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CHROMATOGRAPHIC METHOD FOR KINETIC STUDY OF HETEROGENEOUS REACTIONS

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SUMMARY

The advantages of chromatographic methods in the investigations of complex multistage processes proceeding with a change in state of aggregation with time and temperature are demonstrated by application to a kinetic study of the formation and decomposition of ammonium phosphates.

INTRODUCTION

There has been an increasing tendency to apply gas chromatography (GC) to physicochemical investigations of gas–condensed phase systems, including the equilibrium and kinetics of chemical reactions in the presence of gaseous components[1–4]. The application of a number of chromatographic methods to the study of the equilibria of chemical processes, specifically thermal decomposition of ammonium phosphates, is described elsewhere[2].

The special features and advantages of chromatographic methods, applied to complicated multistage processes and kinetic investigations, are considered in the present paper, using the formation and decomposition of ammonium phosphates as an example. It should be pointed out that literature kinetic data on mono- and diammonium phosphate formation are scarce, and kinetic data on the thermal decomposition of the phosphates are limited and contradictory.

The formation of ammonium dihydrogenphosphate and diammonium hydrogenphosphate by interaction of ammonia and phosphoric acid and their thermal decomposition were studied in a gas–liquid–solid system (GLS). This process is accompanied by a change in composition and in the state of aggregation.

Since the use of conventional methods for kinetic studies of such heterogeneous systems necessitates the construction of special equipment, and the experiments are time-consuming and labour-intensive, the complexity in providing comparable experimental conditions for studying individual reactions is a serious limitation. Thus it seemed useful to employ chromatographic methods and apparatus, which are highly sensitive, rapid and capable of being varied over a wide range of experimental conditions.

EXPERIMENTAL

Our methods are based on a reactor in direct combination with a gas chromatograph: an U-shaped reactor is included in the gas chromatograph before the measuring cell of the detector. Two different methods were developed for studying the phosphoric acid ammoniation process:

(1) A flow method variant, where a microdrop of phosphoric acid is injected with a syringe into a flowing mixture of ammonia and helium and the kinetics of the loss of ammonia from the stream is registered by a conductivity detector. The amount of phosphoric acid was varied in the range of 1–5 μl, with acid concentrations in the range of 50–88.5% (w/w) and ammonia concentrations from 1.5 to 40% (v/v). Preliminary experiments showed that the delay time of readings did not exceed 2–3 s, the dead volume of the system was 1–3 ml and the broadening of the kinetic curve is insignificant if the reactor volume and connections are reduced to a minimum.

(2) A pulse variant of the chromatographic method, where an amount of ammonia in a stream of helium is passed over phosphoric acid supported on the inert material Porochrom (silica support, Porochrom-111; Yerevan, U.S.S.R.), particle size 0.3–0.6 mm, surface area 1.1 m^2/g. In this series of experiments the content of acid mixed with the inert material was varied in the range of 5–40% (w/w), which corresponds to a change in acid layer thickness from $3 \cdot 10^{-2}$ to $37 \cdot 10^{-2}$ μm, assuming that the coating of the support is uniform. The ammonia concentration in the pulse was varied from 5 to 100% (v/v), the temperature from −70 to 80°C, the volume of ammonia from 0.2 to 5.0 ml and the reagent contact time from 0.1 to 10 s.

In our earlier publication[1] we showed that it is possible to apply GC to measurement of the evolution rate of gaseous products in topochemical processes. The application of a gas chromatograph provided with a katharometer for measuring the evolution kinetics of gaseous products of thermal decomposition processes was considered and the conditions where the detector signal intensity is directly proportional to the reaction rate were established. In the present study, this method was applied to the kinetics of thermal decomposition of ammonium phosphates both in the solid and molten states. For this purpose a differential flow method was used. To study the decomposition of the melts of ammonium phosphates, a sample was prepared by coating Porochrom with a layer of ammonium dihydrogenphosphate from solutions of different concentrations; the content of phosphates in the mixture with the inert support was varied in the range of 1–40% (w/w) (the calculated thickness of a layer from $0.6 \cdot 10^{-2}$ to $40 \cdot 10^{-2}$ μm).

For simultaneous recordings of the ammonia and water evolved, the flow was diverted after the reactor and two detectors were used; thus kinetic elution curves were recorded of the sum of the ammonia and water and of the ammonia alone, following the absorption of water in the U-tube with dry potassium hydroxide. The experiments were carried out under isothermal conditions and programmed heating of samples.

The measurements of the concentrations of the gaseous reagents and quantities were carried out on an absolute calibration basis. The scattering of the kinetic results in parallel experiments was as follows: for a case with an acid drop ammoniation in the ammonia flow, of the order of ±15% (relative); by a pulse method, ±7%; phosphate thermal decomposition, ±10%.

RESULTS AND DISCUSSION

Fig. 1 presents characteristic curves for ammonia absorption from the flow under phosphoric acid drop ammoniation; the process starts with a maximum rate and the rate sharply decreases with time. The visual observations show that upon introduction a drop grows turbid instantly, due to the formation of a product crust; mechanical disintegration of the crust causes a "sharp increase" in the rate of the process (ab region, curve 1). The complete ammoniation to diammonium phosphate is not attained. An increase in ammonia concentration from 1.5 to 40% (v/v) enhances the extent of ammoniation from 1 to 60%.

In the case of the pulse method, the integral kinetic curves have been obtained by summing the quantities of ammonia absorbed and the pulse contact times in a number of single pulses. Preliminary experiments showed that the results do not depend on the duration between pulses. Irrespective of the experimental conditions varied with in the above limits (low temperatures excluded), a certain number of pulses are absorbed completely; then, a partial "skip" of ammonia is observed.

The dependence of the ammoniation extent on the quantity of ammonia introduced while varying the acid layer thickness on the inert support is presented in Fig. 2. (acid concentration 88.5%, w/w). The complete absorption of ammonia pulses (without skips) was observed in the AB regions of the curves, marked with dotted lines; therefore, the ammoniation rate in these regions is greater, compared with that for ammonia pulses passing through the condensed phase. It is seen that a constant quantity AB′ of ammonia is absorbed in these AB regions independent of the film thickness coated. Stoichiometric calculations of diammonium phosphate formation show that the quantity AB′ of ammonia result in ammoniation of an acid layer of

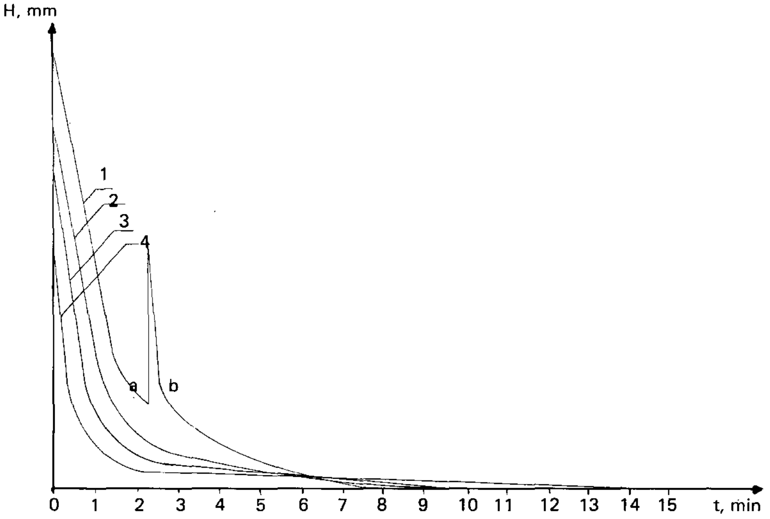

Fig. 1. Kinetic curves for phosphoric acid drop ammoniation (concentration 55.6%; temperature 25°C; drop size 3 μl); H = detector signal intensity; Ammonia concentrations in the flow, % (v/v); 1, 40.3; 2, 29.5; 3, 9.5; 4, 4.1.

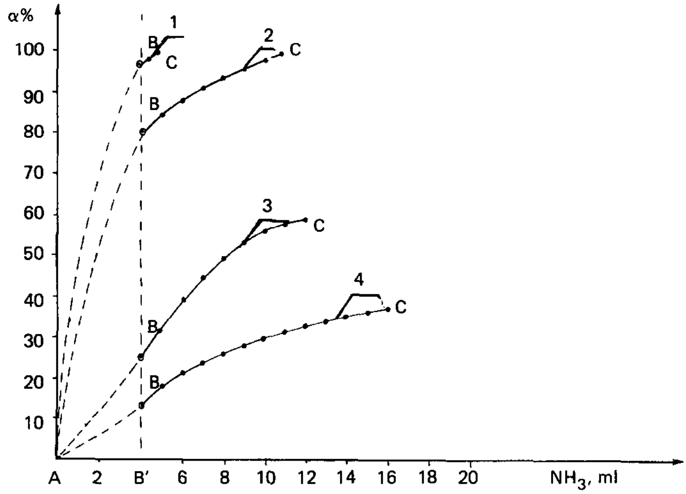

Fig. 2. The dependence of the phosphoric acid ammoniation extent on the quantity of ammonia introduced: ammonia concentration in the pulse 100% (v/v); temperature 25°C. Acid film thicknesses (μm): 1, $0.5 \cdot 10^{-1}$; 2, $0.67 \cdot 10^{-1}$; 3, $1.61 \cdot 10^{-1}$; 4, $3.67 \cdot 10^{-1}$.

thickness $2 \cdot 10^{-2}$ μm. In the regions BC the extent of ammonia absorbed from a single pulse depends on the experimental conditions. The AB region increases with decreasing acid concentration, and does not depend on the contact time, the ammonia concentration in the pulse or the temperature (an ammonia skip from the first pulse was recorded only when the temperature decreased below −40°C).

The pulse method of ammoniation of monoammonium to diammonium phosphate has been performed according to the scheme $S_1 + G \rightarrow S_2$, where S and G are the solid and gas, respectively, and as shown the rate of the reaction is negligibly small.

The evaluation of all data on phosphoric acid ammoniation has been carried out according to a scheme comprised of the following steps: dissolution and reaction of ammonia and phosphoric acid; diffusion in the liquid phase; crystallization of phosphates; diffusion of ammonia through a layer of solid product to the interface with a liquid phase. The results obtained permit the conclusion that, under the conditions studied (temperature 20–25°C, acid concentration 50–88.5%, w/w), layer-by-layer ammoniation of the liquid in the droplet or film takes place. The process is limited by ammonia diffusion through a layer of product. The minimum thickness of the phosphate layer, $2 \cdot 10^{-2}$ μm, the formation of which causes screening of the liquid phase, and, in fact, the end of the ammoniation process, has been evaluated.

The investigation of the phosphate thermal decomposition kinetics has shown that an appreciable decomposition starts at 80 and 105°C for di- and monoammonium phosphates, respectively. The decomposition of diammonium phosphate occurs with the evolution of ammonia alone and the formation of ammonium dihydrogenphosphate; the latter decomposes to form simultaneously ammonia and water, the proportion of which varies depending on the temperature and extent of decomposition. The solid-phase phosphate decomposition may proceed up to 160–165°C. Fig. 3 shows kinetic curves for the decomposition of solid diammonium phosphate; it is

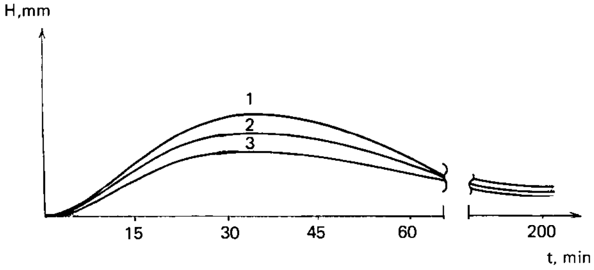

Fig. 3. Kinetic curves for thermal decomposition of diammonium phosphate: 1, 95; 2, 87; 3, 81°C.

clear that the process accelerates with time. The activation energies for the solid phase decomposition were determined from the dependence of the maximum process rate on temperature according to the Arrenius plot, being 75 and 58 kJ/mol for di- and monoammonium phosphates, respectively. The transformation to a melt takes place in the temperature range 165–190°C and depends on the extent of phosphate decomposition, as the accumulation of decomposition products decreases the temperature of melting of the reaction mixture.

The monoammonium phosphate decomposition in the melt starts with a maximum rate; subsequently the rate depends on the melt layer thickness on the support (Fig. 4). Analysis of the kinetic data reveals three reaction regions. For very thin films of melts, $< 1 \cdot 10^{-2}$ μm, there exists a kinetic region (ab) where the rate of the process does not depend on the layer thickness and is determined by the decomposition of melted monoammonium phosphate; it is satisfactorily described by a first-order equation. The apparent activation energy of the decomposition is 63 kJ/mol. At high amounts of ammonium dihydrogenphosphate on the support ($> 30 \cdot 10^{-2}$ μm), the decomposition rate is not dependent on the film thickness (region cd). It is assumed that under these conditions the process is limited by diffusion of the melt components to the interface with the gaseous phase (diffusion region). The linear

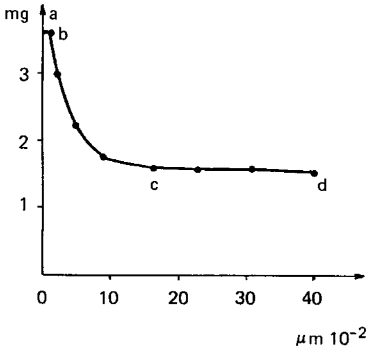

Fig. 4. Dependence of the amount of gaseous products evolved within 2.5 min on the monoammonium phosphate layer thickness.

dependence of the quantity of decomposition products evolved on $\sqrt{t}$ for a large layer thickness, according to the Fick diffusion equation, conforms indirectly a diffusion mechanism. The apparent activation energy of diffusion of the melt components is 33 kJ/mol. There is a transition region between the above two, where the rate of the process depends on the melt layer thickness. It is expected that the nature of the above-mentioned kinetic and diffusion conditions of the process is overlapped in this region (region bc).

CONCLUSION

The results of this investigation of the formation and decomposition processes of ammonium phosphate demonstrate extensive possibilities for the application of chromatographic methods to the study of the macrokinetics and nature of separate stages of complicated heterogeneous processes proceeding in the presence of gaseous reagents.

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