PHOTOREACTIONS SENSITIZED BY THE HALOGENS[1]

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In a series of photochemical reactions, the halogens are the active light-absorbing component. The halogens enter directly into some of the reactions, in others they merely act as sensitizers. As is well known, sensitized reactions may take place in the gaseous, liquid, or solid phase. This paper will deal mainly with homogeneous gas reactions sensitized by the halogens.

When a molecule absorbs light, one of a number of things may happen; the molecule may be excited, dissociated, or predissociated, or possibly even ionized. Fortunately the nature of the absorption spectrum often indicates what happens to the molecule when it absorbs a light quantum, that is, the absorption spectrum indicates the nature of the primary photochemical act.

According to spectroscopic evidence, the primary photochemical process in chlorine is dissociation. In bromine above 5107 Å. and in iodine above 4989 Å. the primary process is excitation, but evidence points to this excitation being converted into dissociation by collision if foreign gases are present, which is always the case in photosensitization experiments (7, 40). Therefore, the photochemical reactions sensitized by the halogens are probably always initiated by free atoms. Examples discussed in this paper show that this assumption provides a satisfactory explanation of the facts.

THE ACTION OF CHLORINE

1. The decomposition of ozone

Chlorine sensitizes the decomposition of ozone, both thermally and photochemically, oxygen being produced. With less than 7 per cent ozone, the quantum yield is about 3. The reaction is zero order with respect to ozone concentration until the ozone is practically all decomposed, when the rate suddenly increases. A similar sudden increase in rate is

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observed for nitrogen trichloride (1, 4, 24). When higher ozone concentrations are used, a chain reaction appears and quantum yields up to 60 have been observed. With increasing ozone concentration or decreasing chlorine concentration, the reaction approaches the $I_{\text{abs.}}^{1/2}$ type. At the same time, the reaction becomes sensitive to small temperature changes and to changes in surface (16). The formation of ClO_2 and ClO_3 as intermediate products can be shown, and under suitable conditions Cl_2O_6 separates out on the walls of the vessel as a red liquid (24, 27). Chlorine heptoxide is also formed under certain conditions. Chlorine heptoxide is relatively inert, but ClO_3 undergoes various reactions, such as thermal and photosensitized decomposition reactions, with ozone (27). As a simplified mechanism for this reaction, we suggest:

$$Cl_2 + h\nu \rightarrow Cl + Cl \tag{1}$$

$$Cl + O_3 \rightarrow ClO + O_2 \tag{2}$$

$$ClO + O_3 \rightarrow ClO_2 + O_2 \tag{3}$$

$$\left.\begin{array}{ll} ClO_2 + O_3 \rightarrow ClO_3 + O_2 & (4) \\ ClO_3 + O_3 \rightarrow ClO_2 + 2O_2 & (5) \end{array}\right\}\text{chain}$$

Reactions 4 and 5 are known definitely to take place.

$$2ClO_3 \rightarrow Cl_2O_6 \tag{6}$$

Goodeve and Todd (14) state that this oxide exists mainly as ClO_3 in the gas phase but as Cl_2O_6 in the liquid phase. Instead of reaction 2, Rollefson and Burton (26) propose

$$Cl + O_3 \rightarrow ClO_3$$

They also suggest that ClO_4 is formed, to account for the formation of chlorine heptoxide.

$$ClO_3 + O_3 \rightarrow ClO_4 + O_2$$

$$ClO_4 + ClO_3 \rightarrow Cl_2O_7$$

It will be realized that when the various possible thermal and photo reactions of the intermediates are taken into account, the reaction is scarcely as simple as Bonhoeffer supposed (quantum yield = 2) in 1923.

2. The decomposition of chlorine monoxide

Chlorine photosensitizes the decomposition of chlorine monoxide (2), the rate of decomposition being proportional to the amount of light absorbed. The quantum yield is 2, the same as for the direct photodecomposition. This can be very satisfactorily explained by the following mechanism: From spectroscopic evidence the mechanism of the direct decomposition is

$$Cl_2O + h\nu \rightarrow ClO + Cl$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO$$

followed by reactions of ClO such as

$$2ClO \rightarrow Cl_2 + O_2$$

The mechanism suggested for the sensitized reaction is

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO$$

$$2ClO \rightarrow Cl_2 + O_2$$

leading to the same quantum yield as before.

3. The decomposition of ClO_2 *and* ClO_3

Experiments have not yet been done on the chlorine-sensitized decomposition of ClO_2, although there is no doubt that it would go as readily as the bromine-sensitized decomposition to be described in the next section. Preliminary experiments have recently been done on the sensitized decomposition of ClO_3 (18). Gaseous ClO_3 absorbs in the ultraviolet with a threshold at about 3500 Å. (13). Consequently, with the maximum pressure of ClO_3 possible at 3°C., very little light is absorbed at 3650 Å. On adding chlorine and insolating with 3650 Å., a sensitized reaction takes place, the quantum yield being about 0.7. In calculating this quantum yield, the overall photoreaction was assumed to be

$$2ClO_3 \rightarrow Cl_2 + 3O_2$$

and the reaction was followed by the pressure change on a glass spoon gauge. More work has to be done on this reaction before a mechanism can be put forward.

4. The decomposition of nitrogen trichloride

The chlorine-sensitized decomposition of nitrogen trichloride has been extensively studied (15). The reaction is of zero order with respect to nitrogen trichloride until the reaction is nearly complete; then a semi-explosive reaction occurs. With a high chlorine pressure, the quantum yield approaches a limiting value of 2. The primary action is

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (1)$$

which is followed by

$$NCl_3 + Cl \rightarrow NCl_2 + Cl_2 \qquad (2)$$

The NCl_2 then reacts, producing chains that are short at ordinary temperature.

$$NCl_2 + NCl_3 \rightarrow N_2 + 2Cl_2 + Cl \qquad (3)$$

While the quantum yield is independent of 2.5-fold variation of surface, there are some indications that the state of the surface may enter indirectly as a factor in the decomposition. In vessels that have been freshly washed, quantum yields 50 per cent higher than usual are occasionally observed. Chain rupture is supposed to be due to

$$Cl + NCl_3 + X \rightarrow NCl_4 + X^* \qquad (4)$$

$$2NCl_4 + (\text{surface catalyst}) \rightarrow N_2 + 4Cl_2 \qquad (5)$$

It can be shown that, using this mechanism,

$$(NCl_2)\ (NCl_3) = \text{constant}$$

The semi-explosive termination might therefore be due to the building up of the intermediate product, NCl_2, as (NCl_3) approaches zero. The sudden increase in (NCl_2) might cause other heat-producing reactions such as

$$NCl_2 + NCl_2 \rightarrow N_2 + 2Cl_2$$

to become important, producing a sudden rise in pressure.

5. *Oxidations*

Chlorine also acts as sensitizer in a number of extremely interesting oxidation reactions of simple carbon compounds (29). For example, chlorine and carbon monoxide unite to form phosgene, but in the presence of oxygen the formation of phosgene is practically completely suppressed and a sensitized formation of carbon dioxide takes place (for a summary see, for example, reference 5). It seems probable that the radical COCl is formed as an intermediate. This radical reacts preferentially with oxygen, forming a peroxide which gives rise to a chain reaction in which the halogen is reformed and the organic substance oxidized with a quantum yield that may amount to about 10^3 molecules per quantum.

$$Cl_2 + h\nu \rightarrow 2Cl \qquad (1)$$

$$Cl + CO + M \rightarrow COCl + M \qquad (2)$$

$$COCl + O_2 \rightarrow CO_3Cl \qquad (3)$$

$$CO_3Cl \rightarrow CO_2 + ClO \qquad (4)$$

$$ClO + CO \rightarrow CO_2 + Cl \qquad (5)$$

The chain carrier in this case is probably ClO.

Chloroform and chlorine give carbon tetrachloride in the light, but in the presence of oxygen phosgene is formed almost quantitatively with a quantum yield of about 100 (9, 31).

$$Cl_2 + h\nu \rightarrow Cl + Cl \tag{1}$$

$$Cl + CHCl_3 \rightarrow CCl_3 + HCl \tag{2}$$

$$CCl_3 + O_2 \rightarrow CO_2Cl_3 \tag{3}$$

$$CO_2Cl_3 \rightarrow COCl_2 + ClO \tag{4}$$

$$ClO + CHCl_3 \rightarrow HCl + COCl_2 + Cl \tag{5}$$

Here the radical CCl_3 appears to form a peroxide, which yields $COCl_2$ and a chain carrier ClO.

Experiments recently carried out in this laboratory indicate that reaction 5 actually does take place when chloroform reacts with a ClO radical, prepared by shining light on ClO_2.

$$ClO_2 + h\nu \rightarrow ClO + O$$

This and similar reactions are being investigated in detail.

Franke and Schumacher (12) have investigated the kinetics of the chlorine-sensitized oxidation of trichlorobromomethane. Phosgene is produced, and quantum yields up to 400 have been measured.

$$Cl_2 + h\nu \rightarrow Cl + Cl \tag{1}$$

$$Cl + CCl_3Br \rightarrow CCl_3 + BrCl \tag{2}$$

$$CCl_3 + O_2 \rightarrow CO_2Cl_3 \tag{3}$$

$$CO_2Cl_3 \rightarrow COCl_2 + ClO \tag{4}$$

$$ClO + CCl_3Br \rightarrow COCl_2 + \begin{cases} Cl_2 + Br \\ BrCl + Cl \end{cases} \tag{5}$$

$$CO_2Cl_3 + ClO \rightarrow COCl_2 + O_2 + Cl_2 \tag{6}$$

A mixture of tetrachloroethylene and chlorine forms hexachloroethane on illumination, but in the presence of oxygen trichloroacetyl chloride is formed (11).

$$Cl_2 + h\nu \rightarrow Cl + Cl \tag{1}$$

$$Cl + C_2Cl_4 \rightarrow C_2Cl_5 \tag{2}$$

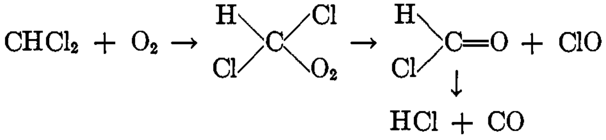
$$C_2Cl_5 + O_2 \rightarrow C_2Cl_5O_2 \tag{3}$$

$$C_2Cl_5O_2 \rightarrow CCl_3\cdot COCl + ClO \tag{4}$$

$$ClO + C_2Cl_4 \rightarrow CCl_3\cdot COCl + Cl \tag{5}$$

Trichloroethylene similarly gives dichloroacetyl chloride (22).

In order to clarify some of the foregoing oxidations, Brenschede and Schumacher investigated the reactions of methane, methyl chloride, methylene chloride, and formaldehyde with oxygen and chlorine and light (6). Methane yields mainly carbon dioxide; methyl chloride yields more carbon monoxide; methylene chloride yields carbon monoxide and phosgene in the ratio 10:1. In the last reaction the radical $CHCl_2$ apparently reacts with oxygen, forming a peroxide which yields formyl chloride and a chain carrier. Chlorine is practically not used up in the reaction.



Formyl chloride undergoes either a thermal or chlorine-sensitized decomposition, yielding hydrogen chloride and carbon monoxide (28). The formation of a peroxy compound in the methane reaction was shown by streaming experiments in which the products were frozen out in a trap at −95°C. A small amount of oily liquid was obtained which gave a positive peroxy test with titanic acid.

In each of these oxidation reactions, an intermediate compound with a trivalent carbon is formed, either by abstracting an atom such as hydrogen or bromine from an organic compound or by adding on a halogen atom to a C=C double bond. The radical formed reacts with oxygen, producing a peroxide which gives rise to a chain reaction in which the halogen is reformed and various oxidation products result. It is also typical that the sensitized oxidations only take place at a temperature below 150°C., owing to the ease of decomposition of the peroxide. The following equations summarize the overall reactions of the radicals:

$$COCl + O_2 = CO_2 + ClO$$

$$CCl_3 + O_2 = COCl_2 + ClO$$

$$C_2Cl_5 + O_2 = CCl_3COCl + ClO$$

$$C_2HCl_4 + O_2 = CHCl_2COCl + ClO$$

$$CHCl_2 + O_2 = CO + HCl + ClO$$

A general reaction mechanism can be written for the above oxidations:

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (1)$$

$$Cl + X \rightarrow R + HCl, \text{ or} \qquad (2)$$

$$Cl + X^1 \rightarrow R^1$$

$$\text{R (or R}^1) + O_2 \rightarrow \text{P} \qquad (3)$$

$$\text{P} \rightarrow \text{Products} + \text{ClO} \qquad (4)$$

$$\text{ClO} + \text{X} \rightarrow \text{Products} + \text{Cl} \qquad (5)$$

X is a halogenated hydrocarbon (X^1 unsaturated); R (or R^1) is the radical formed; and P is a peroxy compound.

THE ACTION OF BROMINE

1. *The decomposition of ozone*

The thermal decomposition of ozone is catalyzed by bromine, the oxide $(Br_3O_8)_n$ being formed as an intermediate compound (20). Other oxides, Br_2O and BrO_2, are known and their formation may precede the formation of $(Br_3O_8)_n$. Using low concentrations of bromine and ozone, a photoreaction can be measured, the reaction being a chain reaction with a quantum yield of about 30 (4, 32). It is interesting to note that the quantum yields at 3650 and 5460 Å. are the same, indicating that practically every bromine molecule absorbing a quantum at 5460 Å. dissociates into atoms. The chain is probably propagated by an unstable oxide of bromine, possibly BrO. Indeed, the decompositions of ozone photosensitized by chlorine and bromine, respectively, resemble one another in many respects.

2. *The decomposition of chlorine monoxide*

Chlorine monoxide undergoes a bromine-sensitized decomposition using light of wave length 5460 Å. (7). The reaction involves short chains and some chlorine dioxide is formed. The quantum yield is 4.3 at 19°C., and the ratio of the quantum yields in the direct and sensitized reactions is practically unity. This suggests that, apart from the primary act of light absorption, the sensitized and unsensitized reactions have essentially similar mechanisms. In all probability, 5460 Å. produces bromine atoms, either directly or indirectly, and a possible mechanism is therefore;

$$Br_2 + h\nu \rightarrow (Br_2^*) \rightarrow 2Br \qquad (1)$$

$$Br + Cl_2O \rightarrow BrCl + ClO \qquad (2)$$

$$2BrCl = Br_2 + Cl_2 \qquad (3)$$

Quantum yields greater than 2 and the formation of ClO_2 might be due to

$$ClO + Cl_2O \rightarrow Cl + Cl_2 + O_2 \qquad (4)$$

and

$$ClO + Cl_2O \rightarrow ClO_2 + Cl_2 \qquad (5)$$

Chains could be terminated by

$$Cl + Cl + M \rightarrow Cl_2 + M$$

$$ClO + ClO \rightarrow Cl_2 + O_2$$

$$Cl + ClO + M \rightarrow Cl_2O + M$$

$$Cl + ClO_2 \rightarrow Cl_2 + O_2$$

The relative importance of these reactions has not yet been determined. It is, of course, possible that ClO may react with bromine,

$$ClO + Br_2 \rightarrow BrO + BrCl$$

but, thus far, experiments to prove or disprove this suggestion are lacking.

3. *The decomposition of chlorine dioxide*

Bromine also sensitizes the decomposition of chlorine dioxide (33). At 15°C. the reaction is accompanied by a pressure decrease and the formation of Cl_2O_6. If insolation is continued, the pressure subsequently increases, owing to the photosensitized decomposition of Cl_2O_6 (or ClO_3). At 30°C. the reaction is accompanied by an increase in pressure and the formation of chlorine and oxygen. By introducing water into the reaction cell, troublesome side reactions can be eliminated and the effect of varying different factors studied. It is found that the quantum yields at 3650 and 5460 Å. are equal, indicating that the reaction at 5460 Å. probably also proceeds by way of bromine atoms and not by way of an excited molecule. The quantum yields for the sensitized and unsensitized reactions are also equal, indicating that, apart from the primary act of light absorption, the mechanisms for the two reactions are similar. In the direct reaction the mechanism probably is:

$$ClO_2 + h\nu \rightarrow ClO + O$$

$$ClO_2 + O + M \rightarrow ClO_3 + M$$

followed by reactions of ClO and ClO_3.

For the sensitized reaction Schumacher (30) has suggested a mechanism involving bromine atoms:

$$Br_2 + h\nu \rightarrow 2Br$$

$$Br + ClO_2 \rightarrow BrCl + O_2$$

$$2BrCl = Br_2 + Cl_2$$

However, since the main product of the reaction is Cl_2O_6, this mechanism has to be rejected. Another possibility would be

$$Br_2 + h\nu \rightarrow 2Br$$
$$Br + ClO_2 \rightarrow BrO + ClO$$
$$BrO + ClO_2 \rightarrow ClO_3 + Br$$

which would give the same products as the direct photoreaction. In view of the existence of other oxides of bromine, it does not seem to be particularly objectionable to postulate the existence of BrO.

4. The decomposition of ClO_3

The decomposition of ClO_3 is sensitized by bromine, but thus far quantitative experiments are lacking (33).

5. The decomposition of dibromotetrachloroethane

The bromine-sensitized decomposition of gaseous dibromotetrachloroethane has been studied (8). Using 4360 Å. and a temperature of about 150°C. tetrachloroethylene is produced, the quantum yield varying from 1 to 40. The mechanism is essentially similar to that of the iodine-sensitized decomposition of ethylene iodide in carbon tetrachloride solution.

$$Br_2 + h\nu \rightarrow 2Br$$
$$Br + C_2Cl_4Br_2 \rightarrow C_2Cl_4Br + Br_2$$
$$C_2Cl_4Br \rightleftarrows C_2Cl_4 + Br$$
$$Br \xrightarrow{\text{wall}} \tfrac{1}{2} Br_2$$
$$Br + Br + M \rightarrow Br_2 + M$$

6. The decomposition of dibromodichloroethane

Bromine sensitizes the decomposition of dibromodichloroethane (23), the quantum yield being about 12.

7. The decomposition of bromophosgene

The decomposition of bromophosgene is accelerated by bromine plus light, but the quantum yield is small (4).

8. The decomposition of nitrous oxide

Bromine also photosensitizes the decomposition of nitrous oxide at 650°C. (17).

$$Br_2 + h\nu \rightarrow Br + Br$$
$$N_2O + Br \rightarrow BrO + N_2$$
$$N_2O + BrO \rightarrow Br + O_2 + N_2$$

9. Oxidations

Bromine sensitizes the oxidation of bromotrichloromethane to phosgene (12). Using 4360 Å. and $(CCl_3Br) < 4(Br_2)$, the quantum yield does not exceed 4, and thereby differs quite markedly from the yield for corresponding chlorine-sensitized reaction. The first steps in the reaction are:

$$Br_2 + h\nu \rightarrow Br + Br \tag{1}$$

$$CCl_3Br + Br \rightarrow CCl_3 + Br_2 \tag{2}$$

$$CCl_3 + O_2 \rightarrow COCl_2 + ClO \tag{3}$$

The lower quantum yield in this case is thought to be due to the removal of the chain carrier by the reaction,

$$ClO + Br_2 \rightarrow BrO + BrCl \tag{4}$$

It is then assumed that BrO reacts with bromotrichloromethane to form phosgene, without regenerating the chain carrier.

$$CCl_3Br + BrO \rightarrow COCl_3 + Br_2 \tag{5}$$

$$2COCl_3 \rightarrow 2COCl_2 + Cl_2 \tag{5a}$$

This mechanism leads to a limiting quantum yield of 4. If $(CCl_3Br) > 4(Br_2)$, ClO reacts with CCl_3Br, leading to chain formation and a quantum yield greater than 4 (see equation 5 in the chlorine-sensitized reaction).

In contrast to the corresponding chlorine-sensitized reaction, bromine does not sensitize the oxidation of carbon monoxide (21). A number of further oxidations sensitized by bromine have been carried out in carbon tetrachloride solution, but will not be dealt with here (10, 19).

THE ACTION OF IODINE

While iodine sensitizes many reactions, very few of these have been investigated in the gas phase. The only one that will be mentioned is the decomposition of nitrous oxide, which is accelerated by light in the presence of iodine (17).

From the above survey, it is clear that all the halogen-photosensitized gaseous reactions thus far known can be explained by chemical mechanisms involving halogen atoms.

SUMMARY

Spectroscopic evidence indicates that the sensitizing action of chlorine is practically always due to chlorine atoms. For bromine, when λ is less than 5107 Å., reaction will be by way of bromine atoms. Experiments using 5107–6290 Å. also probably involve bromine atoms, although the possibility of reaction due to excited bromine molecules cannot be wholly ruled out. Iodine atoms are produced in photosensitization experiments

involving iodine and λ less than 4989 Å. Experimental evidence also favors the production of iodine atoms using λ up to 6200 Å.

Mechanisms in accordance with the above are advanced for a number of chlorine-sensitized decomposition reactions and for a number of chlorine-sensitized oxidation reactions. In the oxidation reactions, an intermediate compound with a trivalent carbon is formed which reacts with oxygen forming a peroxide, giving rise to a chain reaction. Reactions sensitized by bromine and iodine are also discussed.

It appears that all the halogen-sensitized photoreactions thus far known can be explained by chemical mechanisms involving halogen atoms.

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