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APPLICATION OF CIRCULATION TECHNIQUES FOR STUDYING THE KINETICS OF CHEMICAL REACTIONS BY MEANS OF REACTION GAS CHROMATOGRAPHY

V. G. BEREZKIN AND V. E. SHIRYAEVA
Institute of Petrochemical Synthesis, Moscow (U.S.S.R.)

SUMMARY

The use of circulation arrangements is proposed for the study of homogeneous and heterogeneous chemical reactions by the pulse method. The Diels–Alder reaction of isoprene with maleic anhydride was studied by the pulse method in a circulation apparatus. The value of the activation energy obtained is in good agreement with previously published results.

INTRODUCTION

The application of gas chromatographic techniques to kinetic research has led to considerable progress in the study of chemical reactions and their mechanisms and kinetics. Pulse chromatographic methods offer valuable possibilities for studying reaction kinetics. The pulse method was first suggested by KOKES *et al.*[1]. The pulse method of investigating the kinetics of chemical reactions consists of injecting a portion of a volatile compound into the carrier gas flow at the entrance of the reactor column so that the changes in the concentration of this compound give information on the reaction that takes place in the reactor column. In pulse methods, the chemical reaction and its analysis are thus combined into a single method.

An important contribution to the development of chromatographic methods for investigating catalytic processes was made by ROGINSKII *et al.*[2], who brought attention to some features of chemical reactions in chromatographic reactors. GIL-AV AND HERZBERG-MINZLY[3] applied the direct pulse method to the study of reaction kinetics in the liquid phase when investigating the reaction of conjugated dienes with chloromaleic anhydride. Further development of this method made it possible to determine the sequence of the reaction steps with respect to the second non-volatile component, as well as the velocity constant of the bimolecular reaction[4]. A critical review with many methodological and technical suggestions has been published[5].

The present paper describes the use of a circulation arrangement of apparatus for studying the kinetics of chemical reactions. The idea of circulation arrangements was first developed by MARTIN[6], and a number of workers[7–9] further developed this method. The circulation arrangement makes it possible to use columns with only a small amount of the liquid phase or catalyst being investigated, to measure the kinetic parameters at lower temperatures, and to determine the degree of transformation for various durations of contact in a single experiment.

THEORETICAL

Fig. 1 shows schematically the change in the concentration of a volatile substance in the chromatographic reactor at three moments of time, t_1, t_2 and t_3, for use in studying the kinetics of liquid-phase irreversible reactions by the pulse method. A portion of the component A enters the chromatographic reactor, where a solution of the second non-volatile reagent B in a non-volatile solvent serves as the stationary liquid phase. The concentration of the second reagent, B, is one or two orders of magnitude higher than that of the volatile component, A($C_B \gg C_A$). This makes it possible to realize conditions under which the kinetics of volatile-component reactions are described by a first-order equation. Hence, during an experiment, it is possible to determine accurately and simply the concentration of substance A both before and after the reaction, the temperature of the experiment (reaction), the concentration of substance B and the duration of the reaction. These data are sufficient to enable the first-order rate constant, k, to be determined from the equation:

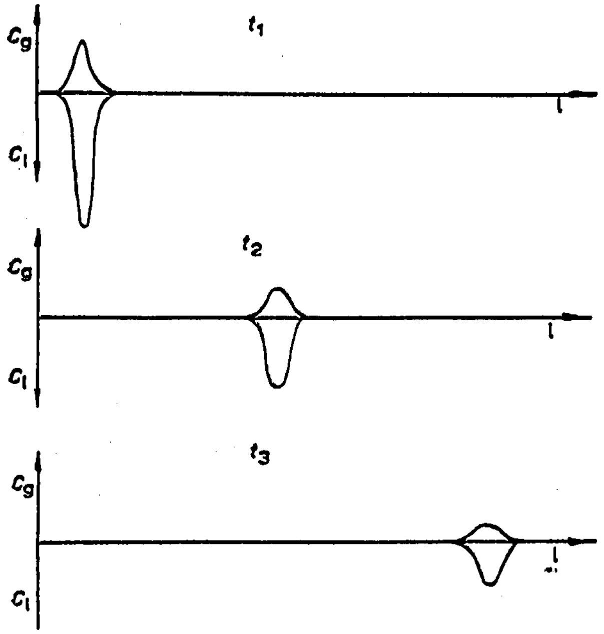


Fig. 1. Variation of reagent concentration with time in the chromatographic reactor. C_g = concentration of a volatile substance in the gaseous phase, C_l = concentration of a volatile substance in the liquid phase, l = length of a reaction layer.

$$k = \frac{2.3 \log\left(\frac{C_{0A}}{C_A}\right)}{C_B{}^n t}$$

where C_{0A} = initial concentration of component A; C_A = final concentration of component A; C_B = concentration of component B; t = duration of contact; and n = reaction order with respect to component B.

It should be noted that the results obtained in liquid-phase reactions are usually simpler to interpret, unlike heterogeneous catalytic reactions, and the kinetic characteristics obtained usually coincide with the results obtained under static conditions. The advantages of the chromatographic method have been shown earlier[10].

EXPERIMENTAL AND RESULTS

As an example of an application, the described method was applied to the study of the kinetics of the Diels–Alder reaction of isoprene with maleic anhydride. Under the conditions under consideration, this reaction proceeds in the kinetic-dependent region. The two columns (reactors) used for the reaction were connected into a circulation circuit (Fig. 2). An LHM-8M instrument with a thermal conductivity detector was used as a chromatograph. One of the reagents, maleic anhydride, was deposited on Chromosorb-P at a level of 15 % in the form of tricresyl phosphate solution saturated at 35°. Tricresyl phosphate was used as the solvent so as to extend the applicable temperature range of the reaction (as the melting point of the maleic anhydride is 55°) and to increase the duration of contact of the reactants. The concentration of the maleic anhydride in tricresyl phosphate was 0.358 g/ml at 35°. The prepared sorbent was placed in two thermostated reactors, each being a copper column 210 cm long and 0.2 cm in diameter. It was verified experimentally that during the time necessary to carry out a series of experiments at different temperatures, the concentration of the maleic anhydride in the liquid phase changed only to a negligible degree.

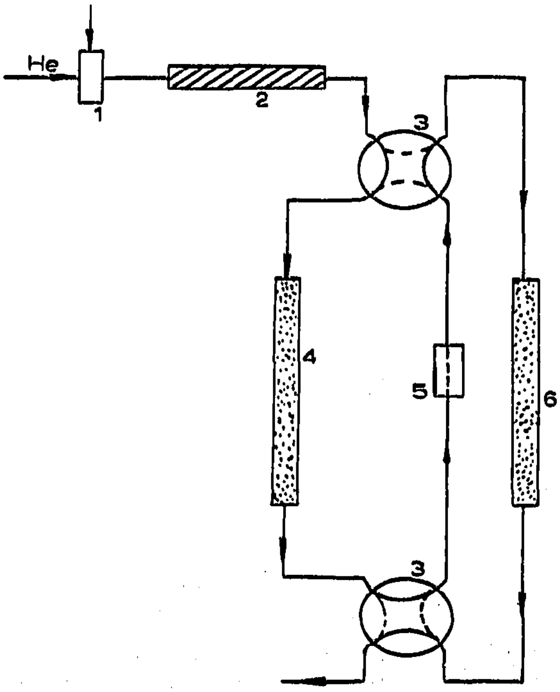
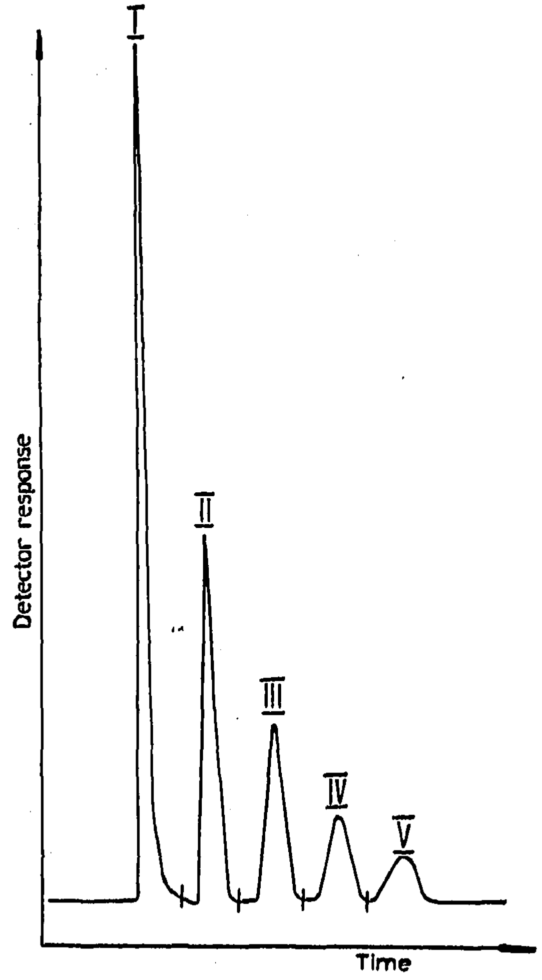


Fig. 2. Circulation arrangement for studying chemical reaction kinetics by the gas chromatographic technique. 1 = Sample injection device; 2 = separation column; 3 = eight-way tap; 4 = first reactor; 5 = indicating cell; and 6 = second reactor.

Isoprene was fed in pulses into the reactor inlet. The injected reactant can be separated from impurities by separation on a chromatographic column situated before the reactor. This eliminates the need for preliminary purification of the initial reagent.

A sample injection device (1) feeds a sample into the separation column (2), from which it enters the first reactor (4) through an eight-way tap (3). After passing through the first reactor, the sample enters the indicating cell (5) of the detector through the eight-way tap. When the detector readings indicate that the sample has completely passed from the first into the second reactor (6), the tap is switched into the position shown in Fig. 2 by dotted lines. After the second reactor (6), the sample again passes into the sensing cell of the detector, and then back into the first reactor (4). After this, the tap is again turned to its initial position and the cycle is repeated. Circulation may be continued until complete absorption of the diene has occurred.

A chromatogram obtained with isoprene after several single cycles is shown in Fig. 3. The course of the reaction was followed according to changes in chromatographic peak areas obtained after passing the reactants through the first reactor (this



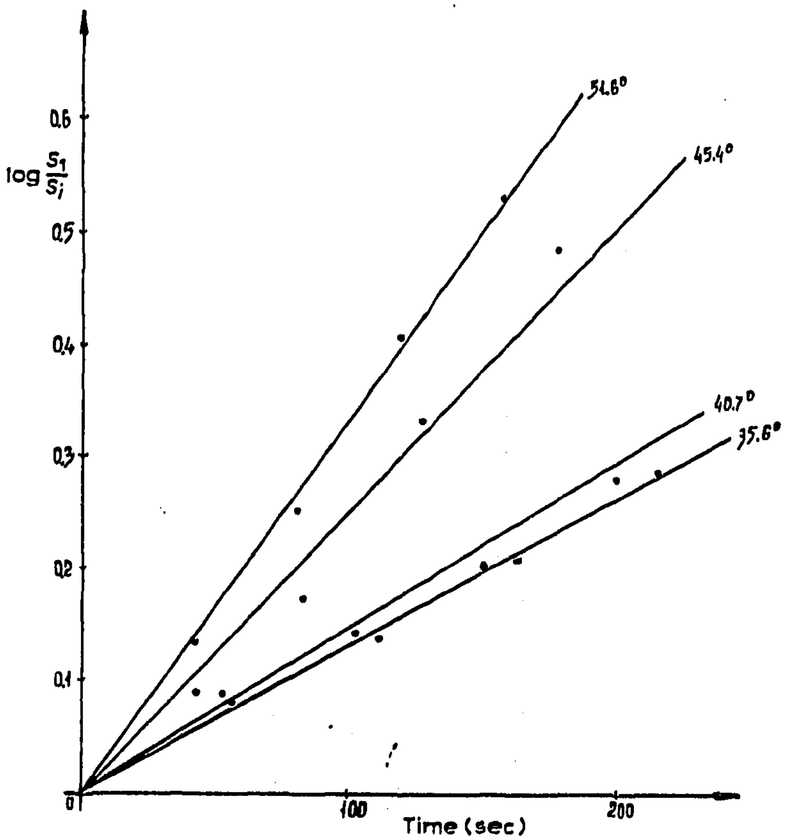


Fig. 3. Chromatographic trace for isoprene during five circulations. Peaks I–V are peaks of isoprene. The areas of the peaks are proportional to the concentration of isoprene after each circulation.

Fig. 4. Variation of log (S_1/S_i) with reaction time for isoprene at various temperatures. S_1 and S_i are isoprene peak areas after successive passages from the first to the ith column (reactor).

value was taken as the initial one). The contact time was determined as the net retention time of isoprene after passing through the first reactor ($t = 0$).

Fig. 4 shows relationships between $\log(S_1/S_t)$ and contact time for the reaction of isoprene with maleic anhydride. From the results obtained the velocity constant of this reaction can be calculated.

The activation energy of the reaction was calculated from the relationships between the velocity constants and temperature (Fig. 5) by the least-squares method.

Table I shows that the value of the activation energy obtained by the proposed method is in good agreement with the published value[11].

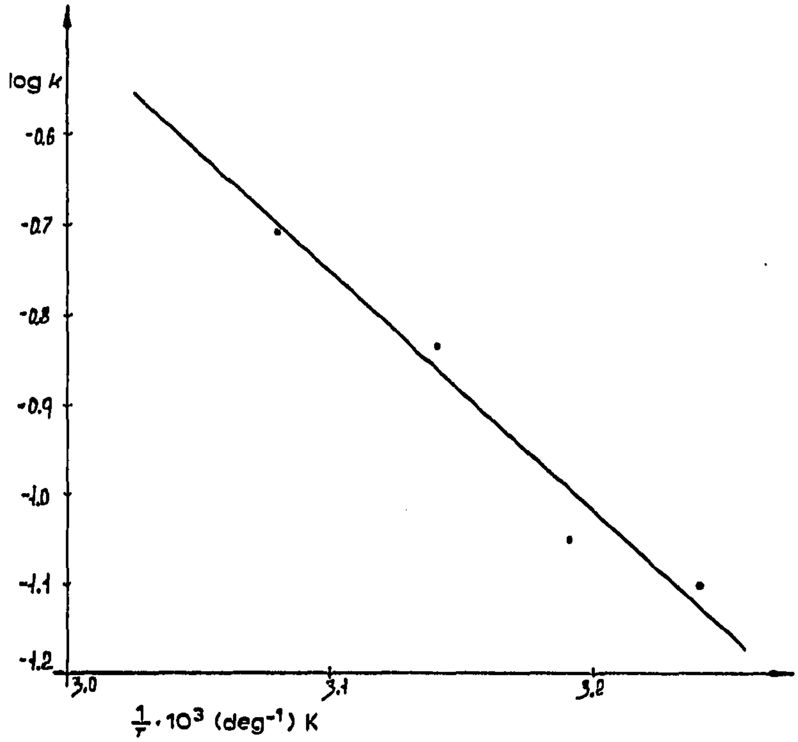


Fig. 5. Temperature dependence of velocity constants for the reaction of isoprene with maleic anhydride.

TABLE I

KINETIC PARAMETERS FOR THE REACTION OF ISOPRENE WITH MALEIC ANHYDRIDE

Reaction velocity constant (min^{-1})				*Activation energy (kcal/mole)*	
35.6°	*40.7°*	*45.4°*	*51.6°*	*This work*	*Ref. 11*
0.181	0.203	0.334	0.451	12.1 ± 0.9	12.2

CONCLUSIONS

The proposed circulation arrangement and pulse chromatographic method have been evaluated for the measurement of kinetic parameters of reactions. It is clear that not only homogeneous and heterogeneous (catalytic) reactions, but also adsorption and absorption phenomena, can be followed by this method.

The usefulness is shown by the example of determining the kinetic parameters of the reaction of isoprene with maleic anhydride. The measured value of the activation energy is in good agreement with the value obtained previously by another method.

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