100. Laser Flash Photolysis of Chloranil in Solution

by **Elisabeth Guerry-Butty, Edwin Haselbach***, **Cécile Pasquier**[1]), and **Paul Suppan***
Institute of Physical Chemistry, University of Fribourg, Pérolles, CH-1700 Fribourg

and **David Phillips**
The Royal Institution of Great Britain, Albemarle St., London WI, U.K.

Dedicated to Prof. *Albert Eschenmoser* on the occasion of his 60th birthday

(8.III.85)

Chloranil (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione; C) in deoxygenated acetonitrile shows transient absorptions which are assigned to the radical anion $C^{\overline{\cdot}}$ and to the triplet $^3C^*$. The absorption due to $C^{\overline{\cdot}}$ rises 'instantly' during the 12 ns laser flash and then more gradually in a time of µs. This observation is explained as electron capture from neat acetonitrile by photoexcited C taking place from both its singlet and triplet states with rate constants estimated as 10^9 and 10^4 $s^{-1}M^{-1}$, respectively.

Introduction. – Chloranil (*2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione;* **C**) is a well-known electron acceptor, and it has been used successfully for the preparation of aromatic radical cations in solution [1]. In such cases, the electron transfer takes place between the excited triplet state ^{3}**C*** and the ground state of the aromatic molecule (*e.g.* naphthalene) in a polar solvent such as propionitrile. Acetonitrile (MeCN) was found to be unsuitable for such studies because of the formation of the radical anion $C^{\overline{\cdot}}$ in the absence of any aromatic donor, but the process of electron capture from a neat polar non-protic solvent by photoexcited **C** has not been investigated in detail so far. In this paper, we describe the behaviour of photoexcited **C** in several neat solvents to understand the process of its electron capture from the surrounding medium.

Results and Discussion. – 1. *Absorption Spectra of* **C** *in Various Solvents.* At the outset of this work it was found necessary to clear up some ambiguities [2] in the solvent dependence of the UV/VIS absorption spectra of **C**. *Fig. 1* and *Table 1* show the absorption spectra of **C** in the solvents cyclohexane (n_1), $CHCl_3$ (n_2), MeCN (n_3), EtOH (n_4), Et_2O (a_1), *p*-dioxan (a_2), THF (a_3), and benzene (a_4). In the solvents n_1–n_4, the first absorption band of **C** is always located around $\lambda_{max} \sim 370$ nm and is assigned to a π–π^* transition [2][2]). On the other hand, a remarkable spectral change occurs in the ether-type solvents a_1–a_3 and in benzene *(Fig. 1)*. This change from the 'normal' spectrum of **C** in solvents n_1–n_4 to the 'anomalous' spectrum in solvents a_1–a_4 obviously cannot be explained by a general dielectric solvent effect. It also does not result from a chemical

---

[1]) Present address: Institute of Organic Chemistry, University of Fribourg, Pérolles, CH-1700 Fribourg.

[2]) The n–π^* band which is clearly observed in the spectrum of *p*-benzoquinone in non-polar solvents [2] cannot be observed for **C**. It is probably blue-shifted by the effect of the four Cl-atoms and is hidden under the first more intense π–π^* band.

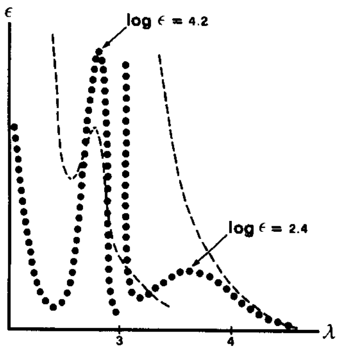

Fig. 1. *Absorption spectra of chloranil in MeCN* (● ● ●) *and in THF* (---) *at concentrations* 3×10^{-3} M (right) *and* 1.6×10^{-4} M (left). Abcissa: nm × 100.

reaction, since by evaporating the solvent from a solution of **C** in THF the normal absorption spectrum of **C** is recovered by redissolving the residue in MeCN. It is, therefore, probable that the latter spectral change is due to the formation of some ground-state complex between **C** and the ether-type solvents or benzene, solvents which exhibit good electron donor properties. In these solutions, therefore, the lowest-energy excited state presumably corresponds to a charge-transfer state involving **C** and the solvent rather than to a molecular state of **C**. Since our principal aim was to study the electron capture properties of *molecular* states of **C**, a clear distinction between the behaviour of excited **C** in solvents n_1–n_4 and solvents a_1–a_4 must be accomplished.

Table. *Absorption Spectral Data for Chloranil in Various Solvents* (wavelength in nm)

Solvent		$\lambda_{1\,max}$	log ε	$\lambda_{2\,max}$	log ε
n_1	Cyclohexane	370	2.4	290	4.2
n_2	$CHCl_3$	375	2.37	292	4.23
n_3	MeCN	367	2.4	288	4.2
n_4	EtOH	365 (sh)	2.3	288	3.9
a_1	Et_2O	–	–	284	4.2
a_2	1,4-dioxan	–	–	287	4.2
a_3	THF	–	–	283	4.12
a_4	benzene	330 (sh)	3.35	–	[a]

[a]) This region is inaccessible due to solvent absorption.

2. *Flash Photolysis of* **C** *in Various Solvents.* The transient absorption spectra of a 10^{-2} M deoxygenated solution of **C** in MeCN in the region of 400–700 nm are shown in *Fig. 2*; the excitation pulse is provided by a nitrogen-filled excimer laser (emission at 337 nm, pulse energy 3 mJ). The absorption in the 450-nm region is assigned to the radical anion C^{-} according to [1]; this assignment is further confirmed by transient photocurrent measurements, as discussed below. The absorption in the 510-nm region is due to the triplet $^3C^*$ [1]. From *Fig. 3*, we note that the absorption due to C^{-} rises 'instantly' during the life-time of the 12 ns flash; this steep rise is then followed by a gradual rise which nears completion after ~ 10 µs. The triplet absorption, on the other hand, decays with a half life of ~ 1 µs. The integrated triplet absorption decay matches the slow rise of the C^{-} absorption *(Fig. 4)*, suggesting that the latter is due to an electron transfer reaction of $^3C^*$ with MeCN. In an aerated solution of **C** in MeCN flashed under identical conditions,

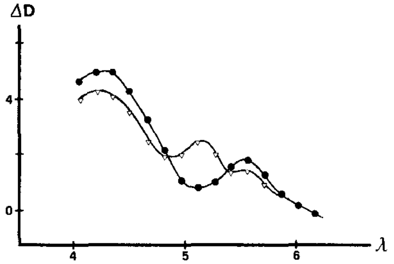

Fig. 2. *Transient absorption spectra of a deoxygenated solution of 10^{-2} M chloranil in MeCN.* ▽ : 20 ns; ● 10 µs. Abcissa: nm × 100; ordinate: D × 10^{-2}.

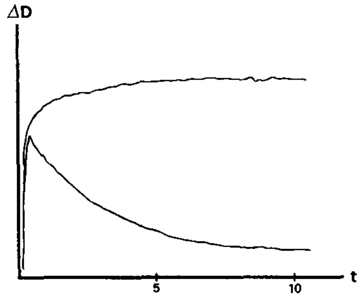

Fig. 3. *Transient absorptions of a deoxygenated solution of 10^{-2} M chloranil in MeCN at 436 and 509 nm.* Time t in µs.

only the fast rise of $C^{\bar{\cdot}}$ is observed near 430 nm, the triplet absorption being undetectable at 510 nm.

When the laser pulse intensity is attenuated by calibrated neutral-density filters, it is found that the transient optical densities throughout the 400–700 nm region follow linearly the filter transmission. These measurements were repeated with a frequency-tripled YAG laser (355 nm, 12 mJ) of higher energy and higher photon density (see *Experimental*) with 6.5 × 10^{-3} M solutions of **C**. In this case, a different result was obtained for the $C^{\bar{\cdot}}$ absorption: instead of a slow rise following the instant absorption increase mentioned above, the absorbance shows a fast *decay* immediately after the initial rise *(Fig. 5)*. The remarkable difference must be due to the higher concentration of radical ions produced under these conditions, since the fast decay can be reduced and eventually suppressed when the laser pulse intensity is reduced by means of filters *(Fig. 5)*.

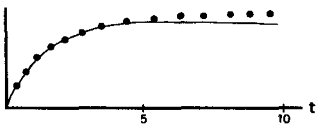

Fig. 4. *Integration of the triplet absorption* (●) *and rise of the 436-nm absorption attributed to* $C^{\bar{\cdot}}$. Time t in µs. Ordinate: arbitrary units.

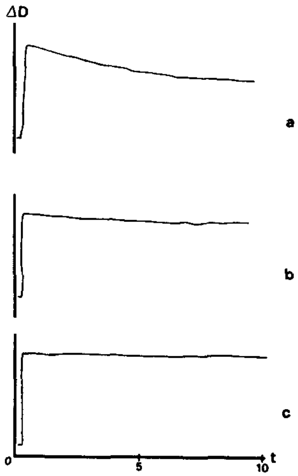

Fig. 5. *Transient absorption at 436 nm of a deoxygenated solution of chloranil in MeCN with YAG frequency-tripled laser excitation at various relative energies* (the initial absorptions are brought to the same scale). a: no filter; b: filter with D = 0.5; c: filter with D = 1. Time t in µs.

Apparently, with higher initial ion concentrations higher bimolecular rates of charge recombination occur[3]).

The optical density due to $C^{\cdot-}$ also follows linearly the laser pulse intensity after 10 µs, which suggests that it is formed in a monophotonic process.

The effect of **C** concentration was also investigated: the optical densities of the transient follow linearly the fraction of laser light absorbed by the sample. This suggests that $C^{\cdot-}$ arises from electron capture by excited **C** from MeCN and not through the bimolecular process $C^* + C \rightarrow (C_2)^* \rightarrow C^{\cdot-} + C^{+}$, which may be feasible in the solvent used.

In deoxygenated MeCN a transient photocurrent is observed when a 1.7×10^{-3} M solution of **C** is flashed with the YAG laser. The current rises 'instantly' and passes through a maximum after about 2 µs; it then decays to about half its maximum value and shows little variation after 10 µs (*Fig. 6*). When the laser intensity is reduced by means of filters, it is found that the transient photocurrent intensity varies linearly with the laser intensity (*Fig. 7*).

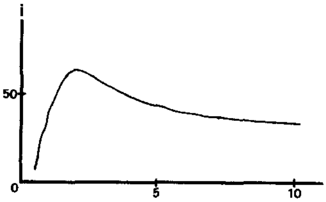

Fig. 6. *Transient photocurrent* (in µA) *in a deoxygenated solution of 1.7 × 10⁻³* M *chloranil in MeCN.* Time t in µs.

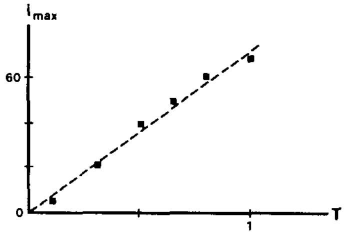

Fig. 7. *Peak transient photocurrent* i_{max} (in mA) *of* Fig. 6 *as a function of laser intensity.* T: filter transmission.

In $CHCl_3$, neither triplet absorption nor photocurrent could be observed but a relatively weak transient absorption in the wavelength region around 450 nm can be attributed to **C** semiquinone neutral radical (see [3]) resulting from H-abstraction by **C***. The lack of triplet absorption is probably due to its fast radiationless deactivation to the ground state resulting from the heavy-atom effect of the three Cl-atoms; no radical ions are found because of the low polarity of $CHCl_3$.

Concerning solvents of the a group, it is found that in deoxygenated benzene (8×10^{-4} M solution of **C**), only the absorption attributable to $^3C^*$ (510 nm) is observed with a decay time of ~ 1 µs. In deoxygenated THF (2×10^{-3} M solution of **C**), there is in addition a strong transient absorption in the region around 450 nm. This is in agreement with previous assignments of this transient as the semiquinone radical resulting from H-abstraction by $^3C^*$ from THF, a solvent of relatively low polarity but being a good H-donor [3]. No transient photocurrent could be observed in either THF or in benzene.

The above mentioned transient photocurrent measurements establish clearly the presence of charge carriers when **C** is flash-photolyzed in MeCN, but their absence in all other solvents investigated in this work. Both $^1C^*$ and $^3C^*$ appear to react with MeCN in a monophotonic process of electron capture by the solute from the solvent: $^1C^*$ or $^3C^* + (MeCN)_n \rightarrow C^{\cdot-} + (MeCN)_n^{+}$. In MeCN, therefore, the yield of $^3C^*$ must be lower

---

[3]) Overall chemical reactions of $C^{\cdot-}$ can be excluded, since there is no spectral change in the solution after prolonged irradiation.

than unity in view of the relatively fast electron capture by $^1C^*$ from the solvent. An estimate of the rates of these two processes can be as follows.

From the extinction coefficient $\varepsilon_{max} = 250$ of the first π–π^* transition of **C** a natural radiative lifetime of 400 ns can be estimated for its S_1 state. Since no fluorescence is detectable in any solvent, an upper limit of 10^{-4} can be given for its quantum yield in view of our experimental detection limit. The rate constant of radiationless deactivation of S_1 in absence of any quenching reaction (*e.g.* in benzene) is, therefore, at least 10^{10} s^{-1}, and this corresponds probably to the intersystem-crossing rate $S_1 \rightarrow T_1$ of this halogenated quinone. Furthermore, the fact that in MeCN both the instant rise of $C^{\overline{\cdot}}$ and the absorption by $^3C^*$ are observed suggests that the rate of intersystem crossing and of electron capture by S_1 must be similar. Since neat MeCN has a concentration of about 10M, the second-order rate constant for electron capture by S_1 from MeCN must be k_{et} ($^1C^*$) $\geqslant 10^9$ s^{-1}M^{-1}. Electron capture by T_1 is very much slower, as shown by the similar decays of the $^3C^*$ absorption in benzene ($k_d \approx 10^6$ s^{-1}) and in MeCN, where the lifetime of $^3C^*$ is according to our measurements only some 10% shorter. The pseudo-first-order rate constant for electron capture by T_1 is, therefore, $\sim 10^5$ s^{-1}, yielding a second-order rate constant k_{et} ($^3C^*$) $\approx 10^4$ s^{-1}M^{-1}.

MeCN would not be considered a good electron donor, given its gas-phase ionization potential of 12.21 eV [4]. The proposed electron capture process may, therefore, at first sight appear unlikely on energetic grounds. It is interesting, therefore, to discuss it on the basis of the *Rehm-Weller* equation [4]

$$\Delta E = E_{ox} + E_{red} - E^* - C \qquad (1)$$

E_{red} (**C**) is -0.02 V *vs.* SCE [1]. The excited state energies E^* are ~ 3 eV for $^1C^*$ (approximate onset of the first absorption band) and 2.13 eV for $^3C^*$ [1]. A difficult quantity to evaluate is E_{ox} for neat MeCN for which a lower bound value of 4 V *vs.* SCE can be assumed according to electrochemical data [5]. Alternatively, a value of 4.8 V for this quantity can be estimated from the gas-phase ionization potential of MeCN of 12.21 V [6], the solvation energy of ~ 3.1 eV of MeCN$^+$ in MeCN calculated from the *Born* equation $E_{solv} = -e^2/2r$ (r being the ion's cavity radius of 200 pm assuming spherical molecules and densest packing), and a SCE potential *vs.* vacuum of 4.26 V [7].

For the *Coulomb* term C, we use a slightly modified form of the one used in the original *Rehm-Weller* equation, since in our case the initially formed ion pair is not separated by solvent molecules, and the only screening effect results from the solute and solvent polarizabilities. Hence

$$C = -\frac{e^2}{n^2 d} \qquad (2)$$

where $n \cong 1.3$ is the mean refractive index of **C** ($n \cong 1.4$) and of MeCN ($n \cong 1.2$). With an ion separation of 300 pm, the *Coulomb* term comes then to ~ 2.2 eV. The overall energy balance ΔE for electron capture by $^1C^*$ is, therefore, ~ -1 eV, while it is ~ -0.1 eV for $^3C^*$, both processes being energetically feasible. It is interesting to note that the rate constants for electron transfer in an intramolecular donor/acceptor system are given as $k_{et} = 10^9$ s^{-1} for $\Delta E = -1$ eV and $k_{et} = 10^5$ s^{-1} for $\Delta E = 0$ [8], in general agreement with the findings in our 'pseudo-intramolecular' system **C*** and adjacent MeCN, forming some sort of supermolecule for the process in question. The ratio of 10^4 between the rate constants may accordingly result simply from the 1 eV energy difference between these two states. We note finally that both these processes would be predicted to be energetically unfeasible using the usual expression for the *Coulomb* term $C = -e^2/\varepsilon d$ given ε(MeCN) = 35.

Conclusion. – We conclude that both $^1C^*$ and $^3C^*$ are quenched by electron transfer from neat MeCN, a solvent usually not considered to be a good electron donor. Close contact between the partners is clearly an essential requirement for the process to be energetically feasible since only then does the *Coulomb* term *C* in *Eqn. 1* take a form which results in a sufficient stabilization of the initially formed ion pair. We further conclude that studies of the present kind may lead to equivalent insight into intrinsic (*i.e.* diffusionless) electron-transfer rates as recently investigated with intramolecular donor/acceptor systems [7].

Experimental. – Chloranil (*Fluka, puriss.*) was twice recrystallized from UV-grade benzene and then sublimed. MeCN (*Fluka*, UV-grade) was dried over P_2O_5 for 3 h prior to distillation. THF and $CHCl_3$ (both *Fluka*, UV-grade) were redistilled. All other solvents were *Fluka* UV-grade and were used without further purification.

For the flash-photolysis experiments a right-angle irradiation-detection set-up was used. The samples (~ 5 ml) were held in 10 × 20 mm pathlength silica cells fitted with a septum to allow passage of N_2 or Ar through the soln. Deoxygenation was performed by bubbling the inert gas for 10 to 15 min. The monitoring beam from a 100-W high-pressure Hg arc was monochromatized through a wavelength-graded interference filter (*Barr & Stroud* model *MS-1*) and collimated through a 2-mm diameter, 20-mm long section of the sample just behind the silica window. The light intensity was measured by a photomultiplier tube (*EMI 9785Q*) through 50 Ω, 200 Ω or 1 kΩ anode load resistors depending the time constant and amplification required. With the 50-Ω resistor the total instrumental response time is estimated to be below 2 ns (the fluorescence decay of *Rhodamine 6 G* with a lifetime of 3.9 ns can be observed by deconvolution of the laser pulse). The kinetic traces were displayed on a fast-storage oscilloscope (*Tektronix 7834*) and digitized by means of a vidicon digitizer described previously [9].

An excimer laser (*Oxford-Lasers* model *KX-1*) filled with 100 mbar of N_2 was used for irradiations at 337 nm, the pulse energy being 3 mJ with a pulse duration of about 12 ns. This beam was focussed on a 2 × 20 mm area of the sample, the concentration of which was such that over 50% of the 337-nm light was absorbed in a 2-mm path behind the window. The irradiated *observed* sample volume was, therefore, ~ 40 µl. The number of photons per pulse of 3 mJ at 337 nm being ~ 5×10^{15}, the number of excited molecules formed initially in the volume is of the order of 2×10^{15}. On the other hand, the number of ground-state molecules present in the sample is ~ 2.5×10^{19} for a 10^{-3} M soln. Thus, even in the least concentrated samples, only one molecule in 10^4 absorbs a photon. Under such conditions ground-state depletion is negligible and double-photon processes are unlikely.

For irradiations at 355 nm a YAG laser (*JK-Lasers* model *2000*) was used at the frequency-tripled wavelength (the fundamental and the frequency doubled beams were eliminated by a prism). The 355-nm pulse energy was measured as 12 mJ, the pulse duration being about 22 ns. The laser beam was of circular cross section (6 mm diameter) and the irradiated area of the sample was 28 mm^2. The density of excited molecules formed at 355 nm irradiation was *ca.* (12 mJ/28 mm^2)/(3 mJ/40 mm^2) ≅ 6 times larger than for irradiation at 337 nm, for solns. of similar optical densities.

Transient photoconductivity measurements were achieved with the same cells and the same irradiation arrangements, the septum being replaced by a *Teflon* stopper fitted with two Pt electrodes and with tubes to allow passage of an inert gas for deoxygenation. The electrode area was 3.6 mm^2, the inter-electrode distance was 5 mm. The DC voltage applied between the electrodes could be varied (power supply *Bertan 205 A*) but a constant voltage of 500 V was used. The current was converted to voltage by a resistor giving a time constant of 20 ns for this mode of detection. As noticed previously [1], a dark current passes through the sample when the 500-V potential difference is applied. This dark current increases slowly in time and it is, therefore, probable that under these conditions a slow electrolytic decomposition of the soln. takes place. Therefore, it is important to apply the 500-V for short periods only and to proceed with the measurements rapidly (*e.g.* in 10 s). In our experiments, the dark current was about 300 µA and the peak transient photocurrents about 70 µA.

The kinetic photocurrent curves were displayed on the *Tektronix* oscilloscope and digitized in the same manner as the optical traces. All experiments were performed at 20 ± 2°.

REFERENCES

[1] R. Gschwind, E. Haselbach, *Helv. Chim. Acta* **1979,** *62,* 941; H. D. Roth, M. L. M. Schilling, P. G. Gassman, J. L. Smith, *J. Am. Soc.* **1984,** *106,* 2711 and references therein.

[2] H. P. Trommsdorff, J. Kahane-Paillons, *Spectrochim. Acta* **1967,** *23A,* 1661; H. P. Trommsdorff, P. Sahg, J. Kahane-Paillons, *ibid.* **1970,** *26A,* 1135.

[3] K. Kawai, Y. Shirota, H. Tsubomura, H. Mikawa, *Bull. Chem. Soc. Jpn.* **1972,** *45,* 77.

[4] D. Rehm, A. Weller, *Z. Phys. Chem. (Wiesbaden)* **1970,** *69,* 183.

[5] M. R. Rifi, F. H. Covitz, 'Introduction to Organic Electrochemistry', Dekker, New York, 1974, p. 101.

[6] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, S. Iwata, 'Handbook of photoelectron spectra of fundamental organic molecules', Halsted Press, New York, 1981.

[7] A. Henglein, *Pure Appl. Chem.* **1984,** *56,* 1215.

[8] J. R. Miller, L. T. Calcaterra, G. L. Closs, *J. Am. Chem. Soc.* **1984,** *106*, 3047; P. Pasman, F. Rob and J. W. Verhoeven, *ibid.* **1982,** *104,* 5127.

[9] M. Gremaud, P.-H. Chassot, P. Suppan, *Chimia* **1983,** *37,* 379.