

**DEHYDROGENATION OF SUBSTITUTED ALCOHOLS TO ALDEHYDES
ON ZINC OXIDE–CHROMIUM OXIDE CATALYSTS**

Daniela GULKOVÁ and Miloš KRAUS

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchbát*

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Sixteen primary alcohols of the structure RCH_2OH ($R = CH_3, C_2H_5, (CH_3)_2CH, (CH_3)_3CCH_2, HOCH_2, CH_3OCH_2, C_6H_5, C_6H_5CH_2, C_6H_5OCH_2, ClCH_2, BrCH_2, F_3C, CNCH_2, (CH_3)_2NCH_2, (C_2H_5)_2NCH_2$ and tetrahydrofurfuryl) were explored for the possibility of obtaining the corresponding aldehydes by dehydrogenation on solid catalysts. Various catalysts were tested and two zinc oxide–chromium oxide catalysts were selected for further work because their activity and selectivity was satisfactory; moreover, the selectivity could be improved by addition of sodium into the catalysts and of water into the feed. The reaction was performed in the temperature range 250 – 450 °C and at atmospheric pressure. 2-Chloroethanol, 2-bromoethanol, ethylene glycol, 2-cyanoethanol and 2-(*N,N*-diethylamino)ethanol decomposed and deactivated the catalyst. The other alcohols were studied from the point of kinetics of dehydrogenation, which was described by a Langmuir–Hinshelwood type rate equation (3), and of substituent effects on rate, which were correlated by Taft equation (1) with the slope $\rho^* = -1.46$. The preparative value of catalytic dehydrogenation for obtaining substituted aldehydes was confirmed by prolonged runs and isolation of the aldehydic product by distillation using as the feeds 2-methoxyethanol and 2-(*N,N*-dimethylamino)ethanol, respectively.

Catalytic dehydrogenation of primary or secondary alcohols to aldehydes or ketones, respectively, is the basis of some industrial processes for production of simple carbonyl compounds like acetaldehyde, acetone, 2-butanone and some others. However, the dehydrogenation is not used in case of substituted alcohols, i.e. the compounds containing beside the hydroxyl group also some other substituents. Oxidation by reagents like chromic acid is preferred but it brings the problem of disposal of the inorganic products from spent oxidant. For the production of some speciality chemicals, substituted aldehydes and ketones are needed as intermediates in increased amounts and, therefore, it is of interest to explore the catalytic dehydrogenation of substituted alcohols as a process which can be easily scaled-up and which is better acceptable from the point of ecology. The primary problem is how a substituent will withstand the contact with a solid catalyst and the next question is how a substituent will influence the rate of alcohol dehydrogenation. Until now, no systematic study on this subject has been published.

The effect of alkyl chain structure on the rate of dehydrogenation of 1- and 2-alkanol RCH_2OH and $RCH(OH)CH_3$ has got some attention¹⁻⁸. Quantitative correlations of structure effects on rate by the Taft equation⁹

$$\log k_{rel} = \rho^* \sigma^* \quad (1)$$

have been published⁴⁻⁸ (k_{rel} is rate constant relative to the value for $R = H$ or CH_3 , respectively, σ^* is a parameter characterizing the substituent R and ρ^* is the reaction parameter which value is specific for the interaction between the reaction centre of a given series of alcohols and the active centre of the used catalyst). The range of σ^* values for alkyl groups is relatively small (0.3) and therefore the correlations are not convincingly proven. Substituents containing hetero atoms (halogens, N, O) which span a broader range of σ^* values (more than 2) would give better evidence on the direction of electronic influence.

Catalytic activity for dehydrogenation of alcohols is found with a number of oxides and metals. The most active and selective are copper, zinc oxide, chromium oxide and mixtures $ZnO-Cr_2O_3$, which have been studied also in this Laboratory^{6,7,10}. In the present work, we have used the catalysts prepared by coprecipitation of zinc and chromium hydroxides and by subsequent calcination of the mixture into oxidic form. Some preparation variables were a part of the study but its main goal was the influence of substituents, containing hetero atoms, on the feasibility of preparation of substituted aldehydes by catalytic dehydrogenation of primary substituted alcohols.

EXPERIMENTAL

Materials

All alcohols used as reactants have been distilled over a 30 cm column with wire spirals and kept over calcined molecular sieve 3A. Their purity has been checked by gas chromatography. Their origin and boiling points were as follows: ethanol (České lihovary, Prague, 99.9%), b.p. 78 °C; 1-propanol (Lachema, Brno), b.p. 97 °C; 2-methyl-1-propanol (Fluka, Buchs), b.p. 108 °C; 3,3-dimethyl-1-butanol (Fluka, Buchs), b.p. 143 °C; 2-phenylethanol (Ventron, Karlsruhe), b.p. 219 °C; 2-methoxyethanol (Milton Industrial Estate), b.p. 125 °C; 2-phenoxyethanol (Lachema, Brno), b.p. 245 °C; 2,2,2-trifluoroethanol (Fluka, Buchs), b.p. 74 °C; tetrahydrofurfuryl alcohol (Lachema, Brno), b.p. 174 °C; 2-chloroethanol (Lachema, Brno), b.p. 132 °C; 2-bromoethanol (Lachema, Brno), b.p. 150 °C; 2-cyanoethanol (Lachema, Brno), b.p. 221 °C; ethylene glycol (Lachema, Brno), b.p. 197 °C; 2-(N,N-diethylamino)ethanol (Lachema, Brno), b.p. 161 °C. 2-(N,N-Dimethylamino)ethanol was prepared according to ref.¹¹ with some modifications: Toluene (300 ml) and 50 ml of ethanol was cooled to -10 °C and mixed with chilled dimethylamine (90 g). The mixture was stirred and cooled to 0 °C while 2-chloroethanol (180 g) was added dropwise during 4 h. After standing overnight, the product was mixed with a solution of 85 g NaOH in 350 ml water. The lower layer was saturated with K_2CO_3 and the organic layer was distilled over a column; b.p. 134 °C. 1-Methoxy-2-propanol was prepared from 1,2-epoxypropane and sodium methoxide according to ref.¹².

Catalysts

The catalysts were both commercial samples and laboratory preparations. The industrial catalysts were: G 13 (Girdler-Südchemie, München), 42% CuO, 26% Cr₂O₃; G 66B (Girdler-Südchemie, München), 32% CuO, 62% ZnO; R 3-11 (BASF, Ludwigshafen), 30% Cu and promoters on unspecified carrier; Cu/kieselguhr (Synthesia, Pardubice), 52% Cu after reduction; Cu/silica (Naflochim, Bourgas); ZnO-Cr₂O₃ (methanol catalyst from Leuna-Werke, Leuna), 61% ZnO, 21% Cr₂O₃, surface area (BET) 41 m² g⁻¹, pore volume 0.43 cm³ g⁻¹.

The kinetic measurements were performed with the ZnO-Cr₂O₃ catalyst prepared in the following way: To a solution containing 245 g Cr(NO₃)₃ · 9 H₂O and 105 g Zn(NO₃)₂ · 6 H₂O in 3 l water a solution of 45 g NH₃ in 650 ml water added gradually under vigorous stirring. The precipitate was washed four times by decantation using 3 l distilled water each time, then filtered off by suction and washed with further 2 l of water. The solid was dried for 6 h at 120 °C and calcined in a stream of nitrogen at 550 °C for 3 h. The product was crushed to smaller particles and different fractions were sieved out. Every fraction was separately mixed with a 1% solution of NaOH into a thin slurry, filtered off and dried at 100 °C. The catalysts contained 30.4% Zn, 38.4% Cr and 1.0% Na, its surface area (BET) was 40 m² g⁻¹ and a pore volume 0.93 cm³ g⁻¹.

Apparatus and Procedure

A standard glass flow reactor containing for kinetic runs 0.05 to 1 g and for preparative experiments about 10 to 50 g of the catalysts was used. The alcohols were fed from a syringe driven by an electric motor with variable speed, the gases were taken from pressure flasks. Traces of oxygen were removed from nitrogen by absorption into a reduced manganese oxide-magnesium oxide-chromium oxide mixture, from hydrogen by reaction on a palladium deoxo catalyst. Both gases were dried by molecular sieve 5A. The temperature of the catalyst was measured inside a thermocouple well in the middle of the bed and it was controlled automatically using a resistance thermometer placed outside of the reactor. The liquid products were separated by cooling the reactor effluent to -78 °C and analyzed gas-chromatographically. The ratio of unreacted alcohol to formed aldehyde was determined from peak areas given by a FID sensor. It has been found for five alcohol-aldehyde pairs that the factor converting the ratio of peak areas to molar ratio is always 1.33 and this value was used for all reaction products.

For activity, selectivity and kinetic measurements, the catalyst sample (grain size 0.16 - 0.40 mm) was mixed with equal volume of glass beads and layers of the beads were placed in front of and behind the catalyst bed. The catalyst was activated by heating at 400 °C for 2 h in a stream of hydrogen (3 l h⁻¹). Hydrogen stream was replaced by nitrogen, the temperature was lowered to the desired level (in case of kinetic measurements to 360 °C), feeding of alcohol was started and nitrogen flow was adjusted to the value needed for obtaining the required partial pressure of the alcohol (0.020 - 0.095 MPa). The feed rate of the alcohol was 0.04 - 0.81 mol h⁻¹. The overall pressure was atmospheric (0.10 MPa). When the repeated analyses of the product indicated attainment of the steady-state conversion, two successive samples were analyzed three times and from all six conversion values an average was calculated which was used for evaluation of kinetics. For every partial pressure, a fresh catalyst sample was used and measurements at standard conditions preceded and closed the kinetic runs, in order to check catalyst activity.

For treatment of data, a graph of conversion of the alcohol x_A vs reciprocal space velocity W/F_A^0 (where W is a catalyst weight, F_A^0 alcohol feed rate) was plotted. From the linear dependence at the origin, which usually included four points, the initial reaction rate r_A^0 was calculated as an average of the ratio $r_A^0 = x_A / (W/F_A^0)$ in mol h⁻¹ kg_{cat}⁻¹. Prior to kinetic measurements, experiments with different grain size of the catalyst and 1-propanol as the feed confirmed that with the fraction 0.16 - 0.40 mm pore diffusion does not affect the rate. Similarly, experiments with variable feed rate and catalyst weight but at constant W/F_A^0 ratio showed the absence of retardation by external diffusion.

The error of kinetic measurements was estimated by repeated experiments with 1-propanol and the laboratory ZnO–Cr₂O₃ catalyst to be 4.2% of the r_A^0 values. The temperature was kept constant within ± 0.5 K.

RESULTS AND DISCUSSION

Catalyst Selection

Dehydrogenation of alcohols to aldehydes or ketones is a reversible reaction which equilibrium is strongly temperature dependent. Thermodynamic calculations show relatively small influence of alcohol structure (within the series of primary and secondary alcohols, respectively) on equilibrium conversion and it can be stated that, in general, under 250 °C and at atmospheric pressure, the attainable conversion of an alcohol into the corresponding carbonyl compound is small and for almost total conversion, temperatures over 500 °C are needed. However, high reaction temperature has several drawbacks. First, side reactions, especially cracking, are more pronounced and some side products block and deactivate the catalysts. The extent of this may be higher with substituted alcohols. Second, copper, which is an excellent catalyst for alcohol dehydrogenation, sinters and loses activity at temperatures over 320 °C (cf. ref.¹⁰). Third, the dehydration of alcohols to olefins and water accompanies often the dehydrogenation (cf. ref.⁸) and because its activation energy is usually higher, its participation increase with temperature.

Thus, for dehydrogenation of substituted alcohols in good yields in a single pass, a catalyst is needed which would allow to work at about 400 °C and higher, with low or suppressed dehydration activity and good thermal stability.

Figures 1a – 1d demonstrate the effect of reaction temperature on the activity and selectivity (selectivity defined as molar ratio of produced aldehyde to converted alcohol) in the reaction of 1-methoxy-2-propanol over various catalysts. As can be expected, in all cases the over-all conversion increases and the selectivity decreases with increasing temperature. In general, the selectivity was unsatisfactory at reasonable conversion and therefore, we have looked for ways of improving it.

The first attempt concerned thermal treatment of the ZnO–Cr₂O₃ catalyst. The precursor of the laboratory catalyst was calcined at 500, 550 and 600 °C, respectively, and tested at 390 °C, with partial pressure of 1-methoxy-2-propanol in the feed (the rest being nitrogen) $p_A^0 = 0.08$ MPa, space time $W/F_A^0 = 100$ g h mol⁻¹. The conversion was in all these cases 96 – 98% but the selectivity increased with the calcination temperature, being 10, 42 and 43%, respectively.

Next step was to increase the selectivity of ketone formation by chemical modification of the catalyst. It is known (e.g. ref.⁶) that addition of alkali to oxide catalysts suppresses the dehydration activity. Both the commercial and laboratory ZnO–Cr₂O₃ catalysts, impregnated with 1 wt.% of Na⁺ (see Experimental) showed almost unchanged dehydrogenation activity and decreased dehydration activity. At conditions

given in the preceding paragraph, the conversion with the alkalinized laboratory sample calcined at 500, 550 and 600 °C, respectively, was around 95% and the selectivity was 52, 70 and 50%, respectively. Also the selectivity of the commercial sample calcined at 550 °C increased from 50 to 76% as the result of sodium addition.

On the basis of these findings, the laboratory ZnO-Cr₂O₃ catalyst, calcined at 550 °C and with 1 wt.% of Na⁺ added was selected for kinetic and structure effects studies. It

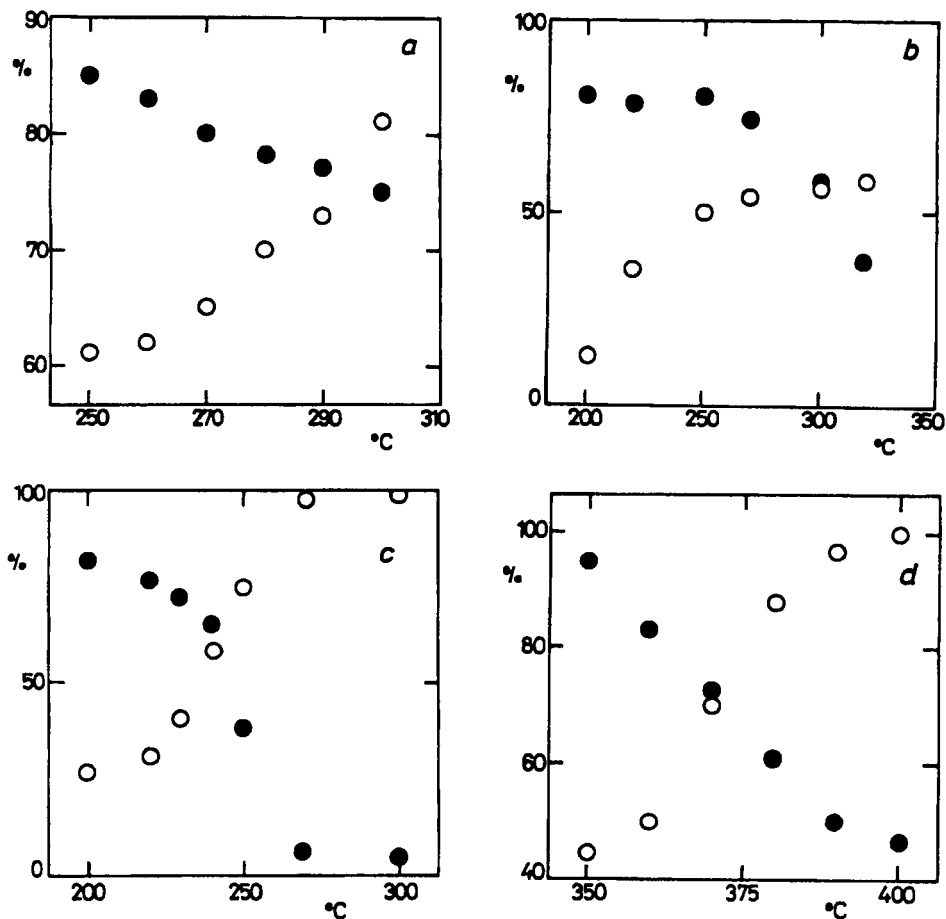


FIG. 1

Influence of reaction temperature on over-all conversion (O) and on selectivity (●) of dehydrogenation of 1-methoxy-2-propanol to 1-methoxy-2-propanone. Partial pressure of the alcohol in the feed $p_A^0 = 80$ kPa, space time $W/F_A^0 = 100$ h g mol⁻¹. a Cu/kieselguhr, b G 13, c G 66B, d commercial ZnO-Cr₂O₃ catalyst

showed a steady activity with time; after conversion decrease in the first hour on stream, its activity remained constant for many hours (Fig. 2).

Preliminary measurements included also pretreatment of the catalyst in nitrogen or hydrogen streams at different temperatures. However, it was found that in all cases the same activity was obtained, only the time of reaching it was different. Figure 3 gives some examples; it follows from these data that formation of the active surface, very probably by reduction either by hydrogen or the reaction mixture, is necessary.

Selection of Reactants

First experiments with 1-methoxy-2-propanol have indicated the possibility to obtain the corresponding carbonyl compound, 1-methoxy-2-propanone, by dehydrogenation on a solid catalyst. The next step was to prove the same for transformation of substituted primary alcohols to aldehydes. A broad experimental survey showed which substituents can resist the action of the $\text{ZnO-Cr}_2\text{O}_3$ catalyst. The tests with a series of substituted ethanols excluded several compounds which can easily form vinyl derivatives by splitting off hydrogen chloride or bromide (2-chloroethanol or 2-bromoethanol) or water (ethylene glycol or 2-cyanoethanol). With these reactants, the liquid

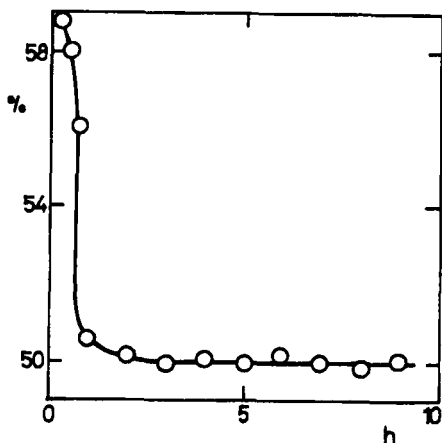


FIG. 2

Change of conversion with time-on-stream in the dehydrogenation of 1-methoxy-2-propanol at 360 °C, $p_A^0 = 60$ kPa, $W/F_A^0 = 100$ h g mol⁻¹ on laboratory $\text{ZnO-Cr}_2\text{O}_3$ catalyst

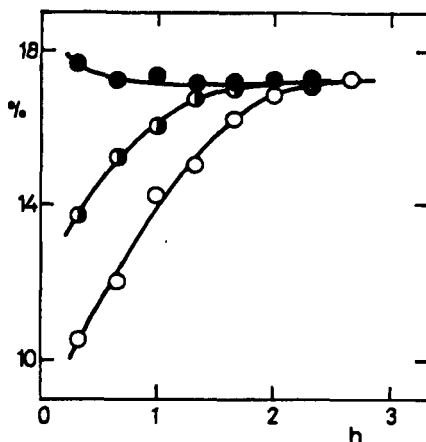


FIG. 3

Influence of activation on the activity of commercial $\text{ZnO-Cr}_2\text{O}_3$ catalyst in the dehydrogenation of 1-propanol at 350 °C, $p_A^0 = 50$ kPa, $W/F_A^0 = 100$ h g mol⁻¹. ○ Nitrogen, 2 h at 350 °C; ◐ hydrogen, 2 h at 350 °C; ● hydrogen, 2 h at 400 °C

products were dark and contained no aldehyde; the catalyst was deactivated rapidly. Similar rapid decay of the catalyst was observed with 2-(N,N-diethylamino)ethanol.

As suitable for further study appeared primary and secondary alcohols with fluoro, methoxy, phenoxy, phenyl and N,N-dimethylamino groups and also tetrahydrofurfuryl alcohol. Four aliphatic primary alcohols (ethanol, 1-propanol, 2-methyl-1-propanol and 3,3-dimethyl-1-butanol) were included into the kinetic study in order to connect the present work with published⁴⁻⁸ correlations of structure effects on rate in which only unsubstituted alkanols were used. Also benzyl alcohol reacted readily giving benzaldehyde but, as this aldehyde is easier to obtain than the alcohol, this reaction was not followed further.

Beside 1-methoxy-2-propanol some other secondary alcohols have been studied and the result will be treated in subsequent paper¹³.

Kinetics

The measurements of alcohols dehydrogenation at 360 °C and at different partial pressure of the reactant in the feed and flow velocity yielded dependences of initial reactions rate r_A^0 on initial partial pressure p_A^0 (for treatment of conversion data see Experimental) in the range $p_A^0 < 0.02 - 0.10 >$ MPa and r_A^0 up to 600 mol h⁻¹ kg_{cat}⁻¹. This dependences have been used for finding a suitable rate equation which was selected by Marquardt's non-linear optimization procedure from a series of expressions of the type

$$r_A^0 = \frac{k_1 (p_A^0)^a}{[1 + k_2 (p_A^0)^b]^c} \quad (2) - (13)$$

The values of exponents a , b and c are given in Table I. Equation (2) has adjustable exponent α , i.e. it corresponds to the power-law rate equation; the others are Langmuir-Hinshelwood type. The data sets consisted of 17 pairs $r_A^0 - p_A^0$ for 1-propanol,

TABLE I
Exponents of the rate equations (2) - (13)

Eq.	a	b	c	Eq.	a	b	c
(2)	α	0	0	(8)	1	0.5	3
(3)	1	1	1	(9)	0.5	1	1
(4)	1	1	2	(10)	0.5	1	2
(5)	1	1	3	(11)	0.5	1	3
(6)	1	0.5	1	(12)	2	1	2
(7)	1	0.5	2	(13)	2	1	3

9 for the remaining alcohols. The sum of squared deviations of experimental and calculated values Q_{\min} was used as the criterion of fit. Their testing according to Beale¹⁴ on 95% probability level allowed to discriminate several best fitting equations. Equation (3) was among them for all alcohols, on first or second place, and therefore, the comparison of alcohol reactivity is based on it. Two examples of the fit of calculated $r_A^0-p_A^0$ dependences and experimental data are presented in Fig. 4.

In case of 1-propanol, the measurements of initial reaction rates were supplemented by estimation of the influence of the product (propanal) on rate. Five 1-propanol-propanal feeds containing 1.5, 3.0, 6.0, 12.0 and 15.0 mole % of the aldehyde, respectively, were used for measurements of initial reaction rates at different partial pressures of 1-propanol in the feed. The retardation of dehydrogenation was appreciable. On the contrary, the presence of hydrogen in the feed had no effect on rate. The treatment of data on propanal influence allowed to find best-fitting complete rate equation

$$r = \frac{k K_A p_A}{1 + K_A p_A + K_R p_R} \quad (14)$$

when in Eq. (3) $k = k_1/k_2$, $K_A = k_2$ is substituted in the Langmuir-Hinshelwood sense and the term for propanal competitive adsorption $K_R p_R$ is added. The meaning of k is rate constant of the surface reaction, K_A and K_R denote adsorption coefficients of 1-propanol and propanal, respectively.

The values of rate constants and adsorption coefficients for all alcohols calculated by Eq. (3) are summarized in Table II.

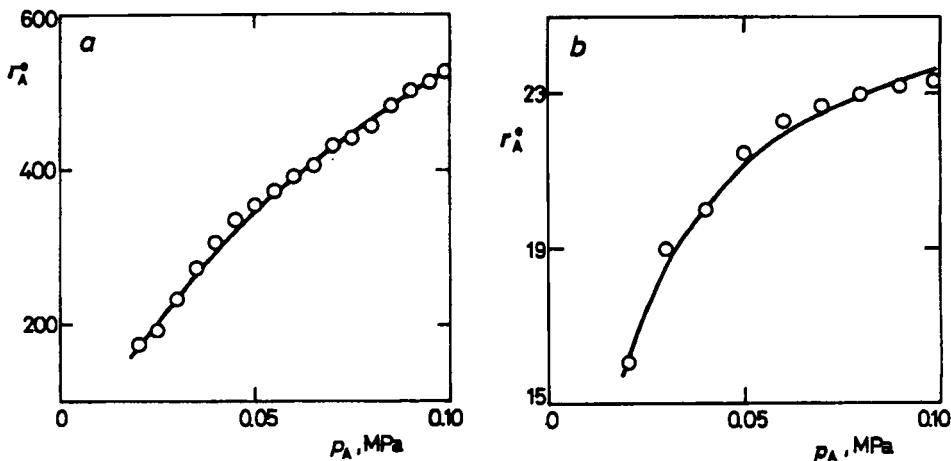


FIG. 4

Examples of the fit of Eq. (3) (curves) to experimental data for 360 °C (points) on the dehydrogenation of a 1-propanol, b 2-phenoxyethanol

Correlation of Alcohol Reactivity

The set of rate constants k in Table II makes it possible to apply linear free energy relationships, specifically the Taft equation (1) or its broader form¹⁵ with added term for steric influence

$$\log k_{rel} = \rho^* \sigma^* + \partial E_S \quad (15)$$

for correlation of structure effects on rate. The least-square treatment of the data using σ^* and E_S values from ref.¹⁶ revealed a fairly good correlation between $\log k_{rel}$ and σ^* for substituents R in RCH_2OH . The correlation coefficient for nine alcohols (no σ^* value for tetrahydrofurfuryl substituent was found in the literature) was 0.924. When the deviating point for 2-phenylethanol was excluded the correlation coefficient increased to 0.992. The omission of the $C_6H_5CH_2$ substituent seems to be justified by observation of appreciable dark deposit which was formed in the vaporizing and preheating sections of the reactor in experiments with 2-phenylethanol.

The attempts to correlate the rate constants with steric constants E_S or the constants $E_S^{\%}$ corrected for hyperconjugation (values from ref.¹⁷) were unsuccessful. The correlation coefficients for the second term in Eq. (15) were low for both sets of steric constants. The plots of $\log K_A$ against σ^* , E_S or $E_S^{\%}$, respectively, gave scatter diagrams.

TABLE II
Values of rate constants k ($\text{mol h}^{-1} \text{kg}_{cat}^{-1}$) and adsorption coefficients K_A calculated by Eq. (3) for ten primary alcohols

Alcohol	k $\text{mol h}^{-1} \text{kg}_{cat}^{-1}$	K_A MPa^{-1}
Ethanol	663	24.4
1-Propanol	1 115	9.1 ^a
2-Methyl-1-propanol	1 589	6.5
3,3-Dimethyl-1-propanol	679	54.6
2-(N,N-Dimethylamino)ethanol	153	5.9
2-Phenylethanol	45	27.6
2-Methoxyethanol	74	3.7
2-Phenoxyethanol	27	77.0
2,2,2-Trifluoroethanol	0.8	21.4
Tetrahydrofurfuryl alcohol	7.9	21.3

^a $K_R = 755 \text{ MPa}^{-1}$ (for propanal).

The slopes of the lines in Fig. 5 ($\rho^* = -1.42$ for the series with 9 points and $\rho^* = -1.46$ for the 8-membered series) indicate a decrease of reactivity with increasing electronegativity of the substituent. This is in agreement with observation of Sun and Wang³ for the dehydrogenation of primary unsubstituted aliphatic alcohols on a chromium oxide-copper oxide catalyst (their data gave $\rho^* = -0.7$, cf. ref.¹⁸). However, this finding contrasts with repeated observation of positive values of ρ^* for dehydrogenation of unsubstituted secondary alcohols, both on metals^{4,5} and oxides⁶⁻⁸.

There is no clear mechanistic meaning for the sign of the ρ^* parameter because its value is a relative quantity based on the influence of substituents on the rate of ester hydrolysis for which Taft⁹ has set by definition $\rho^* = 2.48$. Thus, the difference of the ρ^* values for the dehydrogenation of primary and secondary alcohols, respectively, may be an expression of the extent of electronic influence on reaction centre, but in the same direction, and not of its reversion.

The value of the σ^* constant for tetrahydrofurfuryl group is not available (ref.¹⁶). Using the rate constant of dehydrogenation of tetrahydrofurfuryl alcohol, its value can be estimated from Fig. 5 as 1.2, i.e. near to that for the CH_3OCH_2 substituent as could be expected.

Preparative Experiments

For proving the feasibility of alcohol dehydrogenation for preparation of substituted aldehydes, two alcohols have been studied in detail from this point of view, namely 2-methoxyethanol and 2-(*N,N*-dimethylamino)ethanol. Alkalized commercial $\text{ZnO-Cr}_2\text{O}_3$ catalyst was applied.

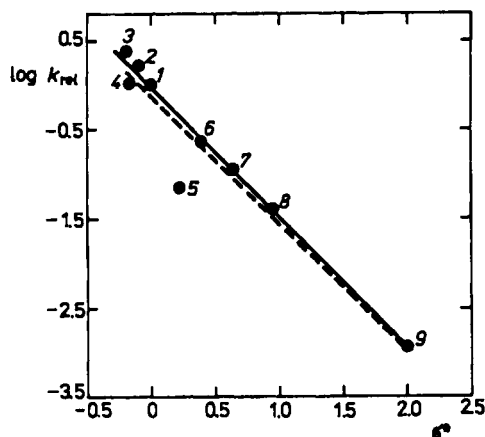


FIG. 5
Correlation of rate constants k for 360 °C in the coordinates of the Taft equation (1). 1 Ethanol, 2 1-propanol, 3 2-methyl-1-propanol, 4 3,3-dimethyl-1-butanol, 5 2-phenylethanol, 6 2-(*N,N*-dimethylamino)ethanol, 7 2-methoxyethanol, 8 2-phenoxyethanol, 9 2,2,2-trifluoroethanol. Full line correlation without 2-phenylethanol (point 5) dotted line correlation including this compound

Preliminary experiments with 2-(N,N-dimethylamino)ethanol in the temperature range 370 – 390 °C, space time 0.025 – 0.226 h kg_{cat} mol⁻¹ have shown that conversion between 40 to 100% can be achieved with selectivity 70 to 10%, decreasing with increasing conversion. A compromise was accepted and following reaction conditions were used: temperature 370 °C, catalyst weight 9 g, space time 0.226 h kg_{cat} mol⁻¹. The reaction was run for 76 h and the liquid product contained according to GLC analysis 54 mole % unreacted alcohol, 31 mole % 2-(N,N-dimethylamino)acetaldehyde, 8.5 mole % acetaldehyde and several unidentified compounds in small amounts. Distillation of it gave 74 g (CH₃)₂NCH₂CHO, b.p. 110 °C, that is 28 mole % yield based on (CH₃)₂NCH₂CH₂OH.

In case of 2-methoxyethanol, the previous experience that water supresses dehydration on oxide catalysts was utilized and the dehydrogenation was made with 20 wt.% of water in the feed. The conversion was affected by its presence only to about 15 rel.%. Preliminary experiments (Fig. 6) indicated the possible range of conversions and selectivities but showed also strong retardation of the reaction by the formed product, in accord with the kinetic study on 1-propanol dehydrogenation. The preparative experiment was run at 390 °C, with catalyst weight 50 g and space time 0.97 h kg_{cat} mol⁻¹. The liquid product collected during 53 h contained according to GLC analysis 20 mole % unreacted 2-methoxyethanol, 45 mole % 2-methoxyacetaldehyde, 16 mole % acetaldehyde and 12 mole % methanol (beside water). Distillation yielded 77 g 2-methoxyacetaldehyde, b.p. 92 °C, that is 38% of theory based on fed alcohol.

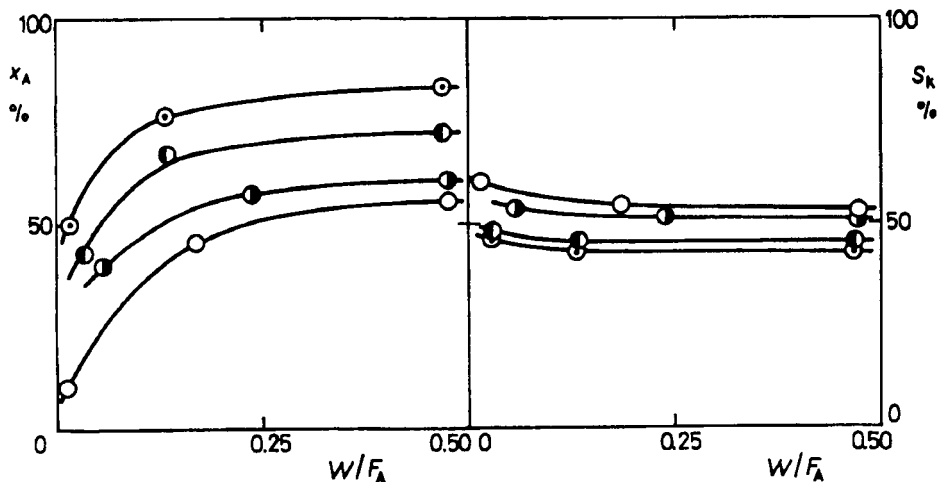


FIG. 6

Dehydrogenation of 2-methoxyethanol on commercial alkylized ZnO–Cr₂O₃ catalyst. Influence of space time W/F_A^0 (in h kg_{cat} mol⁻¹) on conversion x_A and selectivity of aldehyde formation S_k . Temperature, °C: ○ 370, ● 380, ● 390, ⊙ 400

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