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177. Kinetics of Ethylene Oxidation on a Supported Silver Catalyst

by **Hans Rudolf Dettwiler, Alfons Baiker** and **Werner Richarz**

Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule, CH-8092 Zürich

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Summary

The kinetics of ethylene oxidation by air over a supported silver catalyst were investigated in the temperature range 490-620 K. The reaction network was found to be triangular. Under virtually constant oxygen partial pressure (0.2 bar), the following rate relationships, (in mol $g^{-1}s^{-1}$) were found: (formulae in curved brackets denote partial pressures)

$$r_1 = k_1 \frac{(C_2H_4) \cdot K_{C2H4}}{1 + (C_2H_4) \cdot K_{C2H4}} \qquad C_2H_4 + \tfrac{1}{2}\,O_2 \xrightarrow{k_1} C_2H_4O$$

$$r_2 = k_2 \frac{(C_2H_4) \cdot K_{C2H4}}{1 + (C_2H_4) \cdot K_{C2H4}} \qquad C_2H_4 + 3\,O_2 \xrightarrow{k_2} 2\,CO_2 + 2\,H_2O$$

$$r_3 = k_3\,(C_2H_4O) \qquad C_2H_4O + 5/2\,O_2 \xrightarrow{k_3} 2\,CO_2 + 2\,H_2O$$

where:

$$k_1 = 40.69 \exp\left[-\frac{76\,970}{R \cdot T}\right], \quad [\mathrm{mol} \cdot g^{-1} \cdot s^{-1}]\, T > 490\ K;$$

$$k_2 = 1.34 \exp\left[-\frac{63\,070}{R \cdot T}\right], \quad [\mathrm{mol} \cdot g^{-1} \cdot s^{-1}]\, T > 490\ K;$$

$$k_3 = 9.51 \cdot 10^3 \exp\left[-\frac{85\,280}{R \cdot T}\right], \quad [\mathrm{mol} \cdot g^{-1} \cdot s^{-1} \cdot bar^{-1}]\, T > 530\ K;$$

$$K_{C2H4} = 1.84 \cdot 10^{-4} \exp\left[\frac{53\,550}{R \cdot T}\right], \quad [bar^{-1}]$$

R is expressed in $J \cdot mol^{-1} \cdot K^{-1}$.

The given rate expressions are discussed in the framework of earlier kinetic investigations.

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Introduction. - Since *Lefort*'s original description of the process [1], the oxidation of ethylene has been the subject of numerous investigations [2] [3]. The reported kinetic equations extend from empirical correlations to complicated rate equations, mostly of the *Langmuir-Hinshelwood* type. Some of these equations account for the observed inhibiting effect of reaction products. Differences in the reported kinetic equations and mechanism are primarily due to opposing opinions about the type of chemisorbed oxygen present at the catalyst surface and to the different kinds of supported or unsupported silver catalysts which were used for the investigations. The result of these various individual efforts is therefore not a generally accepted rate equation but a variety of relationships, valid under the conditions reported. In the present work, we studied the kinetics of ethylene oxidation over a supported silver catalyst in the temperature range 490-620 K and in the presence of excess oxygen.

Experimental. - *Apparatus.* The apparatus *(Fig. 1)*, which was used for the kinetic measurements, consisted of a gas metering system, a Pyrex U-tube reactor (i.d. 1 cm) and a gas chromatograph (*Carlo Erba,* Mod. Fractovap 2200) equipped with a HW-detector and a sample valve. The reactor tube was thermostated by a temperature controlled silicon oil bath.

Analysis. The GC. analysis was carried out by means of a *Porapak* S Column (1 m×4 mm). Column temperature was 100° and helium flow rate 0.68 $cm_s^3 s^{-1}$. Calibration was carried out with each species.

Catalyst. This was prepared by impregnation of pumice particles of 0.75 mm average diameter: 60 g lactic acid (90%) was heated to 80° on a water bath. 20 g silver oxide *(Fluka AG)* and 0.5 cm^3 H_2O_2 (30%) were then added in small portions to the continuously stirred solution. After the silver oxide had dissolved completely the solution was diluted with 50 cm^3 distilled water. The impregnation was carried out with the above solution in a rotating evaporator containing 200 g of pumice. After impregnation the excess liquid was removed and the particles were cooled. To decompose the silver lactate the catalyst was then slowly heated to 400° under nitrogen. After 20 h the catalyst was removed from the furnace, cooled in a nitrogen flow and weighed. No further treatment was given to the catalyst before its use in the reactor. The catalyst had the following properties: silver content, *ca.* 8%; specific BET-surface, 1.6-2 m^2 g^{-1}; specific pore-volume, 0.452 cm^3 g^{-1}; mean pore diameter, $7 \cdot 10^3$ nm;

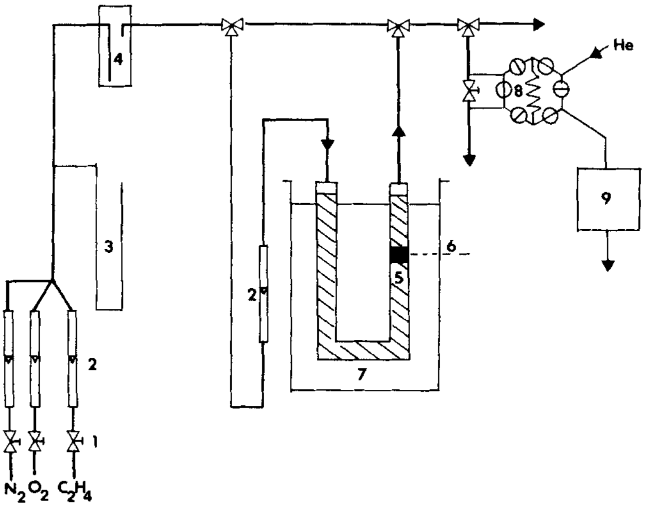

Fig. 1. *Apparatus*
1 low flow valves
2 flow meters
3 manometer
4 drying unit
5 reactor
6 thermocouple well
7 oil bath
8 sampling valve
9 gas chromatograph

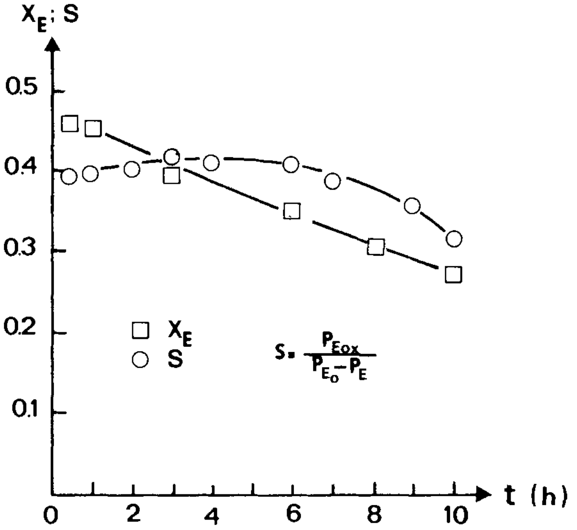

Fig. 2. *Long term behaviour*
T = 573 K
$(C_2H_4) = 0.03$ bar
$(O_2) = 0.2$ bar

apparent density, 1.18 g cm^{-3}; true density, 1.68 g cm^{-3}. Mean pore diameter and specific pore volume have been determined by the mercury penetration method.

Procedure. Before starting with the experimental runs, the reactor temperature was adjusted to a given value. Gas samples were taken approximately 20 to 30 min after setting the desired flow rates. The mol fractions of ethylene oxide and carbon dioxide in the product stream were obtained from the chromatogram with the aid of calibration curves. The concentration of water was assumed to be equal to the measured concentration of carbon dioxide. Average reaction rates were calculated, based on the assumption of a differential reactor (conversion $\leqslant$ 10%). The calculated reaction rates are therefore assumed to correspond to the average partial pressures of reactants and products in the reactor. Temperature gradients were small enough to be neglected.

Results. - *Long term behaviour, mass transfer and reaction network.* The long term behaviour of the catalyst was tested during preliminary runs. *Figure 2* shows the declining activity and selectivity observed during these experiments. The kinetic measurements were carried out in the first min, where the activity and selectivity could be assumed to be approximately constant (loss of activity less than 3%).

Figure 3 shows the measured selectivity as a function of gas flow rate and temperature at constant contact time. The selectivity increases with increasing gas flow rates, but with flow rates greater than 45 $cm_s^3 s^{-1}$ (Re_d[1]) $\geq$ 10.5) the influence becomes very small. In order to avoid the disguise of the kinetic measurements by gas flow rate influences, all experiments were carried out with a gas flow rate of 45 $cm_s^3 s^{-1}$. The absence of mass transfer limitation of the reaction under the conditions of the kinetic experiments was assured by applying the test criterion of *Mears* [4]. The estimated *Damköhler* number amounted to Da = 0.053 at 670 K and indicated that the reaction was not limited by mass transfer (Da $\ll$ 1).

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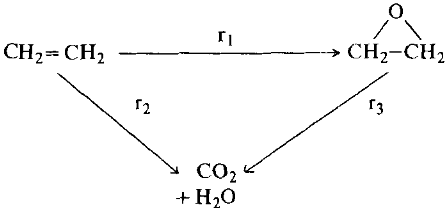
[1] Re_d is the *Reynolds* number referred to the catalyst particle diameter: $Re_d = m^* \cdot d/\mu$, where m^* = mass flow rate per unit cross-sectional area, d = catalyst-particle diameter and μ = dynamic viscosity.

Figure 4 showing selectivity *versus* conversion, substantiates that with the catalyst used the following reaction network has to be considered.



Kinetics. For the quantitative kinetic analysis, only those experimental runs where ethylene conversion was less than 10% were used for the determination of the reaction rates. The differential reactor experiments were evaluated by means of the following relationship: $r_i = -\frac{1}{w}\cdot\frac{\Delta N_i}{\Delta t} = -\frac{1}{w}\cdot\Delta N_i^* = \frac{1}{w}\cdot N_i^*\cdot X_i$ where r_i reaction rate (mol $s^{-1}g^{-1}$), w catalyst weight (g), N_i^* molar flow rate (mol s^{-1}), X_i conversion (–).

Figure 5 shows the measured rate of ethylene consumption as a function of the ethylene partial pressure at different temperatures and under virtually constant oxygen partial pressure (0.2 bar). A first order dependence of the ethylene reaction rate on oxygen partial pressure in the temperature range 493-623 K is indicated in *Figure 6.*

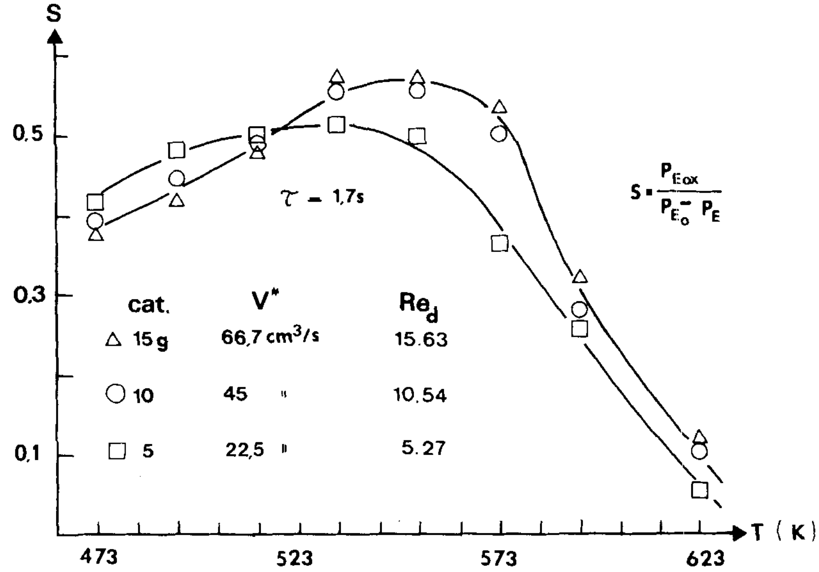


Fig. 3. *Selectivity* versus *gas flow rate and temperature at constant contact time* $\tau = V/V^*$. V = volume of fixed bed, V^* = gas flow rate; (C_2H_4) = 0.03 bar; (O_2) = 0.2 bar

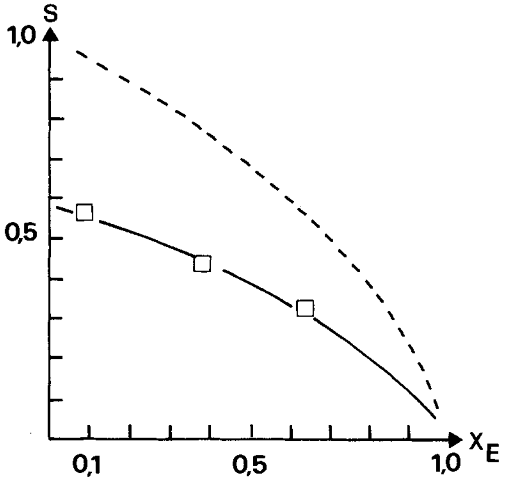


Fig. 4. *Selectivity* versus *conversion*
T = 523 K (--- expected dependence of S on X_E in the case of pure consecutive reaction)

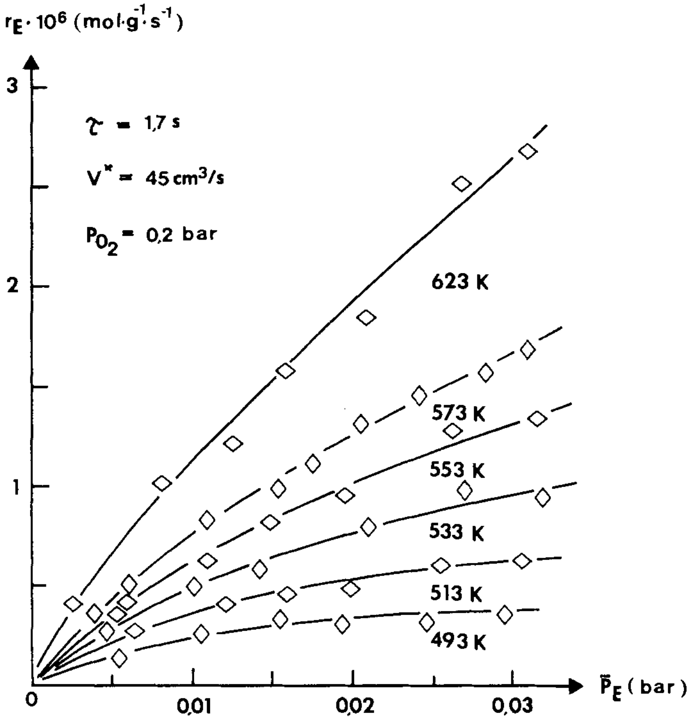


Fig. 5. *Measured rate of total ethylene consumption as a function of ethylene partial pressure and temperature*

The oxidation of ethylene oxide was studied separately and *Figure 7* shows the determined dependence of the rate on the ethylene oxide partial pressure. In the temperature range 533–623 K and under the given partial pressure conditions (excess oxygen), the rate r_3 was first order with respect to the ethylene oxide partial pressure.

$$r_3 = k_3(C_2H_4O). \tag{1}$$

The measured selectivity $S = \frac{(C_2H_4O)}{(C_2H_4)_0 - (C_2H_4)}$ for the oxidation of ethylene to ethylene oxide as a function of temperature is shown in *Figure 8*. The reaction rates r_1 and r_2 were derived assuming that the ethylene oxid formed by r_1 reacts further with rate r_3 and utilizing the measured selectivity S *(cf. Figure 8)* as well as the reaction rate obtained for total ethylene consumption r_E.

The determined reaction rates r_1 and r_2 are in accordance with the following relationships:

$$r_1 = k_1' \cdot (O_2) \frac{(C_2H_4) \cdot K_{C2H4}}{1 + (C_2H_4) \cdot K_{C2H4}} \tag{2}$$

$$r_2 = k_2' \cdot (O_2) \frac{(C_2H_4) \cdot K_{C2H4}}{1 + (C_2H_4) \cdot K_{C2H4}} \tag{3}$$

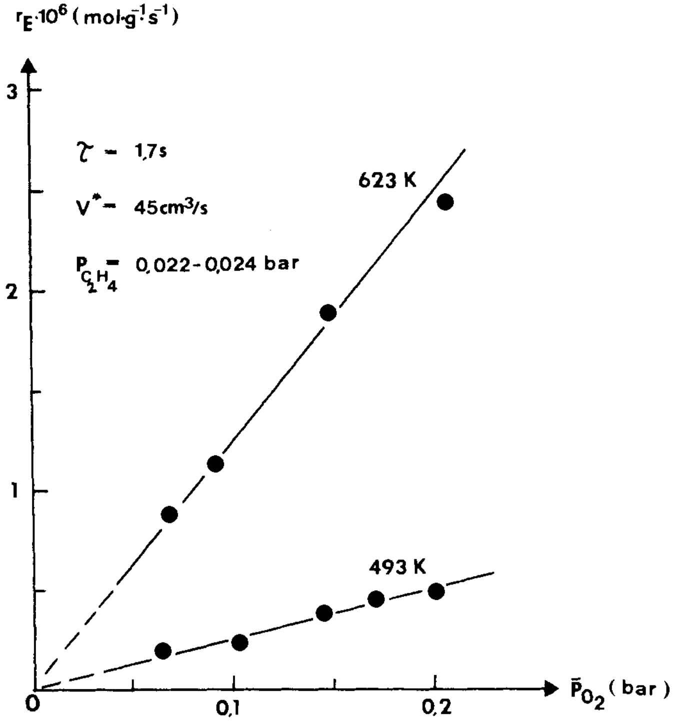


Fig. 6. *Dependence of the rate of total ethylene consumption on the oxygen partial pressure*

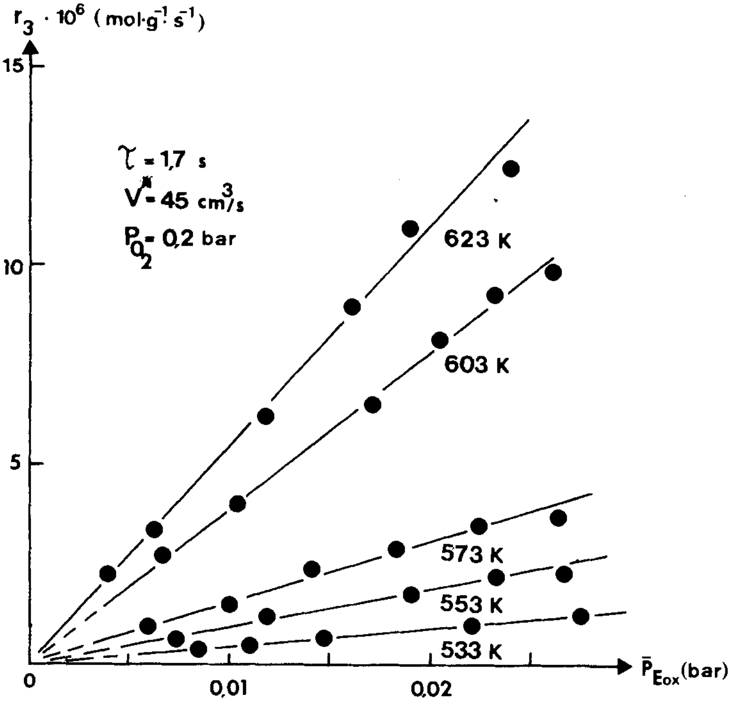


Fig. 7. *Rate of ethylene oxide oxydation as a function of ethylene oxide partial pressure and temperature*

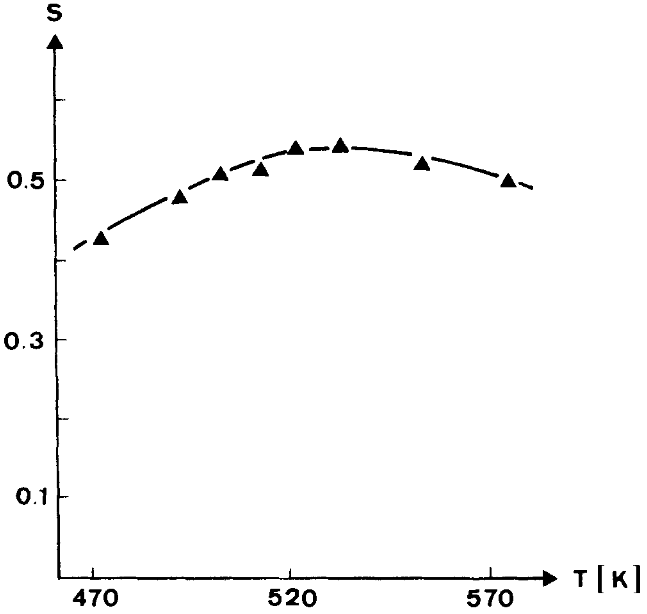


Fig. 8. *Dependence of Selectivity S on reaction temperature at low conversion* ($X_E \leq 0.1$)

where quantities between curved brackets denote partial pressures and K_{C2H4} (bar^{-1}) is the adsorption equilibrium constant of ethylene. The rate equations (2) and (3) correspond to a *Langmuir-Hinshelwood* expression with the assumptions: surface reaction controls, ethylene and oxygen are competing for different sites on the surface and oxygen is only weakly adsorbed.

$$r = k\,\theta_{C2H4} \cdot \theta_{O2} = k\,\frac{(C_2H_4) \cdot K_{C2H4}}{1+(C_2H_4) \cdot K_{C2H4}} \cdot \frac{(O_2) \cdot K_{O2}}{1+(O_2) \cdot K_{O2}}. \qquad (4)$$

With $1 \gg (O_2)K_{O2}$ equations (2) and (3) are obtained.

The assumption of ethylene and oxygen having affinity to different sites on the surface is well documented [11]. In the case of excess oxygen, (2) and (3) can

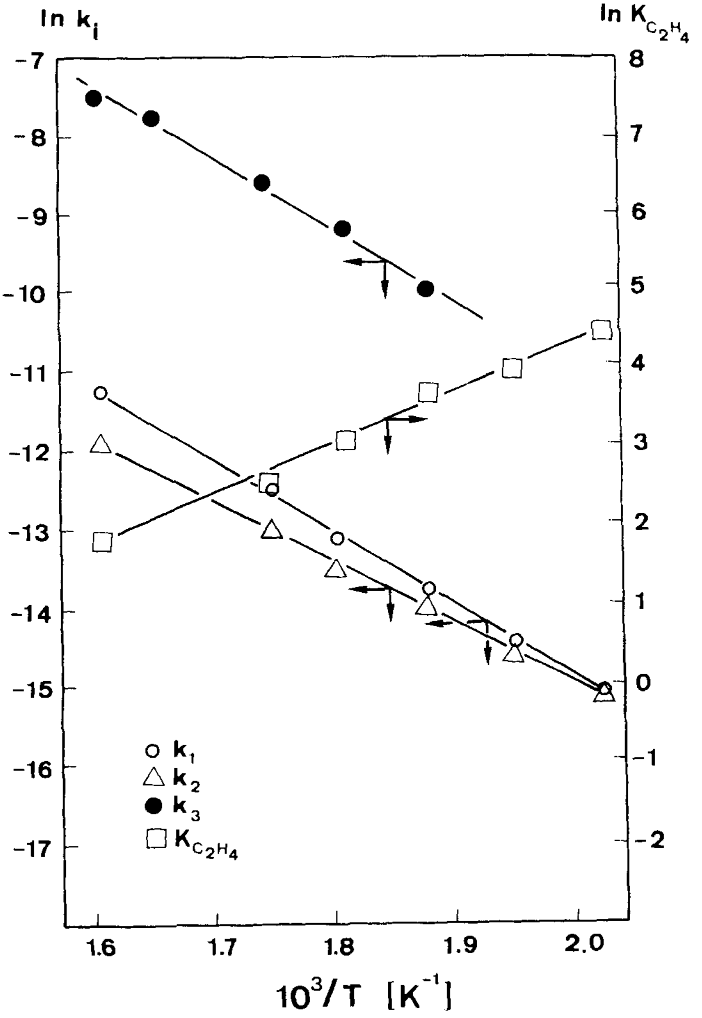


Fig. 9. *Temperature dependence of rate constants and adsorption equilibrium constant*

Table 1. *Rate equations for r_1*

Rate expression r_1	Reaction conditions	Activation Energy E_a Heat of adsorption Δq_0		Ref.
		E_a kJ mol^{-1}	Δq_0 kJ mol^{-1}	
$k(C_2H_4)$	$(C_2H_4) = 0.0134$-0.0536 bar $(O_2)_{air} = 0.0402$-0.1609 bar Cat: Ag/glass wool fibers $T = 536$ K	67	-	[5]
$k(O_2)$	$(C_2H_4) = 0.0204$-0.18 bar $(O_2)_{air} = 0.21$-0.176 bar Cat: Ag(Ba)/ Carrier not specified $T = 497$-547 K	50	-	[6]
$k(C_2H_4)^{0.3}(O_2)^{0.7}$	$(C_2H_4) = 0.92$-0.153 bar $(O_2) = 0.11$-0.866 bar Cat: Ag(Ba)/Alumina $T = 513$-533 K	81	-	[7]
$k(O_2)$ $((O_2) > 0.1$ bar$)$	$(C_2H_4) = 0.1$-0.8 bar $(O_2) = 0.2$-0.6 bar Cat: Ag(Ba)/Korund $T = 513$ K	82	-	[8]
$k(C_2H_4)^{0.5}$	$(C_2H_4) = 0.0016$-0.054 bar $(O_2)_{air} = 0.213$-0.202 bar Cat: Ag/Alumina $T = 523$-573 K	36	-	[9]
$k(O_2)$	$(C_2H_4) = 0.561$ bar $(O_2) = 0.0966$ bar Cat: Ag/Alumina $T = 448$-523 K	-	-	[10]
$\sim k(C_2H_4)(O_2)^{3/2}$	$(C_2H_4) = 0.026$-1.32 bar $(O_2) = 0.061$-1.32 bar Cat: Ag/Alumina $T = 493$ K	-	-	[11]
$\sim k(C_2H_4)(O_2)^{3/2}$(low$(O_2)$) $k(C_2H_4)(O_2)^{-0.3}$(high(O_2))	$(C_2H_4) = 0.026$-0.062 bar $(O_2) = 1.31$-13.1 bar Cat: Ag/Alumina $T = 493$ K	-	-	[12]
$k(C_2H_4)^{-0.03}(O_2)^{0.91}$	$(C_2H_4) = 0.1$-0.9 bar $(O_2) = 0.1$-0.9 bar Cat: Ag precipitated $T = 494$ K	-	-	[13]
$k \cdot \frac{K_{C_2H_4}(C_2H_4)}{1 + K_{C_2H_4}(C_2H_4)}$	$(C_2H_4) = 0.002$-0.03 bar $(O_2) = 0.05$-0.2 bar Cat: Ag/Pumice $T = 493$-623 K	77	54	present work

Table 2. *Rate equations for r_2*

Rate expression r_2	Reaction conditions	Activation Energy E_a Heat of adsorption Δq_0		Ref.
		E_a kJ mol^{-1}	Δq_0 kJ mol^{-1}	
$k(C_2H_4)$	$(C_2H_4) = 0.0134–0.056$ bar $(O_2)_{air} = 0.0402–0.1609$ bar Cat:Ag/glass wool fibers T = 536 K	67	–	[5]
$k(O_2)$	$(C_2H_4) = 0.0204–0.18$ bar $(O_2)_{air} = 0.21–0.176$ bar Cat:Ag(Ba)/Carrier not specified T = 497–547 K	63	–	[6]
$k \cdot \frac{K_{O_2}(O_2)}{1+K_{O_2}(O_2)}$	$(C_2H_4) = 0.1–0.8$ bar $(O_2) = 0.2–0.8$ bar Cat:Ag(Ba)/Korund T = 533 K	138	80	[8]
$k(C_2H_4)^{0.25}$	$(C_2H_4) = 0.0016–0.134$ bar $(O_2) = 0.213–0.186$ bar Cat:Ag/Alumina T = 433–493 K	31	–	[9]
$k(O_2)$	$(C_2H_4) = 0.561$ bar $(O_2) = 0.0966$ bar Cat:Ag/Alumina T = 448–523 K	–	–	[10]
$\sim k(C_2H_4)(O_2)^2$	$(C_2H_4) = 0.026–1.32$ bar $(O_2) = 0.061–1.32$ bar Cat:Ag/Alumina T = 493 K	–	–	[11]
$\sim k(C_2H_4)(O_2)^{3/2}$(low$(O_2)$) $k(C_2H_4)(O_2)^{-0.3}$(high(O_2))	$(C_2H_4) = 0.026–0.062$ bar $(O_2) = 1.31–13.1$ bar Cat:Ag/Alumina T = 493 K	–	–	[12]
$k(C_2H_4)^{-0.2}(O_2)^{1.1}$	$(C_2H_4) = 0.1–0.9$ bar $(O_2) = 0.1–0.9$ bar Cat:Ag precipitated T = 494 K	–	–	[13]
$k \cdot \frac{K_{C_2H_4}(C_2H_4)}{1+K_{C_2H_4}(C_2H_4)}$	$(C_2H_4) = 0.002–0.03$ bar $(O_2) = 0.05–0.2$ bar Cat:Ag/Pumice T = 493–623 K	63	54	present work

be simplified by considering the oxygen partial pressure as a constant according to $k_i = k'_i\,(O_2)$ leading to the equations:

$$r_i = k_i \frac{(C_2H_4) \cdot K_{C2H4}}{1 + (C_2H_4) \cdot K_{C2H4}} \tag{5}$$

where i = 1 and 2.

From the evaluated kinetic data, we obtained the following *Arrhenius* relationships for the three reaction rate constants: $k_1 = 40.69 \cdot \exp\,[-76\,970/R \cdot T]$, $[\mathrm{mol} \cdot \mathrm{g}^{-1} \cdot \mathrm{s}^{-1}]$; $k_2 = 1.34 \cdot \exp\,[-63\,070/R \cdot T]$, $[\mathrm{mol} \cdot \mathrm{g}^{-1} \cdot \mathrm{s}^{-1}]$; $k_3 = 9.51 \cdot 10^3 \cdot \exp\,[-85\,280/R \cdot T]$, $[\mathrm{mol} \cdot \mathrm{g}^{-1} \cdot \mathrm{s}^{-1}\,\mathrm{bar}^{-1}]$; where R is expressed in $\mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$.

The adsorption equilibrium constant K_{C2H4} was estimated by a non linear least square regression method and was in accordance with:

$$K_{C2H4} = 1.84 \cdot 10^{-4} \cdot \exp\left[\frac{53\,550}{R \cdot T}\right].$$

The *Arrhenius* plots of k_1, k_2 and k_3 as well as a *Van't Hoff* plot of $K_{C_2H_4}$ are summarized in *Figure 9*.

Discussion. - *Tables 1-3* give a survey of the kinetic rate equations which have been reported for r_1, r_2 and r_3, respectively. Despite the variety of proposed rate equations, there are some general characteristics with respect to the present work.

Several investigators [5] [6] [10] [12] reported the same partial pressure dependence for both reaction rates, r_1 and r_2. Moreover r_1 and r_2 show apparent activation energies of almost the same magnitude [5] [6] [9]. Most investigators [5] [10]

Table 3. *Rate equations for r_3*

Rate expression r_3	Reaction conditions	Activation Energy E_a Heat of adsorption Δq_0		Ref.
		E_a kJ mol^{-1}	Δq_0 kJ mol^{-1}	
$k(C_2H_4O)$	$(C_2H_4) = 0.0134\text{-}0.0536$ bar $(O_2)_{air} = 0.0402\text{-}0.1609$ bar Cat:Ag/glass wool fibers T = 536 K	-	-	[5]
$k \cdot \frac{K_{C_2H_4O}(C_2H_4O)}{1 + K_{C_2H_4O}(C_2H_4O)}$	$(C_2H_4) = 0.2\text{-}0.5$ bar $(O_2) = 0.2\text{-}0.8$ bar Cat:Ag(Ba)/Korund T = 533 K	54	21	[8]
$k(C_2H_4O)(O_2)$	$(C_2H_4) = 0.02$ bar $(O_2)_{air} = 0.2058$ bar Cat:Ag/Carrier not specified T = 560 K	71-80	-	[14]
$k(C_2H_4O)^{0.5}$	$(C_2H_4) = 0.0016\text{-}0.054$ bar $(O_2) = 0.213\text{-}0.202$ bar Cat:Ag/Alumina T = 523-572 K	48	-	[9]
$k(C_2H_4O)$	$(C_2H_4) = 0.0128\text{-}0.0488$ bar $(O_2)_{air} = 0.2114\text{-}0.2046$ bar Cat:Ag/Alumina T = 473-558 K	-	-	[10]
$k(C_2H_4O)$	$(C_2H_4) = 0.005\text{-}0.025$ bar $(O_2) = 0.2$ bar Cat:Ag/Pumice T = 533-623 K	85	-	present work

[14] found first order dependence of r_3 on the ethylene oxide partial pressure. At low ethylene oxide partial pressures the rate expression reported by *Fognani & Montarnal* [8] can also be considered to be approximately first order with respect to ethylene oxide, because the ethylene oxide is reported to be only weakly adsorbed ($q_0 \sim 21$ kJ mol^{-1}).

The vast majority of the reported rate equations were derived without taking into account inhibition by the products and it is likely that some kinetic results were affected by inhibition, especially those where the kinetics were derived from measurements at higher conversion. The inhibition by the reaction products has been studied carefully by *Metcalf & Harriot* [12]. They reported a rapidly reversible inhibition effect by carbon dioxide and water, while the inhibition by ethylene oxide was found to be only slowly reversible. Although there are some similar characteristics in the reported rate equations, the derivation of the mechanisms on the basis of these kinetic investigations proved to be questionable and speculative. Some mechanisms which have been proposed on the basis of further information, as adsorption and tracer studies are discussed in references [3]. The best word on the question about mechanism will come only from investigations which identify the surface intermediate directly under reaction conditions, as has been done by *Force & Bell* [14].

Conclusion. - In the temperature range 490-620 K, catalytic oxidation over a supported silver catalyst is a triangular reaction network. In the investigated partial pressure range ($P_{C_2H_4} = 0.002$-0.03 bar and $P_{O_2} = 0.05$-0.2 bar) the partial oxidation to ethylene oxide and the total oxidation to carbon dioxide and water show the same partial pressure dependence and the apparent activation energies are almost of the same magnitude. The ethylene oxide oxidation rate is first order with respect to ethylene oxide. At low ethylene conversion ($X_E \leqslant 0.1$) the selectivity obtained with respect to ethylene oxide is about 0.55.

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