

# THE THERMAL, ELECTRONIC AND PHOTOCHEMICAL DECOMPOSITIONS OF SOLID BODIES

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The photochemistry of solids has received relatively little attention, if one excepts numerous studies on the silver halides made in connection with the photographic process (1). A few quantitative studies of the rate of thermal decomposition of solids have been made, but, in general, little is known other than the products of the reactions. The effects of alpha and beta particles on solids have been observed (2), but the chemical effects of slow-moving electrons on solids have received little or no attention. Theoretical considerations underlying the various modes of decomposition are in a very rudimentary stage. It is the purpose of this article to bring together the existing data on these subjects and to point out certain theoretical difficulties and possibilities.

The reason for the sparsity of the data on the reactions of solids is not difficult to find. The following types of reaction seem to be evident: (1) those for which all of the products are gaseous; (2) those in which the solids, in decomposing, leave a solid residue. In the former case the products may have relatively little effect on the course of the reaction unless they are highly adsorbed by the remaining solid. It is true that the rate of reaction may seem to depend markedly on the method used for its determination, for the process of diffusion of the gaseous products through the crystal lattice may be an important factor. Fortunately, however, this effect may be neglected in many cases. Thus any method depending on the evolution of a gas would give

a true measure of the reaction rate only after a steady state had been reached. In some cases the reaction may be limited to the surface molecules, and diffusion would not be of importance. For

TABLE I  
Thermal decomposition of solids

SUBSTANCE	TEMPERATURE RANGE	<i>E</i> cals./mole	CRYSTAL FORM	<i>T</i> <sub>1</sub> (K = 0.01) ABSOLUTE	<i>E</i> / <i>T</i> <sub>1</sub>	REFERENCE
	°C					
FeCO <sub>3</sub> (siderite).....	491-581	85,500	Trigonal	773	111	(14)
CoCO <sub>3</sub> (dry crystals).....	427-477	72,400 <sup>a</sup> 82,200 <sup>b</sup>	Trigonal	713 738	102 111	(14)
ZnCO <sub>3</sub> (zincspar).....	407-452	95,000	Trigonal			(14)
PbCO <sub>3</sub> (cerrussite).....	320-350	69,600 <sup>c</sup>	Rhombic	602	116	(14)(15)
Hg <sub>2</sub> CO <sub>3</sub> (precipitated) <sup>d</sup> .....						
Ag <sub>2</sub> O <sup>e</sup> (dried crystals).....	327-353	31,000 <sup>f</sup>	Cubic			(16)
Ag <sub>2</sub> CO <sub>3</sub> (dry crystals).....	239-253	40,000 <sup>g</sup>				(17)
Ag <sub>2</sub> CO <sub>3</sub> (amorphous) <sup>h</sup> .....	227-268					(17)(18)
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (anhydrous).....	130-170	52,100	Rhombic-bi- pyramidal	457	114	(19)
MgCO <sub>3</sub> (magnesite).....	416-487	110,000 <sup>i</sup> 204,000 <sup>k</sup> 84,000 <sup>l</sup>	Rhombic			(20)
CdCO <sub>3</sub> (precipitated).....	376-410	50,000 <sup>m</sup>	Trigonal	756	111	(21)
KClO <sub>3</sub> (crystals).....	100-255		Mono- clinic			(22)

<sup>a</sup> Reaction:  $2 \text{CoCO}_3 = \text{CoCO}_3 \cdot \text{CoO} + \text{CO}_2$ . <sup>b</sup> Reaction:  $\text{CoCO}_3 \cdot \text{CoO} = 2 \text{CoO} + \text{CO}_2$ . <sup>c</sup> Reaction:  $2 \text{PbCO}_3 = \text{PbCO}_3 \cdot \text{PbO} + \text{CO}_2$ . <sup>d</sup> Autocatalysis by Hg<sub>2</sub>O. Results not reproducible owing to effect of impurities and decomposition of catalyst. <sup>e</sup> Autocatalysis by Ag. Temperature Coefficient = 1.53. <sup>f</sup> Calculated from data given by Lewis. <sup>g</sup> Calculated by authors. Data not constant. Temperature Coefficient = 2.14. <sup>h</sup> Decomposes to give unstable intermediate (oxycarbonate) which acts as autocatalyst. <sup>i</sup> Calculated by authors for reaction  $2 \text{MgCO}_3 = \text{MgCO}_3 \cdot \text{MgO} + \text{CO}_2$  for range 416-426°C. <sup>k</sup> Calculated by authors for reaction  $\text{MgCO}_3 \cdot \text{MgO} + 2 \text{MgCO}_3 = 3 \text{MgO} \cdot \text{MgCO}_3 + 2 \text{CO}_2$  for range 452-462°C. <sup>l</sup> Calculated by authors for reaction  $3 \text{MgO} \cdot \text{MgCO}_3 = 4 \text{MgO} + \text{CO}_2$  for range 470-487°C. Only one of these three reactions has a specific reaction rate near 0.01. <sup>m</sup> Calculated by authors. An induction period is found. Temperature coefficient = 2.02.

the second type of reaction, diffusion is often of importance and, in addition, the products of the reaction remain in intimate contact with the unreacted molecules, a fact which may lead to various secondary phenomena, such as autocatalysis.

These difficulties are present in all three classes of decomposition discussed in the present article. They are particularly difficult to overcome in studies of decomposition by radiation and by electron bombardment, for the amount of reaction is usually small and its detection difficult. Gas evolution methods are usually the most convenient to employ, but care is necessary because of adsorption.

#### THE THERMAL DECOMPOSITION OF SOLIDS

Table 1 gives a fairly complete list of the thermal decompositions of solids which have been studied from the standpoint of reaction rate. In nearly all, if not all, cases where the rate can be determined without ambiguity, the variation with temperature is satisfactorily given by the Arrhenius equation

$$K = A e^{-E/RT} \quad (1)$$

where  $K$  is the specific reaction rate,  $A$  is a constant,  $E$  the "heat of activation" or critical increment per gram-molecule,  $R$  the gas constant per gram-molecule per degree and  $T$  the absolute temperature. The reactions usually obey the equation for a unimolecular reaction

$$-dM/dt = K M \quad (2)$$

where  $M$  represents the amount of solid in convenient units and  $t$  is the time. In some cases, however, the rate is proportional to the surface of the solid instead of to its mass, and, in addition, the equation sometimes needs modification because of such phenomena as autocatalysis. An attempt has been made to point out facts of this nature in the footnotes to the table.

It has been shown for bimolecular gas reactions that  $E/T$  is nearly constant when various reactions are compared for identical values of  $K$  (3). Such a comparison is shown in table 1 for the decomposition of solids, the value  $K = 0.01$  being chosen for the calculations. In many cases it was impossible to obtain the rate constants directly from the data given by the authors. The values of  $E/T$  show a surprising constancy, however. While the data on the decomposition of solid  $\text{KClO}_3$  are not entirely satis-

factory, this substance almost certainly does not follow this generalization. It would be unwise, therefore, to make too broad a statement on the basis of the values given in the table, although it is possible that the relationship would be valid for those reactions for which catalytic effects are not important.

Theories of the mechanism of gaseous reactions have attained some success in the past few years in accounting for the rate of reaction on the basis of collisions (3, 4, 5, 6, 7, 8, 9). The complexity of the molecules has been considered, and the distribution of the energy among the various degrees of freedom has been treated with the aid of statistical mechanics. Thus far these theories may be said to be in a somewhat empirical stage, for the number of degrees of freedom which must be used in the calculations can not be obtained from any molecular model. Definite information as to the nature of the bond which must be activated is usually lacking. One may say, however, that it is possible to account for the magnitude of most homogeneous gas reactions by such calculations. Introduction of the ideas of pre-dissociation (10) (11) and further studies of the energy levels in complicated molecules will undoubtedly lead to more satisfactory results in the future.

Few attempts have been made to account for reaction rates in solution. Here it is difficult to treat the problem on the basis of collisions. One or two attempts have been made to account for the reaction rates of solids (12) (13).

For homogeneous gas reactions the order of magnitude of the "heat of activation" is from  $10^4$  to  $10^5$  calories per mole. In general, the heats of activation are not related to any frequencies in the absorption spectra of the reacting gases by the simple equation of the quantum theory  $E = Nh\nu$ , where  $N$  is Avogadro's number,  $h$  is Planck's constant expressed in the proper units and  $\nu$  is the frequency. Numerous attempts to find such a relationship have been made as a result of the interest aroused by the radiation hypothesis (23). In most theories of gas reactions it is customary to assume that the relative kinetic energies of two molecules at impact, plus the internal energies of the two molecules, must exceed  $E/N$  in order to make reaction possible.

Reaction must occur during the interval between such an activating collision and a subsequent deactivating collision. During this interval the proper bond in the molecule must acquire a certain minimum amount of energy.

In the case of the thermal decomposition of solids it is difficult to arrive at any satisfactory formula for the possible number of activated bonds. If the solid is thought of as a system made up of a large number of harmonic oscillators, the fraction in any given quantum state would be given by the expression

$$P_1 = \frac{P_E e^{-E/kT}}{\sum P_j e^{-E_j/kT}} \quad (3)$$

where  $P_E$  is the *a priori* probability of the state under consideration and the summation in the denominator is to be taken over all possible states. If the *a priori* probabilities are all taken equal to unity, and there is an infinite succession of states close together, it is found that the fraction of oscillators with an energy greater than  $E_0$  will be  $e^{-E_0/RT}$  ( $E_0$  in energy units per mole and  $R$  in the same energy units per mole per degree). If now an oscillator must possess an energy greater than  $E_0$  as a prerequisite to decomposition, the specific reaction rate will be given by the equation

$$K = A e^{-E_0/RT} \quad (4)$$

This is identical with equation (1) in form.  $A$  would be a constant depending on the chance of reaction after activation. On the basis of this simple picture, therefore,  $A$  could not exceed the fraction of a group of molecules which could become activated in the proper time unit corresponding to  $K$ .

We find that the values of  $K$  for the thermal decomposition of anhydrous oxalic acid may be represented (19) by the equation

$$\log_{10} K = 22.859 - 11370/T \quad (5)$$

so that  $E = 52100$  calories per mole.  $K$  is expressed in mins.<sup>-1</sup>. Thus at a temperature of 443° K. (which is in the range of temperatures used in the investigation),  $K_{443} = 1.56 \times 10^{-3}$ , or if the unit of time is changed to seconds,  $K_{443}^1 = 2.6 \times 10^{-5}$ . Therefore

$$e^{-52100/1.99 \times 443} = 2.16 \times 10^{-26}, \quad A = 1.20 \times 10^{21} \text{ secs.}^{-1} \quad (6)$$

The quota of active molecules must be restored  $1.2 \times 10^{21}$  times per second in order to maintain the rate of reaction. Without more specific knowledge of the solid state it is difficult to estimate whether this figure is at all reasonable. It is extremely probable that our treatment of the solid as a system of harmonic oscillators is entirely too simplified. Indeed, it is reasonable to suppose that the amplitude of oscillation may not have all values (except, perhaps, for oscillators on the surface). Suffice to say, however, that this value of  $A$  is larger than can be accounted for satisfactorily in homogeneous gas reactions.

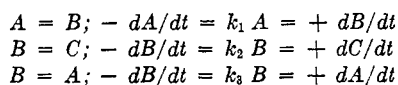
Kassel (13) has considered the difficulties involved in interpreting the high rate of variation with temperature of the decomposition of calcium carbonate hexahydrate (13a), and has come to the conclusion that it is possible to explain the data satisfactorily by postulating a step-wise reaction. We shall show in the next few pages one method of treating the problem by introducing two steps, one of which is reversible. There is no very good reason for postulating such steps for the solids mentioned in table 1. It is conceivable, however, that any solid decomposition involves a rearrangement in space of some atom or groups of atoms, and that either reversion to the initial state or production of a new compound may result from this new configuration.

The recent work of Hume and Colvin (13a) on the decomposition of potassium oxalate hemihydrate indicates a very high temperature coefficient. It is doubtful whether either this reaction or the previously mentioned decomposition of calcium carbonate hexahydrate studied by Topley and Hume (12) can be accounted for entirely by a mechanism involving steps. The reaction takes place undoubtedly at an interface and the treatment given by these authors seems adequate.

The possibility must not be ignored, however, that some modified distribution law must be used, and that the quota of active molecules as calculated above is entirely wrong. Thus it might be possible to treat each unit in the crystal lattice as an entity, and obtain a value for the probability of its possessing a certain energy of oscillation. Upon ascribing a certain number of degrees of freedom to each unit, it would be possible to calculate

the chance that any one degree of freedom would possess the requisite energy for reaction. This treatment of the problem would be analogous to that used for gas reactions. Such a treatment, however, will scarcely account for the magnitude of  $A$ , and similar difficulties are encountered for the other solids given in table 1 for which the values of  $E/T_1$  are about 111. Consequently, this line of attack will not be pursued further in this article, and we shall confine ourselves to the demonstration that most of the facts may be accounted for by assuming a step-wise reaction.

Let us assume the following mechanism



In the steady state we may assume that the amount of  $B$  will remain constant and we may write

$$B = \frac{k_1 A}{k_2 + k_3}$$

and the rate of the observed reaction will be

$$+dC/dt = \frac{k_1 k_2 A}{k_2 + k_3}$$

Put

$$k_1 = a e^{-E_1/RT}; k_2 = b e^{-E_2/RT}; k_3 = c e^{-E_3/RT}$$

and

$$K = \frac{k_1 k_2}{k_2 + k_3}$$

It can now be shown that

$$\ln K = -\frac{E_1 + E_2 - E_3}{RT} - \ln(e^{-(E_2 - E_3)/RT} + c/b) + \ln a \quad (7)$$

Referring to equation (5) we may put

$$E_1 + E_2 - E_3 = 52108 \quad (8)$$

and

$$a = 10^{22.859 - (E_1 - E_3)/2.3 RT} + 10^{22.859} c/b \quad (9)$$

It now remains to test the equations for their applicability to the experimental data. If we put  $E_1 = E_2 = 30054$  and  $E_3 = 8000$ , then  $c/b$  must have a small value in order to give a reasonable value to  $a$ . Let us assume that  $c/b = 10^{-10}$ . Then at  $443^\circ\text{K.}$ ,  $a = 8.218 \times 10^{12}$ . If  $a = b$ , we find that  $c = 0.822 \times 10^3$ . Therefore it can be shown that  $k_1 = 1.294 \times 10^{-2} = k_2$ , and  $k_3 = 9.43 \times 10^{-2}$  if the time is taken in minutes. Thus the quota of molecules in the active state would only need to be restored  $1.4 \times 10^{11}$  times per second for the first and second reactions and only 10 to 100 times per second for the reverse reaction. If the reaction is purely on the surface and only one molecule in  $10^5$  is on the surface, the active quota would only need to be restored  $1.4 \times 10^{16}$  times per second for the forward reactions. There should not be a great deal of difficulty in accounting for this rate of activation.

At a temperature of  $413^\circ\text{K.}$ , if  $c/b$  is still  $10^{-10}$ ,  $k_1 = 9.76 \times 10^{-4} = k_2$ , and  $k_3 = 4.38 \times 10^{-2}$ . The value of  $K$  calculated from these figures is  $2.13 \times 10^{-5}$ , which agrees with that obtained from equation (5). It would be impossible, from the experimental data, to detect the small variation with temperature necessitated by equation (9).

One other explanation is possible in the case of certain solids. Christiansen and Kramers (24) have postulated that a molecule on decomposing may transmit its excess energy to those immediately surrounding it, thereby producing a 'chain' reaction. This type of process might occur if the heat of reaction is small compared to the heat of activation. If the reaction is endothermic, the heat of activation divided by the heat of reaction would give approximately the number of molecules which might decompose in such a chain, providing the second molecule did not require the same heat of activation as the first. If the reaction is exothermic, an indefinitely large number of molecules might decompose in such a chain.



Such considerations as these may be of importance in some cases, but most of the solids mentioned in table 1 decompose with the absorption of energy, so that the explanation of the magnitude of the reaction rate must undoubtedly be found elsewhere.

Equation (1) has been derived by Tolman (25) in the form

$$\frac{d \ln K}{dT} = \frac{\bar{E} - \bar{E}}{RT^2}$$

where  $\bar{E}$  is the average energy of the molecules which react and  $\bar{E}$  is the average energy of all the molecules. As we have seen, most of the reactions of solids require a large difference between these energy terms. Hence some mechanism must be found which gives a larger quota of active molecules than can be obtained on any simple hypothesis.

Before concluding this section on the thermal decompositions of solid bodies, we must return to a fact which has been pointed out several years ago by Langmuir,—namely, that reactions are most apt to occur at an interface. The introduction of an interface into a solid body may lead to effects which have not been considered in this article. For example, the size of the interface and the character of its growth may suffer abnormal variations with temperature. Indeed, some work indicates that *perfect* crystals will not decompose unless they are first transformed either by scratching or by pressure. This would indicate that reproducibility should be difficult of attainment in studies of thermal decomposition. It can be shown, however, that one method of treating the problem of the interface mathematically leads to results identical in form with the step-wise reaction which we have postulated in the preceding paragraphs. In the case of oxalic acid, no interface between solid phases seems possible. The reaction probably takes place on the surface of the crystals.

The values of  $E/T$  may show an agreement which is of no theoretical significance. The fact that most of the solids considered are carbonates and that even oxalic acid decomposes to liberate carbon dioxide, may indicate, simply, a regularity in decompositions of this class. Further studies of other types of solid body will be necessary to decide this question definitely.

The large values of  $E/T$  indicate, however, that the fraction of active molecules must be small according to any simple theory of reactions taking place in one step which has been proposed. If the reaction is restricted to an interface (which would limit the number of molecules capable of activations to a small fraction of the total), the  $A$  terms for the molecules in the zone of action would be much larger than the figures we have given and the difficulty in their explanation would be correspondingly greater. It seems entirely possible, however, that the distribution law for solid bodies is not as yet fully understood and that the future may bring forth a satisfactory explanation along altogether different lines. The new quantum mechanics leads us to believe that this may not be an impossible development in the very near future.

#### THE PHOTOCHEMICAL DECOMPOSITION OF SOLIDS

Little information on the photochemical decomposition of solids is recorded in the literature. Several obvious difficulties are encountered in this type of work.

The determination of the quantum efficiency of a reaction of a solid would necessitate a measurement of the intensity of the incident as well as of the scattered radiation. This latter involves great difficulties and probably has never been carried out with entirely satisfactory precision. It may be estimated by means of a thermopile, which is moved into various positions with respect to the solid being irradiated. The total amount of scattered radiation would be obtained by integrating over a complete sphere (26).

As a result of these considerations, measurements of the photochemical decompositions of solids usually are restricted to an approximate determination of the effective wave lengths and of the decomposition products. We shall cite several photochemical reactions of solids to indicate the nature of the information available.

The rearrangement of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid was first studied by Lobry de Bruyn (27), who found that a solid solution of the acid in the aldehyde was formed. Bowen, Hartley and Scott (28) found that the quantum efficiency of this

reaction was about 0.5, neglecting scattered radiation. Padoa (29) investigated the reaction of single crystals in polarized light, and established that there were distinct differences in the speed of reaction according to the orientation of the crystal to the plane of polarization. Weigert and Brodmann (30) have studied this reaction in solution and find a quantum efficiency of about 0.5 independent of wave length. They find that the assumption of anisotropy of single molecules in solution offers a satisfactory explanation of their results.

Many examples of phototropy (31), or change in color upon irradiation, are known for solids. 1-Keto-2,3,4-tetrachloronaphthalene, which is normally yellow, becomes green under the influence of visible radiation (32). The yellow hydrazones of aromatic aldehydes,  $R_1-CH=N-NH-R_2$ , become rose, orange, purple or red brown (33). Many other examples could be given. The theory underlying these changes is not entirely satisfactory. It is probable that a single theory would not be adequate to explain all of the phenomena (34). Weigert (35) has discussed various aspects of photodichroism and photoanisotropism (35a).

The action of radiation on solid cinnamylidenemalonic acid, first investigated by Riiber (36), gives probably diphenyltetramethylenediethenyldicarboxylic acid under the influence of light. Bowen, Hartley and Scott (28) find the quantum efficiency to be about unity.

Renz (37) studied the action of sunlight on  $TlCl$ , both as a solid and in contact with various solutions. He found that the color became darker and that various compounds of thallium and chlorine were formed. He also investigated  $TiO_2$ ,  $CeO_2$  and  $Nb_2O_5$  in a somewhat similar manner (38). Reaction was observed in all cases.

Many qualitative photochemical effects have been recorded, but an examination of the literature shows that few substances have been investigated from the standpoint both of thermal reaction rate and of photochemical reaction rate. Berthelot and Gaudechon (39) studied the photochemical decomposition of anhydrous oxalic acid and found that carbon dioxide, carbon

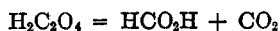
monoxide, hydrogen and traces of formic acid were formed. They allowed the solid to reach a temperature of 95°C. due to the proximity of the quartz mercury arc lamp. The decomposition was found to take place at wave lengths below 300 m $\mu$ . Subsequent work (19) (40) has shown that the decomposition requires even shorter wave lengths, below 250 m $\mu$ , and that decrease in wave length leads to an increase in rate of decomposition. Whether this implies an increase in quantum efficiency or simply an increase in absorption was not ascertained. The hydrate was found to decompose much more rapidly than the anhydrous material. A period of induction was noted. This was explained as due to the relatively slow diffusion of the decomposition products out of the crystal. It may have been only an apparent effect due to the adsorption of the products by the surface of the crystals and the glass wall. Support for this statement is found in the effect of long continued evacuation. The length of the induction period was markedly increased thereby.

The theoretical interpretation of the wave length required for photochemical decomposition of oxalic acid is not certain. We have already seen that some special postulate is probably needed to afford an explanation of the rate of thermal decomposition, and hence the apparent energy of activation would probably bear no relationship to the wave length of light necessary to cause photochemical decomposition. Solutions of oxalic acid are decomposed by wave lengths somewhat longer than those necessary for the decomposition of the solid.

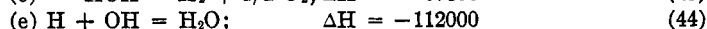
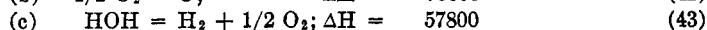
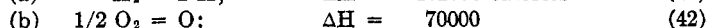
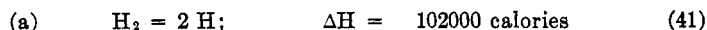
The action of the light may cause an increase in vibration quantum number of some of the bonds lying near the surface with the possibility that direct dissociation may result if the frequency is higher than that of the convergence limit. The chance of such a large increase in vibration quantum number without change in electron level is usually small. Or the phenomenon of pre-dissociation may be of importance (10) (11). In this case the excitation to a higher level may be followed by a change in electronic level resulting in dissociation.

It may be of interest to inquire whether the radiation which causes decomposition might not produce dissociation directly

instead of activation. Since the reaction is probably to be represented by the equation



the primary step may be the removal of a hydrogen atom. The heat of dissociation of the -O-H bond is not known, but it may be assumed to be similar to that required to dissociate an isolated OH radical into an oxygen and a hydrogen atom. The energy required for the latter may be obtained from the following heats of reaction:



Adding



If the action of radiation were to remove a hydrogen atom without the production of an excited residue, a wave length of about 240 m $\mu$  could be calculated as necessary. The fact that this is in agreement with experiment may, of course, be an accident. It is obvious, however, that dissociation may be brought about by the radiation necessary to cause dissociation.

By the use of monochromatic light it has been shown that KClO<sub>3</sub> decomposes for wave lengths below about 280 m $\mu$  (45). The quantum efficiency is low. It is interesting to note that the wave length does not differ greatly from that required for oxalic acid, whereas the heat of activation for the thermal reaction is much lower, although its value is uncertain.

The photochemical decomposition of formic acid in the solid state has also been investigated (46). The quantum efficiency was about 1/50, neglecting scattered radiation. Only wave lengths below 300 m $\mu$  were effective.

In conclusion, we may state that although little information of a precise nature with regard to photochemical decompositions of solids is available, the facts warrant the adoption of principles similar to those used for other systems. Absorption by a solid

usually occurs in broad bands instead of in sharply defined lines. Nevertheless, dissociation and pre-dissociation may be thought of as occurring for surface molecules. No obvious relationship exists, in the few cases available for comparison, between the wave length of the radiation necessary for photochemical decomposition and the thermal heat of activation.

In this discussion mention of the silver halides has purposely been avoided, as they are discussed adequately in other reviews.

#### THE DECOMPOSITION OF SOLIDS BY ELECTRON BOMBARDMENT

The study of ionization and resonance potentials for gases has served to show the exactness of the relation

$$eV = h\nu \quad (10)$$

in such cases that an atom or molecule may be raised to some definite energy level by electron bombardment and may return to its normal state with the emission of radiation.

Direct dissociation of molecules into normal atoms is rarely, if ever, brought about by electron bombardment. The probability of increasing the rotational energy to the point of causing dissociation by such a process seems to be extremely small. Similarly, the chance of increasing the vibration level to such a point is negligible. However, dissociation may be brought about simultaneously with a change in electron level. The products of dissociation may be, in such a case, either a normal and an excited atom, or an ion and a normal atom.

It is now generally agreed that the dissociation of hydrogen into two normal atoms involves the absorption of energy corresponding to about 4.46 volts (41). Inelastic collisions between electrons and hydrogen molecules are not observed at this potential, however. Ionization of hydrogen molecules is produced at a potential of about 16 volts and the product is an  $H_2^+$  ion (47). This ion may dissociate into an  $H^+$  ion and a normal atom upon collision. Dissociation of the molecule into one normal atom and an atom in the 2 quantum state would require an energy corresponding to 14.63 volts. This process may be brought about by electron bombardment, as well as by radiation of wave length less than 84.94  $m\mu$  (48).

Somewhat similar relationships are obtained for other molecules. Therefore, if dissociation is to be brought about, either electron bombardment or radiation may be used. If a molecule is dissociated by radiation the following sets of products may be observed: (a) two normal atoms; (b) one normal and one excited atom; (c) two excited atoms; (d) one atomic ion and one neutral atom; (e) one atomic ion and one excited atom; (f) two atomic ions (one positive and the other negative). Not all molecules will exhibit these six different modes of dissociation. For each electron state of the molecule there will be a convergence frequency which will correspond to dissociation. It seems that dissociation by electron bombardment almost never occurs except when it accompanies a change in electron state. The first of these possibilities is, therefore, a rare occurrence when electrons suffer inelastic impact with molecules.

It can be seen from the foregoing that in some cases the relationship  $eV = h\nu$  may enable one to predict what speed of electron will bring about chemical action, but that in other cases no such prediction could be made.

In addition to the foregoing possibilities, dissociation may result by the phenomenon of pre-dissociation. That is, when a molecule is excited to a higher electron level, its energy may exceed that necessary to produce dissociation in some other electron level. Under these conditions a change of electron level may occur and dissociation result. This phenomenon usually leads to a diffuseness of the lines in the absorption bands (10).

Theoretical studies of the solid state from the standpoint of energy levels are in a very elementary stage, but we may assume tentatively that conditions approximate those in gases. One should expect to be able to calculate the speed of electron which would cause reaction for some cases but not in others.

The kinetic energy of electron which will cause chemical reaction has been investigated for a few cases. Thus it is found that when the ionization potentials of nitrogen and hydrogen are exceeded, ammonia will be produced in a mixture of these two gases (49).

The electron bombardment of metals has been studied with

the following objects in view: (a) to ascertain the wave length of x-radiation emitted (50); (b) to ascertain under what conditions ultra-violet radiation is emitted (51); (c) to determine the nature of secondary electron emission (52); (d) to determine the law governing the scattering of electrons by crystals (53).

These studies have shown that the relationship  $eV = h\nu$  holds within the limits of error for the excitation of x-radiation by electron bombardment. There is also some indication that ultra-violet radiation is given off when metals are bombarded by slow-moving electrons according to the same law. The emission of secondary electrons follows laws somewhat similar to those governing the photoelectric effect. The reflection of electrons from crystals follows laws somewhat similar to those governing the scattering of x-radiation. With certain corrections applied, it is found that the wave length of the electron is given by the de Broglie equation (54)  $\lambda_e = h/mv$ , where  $m$  is the mass of the electron and  $v$  its velocity.

The effects of alpha and beta particles on solids have been known qualitatively for many years (2). Thus glass becomes colored in the presence of radioactive materials. The alkali halides are also colored by their action. The change of white to red phosphorus has been investigated.

The effect of slow-moving electrons on non-conducting solids seems to have received little or no attention. There is considerable difficulty in interpreting the results in this case.

When a non-conducting solid is exposed to an electron stream, the surface of the solid should acquire a negative charge until such a point that the electrostatic repulsion prevents any further electrons from reaching it. If, however, there is a slight conduction along the surface, the charge should be gradually dissipated, and electrons should reach the surface with a kinetic energy dependent on the net effect of the various electric fields present.

The effect of electrons of varying kinetic energy has been studied for oxalic acid. The oxalic acid was placed on the pan of a sensitive balance in a vacuum. The pan of the balance was given a positive charge. A filament was used as a source of electrons and the range of velocity was limited by grids in the



usual manner. With the arrangement of grids used, any positive ions formed in the gas between the grids would reach the surface of the solid and tend to neutralize the negative charge on it. If, then, the first few electrons which reach the solid cause decomposition leading to the production of some gas the process might continue. Superimposed on the electronic decomposition there would be photochemical decomposition brought about by radiation produced in the gas phase. This would, in effect, act as an amplifier of the effect being studied.

The results obtained indicated that when the kinetic energy of the electrons reaching the solid reached a value between 4.5 and 5.5 volts, decomposition resulted. Five volts corresponds to a wave length of about  $250 \text{ m}\mu$ , so that the relationship  $eV = h\nu$  would seem to be verified. The number of electrons per molecule of solid decomposing was about  $10^{-3}$ . These results are open to question for the following reasons: (a) the charge on the solid may render the velocity of the electrons uncertain; (b) oxalic acid does not have a negligible vapor pressure at room temperature (55), so that in spite of the removal of the vapor by liquid air, some photochemical decomposition may have resulted, owing to ionization and resonance in the vapor phase; (c) thermal radiation from the filament may cause a slight amount of decomposition. This error should be negligible.

Similar experiments with potassium chlorate (45) indicate that slight decomposition is produced by electrons at 22 volts. An ionization gauge of high sensitivity was used to detect reaction by measuring the pressure increase. Consideration of the probable adsorption of oxygen in the liquid air trap makes it seem probable that decomposition would not have been observed unless 10 to 100 molecules had decomposed per electron. Since the reaction is decidedly exothermic such a figure might not be surprising. We may say tentatively, that the relationship  $eV = h\nu$  does not permit of prediction of the proper speed of electron to cause decomposition in this case.

#### SUMMARY AND CONCLUSIONS

It is found that many solids decompose thermally, and that the heats of activation are rather high. The probability that the

expression  $e^{-E/RT}$  represents the fraction of molecules in the active state has been discussed. It is concluded that the magnitude of the reaction rates may be accounted for by postulating reaction in steps. It is possible, however, that when more is known of the solid state, some mechanism may be available for providing activation rapidly enough.

The photochemical decomposition of solids may be considered in terms analogous to those used for gases. The wave length necessary to produce decomposition may not be calculated from the heat of activation for the thermal reaction.

The various aspects of the electron bombardment of solids have been discussed. It is found that the electron energies necessary to produce decomposition may not be calculated in some cases from the wave length of radiation which causes the same process. It is shown that the decomposition of oxalic acid by electron bombardment may be in agreement with the relationship  $eV = h\nu$ , but that lack of agreement is found for  $\text{KClO}_3$ .

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