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THE CHEMICAL ACTION OF IONISING RADIATIONS ON INORGANIC CRYSTALS

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1. INTRODUCTION

Considerably greater interest has recently been taken in the study of the chemical changes occurring in solids under the influence of ionising radiations. The results of these investigations have especially great prospects of practical application in the search for radiation-resistant materials for the construction of atomic reactors and plant and for intensifying many solid-state reactions of practical importance. These problems are also encountered in developing the technology of the production of artificial radioactive isotopes by irradiating solids in a reactor. It will therefore be useful to reach, from accumulated data, some general conclusions concerning the chemical changes produced by radiations in solids and their influence on the physicochemical properties of the solids.

The experimental data which have accumulated are so extensive and diverse that it is impossible to cover them in a short review. Since fairly complete surveys have appeared[1-13] of the action of radiation on metals and on polymeric materials, we shall confine ourselves to an examination of work on the chemical changes produced by radiation in ionic crystals. The variation in physical properties under these conditions has been considered[14], and therefore we shall disregard this question, too, in the present paper.

2. ACTION OF HEAT, LIGHT, AND IONISING RADIATIONS ON MATTER

In contrast to heat and light quanta, the energy of which is less than, or at best comparable with, that of chemical bonds, the energy of γ-quanta, electrons, or heavy particles formed in radioactive disintegration or in artificial (instrument) sources of radiation — accelerators — is much larger, usually by several orders of magnitude, than the chemical bonding energy, and this governs many specific aspects of radiochemical processes in the solid phase, which distinguish them from photolysis and thermal decomposition.

The action of heat on a solid results in atomic vibrations in the lattice, caused by the greater number of heat quanta; only a few of them correspond to the high-energy limit of the Boltzmann distribution and can lead to rupture of the chemical bond. Under isothermal conditions heat quanta are distributed uniformly throughout the volume of the crystal, and if this alone governed the start of thermal decomposition, the latter could begin at any point in the crystal, and its kinetics would be represented by a first-order equation. But different positions in the crystal are not equivalent in reactivity. Therefore bond rupture takes place at those points in the lattice where at a given instant the bond is for some reason weaker than at other points, and it is this which causes the localisation of the initial centres of thermal decomposition at defects in the crystal.

In the decomposition of solids under the influence of visible light or ultraviolet radiation the energy of the quantum is comparable in magnitude with that of a chemical

bond, and this case should represent the simplest type of decomposition of the solid[15]. Since on exposure the light flux is incident primarily on the surface of the crystal, any chemical interaction between light and matter which does occur is localised mainly at the surface.

Jacobs *et al.*[16] showed, in a study of the kinetics of the photolysis of barium azide as an example, that, by varying the wavelength maximum of the radiation employed, portions of the crystal surface differing in activity can be made to react separately. Thus at $\lambda < 2600$ Å photolysis can occur over the whole surface of the crystal. When $2600 < \lambda < 3300$ Å, photolysis is localised mainly at lattice defects, and at $\lambda > 3300$ Å the photochemical process can take place only if crystal nuclei of metallic barium are already present in the barium azide crystal, the process being localised at the interface between the starting material and the photolysis product.

Photolysis usually ceases when the crystal surface has become covered with a layer of product, which protects the deeper layers of the crystal from the action of light (provided that further development of the reaction by a thermal mechanism, by conversion of the energy of the light quanta into heat energy[17], is excluded).

The rate of photolysis may depend both on the probability of transfer of an electron to the conduction band and on the possibility of its recombining with a positive hole.

The main features of the radiolysis of solids which distinguish it from thermal and photochemical decomposition processes result from the fact that the energy carried by each γ-quantum or high-energy charged particle far exceeds (usually by several orders of magnitude) the energy of a chemical bond in a solid. Therefore only a negligible fraction of the total energy of a γ-quantum or a heavy particle is expended on the initial expulsion or excitation of an electron. The remainder is transferred to the expelled electrons on ionisation, is emitted as a γ-quantum of longer wavelength by the Compton effect, or may even be used up in displacing the atoms or ions from the normal lattice points into the interstices.

The distribution of the portions of the lattice which have been affected by interaction between radiation and matter depends both on the energy and intensity and on the type of radiation. In the case of γ-rays, for example, exposure produces a uniform formation of radiation defects throughout the bulk of the substance[18]. Exposure to particles results in ionisation of the substance predominantly along the track of the particle, and therefore in a non-uniform distribution of radiolysis products both in the volume of the crystal and along the path traversed by the particle in the crystal[18]. The mean free path then depends firstly on the energy and secondly on the nature of the particle itself.

Since the principal chemical effects of the exposure of solids to high-energy radiation (especially γ-quanta and electrons) are produced not by the bombarding particles themselves but by secondary electrons whose energy may vary within extremely wide limits, the elucidation of quantitative relations is extremely complicated, even if the initial exposure is to monochromatic radiation.

In contrast to light, which produces mainly ionisation effects, high-energy rays may also cause ions to be displaced from the normal lattice points into the interstices. The relative proportions of ionisation and displacement effects depend both on the nature of the irradiated material and on the type of radiation and its energy.

At the end of the track the transfer of the energy of the particle to the lattice causes the formation of heat wedges, which represent local hot spots in the crystal, in which the temperature rises sharply for a brief period.

The possibility of a high concentration of energy in a small portion of the lattice on exposure to high-energy particles and ionising radiation was the basis of attempts to initiate the detonation of explosives by irradiation. However, in spite of a large number of investigations with both high explosives and detonators and with various types of radiation — γ-rays, electrons, neutrons, protons, α-rays, fission products[19-28] — attempts at radiation initiation of explosion were unsuccessful (except for cases of the detonation of nitrogen iodide under the influence of α-particles and fission products). According to Bowden[29], this may be because the centres of decomposition thus formed are too small for the production of the local hot spots necessary for conversion of slow thermal decomposition into detonation.

A general and fundamental characteristic of the radiolysis of solids is that the probability of a process occurring is determined not so much by the weakness of the chemical bonds at individual sites in the lattice, which is the case with thermal decomposition and the action of light, as by what conditions exist for restoration of a bond in the lattice after it has been broken. These determining factors may be extremely varied, ranging from the ionisation potential of the cation, in the case of reactions resulting from electron transfer from anion to cation, to the free volume in the lattice of an ionic salt. The latter is of particular importance when the primary stage of radiolysis is the rupture of bonds within a complex ion, as, for example, in the action of high-energy rays on alkali metal nitrates and permanganates[30-34]. In the first case the mechanism of radiolysis of the crystal will be analogous to thermal decomposition and the action of light, while in the second case it may be different.

3. EXPERIMENTAL TECHNIQUE FOR IRRADIATION

The experimental technique for irradiation and for studying the radiolysis products has much in common with that used for studying the photochemical and thermal breakdown of solids. On the other hand, the basic features of radiolytic changes in ionic crystals, which distinguish them from thermal and photochemical processes, require a special technique for the experimental study of the chemical changes produced in solids by irradiation.

For exposure to an external source of X-rays or γ-rays, the specimens are placed in glass or quartz tubes[35-42] or in special vessels which enable the composition and pressure of the gas over the substance to be controlled, and also permit irradiation at low temperatures[34,43-45]. Exposure to neutrons and mixed radiation in the channels of a reactor is effected in a similar manner[46-49].

If decomposition under the influence of the radiation from a radioactive isotope contained in the test salt itself is to be studied, the preparation is simply kept for a certain time in air or in a vacuum[50,51].

In the case of irradiation with electrons (β-rays) there is a possibility of considerable weakening of the electron flux by the walls of the vessel containing the specimen. Therefore either an open vessel is used[52] or, if irradiation in a vacuum or in an atmosphere of an inert gas is required,

a window is made in the vessel and is covered with a material whose absorption of electrons is a minimum (for example beryllium or aluminium foil).

With exposure to low-energy electrons, which are obtained by means of instrument sources, the substance is placed in the actual space of the source. In special equipment described by Groocock and Tompkins[53] an electromagnetic device enables the substance undergoing decomposition to be introduced into the low-energy electron beam between the cathode and the grid.

In contrast to irradiation with γ-rays, when electrons of low and intermediate energies are used allowance must be made firstly for the great probability of non-uniform distribution of radiolysis products between the bulk of the crystals and their surface, and secondly for the possibility of the preparation being heated up in the electron beam at high intensities of the electron flux. The latter may result in thermal decomposition of the specimen as well as radiolysis, which will considerably modify the experimental results. The effect of this source of error in investigations of radiolysis in an electron flux may be diminished to a considerable extent by using pulsed electron accelerators.

When bombardment with heavy particles — ions, protons, deuterons, and α-particles — is used, the same difficulties are encountered to a still greater extent. Moreover, the shortness of the range in air of heavy particles and ions obtained by radioactive disintegration, is an added difficulty, so that exposure must be made either in a vacuum or with the material to be irradiated in direct contact with the source[54-56].

The possibility of obtaining high-energy particles fluxes in artificial sources sometimes permits enclosed specimens to be irradiated through a foil window, but this involves considerable loss of intensity in the foil.

Another very important factor in the method is measurement of the dose absorbed by the specimen. A distinction must be made between measurement of the intensity of the radiation source and measurement of the radiation dose absorbed by the substance, the latter being defined as the energy ΔE absorbed by an element of mass m or volume v of the material[57].

The first of these determinations is extremely important in the design and manufacture of isotopic and instrument sources of radiation, and the second is especially valuable in the study of radiochemical processes.

The absorbed dose can be measured either directly or indirectly, the former often involving great experimental difficulty and sometimes being altogether impracticable. Direct determination of the absorbed dose is usually accomplished by measuring the attenuation of the energy flux in the substance or the quantity of energy absorbed, by means of a standard made of material having the same thickness and approximately the same density but not subject to radiolysis under the given conditions. Thus, for example, Heal[34,43-45] in his work on the action of X-rays on ionic salts used as such a standard a metal disc of the same thickness as the irradiated crystal. This disc was placed in a calorimeter, and the absorbed dose was calculated from measurements of the temperature of the disc during exposure.

The absorbed dose can be measured also by determining the intensity of the dose by means of a ferrous sulphate or a ceric sulphate dosimeter, and then calculating the dose absorbed by the test material, allowing for the difference in electron density of this material and the dosimetric solution[35-42].

With neutron irradiation, measurement of the absorbed dose is also preceded by determination of the neutron flux intensity, which involves measuring the specific activity, after fixed intervals of time, of a cobalt wire introduced into the irradiated space[54,55,58].

The intensity of an electron beam can usually be characterised by the current measured in a Faraday cylinder, or can even be measured with an ordinary ferrous sulphate dosimeter.

4. METHOD OF STUDYING CHEMICAL CHANGES PRODUCED IN SOLIDS BY RADIATION

The above peculiarities of radiolytic processes in solids compared with thermal and photochemical decomposition are responsible for the special features of the technique used to study the chemical changes occurring in solids on irradiation.

These are methods for the rapid determination of the extremely small amounts of the radiolysis product, which can usually constitute only a few hundredths or tenths of a per cent of the total weight of material, and only in rare instances, when high doses are absorbed, can reach a few per cent. Secondly, in the study of chemical radiation effects in solids account must be taken of the distribution of radiolysis products in the bulk of the crystal, which may differ with the type and energy of the radiation used. Thirdly, the possibility of displacement effects as well as ionisation effects during radiolysis must be borne in mind. Displacement effects, which do not usually lead to chemical changes in the crystal, may have a considerable influence both on the chemical changes associated with ionisation and excitation of electrons in a solid under the action of radiation and on the rates of other physicochemical processes involving irradiated solids (for example, thermal decomposition).

The methods employed to study radiochemical reactions should provide for the possibility of following these effects too.

Among the methods employed at the present time to study the products of radiolysis, we may note firstly dissolution of the irradiated crystals in water and determination of the radiolysis products in the aqueous solution by the usual methods of chemical analysis, *i.e.* by the normal procedures of volumetric microanalysis, or even by means of colorimetric, spectrophotometric, potentiometric, and polarographic methods.

If one of the products of radiolysis is a gas, the course of the process can be followed by measuring the quantity of gas evolved in the reaction.

In contrast to the thermal and photochemical breakdown of solids, in which decomposition starts at the surface and gaseous reaction products are evolved immediately, radiolysis occurs throughout the volume of the crystal, and with small degrees of decomposition the gaseous products

remain in the crystal[52]; in order to determine their amount, therefore, this gas must be liberated from the bulk of the crystal.

One of the methods usually employed for this purpose is to heat the irradiated specimens in a vacuum[46] to the melting point or a crystallographic transition point. However, this may yield results which are too high owing to the simultaneous occurrence of thermal decomposition of the salt, which would be accelerated in the presence of solid products of the radiolysis. In addition, the temperature at which appreciable thermal breakdown begins may be lowered[59-61].

The errors associated with the heating up of the specimens are to a considerable extent eliminated in a method for studying the kinetics of radiolysis based on determining the dependence of gas evolution on the degree of dispersion of the crystals being examined, and then extrapolating the gas evolution at a definite dose to zero crystal size. The method was developed in connection with the radiolysis of barium chloride, and then used to study the dynamics of radiolysis with several other inorganic salts[62-64].

Another method for determining the amount of gas formed in a crystal on radiolysis is the microgas-volumetric technique developed by Heal[65] and based on measuring under the microscope the size of the gas bubble liberated when a small, accurately weighed crystal dissolves. This method was used to study the radiolysis of alkali metal azides[34,43,45]. It follows from the principle of Heal's method that it is applicable only if the gas evolved on radiolysis neither reacts with nor dissolves in the solvent crystal. The quantity of gas evolved can be followed also from the change in weight[66] or density[46] of the crystals during radiolysis.

The composition of the gas evolved can be determined by the usual methods of gas analysis[37,46,52] or by mass spectrometry[41,46].

The course of radiolysis can be followed by checking the amount and condition of a solid reaction product. If the initial crystals are colourless or feebly coloured, while the resulting product absorbs light strongly in the visible or ultraviolet range, the dynamics of radiolysis can be studied, especially in the initial stage of the process, by colorimetry[67], photometry[68-70], and spectrophotometry of the irradiated crystals[44,71-73]. The quantity and structure of the new phase which accumulates during radiolysis, and also the accompanying change in degree of imperfection of the crystal, can be studied also by X-ray[18,56,59,74-78] and electron[79-81] diffraction methods.

Electron paramagnetic resonance has become especially important for investigating the nature of the initial centres formed on the radiolysis of ionic crystals by interaction of electrons and positive holes with ionic defects, and of the free radicals which are formed by the rupture of intracrystalline bonds as a result of radiolysis. This method has been used[51,60,82-92] to study the chemical changes caused by radiation in ionic crystals.

Among other physicochemical methods employed to investigate irradiated ionic crystals the following may be mentioned: measurement of heats of solution[38], thermographic and thermogravimetric examination of the crystals[42], determination of the change in ionic and electronic conduction in the crystals after irradiation[53], and the magnetic susceptibility[46,93,94] and mechanical properties of the crystals[74].

5. CHEMICAL CHANGES PRODUCED BY RADIATION IN INORGANIC IONIC CRYSTALS

The nature and extent of the chemical changes in solid ionic crystals depend on the type and energy of the radiation, and also on the nature of the substance undergoing radiolysis. Absorption of radiation results in ionisation and excitation of the electron shells of the ions forming the lattice, and in some cases in their displacement from their normal lattice points into interstices. Chemical changes result mainly from ionisation effects; displacement effects most often entail a change in physical properties.

With binary ionic salts of the alkali metal halide type the action of ionising radiation depends to a considerable extent on the ionisation potential of the cation, since this quantity determines the depth of the potential traps for the capture of electrons by anionic vacancies, which is the initial stage of the radiolysis of these salts. A consequence of the formation of F- and V-centres is the formation, inside the crystals, of metallic particles and halogen atoms, which are uniformly distributed throughout the volume of the crystal in the case of γ-rays or are located in the portions of the crystal adjacent to the surface under the action of particles and electrons of intermediate energy.

The occurrence of chemical changes when these crystals are irradiated is indicated by the solution becoming alkaline and gaseous halogen being formed on dissolution of the salt (a fact known from the earliest work[95]† on the action of radiation), owing to reaction of the primary products of radiolysis with water molecules:

$$e + H_2O \rightarrow OH^- + \tfrac{1}{2}H_2,$$
$$h + Cl^- \rightarrow Cl, \quad 2Cl \rightarrow Cl_2.$$

As a result of the reversibility of the defects, their rate of breakdown increases with rise in temperature and in their concentration, the chemical changes accompanying their formation usually being slight and according to Heal[98] not exceeding 0.1%.

Increases in the ionisation potential of the cation increases the irreversibility of radiolysis and the yield of products, as is the case, for example, in the radiolysis of silver halides[70] and cadmium halides[99] under the influence of X-rays, γ-rays, and electrons, during which far greater yields of reaction products are reached with the same dose absorbed.

In the case of ionic salts containing complex anions or cations specific effects may appear owing to rupture of chemical bonds within the complex ions under the influence of radiation, which may occur in these cases together with the electron transfer from anion to cation usually observed in binary ionic crystals. In this class of salts the radiolysis of azides, nitrates, and perchlorates has been most thoroughly studied.

Heal, Groocock and Tompkins, Sviridov, and Bowden have investigated the breakdown of these salts under the influence of X-rays, electron irradiation, and reactor radiation[18,20,29,43,53,72,74,100-104]. In all cases metallic crystal nuclei are formed, and free nitrogen is evolved in yields which may reach 1–2.5%. As with alkali metal halide crystals, dissolution of irradiated crystals of sodium

† [Refs. 96 and 97 are not indicated in the text. They deal with free Na and Cl in sodium chloride crystals containing colour centres (Ed. of Translation)].

azide makes the solution alkaline, while interaction between the free hydrogen evolved and the nitrogen of the azide ion yields ammonia and hydrazine[98].

Just as with simple binary salts, the radiation yield and the rate of radiolysis of azides become greater the higher the ionisation potential of the cation. The permanence and the irreversibility of the chemical changes produced in solids by the action of radiation also increase.

Nitrates form another group of salts changes in which under the influence of ionising radiation have been studied in some detail. Irradiation of nitrates by X-rays, γ-rays, and electrons as well as reactor radiation usually results in elimination of an oxygen atom from the nitrate ion with conversion of the latter into a nitrite[34-39,41,46,52,105,106]. The oxygen remains trapped in the crystals, and is liberated from them only when the salt is dissolved in water or is heated to its melting point or a polymorphic transition point[46]. Solutions of irradiated nitrates appear[52,98] to have one more alkaline (pH 9–10) than would be expected solely from hydrolysis of the resulting nitrite.

The radiation yield of the process depends on the possibility of recombination of the nitrite ion with oxygen, and is higher the more conditions favour removal of the oxygen atom from the sphere of action of the NO_2^- ion. The radiation yield of nitrites therefore depends, under otherwise identical conditions, on the free volume, which is the difference between the volume of a unit cell of the crystal lattice and that of the ions in it[30-32,46].

In the radiolysis of alkali metal nitrates the radiation yield has been shown[30,31,46] to be higher the greater this free volume (for cations ranging from sodium to caesium). A similar relation is observed also with the nitrates of the alkaline earth metals[32]. In both cases the sequence of chemical stability on radiolysis is the opposite to the order of thermal stability for the same series of salts[107,108]. This is probably because the thermal stability of the nitrates is determined by such factors as, for example, the polarising effect of the cation on the anion, which play a secondary part in radiolysis. A similar relation is observed with other salts too, for example permanganates[33] and bromates[109].

The free volume is usually the main factor when the variation in ionisation potential in a series of salts is slight. When the change in ionisation potential is considerable, its influence, associated firstly with the polarising action which the cation can exert on the anion and secondly with a change in stability of the centres of electron capture, may become predominant, and the radiation stability will then vary in the same sequence as the thermal stability. Thus, for example, the free volumes in silver and sodium nitrates are about the same, while the ionisation potentials of their cations differ strongly (7.54 and 5.1 eV respectively[110]). Therefore the radiation stability of silver nitrate is far less than that of sodium nitrate. The same relation is shown by a comparison of the radiation stability of strontium and lead nitrates[32].

When the radiation stability of complex ionic salts is being studied, account must be taken also of the strength of the bond, within the complex ion, which is ruptured under the influence of γ-quanta or secondary electrons. An example is provided by comparative data on the radiation yields of potassium chlorate and potassium nitrate under the same conditions of irradiation. The energy of the Cl–O bond in the chlorate is 2.38 eV, while that of the N–O bond in the nitrate is 3.65 eV, and hence the radiation yield of oxygen is 4 and 0.8 mole of O_2 per 100 eV in $KClO_3$ and KNO_3 respectively[46].

Results obtained by Proskurnin and Baberkin have shown that the presence of water of crystallisation in the nitrate results in an increase of the radiation yield, owing both to radiolysis of the water and to a diminished probability of recombination of the oxygen eliminated on radiolysis, as a result of interaction with the water molecules[39,40].

Radiolysis of a chlorate by various types of radiation yields oxygen, chloride, hypochlorite, and perchlorate[44,46,60,61]. The first three products are formed as a result of breakdown of the chlorate ion, and the perchlorate ion is produced by interaction of the chlorate ion with oxygen[44]. Radiolysis of solid potassium perchlorate gives chloride and chlorate[43]. During irradiation the chlorate ion may itself break down into the above products.

The decomposition of solid crystalline salts has been noted also when they are used as targets in the preparation of radioactive isotopes[111-114].

Heavy-metal oxalates evolve carbon monoxide and carbon dioxide on irradiation[49,50,56], the oxalate ion being converted into carbonate[50,56], while in several cases the solid product of radiolysis is the metal oxide[49].

In the radiolysis of solid salts of chromic acids by a neutron flux, it has been established that the ability to undergo radiation-induced reduction increases in the sequence $K_2CrO_4 < K_2Cr_2O_7 < K_2Cr_3O_{10} < CrO_3$.[115]

Interesting relations have been obtained for the radiolysis of complex compounds which break down in several stages owing to their complicated composition[116]. The extent of decomposition of complex compounds depends on the ions in both the inner and outer spheres. Thus it is greater for the crystalline hydrates of nitrates than for the anhydrous salts[36,39,40]. This phenomenon can be explained as a consequence of structural changes and of the influence of products from the radiolysis of water[39,40], and also because the field due to the water dipoles separating the nitrate ions from the cations is weaker than the field due to the latter[36]. A comparison of the radiation stability of various platinum complexes (tetra- and hexa-chloroplatinates[117]) showed that, with the same inner sphere, ammonium salts decompose more readily than the potassium salts. Complexes containing different ligands in the inner sphere decompose more rapidly than those with identical ligands; compounds of bivalent platinum are more readily decomposed than quadrivalent platinum compounds; and a *trans*-isomer breaks down more readily than the *cis*-isomer. In the case of oxalate complexes those of a quadrivalent metal prove to be more stable than those of bivalent metals[116].

The above data suggest that in some cases radiolysis may take place by a mechanism similar to that of thermal decomposition, while in other cases it may have a different mechanism.

When the laws governing radiolysis and thermal and photochemical decomposition are the same, as for example in the case of silver oxalate, the breakdown of which probably always involves capture by interstitial silver ions of electrons expelled by radiation, factors which increase the thermal stability will lead to an increase in the radiation stability too. If, however, the laws are different, methods of increasing — or diminishing — the radiochemical

stability must be sought in terms of factors which are specific to radiolysis. Therefore a clear knowledge of what is the mechanism of the radiolysis of solid ionic salts and what factors govern the radiochemical process is absolutely essential in the search for methods of controlling their radiochemical stability.

The rate of radiochemical processes and the yield of the products of radiolysis may be greatly affected by the actual structure of the crystal, involving the presence of both macro- and micro-defects (ionic vacancies, interstitial ions, impurity ions, dislocations, grain boundaries, etc.). The radiochemical stability of ionic crystals will therefore depend very greatly on their mode of preparation [118], their deformation [119-121], and the concentration and type of impurities which have entered the crystal during its preparation or processing [122,123].

The influence of defects in crystals on their radiation stability can be examined in greater detail in the effect of impurities. A change in radiation stability resulting from the introduction of impurities had already been noted in the early work on the action of radiation on ionic crystals (see for example, Refs. 124 and 125), and formed the subject of later investigations on the tendency of ionic crystals containing impurities to become coloured by radiation. It was shown in this work that impurities may influence the radiation stability in the first place owing to a change in the number of breaks in the distribution of dislocations in the crystals resulting from the lack of correspondence between radii and polarisation properties of the impurity ions and the lattice ions which they replace [126,127]. Secondly, impurity ions differing in charge from the lattice ions which they replace lead to the formation in the crystal of additional cationic or anionic vacancies or interstitial ions. This also entails a change in radiation stability, which increases or decreases depending on the type of vacancies and interstitial ions formed [70,128,129].

Finally, a change in the radiation stability of ionic crystals may result from the direct capture of electrons and positive holes by impurity ions, as is observed when certain impurities are introduced into the crystals of alkali metal halides [130,131].

Apart from the effect of defects due to impurities in crystals, which we have examined in detail, radiation stability depends also on the presence of other types of defects [98]. The radiation stability is usually diminished by the presence of defects in crystals, owing to the participation of point defects in the electronic and ionic processes sometimes involved in radiochemical decomposition, the greater probability of the destruction of excitons localised at defects and accompanied by rupture of chemical bonds within complex ions. In the defective regions, moreover, there is a higher probability that ions, atoms, or radicals split off in the initial stages of radiolysis will be removed from the site of primary bond rupture, and therefore the "cage effect", which leads to recombination and is especially important in the case of solids, is diminished [98].

By analogy with what occurs in thermal decomposition [132,133], it is to be expected that the same defects will affect the rate of radiolysis differently depending on the reaction mechanism. For example, it has been shown [69,134] that the addition of cadmium ions, which generate cationic vacancies in the lattice of silver salts, increases the radiation stability of silver oxalate, but diminishes the radiation stability of silver carbonate [68], the decomposition of which involves rupture of bonds within the carbonate ion.

6. EFFECT OF PRELIMINARY IRRADIATION OF SOLIDS ON THE RATE OF TOPOCHEMICAL REACTIONS

Since the accumulation of defects in crystals may lead to a change in the rate of topochemical reactions (as was noted long ago in the literature on topochemistry), the effects of different types of defect varying according to the reaction mechanism, preliminary high-energy irradiation of solids may be expected to exert an appreciable and specific influence on the rate of individual types of topochemical reactions.

Since the effect of preliminary irradiation has been studied most thoroughly in the case of thermal decomposition compared with other types of topochemical reactions, we shall confine our attention first of all to such reactions.

The effect of previous irradiation on the rate of subsequent thermal decomposition had already been noted in the earliest work on the kinetics of thermal decomposition. The facts which have now been accumulated enable some quite definite conclusions to be drawn concerning the nature of the effect.

Among the earliest work was that of Garner and Moon [135] who found that preliminary exposure of barium azide to γ-rays from radium accelerates the subsequent thermal decomposition of this salt. The same effect was shown in later work with preliminary exposure to various types of radiation in the decomposition of barium azide irradiated with X-rays [101,136], of lithium, cadmium [29,131], and lead [137] azides exposed to γ-rays and neutrons, and also of mercury [139,140], silver [101,118,140], lead [142], nickel, and copper [75] oxalates.

Preliminary exposure to γ-rays, X-rays, and neutrons accelerates the subsequent thermal decomposition of the permanganates of potassium [143], rubidium [144], caesium [145], barium [146], and silver [58,147,148], silver carbonate [68], potassium bromate [149], ammonium dichromate [150], and ammonium perchlorate [42,151,152].

Freeman and Anderson [152] compared the formation of the initial reaction centres in the thermal decomposition of ammonium perchlorate crystals which had and which had not been exposed to X-rays. They discovered that, whereas in unirradiated crystals thermal decomposition involves formation of nuclei on the crystal surface and their further growth into the interior, in the thermal breakdown of irradiated crystals formation of nuclei is not confined to the surface, but takes place throughout the volume of the crystal.

This work established that preliminary exposure to ionising radiation may considerably diminish the time required for subsequent thermal decomposition. Exposure to γ- or X-rays causes mainly a shortening of the induction period [143-148]. For the thermal decomposition of the permanganates of potassium [143], rubidium [144], and caesium [145], it was found that the duration of the induction period t and the dose of ionising radiation absorbed in the substance, or the period of exposure τ, are linked by the simple and reproducible formula

$$\log \tau = kt + \text{const.}$$

A similar relation was observed for the shortening of the induction period in the thermal decomposition of barium azide which had been exposed to X-rays [136].

Neutron irradiation has a strong influence on the whole course of thermal decomposition [144,153], which is not confined

to the initial stage, and this is specific to the activation of thermal decomposition by neutron irradiation.

The effect of radiation on the rate of subsequent thermal decomposition by an ionic–electronic mechanism may be changed by the addition of heterovalent ions, which generate cationic or anionic vacancies, as has been shown for the addition of cadmium to irradiated silver oxalate[141].

A detailed study of the mechanism underlying the action of the additive showed[154] that, whereas with preliminary ultraviolet irradiation of the oxalate the additive affects both photolysis and thermal decomposition, with preliminary exposure to γ- and X-rays the diminution in the effect is due mainly to retardation of thermal decomposition in the presence of the additive.

Many questions still remain unanswered and obscure in the effect of radiation on the rate of subsequent thermal decomposition.

In some cases thermal decomposition is accelerated only by neutrons. Thus with lead styphnate monohydrate[153] the rate is unchanged on exposure to γ-rays and to a ^{60}Co source at doses of the order of 1.8×10^8 rad, but it is greatly increased by neutron irradiation in a reactor channel even at comparatively low doses.

The same occurs when manganese oxalate dihydrate is exposed to neutrons or γ-rays[155]. The causes of this phenomenon have been linked[155,156] with the fact that a great proportion of radiation-induced faults resulting in an increased rate of thermal breakdown of irradiated substances are due to displacement phenomena. In the case of lead styphnate, for example, these displacements may occur both as a result of elastic collisions between neutrons and carbon atoms in the styphnate ion and as a consequence of the reaction $^{14}N + n \rightarrow {}^{14}C + p$, which also leads to destruction of the styphnate ion.

It is not clear in what cases a diminution in activation energy can be expected to result from preliminary irradiation. A change in activation energy has been found[143-148] in the subsequent thermal decomposition of permanganates. In other cases, for example the thermal decomposition of silver oxalate exposed to ^{60}Co γ-rays, data have been obtained indicating the absence of such a phenomenon, the change in rate produced being linked mainly with a change in the pre-exponential factor in the Arrhenius equation[134].

The influence of the interval between the time during which irradiation is carried out and the time of thermal decomposition is not yet clear in all its details. With substances such as barium azide, on the one hand, it has been shown that the rate of subsequent thermal decomposition is affected by the length of this interval[101,136]. On the other hand, the length of the interval appears[143-147] to have no effect on the thermal breakdown of the irradiated permanganates of metals in Group I of the Periodic System, but it is extremely important when the interruption occurred — during the induction period, during the autocatalytic phase, or during the time of diminishing reaction velocity following the maximum.

In this connection it is of interest to study the rate of thermal decomposition directly at the instant of irradiation. It has been shown[157] by means of specially designed equipment[158] that exposure of barium azide to X-rays at the instant of thermal decomposition results in a greater increase in reaction velocity than with preliminary irradiation.

Besides the above data, according to which preliminary irradiation may strongly affect the rate of subsequent thermal decomposition, substances are known with which no such activating effect occurs, although their thermal breakdown takes place quite readily. An example is silver oxide, whose rate of subsequent thermal decomposition remains unchanged after preliminary exposure to γ-rays and neutrons over quite a wide range of doses[159]. The same applies to the thermal decomposition of potassium peroxochromate[101].

The criterion determining whether preliminary irradiation will affect the rate of subsequent thermal decomposition is still obscure, and different views are held concerning the mechanism by which the solid is activated.

According to one of these, the main part in the enhanced reactivity of solids resulting from preliminary irradiation is played by the excitation of electrons and ionisation, and ultimately by radiolysis of the solid. The products of radiolysis which appear in the lattice catalyse subsequent chemical reactions in which the irradiated solid is involved, including thermal decomposition processes.

According to another view, developed by Prout and his collaborators[142-147,159,160], the chief result of irradiation is the displacement of ions from normal lattice points into the interstices. In the course of subsequent thermal decomposition when the substance is heated, these defects are annealed, the interstitial ions returning to the lattice points which they had previoysly vacated. Owing to the accompanying evolution of heat, partial decomposition of the solid occurs even before the onset of general thermal decomposition. This decomposition is accelerated by deformation of the original lattice at the starting material–reaction product interface.

In his early papers Prout[160] suggested that this occurs as a result of elastic collisions of Compton electrons, formed in the primary acts of interaction between radiation and matter, with the lattice ions. This hypothesis, however, was not supported by the experimental data, either of other workers[33,136,148] or of Prout himself[161]. He therefore put forward a new hypothesis[161], according to which displacements can occur in the lattice not as a result of elastic collisions between electrons and ions but as a result of one of the possible displacement mechanisms associated with repeated ionisation of the anion in the ionic crystals. The possibility of displacements of this type, even when the energy of the radiation is low, has been shown[162-165] in the case of crystals of alkali metal halides. According to Prout's views, ionisation effects may appear in the rates of subsequent thermal decomposition mainly because of their being involved in processes resulting in displacement of ions from the normal lattice points into the interstitial space.

A critical comparison of these two points of view has shown[166,167] that the increased rate of thermal decomposition resulting from irradiation of solid salts cannot be reduced to displacement effects alone, but is associated to a considerable extent with the catalytic action of radiolysis products form by ionisation effects in the crystal lattice.

The principal objections to Prout's mechanism can be briefly summarised as follows.

1. According to Prout's mechanism in its original form, irradiation of a solid with γ-quanta and electrons of energy less than the threshold value should not produce displacements, and therefore will not accelerate subsequent thermal decomposition. This contradicts experimental results

indicating that irradiation may have a considerable kinetic effect in spite of its energy being far below the threshold value[33,136,148]. The concept of displacements resulting from repeated ionisation of the anion to some extent removes several objections to Prout's theory, but nevertheless does not eliminate them completely. If displacements resulting in activation of the solid are supposed to result from repeated ionisation of the anion and subsequent expulsion of the positively charged remnant from the lattice point, it must be assumed that those salts will be most sensitive to radiation in which the effective charge on the cation is greatest, or in other words the bond between cation and anion is most ionic in character. In compounds with a greater proportion of homopolar bond the probability of expulsion of an anion which has acquired a positive charge should be smaller, and the stability towards radiation therefore greater. If this were so, it would be expected, for example, that potassium permanganate would be more sensitive to irradiation than is silver permanganate. This contradicts experimental results; precisely the opposite is observed[33].

2. Similarly, doubt also arises concerning the validity of the other criterion which, in Prout's opinion, determines the sensitivity of a thermal decomposition to previous irradiation, namely the applicability of the Prout–Tompkins equation to the kinetics of the thermal breakdown. It is known that the applicability of a particular kinetic equation is not sufficient as a criterion of the occurrence of a chemical process in a solid by a given mechanism. Furthermore, direct experimental results are also known which indicate that a reaction which does not fit into the framework of a chain mechanism, and is not represented by the Prout–Tompkins equation, is nevertheless considerably speeded up by preliminary irradiation[68].

The fact that displacement effects play not the chief but a secondary part in the radiolysis of ionic salts is also indicated by results obtained by Henning *et al.*[46] These workers made a comparative study of the radiolysis of potassium nitrate on irradiation with fast neutrons, which lose a large part of their energy in the solid as a result of displacement effects, and with electrons, whose energy was below the threshold value required to produce displacement effects. The radiation yield was found to be about the same in the two cases.

This is confirmed also by calculations[54] showing that the number of displacements produced by each fission fragment of uranium in potassium nitrate crystals is smaller by two orders of magnitude than the number of nitrate ions decomposed per single fission fragment.

It is more likely that activation of the solid results from the appearance, in the crystal lattice after irradiation, of various defects and inclusions of radiolysis products, which catalyse the thermal decomposition. The formation of such inclusions in the lattice will result mainly from the capture of electrons, expelled by radiation into the conduction band, by anionic vacancies, by interstitial cations located at special points in the crystal (for example on dislocation lines), by impurity ions, etc., *i.e.* as a result of ionisation effects.

Displacement effects, which may change the concentration of ionic defects, also can influence the rate of subsequent thermal decomposition of irradiated materials. Sometimes they may even play the main part then, as is the case, for example, in the effect of preliminary neutron irradiation on the thermal breakdown of lead styphnate[156] and manganese oxalate dihydrate[155].

It can therefore be reckoned that in general both ionisation and displacement effects can be involved in the increased chemical reactivity of solids resulting from their preliminary irradiation. In most cases, especially when electromagnetic radiation and heavy corpuscular ionising radiation is used, the predominant part should probably be attributed to ionisation effects.

Apart from thermal decomposition, preliminary irradiation may substantially change the reaction velocity of ionic crystals in topochemical reactions of other types as well.

Preliminary exposure to protons increases the rate of reduction of nickel oxide by hydrogen[168,169] at low temperatures and the rate of dissolution of ferric oxide in hydrochloric acid[170]. Irradiation changes the adsorption capacity and other physicochemical properties of ionic crystals[171,172].

The mechanism of the change in reactivity produced in these substances by irradiation is probably analogous to that in the case of subsequent decomposition, and consists in the accumulation of defects in the crystals of the irradiated substance.

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