layer  $L_2$  (experiments 38, 37 and 39) causes a decrease of the descending slope, while it leaves unaffected the ascending slope. This confirms that the first is equal to  $k_4$ , and the second to  $k_2$ , as eqns. 30 and 13 show.

Multiplying eqn. 30 by  $L_2$  and inverting the result, one obtains the form:

$$\frac{1}{k_4 L_2} = L_1 \frac{a_L}{a_G} \cdot \frac{K}{D_G} + \frac{1}{3D_L} L_2 \quad (34)$$

According to this linear form, by plotting  $1/k_4 L_2$  vs.  $L_2$ , we find  $1/3D_L$  as the slope of the plot and  $L_1 a_L K/a_G D_G$  as its intercept. From the slope,  $D_L$  is calculated, while from the intercept,  $K/D_G$  is found. By then measuring the diffusion coefficient of the products in the carrier gas [9], or by calculating it theoretically [11], one finds the value of the partition coefficient  $K$ . The  $K/D_G$  value can also be found from the results with a stirred solution, by conducting two experiments at the same temperature: one with a defined length  $L_1$  and another without a diffusion column. From the latter experiment we find  $K_L$ , since  $L_1 = 0$ , and then this value is used with the first experiment to calculate  $K/D_G$ .

Both procedures described above can be applied to the results of Tables I and II. Using the descending slopes from experiments 37–39 of Table II, together with the  $L_2$

TABLE I

SLOPES OF THE DIFFUSION BANDS OF BUTENES OBTAINED WITH A STIRRED SOLUTION OF 0.5 cm<sup>3</sup> 85% ORTHOPHOSPHORIC ACID CONTAINING 1–15 μl 2-BUTANOL

In expt. 27, 3 μl of 2-butanol was dissolved in 1.5 cm<sup>3</sup> of 85% orthophosphoric acid.

Expt. No.	T(K)	$L_1$ (cm)	$\bar{V}$ (cm <sup>3</sup> min <sup>-1</sup> )	Descending slope ( $\cdot 10^{-4} \text{ s}^{-1}$ )				Ascending slope ( $\cdot 10^{-4} \text{ s}^{-1}$ )	
				A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	B <sup>b</sup>	C <sup>c</sup>
14	433.2	50	20	—	1.220	1.106	—	9.463	—
15	443.2	50	20	—	1.297	1.276	—	8.965	10.68
21	393.2	0	30	6.174	5.922	5.672	—	—	—
22	413.2	0	30	—	16.08	—	—	—	—
24	433.2	0	30	—	—	—	32.99	—	—
26	413.2	0	13.3	—	—	—	18.56	—	—
27	413.2	0	26.5	—	—	—	9.655	—	—

<sup>a</sup> 1-Butene + 2-methylpropene.

<sup>b</sup> *cis*-2-Butene.

<sup>c</sup> *trans*-2-Butene.

<sup>d</sup> Mixture of all butenes.

TABLE II  
SLOPES OF THE DIFFUSION BANDS OF BUTENES OBTAINED WITH A QUIESCENT SOLUTION OF 2-BUTANOL IN 85% ORTHOPHOSPHORIC ACID

Expt. No.	T (K)	L <sub>1</sub> (cm)	L <sub>2</sub> (cm)	V̄ (cm <sup>3</sup> min <sup>-1</sup> )	2-Butanol (μl) + orthophosphoric acid (cm <sup>3</sup> )	Descending slope (· 10 <sup>-4</sup> s <sup>-1</sup> )				Ascending slope (· 10 <sup>-4</sup> s <sup>-1</sup> )			
						A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	D <sup>d</sup>
2	428.7	50	0.52	30	15 + 0.5	—	—	—	3.683	—	—	—	15.78
9	429.2	50	0.52	17	15 + 0.5	—	—	—	1.914	—	—	—	14.65
10	429.2	50	0.52	10	15 + 0.5	—	—	—	2.488	—	—	—	—
12	433.2	50	0.52	25	15 + 0.5	—	—	0.6259	—	0.5904	—	7.383	9.348
16	433.2	50	0.52	20	5 + 0.5	—	—	1.099	—	1.189	—	8.151	6.957
18	463.2	50	0.52	20	5 + 0.5	4.168	—	2.206	—	2.486	—	—	—
25	433.2	0	0.52	30	1 + 0.5	—	—	—	—	—	—	26.06	—
38	408.2	35	0.41	30	0.5 + 0.25	—	—	—	—	—	—	3.920	—
37	408.3	35	0.52	30	1 + 0.5	—	—	—	—	—	—	2.751	9.509
39	408.2	35	0.64	30	2 + 1	—	—	—	—	—	—	2.045	9.234
													9.300

<sup>a</sup> 1-Butene + 2-methylpropene.

<sup>b</sup> *cis*-2-Butene.

<sup>c</sup> *trans*-2-Butene.

<sup>d</sup> Mixture of all butenes.

values given, it is found, by plotting  $1/k_4L_2$  vs.  $L_2$  (with a correlation coefficient  $r = 0.9973$ ), that  $D_L = 5.41 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and  $K/D_G = 1.066 \cdot 10^6 \text{ m}^{-2} \text{ s}$ . This value for  $D_L$  has the correct order of magnitude for diffusion coefficients in liquids. From experiments 14 and 24 of Table I (both at 433.2 K),  $K_L = 1.7155 \cdot 10^{-5} \text{ m s}^{-1}$  and  $K/D_G = 3.191 \cdot 10^6 \text{ m}^{-2} \text{ s}$ . Both  $K/D_G$  values, although at temperatures differing by 25 K, have the same order of magnitude. The calculated [11] values of  $D_G$  for butenes at 408.2 and 433.2 K (at the pressure of the experiments) are  $1.77 \cdot 10^{-5}$  and  $1.24 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$ , respectively. Using these values, we find for  $K$  18.9 and 39.6, respectively.

(4) From the ascending slopes of Table II, representing  $k_2$ , and the values pertaining to the mixture of all butenes ( $D$ ), an activation energy for the first-order reaction is calculated. It is  $34.1 \text{ kJ mol}^{-1}$ .

## CONCLUSIONS

The results presented in the previous section are by no means exhaustive for the reaction of dehydration of 2-butanol to butenes. It was simply used as a probe reaction to indicate the potentiality of the RF-GC technique for studying homogeneous catalysis. It has become obvious from the discussion of the results that some physicochemical parameters pertaining to the reaction and emerging from the theoretical treatment of the experimental data are not easily accessible by other conventional techniques. There remains to apply the theoretical analysis in other homogeneous reactions, or even to the same family of reactions, varying the experimental parameters, like  $L_1$ ,  $L_2$ ,  $T$ ,  $\dot{V}$ , etc., more widely.

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