

Communications

Inadvertent Photolysis: Formation of Phosgene

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Received 18 January 1984; accepted 27 February 1984

The formation of phosgene from chlorine and carbon monoxide on exposure to visible light from normal laboratory illumination is attributed to inadvertent photolysis. This observation involving the light-sensitive chlorine species has been made during laboratory simulation studies of the Venus atmosphere. The overall reaction, $\text{CO} + \text{Cl}_2 = \text{COCl}_2$, is assumed to occur through the formation of intermediate species COCl .

During our laboratory simulation studies of the Venus atmosphere, we observed formation of phosgene when a mixture of chlorine and carbon monoxide in a gas cell was exposed to visible region light from laboratory fluorescent tubes. Spontaneous formation of radicals in other systems, due to inadvertent photolysis, was reported recently by Chatgililogu and Ingold¹. After careful evaluation of such spontaneous radical formation in nitroso aromatics, Ingold *et al.* emphasised the need of investigating the effect of ordinary laboratory light from fluorescent tubes, from tungsten filament lamps or even from diffuse day-light on other radical forming processes. Keeping this in view we report here the results of our studies on the formation of phosgene from chlorine and carbon monoxide on exposure to visible region laboratory light.

Chlorine molecules absorb light continuously below 4785 Å leading to their dissociation² into normal $^2P_{3/2}\text{Cl}$ atoms. These atoms can react with a number of organic molecules with the formation of new species. Numerous studies on photochemistry of gases have already been described³.

A cylindrical glass cell (5 cm diameter, 10 cm length) was used. The walls of the cell were of pyrex which allowed all the light of wavelength > 300 nm to pass through. The side windows of the cell were of quartz, suitable for UV studies.

A CARY-15 spectrophotometer was employed for recording the spectra. Chlorine gas employed in the present study was obtained from M/s Matheson (USA). Before use, it was condensed in a liquid nitrogen trap to remove non-condensable impurities such as CO , O_2 , N_2 , etc., if any. After removing the liquid N_2 trap, chlorine was allowed to warm up so that it could be added to the cell to a known pressure;

the gas cell was closed and the excess chlorine in the vacuum line pumped out. Carbon monoxide also of Matheson (purity greater than 99%), was passed through a similar liquid nitrogen trap to remove condensable impurities such as iron carbonyl before adding to the cell. The total pressure of the cell after adding CO to Cl_2 was one atmosphere. This total pressure can be made up either by carbon monoxide or pure nitrogen gas. Pressure of chlorine taken up in the cell was always less than 25 torr, in order to keep the optical density readings for both chlorine and phosgene less than 1.0.

The ultraviolet portion of the spectrum of the mixture was recorded immediately in the region 185 nm to 360 nm. The initial spectrum (Fig. 1) showed only four absorption peaks—at 330 nm due to chlorine, and at 1927 nm, 1991 nm and 2062 nm due to carbon monoxide.

The gas cell was removed from the spectrometer compartment and exposed to the normal room light from the fluorescent tubes. As the walls of the cell were of pyrex glass, all the room light with wavelength less than 300 nm was cut off and light with wavelength greater than 300 nm passed through. The spectrum was recorded again. This procedure of exposing the cell to ordinary laboratory light and then recording its spectrum was repeated frequently after small intervals of time. All such spectra are given in Fig. 1.

It is seen from Fig. 1 that with more and more exposure of the cell to 'room light' the chlorine

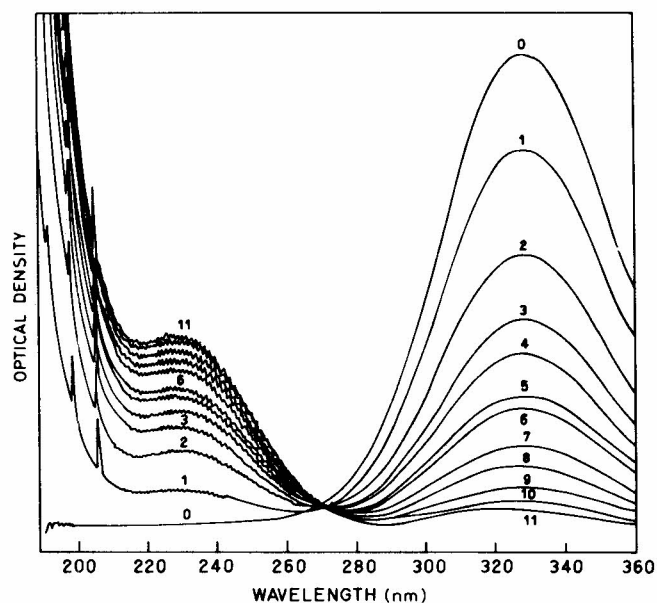
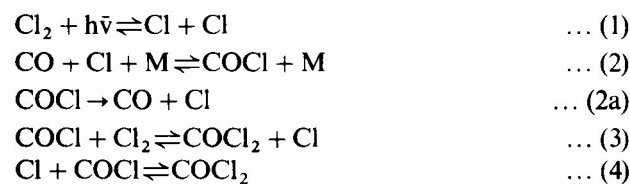


Fig. 1—Formation of phosgene from Cl_2 and CO by absorption of visible light from fluorescent tubes.

absorption band at 330 nm goes on decreasing in intensity with the development of a new peak at 230 nm. This peak grows with the decrease in the intensity of chlorine absorption band. This continues with additional exposure till the chlorine band vanishes completely, i.e. till chlorine is completely used up in the formation of phosgene at 230 nm.

It is interesting to note that decrease in absorption of chlorine peak at 330 nm by two units increases the phosgene absorption at 230 nm by one unit. This implies that the molar extinction coefficients for Cl_2 and Cl_2CO are in the ratio of 2:1. Addition of nitrogen to the system has no effect on the formation of Cl_2CO . But, addition of oxygen retards the rate of formation of phosgene and in the extreme case prevents its formation, favouring oxidation of CO to CO_2 on further exposure to light. This aspect of the photochemical oxidation as applied to the Venus atmosphere forms a separate communication elsewhere, and will not be elaborated here further.

Since carbon monoxide is transparent in the region of wavelengths under investigation, most of the laboratory light falling on the cell is used up in breaking up chlorine molecules into atoms which subsequently react with CO to form phosgene through the intermediate COCl as shown in Scheme 1,

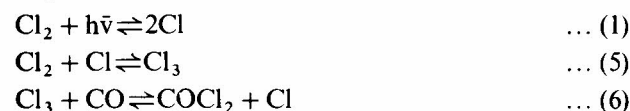


where M is the third body, a chaperon gas.

Scheme 1

Processes (1) and (2) are supposed to be rapid in both directions and the rate of formation of phosgene is controlled by the reaction (3). Reaction (4) is the other possible route of phosgene generation².

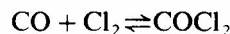
An alternative scheme (Scheme 2) involving Cl_3 intermediate can be represented by the following sequence of reactions,



Scheme 2

Again, the rate of reaction is supposed to be controlled by reaction (6); reactions (1) and (5) are postulated to be rapid in both directions.

The overall reaction can then be written as,



On the basis of these reactions alone, it is difficult to decide between these two possible mechanisms⁴. However, COCl is a more probable intermediate⁵ than Cl_3 .

A similar effect of room light was recorded by Ingold and coworkers¹ when they reexamined the work reported by Ginsburg.

It should be noted, however, that even in the case of 'spontaneous' radical formation, which is reported in the literature to occur in the dark, it is improbable that light was rigorously excluded at all stages of the sample preparation. It is suggested that the role of ordinary laboratory light on other radical forming processes should be investigated.

The identity of phosgene (Cl_2CO) was confirmed in the present experiments by recording its infrared spectrum in another gas cell with NaCl windows employing Perkin Elmer infrared spectrophotometer IR-21.

The author thanks the National Research Council and the National Academy of Sciences of America for the award of a Senior Resident Research Associateship at the NASA Jet Propulsion Lab., Pasadena, California during 1980-82 and he wishes to express his thanks to Dr B V Sreekantan, Director, Tata Institute of Fundamental Research, Bombay for the grant of the study leave.

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