

KINETICS OF THE ADDITION OF TRICHLOROSILANE TO ACETYLENE CATALYSED BY CHLOROPLATINIC ACID ON POLYMER*

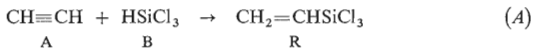
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A macroreticular styrene-divinylbenzene copolymer substituted with cyanomethyl group sorbs chloroplatinic acid from its aqueous solution, and the complex formed catalyses the addition of trichlorosilane to acetylene to give vinyltrichlorosilane. The catalyst containing 1.45% Pt was used to study the kinetics of this reaction at 100°C with the reactants in gaseous phase. Experimental initial reaction rates were correlated by equations derived for heterogeneous catalysed reactions. The addition of the product to the starting mixture resulted in a rate increase, instead of the expected rate decrease. The rate-enhancing effect of vinyltrichlorosilane affected also the dependence of the conversion on contact time, which resembles zero order reaction. Possible reasons of these anomalies in kinetic behaviour are discussed.

One of the catalysts for hydrosilylation of unsaturated organic compounds is chloroplatinic acid coordinated to polymers containing ligand groups¹⁻³. Within the framework of a systematic study of reactions of this type in the present work we were concerned with the kinetics of the addition of trichlorosilane to acetylene (equation (A)) on a catalyst which was prepared by sorption of chloroplatinic acid on a macroreticular styrene-divinylbenzene copolymer bearing cyanomethyl groups. The measurements were performed in an integral flow reactor with reactants in gaseous phase.



EXPERIMENTAL

Catalyst. The support was prepared from a chloromethylated macroreticular styrene-divinylbenzene copolymer (20% divinylbenzene, 0.5–1.5 mm balls, 16.7% Cl, 120 m²/g specific surface area, supplied by Výzkumný ústav syntetických pryskyřic a laků, Pardubice) by reaction with sodium cyanide⁴ in dimethylsulfoxide⁵. A mixture of 100 g of the copolymer and 50 g of NaCN was heated with 400 ml of dimethylsulfoxide in a boiling water bath. The balls were separated and washed with water. After drying they contained 2.6% Cl and 5.8% N (*i.e.* c. 80% conversion) and had a specific surface area of 142 m²/g. Then a solution of 10 g of chloroplatinic acid in

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150 ml of water was poured onto 100 g of the support and the mixture was allowed to stand for 16 h. After separation the catalyst was washed with water (no chloroplatinic acid was extracted), and the dried sample contained 1.45% Pt.

Reactants. Acetylene (pure) from a pressure cylinder was washed with sulphuric acid and passed through the tubes containing solid NaOH, activated carbon, and 5 A molecular sieve. Nitrogen was freed of traces of oxygen by copper and dried by 5 A molecular sieve. Trichlorosilane was a commercial preparation and was purified by distillation; it contained c. 0.1% lower boiling silanes, presumably H_2SiCl_2 .

Apparatus. A reactor was made of glass in the form of a cylinder of 12 mm i.d. and was equipped with a thermocouple well (4 mm o.d.). The catalyst bed had the form of a hollow cylinder with a height of about 2 cm per 1 g of the catalyst. The weighed amounts of the catalyst varied from 1 to 6 g. Trichlorosilane was fed from a temperature-controlled vessel by displacing it with mercury into a stream of acetylene. The temperature in the reactor varied by $\pm 2^\circ C$. The products were condensed at -30 to $-40^\circ C$ and their composition was determined by g.l.c. on a chromatograph with a thermal conductivity detector, hydrogen as a carrier gas (a 0.5 ml/s flow rate), and a column 1.2 m by 0.4 mm which was filled with 5% E 301 silicone elastomer on ground unglazed tiles. The amounts of individual components were determined quantitatively from heights of chromatographic peaks by the method of calibration curves.

Procedure. The catalyst was heated in the reactor in a stream of nitrogen to $130^\circ C$ and kept at this temperature for 1 h. The temperature was decreased to the reaction temperature and the catalyst was heated for another 1 h in a stream of acetylene. Then trichlorosilane was fed into

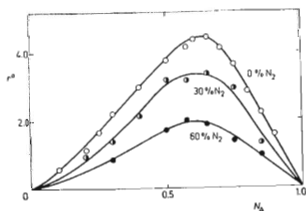


FIG. 1

Dependence of Initial Reaction Rate r^0 (mol/h kg) on the Composition of Feed and on its Dilution by Nitrogen

$N_A = p_A^0 / (p_A^0 + p_B^0)$, A acetylene, B trichlorosilane.

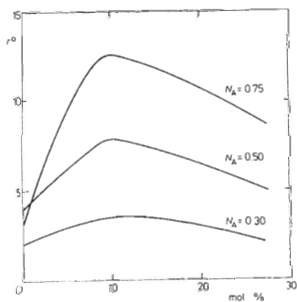


FIG. 2

Dependence of Initial Reaction Rate r^0 (mol/h kg) on the Addition of Vinyltrichlorosilane to Trichlorosilane (in mol %) for Varying Ratios of Trichlorosilane (A) to Acetylene (B)

$$N_A = p_A^0 / (p_A^0 + p_B^0)$$

the reactor. The first portion of the product was discharged and a further portion collected over a 20 min period was analysed. Each day the activity of the catalyst was tested by the experiment carried out under standard conditions, and the ratio of the found to an arbitrarily chosen standard conversion was used as a correction factor for calculating experimental conversions. In this way the errors arising from varying activity of different catalyst samples or from loss of catalytic activity during the measurements were suppressed.

Treatment of data. The values of initial reaction rates r^0 were determined as a ratio of the achieved conversion to the reciprocal space velocity of reaction component W/F_B at a given value of the initial partial pressures of reaction components (p_A^0, p_B^0) at 100°C. In Fig. 1 are the dependences of the initial reaction rates on the trichlorosilane to acetylene ratios with different dilutions by nitrogen, which was used to decrease the total pressure. These 28 sets of the values $r^0 - p_A^0 - p_B^0$ were treated by a combination of a linear and non-linear regression⁶ to verify the suitability of the assumed equations.

RESULTS AND DISCUSSION

A set of initial reaction rates of the addition of trichlorosilane to acetylene at varying partial pressures of reactants was confronted with 30 different rate equations of the three types: with the power equation, with the equations of Langmuir-Hinshelwood kinetics, and with the equations of the so-called redox model⁷. On the basis of the sums of squared deviations S of nonlinear regression from experimental reaction rates, the following six expressions were selected as the best ones:

$$S = 6.17 \quad r^0 = kK_A K_B p_A^0 p_B^0 / (1 + K_A p_A^0 + K_B p_B^0)^4, \quad (1)$$

$$S = 6.21 \quad r^0 = kK_A K_B p_A^0 p_B^0 / (1 + K_A p_A^0 + K_B p_B^0)^3, \quad (2)$$

$$S = 6.32 \quad r^0 = kK_A K_B p_A^0 p_B^0 / (1 + K_A p_A^0 + K_B p_B^0)^2, \quad (3)$$

$$S = 7.20 \quad r^0 = k_1 k_2 p_A^0 p_B^0 / (k_1 p_A^0 + k_2 p_B^0), \quad (4)$$

$$S = 7.38 \quad r^0 = kK_A K_B p_A^0 p_B^0 / [1 + \sqrt{(K_A p_A^0) + K_B p_B^0}]^4, \quad (5)$$

$$S = 7.41 \quad R^0 = kK_A K_B p_A^0 p_B^0 / [1 + \sqrt{(K_A p_A^0) + K_B p_B^0}]^3. \quad (6)$$

In these equations, in which constants k , k_1 , and k_2 denote rate constants and K_A and K_B denote adsorption coefficients, five expressions correspond to the Langmuir-Hinshelwood model (Eqs (1), (2), (3), (5), and (6)). These equations all were derived under the assumption that surface reaction is the rate-determining step. They differ only in assumptions about the number of active centres participating in the rate-determining step and about the mode of adsorption of acetylene (with dissociation or in a molecular way). Eq. (4) corresponds to the redox model, and that in its simplest case⁸. Calculated values are summarized in Table I. Differences

Table I
Values of Constants of Eqs (1)–(6) for 100°C

Constant	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)
k (mol/h kg)	286.4	129.7	33.9	—	530.2	134.8
K_A (atm ⁻¹)	0.41	0.65	1.46	—	0.36	1.04
K_B (atm ⁻¹)	0.86	1.36	3.10	—	0.97	1.66
k_1 (mol/h kg atm)	—	—	—	10.4	—	—
k_2 (mol/h kg atm)	—	—	—	25.7	—	—

in fitting, expressed by values of S , are so small that none of the equations can be denoted as „best”, and therefore it is impossible to draw conclusions about the reaction mechanism from the shape of the curves. These equations are empirical expressions which describe satisfactorily the rate data.

In an additional step of kinetic analysis we wished to find how the reaction rate is influenced by the presence of the product, vinyltrichlorosilane. We therefore made a series of experiments in which the reactor was fed with a mixture of trichlorosilane and vinyltrichlorosilane, and again conversions of trichlorosilane not exceeding 10% were measured. The result was surprising. Instead of the expected decrease in the reaction rate due to competitive adsorption of the product on active sites, we observed the acceleration of the reaction. This effect is apparent from Fig. 2 where the dependences of the reaction rate on the amount of the product in the feed are graphically represented for varying ratios of acetylene to trichlorosilane. The values

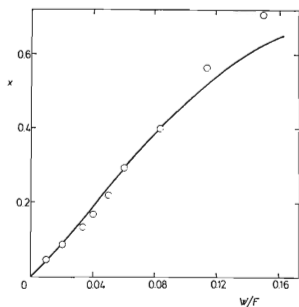


FIG. 3
Dependence of Conversion of Trichlorosilane on Reciprocal Space Velocity of Trichlorosilane W/F (kg h/mol) at 100°C and $p_A^0 = 0.67$ atm, $p_B^0 = 0.33$ atm, $p_R^0 = 0$.

required for these dependences were obtained by interpolation from less distinct dependences for the constant p_A^0/p_R^0 ratio, and that is why points were omitted in Fig. 2. The curves pass through a maximum, which is due to rate acceleration at low concentrations and rate retardation at the higher ones. This effect cannot be described by any equation of the Langmuir-Hinshelwood type extended by a corresponding adsorption term $K_R p_R$ for the product. The same is valid also for Eq. (4). We have therefore assumed that the product changes the properties of the catalytically active complex on the surface of the polymer, which is a platinum compound, for example by its equilibrium coordination as one of the ligands. In such a case there are two complexes on the surface, initial and modified, and their ratio is determined by the partial pressure of the product. We have therefore introduced the term $(1 + K_{PR})$ to Eqs (1) – (6) as a factor modifying some rate constant or some adsorption coefficient. The best (although not quite satisfactory) agreement of experimental with calculated rate constants for the feed containing the product was obtained with a modified equation (4), in which the above factor was multiplied by constant k_1 :

$$r^0 = k_1 k_2 (1 + K_{PR}^0) p_A^0 p_B^0 / [k_1 p_A^0 (1 + K_{PR}^0) + k_2 p_B^0] \quad (7)$$

The lowest sum of squared deviations for 27 experiments and for the values of k_1 and k_2 listed in Table I was obtained for $K = 99 \text{ atm}^{-1}$ with $S = 148$. With other equations, the value of S was several times greater. To further verify Eq. (7), we made measurements in an integral reactor at 100°C with the feed containing acetylene and trichlorosilane in a 2 : 1 ratio at varying space velocity. The results are in Fig. 3 (points), the curve is the integral conversion curve calculated from Eq. (7). The points lie nearly on the line, which confirms the rate-accelerating effect of the product. The agreement of the points with the curve is satisfactory, except in the region of higher conversions. We believe that since the addition is strongly exothermic in this region the conversion was increased due to overheating of the catalyst bed. A rate acceleration of a catalytic reaction by the effect of a product indicates a complex mechanism and has been observed in several cases of homogeneous, or "heterogenized" homogeneous catalysis^{9,10}. A satisfactory explanation has not yet been suggested. Although a certain formal description is possible in our case, no reliable conclusions about the mechanism of the action of the product can be made. The course of the points in Fig. 3 resembles a reaction of zero order. This circumstance was used to estimate the apparent activation energy, by putting directly into the Arrhenius equation the conversions obtained at constant composition of the feed and at constant space velocity at 80, 100, 120, and 140°C . The rate acceleration with temperature was small. In this way the apparent activation energy was found to be $4.4 \text{ kcal mol}^{-1}$.

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