KINETICS AND ADSORPTION ON ACID CATALYSTS. IV.*
KINETICS OF GAS-PHASE DEHYDRATION OF METHANOL ON A SULPHONATED ION EXCHANGER

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The kinetics of dehydration of gaseous methanol in a flow system has been studied at temperatures 111, 131 and 150°C, a macroreticular sulphonated styrene-divinylbenzene ion exchanger being employed as catalyst. The best-fitting rate equation, the rate constants and the adsorption coefficients for the given temperatures have been determined by the method of initial reaction rates using a non-linear regression of the experimental data. The parameters of the Arrhenius and van't Hoff equations have been determined and their meanings are discussed. The number of active centres calculated from the pre-exponential factor is in good agreement with the number of sulphonic acid groups determined analytically.

Several of our recent papers[1~3] on the kinetics of heterogeneous catalytic reactions in the gaseous phase deal with the use of acid macroreticular ion exchangers as models of catalysts with centres of equal activity. Apart from other reactions, we studied the dehydration of tert-butanol to isobutylene[3]. In this connexion we considered it worth while to investigate also the dehydration of an alcohol incapable of giving rise to an olefin, so that the product of dehydration would be the corresponding ether. An example of such alcohol is methanol. The kinetics of its dehydration (*A*)

$$2 \, CH_3OH \quad \rightarrow \quad (CH_3)_2O + H_2O \qquad (A)$$
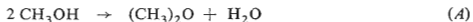
was studied on alumina[4,5] and alumosilicate[6,7]. In the first two papers the rate equations are based on the assumption of a strong adsorption of the reaction components; in the absence of the reaction products these equations may lead to the kinetics of zero order. In the presence of water the second order equation was more appropriate at temperatures 200 to 285°C, with respect to the surface concentration of methanol[4], and the equation of order 0·5 fitted the results at temperatures[5] 145 to 195°C. The latter order was observed even in the absence of water at low partial pressures of methanol[8]. At lower partial pressures the order 0·5 was observed also on alumosilicate[6,7]. Gates and Johanson[9] measured the initial dehydration rates of methanol on a sulphonated non-porous ion exchanger, Dowex 50 X-8, and from these they calculated the apparent activation energy for the temperature range 80—120°C. These authors state[10] that the kinetics of this reaction is best described by an equation of second order with respect to the surface concentration of methanol.

The present paper deals with the dehydration of methanol on the catalyst employed in our previous studies[1-3], viz. a sulphonated macroreticular styrene-divinylbenzene copolymer. The gas-phase initial reaction rates have been determined in a flow system. The objective of the work was to determine the best-fitting rate equation, its constants and their dependence on temperature.

EXPERIMENTAL

Chemicals. Methanol, A.R. (Lachema, Brno), was dried with magnesium and iodine and distilled. After the distillation it still contained 0·6% of water. Bulb nitrogen (Technoplyn, Ostrava) in pressure cylindres was purified by passing through heated copper and dried with a molecular sieve. The catalyst: sulphonated (2·4 mmol —SO_3H-groups per g of the dry catalyst), macroreticular styrene-divinylbenzene copolymer (25% of divinylbenzene), supplied by the Research Institute of Synthetic Resins and Varnishes, Pardubice. It was employed in a dry state (dried at 90°C and 14 Torr), particle size 0·16—0·3 mm. The specific surface area of the dry catalyst, determined by adsorption of nitrogen using the BET method, was 49 m^2/g. Other physical characteristics of this catalyst were described elsewhere[11]. As had been verified thermogravimetrically, the catalyst was stable in the temperature range employed.

Apparatus and procedure. The experimental procedure and the flow apparatus were described previously[1,12]. Methanol was introduced as a liquid, evaporated and its vapour was diluted with a calculated flow of nitrogen. The glass tube reactor (inner diameter 10 mm) was charged with 0·5 g of the catalyst. The maximum fluctuation of the temperature within the bed of the catalyst was ±0·5 to 1°C. After a steady state had been established in the reactor three samples were taken for analysis at selected intervals from the outlet by means of a freezing trap with solid carbon dioxide. The conversion of methanol was determined on the basis of the amount of water produced by the reaction. The liquid reaction product was analysed for the content of methanol and water by gas chromatography in an apparatus with thermal conductivity detection (Vývojové dílny ČSAV, Prague), employing Porapak Q (Waters Associates, Framingham, Mass., USA). The length of the column was 2 m, temperature 110°C, the carrier gas was hydrogen.

Determination of the initial reaction rates. The measurements were carried out at mass feed rates and at a catalyst particle size at which even the much faster reaction of methanol with ethyl acetate[1] was not influenced by external or internal diffusion. The initial reaction rates were determined as slopes of the straight lines expressing the conversion x ($0 < x < 0·1$) as a function of the reciprocal space velocity.

RESULTS AND DISCUSSION

The experimental values of the initial reaction rates, r, at different partial pressures of methanol, p_A, and temperatures 111°C, 131°C and 150°C are plotted in Fig. 1. In deriving the rate equations we first considered that the rate-determining step of the reaction might be adsorption of methanol, the surface reaction of the adsorbed methanol, or desorption of a product. The first and the third possibility could be ruled out from the very shape of the kinetic curves in Fig. 1. If the adsorption were the rate-determining step the dependence of r on p_A would be a linear or even (in the case of a simultaneous adsorption of two methanol molecules) a quadratic function.

Provided that the desorption were the rate-controlling step the initial reaction rate would be independent of the partial pressure of methanol. Therefore, we have considered that the rate-determining step is the surface reaction. In this case 10 different types of rate equations have been derived (Table I) for the studied reaction $2 A \rightarrow R + S$. We have started from the assumption of uniformity of active centres of the catalyst which in the case of the ion exchanger used is very likely true. We have considered that methanol can be adsorbed in a molecular way on one active centre, or on two centres with dissociation, or on two centres without cleavage of the molecule[13]. In some cases (Table I, equation type *3*) we also considered the possibility of simultaneous adsorption of two molecules of methanol on one active centre; this idea was based on the spectral measurements published by Knözinger[14]. Further we have assumed different molecularities of the rate-determining step; we considered that either one molecule reacted in this step (equation types *1* and *2*) or two molecules (equation types *3* to *7*) (an adsorbed molecule of methanol enters in this reaction as such or in the form of its particles produced by dissociation). In case that two molecules participate in the rate-determining step we have considered that the second molecule may not be adsorbed, thus reacting directly from the gaseous phase, or may be adsorbed on other sites of the surface of the catalyst, *e.g.* on the polymeric part of the ion exchanger (equation types *6* and *7*). We also take into account that only one particle of those produced by the dissociative adsorption can react in the rate-determining step (equation types *8* to *10*); this particle reacts alone, or together with a molecule of methanol from the gaseous phase (equation type *8*), or with a molecule of methanol adsorbed molecularly on one (equation *9*) or two (equation *10*) centres of another type.

With the aid of 32 equations derived from the fundamental types in Table I we have evaluated the measured data of the initial reaction rates at the individual temperatures by the method of linear and non-linear regressions[15]. As a criterion we employed the critical value of the sum
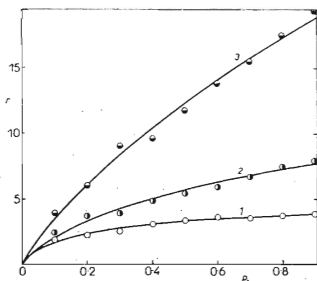

Fig. 1

The Initial Reaction Rate, r [mol h^{-1} kg^{-1}] as a Function of the Initial Partial Pressure of Methanol, p_A [atm]

The points are the experimental values, the curves have been calculated from Eq. (*1a*). 1 111°C, 2 131°C, 3 150°C.

of the squared differences between the calculated and the measured reaction rates[15]. This criterion was not satisfied with models of types 2 and 3, and all models with molecularity 3/2 (type 8 for $n = 1$, types 9 and 10). It was only at 111°C that the models of type 5 satisfied this criterion. Of the equations corresponding to the remaining models, viz. 1, 4, 6, 7 and 8, the eight best ones are given in Table II. It appears that the best-fitting models are those which are based on postulating the adsorption of methanol on two centres (a or $a' = 0.5$).

The best correlating model corresponds to molecularity 1 $(1a)$ with the

$$r = kK_A p_A / [1 + (K_A p_A)^{0.5}]^2 \qquad (1a)$$

TABLE I

The Types of the Rate Equations Employed

Type of equation	Right hand side of the rate equation^a $r = \mathrm{f}(p_A)$	Molecularity of the rate-determining step	Mode of adsorption^b	s^c
1	$kK_A p_A / [1 + (K_A p_A)^a]^s$	1	M1, D	1—4
2	$k[(1 + 8K_A p_A)^{1/2} - 1]^s / 4(4K_A p_A)^{s-1}$	1	M2	2,3
3	$kK_A p_A^2 / [1 + K_A p_A^2]^s$	2	2M	1,2
4	$kK_A p_A^2 / [1 + (K_A p_A)^a]^s$	2^d	M1, D	1—4
5	$kK_A^{1/2} p_A^2 [(1 + 8K_A p_A)^{1/2} - 1]^s / (4K_A p_A)^s$	2^d	M2	2,4
6	$kK_A K_A' p_A^2 / \{[1 + (K_A p_A)^a]^{1/a}[1 + (K_A' p_A)^{a'}]^{1/a'}\}$	2^e	M1, D	—
7	$k\{[(1 + 8K_A p_A)^{1/2} - 1]/16K_A p_A\} \cdot \{K_A' p_A / [1 + (K_A' p_A)^{a'}]^{1/a'}\}$	2^e	M2; M1, D	—
8	$k(K_A p_A)^{1/2} p_A^n / [1 + (K_A p_A)^{1/2}]^s$	$1/2 (n = 0)$ $3/2 (n = 1)^f$	D D	1,2 1,2
9	$k\{(K_A p_A)^{1/2} / [1 + (K_A p_A)^{1/2}]\} \cdot \{K_A' p_A / [1 + K_A' p_A]\}$	$3/2^e$	D; M1	—
10	$k\{(K_A p_A)^{1/2} / [1 + (K_A p_A)^{1/2}]\} \cdot \{[(1 + 8K_A' p_A)^{1/2} - 1]^2 / 16K_A' p_A\}$	$3/2^e$	D; M2	—

^{a} Symbols: k the rate constant. K_A the adsorption coefficient of methanol, p_A the initial partial pressure of methanol. In the cases where the second molecule of methanol adsorbs on other sites of the surface the symbols have the superscript'. ^{b} D designates the adsorption on two centres with dissociation of the molecule ($a = 0.5$), M1 the adsorption without dissociation on one centre ($a = 1$) M2 the adsorption without dissociation on two centres[13], 2M the adsorption of two molecules on one active centre. ^{c} Exponent in the rate equations expressing the number of centres assumed to participate in the rate-determining step. If the value of s exceeds the number of the adsorbed particles even free active centres participate in the rate-determining step. ^{d} The second molecule of methanol may react from the gaseous phase. ^{e} The second molecule of methanol is adsorbed on other sites of the surface. ^{f} The second molecule of methanol reacts from the gaseous phase.

TABLE II
Survey of the Best-Fitting Rate Equations

Order of suitability	Type of equation (Table I)	Values of exponents	Molecularity	Orders of suitability at temperatures °C			Average order
				111	131	150	
1	_1_	$a = 0.5$; $s = 2$	1	3	1	1	1.67
2	_6_	$a = 0.5$; $a' = 1$	2	4	2	3	3.00
3	_8_	$n = 0$; $s = 1$	1/2	1	3	7^a	3.67
4	_1_	$a = 0.5$; $s = 3$	1	6	5	2	4.33
5	_8_	$n = 0$; $s = 2$	1/2	2	4	8^a	4.67
6	_7_	$a' = 0.5$	2	5	7	4	5.33
7	_4_	$a = 0.5$; $s = 3$	2	8	6	5	6.33
8	_4_	$a = 0.5$; $s = 4$	2	7	8	6	7.00

^{a} The sum of the squared deviations exceeded the critical value[15].

following constants: 111°C: k [mol h^{-1} kg^{-1}] = 7.0, K_A [atm^{-1}] = 9.0; 131°C: $k = 28.2$, $K_A = 1.3$, 150°C: $k = 198$, $K_A = 0.22$. The courses of the functions $r = f(p_A)$ calculated from this equation are plotted in Fig. 1. The next model corresponding to molecularity 1 is the fourth one. The models of molecularity 1/2, corresponding to the kinetic equation found by Knözinger[5,8] for the dehydration of methanol on alumina and by Trambouze and coworkers[6,7] for the dehydration of methanol on alumosilicate, very well agreed with experiment at lower temperatures (at 111°C these models are the best ones), but at 150°C they were not consistent with the criterion of the critical value of the sum of the squared deviations. Of the models with molecularity 2 the better fitting were those which postulated two kinds of centres on the catalyst surface for the adsorption of methanol (types _6_ and _7_), but they had three constants. The equations of type _4_ were on the border of the reliability region at all temperatures.

The best-fitting equation type, _1_, is identical with that determined by us previously[3] for the dehydration of tert-butanol on the same ion-exchanger catalyst. This fact suggests that the dehydration of tert-butanol to olefin and the dehydration of methanol to ether have similar rate-controlling steps. Although there are not yet enough data for creating some definite idea on the nature of this step it is possible that it is the formation of a polar species similar to a carbonium ion, formed from a molecule of alcohol adsorbed on two active centres; the rate constant of dehydration of tert-butanol[3] is nearly three orders of magnitude higher than the rate constant of dehydration of a primary alcohol (methanol).

From the rate constants and the adsorption coefficients of methanol, determined for equation (_1a_), we calculated the parameters of the Arrhenius and the van't Hoff equa-

tions. The value of the activation energy (27·3 kcal/mol) is not very different from those determined by Knözinger, with alumina, for some other primary alcohols[16] (25·1—25·5 kcal/mol) and for methanol[5] (25·9 kcal/mol), or by other authors for methanol on alumosilicate[7] (23·6 kcal/mol) or sulphonated ion exchanger Dowex 50 X-8 (~24·5 kcal/mol)[9]. The last value, however, is merely an apparent activation energy, calculated from the temperature dependence of the reaction rate, and the ion exchanger employed, like that used in a kinetic study[10] and unlike ours, was non-porous and cross-linked.

The value of the pre-exponential factor in our study was $k^0 = 2·14 . 10^{16}$ [mol . $. h^{-1} kg^{-1}$]. Provided that the activated complex, like the adsorbed molecules, forms an immobile layer without translation degrees of freedom[7,17], the value of the pre-exponential factor allows us to evaluate the number of active centres per mass unit of the catalyst. If the change in entropy associated with transition of the adsorbed molecules to the activated state is negligible the preexponential factor is given by the expression k^0 [mol $s^{-1} kg^{-1}$] $= (kT/h) L$, where L is the concentration of active centres in mol/kg. From this relation the value of L for our catalyst was calculated as 0·7 mol/kg, i.e. $4·3 . 10^{20}$ active centers per gram of the catalyst. By its order of magnitude this value very well accords with the number of acidic centres of this catalyst determined by titration with a hydroxide[3] or by adsorption of gaseous ammonia[18] (~$14 . 10^{20}$) and can be regarded as confirmation of the physical meaning of the rate constant, determined by this kinetic analysis. For the sake of comparison we give the number of centres determined in a similar way from the kinetic data of the dehydration of methanol on alumosilicate[7] ($2 . 10^{14}$ centres/g) or calculated[7] from Knözinger's data for alumina (~$1 . 10^{16}$). It is natural that these numbers of active centres are lower since far from all of the acidic centres of these catalysts are so acid as sulpho groups, i.e. acid enough to induce the reaction of a primary alcohol. In the dehydration of tert-butanol on the same alumosilicate Trambouze and coworkers[7] determined a value of $1·3 . 10^{19}$ centres/g.

The rather high adsorption enthalpy (−30·5 kcal/mol) indicates a chemical nature of the adsorption of methanol on the acid ion exchanger catalyst and is very close to the value found with alumosilicate[7] (−29·4 kcal/mol). The value of the adsorption entropy ($\Delta S_a^0 = -75$ e.u.) complies with the first and the third Boudart rules[19] concerning the physical meaning of the adsorption parameters in the Langmuir–Hinshelwood equations (it is negative and its absolute value is higher than 10 e.u.), but it is too high in respect to the second and the fourth Boudart rules, even though the latter is only an empirical one. According to the second rule the value of ΔS_a^0 should not exceed the value of the standard entropy of the gaseous substance, which we estimated, for 131°C, by extrapolating the tabulated values[20] at approximately 61 e.u. It must be considered, however, that the adsorption of methanol on two centres probably brings about a steric reorientation of the sulpho groups on the exchanger. If so, it is further probable that the loss of the corresponding degrees of freedom of these groups, associated with the adsorption, raises the value of ad-

sorption entropy to above that which would correspond to the loss of the degrees of freedom of the gaseous substance. Besides, Glasstone, Laidler and Eyring[17] have derived by a theoretical calculation that the formation of an immobile layer by adsorption of a gas on a solid is associated with an entropy change of about 110 e.u., which value, though derived for a differently defined standard state (mol/ml), is still too high also.

REFERENCES

1. Setínek K., Beránek L.: J. Catal. *17*, 306 (1970).
2. Zanderighi L., Setínek K., Beránek L.: This Journal *35*, 2367 (1970).
3. Jeřábek K., Bažant V., Beránek L., Setínek K.: Presented at 5th International Congress on Catalysis, W. Palm Beach, Florida, U.S.A. 1972.
4. Balacéanu J. C., Jungers J. C.: Bull. Soc. Chim. Belges *60*, 476 (1951).
5. Kalló D., Knözinger H.: Chem. Ing.-Tech. *39*, 676 (1967).
6. Figueras F., Nohl A., de Mourges L., Trambouze Y.: Trans. Faraday Soc. *67*, 1155 (1971).
7. Nohl A., Pralus C., Serban G., Figueras F., de Mourges L., Trambouze Y.: J. Chim. Phys. *66*, 2001 (1969).
8. Knözinger H.: Angew. Chem. *80*, 778 (1968).
9. Gates B. C., Johanson L. N.: J. Catal. *14*, 69 (1969).
10. Gates B. C., Johanson L. N.: A.I.CH.E. J. *17*, 981 (1971).
11. Komers R., Tomanová D.: Chem. průmysl *21*, 559 (1971).
12. Šimoník J., Beránek L.: This Journal *37*, 353 (1972).
13. Davidová N., Penčev V., Beránek L.: This Journal *33*, 1229 (1968).
14. Knözinger E.: *Thesis*. University of Munich, 1966.
15. Hančil V., Mitschka P., Beránek L.: J. Catal. *13*, 435 (1969).
16. Knözinger H., Bühl H., Ress E.: J. Catal. *12*, 121 (1968).
17. Glasstone S., Laidler K. J., Eyring H.: *The Theory of Rate Processes*, p. 339. McGraw-Hill, New York and London 1941.
18. Komers R.: Unpublished results.
19. Boudart M., Mears D. E., Vannice M. A.: Ind. Chim. Belge *32*, (Special No, Vol I) 281 (1967).
20. Rossini F. D.: *Selected Values of Chemical Thermodynamic Properties*. V. S. Natl. Bur. Standards, Circular 500, Washington D. C. 1952.

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