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Abstract

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STUDY OF THE KINETICS OF BIMOLECULAR CHEMICAL REACTIONS BY THE PULSE CHROMATOGRAPHIC METHOD

(Presented by Academician V. N. Kondrat’ ev, March 10, 1964)

Recently a method has been proposed for carrying out chemical reactions in a "chromatographic regime" (1,2,3), in which chromatographic separation occurs along with the chemical reaction. It should be noted that the experimental data available in the literature refer only to monomolecular, predominantly catalytic, reactions. In the present work* for the study of a bimolecular reaction by the pulse chromatographic method, one of the reactants was dissolved in a stationary liquid phase (it is also possible to pass a continuous flow of one of the reactants in the gas phase (4)), while the other was introduced in the form of a pulse at the reactor inlet.

(Figure: Fig. 1. General scheme of the chromatographic apparatus. —cylinder; $_1$ and $_2$ —katharometers; —sample-introduction device; —chromatographic column; —reactor; —recording instrument; —gas-flow-rate meter)

Fig. 1. General scheme of the chromatographic apparatus. —cylinder, $_1$ and $_2$ —katharometers, —sample-introduction device, —chromatographic column, —reactor, —recording instrument, —gas-flow-rate meter.

Since, in order to study the kinetics of chemical reactions, it is necessary to use pure compounds, in our work a scheme was used that differs from those described in the literature. Usually the chromatographic column follows the reactor and serves for analysis of the reaction products. In the proposed method the chromatographic column precedes the reactor and therefore makes it possible to study the kinetics of chemical reactions of compounds without first isolating them in pure form. The concentration of the reacting compounds is recorded by two independent detectors—before and after the reactor. In the work, ordinary chromatographic equipment was used (see the scheme in Fig. 1). The use of this scheme makes it possible to obtain the concentrations of the reacting compounds before and after the reaction and the time of their interaction. By varying the concentration of the second nonvolatile component, one can determine the order of the reaction with respect to this component and calculate the rate constant of the bimolecular reaction; this was not taken into account by the authors of work (8), who studied the reaction of a diene pulse with chloromaleic anhydride as the stationary phase only as a pseudo-first-order reaction. In the present work, the kinetics of the diene-synthesis reaction with maleic anhydride was studied for butadiene and isoprene.

The diene-synthesis reaction is practically irreversible for aliphatic dienes in the temperature range investigated (47—77°) (^{5}). The literature (^{6},^{7}) gives kinetic data obtained by measuring the vapor pressure of the reacting mixture for the diene-synthesis reaction with maleic anhydride as a second-order reaction.

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* The work was reported on December 29, 1963, at an expanded seminar at the Institute of Petrochemical Synthesis, Academy of Sciences of the USSR.

Maleic anhydride, in the form of a solution saturated at 45° in tricresyl phosphate (TCP), was applied to brick in an amount of 40% of the weight of the latter. The sorbent thus obtained was placed in a thermostated reactor. Tricresyl phosphate was used as the solvent in order to: 1) broaden the temperature range for studying the reaction kinetics (since maleic anhydride melts at 56° and sublimes noticeably already at 70°), and 2) increase the contact time of the reacting substances.

The concentration of maleic anhydride was 6.5 mol/liter, while the concentration of butadiene introduced into the reactor as a pulse was $\sim 1.5 \cdot 10^{-3}$ mol/liter. Thus, in a single experiment only 0.02% of the maleic anhydride is consumed. When highly sensitive detectors are used with a smaller sample, this value may reach $\sim 10^{-5}\%$, i.e., under these conditions even reversible reactions can be regarded as irreversible. Thus, the concentration of maleic anhydride in this series of experiments remains practically constant. Under conditions of constant maleic anhydride concentration, the expression for the reaction rate constant

$$k = \frac{\lg C_0/C}{C_{\mathrm{MA}} \cdot t}$$

and the diene-synthesis reaction will obey a first-order equation.

(Figure: Fig. 2)

Fig. 2. Dependence of the degree of conversion (S_1/S_2) of butadiene on the change in concentration of the stepwise chromatographic peaks (h_1/h_2). $t =$ 50.5; 60; 74°

(Figure: Fig. 3)

Fig. 3. Dependence of $\lg(h_1/h_2)$ on reaction time for butadiene at different temperatures

As is known [4], the degree of conversion for a first-order reaction is not sensitive to the shape of the pulse. Therefore, the change in pulse shape due to spreading in the reactor should not affect the degree of conversion. This proposition was shown experimentally in the present work by determining the degree of conversion from the areas of the peaks of the reacting compound and from the heights of the stepwise peaks (the latter were obtained as a result of equalization of concentrations in a vessel placed after the chromatographic column). As can be seen from Fig. 2, in both cases identical results were obtained. Therefore, subsequently the degree of conversion was determined as the ratio of peak areas (allowing for the different sensitivities of the two detectors), which is more convenient experimentally. The contact time was determined as the difference in the retention time of the diene before and after the reactor, taking into account the dead time of the reactor.

Figure 3 shows the dependence of $\lg h_1/h_2$ on contact time for the reaction of butadiene with maleic anhydride. These data refer to differ-

experimental conditions: carrier-gas flow rate, temperature, and amount of substance introduced. The straight-line dependences obtained confirm that, under conditions of constant maleic anhydride concentration, the reaction under consideration obeys a first-order equation with respect to the diene.

The proposed method also makes it possible to determine the reaction order with respect to maleic anhydride. For this purpose a series of experiments was carried out with different concentrations of maleic anhydride in tricresyl phosphate, and it was shown that the reaction order with respect to maleic anhydride differs from unity and, in the case of butadiene, is 1.2, while in the case of isoprene it is 0.8. Thus, for the first time the reaction order with respect to both components has been studied, and it has been shown that, when the reaction proceeds in a TKF solution, the reaction order differs from 2, contrary to the assumption of other authors ([6,7]).

(Figure: Fig. 4. Simplified scheme for measuring kinetic characteristics by the relative method. The designations are the same as in Fig. 1)

Fig. 4. Simplified scheme for measuring kinetic characteristics by the relative method. The designations are the same as in Fig. 1

On the basis of the data obtained, the activation energies and rate constants were calculated for the reaction of maleic anhydride with butadiene and isoprene. As follows from the data in Table 1, the activation-energy values measured by the pulse chromatographic method agree well with the literature data ([6,7]). The values of the rate constants differ from those given in the literature, but are of the same order of magnitude.

It should be noted that the kinetic parameters of the reaction can also be determined on a single chromatographic unit with one detector, if the concentration or amount of the reacting substance is determined relative to a nonreacting substance–standard–introduced into the mixture. The scheme of the chromatographic unit for this case is given in Fig. 4. In the first experiment, the relative amount of diene in the initial mixture is determined with the reactor switched off; in the second, the relative amount of diene is determined with the reactor switched on.

Table 1

Kinetic characteristics for the reactions of certain dienes with maleic

anhydride

Dienes	47.5°	49°	57°	59.6°	66°	68.3°	77°	Found	According to (10)
	Rate constants of reaction, l/mol·h	Activation energy, kcal/mol							
Butadiene	1.55		2.8		4.7		7.9	12 ± 0.8	11.7± 0.8
Isoprene		5.75		11.0		16.9		12.1± 1.0	12.2

The relative amounts of diene in the initial mixture without the reactor and with the reactor can be expressed, respectively, as $S_{01}/S_{1\text{ st}}$ and $S_{02}/S_{2\text{ st}}$ (where S_{01} and S_{02} are the areas of the chromatographic peak of the diene in measurements without the reactor and with the reactor; $S_{1\text{ st}}$ and $S_{2\text{ st}}$ are the areas of the chromatographic peak of the standard in the measurement. The rate constant of the reaction was calculated from the equation

$$k = \frac{\lg \dfrac{S_{01}/S_{1\text{ st}}}{S_{02}/S_{2\text{ st}}}}{C_{\text{ma}} t}.$$

By this same method we obtained the value of the activation energy for the reaction of isoprene with maleic anhydride, $E = 12.1$ kcal/mol.

Experimental study of the kinetics of the diene-synthesis reaction of maleic anhydride with isoprene and butadiene showed that the investigated

the reaction is first order with respect to the diene; however, with respect to maleic anhydride the reaction order differs from unity, which does not agree with the assumptions of other authors.

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