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APPLICATION OF GAS CHROMATOGRAPHY IN THE STUDY OF KINETICS OF VOLATILE PRODUCTS EVOLVED IN TOPOCHEMICAL PROCESSES

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SUMMARY

The application of gas chromatography in the differential flow method for the study of the kinetics of the evolution of volatile products in topochemical processes is described. The method was used to study the decomposition of calcium, magnesium and beryllium perchlorates.

INTRODUCTION

The application of gas chromatography (GC) in physicochemical investigations has recently been considerably extended[1]. The use of GC equipment in combination with differential thermal analysis (DTA) for the study of a number of topochemical processes has been demonstrated[2-6].

In these earlier publications, GC was used to determine the composition and amount of gases evolved during topochemical processes.

The present paper deals with the characteristics and advantages of using GC in the differential flow method to obtain kinetic results for the topochemical processes that occur with the evolution of gaseous products.

EXPERIMENTAL

Fig. 1 shows a schematic diagram of the apparatus used. The U-shaped quartz reactor 1 containing the sample is inserted in the flow path of the carrier gas between the comparative and measuring cells of the thermal conductivity detector, the signal of which is registered. The experimental requirements of the kinetic experiments can be met fairly simply by using standard GC equipment.

In order to receive adequate results on the rates of topochemical processes, it is necessary to have a knowledge of and to minimize the influence of factors such as gas evolution–record delay, zone shape distortion of the evolved volatile product owing to diffusion in the flow of carrier gas, external diffusion, heating period and thermal effects of the process.

The delay time and the effect of diffusion were determined experimentally by introducing a rectangular-form gas impulse before the reactor. The delay time of readings at carrier gas velocities of 60–80 ml/min does not exceed 5 sec without or

10–15 sec with the presence of absorbers 2 and 3 in the system. This delay time can therefore be ignored for processes that are not too rapid. During the delay time, diffusion, which causes distortion of the kinetic curve, is also not significant.

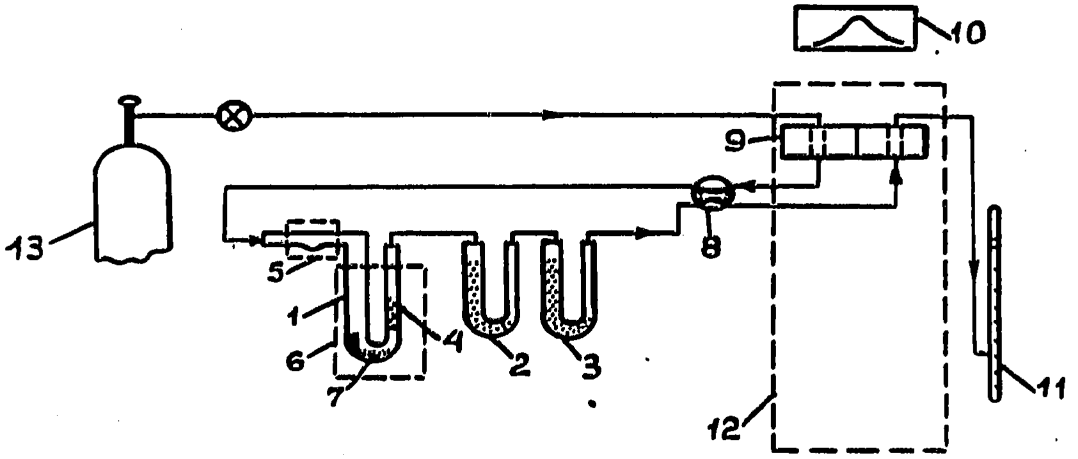


Fig. 1. Schematic diagram of the apparatus. 1 = Reactor; 2, 3 = absorbers; 4 = potassium carbonate layer; 5 = furnace for preliminary heating of the sample; 6 = furnace for heating the reactor; 7 = perchlorate sample; 8 = four-way tap; 9 = katharometer; 10 = recorder; 11 = flow meter; 12 = thermostat; 13 = carrier gas tank.

The use of very small samples (as the detector is highly sensitive) and helium as the carrier gas almost eliminates the effects of the external diffusion of the products and the heat of reaction on the rate of decomposition. The absence of this influence can be shown by establishing the independence of the reaction kinetics from the variation of the helium flow-rate and the sample size. The sample is put into a flat quartz boat in a horizontal section of the reactor and pre-heated in furnace 5. When the reactor is tilted, the boat slides to the lower section, which is heated to the required temperature.

If several gaseous products are evolved during a topochemical process, it is convenient to carry out selective absorption and chemical transformation of the components or separation with the use of combined detectors behind the reactor.

In the course of a decomposition process, the sample in the reactor evolves W (mg/min) of a volatile product at a certain instant of time, t (min), and a linear concentration detector (katharometer) records the response, h (mV), where

$$h(t) = KC(t) \tag{1}$$

which is proportional to the concentration, $C(t)$ (mg/ml), of the volatile product in the carrier gas. In this instance, the concentration of the volatile product is directly proportional to the rate of its evolution and is inversely proportional to the flow rate of the carrier gas, V (ml/min):

$$C(t) = \frac{W(t)}{V} \tag{2}$$

The proportionality factor, K, can be determined by measuring the parameters of the chromatographic band that is formed by a certain amount of a particular volatile component according to the well known chromatographic formula of DIMBAT *et al.*[7]. Thus,

$$h(t) = \lambda W(t) \tag{3}$$

The rate of formation of the volatile product is directly proportional to the height, h, of the curve registered by the recorder (Fig. 2). Therefore the dependence of h on t can be used directly for determining the applicability of a kinetic equation in a differential form. The absolute value of the rate, $W(t)$ (mg/min), can be calculated by using eqn. 3. The amount of product evolved by a certain instant of time, t, is determined from the area under the curve $h(t)$ by using a calibration graph.

DECOMPOSITION OF CALCIUM, MAGNESIUM AND BERYLLIUM PERCHLORATES

The procedure and the apparatus described above were used to study the kinetics of the thermal decomposition of calcium, magnesium and beryllium perchlorates.

Fig. 2 shows the kinetic curves for the evolution of oxygen during the decomposition of calcium perchlorate at a temperature of 430°. The initial portion of Fig. 2a corresponds to the induction period; the rate of evolution is not detectable even with the maximum detector sensitivity. In such an event, the volatile products are accumulated by disconnecting the reactor from the helium flow within 2 min. By blowing out, significant peaks can then be registered. Fig. 2b represents an envelope curve that is drawn through the peak maxima.

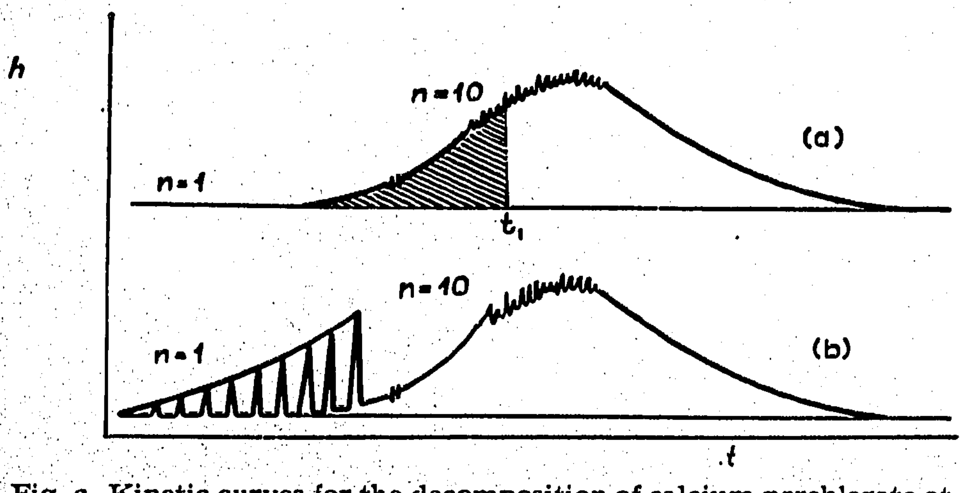


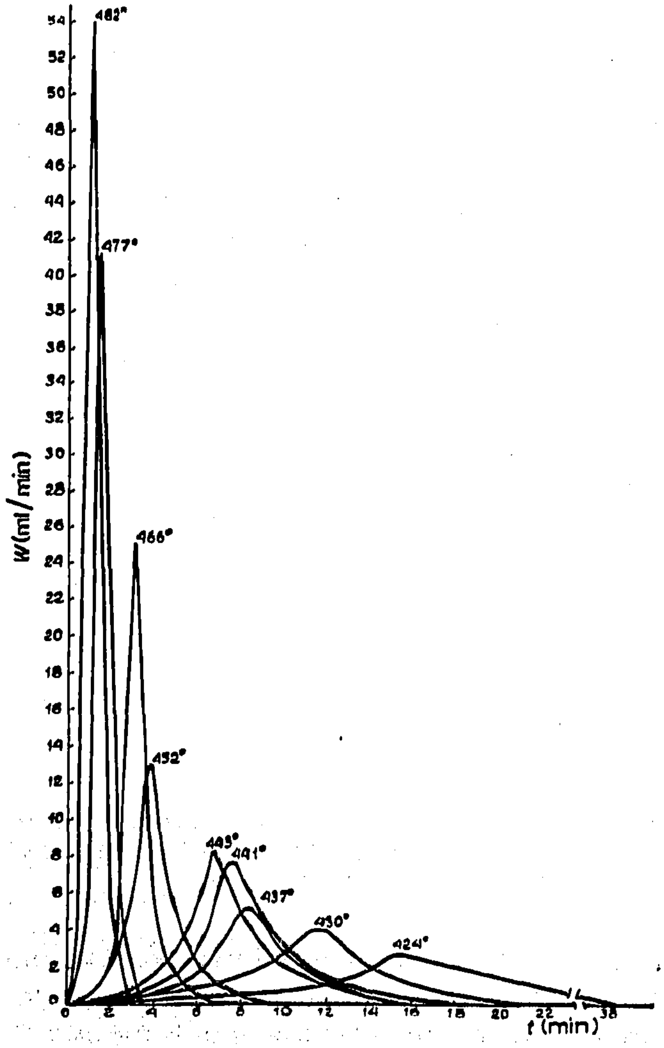
Fig. 2. Kinetic curves for the decomposition of calcium perchlorate at 430°. (a) Continuous recording; $n = 1$, maximum detection for sensitivity; $n = 10$, detector response attenuated by a factor of 10. (b) Recording with periodic disconnection of the reactor from the helium flow.

The decomposition of calcium perchlorate is a very complicated process. On the macro-scale, this process can be interpreted according to the model used for the decomposition of the perchlorates of the alkali metals and some alkaline earth metals[8,9]. At first, the reaction proceeds in the solid phase. Later, when a certain amount of the solid decomposition products has accumulated, relatively fusible compounds are formed and melt micro-zones appear. The decomposition rate in the melt is much higher than that in the solid phase, and the process accelerates as the proportion of the melt increases.

When the melt appears, bubbles of oxygen are evolved and the kinetic curve shows typical noise that results from fluctuations of the oxygen concentration in the helium (Fig. 2).

The maximum rate of decomposition is achieved when a continuous mass of the melt is formed. Later, the decomposition rate falls as a result of a decrease in the perchlorate concentration in the melt and as a result of the solidification of calcium chloride.

Fig. 3 shows the kinetic curves, $W(t)$, for the decomposition of calcium perchlorate over the temperature range 424–482°. The dependence of the reaction rate (up to a maximum) on the amount of oxygen evolved is demonstrated in Fig. 4. The relationship obtained is linear, which agrees with the model described above. The apparent activation energy of the decomposition of calcium perchlorate in this temperature range is 56 cal/mole. It should be noted that there exists a temperature range



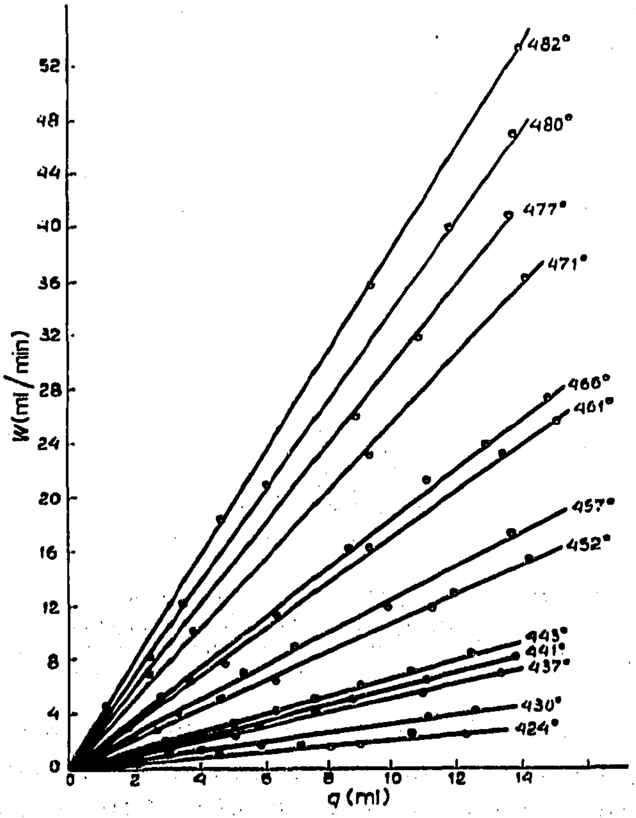


Fig. 3. Kinetic curves for evolution of oxygen during the decomposition of calcium perchlorate.

Fig. 4. Dependence of the decomposition rate (up to a maximum) of calcium perchlorate on the amount (q) of oxygen evolved.

(below 407°) in which the decomposition slowly but almost completely occurs in the solid phase, and the apparent activation energy of the decomposition in the solid phase is 62 cal/mole.

The decomposition of magnesium perchlorate occurs in the solid phase, with oxygen and chlorine being evolved. The kinetic curve for the evolution of oxygen from dehydrated magnesium perchlorate is shown in Fig. 5. Decomposition occurs during temperature-programmed heating at a linear rate of 9°/min. Decomposition proceeds in three stages. In contrast to results published elsewhere[10], it has been established that chlorine is evolved during the course of the whole process. Chlorine was absorbed stepwise in the absorbers and later its amount was determined chemically. U-shaped tubes containing a solution of potassium iodide in glycerol coated on ground quartz were used as absorbers. With such a chemical absorber, it was almost possible to avoid the diffusion of the oxygen zone and a noticeable delay in the detector response. It was also possible to obtain some information on the mechanism of the decomposition of magnesium perchlorate.

The decomposition of the tetrahydrate of beryllium perchlorate is accompanied by the evolution of highly reactive and thermally unstable perchloric acid. We used

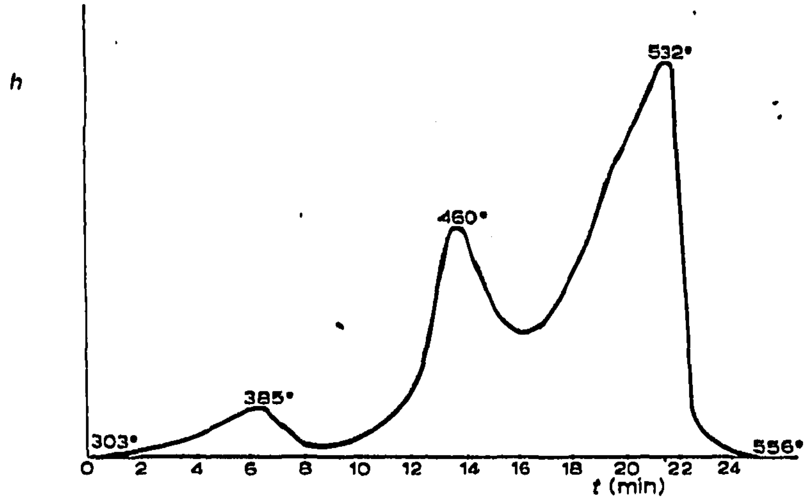


Fig. 5. Curve for evolution of oxygen during decomposition of magnesium perchlorate

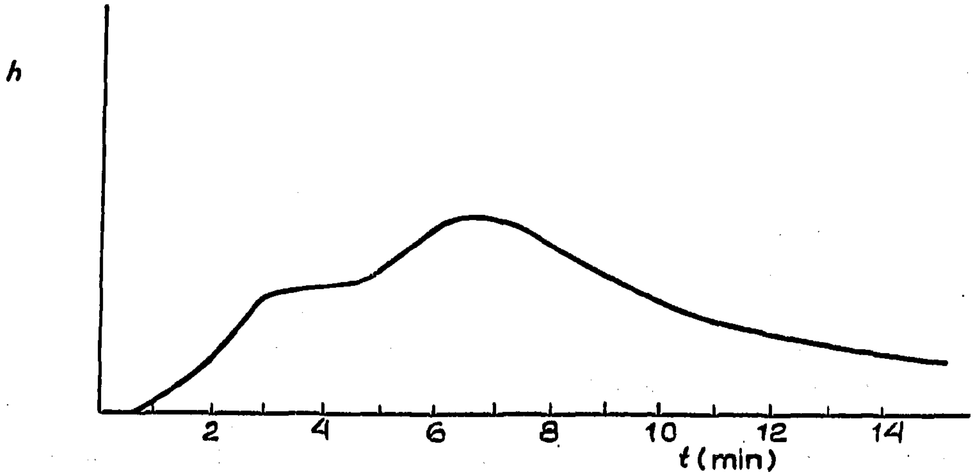


Fig. 6. Curve for decomposition of beryllium perchlorate at a temperature of 225°.

the chemical transformation of perchloric acid to study the kinetics of this process. The layer of pre-heated potassium carbonate 4 (Fig. 1) was put on a grid soldered into the bend of the reactor 1. Perchloric acid, which is evolved during the decomposition of the beryllium perchlorate sample 7, on passing through the carbonate liberates a stoichiometric amount of carbon dioxide, which is detected. It was shown that when using the conditions selected the exchange reaction occured rapidly and quantitatively and the calcium perchlorate formed was not decomposed. The kinetic curve for the decomposition of the tetrahydrate of beryllium perchlorate at 225° is shown in Fig. 6.

CONCLUSION

The examples described show the essential advantages and possibilities of using GC equipment and methods to study the kinetics of the evolution of volatile products in topochemical processes.

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