DETERMINATION OF RATE EQUATIONS OF CATALYTIC OXIDATION OF PROPENE TO ACROLEIN AND ACRYLIC ACID IN THE GAS PHASE

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The kinetics of propene catalytic oxidation to acrolein and acrylic acid was studied in a flow-circulation reactor over a multicomponent oxide catalyst containing molybdenum, cobalt, nickel, iron, bismuth, and potassium. The rate equations were found for the total formation of acrolein and acrylic acid.

The catalytic oxidation of propene to acrylic acid in the gas phase takes place in two steps, and two different catalysts are used which work at different reaction conditions. In the first step, propene is oxidized to acrolein and partly acrylic acid is as well formed. At the present time, the multicomponent oxide catalysts containing molybdenum, tin, vanadium, phosphorus, iron, bismuth, cobalt, boron, antimony, tungsten, tellurium, nickel, *etc.*[1] appear to be applied largely to oxidation of propene to acrolein. On studying the kinetics of propene oxidation to acrolein over multicomponent oxide catalysts, it was found out that the rate of formation of acrolein did not depend on the oxygen partial pressure and is of the first order with regard to propene[2-4]. Boreskov and coworkers[5] then observed the acrolein autocatalytic effect during propene oxidation to acrolein.

The aim of this work was to carry out a detailed study of propene catalytic oxidation to acrolein, to find the respective rate equations, and to propose a reaction scheme of propene oxidation to acrolein.

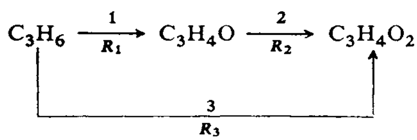
EXPERIMENTAL

All the kinetic measurements were carried out in an apparatus with flow-circulation reactor under the following reaction conditions: catalyst particle size 0·4—0·63 mm, total flow rate of reaction mixture $F = 5\ dm^3/h$, reaction temperature $T = 593$ K, pumping power of circulation pump 200 dm^3/h, reaction mixture composition 5—7 mol % C_3H_6, 8—14 mol % O_2, 10—30 mol % H_2O, 1·5—4 mol % C_3H_4O, 0·25—0·5 mol % $C_3H_4O_2$, the remainder is nitrogen. These conditions ensured that the effect of internal and external diffusion was negligible and that the measurement took place in the kinetic region. The amount of substance of propene before and after the reaction was determined by gas chromatography, the amount of substance of acrolein polarographically, and that of acrylic acid by titration[6]. The kinetic study of propene oxidation was carried out over a multicomponent oxide catalyst of the type $Mo_aCo_bNi_cFe_dBi_eK_fO_x$ which was prepared in accordance with patent[7].

RESULTS AND DISCUSSION

On studying the influence of oxygen, water, propene, acrolein, and acrylic acid on the kinetics of propene oxidation, it was found out that the total rate of acrolein formation R_A did not depend on the partial pressure of oxygen and water, increased with increasing the propene partial pressure and decreased on adding acrolein or acrylic acid into the initial reaction mixture. The characteristic feature of the rate of acrolein formation is a passage through a maximum in dependence on the propene conversion x_P. On oxidizing propene, acrylic acid is formed in addition to acrolein (carbon dioxide is formed in slight amount owing to a high selectivity of the catalyst to acrolein).

Whereas acrolein is formed directly from propene, acrylic acid forms, as it follows from experimental data, partly by a consecutive reaction from acrolein and partly by a side reaction directly from propene, according to the reaction scheme (Scheme 1).



SCHEME 1

The total rate of acrolein formation R_A is given by the relation $R_A = R_1 - R_2$, and the total rate of acrylic acid formation R_K by the relation $R_K = R_2 + R_3$. To be able to establish the forms of rate equations for R_1, R_2, R_3 from the measured values of rates R_A, R_K, it was necessary to study the separate oxidation of acrolein over the same catalyst and, on the basis of the experimental data obtained, to determine a preliminary form of reaction rate R_2 which corresponds to the reaction rate of formation of acrylic acid from acrolein. For the reaction rate R_2, the equation was proposed in a general form

$$R_2 = k_2 \cdot p_A^n/(1 + K_2 p_K + K_3 p_A)^m \,, \qquad (1)$$

where $n = 1, 2$, $m = 1, 2$, p_A is the acrolein partial pressure and p_K the acrylic acid partial pressure.

The equations were converted to a linear form and treated graphically. From the combinations of possible exponents n and m complies only the equation in the form

$$R_2 = k_2 \cdot p_A^2/(1 + K_2 p_K + K_3 p_A) \,, \qquad (2)$$

where the orientation values of constants were obtained by numerical calculation: $k_2 = 1{\cdot}26 \,.\, 10^{-14}\ \text{mol s}^{-1}\,\text{g}^{-1}\,\text{Pa}^{-2}$, $K_2 = 3{\cdot}21 \,.\, 10^{-3}\ \text{Pa}^{-1}$, and $K_3 = 2{\cdot}22 \,.\, 10^{-4}\ \text{Pa}^{-1}$. In linearized form Eq. (*2*) takes the form

$$p_A^2/R_2 = 1/k_2 + K_2 p_K/k_2 + K_3 p_A/k_2 \,. \qquad (3)$$

If the left-hand side of Eq. (*3*) is denoted by Y_m and the right-hand one by Y_c, then if Eq. (*3*) is valid, it must hold $Y_c = Y_m$, which is very well fulfilled for the measured data of acrolein oxidation to acrylic acid (Fig. 1). If propene is present in the reaction mixture, it is necessary to add a term referring to its adsorption on the catalyst surface to the denominator of Eq. (*2*). This was done after the complete solution of kinetics of the entire system. To determine the form of rate equation for $R_1 = R_A + R_2$, it was necessary to calculate, in the first approximation by means of Eq. (*2*), the values of rates R_2 for all the values of rates R_A found experimentally.

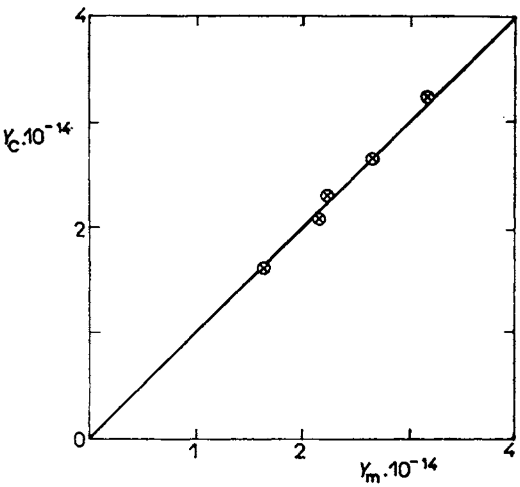


FIG. 1

Dependence of the left-hand side of Eq. (*3*), denoted by Y_m ($\text{Pa}^2\,\text{s g mol}^{-1}$), on the right-hand side of Eq. (*3*), denoted by Y_c ($\text{Pa}^2\,\text{s g mol}^{-1}$), for oxidation of acrolein to acrylic acid

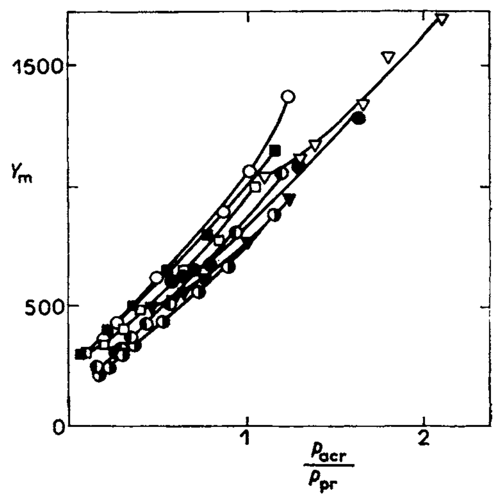


FIG. 2

Dependence of the left-hand side of Eq. (*6*), denoted by Y_m ($\text{s}^{1/2}\,\text{g}^{1/2}\,\text{mol}^{-1/2}$), on the ratio p_P/p_A for different molar compositions of reaction mixture (initial content 12% O_2 and 20% H_2O). ○ 3% C_3H_6; ◐ 5% C_3H_6; ◑ 7% C_3H_6; ● 5% C_3H_6, 1·5% C_3H_4O; ▽ 5% C_3H_6, 4% C_3H_4O; ▼ 7% C_3H_6, 1·5% C_3H_4O; □ 5% C_3H_6, 0·25% $C_3H_4O_2$; ■ 5% C_3H_6, 0·5% $C_3H_4O_2$. The remainder of reaction mixture is nitrogen

The reaction rate R_1 passes through a maximum in dependence on propene conversion, which indicates that it is probably proportional to the $p_P \,.\, p_A$ product (p_P is propene partial pressure) or that it can be described by rate equations of bimolecular reactions over the catalyst surface[8].

Several equations were proposed which describe the above-mentioned facts. These equations were linearized nad graphically treated. The equation

$$R_1 = k_1 p_P \,.\, p_A/(1 + K_1 p_P + K_2 p_K + K_3 p_A)^2 \qquad (4)$$

proved to be best. When linearized, it takes the form

$$(p_A/p_P \,.\, R_1)^{1/2} = K_1/k_1^{1/2} + 1/p_P \,.\, k_1^{1/2} + K_2 p_K/p_P \,.\, k_1^{1/2} + K_3 p_A/p_P \,.\, k_1^{1/2} \,, \qquad (5)$$

and can be rewritten into

$$Y_m \equiv (p_A/p_P \,.\, R_1)^{1/2} = A + B/p_P + C \,.\, p_K/p_P + D \,.\, p_A/p_P \equiv Y_c \,. \qquad (6)$$

Fig. 2 illustrates the dependence of Y_m on p_A/p_P. The coefficients A, B were determined from values of Y_m extrapolated to the zero value of p_A/p_P from measured curves when only propene, water, and nitrogen were present in feed. The coefficient C was as well determined from extrapolated values of curves when acrylic acid in addition was present in feed. The coefficient D was then calculated numerically from an arbitrary point of measured curves (it did not concern the curves, however, where acrolein was present in feed). The found values of the coefficients are as follows: $A = 60\ g^{1/2}\ s^{1/2}\ mol^{-1/2}$, $B = 5{\cdot}38 \,.\, 10^5\ Pa\ g^{1/2}\ s^{1/2}\ mol^{-1/2}$, $C = 1\ 234\ g^{1/2}\ s^{1/2} \,.\, mol^{-1/2}$, $D = 377\ g^{1/2}\ s^{1/2}\ mol^{-1/2}$. If the right-hand side of Eq. (*6*) is denoted by Y_c, and the dependence of Y_m on Y_c is plotted, then if Eq. (*6*) is valid, the measured points must lie on a straight line with slope equal unity.

It is evident from Fig. 3*a* that Eq. (*6*) describes very well the experimental points with pure propene and acrylic acid in feed. If acrolein is present in the reaction mixture already in feed, the numerical values of Y_c are substantially lower. Here the content of propene in the reaction mixture makes no difference but the difference $Y_m - Y_c$ is directly proportional to the partial pressure of feed acrolein. From it follows that on the right-hand side of Eq. (*8*) is added another term $E \,.\, p_A^0$ (p_A^0 is the initial partial pressure of acrolein), where the coefficient E has the value $E = 8{\cdot}8 \,.\, 10^{-2}\ g^{1/2}\ s^{1/2}\ mol^{-1/2}\ Pa^{-1/2}$. This additional adsorption term can be explained by the presence of an impurity in acrolein which is sorbed on the catalyst surface.

With respect to the term $E \,.\, p_A^0$ in Eq. (*6*) and on using the coefficients A, B, C, D obtained by extrapolation, the relation between the measured Y_m and calculated Y_c is illustrated in Fig. 3*b*. The determination of accurate form of the rate equation of R_1 allows to determine the final form of the rate equation for R_2 and R_A. The oxidation of acrolein to acrylic acid takes place over the same catalyst as the oxidation of propene to acrolein and consequently the same terms, resulting from the adsorption of single components, must occur in the denominator as in equation for R_1, however, the exponent must be different. The total rate of acrolein formation R_A can be expressed by the relation

$$R_A = k_1 \cdot p_P \cdot p_A/(1 + K_1 p_P + K_2 p_K + K_3 p_A + K_4 p_P \cdot p_a^0)^2 - \\ - k_2 \cdot p_A^2/(1 + K_1 p_P + K_2 p_K + K_3 p_A + K_4 p_P \cdot p_A^0) . \quad (7)$$

Determination of the constants was carried out by weighted nonlinear regression (simplex method) by means of a computer. Approximate values of the constants, serving as starting values for the nonlinear regression, were determined from the known values of coefficients *A*, *B*, *C*, *D*, *E*. The more accurate values of the constants obtained by nonlinear regression are as follows: $k_1 = 3{\cdot}87 \cdot 10^{-12}$ mol s^{-1} g^{-1} Pa^{-2}, $k_2 = 2{\cdot}57 \cdot 10^{-14}$ mol s^{-1} g^{-1} Pa^{-2}, $K_1 = 8{\cdot}63 \cdot 10^{-5}$ Pa^{-1}, $K_2 = 2{\cdot}12 \cdot 10^{-3}$ Pa^{-1}, $K_3 = 9{\cdot}38 \cdot 10^{-4}$ Pa^{-1}, $K_4 = 1{\cdot}40 \cdot 10^{-7}$ Pa^{-2}.

From the graphic illustration (Figs 4*a*, *b*, *c*) of the dependences of R_A on propene conversion x_P it is evident that Eq. (7) represents well the experimentally found values of R_A both for the reaction mixtures with propene in feed and for reaction

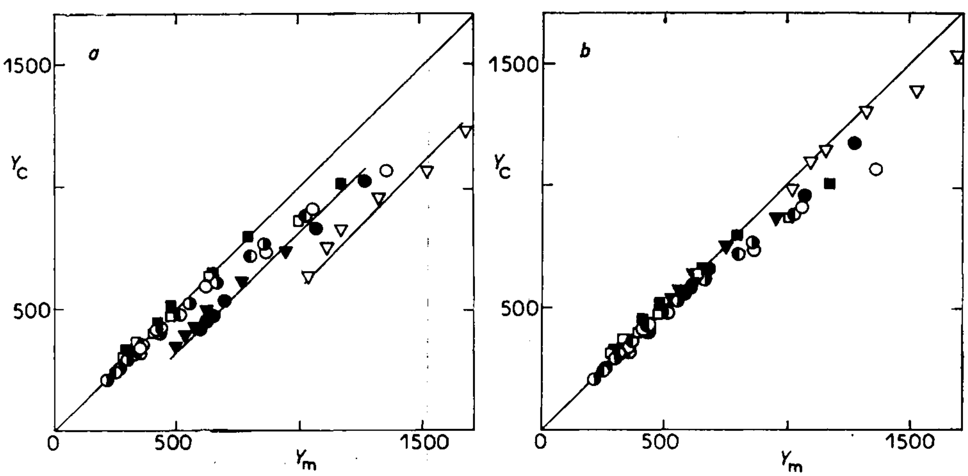


FIG. 3

Dependence of the left-hand side of Eq. (*6*), denoted by Y_m ($s^{1/2}$ $g^{1/2}$ $mol^{-1/2}$), on the right-hand side of Eq. (*6*), denoted by Y_c (the same dimension), for oxidation of propene to acrolein (for point symbols see Fig. 2). *a* without correction for initial partial pressure of acrolein; *b* after inserting correction for initial partial pressure of acrolein mixtures with acrolein and acrylic acid in feed, and describes as well the measured data for the separate oxidation of acrolein to acrylic acid (Fig. 5). The accurate form of equation for the reaction rate R_2 allows to determine the values of reaction rates $R_3 = R_K - R_2$ from the total reaction rate of formation of acrylic acid R_K. On the basis of found knowledge, several forms of rate equations for R_3 were

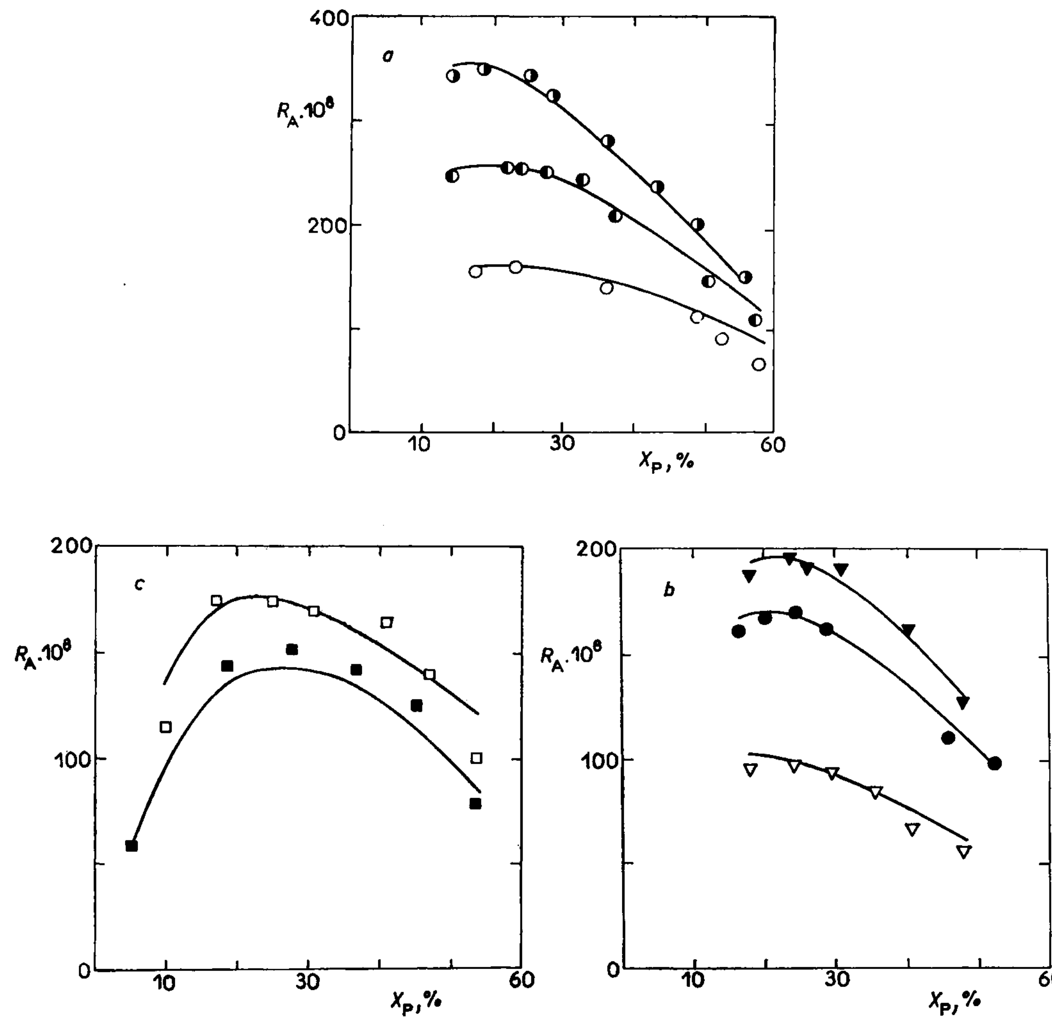


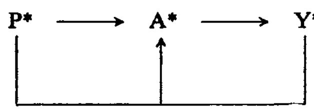
FIG. 4

Dependence of the total reaction rate of acrolein formation R_A on propene conversion (for point symbols see Fig. 2). *a* with propene in feed; *b* with propene and acrolein in feed; *c* with propene and acrylic acid in feed proposed whose validity was preliminary verified by linearizing and plotting. The total rate of formation of acrylic acid R_K is described best by the equation

$$R_K = k_2 \,.\, p_A^2/(1 + K_1 p_P + K_2 p_K + K_3 p_A + K_4 p_P \,.\, p_A^0) + k_3 \,.\, p_P \,.\, p_A/ /(1 + K_1 p_P + K_2 p_K + K_3 p_A + K_4 p_P \,.\, p_A^0)^3 \,. \qquad (8)$$

Equation (*8*) was subjected to nonlinear regression (by simplex method), the optimum value of constant k_3 being sought (the remaining constants firmly given – see constants of Eq. (7)). The found constant k_3 has the value of $6{\cdot}49 \,.\, 10^{-13}$ mol . . s^{-1} g^{-1} Pa^{-2}. Agreement of Eq. (*8*) with the measured data is not so good as with Eq. (7). The reason is small accuracy of the determination of acrylic acid which is formed during the oxidation of propene at most up to 6%.

The suggestion of kinetic scheme of propene oxidation to acrolein stems from the found forms of rate equations for R_1, R_2, R_3. In the rate equation for R_1, the product $k_1 \,.\, p_P \,.\, p_A$ is a characteristic feature which gives evidence of autocatalytic character of the propene oxidation to acrolein. The autocatalytic character can be modelled by a block of two consecutive reactions with a side reaction of reactant and of final product with a slow first step[9]. The kernel of the scheme proposed forms an autocatalytic block of adsorbed propene P* and particle Y* in the form (Scheme 2):



SCHEME 2

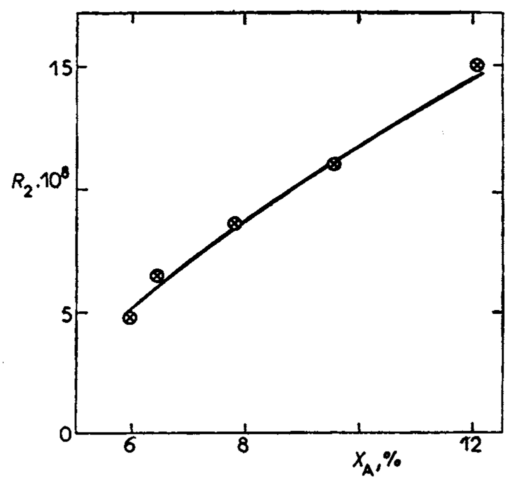
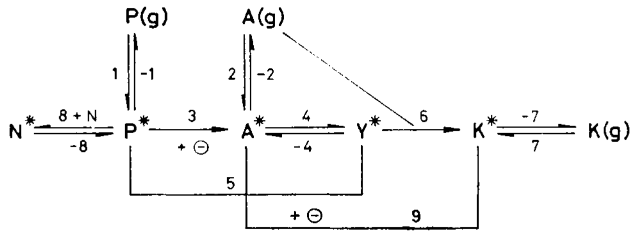


FIG. 5

Dependence of the total reaction rate of acrolein decrease R_2 on acrolein conversion x_A for oxidation of acrolein to acrylic acid

The found rate equations are to be interpreted by Scheme 3 whose kinetic equations, on the assumption of adsorption equilibria, lead to Eqs (7) and (*8*). Scheme 3 expresses also the fact that when feeding acrolein into the reaction mixture, a decrease of rate of acrolein formation occurs owing to an impurity N. The acrolein used was 95%, and higher purity has not been achieved even by repeated distillation on a multiplate column. In Scheme 3, asterisk denotes particles in adsorbed state.



SCHEME 3

Scheme 3 is based on the idea that propene is adsorbed on the catalyst surface and the adsorbed propene P* is formed. From P* arises in step 3, with the participation of free active centre of catalyst$^{\ominus}$, adsorbed acrolein A* being in equilibrium with the particle Y* which is able together with adsorbed propene to form additional acrolein A* (step 5). Acrylic acid is formed partly by the consecutive reaction (step 6) when particle Y* reacts with acrolein A in gaseous state and partly by the side reaction (step 9). Chemical interpretation of particles P*, A*, Y* is discussed in another work[10].

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