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Note

Device for gas chromatographic analysis, with mass balance, of gaseous reacting mixtures in a static reactor

J. C. DÉCHAUX

Laboratoire de Cinétique et Chimie de la Combustion, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq Cedex (France)

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Gas-phase chromatography is a convenient and direct method for the study of gaseous reacting mixtures, and during the last two decades it has been perhaps the most popular technique among the common routine methods. In many cases, there is no substitute for this technique particularly when very complex mixtures are to be analyzed.

The object of many experiments on kinetics is to construct a mechanistic model for a reaction process[1]. At the moment, the goal is to obtain a model which is as exhaustive as possible, and this requires a knowledge of the nature of every molecular moiety involved in the reaction; the transient species are detected or postulated. Consequently, it is very useful to achieve, with respect to the products analyzed, a mass balance of nearly 100% between the starting reagents and the products obtained. In fact this is rarely the case, but, if realized, it indicates that no noticeable product has been overlooked. The kinetic scheme deduced is thus more reliable.

Kinetic studies are conducted either in flow or static systems, and various gas chromatographic (GC) devices have been described[2–6]. One of them[7] allows one to check mass balances in a static reaction vessel, but is restricted to mixtures containing a large excess of a liquid-nitrogen-condensable product, namely water or nitromethane. In this paper a more general device will be described. A static reactor is used comprised of a cylindrical Pyrex vessel (length 14 cm, volume 790 cm^3). To measure the pressure change resulting from the reaction a Bell–Howell pressure transducer is employed; the light emission is monitored by using a photomultiplier. The reaction vessel is enclosed in a furnace allowing a slight temperature gradient along the reactor axis (less than one degree).

EXPERIMENTAL

The apparatus is illustrated in Fig. 1. It comprises a static reactor of exactly known volume, V_R, and temperature, T_R, and which contains the reaction medium. The heatable pressure-transducer (Bell-Howell 4100) allows one to record the variation of pressure *versus* time inside the reactor. When opening the stopcock A, at any time t of the reaction, a sudden expansion takes place from the reaction vessel to a heated expansion volume which comprises:
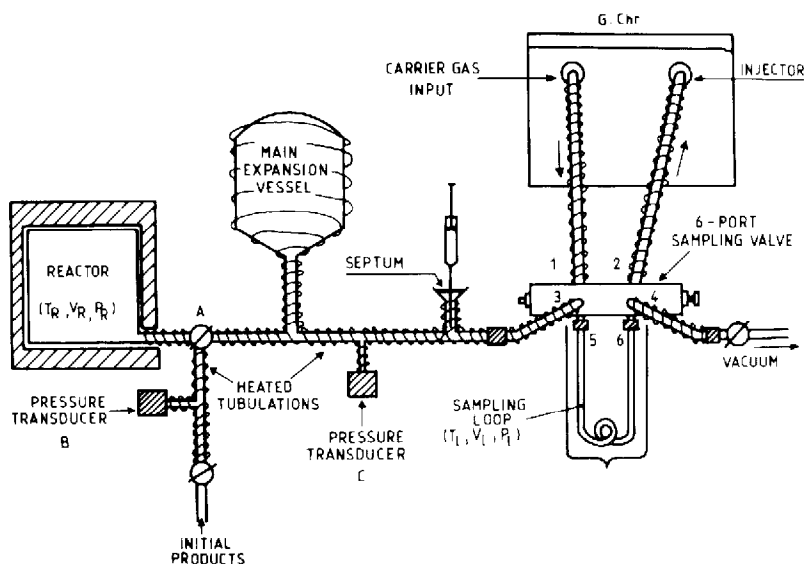
Fig. 1. Scheme of the device. A = Expansion stopcock, allowing a sudden expansion from the reaction vessel to the heated expansion volume; B = heatable pressure transducer, to record the variation of pressure *versus* time inside the reactor; C = heatable pressure transducer giving, after expansion, the pressure in the expansion volume; 1 = carrier gas input to the sampling loop, or directly to the gas chromatograph; 2 = carrier gas output to the chromatograph; 3 and 4 = connections between expansion volume and sampling loop; 5 and 6 = gas entering and leaving the sampling loop.

a main expansion vessel, with a volume suitable for suddenly stopping the reaction inside the reactor, as soon as the stopcock A has been opened. For example, when studying the $C_2H_6 + O_2$ reaction near 350°C and a total initial pressure of 600 Torr with a reactor volume of 790 cm³, the volume of the main expansion vessel was nearly 1000 cm³;

a heatable pressure-transducer C (Bell-Howell 4100) which gives (*versus* time) the pressure inside the expansion volume;

a chromatographic septum fixed inside a female "rotulex" union (Sovirel 692) with the PTFE O-ring removed; the septum is kept in position by a male union and a spring-holder. It allows the injection of gases or liquids by a syringe for calibration;

a heated Type 6-port gas-sampling valve (Varian 57-36-00) which is continuously swept by carrier gas. Two positions are possible for the piston: in one position, the carrier gas enters at 1 and leaves at 2, bypassing the sample loop; at the same time, the sampling loop is connected to 3 and 4, *i.e.*, to the expansion volume, and can receive the sample coming from the reactor. Movement of the piston connects the carrier gas input 1 and the injector 2 via the sampling loop, flushing the content of the latter into the gas chromatograph.

The gas chromatograph used is a Varian Model 1800 having a thermal conductivity detector and 1/4 in. O-diameter columns. The peak areas are measured by using a Perkin-Elmer integrator, Model Sigma 2. The products can be injected directly through a septum by using a syringe, or by a gas-sampling valve, shown in Fig.

RESULTS AND DISCUSSION

Precautionary measures

The sample flushed into the injector via the tube 2 must have the same composition as the sampled reacting mixture at the time *t*. This requires:

a leak-free expansion volume, which can easily be checked by using the pressure-transducer C;

a leak-free sampling valve. This condition was met with the valve used; no leak of the carrier gas (4 bar) could be observed, even when the expansion volume was at zero pressure;

no condensation should be observed, *i.e.*, the expansion volume, tubing, pressure-transducer and valve should be heated sufficiently and regularly. Irreproducibility of results is often a sign of condensation. To check for any condensation, it is adequate to measure, *versus* time using pressure-transducer C the pressure inside the expansion volume after expansion: it must be constant. It is also convenient to inject into this volume through the septum various increasing quantities of condensable products, compare them to the quantities obtained by the analysis and to check whether a pressure limit is obtained for the largest injections. This limit corresponds to the condensation of a given product. A calculation is made (law of perfect gases) of the pressure that must be obtained after expansion, the ratio of the reactor volume/expansion volume being measured (see later);

no reaction must occur, after expansion, in any part of the expansion volume: this can be checked approximately by monitoring the pressure inside the expansion volume (if condensation has been ruled out);

the duration of the sampling must be as short as possible, compared with the duration of the reaction studied. Note that the main expansion vessel has to be placed between the reactor and the sampling loop. In the latter, because of the small diameter of the internal connections of the sampling valve, the expansion is not immediate and can last about 25 sec. In the first case it lasts about 2 sec. It is obvious that the described device is suitable for reactions where the duration is at least several tens of seconds;

no chemical reaction should occur in the sampling loop and the carrier gas output from the valve to the chromatograph injector; this point may seem trivial, but in the present case (reaction: oxidation of C_2H_6 by O_2) it was obvious that two products of this reaction, namely C_2H_4 and CO, reacted rapidly with the carrier gas, H_2, with the catalytic effect of the copper tubing used, the temperature of the latter being 120°C and the H_2 pressure 4 bar. Abnormal evolutions, compared to literature data were obtained, moreover, the injection of pure C_2H_4 in the expansion vessel gave, after entering the sampling loop and the copper tubing 2, two peaks of nearly equal areas: one corresponding to the initial ethylene, the other to ethane formed upon hydrogenation. When using, under the same conditions, tubing at room temperature, no ethane was obtained. So stainless-steel tubing was employed and helium as carrier gas.

Calibrations and calculations

The pressure in the reactor divided by the pressure in the expansion volume after expansion, $A = P_R/P_1$, must be experimentally determined, the pressure-trans-

ducer and tubing temperatures being fixed. This ratio depends slightly on the reactor temperature.

The ratio, B, of the number of moles, N_R, in the reactor at the sampling time divided by the number of moles, N_1, in the loop after sampling has to be calculated. By applying the law of perfect gases we have

$$N_R = \frac{P_R V_R}{R T_R} = \frac{A P_1 V_R}{R T_R} \text{ and } N_1 = \frac{P_1 V_1}{R T_1}$$

which gives $B = A V_R T_1 / T_R V_1$ (dimensionless). If it is convenient, for instance for computer simulation[8], to determine directly the concentration, C_R (mol l^{-1}), of a given product inside the reactor of volume V_R, we write:

$$C_R = \frac{N_R \cdot 10^3}{V_R} = \frac{10^3 \cdot B}{V_R} \cdot N_1$$

The ratios A and B are valid for total or partial pressures, or number of moles. Having determined the number of moles, N_1, of any product in the loop, we are able to calculate the concentration, C_R, of the same product in the rector.

The law of perfect gases applied to the initial reactants allows one to calculate the initial number of C, H and O atoms. When all analyses are considered complete (chromatographic and others where necessary), we calculate the numbers of C, H and O atoms in the products formed and the unreacted starting materials. It is obviously desirable to find a number as near as possible to the number of atoms in the initial reactants.

Applications

This device has been used to study the slow oxidation of various alkanes, namely methane, ethane and propane, in order to compare experimental and computer-simulated results.
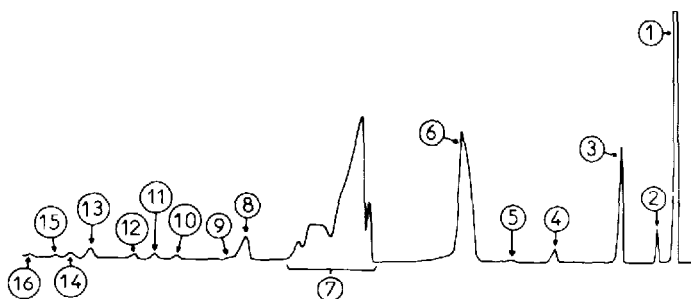

Fig. 2. Chromatogram of the products obtained from the slow oxidation of propane. Peaks: 1 = N_2 + O_2; 2 = CH_4 (t_R = 4 min 12 sec); 3 = CO_2 (t_R = 8 min 30 sec); 4 = C_2H_4 (t_R = 16 min 48 sec); 5 = C_2H_6 (t_R = 21 min); 6 = H_2O (t_R = 23 min 20 sec); 7 = resolved peak (mixture of C_3H_8, CH_3OH, CH_3CHO, C_3H_6); 8 = $(CH_2)_2O$ (t_R = 44 min 5 sec); 9, 10 = unidentified; 11 = C_2H_5OH (t_R = 53 min); 12 = unidentified; 13 = propylene oxide + acrolein (t_R = 59 min 6 sec); 14 = acetone + propanal (t_R = 61 min 5 sec); 15 = isopropanol (t_R = 62 min 35 sec); 16 = 1-propanol (t_R = 65 min).

TABLE I

C, H AND O MASS BALANCES OBTAINED IN THE SLOW OXIDATION OF CH$_4$[9]

Reaction time (min)	Carbon balance (%)	Hydrogen balance (%)	Oxygen balance (%)
1	98.0	99.4	101.0
2	99.7	99.5	101.2
3	103.0	100.0	97.3
4	101.8	99.1	98.9
5	99.7	98.7	100.0
6	97.0	98.1	101.2

An example of a chromatogram of propane oxidation products is presented in Fig. 2. The chromatographic conditions were: 10 ft. × 1/4 in. O.D. column packed with Porapak Q (50–80 mesh); carrier gas, helium at 60 ml/min; initial temperature, 45°C. The temperature was held at 45°C for 12 min after injection, then linearly programmed at 4°C/min to 24 min, then at 2°C/min to 40 min, then at 4°C/min. Note that similar chromatograms were obtained for the oxidation of methane and ethane; however, in the case of methane, few C$_2$ and C$_3$ products are detectable, as are C$_3$ products in the case of ethane.

In the case of methane, the products detected were: CH$_4$, O$_2$, CO, H$_2$O, CO$_2$, CH$_3$OH, H$_2$ and C$_2$H$_6$; O$_2$ and CO were measured on a 5A molecular sieve, H$_2$O$_2$ and H$_2$CO by polarography. Mass balances were calculated for various reaction times and are near 100%, as can be seen in Table I. Under these conditions, such a result clearly indicates that no noticeable product has been missed, and the results can be used for kinetic or preparative purposes. They have been used as a basis to check the validity of a kinetic mechanism supposed to be representative of the reaction. The following species were considered: CH$_4$, O$_2$, H$_2$O, CO, CO$_2$, H$_2$O$_2$, H$_2$CO, C$_2$H$_6$, H$_2$, CH$_3$OH, CH$_3$O$_2$H, HCO$_3$H, OH, HO$_2$, CH$_3$, CH$_3$O, CH$_3$O$_2$, HCO, H, CH$_2$OH and HCO$_3$. The mechanism is based on the mutual interactions of these 23 species, which represent the major molecular products detected by analysis, and the various free radicals which have been detected or postulated. We have to set up a model as complete as possible (124 reactions), and choose the rate constants. A review of the rate constants indicates that they could be roughly classified as follows:

accurately known rate constants, for example for the reaction CO + OH → CO$_2$ + H;

approximately known rate constants, but about which some uncertainty holds, for example the reaction RCO → R + CO;

rate constants obtained only by estimation by analogy, for example by comparison with those for similar reactions. Proceeding successively by trial and error to adjust some concentrations, for a given product there are three possible solutions: variation of rate constants of formation, variation of rate constants of consumption and variation of the concentrations of the radical and molecular precursor species. These trials are complicated, and it was necessary to compute the rate of each reaction at any moment. Clearly, attempts were made to modify the more important reactions; the minor reactions for a given product are practically not adjustable. Some dubious

constants were modified during the trials in order to fit experimental and simulated curves. The results allow one to suggest likely values for some constants.

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