CHEMICAL ACTION IN THE GLOW DISCHARGE. XV

Reactions Preceding Ignition

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Unusual opportunities for the study of the factors underlying ignition are offered by the glow discharge, since within the discharge are to be found positive ions, atoms, excited molecules, and electrons of known energy content. All of these are present under conditions fairly well known and controllable by the investigator.

The glow discharge may be produced in a cold electrode tube at pressures ranging from a hundredth of a millimeter to several centimeters. The discharge itself consists of the Crookes dark space adjacent to the cathode, followed in order by the negative glow, the Faraday dark space, and the positive column which extends to the anode. Any of these regions, except the Crookes dark space, may be eliminated by moving the anode towards the cathode, without changing the characteristics of the remaining regions.

The potential drop across the Crookes dark space is 300 volts or more, depending on the conditions of the experiment, the actual gradient often being 1000 volts per centimeter. The length of the dark space is about one-half a mean free path between ionizing collisions for an electron of energy corresponding to the cathode potential drop. The potential drop in the negative glow is negligible. The length of the negative glow in various gases corresponds exactly to the range of electrons possessing an energy equal to the full cathode potential drop as given by Lehmann (4). This makes it possible to use directly the data of Lehmann in computing the number of positive ions formed per electron in the negative glow.

The Faraday dark space is a low energy region in which the electrons leaving the negative glow are accelerated until they reach the ionization potential of the gas, at which point the positive column sets in. The gradient in the Faraday dark space is usually of the order of 20 to 25 volts per centimeter. The positive column is a region of low energy ionization. The average energy of the electron is from 6 to 8 volts, indicating that the maximum energy does not materially exceed the ionization potential. The gradient is of the order of 15 to 20 volts per centimeter.

Chemical reactions which may be produced in the glow discharge are of two general types, propagating and non-propagating. Under controlled conditions it is possible to study the reaction in explosive mixtures without propagation. By varying the conditions of the experiment, reaction chains can be introduced to study the factors influencing the reaction through various degrees of propagation until ignition occurs.

A detailed description of the various reactions studied has been presented in a series of articles (1).

NON-PROPAGATING REACTIONS

Typical reactions studied under non-propagating conditions are the synthesis of ammonia, the oxidation of nitrogen, the formation of ozone, the oxidation of hydrogen, the oxidation of carbon monoxide, and the oxidation of methane. The decomposition of ammonia, nitrogen dioxide, nitrous oxide, water, methane, and carbon monoxide have also been studied. It should be pointed out that in these studies conditions were so arranged that only the forward reaction was in evidence; any possible back reaction was completely, or almost completely, eliminated from the experiment.

Since all these reactions as they occur in the discharge possess marked similarities in character, the various factors influencing the rate of reaction will be described for the entire series, rather than for individual cases.

1. Portion of the discharge in which the reaction occurs

The Crookes and Faraday dark spaces appear incapable of inducing reactions. All reactions occur readily in the negative glow except the synthesis of ozone, failure in this case being apparently due to the difficulty in eliminating the back reaction. Under no conditions has it been found possible to ignite explosive mixtures in the negative glow, although slight evidence of chains was observed at high current densities. In the positive column both propagating and non-propagating reactions may be produced; at low current densities chains are inappreciable even in the most explosive mixtures.

2. Effect of pressure

The rate of reaction in the negative glow is independent of the pressure over the range investigated (20 mm. to 0.2 mm.). The characteristics of the glow are difficult to control over a greater pressure range. The absence of a pressure effect shows the reactions to be of zero order. In consequence it is possible to state definitely that the reaction must be initiated by specific reaction centers, rather than by regions of high energy density. In addition it is evident that any state which is in equilibrium with

any other state does not participate in the reaction; thus the reaction $A + B_2 \rightarrow AB_2$ will show a pressure coefficient if an $A_2 \rightleftharpoons 2A$ equilibrium exists in the gas.

3. Effect of current

The rate of reaction is proportional to the current over as wide a range as can be studied. The immediate interpretation of this fact is that the reaction is initiated by specific reaction centers, formed presumably by direct electron impact. Interaction between these primary reactive states, or conditions involving the interaction of primary with other excited states formed in the discharge, can be eliminated from the reaction mechanism; likewise the formation of initial reactive centers by the interaction of non-reactive primary states can be excluded; all of these possibilities require the rate to be dependent on some higher power of the current.

The rate of production of positive ions in the discharge is known to be independent of the pressure, and proportional to the current over the region where the voltage remains constant. The intensity of the characteristic spectrum of the discharge indicates that the concentration of atoms and excited molecules is dependent on the pressure and the current density. Direct measurements of the atom concentration in the discharge by Crew and Hulburt (3) also confirm this contention. The natural conclusion to be drawn, therefore, is that the initial reaction centers are positive ions formed by direct electron impacts.

4. Effect of temperature

Reactions in the negative glow are unique in that they possess either a a zero or a negative temperature coefficient. Even the oxidation of hydrogen occurs at the same rate over a 400°C. change in temperature. The complete absence of a positive temperature coefficient is of particular significance in this study of the nature of the initial reaction centers, since it shows that these centers contain within themselves all the energy necessary for reaction. Reaction occurs, therefore, between the original active centers and normal molecules.

5. Effect of added gases

In syntheses the rate of reaction is always accelerated by the addition of the reacting gas having the higher ionization potential, and retarded by addition of the gas with the lower potential. To illustrate: in the oxidation of hydrogen the rate for $2H_2$–O_2 mixture is 6.5 molecules per electron of current, in an $8H_2$–O_2 mixture it is 8.0 molecules per electron, while in an H_2–$2O_2$ mixture it is only 3.5 molecules per electron.

Additions of foreign gases to combining mixtures, with the exception of

helium, retard the rate in proportion to the extent to which they absorb energy. Helium, with its high ionization potential of 24.5 volts, accelerates the rate up to a partial pressure of about 50 per cent. The general

TABLE 1

M/N ratios

REACTION	$\frac{M}{e}$	$\frac{M}{N_T}$	$\frac{M}{N_R}$	T °C.
$N_2 + 3H_2 = \underline{2NH_3}$	0.82	$\frac{0.82}{8.0} = 0.1$	$\frac{M}{N_2^+} = \frac{0.82}{4.5} = 0.2$	−183
$\underline{NH_3} \rightarrow N_2 + 3H_2$	3.7	$\frac{3.7}{8.0} = 0.46$		+20
$N_2 + 2O_2 = \underline{2NO_2}$	0.92	$\frac{0.92}{7.8} = 0.12$	$\frac{M}{N_2^+} = \frac{0.92}{2.7} = 0.35$	−183
$\underline{2NO_2} \rightarrow N_2 + 2O_2$	20.0	$\frac{20}{13} = 1.55$		+170
	60.0	$\frac{60}{13} = 4.65$		+20
$\underline{2N_2O} \rightarrow 2N_2 + O_2$	14.0	$\frac{14}{7} = 2.0$		+22
	14.0	$\frac{14}{7} = 2.0$		+500
$2H_2 + O_2 = \underline{2H_2O}$	6.5	$\frac{6.5}{10} = 0.65$	$\frac{M}{H_2^+} = \frac{6.5}{5} = 1.3$	−183
$2CO + O_2 = \underline{2CO_2}$	6.5	$\frac{6.5}{9} = 0.72$	$\frac{M}{CO^+} = \frac{6.5}{6.0} = 1.1$	−183
$CH_4 + 2O_2 = \underline{CO_2 + 2H_2O}$	10.5	$\frac{10.5}{8.3} = 1.3$	$\frac{M}{CH^+} = \frac{10.5}{2.8} = 3.8$	−183
$\underline{2CH_4} \rightarrow C_2H_4 + 2H_2$	3.1	$\frac{3.1}{7.8} = 0.4$		−183

M in syntheses is the number of molecules formed; in decompositions the number decomposing.

N_T is the total number of positive ions formed per electron of current.

N_R is the number of positive ions of reactant having the higher ionization potential.

e denotes electrons of current in the outer circuit.

conclusion may be drawn, therefore, that ions of the reacting gas having the lower ionization potential and ions of inert gases, except helium, are relatively ineffectual in initiating reactivity.

In decompositions the addition of foreign gases may or may not retard the rate, depending on the specific nature of the reaction. In the decomposition of nitrous oxide the rate is decreased by foreign gases to the extent to which they reduce the number of N_2O^+ ions as computed from the relative stopping power for electrons. The decomposition of nitrogen dioxide, on the other hand, is actuated by foreign ions almost as readily as by NO_2^+ ions.

6. Comparative ion efficiency

Since the length of the negative glow is exactly equal to the range of electrons for corresponding voltages as given by Lehmann, it seems justifiable to use Lehmann's values for the number of electron volts required to produce an ion pair, in computing the number of positive ions formed per electron in the negative glow. In making the calculations the positive ion current to the cathode was neglected, since it represents only a small per cent of the total current (2). In cases where the number of electron volts required to produce one ion pair has not been determined by Lehmann, 45 was used as an average value.

In syntheses the number of molecules formed is used in the calculations, while in decompositions the number decomposed is considered. M refers to the number of the various molecules underlined. The M/N ratios are given in table 1 for both the total number of ions and for those ions having the higher ionization potential.

It is interesting to note that the M/N ratios computed above compare favorably with the values obtained by Lind with α-rays (5). The conspicuous fact to observe is that the ratios are all small, and that in no instance is it necessary for the initial reaction center to collide with more than three molecules for the reaction to go to completion.

PROPAGATION REACTIONS

The various factors which determine the reactivity in the discharge respond in an entirely different manner for propagation reactions from that described for initial reaction centers. Nevertheless, it is possible, by gradual changes in the experimental conditions, to follow the reaction from the initial zero-order type through various stages involving reaction chains until the ignition point is reached.

1. The effect of pressure, current, and temperature

The reactivity in the positive column for explosive mixtures exhibits a marked interdependence between pressure, current, and temperature. For each explosive mixture a combination of these three factors can be chosen below which the rate is of zero order, the reaction behaving exactly

as that in non-explosive mixtures. Above these particular conditions the rate increases nearly hyperbolically with pressure, more nearly exponentially with current, and moderately with temperature; in the hydrogen–oxygen reaction a 300°C. rise above room temperature increases the rate eightfold. Ignition occurs when the rate versus current, temperature, or pressure curve becomes asymptotic with the rate axis. Ignition can be induced in the positive column when the total expenditure of energy in this region is less than one two-hundredths of that being expended in the negative glow where the reaction is strictly zero order.

The rapid increase in rate with current suggests that energy states formed in the discharge other than those serving as initial reaction centers are involved in the chain mechanism. The positive temperature coefficient indicates that the reaction chains are favored by high thermal states in the gas. The pressure effect, as will be seen in the next paragraph, results largely from a retardation in the rate of diffusion of the various contributing energy centers out of the path of the reaction chain.

2. The effect of added gases

The influence of added gases on the rate of reaction is in distinct contrast to that described for non-propagating reactions. The addition of various gases accelerates the rate to the extent to which diffusion is retarded. This is illustrated in the hydrogen–oxygen case in which hydrogen, helium, a mixture of hydrogen and oxygen ($2H_2:O_2$), water vapor, argon, nitrogen, oxygen, and nitrous oxide enhance the rate, the effect increasing in the order named. These results indicate that high energy states are necessary for the maintenance of the reaction chains, or, conversely, that the chains will tend to break upon entering a region of normal energy density.

MECHANISM OF REACTION

The results that have just been described make it possible to draw certain general conclusions concerning the reaction processes involved in the glow discharge; these conclusions are independent of any specific mechanism of reaction.

1. The reaction is induced by initial reaction centers. These centers are some energy-rich molecular state, and not regions of high energy density.

2. The initial reaction centers are formed only by primary processes occurring in the discharge, presumably by direct electron impact.

3. Non-propagating reactions occur when the reaction centers collide with normal molecules. Energy over and above that contained in the initial centers is unnecessary for the reaction.

4. Propagation occurs in explosive mixtures when the initial reaction

centers, or these centers associated with normal molecules, collide with energy-rich molecular states.

5. Processes which retard diffusion tend to enhance the effect of propagation, and to lower the energy input necessary for ignition.

Any detailed mechanism that may be suggested for the processes involved in the reaction about the active centers entails considerable speculation; in consequence an attempt to outline such a mechanism must be considered merely as a working hypothesis. It is definite, however, that any tenable mechanism must conform to the observed facts outlined above.

There is considerable evidence to suggest that the primary reaction centers are positive ions formed by direct electron impact in the discharge. The fact that the temperature coefficient is zero or negative for non-propagating reactions argues against the initial centers being atoms or excited molecules, since photochemical reactions which have been assigned to these states usually possess a positive temperature coefficient. Insofar as data are available the results indicate that the negative temperature coefficient for the rate can be correlated with the temperature coefficient for the dielectric constant of the gases present. Since the forces involved in the association of neutral molecules about an ion have been shown by Loeb (6) to be a direct function of the dielectric constant of the molecules, the apparent relationship between temperature and dielectric constant suggests some type of cluster mechanism.

The fact that propagation occurs in the positive column but not in the negative glow may result from one of two possibilities: Either some active state is formed in the positive column and not in the negative glow which gives rise to reaction chains, or else some condition exists in the negative glow and not in the positive column which is detrimental to chain formation. While the data are insufficient to determine which of these two possibilities is correct, it seems very doubtful that any active state can be produced in the positive column that is not formed in greater abundance in the negative glow. The zero-order conditions prevailing in the negative glow suggest that the life of the active centers in the gas phase is too short to permit the development of reaction chains.

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