KINETIC ANALYSIS OF COUPLED GAS PHASE OXIDATION REACTION OF SECONDARY ALCOHOLS ON IRIDIUM*

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Kinetics of partial gas phase oxidation of 2-butanol (B) and 4-methyl-2-pentanol (M) to ketones on Ir/C catalyst at 150°C has been studied. In single reactions alcohol B was 4—7 times more reactive than alcohol M, in competitive reactions the latter was twice as reactive as the former. Separate treatment of rate data for single and competitive reactions of both alcohols showed that each set could be described by nearly the same set of equations on 99% confidence level, including, of course, very different kinetic models. Confrontation of the kinetics of single and competitive reactions (comparison of the values of corresponding constants of rate equations) and the analysis of relative reactivities revealed the unfitness of Langmuir–Hinshelwood and redox models in this case. A model taking into account nonhomogeneity of the surface and a model derived on the basis of a chain mechanism would be able to describe better and in consistent way the kinetics of single and competitive reactions as well as the observed inversion of the reactivity of studied alcohols.

In treatment of data on heterogeneous catalytic reactions several different kinetic models have been frequently found suitable, which could not be distinguished by using only statistical criteria. Further information about reaction system is therefore necessary in order that the most probable model be defined. One of the possible sources of such an information is the study of elementary processes and unstable intermediates on catalyst surface by modern physical methods. In addition to this molecular approach, the results of which do not have to be always in unambiguous relation to the reaction kinetics, one can also utilize approach which is of phenomenological nature. If one changes in a controlled way some property of the reaction system, even without detailed knowledge of the reaction mechanism one can deduce how, according to the individual models, the system would reflect this change. By comparison of the observed behaviour with that predicted, the validity of the model investigated can be either supported or rejected.

On studying catalytic reactions by this way, variation in the structure of reactants or in reaction temperature have been most frequently utilized. Controlled changes of catalyst properties were used *e.g.* in the analysis of kinetic models of some reactions catalysed by organic ion exchangers[1]. Another possibility is to change the number of reactants and reactions in the system, *i.e.* to study mutual influencing of reactions on going from single reactions to a coupled system. When studying some consecutive and parallel reactions in the gas phase[2] (for example hydrogenation, transesterification or decarboxylation reactions) we hav found that their kinetics can be described by Langmuir–Hinshelwood model with very similar values of the constants found independently by the analysis of single and coupled reactions.

Type of the reactions that has so far been little investigated from this point of view are heterogeneous catalytic oxidation reactions. On the other hand, these are the reactions for which most different kinetic models can be found in literature. Besides the equations of Langmuir–Hinshelwood type, data could be frequently described by equations of redox type[3] and also equations based on the assumption of nonhomogeneity of the catalyst surface were used[4]. In this work we intended to verify whether the study of a coupled system, especially competitive reactions, yields information needed for the more detailed analysis of the suitability of individual kinetic models. In competitive system there exists mutual influencing of reactions and the correct model should be able to describe this influencing, *i.e.* it ought to fit kinetic data for both single and competitive reactions without being necessary to readjust the parameters for the competitive system.

For this study we have chosen partial oxidation of secondary alcohols to ketones (equation (A)).

$$R\text{---}CH_2\text{---}CH(OH)\text{---}CH_3 + 0.5\,O_2 \;\rightarrow\; R\text{---}CH_2\text{--}CO\text{---}CH_3 + H_2O \tag{A}$$
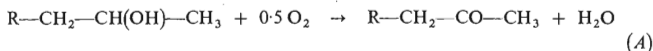
This reaction is irreversible and its kinetics has been described in literature using the above mentioned types of kinetic models (*cf.* review in ref.[5]). A suitable pair for competitive experiments proved to be 2-butanol ($R = CH_3$) and 4-methyl-2-pentanol ($R = (CH_3)_2CH$); the reaction was catalysed selectively by iridium on active charcoal[6] at 150°C.

EXPERIMENTAL

Compounds

2-Butanol, analar grade (Reanal, Budapest) was dried over anhydrous magnesium sulphate, shaken with active charcoal and rectified (b.p. 99—99.5°C). 4-Methyl-2-pentanol was partially commercial product (purum, Fluka AG, Buchs SG) and partially the substance was prepared by Grignard synthesis from isobutyl bromide and acetaldehyde using the procedure reported for preparing 4-methyl-2-butanol[7]. The product so obtained was rectified. Both samples were combined, dried and purified (b.p. 130.5°C), similarly as 2-butanol. According to gas chromatographic analysis, the product contained 0.2% of the starting ketone as the only admixture.

Catalyst (0.5% iridium on active charcoal). Granulated (0.25—0.5 mm) active charcoal (Chema, Prague-Chvaly) was boiled in concentrated HCl, washed, boiled in distilled water and dried at 150°C. Then it was impregnated with ammonium hexachloroiridate solution while stirring

(1·15 g per 100 g of charcoal), after 2 h it was separated by filtration with suction and dried at 145°C. The catalyst was reduced at 200°C for 2 h in a stream of electrolytic hydrogen (Technoplyn, Prague), cooled to 50°C, hydrogen was replaced by nitrogen and finally the catalyst was shortly flushed with air at ambient temperature.

Apparatus

Measurements were carried out at atmospheric pressure. Basic features of the glass flow apparatus used were reported earlier[8,9]. Air was taken from central pressure distribution and was purified by a cellulose cotton wool filter, nitrogen (for lamps, Technoplyn, Prague) was taken from pressure cylinder. The gases were dried and freed from CO_2 by solid potassium hydroxide. Liquid reactants were fed by a linear feeding device to an evaporator where their vapours were mixed with air or with its mixture with nitrogen. Vapour mixture then passed through a layer of the catalyst (0·02—0·20 g) which was diluted by threefold volume of glass balls. The catalyst was placed in a U-shaped reactor made from a glass tube (i.d. 10 mm) and a thermocouple well (e.d. 5 mm) reached to its layer. The reactor was heated by a thermostatted electric oven with forced air circulation, the temperature within the catalyst bed was kept at $150 \pm 0.5°C$.

Analysis

Gaseous reaction products were introduced periodically *via* a sampling valve to a gas chromatograph equipped with a flame ionisation detector and an integrator. The column with i.d. 4 mm was 1 m long, nitrogen was used as a carrier gas. In the case of single reactions (separation of alcohol from the ketone formed) the column was packed with 15% diglycerol on Celite (oven temperature 102°C), in the case of competitive reactions (separation of 2-butanol, 4-methyl-2-pentanol and corresponding ketones) we used 8% diglycerol +7% Carbowax 1000 on Chromosorb W at 96°C. Conversions were determined from the ratios of integral chromatographic peaks of ketone and alcohol with the use of previously made calibrations. For further treatment we took the mean values of 4—6 determinations of conversion carried out successively after steady state conditions had been established in the reactor.

Kinetic Measurements and Treatment of Data

It was first verified that under the conditions used the uncatalysed oxidation did not take place and that the rate of catalytic reaction was not affected by external or internal diffusion. Some differences in the steady state activity of fresh catalyst sample and a decrease in the catalyst activity with time (approximately 10% rel. after 8 h) have been observed. These changes were corrected by carrying out periodically reference experiments and by relating the experimental reaction rate to the chosen standard activity of the catalyst. It was also checked that changes in the catalyst activity do not influence the relative reactivities of 2-butanol and 4-methyl-2--pentanol.

Kinetics measurements were made at alcohol conversions to 3%, for which case it holds that

$$x_A = r_A(W/F_A). \qquad (1)$$

As the value of the initial reaction rate r_A for a given combination of partial pressures we used the arithmetic mean from r_A values calculated according to relation (*1*) from conversions obtained at 3—4 different W/F_A values. Experimental kinetic data were treated by nonlinear regression using the Marquardt method[10]. Minimised function was the sum of squared deviations

of experimental from calculated initial reaction rates. Estimation of confidence intervals of the constants of kinetic models was carried out on 95% confidence level by two ways. The first one was based on the estimation of standard deviations computed with the aid of ERRCALC programme[11], the second included the search for all the combinations of the constants for which the value of minimised function for a given model did not exceed the critical value[12]. The lowest and highest value of each constant from this set of combinations were considered as limit values of the confidence interval.

RESULTS AND DISCUSSION

Data

We have determined 25 values of initial reaction rates for the oxidation of 2-butanol and 25 values for the oxidation of 4-methyl-2-pentanol. Partial pressures of the alcohols were changed within $2-50$ kP interval, those of oxygen from $1\cdot2$ to 19 kPa and total pressures (alcohol + oxygen) from 10 to 57 kPa. We have further determined 32 values of initial reaction rates for the oxidation of both alcohols in the competitive system, varying butanol to methylpentanol molar ratios from $0\cdot33$ to $4\cdot0$, the sum of partial pressures of both alcohols from $10-25$ kPa and oxygen partial pressure from $10-19$ kPa. Ratios of initial reaction rates r_B/r_M (the so called relative reactivities) in the competitive system did not show any trend in dependence on either oxygen partial pressure or on the sum of partial pressures of both alcohols.
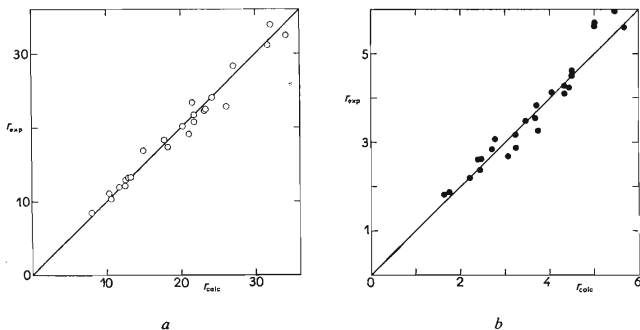

Fig. 1

Relationship Between Experimental Initial Reaction Rates r_{exp} (mol h^{-1} kg^{-1}) and r_{calc} Values Calculated According to Eq. (2) For Single Reactions

a Oxidation of 2-butanol ($k'_A = 5\cdot40$ mol h^{-1} kg^{-1} kPa$^{-1\cdot5}$; $K_A = 0\cdot084$ kPa^{-1}; $K_0 = 0\cdot0001$ kPa^{-1}); b oxidation of 4-methyl-2-pentanol ($k'_A = 2\cdot36$ mol h^{-1} kg^{-1} kPa$^{-1\cdot5}$; $K_A = 0\cdot208$ kPa^{-1}; $K_0 = 0\cdot002$ kPa^{-1}).

For the competitive system preliminary experiments were also made in which reaction rates were not evaluated but only the ratios of obtained conversions x_B/x_M for a series of different initial ratios of both alcohols $(p_B/p_M = 0.33$ to $10.7)$, without determining the absolute values of partial pressures. By this way 26 values of x_B/x_M were obtained.

The difference between the relative reactivities determined from the initial reaction rates of separately reacting alcohols and those obtained from the rates observed for the competitive system is worthy mentioning. In single reaction, 2-butanol was always more reactive (Fig. 1); r_B and r_M values measured for the same partial pressures of both alcohols were in the ratio 4.2 to 7.4 (the higher values were found for the higher partial pressures of the alcohol). In the competitive system (Fig. 2), 2-butanol was less reactive than 4-methyl-2-pentanol; r_B/r_M values determined in experiments carried out at the same partial pressures of both alcohols were always close to 0.55. This inversion of the relative reactivity resulted from the fact that the presence of 4-methyl-2-pentanol had a strong rate-retarding effect upon the reaction of 2-butanol, while the rate of the reaction of 4-methyl-2-pentanol was not significantly influenced by the presence of 2-butanol.

Equations of Langmuir–Hinshelwood (LH) and Redox (RE) Type

To describe the experimental data, we have attempted first to use the equations of LH type (33 equations) and of RE type (9 equations), the basic forms of which are summarized in Table I. Treatment of the initial reaction rates for both butanol and methylpentanol showed that on 99% confidence level the experimental data are fitted by two equations of LH-I type with exponents

$$a = 1 ; \quad a' = b = b' = 0.5 ; \quad c = 3 \quad \left(\text{Eq.}(2)\right)$$

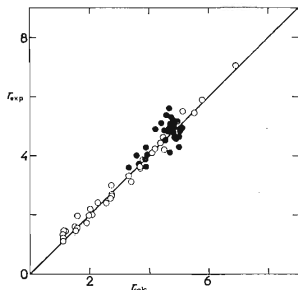$$a = a' = b = b' = 0.5 ; \quad c = 2 \quad \left(\text{Eq.}(3)\right),$$

FIG. 2

Relationship Between Experimental Initial Reaction Rates r_{exp} (mol h^{-1} kg^{-1}) and r_{calc} Values Calculated According to Eq. (2a) for Competitive Reactions

○ Oxidation of 2-butanol ($k'_B = 2.6$ mol . h^{-1} kg^{-1} kPa$^{-1.5}$; $K_B = 0.022$ kPa^{-1}; $K_M = 0.25$ kPa^{-1}; $K_0 = 0.0065$ kPa^{-1}); ● oxidation of 4-methyl-2-pentanol ($k'_M = 6.3$ mol h^{-1} kg^{-1} kPa$^{-1.5}$; $K_B = 0.0001$ kPa^{-1}; $K_M = 0.62$ kPa^{-1}; $K_0 = 0.0036$ kPa^{-1}).

TABLE I
Basic Forms of Equations of Langmuir–Hinshelwood and Redox Type Used

Denotation	Equation	Exponents	Note
LH-I	$$r_A = \frac{k_A P_A^a P_O^b}{[1 + (K_A P_A)^{a'} + (K_O P_O)^{b'}]^c}$$	$a, b, a', b' = 0; 0.5; 1$ $c = 1; 2; 3; 4$	alcohol and oxygen adsorbed on the same sites
LH-II	$$r_A = \frac{k'_A P_A^a P_O^b}{[1 + (K_A P_A)^a]^c [1 + (K_O P_O)^{b'}]^c}$$	$a, b, b' = 0.5; 1$ $c = 1; 2$	alcohol and oxygen adsorbed on different sites
LH-III	$$r_A = \frac{k'_A P_A P_O^b}{\{[1 + (K_O P_O)^{b'}]^2 + 4 K_A P_A\}^{0.5} + 1 + (K_O P_O)^{b'}]^c}$$	$b = 0.5; 1$ $b' = 0; b$ $c = 2; 3; 4$	alcohol adsorbed on two sites without dissociation; the sites are identical for both components
RE-I	$$r_A = \frac{k_A P_A^a P_O^b}{k_A P_A^a + P_O^b}$$	$a, b = 0.5; 1$	two steps comparable in rates
RE-II	$$r_A = \frac{k'_A P_A^a P_O^b}{(k'_A/k_2) P_A^a + P_O^b + (k'_A/k_3) P_A^a P_O^b}$$	$a = 1; 2$ $b = 0.5; 1$	three steps comparable in rates
RE-III	$$r_A = \frac{k'_A P_A P_O^{0.5}}{[1 + (K_A P_A)^{a'}]\{[1 + (K_A P_A)^{0.5}]^c P_O^{0.5} + k_A K_A P_A\}}$$	$a' = 0.5; 1$ $c = 0; 1$	two steps comparable in rates (as in RE-I) with preceding fast adsorption of alcohol

by one equation of LH-II type with exponents

$$a = 1 ; \quad b = b' = 0.5 ; \quad c = 1 \quad (\text{Eq. } (4))$$

and by one equation of RE-I type with exponents

$$a = 1 ; \quad b = 0.5 \quad (\text{Eq. } (5)) .$$

These equations could not be distinguished with the use of Beale criterion[13]; only for the rate data obtained with butanol the fit by Eq. (5) was somewhat worse. The fitness of the best Eq. (2) to the initial reaction rates of single reactions is seen from Fig. 1.

Data for competitive reactions were treated with the use of four equations mentioned above (Eqs (2)—(5)). The LH equations (2)—(4) were modified in the usual way, by extending them by the adsorption term of the competing substance (see *e.g.* Eq. (2a)).

$$r_{B(M)} = k'_{B(M)} p_{B(M)} p_0^{0.5} / [1 + (K_B p_B)^{0.5} + (K_M p_M)^{0.5} + (K_0 p_0)^{0.5}]^3 . \quad (2a)$$

TABLE II

Confidence Regions for Constants of LH and RE Equations

Eq.	Constant[a]	From single reactions of alcohol		From competitive reactions of alcohol	
		B	M	B	M
(2), (2a)	k'_B	4·0— 6·8	—	1·8— 3·4	—
	k'_M	—	1·6— 3·1	—	2·4— 10·2
	$K_B \cdot 10^2$	3·7—13·1	—	0·8— 3·6	0— 0·1
	$K_M \cdot 10^2$	—	11·2—30·4	12·7—36·7	33·6— 90·2
	$K_O \cdot 10^2$	0— 0·1	0— 0·6	0— 1·7	0— 1·8
(4), (4a)	k'_B	2·3— 3·5	—	0·5— 1·3	—
	k'_M	—	0·7— 1·4	—	0·9— 3·5
	$K_B \cdot 10^2$	22·5—33·5	—	6·1—19·3	0
	$K_M \cdot 10^2$	—	42—78	35—85	52—164
	$K_O \cdot 10^2$	0— 0·2	0— 0·5	0—6·5	0— 8·2
(5), (5a)	k'_B	7·6—11·9	—	1·5—2·9	—
	k'_M	—	2·5— 3·7	—	2·7— 7·5
	k_B	0·8— 1·3	—	0·3— 0·7	0
	k_M	—	1·5—2·5	1·4—3·3	2·0— 6·2

[a] Dimensions of the constants: k'_B, k'_M in Eq. (2), (2a), (4), (4a): mol h^{-1} kg^{-1} kPa$^{-1.5}$; in Eq. (5), (5a): mol h^{-1} kg^{-1} kPa^{-1}; K_B, K_M, K_O : kPa^{-1}; k_B, k_M : kPa$^{-0.5}$.

By modification of the RE equation (5) one gets Eq. (5a) for the oxidation of alcohol B or M in the competitive system

$$r_{B(M)} = k'_{B(M)}p_{B(M)}p_0^{0.5}/(k_B p_B + k_M p_M + p_0^{0.5}) .\qquad (5a)$$

Eq. (3) can be disregarded based on the result of the nonlinear regression of rate data for competitive reactions; the remaining three equations described the results similarly well. The agreement between experimental and calculated data obtained by using Eq. (2a) and the constants optimised for the competitive system is evident from Fig. 2.

On treating data for single reactions of butanol and methylpentanol by LH and RE equations a very good fitness of these equations to experimental data has been obtained. This has been frequently the reason why these models were accepted in literature for description of the kinetics of heterogeneous catalytic oxidation. Even in treating data for the competitive reactions we have found a good fitness of these models. However, concerning the suitability of LH and RE models for description of the kinetics of catalytic oxidation of alcohols, a different situation arises when one analyses the values of their constants. In a relevant model, each constant should have identical value (within confidence interval), irrespective of whether it was obtained from data for single or competitive reactions. As it is seen from Table II, this requirement is fulfilled for all three examined models in the case of the constants which relate to methylpentanol (k'_M, K_M or k_M) and for LH model also the constants which relate to oxygen (K_0). In contradistinction to this, different values of constants relating to butanol (k'_B, K_B or k_B) have been obtained on the basis of data for single and competitive reactions (even with confidence interval being taken into account). Furthermore, mutual comparison of $K_B(k_B)$ values for the competitive system, where these constants were determined twice (once from rate data for butanol and once from the effect of this alcohol on the rate of the reaction of methylpentanol), points to important controversy.

In order to illustrate how markedly different are the results obtained by treatment of single and competitive reactions, in Fig. 3 are plotted experimental reaction rates in the competitive system against the rates calculated according to Eq. (2a) for the competitive system from the values of the constants for single reactions. A similar picture is obtained also for LH equation (4a) and RE equation (5a).

Another result which shows the unsuitability of LH and RE equations is provided by treatment of the relative reactivities of both alcohols in the competitive system. For all the LH and RE equations from Table I, extended for the competitive system it follows that

$$\frac{r_B}{r_M} = \frac{dx_B/d(W/F_B)}{dx_M/d(W/F_M)} = \frac{dx_B p_B}{dx_M p_M} = \frac{k'_B}{k'_M}\left(\frac{p_B^*}{p_M^*}\right)^a = R_{B/M}\left(\frac{p_B^*}{p_M^*}\right)^a ,\qquad (6)$$

since in the extended form for the competitive system they have common denominators which can be reduced, and since $F_B = F y_B$; $F_M = F y_M$ and $y_B/y_M = p_B/p_M$. This relation (6) makes it possible to determine in rate equations the exponent a from data on relative reactivities. By using this relation we treated first preliminary conversion data x_B/x_M vs p_B/p_M (after substitution of $p^*_{B(M)} = p_{B(M)}(1 - x_{B(M)})$) and determined the exponent $a = 0.67 \pm 0.16$ and the constant $R_{B/M} = 0.54 \pm 0.06$. By means of Eq. (6) for the initial conditions (where $p^*_B/p^*_M \approx p_B/p_M$) we further treated the values of the ratios of initial oxidation rates of both alcohols r_B/r_M for the competitive system in dependence on the p_B/p_M ratio, and by nonlinear regression of these data we found that $a = 0.663 \pm 0.033$ and $R_{B/M} = 0.544 \pm 0.016$.

The obtained value of the exponent $a = 0.66$ to 0.67 is at variance with LH and RE models which admit only certain discrete values (0·5; 1; 2; ...); in Eqs (2), (4) and (5) which fit best the rate data, a equals to 1. Also the value of the constant $R_{B/M} = k'_B/k'_M = 0.544 \pm 0.016$ which was determined from the relative reactivities in the competitive system differs significantly from the values calculated from k' constants for single reactions; for Eq. (2) $k'_B/k'_M = 2.3 \pm 1.0$, for Eq. (4) it is 2.8 ± 1.1 and for Eq. (5) it equals to 3.2 ± 1.2.

The above mentioned deficiencies are not done away even by introducing into LH equations the so called unavailability factor of sites due to the isolation or steric hindrance of sites by the molecule of the bulkier reactant according to Lih's ideas[14]. Thus, for all the results obtained it follows that the equations of LH and RE type are incapable of describing the kinetics of single and competitive oxidation of secondary alcohols in a consistent way as well as they are not able to express the mutual influencing of these reactions in the competitive system. It seems therefore likely
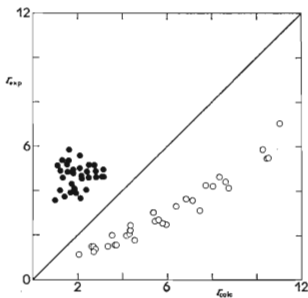

FIG. 3

Relationship Between Experimental Initial Reaction Rates for Competitive Reactions r_{exp} (mol h^{-1} kg^{-1}) and r_{calc} Values Calculated According to Eq. (2a) by Using Values of Constants for Single Reactions (see text for Fig. 1)

○ Oxidation of 2-butanol; ● oxidation of 4-methyl-2-pentanol.

that the mechanism of oxidation reactions on the catalyst employed does not correspond to such simple models. For that reason we had to consider also other kinetic models of more complex type.

Equations Considering Nonhomogeneous Catalyst Surface (NH Models)

Equations of this type were derived by a procedure reported by Temkin and Kiperman[4] for uniformly nonhomogeneous catalyst surface which is characterized by the relation

$$dq/ds = -\text{const.} = -fRT, \tag{7}$$

where ds is the differential fraction of the sites whose heat of adsorption lies between q and $q + dq$; f is a constant. We assumed first that the constant f has identical value for all the components and derived for five variants of the mechanism of surface reaction the equations of type NH-I

$$r_A = k'_A p_A^a p_0^b / [K_A p_A + (K_0 p_0)^{b'}]^d,$$

where $a = 1; 2$, $b = 0.5; 1$, $b' = 0.5; 1$ and d is a parameter (generally not an integer number). In treatment of data for single reactions the equation with exponents

$$a = 1; \quad b = b' = 0.5 \quad (\text{Eq. (8)}),$$

fit the experimental data and was equivalent to the best LH and RE equations on 99% confidence level. After its extention for the competitive system, this equation described with the same reliability also data for competitive reactions. The analysis of the constants for single and competitive reactions and the results of treatment of the relative reactivities revealed, however, discrepancies in all points for which LH and RE equations had to be considered unsuitable. Thus, for the same reasons as in the previous case, all the equations considering a nonhomogeneous surface with the same distribution function of the reactants have been rejected.

If, one the other hand, on supposes different distribution functions for both alcohols on nonhomogeneous catalyst surface $(f_B \neq f_M)$, i.e. the dependence of the heat of adsorption and activation energy on the degree of the surface coverage is steeper for one alcohol compared to the other, the reaction rate of the alcohol with the higher f value will be more influenced by the addition of the other competing alcohol than the reaction rate of the alcohol with the lower f value. Such a model could thus describe the observed very strong mutual influencing of reactions and perhaps also the inversion of the relative reactivity better than the models discussed so far.

The rate equation for this model can be derived again by the general procedure reported by Kiperman[4]. Several simplifying assumptions have to be, however,

introduced: the adsorption of oxygen on other sites compared to the adsorption of alcohols, the adsorption of each alcohol in the region of medium coverage of the surface, both alcohols (*i.e.* their sum) occupying nearly completely the surface; as followed from experimental data, this assumption is justified. Rate equations for this model (NH-II) have the following form

$$r_B = k'_B (p_B/p_M)^m p_0^n \tag{9}$$

$$r_M = k'_M (p_M/p_B)^{m'} p_0^n , \tag{10}$$

where

$$m = (1 - \alpha_B) f_B / (f_B - f_M) , \tag{11a}$$

$$m' = (1 - \alpha_M) f_M / (f_M - f_B) \tag{11b}$$

and $n = b (1 - \alpha_0)$; α_B, α_M and α_0 are constants of the linear dependence[4] of the activation energy on the heat of adsorption of reactants, the value of which vary from 0 to 1. For single reactions the following expression would correspond to Eqs (9) and (10)

$$r = k p_A p_0^b / [(K_A p_A)^{\alpha_A} (K_0 p_0)^{\alpha_0 b}] = k' p_A^{(1 - \alpha_A)} p_0^{b(1 - \alpha_0)} , \tag{12}$$

in which $b = 0.5$; 1; 2. Data for single reactions were treated by Eq. (12) and those for competitive reactions by Eqs (9) and (10). These equations fit well experimental data and on 99% confidence level they were equivalent in reliability (with the exception of Eq. (12) for methylpentanol) to Eqs (2), (4), (5) and (8) (Table III).

The values obtained for parameters of Eqs (9), (10) and (12) are listed in Table IV. In the analysis of the values of these constants one cannot compare k'_B and k'_M values for single reactions with those for competitive reactions since k'_B and k'_M for these cases are differently complex functions of a series of other constants (among others also α_B, α_M, f_B, f_M) the values of which are not known. However, such a comparison can be made for the values of the exponents in the rate equations. Taking into account the confidence region found (Table IV), the values of the exponent n at partial pressure of oxygen can be regarded as identical for both butanol and methylpentanol reactions, and that in single as well as in competitive reactions. The sign of exponents m and m' is also of interest. It is reasonable to assume that the heat of adsorption will either increase or decrease for both alcohols with the activity of catalyst sites (*cf.* Eq. (7)) and that f_B and f_M have the same sign. Then (since $f_B \neq f_M$) it follows from the analysis of Eqs (11) for exponents m and m' that one of them must be positive and the second one negative, which was proved experimentally (Table IV).

Also the results of the treatment of relative reactivities support the NH-II model.

From comparison of the quotient of Eqs (9) and (10) with Eq. (6) one obtains (for initial conditions $p_B^*/p_M^* = p_M/p_M$)

$$r_B/r_M = (k_B'/k_M')(p_B/p_M)^{m+m'} = R_{B/M}(p_B/p_M)^a \qquad (13)$$

from which it follows that $a = m + m'$. This is the case. It was found by treatment of the relative reactivities that $a = 0.663 \pm 0.033$ and by direct treatment of the rate data for competitive reactions (Table IV) that $m + m' = 0.66 \pm 0.10$. A similar

TABLE III
Relative Values of the Sum of Squared Deviations Q for Best Equations

Model	Eq.	Single reactions		Competitive reactions	
		Q_B	Q_M	Q_B	Q_M
LH-I	(2), (2a)	1·314	1·319	1·041	1·694
LH-II	(4), (4a)	1·310	1·452	1·357	1·000
RE-I	(5), (5a)	2·508	1·022	1·439	1·118
NH-I	(8)	1·000	1·000	1·429	1·102
NH-II	(9), (10), (12)	1·473	3·022	1·112	1·666
CH	(16), (17), (18)	1·380	1·030	1·000	1·089

For better comparison, the values of the sum of squared deviations are expressed relatively, i.e. they are related to the value of the sum of squared deviations for the model which fit best a given set of data. Critical value of the sum of squared deviations[13] for 99% confidence level equals to 1·66 in most cases or it is close to this value.

TABLE IV
Values of Parameters of NH-II Model

| Eq.	Parameter	For reaction of alcohol	
		B	M
(12) [single reactions]	k_A' (mol h^{-1} kg^{-1} kPa$^{-(1-\alpha_A)n}$)	4·1 $\pm$ 0·6	0·95 $\pm$ 0·23
	$(1-\alpha_A)$	0·25 $\pm$ 0·03	0·17 $\pm$ 0·05
	$b(1-\alpha_0) = n$	0·46 $\pm$ 0·05	0·45 $\pm$ 0·09
(9), (10) [competitive reactions]	k_A' (mol h^{-1} kg^{-1} kPa^{-n})	0·88 $\pm$ 0·24	1·76 $\pm$ 0·49
	m (m')	0·69 $\pm$ 0·05	−0·03 $\pm$ 0·05
	n	0·38 $\pm$ 0·14	0·35 $\pm$ 0·15

agreement was also established for $R_{B/M}$ ($= 0.544 \pm 0.016$) and k'_B/k'_M ratio ($= 0.57 \pm 0.24$).

Consistency in the results of treatment of single and competitive rate data (although not quite unambiguous due to simplification used to derive the rate equations) and especially the agreement of the values of m and m' with both theory and the results of treatment of the relative reactivities differentiates this kinetic model NH-II from those discussed so far. For all these models (LH, RE and NH-I) the fractional value of the exponent a at the partial pressures of alcohols obtained from the relative reactivities ($a = 0.66 \pm 0.03$) was at variance with the assumptions.

Model Based on Chain Mechanism of Oxidation (CH Model)

This model could also describe the observed mutual influencing of the reactions, since in this case the active species formed from one alcohol can be expected to interact with molecules or species formed from the other one. In order to examine generally the ability of this model to describe the observed results, we formulated the simplest oxidation chain mechanism. We were not concerned either with variants of reaction mechanism, a great number of which could be proposed, or with the nature of active species (free radicals or ion or other active forms). This question is irrelevant as far as formulation of the rate equation is concerned.

In constructing the model we adopted the concept commonly accepted for homogeneous oxidation of hydrocarbons or alcohols[15-17]. These ideas have in fact been applied also to the explanation of some heterogeneous catalytic oxidations[16,18-20] in the liquid phase. According to them[15] the propagation cycle involves the following steps

$$A^* + O_2 \quad \rightarrow \quad AO_2^* \qquad\qquad (B)$$

$$AO_2^* + A \quad \rightarrow \quad AO_2H + A^*$$
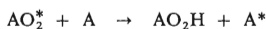
the first one being considered as fast (denotation * means active species, A is the substance to be oxidised); the peroxy compound AO_2H then yields ketone by a fast reaction which is the final oxidation product. The termination is presumed to proceed via peroxy species AO_2^*

$$2\, AO_2^* \quad \xrightarrow{\ k_t\ } \quad \text{unreactive products.} \qquad\qquad (C)$$
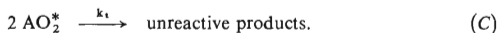
Such a scheme can be described by Eq. (14)

$$r = \left[k_p/(2k_t)^{0.5} \right] p_A r_i^{0.5} , \qquad\qquad (14)$$

where r_i is a nonspecified rate of initiation. We considered a number of initiation mechanisms on the catalyst surface; the experimental data for single reactions were

best described by the model according to which the initiation involves the interaction of adsorbed oxygen atoms with alcohol molecules, which can be expressed by Eq. (15) (slow step of initiation mechanism comprises dissociation of adsorbed oxygen molecules to atoms)

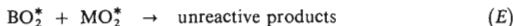$$r_i = k_i p_0 / (1 + K_0 p_0 + K_A p_A)^2 . \qquad (15)$$

After introducing Eq. (15) into Eq. (14) one obtains Eq. (16) for the rate of the oxidation of individual alcohols.

$$r = \left[k_p k_i^{0.5} (2k_i)^{0.5} \right] p_A p_0^{0.5} / (1 + K_A p_A + K_0 p_0) =$$
$$= k'_A p_A p_0^{0.5} / (1 + K_A p_A + K_0 p_0) . \qquad (16)$$

In deriving the rate equations for competitive reactions we used the procedure reported by Boudart[15] for homogeneous competitive oxidation of two hydrocarbons. In addition to normal propagation and termination steps (see Schemes (B) and (C)), in the case of the competitive system also cross-propagation steps

$$BO_2^* + M \rightarrow BO_2H + M^* \qquad (D)$$

$$MO_2^* + B \rightarrow MO_2H + B^* \qquad$$
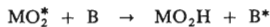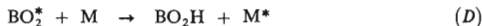
and cross-termination step

$$BO_2^* + MO_2^* \rightarrow \text{unreactive products} \qquad (E)$$

should be taken into account.

It is the competition for active species in the cross-propagation steps which could be the reason for the strong mutual influencing of competitive reactions. Using this scheme and steady state approximation on gets the following expression for the rate of the oxidation of alcohols in the competitive system

$$r_B = k^* p_B p_0^{0.5} (A_1 p_B + p_M) / U \qquad (17)$$

$$r_M = k^* p_M p_0^{0.5} (A_2 p_M + p_B) / U , \qquad (18)$$

where $U = (1 + K_B p_B + K_M p_M + K_0 p_0)(C_1 p_B^2 + C_2 p_B p_M + C_3 p_M^2)^{0.5}$ and $k^* = k_i^{0.5}$; A_1, A_2, C_1, C_2 and C_3 are different arrangements of the rate constants of propagation and termination steps. It is assumed that the mechanism of initiation process is the same as in the case of single reactions, only Eq. (15) is extended by inclusion of the adsorption term of the competing alcohol.

Eqs (*17*) and (*18*) fit very well the experimental data for competitive reactions, and Eq. (*16*) described well single reactions of both alcohols (Table III). The consistency of the obtained sets of constants can be analysed analogously as in the case of previous models. Constants k^*, C_1, C_2 and C_3 for the competitive system should be the same both as those determined from rates of the oxidation of butanol and as those obtained from rates of the oxidation of methylpentanol. If one compares these constants, which are listed in Table V, this assumption can be regarded as fulfilled. The agreement between the constants for single and competitive reactions can be estimated only partially. The values of K_0, K_B and K_M constants were determined from single reactions and their use for competitive reactions in optimisation of the other constants in Eqs (*17*) and (*18*) led to a good agreement with the experimental data (Table III). The other constants cannot be compared individually, since constants A_1, A_2, C_1, C_2, C_3 and k^* are present only in Eqs (*17*) and (*18*) and the k'_A constant only in Eq. (*16*). If we compare, however, the limit forms of Eqs (*17*) and (*18*) for competitive reactions (when $p_M = 0$ or $p_B = 0$) with Eq. (*16*) for single reaction (k'_A is either k'_B or k'_M) we see that the following expressions should hold for the relations between the constants:

$$k'_B = k^* A_1 / C_1^{0.5} \qquad (19)$$

$$k'_M = k^* A_2 / C_3^{0.5} \qquad (20)$$

Let us compare now *e.g.* the experimentally found constants C_1 and C_3 with the values calculated according to Eqs (*19*) and (*20*) using the remaining constants. By

TABLE V
Confidence Regions for Constants of Eqs (*17*) and (*18*)[a] for Competitive Reactions

Constant[b]	From rates of the reaction of alcohol	
	A (Eq. (*17*))	B (Eq. (*18*))
k^*	8·0 — 9·4	8·0 — 9·7
C_1	0 — 4·0	0 — 2·0
C_2	30 — 58	15·8 — 30·2
C_3	73 — 101	86 — 128
A_1	0·164 — 0·206	—
A_2	—	1·05 — 1·25

[a] Constants K_B (= 0·41 kPa^{-1}), K_M (= 0·80 kPa^{-1}) and K_O (= 0·027 kPa^{-1}) were taken from the results of the treatment of single reactions (Eq. (*16*)); [b] dimension of constant k^* is (mol . . h^{-1} kg^{-1} kPa$^{-1.5}$), the other constants are dimensionless.

substitution of k'_B ($= 3.9$ mol h^{-1} kg^{-1} kPa$^{-1.5}$) and k'_M ($= 1.3$ mol h^{-1} kg^{-1} . . kPa$^{-1.5}$) found by treatment of single reactions, and A_1, A_2 and k^* from Table V for competitive reactions, we calculated the C_1 constant which lies in 0.11 to 0.25 region and the C_3 constant which lies in $42-87$ region. These are the values from the intervals $0-2$ and $86-101$, respectively, found by direct treatment of the experimental data (Table V). This agreement speaks for the consistency of the results of treatment of the kinetics of single and competivie reactions by the model of chain mechanism.

This model describes also the relative reactivities and their inversion on going from single reactions of both alcohols to the competitive system. For the relative reactivities r_B/r_M in the competitive system one gets from the quotient of Eq. (17) and (18) the following relation

$$r_B/r_M = (A_1 p_B^2 + p_B p_M)/(A_2 p_M^2 + p_B p_M) . \qquad (21)$$

If the values of A_1 and A_2 from Table V are put into Eq. (21), one obtaines for the same partial pressures of both alcohols ($p_B = p_M$) the value equaling to 0.55, which is in good agreement with the experiment and expresses the observed fact that in the competitive system methylpentanol is twice as reactive as butanol. If one divides Eq. (17) by Eq. (18) in their limit forms for the reactions of individual alcohols ($p_M = 0$ or $p_M = 0$), one obtaines the relation (22).

$$r_B/r_M = (k'_B p_B/k'_M p_M) \left[(1 + K_0 p_0 + K_M p_M)/(1 + K_0 p_0 + K_B p_B)\right] . \qquad (22)$$

With regard to the fact that experimentally found k'_B/k'_M ratio equals to 3 and $K_M > > K_B$, the relative reactivity of separately reacting alcohols (at identical partial pressures $p_B = p_M$) will be always higher than 3 (in the favour of butanol) and will increase with the total pressure of both alcohols, which was experimentally established.

The model of chain mechanism, even though considerably simplified could in principle be able to describe in consistent way the kinetics of single and competitive reactions and to account for the mutual influencing of the reactions and the change in the relative reactivity in the competitive system. We did not succeed in proving the so-called heterogeneous-homogeneous mechanism, which might take place during chain oxidation reaction. We were not able to establish the effect of the free volume in the catalyst bed and to detect mass spectrometrically[21] the evolution of active species to the gas phase.

CONCLUSION

Confrontation of the kinetics of competitive and single reactions proved to be an efficient tool of the analysis of the suitability of kinetic models of heterogeneous catalytic reactons. For the oxidation of secondary alcohols to ketones on the iridium

catalyst studied by us the utilization of this approach allowed to conclude that its kinetics cannot be satisfactorily described by such simple models as are Langmuir--Hinshelwood or redox ones, even though they describe the kinetics of single reactions very well. Neither more sophisticated LH models (*e.g.* those involving the unavailability factor of sites for the adsorption of some of the reactants) or RE models (*e.g.* those with three comparatively fast steps) did not lead to improvements. The oxidation mechanism and the model of catalytic surface are obviously more complex in the case under study. It seems very likely that nonhomogeneity of the surface or chain mechanism, or both simultaneously, play an important role in the kinetics of oxidation reaction. The preference of the former or the latter model could not be proved. These models are better suited to describe the different behaviour of single and competitive reactions, among others also for the fact that they include some processes which can take place only in the competitive system. This leads to the introduction of some additional constants which are not present in the equations for single reactions.

LIST OF SYMBOLS

$a, a', b, b', c, d, m, m', n$	exponents in rate equations
a	the exponent in the numerator of rate equations at alcohol partial pressure
A_1, A_2	constants in the numerator of rate equations *(17)* and *(18)*
C_1, C_2, C_3	constants in the denominator of rate equations *(17)* and *(18)*
f	the constant characterizing the nonhomogeneity of active sites in Eq. *(7)*
F	flow rate of reactants
F/W	space velocity
k'_A, k'_B, k'_M	overall constants in the numerator of rate equations
k^*	the constant in the numerator of rate equations *(17)* and *(18)*
k_A, k_B, k_M	constants in the denominator of the rate equations of RE type
k_2, k_3	rate constants for the second and third steps in the redox RE-II equations
k_i, k_p, k_t	the rate constants of initiation, propagation and termination in the chain mechanism
K_A, K_B, K_M, K_0	adsorption coefficients
p	initial partial pressure
p^*	partial pressure after conversion x was attained
q	heat of adsorption
Q	relative value of the sum of squared deviations of experimental and calculated initial reaction rates
r	initial reaction rate
r_{exp}, r_{calc}	experimental and calculated value of the initial reaction rate
r_i	initiation rate in the chain mechanism
r_B/r_M	the relative reactivity of 2-butanol with respect to 4-methyl-2-pentanol

$R_{B/M}$	the overal constant in Eq. (6), equaling to k'_B/k'_M
T	absolute temperature
W	catalyst mass
x	degree of conversion of a given alcohol
y	molar fraction
α	constant of the linear relationship between the activation energy and the heat of adsorption (cf.[4])

Denotation of Reactants

A	alcohol or the compound to be oxidised in general
B	2-butanol
M	4-methyl-2-pentanol
O	oxygen
A*, AO_2^*, B*, BO_2^*, M*, MO_2^*	active species in the schemes $(B)-(E)$

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