6. A Transient Ion Pair ($CCl_3^+ \cdot Cl^-$) in Irradiated Liquid CCl_4: Evidence for a 'Delayed' Geminate Ion Neutralisation

(Preliminary communication)

by **Rolf E. Bühler** and **Bendicht Hurni**[1])

Laboratory for Physical Chemistry, ETH-Zentrum, 8092 Zürich, Switzerland

Zum Andenken an Prof. Dr. *Heinrich Labhart*

(16.XI.77)

Summary

Detailed cation scavenger studies in pulse-irradiated pure, liquid CCl_4 reveal that the 500 nm absorption has both, neutral and cationic characteristics, and that CCl_4^+ must be the precursor. It is shown that all experimental results are compatible with the following ion neutralisation mechanism: $CCl_3^+ + Cl^- \rightarrow (CCl_3^+ \cdot Cl^-) \rightarrow CCl_4$.

The 500 nm band is assigned to the CCl_3^+-cation (free or complexed). Its neutralisation therefore does not occur on ion recombination, but is delayed by the life time of the ion pair: $\tau_{1/2}$ (ion pair) $= 33 \pm 3$ ns at $-22°C$ with activation energy of 10.9 ± 2.1 kJ/mol. Possible reasons for the ion pair stability are briefly discussed.

Introduction. – In non-polar systems all radiation initiated ions neutralize eventually each other. These processes are generally well known. They can be categorized into a very fast part of geminate ion recombination, typically with non-homogenous kinetics, and into a slower part of free ion neutralisation with homogeneous kinetics. On neutralisation these ions are known to either reform the original species in ground state, or in excited state, possibly followed by radical production, and if the ions react or dissociate before neutralisation other neutral fragments may be formed.

In this communication we report about a non-polar system, in which the original ions recombine in a first step to form ion pairs (possibly contact pairs), which then neutralize in a second slower step by a unimolecular decay process. The initial ion recombination corresponds to the actual geminate process; the first order decay of the ion pairs can be called a 'delayed neutralisation'. The optical absorptions of the transient ions involved disappear by first order kinetics related to the ion pair decay and not by the geminate, non-homogenous kinetics.

The actual ionic processes occuring in liquid carbon tetrachloride under ionising radiation were not well understood sofar [1], although much experimental

---

results from product analysis [2], from low temperature matrix studies with poly-crystalline CCl_4 [3] and from several pulse radiolysis studies in liquid CCl_4 [4–6] were published. Neither the assignment of the cationic absorption in the visible at about 500 nm, nor the interpretation of its two step decay mechanism were satisfactory. In this paper the main results and arguments will be presented which led to the assignment of the 500 nm band to the CCl_3^+-cation within an ion pair $(CCl_3^+ \cdot Cl^-)$ and to the understanding of the reaction mechanism involved[2]).

Experimental Part. – The technique of pulse radiolysis with the accelerator Febetron 705 *(Hewlett Packard)* for 2 MeV-electrons has been described elsewhere [8]. The sample temperature was held constant to within ± 0.2 K by a nitrogen-gas-cryostat. CCl_4 *(Fluka, spectrograde)* and Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane, Frigen-113 from *Hoechst)* were dried 3 times for 6 h over molecular sieve A3, A4 or A5 and fractionated through a 'Fischer-Spaltrohrkolonne'[3]). The final impurities were estimated to be < 10 ppm (GC.). A preirradiated CCl_4-sample followed by the above treatment gave identical results to the samples without preirradiation. The cation scavengers aniline, cyclohexane and cyclohexene *(Fluka, puriss.)* were purified by vacuum distillation; tetramethyltin *(Fluka, purum)* and biphenyl *(Fluka, puriss.)* were used as received.

Results. – The transient spectrum as measured at different times after a 50 ns pulse in CCl_4 of $-22°$ is shown in *Figure 1*. The dose is 20 ± 1 krad and the temperature just above the m.p. The band maximum ($\lambda_{max} = 500 \pm 10$ nm) and the band width (FWHM = 160 nm) do correspond to the band as measured by *Cooper & Thomas* [4] at room temperature. The band however does not show any fine structure. The absorption from 400 to 600 nm decays uniformly and is not affected in band position and shape by added scavengers, except for the overlap of possible scavenger cation absorption. The 500 nm band as recorded in pure CCl_4 decays in two steps: a fast process of 1st order kinetics *(Fig. 2)* covering about 95% of the total decay, followed by a slow process of 2nd order. From the present measurements at $-22°$ and the published rate at room temperature [4] the activation energy of the first order process is estimated to be 10.9 ± 2.1 kJ/mol $(2.6 \pm 0.5$ kcal/mol) (see *Table 1*).

Table 1. *The first order half life of the absorption at 500 nm in the CCl_4-Freon-113-system*

Composition		$\tau_{1/2}$ (ns) at 500 nm		
CCl_4	Freon-113	$-34°$	$-22°$	$+23°$
pure	–	–	33 ± 3	15 ± 2 [4]
solvent	10^{-1}M	–	33 ± 3	–
90%	10%	–	33 ± 3	–
50%	50%	–	–	23 ± 2
10%	90%	–	47 ± 5	–
5×10^{-1}M	solvent	48 ± 5	–	–
10^{-1}M	solvent	–	–	20 ± 5
5×10^{-2}M	solvent	52 ± 8	–	–
–	pure	2nd order[a])	–	2nd order[a])

[a]) The absorption at 500 nm is due to the Freon-anion ($\lambda_{max} = 440$ nm) [7]. The corresponding Freon-cation ($\lambda_{max} = 380$ nm) [7] shows an identical decay, as expected for a neutralisation process.

[2]) Full details will be published later. See also [7].
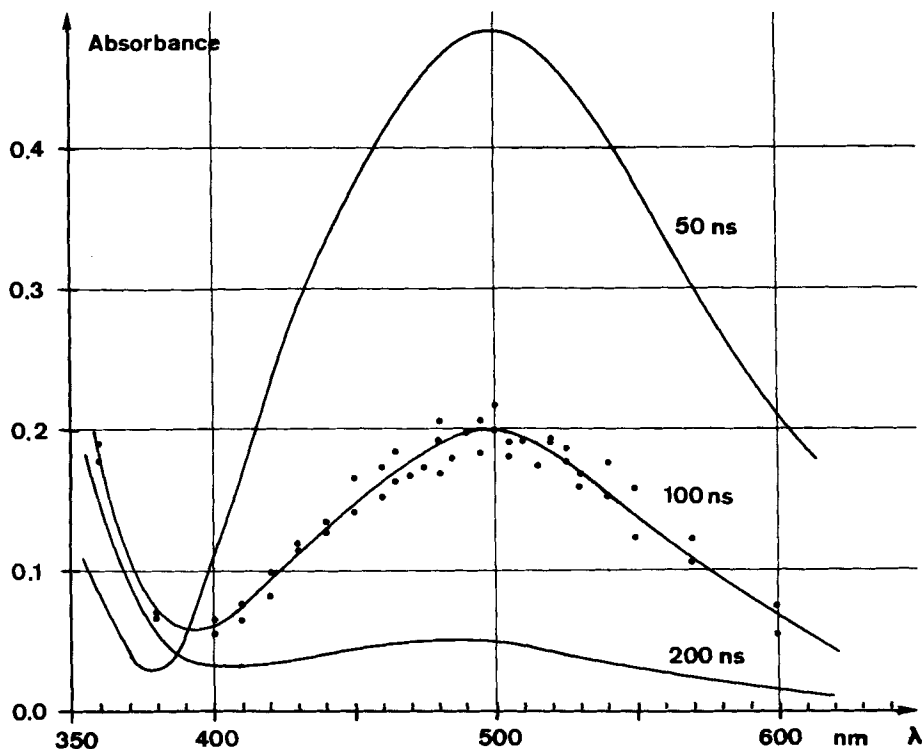[3]) *Fischer,* Labor- und Verfahrenstechnik, Bonn–Bad Godesberg D.

Fig. 1. *Transient spectra in irradiated pure CCl_4 at* $-22°$ *for 50 ns, 100 ns and 200 ns delay after start of irradiation pulse* (50 ns corresponds about to pulse end). For clarity experimental points are given for 100 ns delay only. Dose $= 20 \pm 1$ krad

Already *Cooper & Thomas* [4] have shown that this visible band responds to cation scavengers. Our extension on these scavenger studies produces the following results (compare with *Table 2*).

1) All cation-scavengers used having an ionization potential I_p(scav) smaller than $I_p (CCl_4) = 11.47$ eV [9] (or 11.28 eV [10]) do reduce the pulse-end absorbance of the visible band, however, have no effect on the life time *(Table 2)*. This is also true for the scavengers tetramethyltin ($I_p = 8.25$ eV), aniline ($I_p = 7.7$ eV) and N,N-dimethylaniline ($I_p = 7.14$ eV) which all have an ionisation potential smaller than the one of CCl_3 radicals ($I_p (CCl_3) = 8.78$ eV). This is particularly important in connection with the expected decay of the CCl_4^+ cation into CCl_3^+. For the scavengers aniline, N,N-dimethylaniline and cyclohexene the corresponding absorptions of the scavenger cations are observed.

2) Freon-113 (CCl_2F-CF_2Cl) with $I_p = 11.99$ eV $> I_p (CCl_4)$ does not show any effect on the visible band of the CCl_4-system as expected. However in a solution of 0.1M CCl_4 in Freon-113 the 500 nm band appears in competition to the Freon-113-cation band at 380 nm [7], indicating charge transfer from the Freon cation to the CCl_4.

Table 2. *Results of scavenger studies*

Scavenger (I_p from [9])	Conc.	Decay rate constant (s^{-1}) measured at 500 nm	Maximum absorbance at 500 nm (pulse end)
–[a])	–	$(2.1 \pm 0.3) \times 10^7$	0.145 ± 0.015
Cyclohexane ($I_p = 9.88$ eV)[c])	10^{-2} M	$(2.5 \pm 0.15) \times 10^7$	0.100 ± 0.010
	3×10^{-2} M	$(2.3 \pm 0.1) \times 10^7$	0.093 ± 0.010
	10^{-1} M	$(2.7 \pm 0.3) \times 10^7$	0.073 ± 0.014
Cyclohexene ($I_p = 8.94$ eV)[c])	10^{-2} M	$(2.5 \pm 0.2) \times 10^7$	0.109 ± 0.010
$Sn(CH_3)_4$ ($I_p = 8.25$ eV)[b])	10^{-2} M	$(2.5 \pm 0.2) \times 10^7$	0.105 ± 0.017
	3×10^{-2} M	$(2.6 \pm 0.25) \times 10^7$	0.088 ± 0.008
	10^{-1} M	$(2.0 \pm 0.2) \times 10^7$	0.072 ± 0.005
Aniline ($I_p = 7.70$ eV)[c])	10^{-3} M	$(2.3 \pm 0.2) \times 10^7$	0.127 ± 0.012
	10^{-2} M	$(2.1 \pm 0.25) \times 10^7$	0.033 ± 0.002

[a]) CCl_4 as pure solvent ($I_p(CCl_4) = 11.47$ eV[c])).   [c]) Photoionization data.
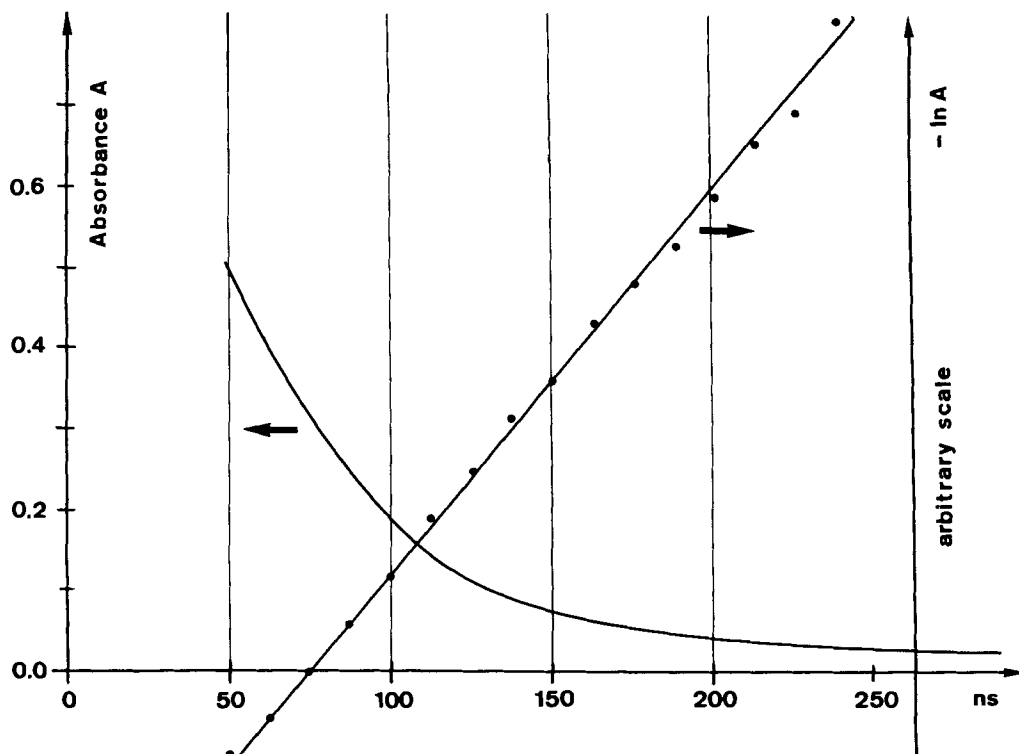[b]) Electron impact data.

Fig. 2. *Rate curve and 1st order plot for the decay of the 500 nm absorption in pure CCl_4 at $-22°$*. The time given is from start of irradiation pulse

3) In pure Freon-113 at $-34°$ the Freon cation disappears by a 2nd order process as would be expected for a free ion neutralisation. With 0.1 M CCl_4, however, the 500 nm band which then competes with $Freon^+$ decays again by 1st order, just as in the CCl_4 solvent *(Table 1)*.

Discussion. – From our results three principal conclusions can be drawn:

1) *The CCl_4^+-cation must be precursor to the 500 nm-species.* This is shown by the behaviour of the band relative to the cation scavengers, particularly by the inability to change its lifetime, and by the effect on the maximum absorbance *(Table 2)*. This generally conforms with the idea of a highly unstable, very short lived CCl_4^+ cation[4]).

2) *The 500 nm-species behaves like a cation.* The absorption decays in two steps of different kinetics: a very fast major part corresponding to the idea of geminate ion recombination and a slow part of 2nd order corresponding to the free ion recombination. An initial yield for the slow part (G_{slow}) can be estimated from the competition studies with aniline as the cation scavenger. By assuming that the absorption coefficient ε (aniline$^+$) = 2000 M^{-1} cm^{-1} (420 nm) [11] from aqueous solutions can also be used in CCl_4 solutions, one finds $G_{slow} = 0.10$. This corresponds quite well to the known free ion yield $G_{fi} = 0.096$ [12]. Similarly we find the maximum yield (from the 500 nm absorption) at the end of our 50 ns pulse in CCl_4 at $-22°$ to be $G_{max} = 2.0$. For the results by *Cooper & Thomas* [4] in CCl_4 at room temperature one derives in the same way a $G_{max} = 4.8$ at the end of their 12 ns pulse. These G_{max}-values correspond quite well to the expected total ion yields for such experimental conditions. Since it can be expected that the negative entity is Cl^-, from the dissociative electron attachment to CCl_4, the 500 nm absorption cannot be due to an anion.

3) *The 500 nm-species behaves like being neutral.* No one of all cation scavengers with ionisation potentials ranging from 7.14 eV to 11.99 eV were able to affect the 500 nm-decay rate; the only effect was competition with the precursor. The fast part of the 500 nm decay, which was discussed in the previous paragraph as being due to the geminate ion recombination should follow some function of erfc $\sqrt{\lambda t}$ (λ being a parameter) (see *e.g.* [13]). There is no way of adjusting such a function to the experimental decay curve, which actually follows good 1st order kinetics. Also, a crude estimate about the rate of recombination of such geminate ions in CCl_4 calls for a much faster process than was detected.

All three conclusions ask for a cation within a neutral species, which decays dominantly by 1st order and has CCl_4^+ as its precursor. The following mechanism is able to explain these facts:

There are two fast initial processes:

---

[4]) For a very long time the CCl_4^+ cation was considered as purely dissociative. Today there is a tendency to assume a shallow minimum for (CCl_3^+-Cl), however of unknown depth [10]. Our scavenger experiments indicate a much longer life time of CCl_4^+ than hitherto assumed.

$$CCl_4^+ \longrightarrow CCl_3^+ + Cl \tag{1}$$

$$e + CCl_4 \longrightarrow CCl_3 + Cl^- \tag{2}$$

They are succeeded by the following mechanism of ion recombination:

$$CCl_3^+ + Cl^- \xrightarrow{\ (3)\ } (CCl_3^+ \cdot Cl^-) \xrightarrow{\ (4)\ } CCl_4$$

The 500 nm absorption is due to the CCl_3^+ cation, either as a free ion or as partner within the ion pair. In the latter case it behaves like a neutral species relative to cation scavengers. The initially formed CCl_4^+ cation decays faster than our experimental time resolution but slow enough, so that the cation scavengers are able to interfere with that decay[4]).

During the fast geminate ion recombination, reaction (3) is also faster than our experimental time resolution. The observed 1st order decay corresponds to reaction (4) with $k_4 = (2.1 \pm 0.3) \times 10^7 s^{-1}$ at $-22°$. Reaction (4) is the rate determining step. During the slow free ion recombination reaction (3) is slower than the unimolecular decay of the ion pair (reaction (3) being rate determining). The observed slow 2nd order decay of the 500 nm absorption therefore corresponds to the free ion recombination (3).

There is also the possibility of an alternative ion-mechanism:

$$CCl_4^+ + Cl^- \xrightarrow{\ (3')\ } Cl + (CCl_3^+ \cdot Cl^-) \xrightarrow{\ (4')\ } Cl + CCl_4$$

Such a process can be important if the life time of the CCl_4^+-cation actually turns out to be much longer than assumed sofar[4]). Both mechanisms (reactions (3) and (4) or (3') and (4')) are based on the formation of an ion pair ($CCl_3^+ \cdot Cl^-$). There must be a reason for the stability of such ion pairs. Only brief mentioning of two types of possible arguments will follow here:

1) CCl_3^+ is a planar cation [14]. On neutralisation with Cl^- the structure has to change to tetraedric symmetry. The experimental activation energy for the ion pair disappearance might have something to do with this structural change. Further support comes from the decay kinetics as found in the CCl_4-Freon-113 system: In all cases where a CCl_3^+ cation neutralizes (with Cl^- or Freon-113$^-$) the decay kinetics is of 1st order. In the systems where the Freon cations neutralize (with Cl^- or Freon$^-$) the decay kinetics is of 2nd order. This might be related to the structure of the Freon cation, which, in contrast to the CCl_3^+, is expected to be close to the parent molecule, therefore indicating lack of ion pair stability.

2) CCl_4 may yield some solvation either due to its polarizability or due to its capability to act as electron acceptor. Complex formation of aromatic hydrocarbons with CCl_4 is well known (see e.g. [15]). In particular the ion-molecule complex ($I^- \cdot CCl_4$) as studied by Symons et al. [16] has strong relations to the solvation of Cl^- in the ion pair.

Further experiments are in progress. A detailed report will be published later.

REFERENCES

[1] *R. E. Bühler*, 'Radiation Chemistry of the Carbon-Halogen Bond', in S. Patai (editor), Chemistry of the Carbon-Halogen Bond (Part 2), J. Wiley, 1973.

[2] *N. E. Bibler*, J. phys. Chemistry *75*, 24 (1971), and many earlier papers cited therein. Also our own unpublished data.

[3] Summary of the matrix studies by *W. H. Hamill*, in E.T. Kaiser, L. Kevan (editors), 'Radical Anions', Interscience 1968, chapter 9.

[4] *R. Cooper & J. K. Thomas*, Adv. chem. Ser. *82*, 351 (1968).

[5] *R. E. Bühler*, Helv. *51*, 1558 (1968).

[6] *H. D. Burrows, D. Greatorex & T. J. Kemp*, J. phys. Chemistry *76*, 20 (1972).

[7] *B. Hurni & R. E. Bühler*, Chimia *29*, 526 (1975); (abstract only) and *B. Hurni*, Thesis ETH-Zürich No. 5611, 1975.

[8] *B. Hurni, U. Brühlmann & R. E. Bühler*, Radiat. phys. Chemistry *7*, 499 (1975).

[9] *F. H. Field & J. L. Franklin*, 'Electron Impact Phenomena', Acad. Press, 1970, revised edition.

[10] *A. S. Werner, B. P. Tsai & T. Baer*, J. chem. Physics *60*, 3650 (1974).

[11] *E. J. Land & G. Porter*, Trans. Farad. Soc. *59*, 2027 (1963); and *A. Wigger, W. Grünbein, A. Henglein & E. J. Land*, Z. Naturforsch. *24b*, 1262 (1969).

[12] *W. F. Schmidt & A. O. Allen*, J. chem. Physics *52*, 2345 (1970).

[13] *S. J. Rzad, P. P. Infelta, J. M. Warman & R. H. Schuler*, J. chem. Physics *52*, 3971 (1970).

[14] *M. E. Jacox & D. E. Milligan*, J. chem. Physics *54*, 3935 (1971).

[15] *R. Foster*, 'Organic Charge Transfer Complexes', Acad. Press, 1969, p. 408.

[16] *M. J. Blandamer, T. E. Gough & M. C. R. Symons*, Trans. Farad. Soc. *62*, 301 (1966).