

ON THE PHOTOOXIDATION OF GASEOUS HCCl_3 and ClO RADICAL FORMATION

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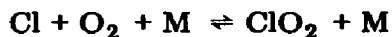
Summary

The photolysis of HCCl_3 in the presence of O_2 or O_3 was investigated at 25 °C and for $\lambda \geq 185$ nm. In the presence of O_2 , HCCl_3 is photooxidized by a long chain process which leads to the production of COCl_2 , Cl_2 , HOCl and HCl . In the presence of O_3 , COCl_2 and HCl are the main photoproducts.

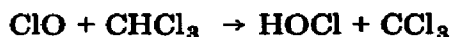
The formation of ClO was studied and two likely mechanisms are indicated, namely



and



ClO radicals disappear according to the reactions



and



The absorption spectrum of HOCl was investigated and it is concluded that there is no absorption band at about 330 nm.

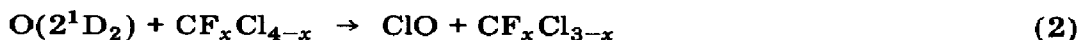
1. Introduction

The last few years have seen considerable interest in the ClO stratospheric cycle and several studies have been devoted to the photooxidation of chloroalkanes or fluorochloroalkanes.

In addition to the well-known reactions of the chlorine atom with O_2 and O_3 which form ClO , this radical also appears in the stratosphere as the result of the reaction of excited oxygen atoms with chloroalkane molecules, *i.e.*



The ClO radical is at the heart of the formation of the HOCl molecule, the potential role of which in stratospheric chemistry has, to our knowledge, been neglected prior to 1976. Prasad *et al.* [1] have emphasized the importance of this saturated and relatively inert compound which can serve as a reservoir of atmospheric chlorine. As a consequence, a better knowledge of the mechanisms of the photooxidation of haloalkanes initiated either by oxygen atoms or by chlorine atoms seemed to be desirable. Several reported results [2 - 7] have helped in the understanding of such mechanisms and the main product of the oxidation appears to be a carbonyl halide. Using flash photolysis Gillespie *et al.* [8] have observed the formation of ClO directly according to reaction (2):



Secondary formation of ClO from the $\text{CF}_x\text{Cl}_{3-x}$ radicals and O_2 is also clearly evident. However, the mechanisms of formation and destruction of the ClO radical during the photooxidation of the haloalkanes are not yet totally understood.

More recently Sanhueza [5] has studied the photooxidation of HCCl_3 at 366 nm in the presence of O_2 and Cl_2 . A chain process produces COCl_2 with a yield equal to the yield of HCCl_3 disappearance.

The various studies concerned with the photooxidation of haloalkanes call for CX_3O_2 as an intermediate, *e.g.* the reactions of the peroxy radical CCl_3O_2 with NO [9] and with chlorine atoms [8]. As part of our research programme [10 - 13] to study the photoreactions of haloalkanes in connection with their atmospheric photodissociation, we now consider the photolysis of HCCl_3 in the presence of O_2 or O_3 , in a wavelength range corresponding essentially to the solar UV radiation reaching the stratosphere and not the troposphere, *i.e.* the "window" between 185 and 227 nm corresponding to a weaker absorption by O_2 and O_3 and consequently to a deeper penetration of these wavelengths in the stratosphere [14].

2. Experimental

The HCCl_3 is purified by distillation under vacuum before use, its purity being controlled by its IR spectrum.

O_3 , prepared by the photolysis of O_2 , is then trapped at -126.5°C and O_2 is pumped off.

The photolysis is carried out at room temperature with standard equipment for steady irradiation. A suprasil cell (10 cm in length and 5 cm in diameter) is used. A deuterium lamp (200 W) is the light source, the unfiltered emission corresponding to $\lambda \geq 185$ nm and the maximum emission being at 220 nm. Near 300 nm the light flux is only 20% of the maximum flux.

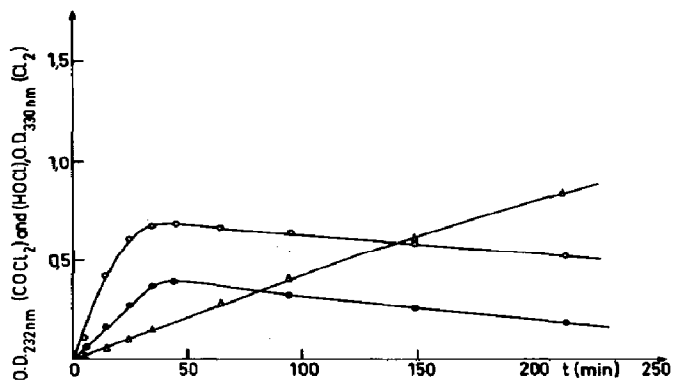


Fig. 1. The formation of COCl_2 (\circ), HOCl (\bullet) and Cl_2 (\triangle) vs. time (pressure of HCCl_3 , 55 Torr; pressure of O_2 , 107 Torr).

The analysis of the photoproducts is performed by gas chromatography, and by UV and IR absorption spectroscopy.

3. Results

3.1. Photolysis of HCCl_3 in the presence of O_2

The products of the photolysis were analysed for HCCl_3 pressures in the range 10 - 100 Torr and O_2 pressures between 10 and 120 Torr, after irradiation times varying from 10 to 60 min. Some of the irradiations were prolonged to 8 - 10 h.

A chain process is involved in the disappearance of HCCl_3 , and COCl_2 , HCl , Cl_2 and HOCl are produced; the formation of Cl_2 is directly proportional to the irradiation time. After the complete destruction of HCCl_3 , a decrease in concentration of the photoproducts is observed; only the concentration of Cl_2 continues to increase with the irradiation time (Fig. 1). The formation of CO_2 accompanies the disappearance of COCl_2 .

COCl_2 is the major product of the photooxidation and the rate of its formation is equal to the rate of HCCl_3 destruction, as previously observed by Sanhueza [5]. The rates of formation of COCl_2 and HOCl are proportional to the pressure of HCCl_3 (Fig. 2). The increase in the concentration of Cl_2 is quasi-linear during the first few hours (Fig. 1). After the complete consumption of HCCl_3 , the UV spectrum of the photolysis products exhibits an absorption maximum at 195 nm (attributed to COCl_2), an absorption maximum at 232 nm (attributed to COCl_2 and also to HOCl) and an absorption maximum at 330 nm (attributed to Cl_2).

When the absorption due to COCl_2 (analysed by chromatography or IR spectroscopy) is subtracted, observation of the 232 nm absorption permits the formation and disappearance of HOCl to be followed. The formation of Cl_2 is monitored by the absorption maximum at 330 nm (Fig. 3).

The characteristic IR absorption bands (cm^{-1}) used to identify the products and to monitor their evolution are the following:

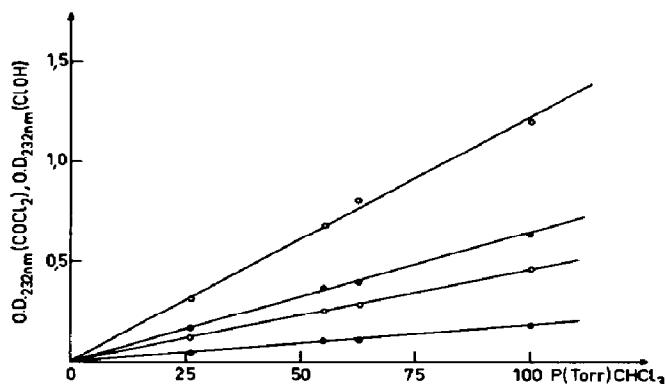


Fig. 2. The optical density (OD) at 232 nm after irradiation times of 10 and 60 min vs. the pressure of HCl_3 : \circ , COCl_2 ; \bullet , HOCl . ($\epsilon_{232\text{nm}}(\text{COCl}_2) = 22 \text{ l mol}^{-1} \text{ cm}^{-1}$; $\epsilon_{232\text{nm}}(\text{HOCl}) = 123 \text{ l mol}^{-1} \text{ cm}^{-1}$.)

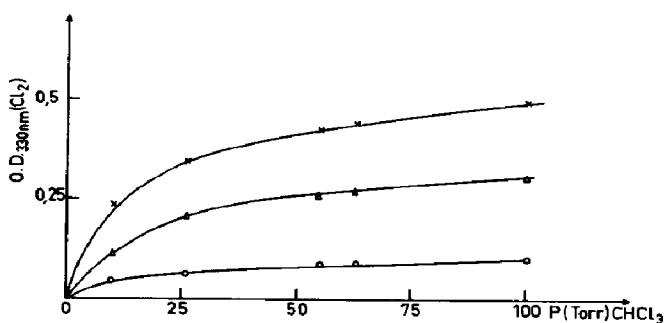


Fig. 3. The optical density (OD) of Cl_2 after various irradiation times vs. the pressure of HCl_3 : \circ , 20 min; \triangle , 60 min; \times , 100 min. ($\epsilon_{330\text{nm}}(\text{Cl}_2) = 80 \text{ l mol}^{-1} \text{ cm}^{-1}$.)

HCl_3	COCl_2	HCl	CO_2	HOCl
1238	1860	2600 - 3100	2347	3600 - 3750

The IR absorption spectrum of HOCl has been investigated by several workers [14 - 16] and, in spite of some difficulties arising from the mode of preparation which does not totally exclude the presence of water, characteristic bands have been observed. The bands corresponding to the O-H stretching vibrations, to the bending vibrations and to the O-Cl stretching vibrations are centred at 3600 , 1240 and 740 cm^{-1} respectively.

In the present study the spectra overlap, thus making the identification difficult. In particular, the IR spectrum of COCl_2 shows an absorption in the range $3600 - 3700 \text{ cm}^{-1}$. Nevertheless, two bands centred at 3710 and 3735 cm^{-1} , which do not appear in the spectrum of COCl_2 , and the band at 1240 cm^{-1} , which can be observed when HCl_3 is absent and when COCl_2 is present at low concentration, permit HOCl to be identified.

Under our experimental conditions the following chain reactions have to be considered:



The photolysis of O_2 produces oxygen atoms in a ^3P state:



This dissociation is followed by ozone formation:



The mechanism of ClO formation will be discussed later. It leads to the reactions



After the complete destruction of HCCl_3 the relative proportion (%) of photoproducts formed by reactions (3) - (12) is the following:

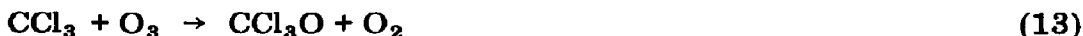
— HCCl_3	COCl_2	HCl	HOCl	Cl_2
100	95 ± 5	70 ± 5	12 ± 2	8 ± 1

These percentages refer to the initial concentration of HCCl_3 and were observed on irradiating (45 min) a mixture of HCCl_3 (55 Torr) and O_2 (107 Torr).

3.2. Photolysis of HCCl_3 in the presence of O_3

Only COCl_2 and HCl are formed in notable amounts and with rates which are close to those observed in the presence of O_2 . HOCl was not identified and only traces of Cl_2 were recorded. The irradiations lasted for less than 1 h.

Reactions (3) and (4) are followed by



The O_3 molecules are photolysed and form excited oxygen atoms:



We note that reaction (8) does not occur, or occurs very little. The same conclusion holds for reactions (11) and (12) of the ClO radical.

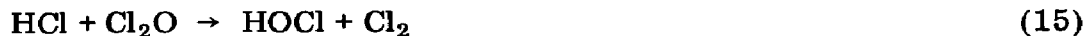
4. Discussion

From a consideration of previous studies [4, 5, 8, 9] and of our results, it seems that reactions (4), (5) and (7) are essential for the long chain process of the photooxidation. Accordingly it is suggested that the formation of COCl₂ occurs by the proposed mechanism. But, with regard to the products HOCl and Cl₂, several processes can be suggested.

4.1. Formation of HOCl

Reaction (11) is exothermic (7 kcal mol⁻¹) and probably occurs in competition with reaction (12) when ClO radicals are present.

Another reaction recently considered by Niki *et al.* [16], *i.e.*



cannot be excluded. HCl is one of the products and the formation of Cl₂O can be envisaged. However, irradiations prolonged after the complete consumption of the HCCl₃ did not indicate that such a reaction intervenes; a decrease in the HOCl concentration is observed after complete HCCl₃ disappearance.

The rate of formation of HOCl increases similar to that of COCl₂; it is proportional to the HCCl₃ pressure (Fig. 1).

Reactions (4), (11) and (12) are essentially responsible for the formation of COCl₂, HOCl and Cl₂ respectively, CCl₃ radicals adding to O₂ very quickly. Indeed the formation of C₂Cl₆ has been observed only for low pressures of O₂, such that [HCCl₃]/[O₂] > 4.5. Under such conditions there is a competition between reaction (5) and the following recombination reaction:



4.2. Formation of ClO

When HCCl₃ and O₂ are present the absorbed photons lead to chlorine atoms and O(³P) atoms. Following the formation of ozone some excited oxygen atoms can be formed by reaction (14). It is then possible to envisage the following sequence:



Reactions (17) and (18) have been observed directly in systems where Cl_2 is photolysed in the presence of O_2 [17 - 20]. When HCCl_3 is present these two reactions compete with reaction (4). The rate constant of reaction (17a) has been measured by Nicholas and Norrish [21]:

$$k_{17(a)} = 1.7 \times 10^{-33} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1}$$

$$k_4 = 4.6 \times 10^{-4} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} [5]$$

Because of the rates of reactions (4) and (17) in which chlorine atoms participate, we note that for pressures between 100 and 200 Torr (as used in the present study) reaction (17) cannot be neglected, even though there is no direct evidence of its intervention.

The formation of ClO from excited oxygen atoms does not seem to lead to HOCl; indeed when the photolysis is performed in the presence of O_3 , HOCl is not observed. A possible explanation might be that the presence of excited oxygen atoms is both a source of ClO and a cause of the HOCl destruction (see reaction (30)).

From the absence of HOCl, we can say also that reaction (22) is not important for our experimental conditions.



$$k_{22} = 1.8 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} [1]$$

An interesting study made by Gillespie *et al.* [8] concerning the oxidation of halomethyl radicals clearly demonstrates that an important secondary formation of ClO occurs. According to these workers reaction (23)



is negligible, and reactions (5), (6) and (7) do not constitute the complete mechanism. Instead, the very fast reaction (5) is followed by



From the present study it seems that reaction (24) contributes to the formation of ClO; in fact in the presence of O_3 (where the mechanism does not include the intermediate CCl_3O_2), HOCl formed by reaction (11) is not observed.

The competition between reactions (24) and (4) requires the postulation of a long lifetime for CCl_3O_2 . Other reactions of CCl_3O_2 have been studied in analogous systems, particularly the reaction similar to reaction (24) with NO giving NO_2 [9].

We finally conclude that two modes of ClO formation are possible: by the intermediary of reactions (17) and (18), and by reaction (24).

4.3. Formation of Cl_2

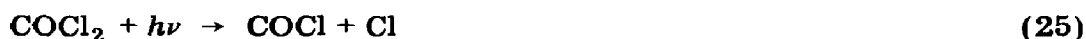
Reactions (8) and (12) give rise to Cl_2 . Under our experimental conditions the recombination of ClO radicals, either direct or indirect [20], is

essentially responsible for the formation of Cl_2 . In the presence of O_3 , in which case HOCl is not observed, Cl_2 is produced in negligible amounts for a total pressure of about 100 Torr. The addition of 200 - 300 Torr of N_2 as a third body is necessary to promote reaction (8).

4.4. Destruction of COCl_2 , HOCl and HCl

For long irradiation times, after the complete disappearance of HCCl_3 , a decrease in the COCl_2 , HOCl and HCl concentrations, an increase in the Cl_2 concentration and the formation of CO_2 are observed (Fig. 1). When O_2 is absent the photodecomposition of these products is very slow; the role of O_2 is therefore obvious.

The formation of CO and of Cl results from the photolysis of COCl_2 [22]:



Oxygen might either collect the atoms and radicals produced by the photolysis or act directly by the following reactions of the excited atoms:



The photolysis of HOCl gives



The following reactions can occur:



After an irradiation time of 8 - 10 h, CO_2 , Cl_2 and very small amounts of H_2O and HCl are the only species present. ClO radicals formed by reactions (27) and (30) disappear by the recombination reaction (12).

Comparing the rate of formation of Cl_2 with the rates of disappearance of COCl_2 and HOCl, an estimation of the UV absorption coefficient of HOCl is obtained. At 232 nm $\epsilon_{232\text{ nm}} \approx 110 \text{ l mol}^{-1} \text{ cm}^{-1}$. This value, although obtained in an indirect way and with the assumption that the absorption at 232 nm is only due to COCl_2 and HOCl, is close to that calculated by Jaffe and Langhoff [23], *i.e.* $\epsilon_{220\text{ nm}} \approx 123 \text{ l mol}^{-1} \text{ cm}^{-1}$. We are currently aiming at a more precise determination of the absorption spectrum of HOCl. Nevertheless it is now possible to say that this spectrum has no maximum at 330 nm; this point is particularly significant in atmospheric chemistry [1].

It should also be emphasized that the photolyses of various haloalkanes such as HCFCl_2 and CH_3CCl_3 , performed under the same experimental conditions, illustrate the influence of the bond dissociation energy of C-H on the yield of the photooxidation products and on the importance of the secondary reactions.

Acknowledgment

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