

LIGHT-INDUCED REACTIONS OF LEUCO CRYSTAL VIOLET

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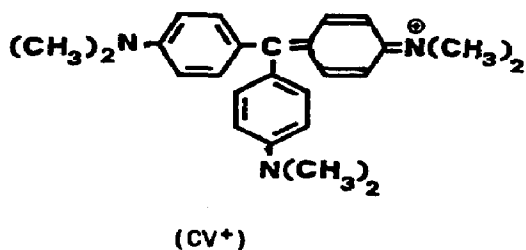
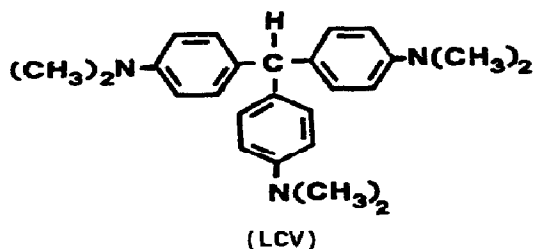
(Received January 27, 1986; in revised form March 14, 1986)

Summary

Leuco crystal violet (LCV) was irradiated in argon-saturated acetonitrile solution with 20 ns flashes of 265 nm or 347 nm light. The formation and the decay of transient species were followed with the aid of optical absorption, phosphorescence and electrical conductivity measurements. Intersystem crossing to the triplet manifold ($^3\text{LCV}^*$) and formation of radical cations ($\text{LCV}^{\cdot+}$) were found to be major routes of the deactivation of electronically excited singlets ($^1\text{LCV}^*$). $^3\text{LCV}^*$ undergoes a very efficient electron transfer reaction with hexachloroxylene, *i.e.* 2,5-dichloro-1,4-bis(dichloromethyl)-benzene ($k = 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) yielding the pentachloroxylyl radical and Cl^- . The former species oxidizes $\text{LCV}^{\cdot+}$ to the blue-coloured crystal violet cation with $k = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. From these results it is concluded that the photo-oxidation of LCV in the absence of O_2 is readily accomplished by means of an electron acceptor which undergoes a dissociative electron transfer reaction with electronically excited LCV and is, in this reaction, converted into a strongly oxidizing radical.

1. Introduction

Triarylmethane dyes are well known for their convertibility from an almost colourless leuco form to an intensely coloured derivative [1]. The conversion is commonly achieved by conventional chemical oxidation. In certain cases, however, this process can be induced by irradiation with light as has been described in the literature [2]. The mechanism of the photo-oxidation of the leuco dyes is still a matter of controversy. The photo-oxidation of leuco crystal violet (LCV) to crystal violet (CV^+)



was the subject of a recent investigation by Hinzmann *et al.* [3]. The transient absorption spectrum (maxima at 490 and 560 nm) observed by these researchers [3] upon laser flash photolysis of LCV in degassed acetonitrile was ascribed to the radical cation LCV^{\ddagger} formed according to the reaction



Neither the transient existence of triplets of LCV nor attempts to detect them were dealt with. MacLachlan [4], however, provided evidence for the formation of triplets of leuco ethyl crystal violet (LECV). He detected the phosphorescence spectrum of LECV at -195°C ($\lambda_{\text{max}} = 420 \text{ nm}$) and observed the formation of naphthalene triplets at room temperature via their T-T absorption spectrum ($\lambda_{\text{max}} = 410 \text{ nm}$) upon irradiation of LECV in ethanol solution containing naphthalene. Naphthalene triplets were formed according to the reaction



MacLachlan also postulated a mechanism for the light-induced oxidation of LECV to the ethyl crystal violet cation (ECV^+) in the presence of carbon tetrachloride (CCl_4), according to which triplets transfer electrons to CCl_4 :



It was proposed [4] that $\text{CCl}_4^{\cdot -}$ is capable of oxidizing LECV^{\ddagger} to ECV^+ according to the reaction



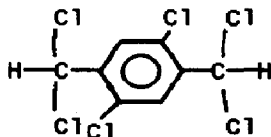
Conventional flash photolysis (halfwidth of flash, $4 \mu\text{s}$) in conjunction with optical absorption measurements revealed [4] that LECV^{\ddagger} possesses an absorption maximum at 480 nm. Nothing was reported in this work concerning the T-T absorption spectrum of the leuco dye.

Because of the discrepancies with respect to both the role of triplets and the assignment of transient absorptions, flash photolysis experiments in conjunction with measurements of electrical conductivity, optical absorption and emission were designed to obtain detailed insight into the triplet formation and photoionization of LCV.

2. Experimental details

2.1. Materials

LCV (Aldrich) was purified by filtration over Al_2O_3 (basic) using ethyl acetate as eluent. 2,5-Dichloro-1,4-bis(dichloromethyl)benzene (HCX)



was synthesized as described elsewhere [5]. It was recrystallized twice from ethanol solution.

Acetonitrile (J. T. Baker, HPLC Gradient Grade) was used without further purification.

The ground state absorption spectra of LCV and HCX are shown in Fig. 1.

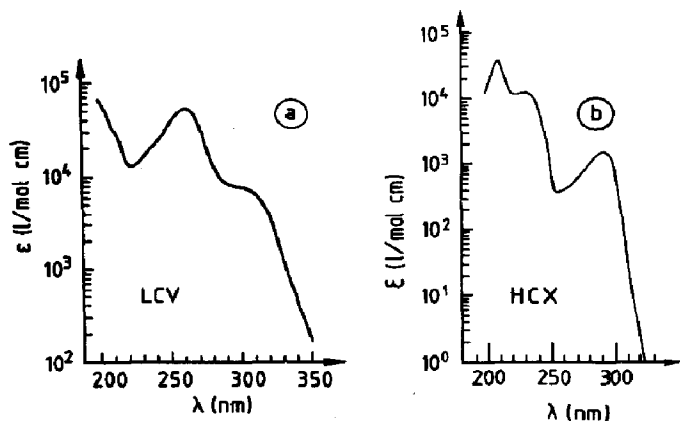


Fig. 1. Ground state absorption spectra of (a) LCV and (b) HCX, recorded in acetonitrile solution at room temperature.

2.2. Flash photolysis experiments

2.2.1. Irradiation of samples

Dilute solutions of LCV (and HCX) in acetonitrile were irradiated in rectangular quartz cells. Deoxygenation of the solution was effected by bubbling with argon. The irradiations were carried out in a front-face configuration either with 347 nm flashes (halfwidth, about 20 ns) from a ruby laser operated with a frequency doubler or with 265 nm flashes (halfwidth, about 15 ns) from an Nd-YAG system equipped with two frequency doublers. In both cases, the absorbed dose was about 1×10^{-5} einsteins l^{-1} per flash.

2.2.2. Detection methods

A conventional technique using a xenon lamp and a photomultiplier operated with five dynodes was used for absorption measurements. For

phosphorescence measurements an RCA 1P28 photomultiplier operated with the full dynode chain together with a gating system was used [6]. Photocurrent measurements were carried out with a quartz cell attached to a flow system. The cell was equipped with a pair of platinum electrodes that were connected to a d.c. set-up [7].

3. Results

In order to get detailed information on the photoreactions of LCV the following experiments were performed in acetonitrile solution.

3.1. Experiments in the absence of 2,5-dichloro-1,4-bis(dichloromethyl)-benzene

3.1.1. Phosphorescence measurements

A strong phosphorescence between 360 and 440 nm was generated during the flash, indicating the formation of triplets according to the reaction



A typical oscilloscope trace and a first-order plot illustrating the formation and decay of the phosphorescence are shown in Fig. 2. The phosphorescence lifetime was 3.5 μs . These results are comparable with those obtained for LECV [4]. In that case, a phosphorescence spectrum with a maximum at 420 nm was observed in ethanol at -195°C .

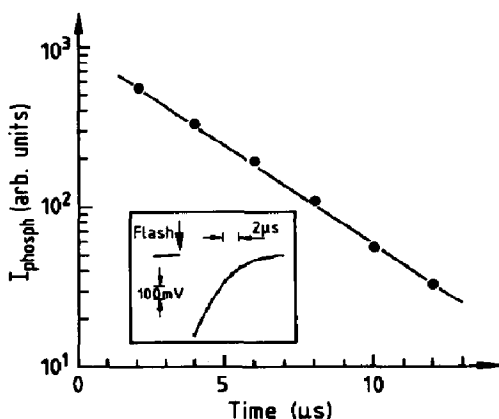


Fig. 2. Decay of the phosphorescence at $\lambda = 370$ nm of LCV (7×10^{-3} M) after irradiation with a 20 ns flash of 347 nm light in argon-saturated acetonitrile solution.

3.1.2. Optical absorption measurements

As can be seen from Fig. 3, at the end of the 20 ns flash a broad transient absorption spectrum with maxima at 400 and 470 nm was recorded in the wavelength region 300 - 650 nm. From the wavelength dependence of

the decay rate it was concluded that this spectrum was composed of spectra of different species: at $\lambda > 520$ nm, the absorption decayed in a single mode according to first-order kinetics with a lifetime $\tau = 3.5 \mu\text{s}$, while at lower wavelengths only a fraction of the initial absorption decayed at this rate. From Fig. 3 it can also be seen that a long-lived absorption spectrum with a maximum at about 400 nm remained after the short-lived portion had decayed. This also can be seen from the oscillograms presented in Fig. 4. From the fact that the short-lived absorption at $\lambda > 520$ nm decayed with the same lifetime as the phosphorescence (see above) this absorption is inferred to be due to triplets of LCV (T-T absorption).

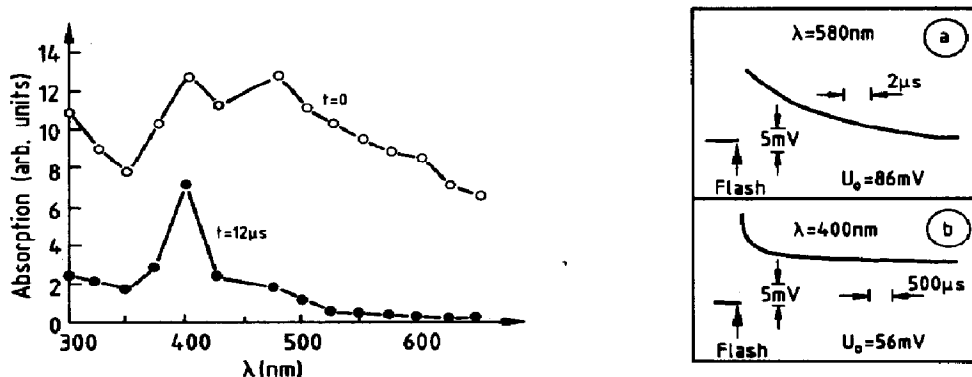


Fig. 3. Transient absorption spectra recorded after irradiation of an argon-saturated acetonitrile solution containing LCV (9×10^{-3} M) with a 20 ns flash of 347 nm light. The upper spectrum was recorded immediately at the end of the flash; the lower spectrum was recorded 12 μs after the flash.

Fig. 4. Oscilloscope traces illustrating the decay of the transient absorption in argon-saturated acetonitrile solution: (a) at 580 nm ($[\text{LCV}] = 7 \times 10^{-3}$ M); (b) at 400 nm ($[\text{LCV}] = 9 \times 10^{-3}$ M). ($\lambda_{\text{inc}} = 347$ nm.)

3.1.3. Electrical conductivity measurements

As demonstrated in Fig. 5, the electrical conductivity of the solution increased during the flash, indicating a rapid photoionization process. Since the triplet lifetime is at least two orders of magnitude longer than the time required for building up the photocurrent (less than 20 ns) it is concluded that the ionization occurs from the singlet state according to the reaction



This result confirms the postulate of Hinzmann *et al.* [3] who claimed that reaction (6) occurred in solution immediately after excitation of LCV with 265 nm light. However, it must be emphasized that the deactivation of singlet excited LCV molecules involves at least two parallel routes including triplet formation and photoionization. As can be seen from Fig. 5, the conductivity decreased according to two modes: the *fast mode*, with a half-life of less than 100 ns, probably reflects an interaction of the electrons with solvent molecules leading to a more stable negatively charged product, which

disappears via neutralization with the positive parent ion (the *slow mode*). The slow decrease followed second-order kinetics.

Relevant to the ionization of LCV from the excited singlet state is previous work with various triarylmethane compounds [8 - 10]. It was shown [10] that compounds such as malachite green leucocyanide undergo ionization quite efficiently from the first excited singlet state upon UV irradiation in polar solvents.

3.2. Experiments in the presence of 2,5-dichloro-1,4-bis(dichloromethyl)benzene

As was pointed out in Section 3.1, photoionization and triplet formation are important primary processes in the photolysis of LCV. In order to study the reactions of the primary species it seemed that it would be interesting to carry out experiments in the presence of an efficient electron scavenger which would stabilize the radical cations $\text{LCV}^{\dot{+}}$. For this purpose, HCX was selected.

The results are described in the following sections.

3.2.1. Optical absorption measurements

As can be seen from Fig. 6, a broad transient absorption spectrum similar to that shown in Fig. 3 was observed at the end of the flash when an acetonitrile solution containing both LCV and HCX was irradiated with 347 nm light. Since HCX does not absorb light at this wavelength (see Fig. 1), identical primary species derived from LCV should be formed in the absence or presence of HCX. However, when inspecting the decay of the transient absorption at different wavelengths, the interference of HCX with

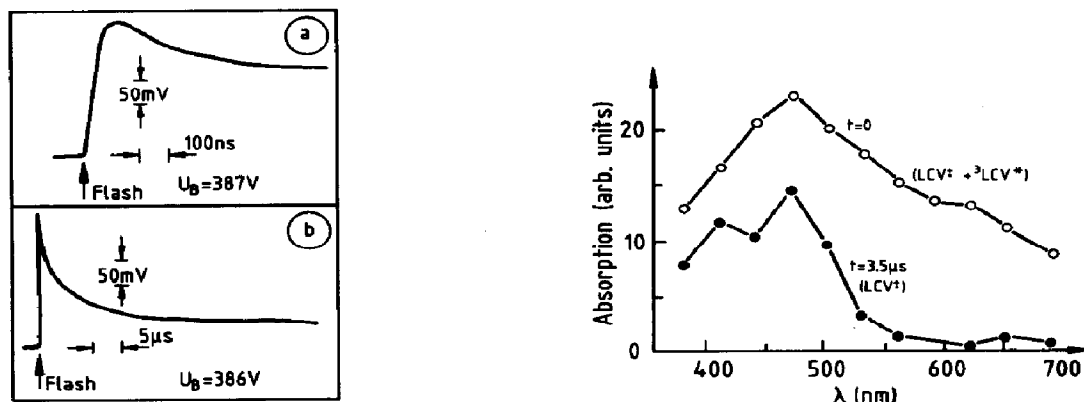


Fig. 5. Oscilloscope traces illustrating the formation and decay of the photocurrent in the photoionization of LCV (3.9×10^{-3} M) in acetonitrile solution by irradiation with a 20 ns flash of 347 nm light.

Fig. 6. Transient absorption spectra recorded after irradiation of an argon-saturated acetonitrile solution containing LCV (9×10^{-3} M) and HCX (2×10^{-5} M) with a 20 ns flash of 347 nm light. Upper spectrum, immediately at the end of the flash; lower spectrum, 3.5 μ s after the flash.

the photoreactions of the primary species of LCV became obvious. The short-lived absorption at wavelengths above 520 nm decayed significantly faster in the presence than in the absence of HCX, indicating that LCV triplets reacted with HCX. It turned out that the first-order rate constant of the decay of the absorption at 580 nm, for example, depended on the HCX concentration according to the equation

$$k_{\text{exp}} = k_0 + k_{\text{T+HCX}}[\text{HCX}] \quad (1)$$

where k_0 and $k_{\text{T+HCX}}$ denote the rate constant of triplet decay in the absence of HCX and the rate constant of the reaction of LCV triplets with HCX respectively. From these measurements $k_{\text{T+HCX}} = 1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ($\pm 10\%$) was obtained.

By the time the T-T absorption had almost totally decayed (about 4 μs), a rather long-lived absorption spectrum with a maximum at 470 nm was observed. While this spectrum, which is attributed to LCV^{\ddagger} , decayed a permanent absorption spectrum with a maximum at 585 nm was generated. This spectrum, which is shown in Fig. 7, is identical with the spectrum of CV^+ . In Fig. 8 typical oscilloscope traces, recorded at 470 and 600 nm, illustrating the simultaneous disappearance of LCV^{\ddagger} and the formation of CV^+ are shown. At both wavelengths, the rapid decay of triplets ($^3\text{LCV}^*$) is seen at the very beginning of the process. Whereas at 600 nm the absorption goes down almost to the zero level prior to the start of the formation of CV^+ , at 470 nm the absorption of the radical cations becomes obvious after the decay of the triplets. The decrease in the absorption of LCV^{\ddagger} is superimposed here by the increase in the absorption of CV^+ (which also absorbs to some extent at 470 nm). It is noteworthy that, in the absence of HCX,

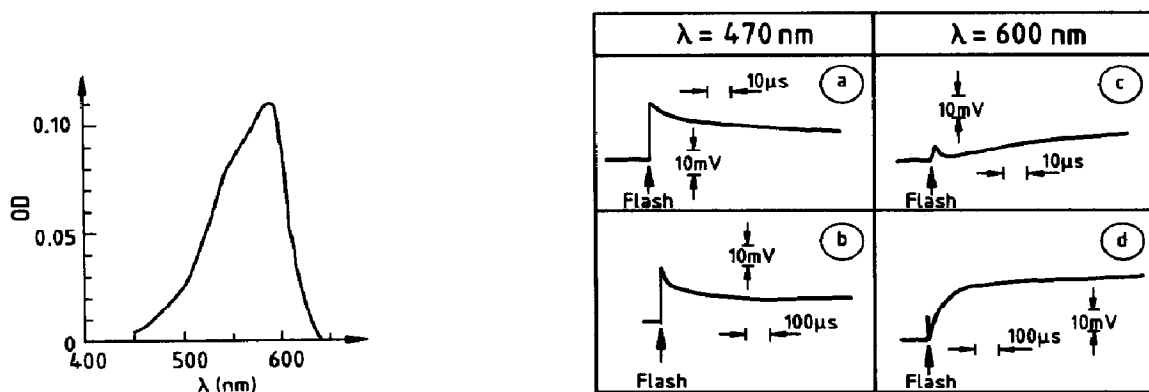


Fig. 7. Optical absorption spectrum of CV^+ formed after irradiation of an argon-saturated acetonitrile solution containing LCV ($4.5 \times 10^{-3} \text{ M}$) and HCX ($2 \times 10^{-5} \text{ M}$) (recorded about 10 min after irradiation with a 20 ns flash of 347 nm light).

Fig. 8. Oscilloscope traces depicting the decay of the optical absorption of LCV^{\ddagger} at 470 nm and the build-up of the absorption of CV^+ at 600 nm in argon-saturated acetonitrile solution ($[\text{LCV}] = 4.5 \times 10^{-3} \text{ M}$; $[\text{HCX}] = 2 \times 10^{-5} \text{ M}$; optical path length, 0.5 cm; $\lambda_{\text{inc}} = 347 \text{ nm}$).

a new permanent absorption band was not formed after the decay of the transient species formed initially.

A significant feature of these experiments is the fact that the formation of CV^+ followed second-order kinetics. This can be seen from Fig. 9. In Fig. 9(a), the increase in the optical density (OD) at 600 nm was plotted according to the equation

$$(\text{OD}_\infty - \text{OD}_t)^{-1} - \text{OD}_\infty^{-1} = \frac{k_2 t}{\epsilon d} \quad (\text{II})$$

where OD_t and OD_∞ denote the optical densities recorded at time t and a long time after the flash and $\text{OD} = \epsilon d[\text{CV}^+]$. ϵ denotes the extinction coefficient and d the optical path length. k_2 is the second-order rate constant. In Fig. 9(b), the first second-order half-life $\tau_{1/2}$ is plotted *versus* the reciprocal absorbed dose. If second-order kinetics were applicable, the following equation should hold:

$$\tau_{1/2} = (k_2[\text{CV}^+])^{-1} \quad (\text{III})$$

The expected proportionality between $\tau_{1/2}$ and the reciprocal absorbed dose D_{abs}^{-1} was found experimentally. Here it is anticipated that $[\text{CV}^+] \propto D_{\text{abs}}$ holds. With $\epsilon = 1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ and $d = 0.5 \text{ cm}$, $k_2 = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was obtained.

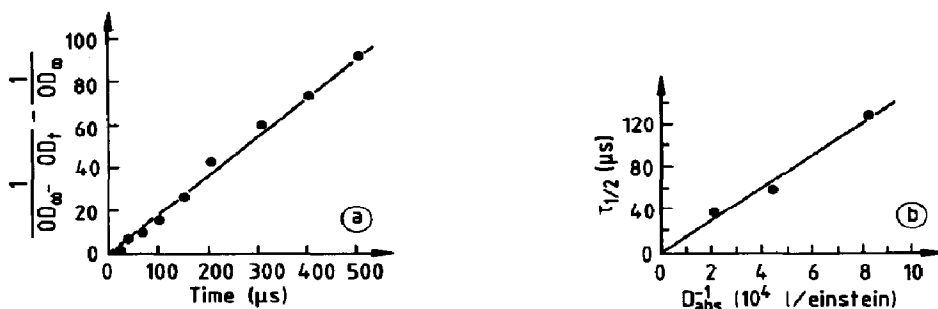


Fig. 9. Kinetic analysis of the formation of CV^+ on the basis of optical absorption measurements at $\lambda = 600 \text{ nm}$ ($[\text{LCV}] = 4.5 \times 10^{-3} \text{ M}$; $[\text{HCX}] = 2 \times 10^{-5} \text{ M}$; solvent, argon-saturated acetonitrile; optical path length, 1 cm; $\lambda_{\text{inc}} = 347 \text{ nm}$). (a) Typical second-order plot according to eqn. (II). (b) Plot of the first second-order half-life as a function of the reciprocal absorbed dose per flash.

3.2.2. Electrical conductivity measurements

In the presence of HCX the electrical conductivity increased in two modes as can be seen from Fig. 10. During the flash the conductivity increased in the same manner as in the absence of HCX. However, an additional increase in the photocurrent in the microsecond range was found when HCX was present. The rate of the slow mode corresponded to the rate of triplet decay measured by following the decay of the T-T absorption. Applying pseudo-first-order kinetics to the slow mode, the rate constant $k_{\text{T}+\text{HCX}} = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ($\pm 10\%$) was obtained. This value compares well

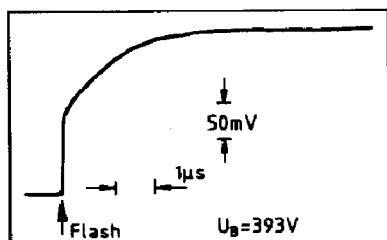
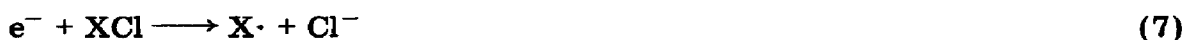


Fig. 10. Oscilloscope trace depicting the formation of the photocurrent in the photoionization of LCV in argon-saturated acetonitrile solution containing HCX ($[LCV] = 2.0 \times 10^{-5} \text{ M}$; $[HCX] = 4.5 \times 10^{-5} \text{ M}$; $\lambda_{inc} = 265 \text{ nm}$).

with $k_{T+HCX} = 1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ obtained by optical absorption measurements. In conclusion, HCX reacts with triplet excited LCV molecules via an electron transfer mechanism.

The initial very fast increase in the electrical conductivity again indicates photoionization of singlet excited molecules according to reaction (6). It is well known that halogenated hydrocarbons are prone to undergo dissociative electron capture processes, which can be described in the case of a chlorinated hydrocarbon XCl as follows:

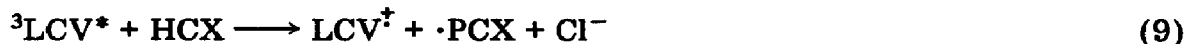


Electrons produced by photoionization are, therefore, assumed to undergo an analogous reaction with HCX:



($\cdot PCX$, pentachloroxylyl radical). The electron adduct is very short lived ($\tau < 10^{-10} \text{ s}$) and, as a consequence, it was undetectable in the present work, where only processes with $\tau > 20 \text{ ns}$ could be time resolved.

The additional increase in the photocurrent in the microsecond range reflects the formation of additional ions, *i.e.* LCV^{\ddagger} and Cl^- . Again, it is feasible to assume that an electron transfer from ${}^3LCV^*$ induces the very fast dissociation of HCX:



4. Discussion

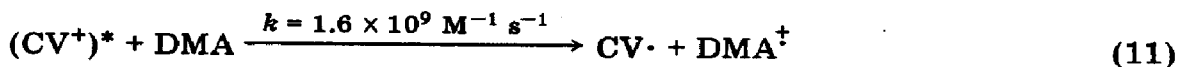
The most striking results of the present work are the following.

(i) Time-resolved electrical conductivity measurements manifested the one-photon ionization of LCV.

(ii) Time-resolved phosphorescence, optical absorption and electrical conductivity measurements revealed that LCV triplets, *i.e.* LCV molecules electronically excited to the lowest triplet state, reacted with HCX (a halogenated hydrocarbon) via an electron transfer mechanism.

On the basis of our present knowledge it is still difficult to formulate a mechanism that explains the photoreactions of LCV in the absence of

electron acceptors such as HCX or O₂. It was clearly shown that under these conditions radical cations (LCV⁺) and triplets (³LCV*) were formed. Moreover, a long-lived transient absorption with a maximum at about 400 nm was found. According to Hinzmann *et al.* [3] the triphenylmethyl-type radical CV·, which can exist in various mesomeric forms, has an absorption maximum at this wavelength. In the present work this was corroborated by exciting CV⁺ at 347 nm in the presence of dimethylaniline (DMA). Under these conditions excited CV⁺ ions reacted via an electron transfer with DMA to form CV·:



From the experimental data obtained so far in the absence of HCX it is difficult to explain how CV· is formed upon irradiation of LCV in acetonitrile. However, it is reasonable to assume that LCV molecules, highly vibrationally excited in the ground state (S₀), are formed in the back reaction of electrons with parent ions:



(LCV^{v*} denotes a vibrationally excited LCV molecule in the ground state (S₀.) If the vibrational energy exceeds the dissociation energy a hydrogen atom is split off:



There is evidence for this mechanism in that the absorption spectrum observed at the end of the flash already possessed a peak at about 400 nm (see Fig. 3). From this observation the occurrence, to some extent, of the neutralization reaction (12) immediately after the photoionization is inferred.

Another route for the formation of CV· might be the dissociation of a small fraction of LCV⁺ according to the equilibrium



as was previously suggested by Hinzmann *et al.* [3].

In the presence of an electron acceptor such as HCX, reaction (12) is prevented and a quite different situation is encountered. The results obtained in this case can be explained by means of the mechanism presented in Fig. 11: the deactivation of triplets can occur via different routes. In contrast to the mechanism claimed by Hinzmann *et al.* [3] both photoionization according to reaction (b-1) and intersystem crossing according to reaction (b-3) are important processes occurring with rate constants above 10⁸ s⁻¹. Thus, at the end of the 20 ns flash the optical absorption of both species, triplets and radical cations, was observed. Electrons formed by reaction (b-1) are effectively scavenged by HCX in a dissociative capture process leading to

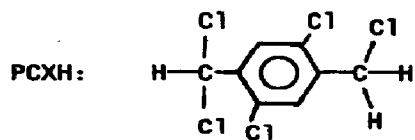
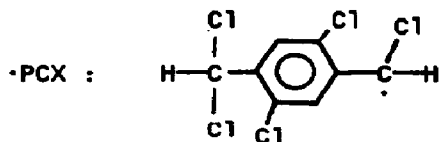
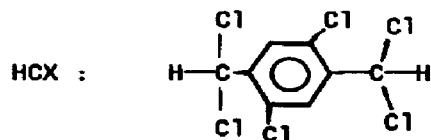
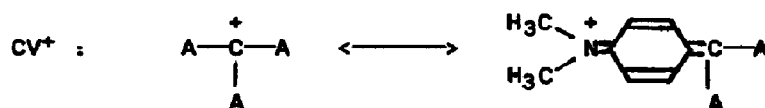
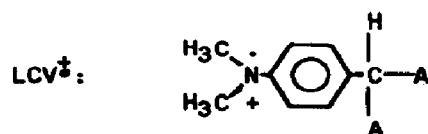
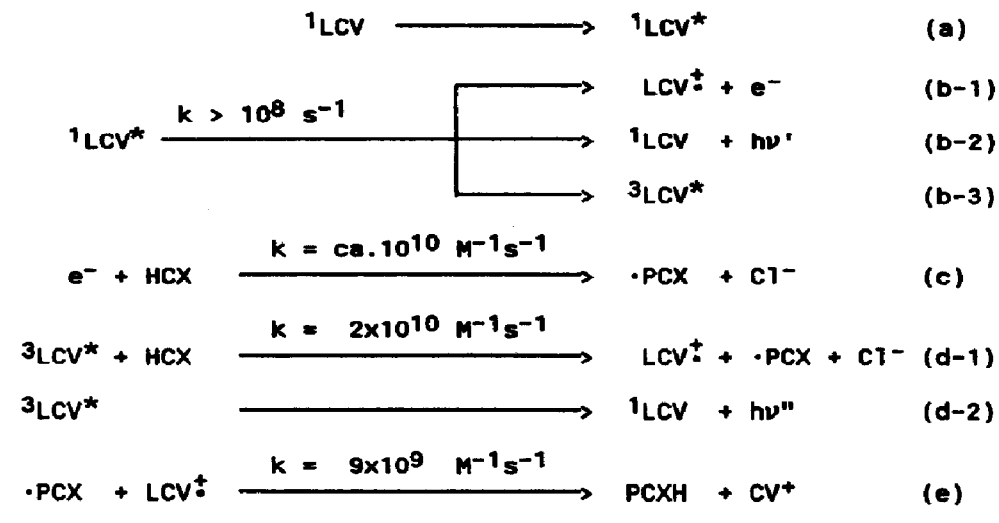


Fig. 11. Mechanism of the photo-oxidation of LCV to CV⁺ in the presence of HCX.

$\cdot\text{PCX}$ radicals and Cl^- ions according to reaction (c). This process, which occurred (as described above) during the flash, causes an increase in the yield of LCV^{\ddagger} radical cations, because it prevents back reactions of electrons with parent ions, *i.e.* with LCV^{\ddagger} . Apart from reaction (b-1), an additional source for LCV^{\ddagger} can be seen to be reaction (d-1), *i.e.* the electron transfer from triplets to HCX. In this way additional $\cdot\text{PCX}$ radicals are also formed. $\cdot\text{PCX}$ radicals are capable of effectively reacting with radical cations LCV^{\ddagger} (reaction (e)), yielding CV^+ . It is assumed that triplet deactivation routes, apart from reaction (d-1), are of minor importance. Therefore, the concentrations of LCV^{\ddagger} and $\cdot\text{PCX}$ should be approximately equal. In this case, the formation of CV^+ is described by the following second-order treatment:



$$[\cdot\text{PCX}] \approx [\text{LCV}^{\ddagger}] \equiv [\text{R}\cdot]$$

$$-\frac{d[\text{R}\cdot]}{dt} = +\frac{d[\text{CV}^+]}{dt} = k_2[\text{R}\cdot]^2$$

$$\frac{1}{[\text{R}\cdot]_t} - \frac{1}{[\text{R}\cdot]_0} = k_2 t$$

$$[\text{CV}^+]_t = [\text{R}\cdot]_0 - [\text{R}\cdot]_t$$

$$[\text{CV}^+]_{\infty} = [\text{R}\cdot]_0$$

$$[\text{R}\cdot]_t = [\text{CV}^+]_{\infty} - [\text{CV}^+]_t$$

$$\frac{1}{[\text{CV}^+]_{\infty} - [\text{CV}^+]_t} - \frac{1}{[\text{CV}^+]_{\infty}} = k_2 t$$

With $\text{OD} = \epsilon d[\text{CV}^+]$ eqn. (II) is obtained.

In conclusion, the oxidative power of HCX with respect to the photo-oxidation of LCV to CV^+ consists of its ability to react rapidly with $^3\text{LCV}^*$ triplets in an electron transfer process which induces the almost simultaneous formation of radicals capable of oxidizing LCV^{\ddagger} .

Acknowledgments

The authors are grateful to Dr. G. Beck for maintaining the flash photolysis set-ups and to Dr. J. Lilie who assisted in the computer evaluation of the data.

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