

## A NEW REACTION: THE PHOTOBREAKDOWN OF ORGANIC COMPOUNDS BY ELECTRON CASCADES

F. GANS

*L.I.R.T.A., Chemin du Couvent, F 91190 Gif-sur-Yvette (France)*

C. TROYANOWSKY and P. VALAT

*Ecole Supérieure de physique et chimie, 10, rue Vauquelin, F 75005 Paris (France)*

### Summary

Organic compounds are destroyed by flashes combining a high energy and long durations. This general photoeffect proceeds through a photoionization and results from an electron cascade, the build up of which depends on both flash duration and energy. The effective process leading to the destructive electron cascade is a photoacceleration of the electrons.

---

### Introduction

We described in previous papers [1, 2] the very general anomalous photolysis observed when organic compounds are illuminated by flashes of high energy and relatively long duration.

These conditions result in a total photodestruction which always forms carbon [2]. It is easily observed by illuminating a sample (whatever its physical state) with flashes of energy up to  $1.5 \times 10^4$  J and duration of a few hundred  $\mu$ s. The reaction has been obtained on many compounds with structures as different as those of benzene, carbon tetrachloride, diethyl oxide, n-hexane, etc. (Table 1). The only molecules which are not destroyed under these experimental conditions are the first saturated alcohols.

### Features of the photodestruction

It can only be observed within given illumination time limits. Steady illumination by a source emitting between 2000 and 20,000 Å only achieves normal photolysis, if any. Similar results are obtained with short flashes:

TABLE 1

Reagent dependence of the destruction threshold

	Joules		Joules
CCl <sub>4</sub>	4400	n-hexane	9000
CHCl <sub>3</sub>	3200	n-heptane	10,000
CH <sub>2</sub> Cl <sub>2</sub>	5750	n-Bu <sub>2</sub> O	5750
CHBr <sub>3</sub>	4400	Et <sub>2</sub> O	13,800
C <sub>2</sub> H <sub>5</sub> Br	5750	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> O	5325
n-C <sub>7</sub> H <sub>15</sub> Br	5750	Ethanol	—
n-C <sub>6</sub> H <sub>13</sub> Br	5325	n-butanol	—
BrCH <sub>2</sub> CH <sub>2</sub> Br	5750	s-butanol	—
Benzene	3300	isobutanol	—
Toluene	4000	t-butanol	8000
C <sub>6</sub> H <sub>5</sub> Br	4000	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	5300
n-pentane	12,000	Diethyl phtalate	7300
		BrCH <sub>2</sub> CH <sub>2</sub> OH	8500

flash-photolysis conditions (500 J, 10  $\mu$ s ) dissociate carbon tetrachloride into the normal Cl<sup>·</sup> and CCl<sub>3</sub><sup>·</sup> free radicals, whereas illumination by a flash of 5000 J within 500  $\mu$ s (at half-peak) leads to carbon formation.

The photodestruction requires a reagent-dependent energy-threshold (Table 1). Below this threshold and whatever the number of successive flashes only normal photolysis is achieved. In our experimental conditions the energy-thresholds range from 3300 J (benzene) to 13,800 J (diethyl oxide). Beyond this threshold the blackening soon becomes a dramatic effect while the reaction can be very violent.

Energy thresholds for destruction are increased (the increase can be more than 100%) when the light is filtered by a sodium chromate solution (0.01 to 1% by wt in water) which absorbs all radiation below 4800 Å. As all the compounds under study absorb below 3000 Å it appears that the photodestruction can occur under conditions where the reagent is radiation-transparent.

### Photonic origin of the photodestruction

The blackening of organic compounds illuminated by a flash of high energy is usually ascribed to a spurious phenomenon: pyrolysis, impurity effect, etc. This is not the case here, where we deal with a photochemical reaction.

Impurities play no part in the reaction. Destruction thresholds are unchanged when soluble impurities are added to the reagent. Insoluble impurities show no more influence. However purified the reagent (see experimental section) the destruction-energy is practically unchanged.

As walls may also play a part in a destructive process we made a few "wall-less" experiments: a thin stream of reagent is run along the axis of the

flash lamp. The photodestruction is observed as under the usual conditions.

Neither can the reaction be a pyrolysis induced by the i.r. part of the radiation, as destruction-thresholds are unaffected if the reagent is illuminated through a copper sulphate aqueous solution which cuts off a part of the near i.r. Moreover, most of our experiments were carried out on carbon tetrachloride which is transparent until the middle i.r.

The destruction can no more be due to a heating of purely thermal origin. It might be thought that the heat generated by the discharge (about 85% of the electrical energy in the flash lamp) induces a very intense heating, resulting in a partial vaporization of the sample. The bubbles would then be adiabatically heated and would lead to a pyrolysis. This view cannot be held as the photodestruction is still observed when the sample is in an evacuated jacket ( $10^{-4}$  Torr) which could not transmit heat.

The fact that the photodestruction is observed when the illumination is performed through an evacuated jacket also rules out any possible role of an external shock-wave. The jacket is longer than the sample cell so that a shock-wave travelling along its walls cannot reach the sample before the end of the flash. As the destruction is no longer observed when black paper is wrapped around the evacuated jacket there is no possibility either of a direct shock-wave effect or of a coupled effect of illumination + shock-wave.

A possible role of an internal shock-wave can also be ruled out as the destruction is obtained even when the reagent is radiation transparent. There can be no such shock-wave when there is no light absorption.

Finally there is no possible role of the electromagnetic field associated with the flash, as photolysis is prevented by wrapping black paper around the sample. Black paper would not stop the electromagnetic field but stops photons, and what is observed is a purely photonic effect.

### Impossibility of a conventional photolysis mechanism

The special and unexpected role of time in this reaction is enough to establish its non-conventional character. It must also be noted that compounds of completely different structures (benzene, carbon tetrachloride, n-hexane) give the same end-product, carbon. It is difficult to think of any *common* conventional mechanism where any reagent would give the same product. It must also be remembered that photolysis still occurs when the reagents are transparent.

Successive photolyses might perhaps be considered. As a filter is never 100% efficient (the more so with a liquid filter such as the ones used), as each flash carries a high light-energy (400 - 2000 J per flash) and as the samples are relatively small (a few ml) it might be imagined that a few photons (normally absorbed by the reagent) could pass through the filter. In the case of  $\text{CCl}_4$ , they would then form  $\text{Cl}^\cdot$  and  $\text{CCl}_3^\cdot$ , which would be

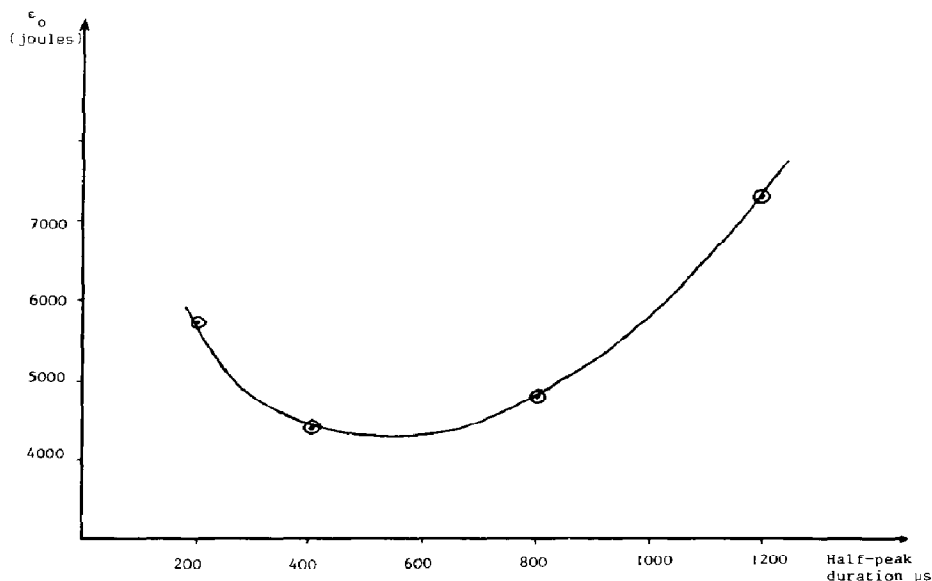


Fig. 1. Time dependence of the destruction threshold.

photolyzed by photons of appropriate energy. The photodestruction would then be the result of the successive photolyses of  $\text{CCl}_4$ ,  $\text{CCl}_3$ ,  $\text{CCl}_2$  and  $\text{CCl}$ .

This idea is not tenable as  $\text{CCl}_3$  absorbs much closer to 2000 Å than carbon tetrachloride itself [3]. The source emission at this wavelength is negligible and it is absorbed by the flash lamp walls, the filter and cell walls as well as by the filter. The probability of such photons reaching the sample is thus very small, and even then would not explain the fact that there is no blackening with steady or very short illuminations.

### Role of time, energy and peak power

We saw that photodestruction can only take place within a given "time-window" and that photolysis remains normal under different conditions. If we compare flash photolysis illumination conditions (500 J, 10  $\mu\text{s}$ , oxygen-filled flash lamp) to our usual ones (5000 J, 500  $\mu\text{s}$ , xenon-filled flash lamp) and take into account that the quantum yield in an oxygen discharge is approximately 1/3 of the yield in xenon, the peak powers in these discharges are in the ratio of 17/10. Although they are quite comparable the results are totally different.

Actually the normal or abnormal character of the photolysis depends on both flash energy and flash duration. This is evident on the curve that plots (Fig. 1) the destruction threshold energy (for  $\text{CCl}_4$ ) against flash duration. If peak power were the determining factor the plot would be a straight line. The presence of a clear minimum shows that both energy and time are independent parameters of the phenomenon.

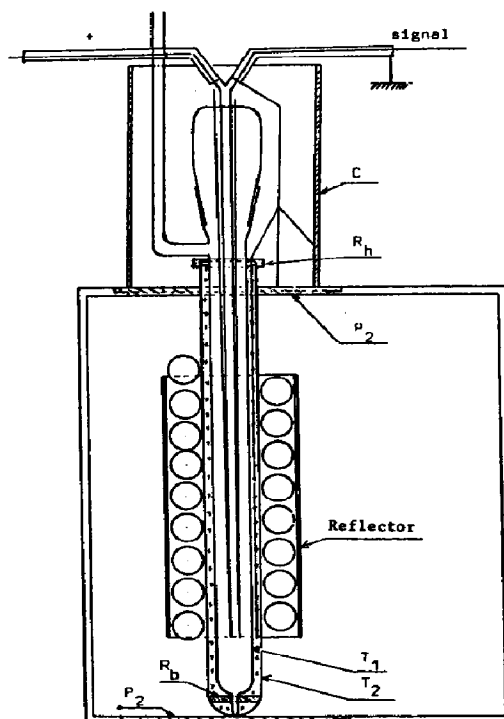
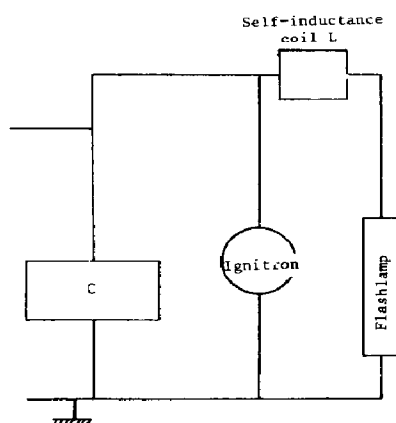


Fig. 2. Short-tailed flashes: block diagram. Fig. 3. Cell for electric measurements.

The fact that  $\text{CCl}_4$  photolysis returns back to normal when illumination times become shorter shows that the photodestruction is a multistep process, one of the steps being slow enough to prevent the photodestruction when excitation becomes too short. The curve (Fig. 1) in some way expresses the propagation condition for the process responsible for the photodestruction.

The major role played by time is confirmed by experiments with flashes where the discharge tail is shortened by having an Ignitron in parallel with the flash lamp (Fig. 2). Although the flash shape is changed the peak power and duration at half-peak remain the same, and the flash energy is reduced by about 20 - 25%. The destruction threshold is then raised by about 100%, which shows the determining influence of that fraction of the energy which is brought in at the end of the flash.

### Role of charged species in the photodestruction mechanism

This influence of charged species can be shown in a number of ways.

(1). The resistivity of a flashed sample drops by several orders of magnitude. With  $\text{CCl}_4$ , a carefully purified sample (resistivity  $10^{14} - 10^{15}$  ohms  $\text{cm}^{-1}$ ) shows after flashing a resistivity of  $10^{10} - 10^{11}$  ohms  $\text{cm}^{-1}$ .

(2). In experiments on gaseous  $\text{CCl}_4$  the reagent resistance becomes zero during the illumination. These experiments are done in a cell (Fig. 3)

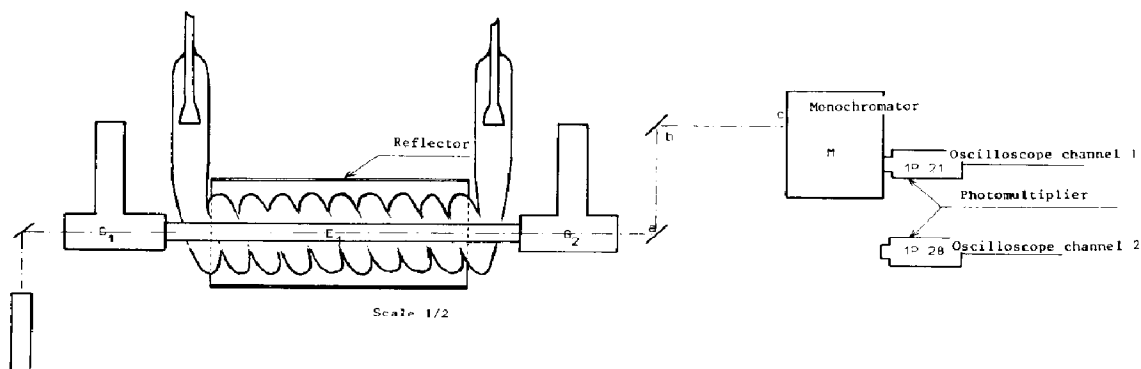


Fig. 4. Experiments at energies below threshold: fluctuation of a laser beam modes. Experimental set-up.

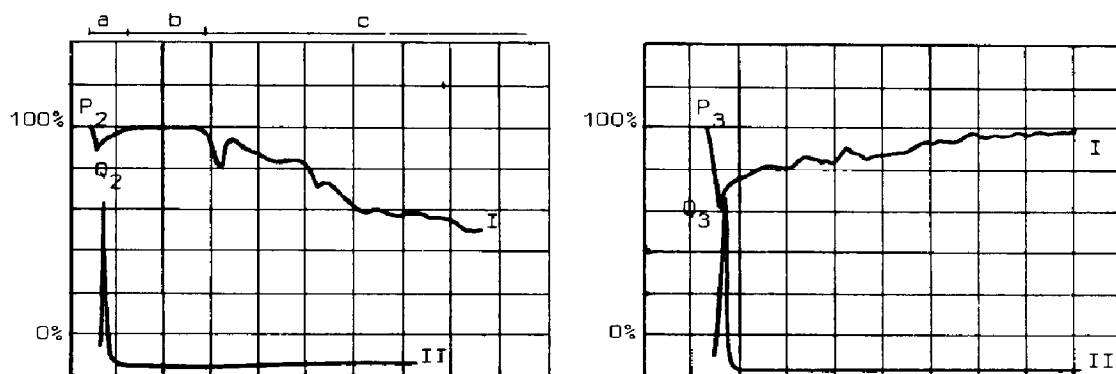


Fig. 5. Reversible drop in optical transmission (7.5 ms/square). I Laser beam transmission; II Flash shape;  $P_n Q_n$ ; drop in laser beam transmission.

Fig. 6. Reversible drop in optical transmission after several flashes: evidence of a cumulative effect (7.5 ms/square). I Laser beam transmission; II Flash shape;  $P_n Q_n$ : drop in laser beam transmission.

equipped with electrodes submitted to a low static voltage. The current flows through the cell before the end of the flash.

(3). Positive ions are formed in the photodestruction. When  $\text{CCl}_4$  in the gaseous state is illuminated with a low voltage applied between electrodes the whole of the carbon is deposited on the cathode. This carbon has therefore appeared exclusively under the form of positively charged ions, which shows that the photodestruction reaction proceeds exclusively through a photoionization.

(4). The influence of charged species also appears in experiments where illuminations are done at energies slightly below the photodestruction threshold. Under such conditions the reagent remains unchanged and the observed phenomena are purely photophysical. A laser beam passes axially through the sample (Fig. 4). Each flash induces a very important fluctuation of the laser modes, which is still apparent many minutes after the

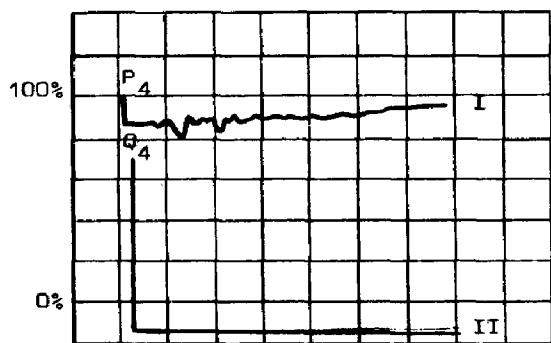


Fig. 7. Laser beam transmission after electrical cleaning of the reagent. (15 ms/square). I Laser beam transmission; II Flash shape;  $P_n Q_n$ : drop in laser beam transmission.

flash. Thermal phenomena account for the long duration fluctuations, which are of no importance. The initial fluctuation, followed on an oscilloscope, is a reversible drop in optical transmission (overall duration 2 - 3 ms). It is a cumulative effect and the drop in optical transmission is much greater after several discharges (Figs. 5 and 6).

This effect is strongly reduced if the cell is equipped with electrodes and submitted for several hours to a static voltage of the order of 10 kV/cm (Fig. 7). This is the "electrical cleaning" technique which is commonly used in the study of dielectrics in order to remove the ions in the medium. It is known that all dielectric materials contain a permanent but very small amount of ions (of unknown nature) originating from friction, cosmic rays, etc. The removal of these ions practically suppresses the perturbation induced by a discharge which is not energetic enough to induce the photodestruction. The latter therefore follows in time a physical process which also involves charged species. The detail of these experiments will be published elsewhere but we shall come back to the importance of this observation.

### Photodestruction mechanism

The phenomena associated with photodestruction are in several points reminiscent of what occurs in the electrical breakdown of dielectrics. The interpretation of this breakdown [4] involves the ions present in a dielectric medium. The applied disruptive voltage forms additional ions and electrons, which are accelerated by the electric field and form electron cascades which are finally responsible for the breakdown.

We have shown the presence and influence of ions in the photophysical and photochemical processes, and the decrease in the photophysical effect when these ions are at least partly removed. We also saw that a photoionization is one of the significant processes during the photodestruction.

We also found that the cascade electrical breakdown, well known in the case of gaseous dielectrics, can be achieved through an illumination. The experiments were done on a number of very pure gases: oxygen, nitrogen,

TABLE 2

Illumination of gases placed under a static voltage: evidence of breakdown from the current intensity at high flash energies

Gas	Flash energy (kJ)	Voltage (kV)	$I_{\text{cell}}$ ( $\mu\text{A}$ )
$\text{N}_2$	2.00	2.00	7
	4.00	2.00	50
$\text{O}_2$	0.00	2.00	0.001
	2.00	2.00	0.001
	6.00	2.00	12.5
	2.00	4.00	10
	3.85	4.00	$4 \times 10^3$
Xe (500 Torr)	2.00	1.00	3
	3.00	1.00	7
	3.85	1.00	$10^3$
	3.50	0.50	13
	4.80	0.50	$5 \times 10^2$
$\text{Cl}_2$ (90 Torr)	2.20	0.25	0.5
	3.20	0.25	1.5
	4.40	0.25	3
	7.20	0.25	250

argon, xenon. These gases fill a cell equipped with electrodes, the applied static voltage being much too low to induce the electrical breakdown. When they are submitted to an illumination of appropriate energy (this apparatus, including the cell, is the same as that used with liquid samples), the current flows through the cell, the electric resistance becoming zero. This is proof of the close relationship between the mechanisms of photodestruction and of electrical breakdown (Table 2).

This analogy must not be pushed too far. We can assume, in our experiments, that the electrons freed under illumination conditions are accelerated during the flash by the associated electromagnetic field. With the energies involved in this case, the field would be of the order of  $5 \times 10^4$  V/cm. If it is assumed that the field is classical and that there is no energy loss of the electrons through collisions, an electron (for a flash of 500  $\mu\text{s}$ ) is very far from gaining enough energy to induce an ionization through collisions.

Actually the photodestruction would rather show a closer relationship to the destructive phenomena induced by giant-pulse lasers. Such destructions have been observed a number of times and are ascribed to a "reverse Bremsstrahlung process" [5]. This name expresses the photoacceleration effect undergone by an electron interacting with the surrounding nuclei or molecules and simultaneously submitted to the field associated with the



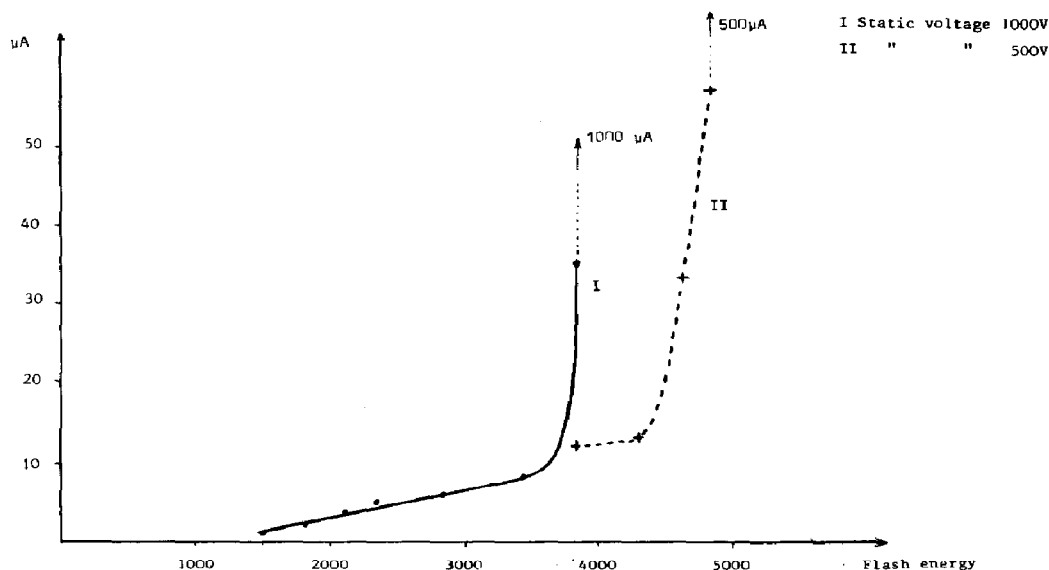


Fig. 8. Photobreakdown of xenon (500 Torr) under a static voltage: current through the cell during illumination.

illumination. The reverse Bremsstrahlung can account, in short times, for the gain of several volt-electrons which is necessary to achieve an ionization.

This photoacceleration effect is what is observed (see preceding section) under the coupled influence of a static voltage and an illumination. The flow of current through the cell is proof that charged species have been accelerated. As the applied voltage is purposely much too low to induce the breakdown the observed destruction (or simple breakdown in the case of a simple gas such as  $O_2$ ,  $N_2$  or Xe) can only result from the illumination and implies the acceleration of electrons.

The lower the value of the static voltage, the higher is the flash energy required to achieve photodestruction (Fig. 8). There is thus a direct correlation between the additional voltage which would induce the electrical breakdown and the supply of energy through illumination.

The role of a reverse Bremsstrahlung is confirmed by the fact that, in a same cell, the photodestruction of  $CCl_4$  requires more energy in the gaseous than in the liquid state. As the dielectric rigidity of a liquid, under a given thickness, is much higher than that of its vapour, only a reverse Bremsstrahlung can account for this fact: as it implies the interaction of electrons with the surrounding matter, this interaction will be much more intense in a condensed than in a gaseous medium.

#### Nature of the primary process

There are two possible hypotheses.

As photodestruction can be achieved under conditions where the reagent is radiation transparent, it seems logical to assume a multiphotonic

process as the primary step raising the reagent to an ionization level.

But it is also possible to imagine a conventional-type absorption by the ions which are always present at very low concentrations in a dielectric. As these ions must be unstable (if not their concentrations would be much higher) they could dissociate easily and free an electron which would be accelerated.

Actually nothing is known about the nature of the ions in dielectric media, but the fact that they are present [4]. It can therefore be imagined that they absorb a part of the impinging radiation, and their poor stability must then result in a free electron.

The idea of a multiphotonic process which would raise the molecule to an ionization level has one drawback: all multiphotonic processes known to this day have involved a laser, usually Q-switched (pulses of 2 - 50 ns, peak powers of 1 - 500 MW) and focussed. The beam area is then such that photonic fluxes are at least  $10^{25}$  photons  $\text{cm}^{-2} \text{s}^{-1}$  and can be as high as  $10^{33}$  photons  $\text{cm}^{-2} \text{s}^{-1}$ .

The use of giant-pulse lasers to achieve multiphotonic processes stems from the fact that only they seem able to give, owing to their high peak powers, the photonic density which is necessary for a phenomenon of low probability. But basically a multiphotonic process does not have to be coherent. In the case of a laser the considered probability is that associated to a purely or nearly purely monochromatic light emission. In our experiments, where photonic fluxes are of the order of  $10^{23}$  photons  $\text{cm}^{-2} \text{s}^{-1}$ , the probability is certainly much higher as the flash lamp emits a continuum. In this case the exciting system contains all the frequencies, the combination of which can supply the energy necessary to reach an ionization level. This must result in a greater probability for a multiphotonic process.

The idea of a multiphotonic primary process seems more believable than that of a conventional absorption by unknown ions but we are not yet able to discriminate between these two possibilities.

### Remarks on the photodestruction mechanism

How the initiating electron is freed is yet unknown but the existence of an electron cascade mechanism results from the resemblance between the electrical breakdown of dielectrics and the results of illuminations on samples of several gases submitted to a low static voltage. These experiments also establish that electrons are accelerated by the illumination, this acceleration adding itself to that which could result from the too low voltage applied between electrodes. The fact of this acceleration implies the intervention of a reverse Bremsstrahlung process, confirmed by the compared energy requirement for the destruction of liquid and gaseous samples of the same compound in the same cell.

The influence of ions in the overall process is already evident below the destruction threshold, as shown by the fluctuations of a laser beam

going through the sample. Ions therefore play already play role in this preliminary step but their presence is not enough to go beyond the photo-physical stage. The electron cascade results from the later acceleration. Electrons must at least have enough energy to ionize the molecule. In a condensed medium this energy is given by a formula of Leach *et al.* [6]:

$$\delta W_i = \frac{n\bar{\alpha}e^2}{a^4}$$

with  $\delta W_i$  = difference between true ionization energy and ionization energy in a condensed medium,

$n$  = number of molecules submitted to the inductive field,

$\bar{\alpha}$  = polarizability,

$e$  = charge of the electron,

$a$  = distance between the charge and the centre of the induced dipole.

In the case of  $\text{CCl}_4$  this energy is of the order of 8.5 - 9 Volt-electrons [7]. This agrees with the idea of a biphotonic process as experiments are usually done in Pyrex cells with a cutoff around 2900 Å (~4.3 Volt-electrons). Actually the flash lamp emission (xenon flash lamp, pressure 300 Torr) is quite poor for wavelengths below 3000 Å, and the assumption of a biphotonic process induced by the only wavelengths near the Pyrex cutoff would result in a very low probability, and also show a clear difference depending on whether Pyrex or silica cells are used. In fact the thresholds are very little influenced by the choice of the cell material (see Table 3). It can be supposed that the first step is an excited state as its lifetime is much greater than that of a virtual state ( $10^{-16}$  s) and that the ionized state is reached in a second step.

The buildup of an electron cascade implies for the electron to have collided with a sufficient number of ionizable molecules. The spatial expression of this condition is Paschen's law, which is not time dependent. But if the electromagnetic field acts during a too short time it is evident that the accelerated charged species will not be able to travel far enough to build a cascade. If illuminations which are too long are used the energy losses of the electron will cancel the gains and no cascade will be able to build itself. When illuminations become too short, the electron velocity will follow the fourth root of the electromagnetic field value [7], as the field is proportional to the square root of the lighting and the electron velocity to the square root of the field. This velocity will increase but poorly for shorter illuminations and no reaction will be possible for too short times. This explains qualitatively the observed minimum of curve (1).

### Chemical processes in photodestructions

Our knowledge of these processes is very limited but photodestruction does not only form carbon. A number of other compounds are formed and remain dissolved in the reagent.

TABLE 3

Dependence of destruction threshold on wall material or optical filter

	Silica	Pyrex	Uranyl nitrate 15 g/l	Sodium chromate 0.1 g/l	Sodium chromate 1.0 g/l
Cutoff $\lambda(\text{Å})$	2200	2900	3200	4400	4700
Bromoform	4400	4400	5900	8000	9000
Benzene	3300	3300	3800	5800	7000
$\text{CCl}_4$	4400	4400	7300	9000	

With  $\text{CCl}_4$  chlorine formation (estimated from its absorption spectrum in the visible) is about ten times greater than that of  $\text{C}_2\text{Cl}_6$  which is the normal product from duplication of  $\text{CCl}_3$ . This could be expected in a reaction that forms carbon, as the abstraction of all chlorine atoms is more probable than the duplication of a primary free radical. V.p.c. analysis shows also the presence of some  $\text{C}_2\text{Cl}_4$  (for energies close to the threshold) and of a compound with a slightly longer retention time than  $\text{C}_2\text{Cl}_6$ . It has to be a  $\text{C}_3$  compound and it has a shorter retention time than  $\text{C}_3\text{Cl}_6$ . It is probably one of the  $\text{C}_3\text{Cl}_4$  isomers.

With benzene an undegassed sample of spectroscopic grade purity forms in a single flash several milligrammes of a heavy compound with the i.r. spectrum of a long-chain phthalic ester.

The discussion of this complicated reaction is outside the scope of this paper. But the study of the products other than carbon should provide additional data on the mechanisms involved. As the reaction always proceeds through a photoionization these photoionization mechanisms could be approached through a study of photodestructions. And as the photodestruction can also be obtained in the solid state (data on benzene and  $\text{CCl}_4$ , Table 4) experiments in the solid state on compounds either pure or diluted in a rigid matrix should open the possibility to reach reaction transients.

### Possible applications of the photodestruction reaction

The most important is certainly the study of photoionization mechanisms. The photodestruction effect does not lend itself easily to optical measurements as carbon formation makes the medium turbid. But electrical measurements are still possible. For solid state experiments the blackening is not homogeneous as it is in a fluid state: carbon is formed in long filaments that cross the sample in all directions. Optical measurements would probably be possible near these filaments, and this could also be possible for dilute solutions in rigid matrices.

TABLE 4

Temperature dependence of the destruction threshold

CCl <sub>4</sub>		Benzene	
T (°C)	Joules	T (°C)	Joules
61.5	4050	63	3250
44	4050	43.5	3350
23	4400	23	3925
-20	4400	5	3925
-40	6800	2	4050
-60	7800	-2	4050
		-20	5750
		-40	6500
		-60	7625

Why some molecules cannot be destroyed by this quite general reaction should also be studied. It is the case of the first saturated alcohols. Electron scavenging is not responsible for this behaviour, as the addition to the reagents of electron scavengers (N<sub>2</sub>O, SF<sub>6</sub>) does not affect the destruction thresholds. Moreover, it must be remembered that most experiments were done on carbon tetrachloride which is an efficient scavenger.

The understanding of this resistance to destruction would be useful to the operation of immersion lasers. We described in previous papers [7, 8] such a solid-state laser, in which small pieces of the doped solid are immersed in a liquid with the same refractive index for the laser wavelength. Such a laser has been easily operated at low or medium pump energies, but photodestruction prevents its use at high pump energies. The photodestruction can be limited by the use of the most destruction-resistant liquids, but they must have the same refractive index as a glass, which restricts the choice to compounds with indices in the 1.50 - 1.60 range. Another improvement is in the use of sodium chromate filters and of "short-tailed flashes", the latter raising the destruction-thresholds by about 100%. But nothing could be better than the use of really photostable liquids if such liquids can be shown to exist in such illumination conditions.

There is no reason why the photodestruction reaction should be limited to organic molecules. They were the ones studied here and their destruction is made visible by carbon formation, but an electron cascade should be as efficient in the case of inorganic compounds.

Finally, it could be mentioned that a high photonic flux impinging within a relatively long time are conditions that do not seem very different from those achieved by nature in lightning. As conditions around a lightning flash are, in the view of some, responsible for the buildup of some

prebiotic molecules, it might be of interest to look for the formation of such compounds under these experimental conditions.

## Experimental

### *Illuminations*

The energy is usually supplied by Sangamo capacitors (60  $\mu\text{F}$ , 10 kV max., self-inductance 0.8  $\mu\text{H}$ ). Three to five capacitors are mounted in parallel. The maximal energy is 15,000 J.

For shorter flashes Bosch capacitors KO/MPS were used (7.73  $\mu\text{F}$ , 18 kV max., self-inductance 27 nH).

Half-peak durations are determined by the length of a self-induction coil of 2 mm copper wire. Triggering is done by a Tesla coil around the flash lamp.

The flash lamp is usually helical (10 silica coils, i.d. 12 mm, coil diameter 32 mm, overall length 185 mm, tungsten electrodes), Xe-filled under 300 Torr. Some rectilinear flash lamps have also been used, with the same electrodes and xenon pressure (i.d. 13 mm, 200 mm between electrodes). One to four tubes are used. In the case of multiple tubes triggering is synchronized. All tubes are placed in a polished Al reflector 65 mm in diameter.

For short-tail flashes an Ignitron is mounted in parallel with the flash lamp (Fig. 2).

The reaction cells are fused silica or Pyrex tubes (commonly Pyrex) placed along the axis of the helical flash lamp or parallel to the rectilinear flash lamps. They are longer than the flash lamp in order to prevent tube-ends effects. Various cell diameters were used, the most common being 6 - 7 mm i.d.

Filtering solutions are in a Pyrex jacket between sample and flash lamp. Jacket thickness is 2 - 3 mm. The  $\text{CuSO}_4$  solution is 10 g/l of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

The discharge energy is deduced from the voltage in the capacitors. Pulse shapes are followed by a photodiode or a photomultiplier (RCA 1P21 or 1P28).

The geometry is far from optimal as the flash lamp is distant from the cell, and the reflector diameter is much larger than that of the flash lamp. Destruction energies are therefore comparative as a better geometry would give lower thresholds. Values obtained with helical or rectilinear flash lamps are comparable: rectilinear flash lamps are always placed so that a known compound will give the same destruction energy as with a helical lamp.

Illuminations are done only once on a sample tested above threshold, as the reaction of a sample already containing carbon is always violent: carbon absorbs radiation at all wavelengths and induces a very important heating. Reactions done distinctly above threshold are also violent: the

reagent is ejected (open cell, atmospheric pressure) or explodes (sealed cell under atmospheric or reduced pressure). The amount of carbon produced is very small at threshold value and increases very rapidly with flash energy. As an example, producing 25 mg of carbon from benzene in optimum conditions required about 20 experiments.

#### *Experiments at sub-threshold energies*

The sample cell, horizontal, is along the axis of a helical flash lamp. The beam from a small He-Ne laser passes along the axis of the cell (Fig. 4) and goes (through a monochromator in order to remove stray light) to a 1P21 photomultiplier.

The flash intensity and shape are detected by another photomultiplier which triggers a dual channel oscilloscope (Tektronix 4407) so that both the light pulse and laser beam intensity are displayed.

There is no fluctuation of the laser beam intensity when the cell is empty or when there is no cell on the optical path. The variations in transmission appearing at long times (over 20 ms) in Figs. 5, 6 and 7 come from the heating of the cell by the discharge, which induces temperature gradients and lens effects.

#### *Electrical measurements*

Measurements under illumination conditions are done in the cell shown in Fig. 3, the electrodes being tungsten wire. In some cases these electrodes have been copper-, nickel- or gold-clad, in order to check that the measured values do not depend on electrode material.

Resistivity measurements are done in a cell equipped with square gold-plated electrodes: electrode area  $1 \text{ cm}^2$ , distance 5 mm.

Current intensities in different gases under different pressures are given in Table 4. In an experiment on chlorine it was observed that the breakdown voltage increases with lower pressures, in agreement with Paschen's law. In the experiment on gaseous  $\text{CCl}_4$  all the carbon was deposited on the cathode.

When measurements are done on liquid  $\text{CCl}_4$ , under a 2 kV static voltage, the destruction-threshold is at 4.1 kJ instead of 4.4 kJ when no voltage is applied. With a short-tailed flash the destruction-threshold (under 0.25 kV) is raised up to 6.5 kJ.

#### *Reagent purity and purification*

All reagents are analytical or spectroscopic grade. The main object of purification is dust removal, done by filtering (sintered glass no. 5, then Millipore filters, pore diam. below  $0.1 \mu\text{m}$ ) and repeated cold-wall distillations. The cells are acid-, solvent- and water-cleaned, then heated under vacuum. Passing a laser beam through a purified sample must give no bright point which would indicate the presence of dust particles.

## Acknowledgements

Part of this research has been done on a research contract from the Direction des recherches et moyens d'essais. We had fruitful discussions with a number of colleagues, among whom C. Manus, G. Mainfray, J. Sutton (Commissariat à l'énergie atomique, Saclay) and S. Leach (Photo-physique moléculaire, Orsay).

## References

- 1 F. Gans, C. Troyanowsky and P. Valat, *J. Chim. Phys.*, 70 (1973) 692.
- 2 F. Gans, E. Michel, C. Troyanowsky and P. Valat, *J. Chim. Phys.*, 72 (1975) 309.
- 3 Data supplied by J. Sutton and coworkers, Centre d'études nucléaires, Saclay, DRA-SRIRMA.
- 4 I. Adamczewski, *Ionization, Conductivity and Breakdown in Dielectric Liquids*, Taylor and Francis, London, 1969.
- 5 J. L. Delcroix, *J. Phys. Colloq.* C3 (1968) 29.
- 6 C. Vermeil, M. Matheson, S. Leach and F. Muller, *J. Chim. Phys.*, 61 (1964) 598.
- 7 P. Valat, *Dissertation Univ. Paris VI*, CNRS no. AO 10509 (1974).
- 8 F. Gans, C. Troyanowsky and P. Valat, *C. R. Acad. Sci.*, 270 B (1970) 1343.