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Application of Mass-spectrometry to the Study of the Decomposition Kinetics and Mechanisms of Solids

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The application of mass-spectrometry to the study of the decomposition kinetics and mechanisms of solids is discussed. Different designs of equipment and experimental procedures for studying the kinetics and the mechanism of the primary and the secondary processes in the decomposition of solids are described, and their relative advantages are analysed. Conditions likely to clarify specific aspects of universal importance to the decomposition of solids are formulated, and the advantages of dynamic mass-spectrometry in this type of study are stressed. The most important results of mass-spectrometric experiments on the kinetics and mechanism of the decomposition of solids are reviewed, including the thermal decomposition of inorganic solids, high-temperature reactions involved in the decomposition of solid propellants, the thermal and mechanical degradation of polymers, and other illustrations of the possibilities of the method.
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I. INTRODUCTION

Mass-spectrometry offers valuable information on the composition of materials and on the structure and concentration of molecules, and has an important part to play in the study of complex reaction mechanisms, since it helps to identify unstable intermediates such as atoms and radicals. The application of mass spectrometry to the study of radicals and their reactions in the gas phase and to the study of gas-phase kinetics has been discussed in a number of review articles[1-3]. More recently, mass spectrometry has been extensively used to study the kinetics and mechanisms of the thermal decomposition and evaporation of solids, including ionic and molecular crystals, metals and oxides, and also the pyrolysis of polymers, coal, and explosives. Recent work on the kinetics and mechanism of decomposition of solid propellants at temperatures close the surface temperatures encountered in combustion has made an important contribution to our understanding of the combustion of these solids. Valuable work is also proceeding on the ignition and combustion of solid propellants.

II. GENERAL FEATURES OF THE MASS-SPECTROMETRIC STUDY OF THE KINETICS AND MECHANISM OF THERMAL DECOMPOSITION OF SOLIDS

Studies of the initial stages of the formation and growth of nuclei, in which the amount of material undergoing chemical change is of the order of 0.1–0.001%, are of

fundamental importance to an understanding of the kinetics and mechanism of thermal decomposition of solids. The scope of this work has been considerably extended by the use of mass spectrometers for measuring partial pressures: modern mass spectrometers have extremely high sensitivities (up to 10^{-11} mmHg for Ar). Processes in the condensed phase can be monitored by using a mass spectrometer to determine the composition of the gas phase. Because of the very high sensitivity of the mass spectrometer, decomposition can be studied in single crystals, thus avoiding the complications associated with intercrystalline boundaries and gas diffusion.

The decomposition of many solids (formates, perchlorates, nitrates) is known to occur in different stages, some of which involve only the solid surface, giving rise to primary decomposition products, whilst the subsequent (or secondary) processes involve the gas phase or the solid/gas interface. Hence it is most important to distinguish primary from secondary processes, so as to study them separately and to identify their individual role in the overall process. In order to study only the primary decomposition stages of solids, and to exclude secondary reactions in the gas phase, the pressure in the reaction vessel must be low enough (10^{-4}–10^{-5} mmHg) to ensure that the molecular mean free path is large compared with the dimensions of the vessel. This condition is satisfied when the ion source of a mass spectrometer is used as the reaction vessel. In order to detect unstable, short-lived species such as atoms, radicals, and also molecules of compounds which are involatile at room temperature, and corrosive gases, the sample must be located very close to the ionisation volume (within a few millimeters). This requirement has been observed in most of the published work on the decomposition mechanism of solids (polymers, coal, ionic crystals, solid propellants, oxides).

The method of heating the solid sample deserves special mention: the powerful sources used for flash heating include xenon lamps[4,5], optical arc furnaces[4,6-8], lasers[9], and electrically heated metal strips[10-12] and gauzes[13-14].

Heating by radiation has the advantage that contact between heater and sample is unnecessary, uniform temperature can be obtained throughout the sample (for transparent samples), and fast heating rates (up to 10^6 deg s^{-1}) and high temperatures (several thousands of degrees with laser beams) can be achieved. However, sample temperatures are difficult to measure with these methods of heating. We have used[10-12] a very small sample of the solid ($\sim 10^{-6}$ g) resting on a titanium strip which was heated electrically, other workers[13,14] have used a platinum strip. Fast heating (in 10^{-3} s) was obtained by discharging a capacitor through the strip whilst passing also a continuous electric current to compensate for thermal losses. Temperature constancy (to within 1–2°) could be achieved by suitable choice of the capacitor voltage and of the constant current: this is particularly important in studies of the decomposition kinetics of solids under isothermal conditions. By using small samples (crystallites, or layers a few microns thick in good thermal contact with the heater strip) the heating time can be kept small (of the order of milliseconds) and the temperature gradients can be reduced to a fraction of a degree when heat is absorbed or evolved as a result of decomposition. The temperature of the heater strip (approximately 100 μm thick) was measured by a thin (5 μm diameter) thermocouple spot-welded or stuck to the strip with a heat-resistant cement. Fig. 1 shows the design of an apparatus used[11] to study the kinetics of the isothermal decomposition of solids by a time-of-flight mass spectrometer method.

The decomposition of coals has been studied[13] also under non-isothermal conditions. Coal particles of 60 μm diameter were placed on a grid with holes 50 μm in diameter, and heated at a constant rate of 10^3 deg s^{-1}. In contrast to the previous work[11], the temperature of the sample was varied linearly with time. Assuming first-order kinetics, all the kinetic parameters (activation energy and pre-exponential factor) could be derived from the results of a single experiment. However, because of the need to assume the kinetic order of the reaction, the method is less accurate than the isothermal method, which directly gives the reaction rate as a function of time. This is particularly important in studies of the decomposition of solids, when the reaction can show diffusional limitation or autocatalytic phenomena, and the problem of identifying the kinetic order becomes complicated or even meaningless.

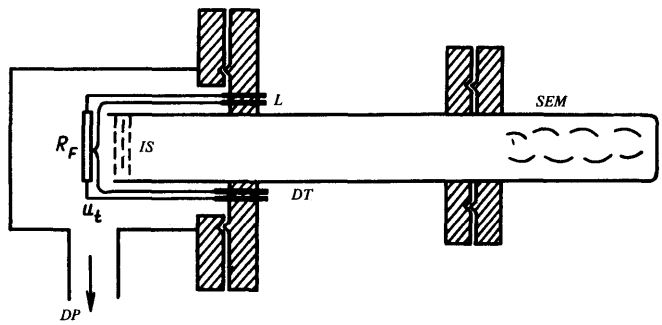


Figure 1. Location of the heater in the ion source of a time-of-flight mass spectrometer[11]: R_F, heater; u_t, thermocouple; *IS*, ion source; *DT*, drift tube; *SEM*, secondary electron multiplier; *L*, electrical leads; *DP*, diffusion pump.

The time constant of the mass spectrometer presents some problems in measurements of the kinetics of fast thermal decomposition reactions in solids. Thus, the most commonly used mass spectrometers, which rely on fixed magnets, can only be used for reactions extending over periods of hours, and their use at elevated temperatures is therefore severely limited. Therefore, dynamic mass spectrometers are far more useful in this type of work: they include time-of-flight mass spectrometers (which have no magnet, and a time constant of 10^{-5}–10^{-4} s), mass spectrometers with a permanent magnet and a variable accelerating potential ($\sim 10^{-2}$ s), quadrupole mass spectrometers, omegatrons, etc.

The design and the areas of application of time-of-flight mass spectrometers have already been discussed[15].

In kinetic studies of the decomposition of solids in the ion source of a mass spectrometer, the most important problem is to establish the relationship between the measured peak intensities and the rates of formation of the gases which contribute to these peaks (i.e. the reaction rates). When the reaction rate is comparable in magnitude to the pumping speed, the rate w_i of formation of the component i is related to the peak intensity I_i; this is proportional to the partial pressure of that component in

the ionisation volume if no other component contributes to the peak, according to the expression[16]:

$$w_i = A\left(\frac{dI_i}{dt} + KI_i\right)$$

where K is the pumping rate constant and A is a proportionality constant related to the sensitivity of the apparatus.

In the limit of a reaction rate much higher than the pumping speed this equation takes the form:

$$w_i = A\frac{dI_i}{dt}.$$

In the opposite limit, when the pumping speed is much higher than the reaction rate, the intensity of the appropriate peak is directly proportional to the latter:

$$w_i = AKI_i = BI_i.$$

In some recent studies[17,18] of the kinetics of polymer degradation using a time-of-flight mass spectrometer with stroboscopic presentation of the signal, which offers a substantially higher sensitivity[19], the constant B had the value $\sim 10^{11}$ molecules s^{-1}.

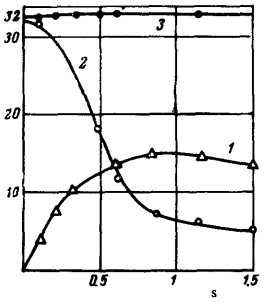


Figure 2. Time dependence at a constant temperature of 310° (see curve *3*) of the intensity of the mass 16 peak (curve *1*) and of the reaction rate (curve *2*), in relative units, during thermal decomposition of ammonium perchlorate in the ion source of a time-of-flight mass spectrometer[11].

Fig. 2, which was obtained in the writer's laboratory[11], shows the time dependence of temperature, intensity of the mass 16 peak, and reaction rate, all in relative units, measured in a study of the thermal decomposition of ammonium perchlorate in the ion source of a time-of-flight mass spectrometer under conditions of comparable pumping speed and reaction rate.

When the decomposition kinetics and mechanism of solids are studied at relatively high pressures (up to 1 atm), secondary reactions in the gas phase cannot be excluded. These add to the difficulty of quantitative mass spectroscopic analysis of gas mixtures (since the measured peak intensities are linearly related to partial pressures in the reactor irrespective of the composition of the gas only if the gas is mixed with a large proportion of an inert diluent) and to the other difficulties of studying gas kinetics a high pressures[1-3]. If the reaction is observed under static conditions, the diffusion time of the decomposition products to the sampling point (or orifice) must be much less than the reaction time. If the reverse is true, the measured rate will be the rate of diffusion of the products from the solid to the orifice rather than the reaction rate. The diffusion time can be significantly decreased by carrying out the reaction under flow conditions using an inert gas stream to carry the reaction products from the sample to the orifice.

Tauerman and coworkers[6-8] studied the volatile products evolved immediately before ignition of two-component solid propellants by a beam of radiation from an optical arc furnace. In this way, the distance between the fuel charge and the conical diaphragm was reduced to 5 mm, and the distance between the orifice and the ionisation volume was 19 mm. The vessel containing the charge was swept with helium at 10–200 mmHg pressure containing 1% of argon as an internal sensitivity standard. This precaution is essential, as the sensitivity decreases when the reaction rate is increased. The apparatus is shown in Fig. 3. The surface temperature of the charge was measured by a thin (50 μm) Chromel–Alumel thermocouple.

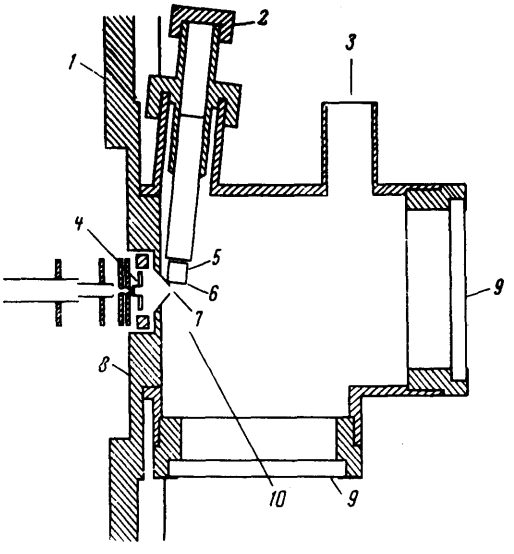


Figure 3. Combustion chamber combined with the ion source of a mass spectrometer[8]: *1*) upper flange of ion source; *2*) sample holder; *3*) to pump; *4*) electron beam; *5*) sample of propellant; *6*) thermocouple; *7*) orifice; *8*) ion source; *9*) quartz viewing port; *10*) radiation from optical arc furnace.

We shall now discuss the most important results obtained by the methods described, and consider concrete examples of the usefulness of the methods.

III. RESULTS OF MASS-SPECTROMETRIC STUDIES OF THE DECOMPOSITION KINETICS AND MECHANISMS OF SOLIDS

1. Decomposition of Inorganic Compounds

Many papers have been written on the thermal decomposition of ammonium perchlorate[10-12,20-24]. Heath and Majer[20], who were among the first to examine this system,

tried to identify the primary decomposition products of ammonium perchlorate in the ion source of a mass spectrometer at 100°. Unfortunately, they used large samples and were therefore unable to exclude secondary reactions in the pores of their sample, where the pressure was probably several order of magnitude higher than in the ion source. As a result, they detected several secondary products (H_2O, NO, NO_2, O_2, Cl_2) as well as the primary product (NH_3). Because of the large distance between the ion source and the sample, and of the modest pumping speed of their apparatus, the authors[20] failed to detect any perchloric acid in the mass spectrum. In order to analyse corrosive gases such as perchloric acid, chlorine, and hydrogen chloride, the time between their formation and detection must be much shorter than their lifetime. (These species disappear as a result of wall reactions.) This condition was evidently not fulfilled in Heath and Majer's work[20]. Since their mass spectrometer was of the static type, with a large time constant, the reproducibility of their results was also poor: the rate of change of the peak intensities was of the same order as the rate of scanning of the mass scale.

More reliable results were obtained in a later study[21] of the main products of the thermal decomposition of ammonium perchlorate at relatively low temperatures (230°). A time-of-flight mass spectrometer was used at pressure of the order of 10^{-3} mmHg. According to the authors[21], the ammonia and perchloric acid formed as primary products did not enter into secondary gas-phase reactions in the hot region of the reaction vessel, and they recombined in the cold regions with formation of NH_4ClO_4. This study included the decomposition of $^{15}NH_4ClO_4$ in order to distinguish the nitrous oxide peak from the background carbon dioxide. The main reaction products at 230° were found to be: water, nitrous oxide, chlorine, and oxygen, together with significant amounts of hydrogen chloride and nitrogen. Hence the equation suggested by Bircumshaw[25], giving H_2O, N_2O, Cl_2, and O_2 as the products, is not completely accurate. A later paper by the same authors[22], dealing with the decomposition kinetics of $^{14}NH_4ClO_4$, $^{15}NH_4ClO_4$, $NH_xD_{4-x}ClO_4$ at 160–230° and 10^{-4}–10^{-7} mmHg, gives the activation energy for the decomposition (28 kcal mole^{-1}) and the ratio of products ($O_2 : N_2O : Cl_2 = 3 : 3 : 2$).

The primary decomposition step of ammonium perchlorate and the decomposition kinetics in a vacuum have been studied in the writer's laboratory[10-12], using time-of-flight mass spectrometry and fast heating techniques. The primary decomposition products were found to be ammonia and perchloric acid. By using small samples (10^{-6}–10^{-5} g), the complicating effects of secondary reactions in the pores between crystallites of the sample were avoided, and the primary decomposition products were identified over the range 280–500°. This work showed that neither decomposition by electron transfer nor breaking of the Cl–O bond play a significant role, and that the main reaction is dissociation of ammonium perchlorate into ammonia and perchloric acid by the scheme

$$NH_4ClO_4(s) \rightarrow NH_3(g) + HClO_4(g), \quad (1)$$

followed by oxidation of the ammonia by the decomposition products of perchloric acid. The mass spectrum of the flash pyrolysis products of ammonium perchlorate is discussed by Boldyrev and coworkers[12]. The spectrum was recorded 1 ms after the onset of decomposition. The perchloric acid spectrum is practically indistinguishable from that obtained by Fisher[26] on an apparatus specially designed for the study of atoms and free radicals. Other papers also discuss the dissociation of ammonium perchlorate into ammonia and perchloric acid[11,27]. The experimental method of studying the kinetics of this reaction has already been described in the previous Section. Ammonium perchlorate crystallites of 10 μm diameter were deposited on the heater strip by evaporation of a droplet of an aqueous or alcoholic solution of ammonium perchlorate. The following relationship was found between the maximum decomposition rate $\left(\frac{d\alpha}{dt}\right)_{max}$ and temperature over the range 280–320°:

$$\left(\frac{d\alpha}{dt}\right)_{max} = 10^{9.09}\exp(-24\,000/RT)\ s^{-1}.$$

Combining this result with data[28] on the equilibrium pressure of ammonia and perchloric acid vapour we obtain a sublimation coefficient $\beta = 8 \times 10^{-2}$ for ammonium perchlorate, which is only a factor of 2 higher than the value reported[29] for the range 230–270° by a different method. The activation energy is lower than a previously published value[29] by 6 kcal mole^{-1}, but higher than another reported value[30] by 2.5 kcal mole^{-1}.

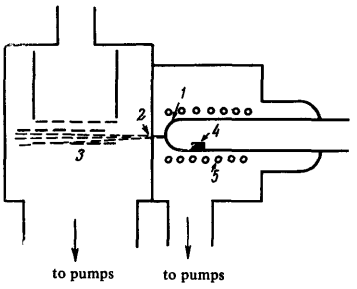


Figure 4. Mass spectrometric assembly for studying the decomposition of solids in the vicinity of the ion source at relatively high pressures[24]: *1*) orifice; *2*) diaphragm; *3*) ion source of time-of-flight mass spectrometer; *4*) sample; *5*) furnace winding.

The decomposition of ammonium perchlorate has been studied[24] at 400° and 20–100 mmHg pressure, i.e. under conditions which did not exclude secondary gas-phase reactions. The combined reaction vessel and effusion orifice used in this work was of molybdenum glass, previously heated to the required temperature. The distance between the orifice and the ionisation volume was a few millimeters, the pumping speed was ~ 100 litre s^{-1}. As a result, unstable particles and corrosive gases could be reliably monitored. The sample was inserted into the heated reaction vessel by magnetic "ram" (Fig. 4). It was located 10 mm from the orifice, and therefore the diffusion time of gas molecules from the sample to the orifice was as short as 0.05 s at 8 mmHg and 0.5 s at 80 mmHg. Because of the shortness of the diffusion path, the procedure allowed the primary decomposition products of ammonium perchlorate (ammonia and perchloric acid) to be detected as well as the secondary products (chlorine, oxygen, nitrous oxide, water, nitrogen, nitric oxide, hydrogen chloride). The measured concentrations of ammonia and perchloric acid were practically the same as the reported[28]

equilibrium pressures of ammonia and perchloric acid over solid ammonium perchlorate:

$$NH_4ClO_4(s) \rightleftharpoons NH_3(g) + HClO_4(g). \quad (2)$$

This confirms the decomposition scheme for ammonium perchlorate proposed by the writer[27] and the hypothesis that the equilibrium corresponding to reaction (2) is maintained during the decomposition. Changes in gas phase composition during the reaction were also observed in the absence and in the presence of iron oxide, and correlated with the catalytic effect of impurities on the dissociation of nitrous oxide.

The dissociation of perchlorates other than ammonium perchlorate has also been investigated. Thus, the kinetics of the thermal decomposition of nitronium perchlorate NO_2ClO_4 has been studied[31] at 100–160° at pressures high enough for the secondary reactions to be significant. The decomposition products are O_2, NO, and Cl_2, the activation energy 15 kcal mole^{-1}. The primary stages in the decomposition of guanidinium perchlorate have been investigated[32] in the ion source of a time-of-flight mass spectrometer. In addition to the reaction previously proposed[33],

$$CH_5N_3 \cdot HClO_4 \rightarrow CN \cdot NH_2 + HClO_4 + NH_3 \quad (3)$$

it was shown that guanidinium perchlorate dissociates by the reaction

$$CH_5N_3 \cdot HClO_4 \rightarrow CH_5N_3 + HClO_4. \quad (4)$$

One-third of the material dissociates by reaction (3), and two-thirds by reaction (4).

An omegatron has been used[34] to study the decomposition of ammonium polymolybdate and polytungstate; ammonia, and molybdenum and tungsten oxides, have been identified as the decomposition products. The accompanying hydrogen and nitrogen are assumed[34] to result from the catalytic decomposition of the ammonia pumped through a layer of molybdenum or tungsten oxide.

The products of the pyrolysis of nickel tetracarbonyl and iron pentacarbonyl have been investigated[35,36]. The mass spectrum of $Ni(CO)_4$ positive ions was established in the mass spectrometer by a method which allowed the molecular beam to be distinguished from the decomposition products formed in the ion source. The evidence for the existence of gas-phase intermediates such as $Ni(CO)_3$ could not be confirmed by sampling the gas from the low-pressure reactor. Appearance potentials and dissociation energies were obtained for the ions $Ni(CO)_x^{+q}$ ($q = 1.2$; $x = 1, 2, 3, 4$).

Bowden and coworkers[37] made a mass-spectrometric study of the kinetics of the thermal dissociation of sodium and thallium azide single crystals. They showed that in the initial stages of dissociation of small NaN_3 single crystals in a vacuum of 10^{-9} mmHg (i.e. close to the ion source of the mass spectrometer) various gases are evolved, such as Ne, Ar, He, and H_2, which are strongly held on the crystal surface by adsorption forces. Subsequently, when the nitrogen lines begin to appear in the mass spectrum, the residual OH^+ and CO_2^+ peaks disappear, obviously as a result of reactions between the background gases and the Na atoms formed by decomposition of the azide. The long induction periods frequently observed in the decomposition of solids can perhaps be ascribed to the disappearance of metal nuclei by reaction with the residual gases.

Many papers, only some of which are mentioned here[38–40], deal with the evaporation mechanism of solids and with the composition of their vapour. Thus, Shchukarev and coworkers[38] have studied the composition of the vapour over the oxides of gallium, thallium, and indium, Mostovskii and Sakseev[39] have examined the vapour over SbS_3 and GeSe. Studies of the evaporation of GeSe have confirmed the view that this compound undergoes little dissociation in the vapour state. The vapours of many solids contain monomers, dimers, and trimers. Due to superposition of the lines, their ratio is often difficult to determine mass-spectrometrically.

Using a time-of-flight mass spectrometer[41,42], the following species have been detected by rapidly heating to 1400–3000° a tungsten wire which had been kept at room temperature in an oxygen atmosphere: O, WO, WO_2, WO_3, W_2O_6, and W_3O_9. These results indicate that only a few per cent of the surface tungsten atoms are oxidised at room temperature. The evaporation products include monomers, dimers, and trimers of WO_3. The activation energy for the evaporation of these oxides is ~ 100 kcal mole^{-1}.

2. Thermal and Mechanical Degradation of Polymers

The kinetics and mechanism of polymer degradation have attracted a great deal of study. Thermal degradation of polymers is known to give rise to a mixture of products of different volatilities[43]. Bradt and coworkers[44,45] published the first papers on the nature of the fractions which are involatile at room temperature but volatile at the temperature of the thermal degradation experiment. In this work, the polymers were decomposed in the immediate proximity of the ion source of a mass spectrometer. The thermal decomposition of polystyrene was shown[44] to produce dimeric and trimeric molecules in addition to the monomer. Analogous results were obtained in a study[46] of the decomposition of polyethylene at 200–330°. The mass spectrum consists of lines which can be assigned to C_nH_{2n+1} ions. The C_4H_9 peak is the strongest in the mass spectrum of the decomposition products of polyethylene at 200°. As the temperature is raised from 200 to 330°, the intensity maximum tends to flatten out and to shift from $n = 4$ to $n = 8$. The degradation is shown to proceed in two stages. In the first stage, mainly at the lower temperatures (~ 200°), the rate is limited by diffusion of light molecules through the polymer. In the second stage, at higher temperatures, the thermal degradation is rate-limiting. The decomposition products of poly(tetrafluoroethylene) and poly(fluoroethylpropylene) have been studied[47] at 350–875° with a time-of-flight mass spectrometer; the flash-pyrolysis products of various polymers have also been studied[16] using a fast pulse of energy from a high-power xenon flash tube. The experimental problems encountered in the study of polymer degradation by mass spectrometry have been discussed in a number of papers[48–50].

The time-of-flight mass spectrometer has been used[17,18,50–53] to study the kinetics and mechanism of the mechanical and thermal degradation of polymers. The polymer samples were fractured and heated close to the ion source of a mass spectrometer, as shown in Fig. 5.

The primary products of the thermal and the mechanical degradation of poly(methyl methacrylate) and polystyrene were shown[51] to have identical mass spectra. Hence it was concluded that the gas evolution accompanying mechanical degradation of these polymers has a thermal origin: the polymer suffers local heating during fracture, and gases are evolved as a result of the rise in temperature. Regel' and Muinov[18] showed that gases are evolved as soon as the load is applied, not only after fracture of the polymer sample. This suggests that decomposition of the polymer sets in as soon as the load is applied. Since the

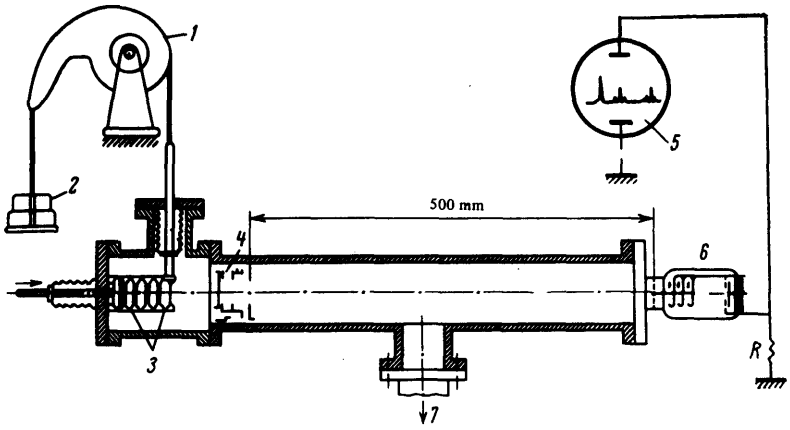


Figure 5. Apparatus for studying the kinetics and mechanism of mechanical degradation of polymers by a time-of-flight mass spectrometric method[52]: *1*) cam; *2*) load; *3*) sample magazine; *4*) source; *5*) mass spectrum; *6*) electron multiplier; *7*) to vacuum pump.

curves of elongation and gas evolution against time are identical, the degradation and deformation processes must be intimately related. The rate of gas evolution is an exponential function of the applied stress. Amelin and coworkers[53] have reported studies of the thermal and mechanical degradation of poly(methyl methacrylate), polystyrene, poly(vinyl chloride), polypropylene, and polyacrylonitrile. They show that the volatile products of thermal and mechanical degradation are identical if the decomposition of the polymer begins in the main chain. When thermal degradation of the polymer involves the removal of side chains, the volatile products are different from those of mechanical degradation. These findings confirm and extend the results of the kinetic theory of degradation, according to which the mechanical fracture processes are related to the thermal degradation of polymers. In a kinetic study[17] of the thermal degradation of poly(methyl methacrylate) and of the methyl methacrylate monomer, initially the activation energy is found to be 30 kcal mole^{-1}, but at a more advanced stage of degradation it becomes ~ 50 kcal mole^{-1}.

3. High-temperature Decomposition of Solid Propellants

Valuable information on the mechanism and the kinetics of the high-temperature decomposition of solid propellants, which play an important part in combustion, can be obtained by fast heating of solid samples to elevated temperatures, and by identifying the decomposition products (including unstable species) in a dynamic mass spectrometer such as a time-of-flight or other instrument with a short time constant. The kinetic parameters of the decomposition reaction can be obtained from a mass spectrometric study of the rate of formation of these products[23]. As a result of the recent developments in the relevant experimental techniques, this type of work has grown considerably in the last few years.

We shall take as our first example a study[4] of the pulsed pyrolysis of nitrocellulose. The source of heat was radiation from an optical arc furnace. Both the characteristics of the source of heat[4,54,55] and the unstable intermediates found in the pulsed pyrolysis of solid organic compounds[4,56,57] have already been described. However, unequivocal identification of these products is far from easy. One of the most important results of this work is the realisation that the composition of the pyrolysis products of cellulose is a function of the rate of heating: this is evident from the data summarised in the Table. For low heating rates up to 300°, using conventional resistance heating, the main decomposition products are water, solid carbonaceous deposits, and volatile organic compounds.

Pyrolysis products of cellulose[4].

Heat source	Electric furnace	Carbon arc	Carbon arc	Xenon flash tube
Thermal flux, cal cm^{-2} s^{-1}		1.5	11	3000 at peak of output
Temperature, °C	up to 350	300	600	600
Heating time	2.7 h	10 s	4 s	$5\cdot10^{-4}$ s
Atmosphere	vacuum	helium	helium	helium
	Products (in wt.%)			
H_2O	19	32	16	28
CO	3	3	13	37
CO_2	?	9	11	4
Volatile organic compounds	51	3	6	30
Tar	2	19	51	none
Solid carbonaceous residue	25	33	3	1
CO/CO_2 ratio	—	0.33	1.2	9.2

With the higher heating rates obtainable from an optical arc furnace (heating time 4–10 s), a large amount of tar is formed and the yield of volatile organic compounds decreases. Under flash pyrolysis with a xenon lamp (heating time ~ 0.5 ms) the main products are volatile

organic compounds (mainly aldehydes and ketones), water, and carbon monoxide. As the heating rate is increased, the CO/CO_2 ratio increases and the molecular weight of the products decreases. Fast heating appears to subdivide the polymer chains into smaller segments. Evidently, pyrolysis in the condensed phase is accompanied by a whole spectrum of chemical reactions in series and in parallel whose probability depends on the heating rate. Useful products can be obtained by controlling the heating rate. Similar effects have been observed during the carbonisation of coal.

The use of a pulsed laser beam for heating coal particles is a new and interesting technique in this area of research[9]. Very small particles of coal (less than 10 μm in diameter, $\sim 10^{-6}$ g) were placed in a quartz tube within the ion source of a time-of-flight mass spectrometer about 10 mm from the ionisation volume, and heated by a pulse of radiation from a focussed laser beam. The energy of the pulse was 0.7 J, corresponding to an energy flux of $\sim$ 100 kW cm^{-2} for a spot diameter of 7 mm. The mass spectrum was recorded 0.2 ms after application of the pulse of radiation. In addition to the stable decomposition products, including polyacetylenes, free radicals (H, C, CH_3) and alkali metal ions (Na^+, K^+) were observed. The mass spectra obtained at low energies of the ionising electrons provide further evidence of the formation of radicals and ions. The temperature of the spot could not be estimated, but it must have reached several thousand degrees, since a considerable amount of atomic carbon was found in the gas phase. The techniques used in this work are suitable for the detection of atoms and radicals in other high-temperature decomposition reactions.

Methods for studying the decomposition of coal under non-isothermal conditions have been developed[13]. The heating rate must be constant, or a known function of time. The method was tested on simple decomposition reactions of solid organic acids, giving rise to water, carbon monoxide, and carbon dioxide, and satisfactory agreement between theory and experiment was obtained. A resistance furnace was used for low heating rates (0.5–0.3 deg min^{-1}), and the decomposition products were led to the detector (a conventional mass spectrometer) by a stream of inert gas. A platinum gauze heater was used for higher heating rates (10^3–10^5 deg min^{-1}), and temperatures were measured by a platinum/platinum–rhodium thermocouple. The decomposition was studied close to the ion source of a time-of-flight mass spectrometer. The highest temperature was 1000°. Assuming first-order kinetics for the formation of ethane by the decomposition of coal, an activation energy of 42.1 kcal mole^{-1} and a pre-exponential factor of 10^{11} min^{-1} were obtained. It was shown that the evolution of methane and hydrogen from coal during pyrolysis is not a first-order reaction, but follows more complex kinetics. The theoretically predicted shift of the maximum reaction rate towards higher temperatures at higher heating rates was confirmed experimentally. Perhaps as a result of the arbitrary assumption of first-order kinetics, the error in the determination of rate constants was as high as two orders of magnitude.

A more satisfactory method of studying the kinetics of fast reactions relies on isothermal conditions, combined with the use of a time-of-flight mass spectrometers[10,11]. The method was applied[58] to kinetic studies of the mechanism of high-temperature decomposition of nitrocellulose. The rates of formation of various decomposition products (NO_2, CH_2O, H_2O, CO, and CO_2) have been studied[58] as a function of reaction time at temperatures (220–280°) close to the surface temperature of pyroxylin guncotton. The reaction was shown to be autocatalytic. The maximum decomposition rate, measured from the rate of formation of the mass 30 peak, is described by the equation

$$W_{max} = 10^{14.4} \exp(-35000/RT)\ s^{-1}.$$

Extrapolation to 220° of the rate of decomposition of nitrocellulose measured[59] at 130–160° in a vacuum of $\sim 10^{-4}$ mmHg (i.e. close to the experimental conditions of the previous investigation[58]) gives a value about an order of magnitude lower than reported in that work[58]. This may be due to a difference in the thickness of the nitrocellulose samples used in the two investigations ($\sim$ 3 μm in Ref. 58, and very much thicker in Ref. 59). The activation energy given in Ref. 58 is lower than the value obtained by other methods[59–61]. The difference may be ascribed to the different methods used to measure the rate constant. In Ref. 58, NO_2, CH_2O, CO, CO_2, and H_2O are chosen as the primary decomposition products although their relative amounts vary during the course of the reaction. The mass spectra of the decomposition products suggest that other nitrogenous species are formed in addition to NO_2 (possibly NO_3).

A series of papers by Dauerman and coworkers[6–8,62] discusses the primary act in the decomposition of nitrocellulose, nitroglycerine, and propellants based on these compounds, under low-pressure combustion and ignition conditions. Their experimental procedure, using a mass spectrometer with a variable accelerating potential has already been discussed (see Fig. 3). Since these experiments were made at relatively high pressures (10–100 mmHg), i.e. under conditions which permit secondary reactions in the gas phase, these workers' claims to have investigated the primary decomposition and combustion products are, to say the least, suspect. Thus, mass spectrometric data on the composition of the high-temperature pyrolysis products of nitrocellulose are quoted[7] in the presence of 10–100 mmHg pressure of helium. Radiant energy from an optical arc furnace is used, and the products are monitored immediately before ignition, at ignition, and during combustion. From an analysis of the intensity ratios of the mass 30 and 46 peaks, they conclude that nitric oxide is predominant among the primary decomposition products, with the reservation that the NO in their experiments could have been formed by decomposition of NO_2. Comparing these results with others[58], obtained under conditions which precluded secondary gas-phase reactions, we conclude that the nitrogen dioxide in Dauerman's experiments[7] must have been converted into NO before reaching the detector. These experiments give no information on the rate of formation of the various components as a function of the extent of conversion of the condensed phase, and in this respect also they differ from our own[58], since they were carried out under non-isothermal conditions of continuously rising temperature. However, in spite of these shortcomings, Dauerman's results[6–8] are very interesting because they reveal the correspondence between the surface temperature of the propellant and the rate of decomposition, thus increasing our knowledge of the processes involved in the ignition and combustion of solid propellants. They lead to the conclusion[6,8,62], very important from the standpoint of the theory of combustion of two-component solid propellants (consisting mainly of nitroglycerine and nitrocellulose), that the main product of the ignition and combustion of these propellants is the NO_3 radical and not NO_2, as previously suggested. This conclusion is based on the fact that the intensity ratio of the mass 46 and mass 30 peaks for the ignition and combustion products at 10 mmHg pressure was well above unity, and that no peaks above mass 46 were found in the

mass spectrum. Fig. 6 shows the time dependence[8] of the intensity of the main ion peaks, which are proportional to the rate of formation of the corresponding gaseous components during ignition of the propellant. The singularities on these curves (points where the differential shows a break) correspond to the moment of ignition and onset of combustion.

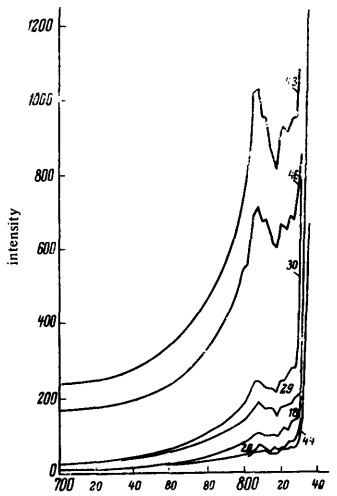


Figure 6. Intensity of various mass peaks as a function of time of irradiation during ignition of solid propellants by radiant energy[8]. The number of ciné-film frames, which is proportional to time, is plotted horizontally. The sample is an uncatalysed D-4 propellant.

Comparing Dauerman's mass spectrum[6,8] with published mass spectra of nitrate esters and other nitro compounds[63], including nitroglycerine, we conclude that it cannot be assigned to any known nitro ester. The mass spectrum was therefore assigned to the NO_3 radical, with the assumption that removal of this radical is the first step in the decomposition of two-component solid propellants (and also of nitroglycerine). However, this conclusion is also debatable, since the observed mass spectrum[6,8,62] could be due to a species (possibly even NO_3) resulting from secondary reactions in the gas phase, e.g. from the gas-phase decomposition of nitroglycerine, which is volatile under the experimental conditions used in that work[6,8,62]. The writer's mass-spectrometric study of the primary products of the decomposition of nitroglycerine compositions at 170–290° in a high vacuum, i.e. in the absence of gas-phase reactions, is also inconsistent with that conclusion[6,8,62]. The value of the mass spectroscopic method in studies of the decomposition of solid propellants is clearly shown in two papers by Dauerman and coworkers[8,64]. Lead stearate—an efficient catalyst for the combustion of two-component solid propellants—is shown[8] to catalyse other condensed-phase chemical reactions of these propellants. The role of the emulsifier in mixed solid propellants based on a butadiene–acrylic acid copolymer has been studied by a similar method[64].

Coats[65] also used the pulsed mass spectrometric method in his study of the thermal decomposition of mixed solid propellants based on ammonium perchlorate. In that work (quoted by Friedman[66]), a thin platinum wire coated with a film (5 μm thick) of the mixed solid propellant was heated to 500–600° in 50 ms by discharging a condenser, and the decomposition products were led to the ion source of a time-of-flight mass spectrometer. Peaks corresponding to hydrocarbon residues, NH_3, $HClO_4$, HCl, and ClO_2 were observed in the mass spectrum.

Recently published work[63,67–73] on the mass spectra of the molecules of individual explosives should prove very valuable in the interpretation of the mass spectra of the decomposition products of solid propellants.

Mass spectrometry has been widely used in recent years to study the kinetics and mechanism of the thermal decomposition of solids. Further developments are being constantly reported, and new fields of application in science and technology are being suggested. The method should prove valuable in areas such as cosmochemistry, the interaction of powerful light beams with matter, and also the study of the combustion mechanism of solid propellants and associated high-temperature, fast reactions. Many unsolved problems remain in all these fields.

REFERENCES

1. V. L. Tal'roze, G. K. Labrovskaya, and A. F. Dodonov, Khim. Nauka i Prom., II, 154 (1966).
2. "Mass Spectrometry", (C. A. McDowell, Editor), New York, 1963, p. 442.
3. "Advances in Mass Spectrometry, 3", Paris, 1964.
4. K. A. Lincoln, Pyrodynamics, 3, 133 (1965).
5. R. Friedman, J. Appl. Polymer Sci., 9, 650 (1965).
6. L. Dauerman, G. E. Solser, and Y. A. Tajima, J. Amer. Inst. Aeronautics and Astronautics, 8, 1501 (1967).
7. L. Dauerman and Y. A. Tajima, J. Amer. Inst. Aeronautics and Astronautics, 8, 1468 (1968).
8. L. Dauerman and Y. A. Tajima, Raketnaya Tekh. i Kosmonavtika, 4, 125 (1968).
9. W. K. Joy, W. R. Lander and E. Pritchard, Nature, 5129, 640 (1968).
10. V. V. Boldyrev, O. P. Korobeinichev, and V. N. Pan'kov, Kinetika i Kataliz, 1, 218 (1968).
11. O. P. Korobeinichev, V. V. Boldyrev, and Yu. Ya. Karpenko, Fizika Goreniya i Vzryva, 1, 33 (1968).
12. V. V. Boldyrev, O. P. Korobeinichev, and Yu. Ya. Karpenko, Izv. Akad. Nauk SSSR, Ser. Khim., 1372 (1968).
13. H. Jüntgen and K. H. Van Xeek, Fuel, 2, 103 (1968).
14. R. Loison and R. Chauvin, Chimie et Industrie, 3, 269 (1964).
15. V. A. Pavlenko, L. N. Ozerov, and A. E. Rafal'son, Zhur. Tekh. Fiz., 64, 581 (1968).
16. V. P. Ageev, N. I. Ionov, and Yu. K. Ustinov, Zhur. Tekh. Fiz., 34, 546 (1964).
17. G. S. Anufriev, O. F. Pozdnyakov, and V. R. Regel', Vysokomol. Soed., 8, 834 (1966).
18. V. R. Regel' and T. M. Muinov, Vysokomol. Soed., 8, 841 (1966).
19. G. S. Anufriev and B. A. Mamyrin, Pribory i Tekh. Eksper., 5, 150 (1964).
20. G. A. Heath and J. R. Majer, Trans. Faraday Soc., 60, 1783 (1964).
21. J. N. Maycock, V. R. P. Verneker, and P. W. M. Jacobs, J. Chem. Phys., 46, 2857 (1967).
22. J. N. Maycock and V. R. P. Verneker, J. Chem. Phys., 47, 3618 (1967).

23. O. P. Korobeinichev, V. V. Boldyrev, V. P. Pan'kov, and Yu. Ya. Karpenko, Abstracts of Papers Presented at the First All-Union Symposium on Combustion and Explosion, FIKhF, Akad. Nauk SSSR, Moscow, 1968.
24. O. P. Korobeinichev, V. V. Boldyrev, Yu. Ya. Karpenko, and N. Z. Lyakhov, Izv. Akad. Nauk SSSR, Ser. Khim., 778 (1969).
25. L. L. Bircumshaw and B. H. Newman, Proc. Roy. Soc. A, 227, 115 (1954).
26. I. P. Fisher, Trans. Faraday Soc., 63, 684 (1967).
27. O. P. Korobeinichev, Kinetika i Kataliz, 5, 1169 (1968).
28. S. H. Inami, W. A. Rosser, and H. Wise, J. Phys. Chem., 67, 1077 (1963).
29. P. W. M. Jacobs and A. Russell-Jones, J. Phys. Chem., 72, 202 (1968).
30. L. L. Bircumshaw and T. R. Phillips, J. Chem. Soc., 4741 (1957).
31. J. N. Maycock and V. R. P. Verneker, J. Phys. Chem., 71, 4077 (1967).
32. V. V. Boldyrev and O. P. Korobeinichev, Izv. Akad. Nauk SSSR, Ser. Khim., 708 (1969).
33. A. Glasner and A. Makovki, J. Chem. Soc., 1606 (1954).
34. M. Onchi and E. Ma, J. Phys. Chem., 67, 2240 (1963).
35. S. M. Schildcront, G. A. Pressley, and F. E. Stafford, J. Amer. Chem. Soc., 89, 1617 (1967).
36. R. E. Winters and R. W. Kisser, J. Inorg. Chem., 3, 699 (1964).
37. R. F. Walker, N. Gane, and F. P. Bowden, Proc. Roy. Soc. A, 294, 417 (1966).
38. S. A. Shchukarev, G. A. Semenov, and I. A. Rat'kovskii, Zhur. Prikl. Khim., 35, 1455 (1962).
39. A. A. Mostovskii and D. A. Sakseev, Zhur. Tekh. Fiz., 34, 1321 (1964).
40. "Condensation and Evaporation of Solids", New York, 1964.
41. B. McCarroll, "Pribory dlya Nauchnykh Issledovanii" (Apparatus for Scientific Research), VINITI, 3, 132 (1967).
42. B. McCarroll, J. Chem. Phys., 46, 863 (1967).
43. S. L. Madorskii, "Termicheskoe Razlozhenie Organicheskikh Polimerov" (Thermal Decomposition of Organic Polymers), Izd. Mir, Moscow, 1967, p. 43.
44. P. Bradt and V. H. Dibeler, J. Res. Nat. Bur. Stand., 50, 201 (1953).
45. P. Bradt and F. L. Mohler, J. Res. Nat. Bur. Stand., 55, 323 (1955).
46. Nakagawa, J. Phys. Soc. Japan, 16, 741 (1961).
47. R. E. Kupel, Analyt. Chem., 36, 386 (1964).
48. K. Gerard, Analyt. Chem., 36, 1402 (1964).
49. G. P. Happ and D. P. Maier, Analyt. Chem., 36, 1678 (1964).
50. A. V. Amelin et al., Pribory i Tekh. Eksper., 4, 152 (1968).
51. V. R. Regel', T. M. Muinov, and O. F. Pozdnyakov, Fiz. Tverdogo Tela, 4, 2468 (1962).
52. V. R. Regel' and T. M. Muinov, Fiz. Tverdogo Tela, 8, 2364 (1966).
53. A. V. Amelin, T. M. Muinov, O. F. Pozdnyakov, and V. R. Regel', Mekhanika Polimerov, 1, 80 (1967).
54. K. A. Lincoln, Appl. Optics, 3, 405 (1964).
55. L. S. Nelson, Science, 135, 296 (1962).
56. K. A. Lincoln, Analyt. Chem., 4, 541 (1965).
57. K. A. Lincoln, "Pribory dlya Nauchnykh Issledovanii" (Apparatus for Scientific Research), 12, 53 (1964).
58. O. P. Korobeinichev, V. V. Aleksandrov, and N. Z. Lyakhov, Izv. Akad. Nauk SSSR, Ser. Khim. (in press).
59. K. K. Andreev and B. S. Samsonov, Symposium "Teoriya Vzryvchatykh Veshchestv" (Theory of Explosives), Trudy Moskov. Khim. Tekhnol. Inst., Izd. Vysshaya Shkola, Moscow, 1967, p. 7.
60. G. B. Manelis, Yu. I. Rubtsov, L. P. Smirnov, and F. I. Dubovitskii, Kinetika i Kataliz, 1, 42 (1962).
61. Yu. M. Grigor'ev, V. I. Lisitskii, and A. G. Merzhanov, "Fizika Goreniya i Vzryva" (Physics of Combustion and Explosion), 4, 512 (1967).
62. L. Dauerman, G. E. Solser, and Y. A. Tajima, J. Phys. Chem., 69, 3668 (1965).
63. R. Boschan and S. P. Smith, Mass Spectra of Nitrate Esters, Nitrite Esters, Nitro Compounds and Several Other Nitrogen Compounds, Naval Ordnance Report, No. 5412, China Lake, California, 23 July 1957.
64. L. Dauerman and G. E. Solser, Raketnaya Tekh. i Kosmonavtika, VINITI, 6, 209 (1968).
65. R. L. Coats, Final Report Research on Combustion of Solid Propellants, Lockheed Propulsion Co., Redlands Calif. 1965, Rept. 641 – F.
66. R. Friedman, Raketnaya Tekh. i Kosmonavtika, 7, 3 (1967).
67. F. Volk and H. Schubert, Explosivstoffe, 1, 2 (1968).
68. J. Momigny, Bull. Soc. roy. Sci., Liège, 25, 93 (1956).
69. J. H. Beynon, R. A. Saunders, and A. E. Williams, Ind. chim. belge, 4, 311 (1964).
70. S. Meyerson, J. Puskas, and E. K. Fields, J. Amer. Chem. Soc., 88, 4974 (1966).
71. J. Collin, Bull. Soc. roy. Sci., Liège, 23, 194 (1954).
72. J. Collin, Bull. Soc. roy. Sci., Liège, 23, 201 (1954).
73. P. T. M. Fraser and N. C. Pane, J. Chem. Soc., B, 6 (1968).

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