

LASER INDUCED PHOTODECOMPOSITION OF IODOFORM

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Summary

Iodoform dissolved in hexane is decomposed by means of a ruby laser pulse at moderate intensity at which two-photon absorption is negligible. The reaction only occurs in the presence of traces of iodine and oxygen. The kinetics is of order 1/2 with respect to the light intensity and iodine concentration and of order 1 with respect to the iodoform concentration. The dependence on the oxygen concentration is more complex: at low concentration oxygen acts as a catalyst giving a reaction rate proportional to the square root of the concentration; at high concentrations oxygen acts as an inhibitor and the rate becomes proportional to the inverse square root of the concentration. A free radical chain mechanism is proposed initiated by oxygen-catalyzed photodecomposition of iodine.

Introduction

Ultra-violet photodecomposition of iodoform producing molecular iodine was first studied by Gibson and Iredale [1] and was found to be of first order with respect to light intensity. The observed quantum yield was equal to one. This reaction takes place in the absence of oxygen but it is known that the presence of oxygen strongly influences the decomposition producing reaction in the dark [2]. Photodecomposition of iodoform has also been obtained by means of a two-photon process using Q-switched ruby laser pulses [3]. Here again it was found that the presence of oxygen could yield dark reactions [3].

It is well known that iodo-compounds are unstable in the presence of visible light. It seemed therefore worthwhile to investigate the one-photon decomposition in the lower frequency region. In the present work long (880 μ s) ruby laser pulses (694.3 nm) were used. It was observed that no decom-

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position took place when iodoform solutions were carefully degassed. Even in the presence of oxygen no reaction was obtained unless traces of iodine were present in the solution. It was also verified that the presence of iodine alone (in the absence of oxygen) is insufficient to produce the reaction. Iodine itself being one of the products of the reaction, it follows that oxygen-catalyzed photodecomposition of CHI_3 is autocatalytic. This observation suggests that the preservation of iodo-compounds depends on the careful removal of any traces of iodine.

Experimental

Iodoform was dissolved in hexane in a closed system under vacuum. The hexane was degassed thoroughly first by repeated freeze-thaw pump cycling and the same process was repeated with the iodoform solution. The solution was then transferred under vacuum into the reaction cell. The solution was handled in the dark to prevent any dissociation of iodoform. The samples containing calibrated amounts of oxygen were prepared by saturating the purified hexane with oxygen. The final equilibrium partial pressure of oxygen above the solution was measured. Samples of low concentrations of oxygen were prepared by allowing the hexane to equilibrate with a large oxygen volume of low pressure. Because of the large relative value of the oxygen volume relative to the reaction cell volume (about 100:1) the initial pressure of oxygen could be taken with negligible error (less than 0.3%) as the partial pressure of oxygen above the solution. The hexane saturated with oxygen was then transferred under vacuum into the reaction cell. Solutions containing small calibrated amounts of iodine were prepared by dissolving iodine in hexane. These solutions were then degassed and mixed with oxygen and iodoform as described above.

The solution samples contained in the reaction cell were irradiated with a ruby laser pulse ($694.3 \pm 0.05 \text{ nm}$, $14,402 \text{ cm}^{-1}$) of $880 \mu\text{s}$ duration having 30 J maximal energy. The diameter of the beam was 14 mm and the scattering angle 2.5 mrad. The cell was 10 cm long and 1.8 cm in diameter and was made of Pyrex. U.v. filters were placed on both sides of the cell to eliminate the scattered light from the Xe lamp. The amount of iodine produced by a single pulse was measured spectroscopically with the aid of a Perkin-Elmer 450 spectrophotometer. The absorption spectrum of iodine in the visible region was taken before and after irradiation and the amount of iodine produced was calculated from the change of o.d. in the 500 nm region, this being the only band of iodine which does not coincide with an absorption band of iodoform. Each sample was irradiated only by a single pulse of the ruby laser and the transmission was checked immediately after irradiation. The spectrum of the samples was then remeasured in half hour intervals of time to ensure that no iodine was produced in the dark.

The initial iodoform concentration was varied from 2.5×10^{-3} to 10^{-2} mol/l and that of iodine from 1×10^{-6} to 7×10^{-6} mol/l. The pressure of

oxygen above the solution was varied between 0.011 and 300 Torr. The energy of the laser pulse ranged from 1 to 15 J. In all these experiments the changes of iodine concentration produced by a single pulse were small and varied between 1×10^{-7} to 15×10^{-7} mol/l.

Commercial iodoform was purified by repeated sublimation under vacuum. Merck's spectroscopic grade hexane was used without additional purification. Fluke's spectroscopic grade hexane was allowed to react with bromine the excess of which was removed with NaHSO_3 . The hexane was then washed, dried and distilled.

The concentration of $[\text{O}_2]$ (in mol/l) was determined from the partial pressure P (in atmospheres) of oxygen above the solution using Henry's law: $X = kP$ where X is the molar fraction of oxygen in the solution and $k = 1.93 \times 10^{-3} \text{ atm}^{-1}$ [4].

Results and Discussion

We have found that iodoform dissolved in hexane is decomposed when subjected to a ruby laser pulse of moderate intensity. Iodoform is transparent in the region of the ruby laser frequency and two photon absorption is negligible [3] at the intensities used (40 kW maximal). It was observed that a pure solution of iodoform in hexane does not produce any photolysis. No decomposition took place unless traces of iodine were present in the solution. It was also verified that the presence of iodine alone in the absence of oxygen is insufficient to produce the reaction. No decomposition took place when iodoform solutions were carefully degassed. Even in the presence of oxygen, no reaction was obtained unless traces of iodine were present in the solution. These observations indicated that the photon energy is absorbed by iodine and that the photolysis of the iodoform is catalyzed by oxygen.

The kinetics of the photolysis of iodoform was studied as a function of iodoform and iodine concentrations, intensity of the laser light and the amount of oxygen in the solution. The photolysis was followed by the amount of iodine produced by a single pulse. The reaction was found to be of first order in iodoform concentration. The change of iodine concentration produced by a single ruby laser pulse *vs.* initial concentration of iodoform is presented in Fig. 1. The dependence of the reaction rate on the intensity of the laser light was of order 1/2. The change of iodine concentration *vs.* the square root of the pulse energy is presented in Fig. 2. Order 1/2 was also obtained for the dependence of the reaction rate on the iodine concentration (Fig. 3). A very complex behaviour was observed on varying the pressure of oxygen above the solutions. Up to a pressure of 3 Torr the rate of photolysis increased with the square root of the oxygen concentration. Beyond this pressure and up to 60 Torr it was observed that the reaction continued in the dark producing extensive dissociation. Above 60 Torr the photolysis depends on the inverse square-root of the oxygen concentration. The logarithm of the change in iodine concentration *vs.* the logarithm of oxygen concentration is plotted in Fig. 4.

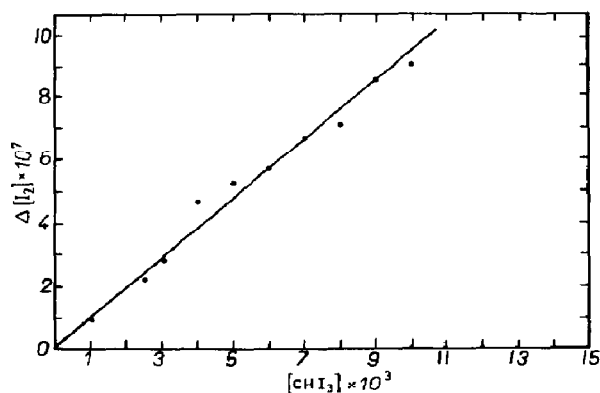


Fig. 1. Change of iodine concentration produced by a single ruby laser pulse vs. initial concentration of iodoform. [N.B. All the concentrations are in mol/l. The parameters relevant to the experiments described by the Figure are $[I_2] = 4.813 \times 10^{-6}$ mol/l, $[O_2] = 2.94 \times 10^{-3}$, pulse energy $E = 7 \pm 0.7$ J; average relative error of the measurements, 4.7%.]

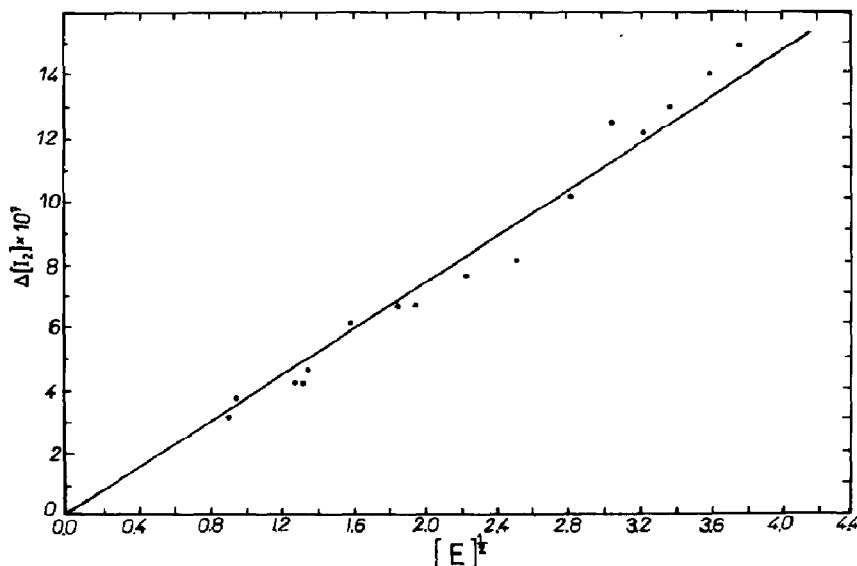


Fig. 2. Change of iodine concentration vs. the square root of the pulse energy (in Joules). The initial concentrations $[I_2]$ and $[O_2]$ were the same as in Fig. 1; $[CHI_3] = 10^{-2}$ mol/l. The average relative error of the measurements was 6.2%.

The square root dependence of the reaction rate on the iodine concentration, the light intensity and the oxygen concentration (at low partial pressures) suggests a free radical chain mechanism initiated by the photodecomposition of iodine. Iodine absorbs very weakly at the laser frequency producing a transition to the $^3\pi_{1u}$ state [5]:



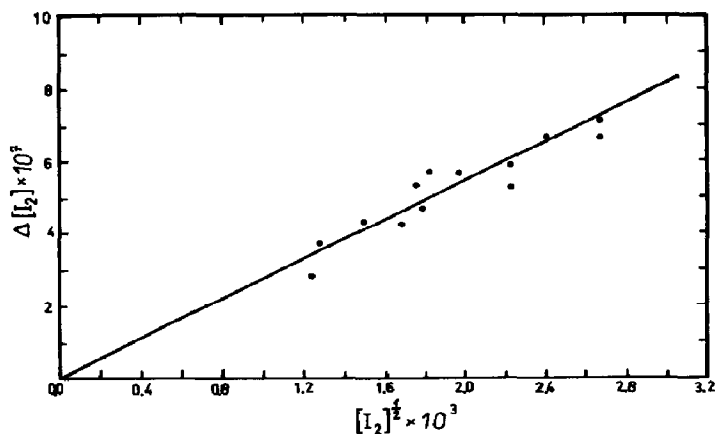


Fig. 3. Change of iodine concentration vs. the square root of the initial iodine concentration. The initial concentrations $[\text{CHI}_3]$ and $[\text{O}_2]$ were the same as in Fig. 2 and the pulse energy was the same as in Fig. 1. Average relative error of the measurements, 7.9%.

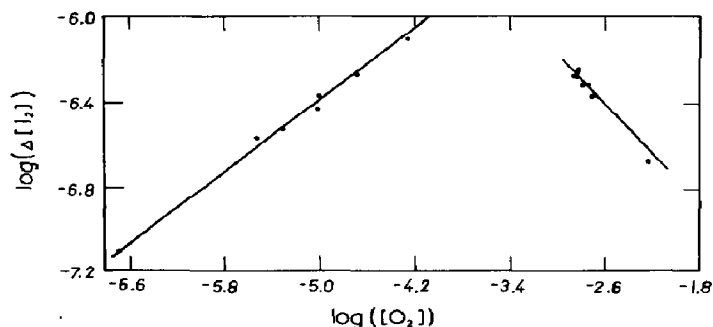


Fig. 4. Change of iodine concentration vs. initial O_2 concentrations. The concentrations $[\text{O}_2]$ are in mol/l. The pulse energy and the initial value of $[\text{I}_2]$ were the same as in Fig. 1. The initial value of $[\text{CHI}_3]$ was 5×10^{-3} mol/l. Average experimental error, 7% at higher O_2 concentrations and 20% at lower O_2 concentrations.

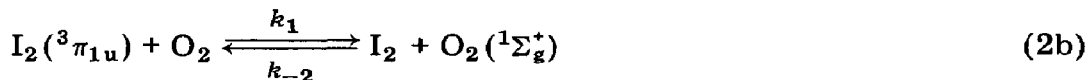
None of the other components of the system absorbs at the laser frequency. In order to explain the influence of oxygen it was first assumed that oxygen enhances the singlet-triplet transition of I_2 . However, no experimental confirmation of this hypothesis could be obtained: it was found that the presence of oxygen does not modify the spectrum of iodine in solution. Complex formation between I_2 and O_2 may therefore be excluded. In the gas phase the excitation of I_2 to the $^3\pi_{1u}$ state at the ruby laser frequency would lead to dissociation. We assume that in the liquid this decomposition is counteracted by the cage effect. The role of the oxygen molecule could then be described either by assuming a Schonberg mechanism [6] of exciplex formation according to the elementary reaction:



followed by dissociation:



or by an energy transfer mechanism [7]:



the oxygen being excited to the singlet state (the $^1\Delta_g$ state of oxygen is 7782 cm^{-1} above the ground state and $^1\Sigma_g^+$ is $13,122 \text{ cm}^{-1}$ above the ground state). The energy stored in the singlet oxygen is then available for reaction according to:



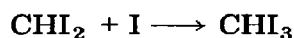
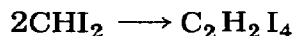
the iodine atom initiates the chain reaction:



the chain is interrupted by the recombination of two iodine atoms:

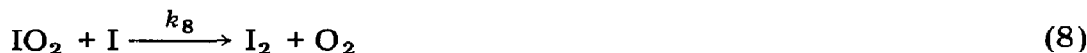


Other interruptions such as:



can be ruled out, since the concentration of CHI_2 is probably much lower than that of I . This is due to the fact that the rate constant k_4 of the endo-ergic reaction step (4) is probably much smaller than k_5 the rate constant of the exoergic step (5).

In order to explain the inhibitory effect of oxygen at high O_2 concentrations we introduce the additional interruption steps:



Assuming steady state conditions the above mechanism leads to the rate equation:

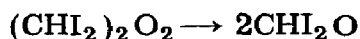
$$\frac{d[I_2]}{dt} = k_4 \left(\frac{k_3 k_2 k_1}{k_{-2} k_{-1}} \right)^{1/2} \frac{(I_L/c)^{1/2} [I_2]^{1/2} [O_2]^{1/2} [CHI_3]}{1 + \frac{k_2 k_3}{k_{-2}} [O_2]^{1/2} (k_6 + \frac{k_7 k_8}{k_{-7}} [O_2]^{1/2})}$$

where I_L is the laser intensity and c is the velocity of light.

Interruption steps such as:



leading to peroxide formation may also occur. These steps probably play a minor role insofar as the overall reaction mechanism is concerned as a result of the lower concentration of CHI_2 radicals compared to that of the iodine atoms. However, the radicals formed by the slow thermal decomposition of the peroxide:



may initiate chain reaction in the dark. This will only affect the region of intermediate oxygen concentration since at low O_2 concentration the steps (9) and (10) will be negligible whereas at high oxygen concentration the chains are very short due to reactions (7) and (8). The relative importance of the slow dark reaction in the intermediate region of oxygen concentration can be explained by the considerable length of the chains due to the low concentration of the radicals in the absence of irradiation thus reducing the probability of chain termination by radical recombination.

The same kind of argument can be used to understand the absence of chain reactions in the case of u.v. [1] and two photon [3] photodecomposition of CHI_3 . In the latter cases the abundance of the iodine atoms produced by the reaction $CHI_3 + h\nu \longrightarrow CHI_2 + I$ has the consequence that the recombination $2I \longrightarrow I_2$ dominates the chain reaction.

References

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