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Controlled rate evolved gas analysis: recent experimental set-up and typical results

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Abstract

The equipment described is designed for the study of complex thermal decompositions. The heating of the sample is carried out under conditions of controlled transformation rate thermal analysis (CRTA) to enhance the information obtained from the computerized quadrupole gas analyser (especially, but not only, by improving the separation between steps). It operates between −20 and +1000°C. The thermolysis of hexahydrated nickel nitrate is briefly examined as an example.

INTRODUCTION

Evolved gas (thermal) analysis (EGA) is the method needed to understand any thermal decomposition of a solid giving rise to several gases. The most popular gas analyser has been, up to now, the quadrupole analyser which is usually oversensitive, although moderate in price. Nevertheless, two conditions must be fulfilled to lead to a clear interpretation, namely (i) there must be no discrimination of the molecules through the device (usually a leak valve) feeding the analyser with a small fraction of the gas flow and (ii) the heating of the sample must be carried out in such a way that the successive steps of the thermolysis are separated as much as possible, so that the gas analysis is meaningful. We previously reported [1,2] that an efficient way to solve these two problems is to use an EGA equipment under conditions of controlled transformation rate thermal analysis (CRTA) [3]. In this way, the rate of production of the gaseous phase is permanently controlled, usually at a low value, so that the whole gas flow may be sent to the quadrupole analyser (with no risk of overpres-

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

sure, no need of gas flow separator and no gas discrimination) and the temperature and pressure gradients through the solid sample may be lowered at will, which may avoid the overlap of successive steps of the reaction.

This paper describes a fully automated and computerized set-up of controlled transformation rate EGA, lists its possibilities and illustrates a few of them with the thermolysis of hexahydrated nickel nitrate. This is the set-up which we have also recently used to study the thermolysis of hexahydrated uranyl nitrate [4,5].

DESCRIPTION OF THE SET-UP

The set-up may be divided in two main parts, one containing the vacuum line and detectors and the other containing the computers and controls.

The sample side and vacuum line

The sample side and vacuum line is illustrated in Fig. 1. Sample A is located in a glass or fused-silica bulb B surrounded with furnace C. This is either a conventional furnace (20–1000°C, but with apparent heating elements, allowing for immediate radiative heating of the sample) or a "refrigerated furnace" (– 20 to + 100°C, simply immersed into a refrigerating liquid bath) in case, for instance, the evolution of water of crystallization has to be studied. The temperature close to the sample is measured with thermocouple D. Sample bulb B is attached, by means of a Cajon VCR 1/4′ fitting, to the vacuum line which is exclusively made of all-metal high-vacuum elements. The main path of the gas flow goes through constriction F (a simple hole through a blind gasket, 10 mm thick), towards a bent pipe G which brings the evolved gas just over the source (i.e. filament H) of quadrupole analyser I (which simply uses a Faraday cup as the detector), before being pumped downwards, towards ionic pump J (fed by an electronic rack) through butterfly valve K. This is a 11 l s^{-1} pump (model P.I-11 from Riber) with two removable titanium electrodes for easy maintenance. This pump has been purposely oversized for continuous use over more than one year with the same set of electrodes. This is partly favoured by use of rotary pump L (connected through a zeolite trap which retains oil vapour), to lower the pressure at the start of each experiment, from 1 bar down to the desired value. Cryogenic pump M (filled with 1 l of zeolite and cooled with liquid nitrogen) is used (two or three times a year) to reach the vacuum of about 10^{-2} mbar needed to start the ionic pump in case it has been stopped. The rest of the time, vacuum valve O remains closed. The vacuum is measured in different ways: by Pirani gauges E or N (PI 101 from Alcatel, pressure range 10^{-4}–100 mbar), by quadrupole analyser I and by ionic pump J (effective pressure range 10^{-8}–10^{-4} mbar).

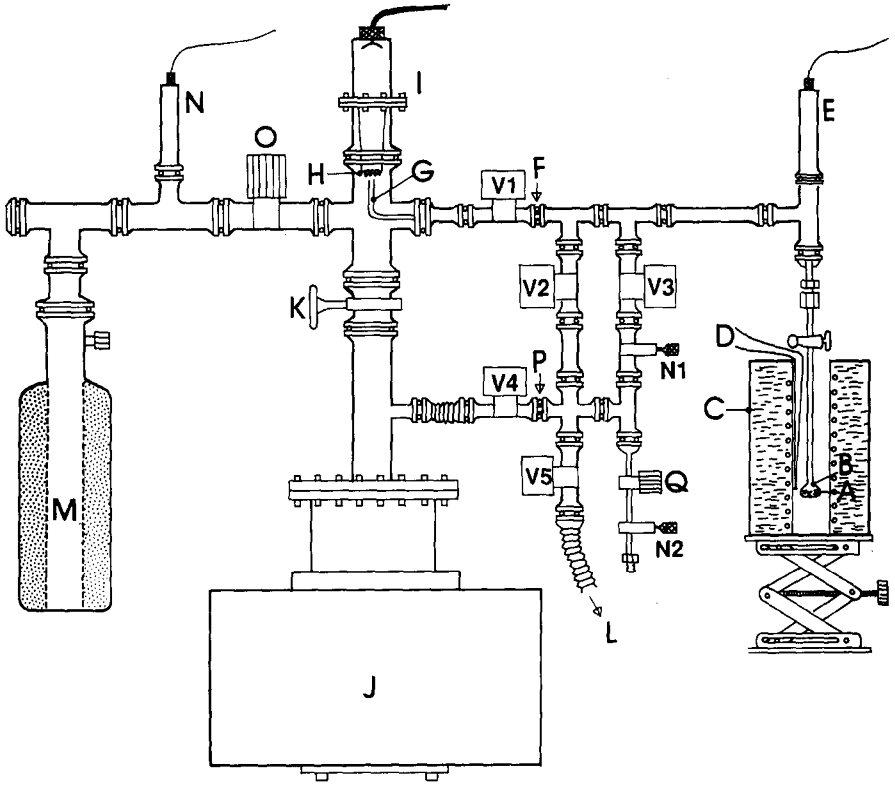

Fig. 1. Controlled transformation rate evolved gas analysis: the sample side and vacuum line.

Another path for the gas evolving from the sample goes through constriction P and electrovalves V2 and V4 directly to the ionic pump. This path is never used alone, but is always associated with the first path (through constriction F) in order to increase the pumping speed, which is needed, as we shall see later, to apply the "rate-jump" method for determining the energy of activation.

A stop-valve Q and a needle valve N2 are also available for the introduction of any gas needed to calibrate the quadrupole gas analyser.

The controlling unit

The connection of the main components and the operation of the controlling unit may be understood with the help of Fig. 2, which is to be examined from left to right.

The raw signals coming from thermocouple D, ionic pump J, Pirani gauges E or N and quadrupole I are processed, by their individual electronic unit, into 0–10 V d.c. analog outputs (linearized in the case of partial

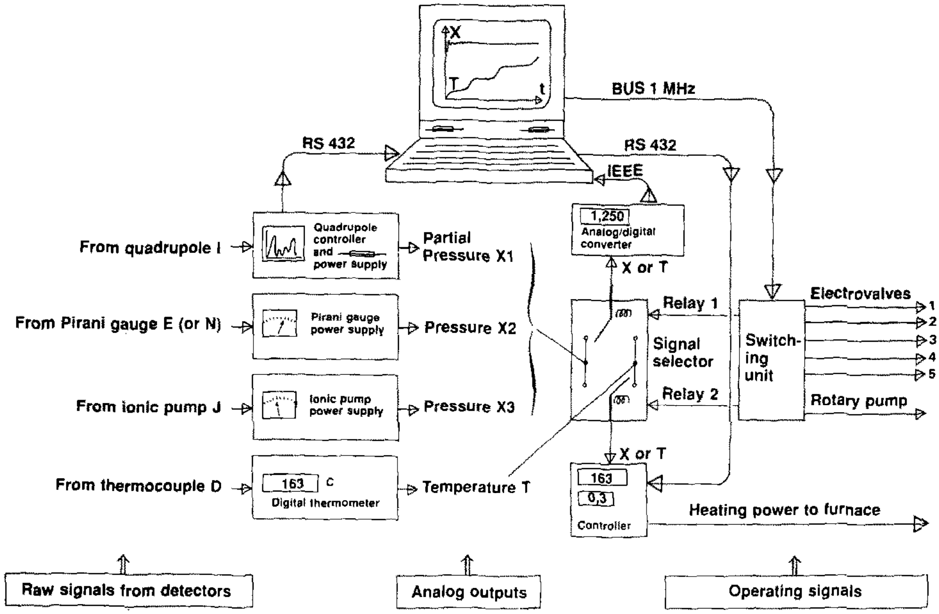

Fig. 2. Controlled transformation rate evolved gas analysis: the controlling unit.

pressure X_1 and temperature T). The quadrupole controller and power supply is a Vacuum Generators PC-Micromass, which includes a PC microprocessor. It may simultaneously deliver eight analogue signals corresponding to eight peaks pre-selected on the spectrum by the operator but only one of them is needed to control the experiment. The others are available, for instance, for continuous external recording. Actually, since these signals may be recorded vs. time and stored using the Micromass software, we found it more convenient to wait for the end of the experiment and then either to transfer the corresponding data files to the main computer (here, Acorn BBC computer, either B series or Master series; it could have been, as easily, a PC computer) or to store them on a diskette (a disk unit is included in the Micromass) for further processing on a standard PC computer.

The analog outputs are sent to the signal selector which has two functions. First, it alternately sends a temperature signal T or a pressure signal p to the analogue/digital converter, for recording by the main computer. This function may also be fulfilled by the scanning unit of the analogue/digital converter and voltmeter, in case it has one built in. The second function is to feed the heating controller with either the temperature signal T (especially to start the experiment with a linear heating rate, or to end it with a temperature plateau) or a pressure signal X (after the onset of the gas evolution from the sample, in order to control the rate of the transformation). The heating controller here is a Microcor III from

CORECI whose settings (P, I and D parameters and also the controlling value of T or X) are sent from the main computer through the RS 432 connection.

The operating signals include the heating power delivered to the furnace by the above heating control, together with the eight signals provided by the switching unit. This unit (Port Com, manufactured by W.D. Interfaces, Leeds, UK, for special use with the Acorn BBC computers) is operated from the 1 MHz port of the main computer. The unit itself operates relays 1 and 2 of the signal selector, valves V1 to V5 of the vacuum line and rotary pump L. The last is mainly in use at the start of the experiment, initially to evacuate the line and sample bulb, simply to save the ionic pump.

CARRYING OUT A TYPICAL EXPERIMENT

Bulb B (see Fig. 1), containing between 10 and 70 mg of sample A, is attached to the vacuum line by means of its Cajon VCR all-metal fitting and its stopcock is open. At the start of the experiment, all electrovalves V1 to V5 are initially closed (these are Alcatel-Lucifer electrovalves of 10 mm bore, normally closed when switched off). Valves V3 and V5 are then opened to let rotary pump K evacuate the line through needle valve N1 whose setting allows smooth pumping, thus avoiding the risk of any spurting out of the sample. Once the pressure measured with the Pirani gauge E has dropped down to about 10^{-1} mbar, then valve V2 is opened to increase the pumping speed. At about 10^{-2} mbar, valves V2, V3 and V5 are closed, the rotary pump is stopped and valve V1 is opened, so that the ionic pump is now used. (Note: the ionic pump, which has a normal power consumption of less than 50 W and which is perfectly silent, is permanently switched on, even in stand-by between experiments.) The gas path is then through constriction F (usually of 1 mm bore and 10 mm long), through quadrupole I and then to ionic pump J.

At this stage the heating control may begin to operate. The experimenter has previously selected the pressure to be controlled (from Pirani gauge E, ionic pump J or quadrupole I) and made the corresponding connection with the signal selector (see Fig. 2). He has fed the main computer (i) with the controlling value of X (say, for instance, 10^{-2} mbar in case the Pirani gauge is used; this will typically lead to a rate of dehydration of about 0.3 mg h^{-1}), (ii) with the initial heating rate he wishes for "launching" the experiment (i.e. reaching the temperature where the gas evolution reaches the required rate; for samples such as hydrated salts which begin to lose a gas phase at room temperature, under vacuum, such an initial heating is not needed) and (iii) with the final temperature of the experiment. The duration of a final temperature plateau may also have been selected if wanted.

Meanwhile the Micromass PC begins to record the height of the eight pre-selected peaks vs. time, whereas the main computer records and displays the basic thermal analysis curve (temperature vs. time, i.e. temperature vs. extent of reaction when the pressure or "vacuum" control allows a constant rate of reaction to be maintained) together with the actual value of the controlled pressure X (also recorded vs. time).

Application of the rate-jump method for determining the apparent energy of activation [6] simply requires here the use of a bypass to increase the pumping rate in a known ratio. This is achieved by using the second constriction P which may be simply made by drilling a gasket (same thickness as that used in F, for instance, 10 mm) with, say, three holes, in parallel and identical to the hole drilled in constriction F. Under these conditions, if it is carefully done, the conductance of constriction P is three times higher than that of constriction F, with no need of any further check or calibration. The automatic application of the method simply needs to keep valves V1 and V2 continuously open and to open valve V4 periodically (say, during 1 h, to obtain a clear "temperature tooth" on the display of the main computer) and close it (during 1 h or more), depending on the desired number of independent measurements of the energy of activation.

It may be necessary to calibrate the height of a given peak (delivered by the quadrupole analyser) not only in terms of absolute pressure but in terms of the flow rate of that gas through the equipment. This is done by fitting a calibrated gas leak (and the associated pure gas supply) to the gas inlet under valve N2. If needed, the gas leak may be previously calibrated by means of a high precision gas volumetric equipment normally used for gas adsorption experiments [7].

POSSIBILITIES OF THE CONTROLLED RATE EVOLVED GAS ANALYSIS (CR-EGA) EQUIPMENT

The equipment described above proved to be quite interesting for its analytical and kinetic possibilities and for its versatility.

Analytical possibilities

The CR-EGA equipment has of course to be compared with more conventional EGA equipment, on which good reviews are available [8]. A few advantages are the following.

(1) Because of the possibility of keeping the rate of gas evolution constant, the equipment lends itself to quantitative determinations which are not possible when neither the pressure nor the gas evolution are controlled [9].

(2) Using an intermediate constriction in or just above the sample bulb, it is possible, in spite of the permanent pumping, to control the residual

pressure above the sample up to a value as high as 100 mbar, which allows selection of the most favourable conditions for a clear-cut separation of successive steps. These conditions also include a low rate of decomposition which leads to small temperature and atmosphere composition gradients within the sample. The present equipment very easily allows us to keep control of reaction rates slow enough to need, if wanted, several weeks for completion of the thermolysis of the sample. Let us also mention that this equipment leaves us the possibility to modify independently, from one experiment to the other, either the residual pressure over the sample (by changing the intermediate constriction) or the specific rate of transformation (by simply changing the starting mass of sample). All this was clearly shown with the thermolysis of hexahydrated uranyl nitrate [5].

(3) Finally, as mentioned in the Introduction, the gas analysis is made more meaningful by elimination of the gas discrimination problem normally encountered with EGA equipment using a carrier gas and bypass pumping: here, the permanent control of the rate of gas evolution ensures that all the gas produced by the thermolysis is sent right to the quadrupole source without any risk of overpressure (we usually keep the pressure in the quadrupole around 10^{-6} mbar during the experiment).

Kinetic possibilities

The use of the rate-jump method for determining the apparent energies of activation [6] has allowed, for instance, more than 100 successive and independent determinations of the energy of activation to be made over the successive steps of the thermolysis of hexahydrated uranyl nitrate [4]. Moreover, these determinations need no preliminary assumption about the mechanism involved. Moreover, in case the rate of transformation is kept constant, the temperature vs. time curve has a quite meaningful shape which immediately allows discrimination between a mechanism controlled by a boundary (the reacting interface), by diffusion or by nucleation and growth of nuclei [10].

Association with other techniques

At any time, the CRTA–EGA experiment may be stopped and the sample, protected in its bulb under vacuum, may then be studied by a non-destructive technique (gas adsorption, NMR, IR spectroscopy, etc.) before being brought back to the CRTA–EGA vacuum line for the study of a further step. The smooth launching of the experiment allows us to get back easily to the thermal analysis curve which would have been recorded if the experiment had not been stopped.

EXAMPLE OF ANALYSIS: THE THERMOLYSIS OF HEXAHYDRATED NICKEL NITRATE

It was of interest to select the case of the complex thermolysis of hexahydrated nickel nitrate, firstly because it leads to a widely used catalyst, nickel oxide, whose properties depend greatly on the conditions of the thermolysis (sometimes carried out after impregnation of an inert catalyst support with an aqueous solution of nickel nitrate, at other times carried out on crystals of various size, etc.). Moreover, large discrepancies are found in the literature between various routes proposed for the thermal decomposition.

Our approach here is to see what happens under well-defined conditions: a residual pressure of 10^{-2} mbar, a pumping rate of about 0.3 mg of water vapour per hour, rate of reaction $d\alpha/dt$ of about 0.006 h^{-1}. Figure 3 shows, from top to bottom, the total pressure controlled from Pirani gauge E, around 10^{-2} mbar (curve P), the thermal analysis curve θ (temperature vs. time) and the corresponding partial pressures (with a logarithmic scale) of the species with relative molar masses 18 and 30 i.e. here H_2O and NO. Table 1 gives the mean relative intensities of seven species along the four

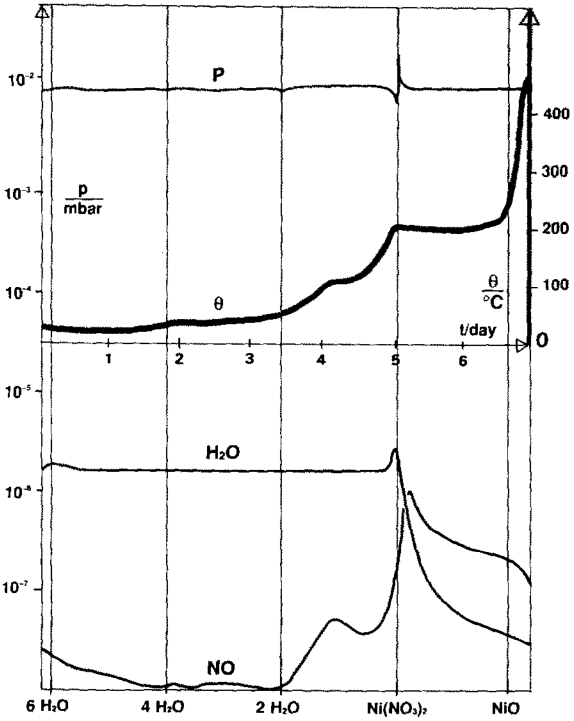

Fig. 3. CR-EGA of hexahydrated nickel nitrate: P, total pressure over the sample; θ, temperature vs. time curve; H_2O and NO, partial pressures in the gas analyser proper.

TABLE 1

Relative intensities (%) of the peaks in the mass spectra recorded during a CR-EGA experiment carried out on hexahydrated nickel nitrate (steps 1–4) and on gibbsite

Species	M/e	1st step	2nd step	3rd step	4th step	Gibbsite
H_2O	18	100	100	100	16	100
HO	17	41	45	41	5	30
	16	9	9	8	26	5
	14	1	1	1	20	0
NO	30	1	1	3	100	0
O_2	32	2	3	2	18	0
NO_2	46	0	0	0	15	0

steps easily seen from the thermal analysis curve. This table clearly shows that water is practically the only gas produced during the first three steps. We have checked (see last column) that the proportion of species with relative masses 18, 17 and 16 was comparable, with our equipment, when we carried out the thermal decomposition of gibbsite, $Al(OH)_3$, which only produces water vapour. We may therefore derive that, in the thermal analysis curve of Fig. 3, the time scale is directly proportional to a mass scale during these first three steps. If we accept that the product of step 3 is the anhydrous nitrate, we may then see that the product obtained at the end of step 1 is the tetrahydrate and at the end of step 2 the dihydrate. What we called step 3 may itself be easily split into two substeps, as if the monohydrate (which, from the literature, does not seem to have ever been isolated) was here an intermediate state. Confirmation of this assumption needs further experiments: we now plan to characterize by X-ray diffraction (and, if necessary, by gas adsorption) the intermediate products and to determine the kinetic equations followed in each step, in order to assess the physico-chemical mechanism of the transformation.

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