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Increased yields of radical cations by arene addition to irradiated 1,2-dichloroethane

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Abstract

Pulse radiolysis in chlorinated hydrocarbon liquids such as 1,2-dichloroethane is a versatile and effective method for the generation of solute radical cations. The addition of a large concentration of toluene or benzene to solutions of 1,2-dichloroethane is found to increase the yield of solute radical cations ($G = 0.68$ molecules $100 \, \text{eV}^{-1}$ in 1,2-dichloroethane (J. Phys. Chem. 83(15) (1979) 1944) by a factor of 2.5. The increased yield is found for solutes which have a potential of $\sim 1.1 \, \text{V}$ (vs. SCE) or below for the $S^{+\bullet}/S$ couple and is due to reaction of the chlorine atom:toluene (π-Cl$^\bullet$) complex with the solute. A similar species forms with benzene. π-Cl$^\bullet$ is formed with a yield of $G = 3.0$, and arises principally as a result of geminate recombination of ions. It has an absorption in the visible with λ_{max} 460 nm, $\varepsilon_{max} = 1800 \, \text{M}^{-1} \text{cm}^{-1}$ and decays with an observed first-order rate constant $k = 1.12 \times 10^6 \, \text{s}^{-1}$. The rate of reaction of the π-Cl$^\bullet$ with added solutes ranges from 2.5 to $5 \times 10^9 \, \text{M}^{-1} \text{s}^{-1}$. The other oxidant present in the 1,2-dichloroethane/toluene solutions is identified as the toluene cation dimer. This is formed from the 1,2-dichloroethane radical cation with bimolecular rate constant $k = 1.35 \times 10^{10} \, \text{M}^{-1} \text{s}^{-1}$ with a radiation chemical yield $G = 0.5$. The rate of reaction of this species with the added solutes is diffusion controlled, $k = 1-2 \times 10^{10} \, \text{M}^{-1} \text{s}^{-1}$.
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1. Introduction

For decades it has been known that pulse radiolysis in chlorinated hydrocarbon liquids can be used to generate radical cations of organic molecules rapidly and efficiently. The cations are generated cleanly in that other products are produced from the solutes only in minor amounts. In solvents such as 1,2-dichloroethane (DCE), radical cations are produced with a yield of $G = 0.68$ molecules $100 \, \text{eV}^{-1}$ (Wang et al., 1979). DCE has frequently been used to produce radical cations and its radiation chemistry is partly understood (Arai et al., 1969; Shank and Dorfman, 1970; Sumiyoshi et al., 1988; Wang et al., 1979).

Here we report that in DCE containing large concentrations of an aromatic solvent (either toluene or benzene), the yield of homogeneously distributed solute cation is increased compared to the yield in neat DCE. The increase in yield is due to the presence of an additional oxidizing species in solution identified as a complex of Cl atom with toluene (or benzene). While oxidation of solutes by solvent cations is nearly diffusion-controlled, oxidation by this second species is slower, resulting in a biphasic growth of solute cations. The species formed in the DCE/toluene and the DCE/benzene systems upon radiolysis are identified and their reactivity and yield investigated.

2. Experimental

1,2-Dichloroethane (Aldrich, HPLC grade) and CCl$_4$ (Mallinckrodt, AR grade) were dried over type 4A

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molecular sieves prior to use. Anhydrous toluene (Aldrich, 99.8%), cyclohexane (Aldrich, HPLC grade) and benzene (Mallinckrodt, AR grade) were used as received. Anthracene, 9,10-dimethylanthracene, 9-methylanthracene, perylene, pyrene, terthiophene and triethylamine were purchased from Aldrich in the highest grade available and were used as received. Biphenyl (Aldrich) was recrystallized three times from ethanol and quaterthiophene (Aldrich) was recrystallized once from toluene prior to use. Bithiophene (Aldrich, 97%), tetramethylphenylenediamine (Aldrich) and triphenylamine (J. T. Baker Chemical Co.) were sublimed prior to use.

This work was carried out at the Brookhaven National Laboratory Laser-Electron Accelerator Facility (LEAF) (Wishart, 2001). Transient absorption was measured using fast detectors and a transient digitizer for times longer than 2 ns (Miller et al., 1998), and with a pulse–probe method, analogous to the laser pump–probe technique, for times to 10 ns. The nanosecond measurements utilized 20 mm quartz cells, a 75 W xenon arc lamp pulsed to a few hundred times its normal intensity and wavelength selection with 40 or 10 nm interference filters. Transient absorption signals were detected with either an FND 100Q silicon ($\leqslant 1000$ nm) diode or a GAP-500L InGaAs (1100–1700 nm) diode and digitized with a Tektronix TDS-680B oscilloscope. Absorption spectra were corrected for the secondary response distortion from the NIR detector (Cline et al., 2002) by normalization of the signal at time t to the signal from the FND100Q silicon diode at the same time.

In pulse-probe measurements, the transient absorbance is determined at a single time delay relative to each accelerator pulse, requiring a few thousand pulses to obtain a kinetic trace. About 50 ml of solution is flowed through a 10 mm cell. The pulsed laser detection system for the picosecond measurements will be described in detail elsewhere. The transmission/time data were analyzed with IGOR Pro software (Wavemetrics). Reaction rate constants were determined using a non-linear least-squares fitting procedure described previously (Miller et al., 1998). Uncertainties for rate constants are quoted as $\pm 2\sigma$ of the rate parameter of the fit. Where not stated, uncertainties are 15%.

The total dose per pulse was determined before each series of experiments by measuring the transient absorption of the hydrated electron in water using $\varepsilon(700\,\text{nm}, e_{aq}^-) = 18500\,\text{M}^{-1}\,\text{cm}^{-1}$ and a yield $G(e_{aq}^-) = 2.97$ molecules $100\,\text{eV}^{-1}$ at $t = 10$ ns. Doses were corrected for the difference in electron density of the organic solvents used compared to that of water. For picosecond data at 1000 nm the radiation dose was determined using the average value for the absorption of the electron in D_2O and in H_2O. For these experiments, the values G (e_{aq}^-, H_2O, 100 ps) = 4.0 (Bartels et al.,

2000), G (e_{aq}^-, D_2O, 100 ps) = 4.4 (Bartels et al., 2000; Singh et al., 1977) and ε (700 nm, e_{aq}^-, D_2O) = 19100 $\text{M}^{-1}\,\text{cm}^{-1}$ (Hart and Anbar, 1970; Singh et al., 1977) were used to calculate the dose. Radiolytic doses of 5–25 Gy were employed. Samples were prepared immediately prior to use. For nanosecond measurements, dissolved oxygen was removed by purging with argon gas for at least 10 min prior to use, then the cells were sealed with septa and parafilm. Unless otherwise indicated, the concentration of toluene used in the binary solutions was 1.57 M and the concentration of benzene was 1.86 M. During irradiation, samples were exposed to as little UV light as possible (via the use of UV cutoff filters) to avoid photodecomposition, no evidence of this occurring was found within the time frames monitored. The measurements were carried out at 21°C.

3. Results and discussion

3.1. Cation formation and increased yield

Fig. 1 shows the absorption spectrum obtained upon radiolysis of millimolar quantities of terthiophene in DCE and in DCE/toluene. The product of radiolysis is identified as the terthiophene radical cation in both solvent systems, known to have absorption maxima at 550 and 850 nm (Emmi et al., 1999b; Wintgens et al., 1994). The inset shows the growth of the terthiophene cation in DCE and a substantially larger growth in DCE/toluene. Similar increases in cation yields are found for a number of solutes, but not all (see Table 1). Identical effects to those found in DCE/toluene solu-
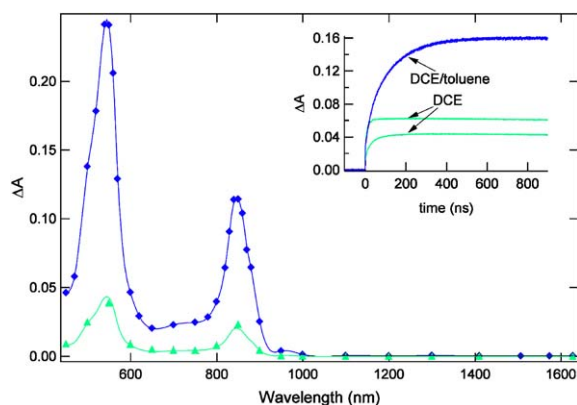

Fig. 1. Spectrum of terthiophene radical cation obtained upon radiolysis of a solution of (a) (▲) 9.2×10^{-4} M 3 T in DCE (D = 10 Gy) and (b) (♦) a solution containing 2.8×10^{-3} M 3 T and 1.57 M toluene in DCE (D = 11 Gy). Inset: Growth of the terthiophene radical cation at 850 nm, conditions from lower trace to upper: 9.7×10^{-4} M 3 T in DCE, 2.8×10^{-3} M 3 T in DCE, 2.8×10^{-3} M 3 T in DCE/toluene. Dose = 19 Gy.

Table 1
Observed rate constants for formation of radical cations of solutes in DCE solutions containing 1.57 M toluene

Solute	E°_{red} (V)[a]	Ref	$k_{(fast)} \times 10^{-10}\,M^{-1}\,s^{-1}$	$k_{(slow)} \times 10^{-9}\,M^{-1}\,s^{-1}$	Yield ratio DCE/ tol:DCE	Branching[b]
Biphenyl	1.91[c]	Mann and Barnes (1970)	1.9±0.1		0.5±0.1	
Pyrene	1.36	Mann and Barnes (1970), Bard and Lund (1978) and Mann and Barnes (1970)	1.7±0.1		—	
2,2′-Bithiophene	1.21[d]	Meerholz and Heinze (1996)	1.1±0.1	1.6±0.1	1.1±0.3	0.18
Anthracene	1.21	Mann and Barnes (1970)	1.5±0.1		0.6±0.1	
9-Methylanthracene	1.14	Fujita and Fukuzumi (1993)	1.1±0.1		0.4±0.1	
9,10-Dimethylanthracene	1.12	Bard and Lund (1978) and Mann and Barnes (1970), Bard and Lund (1978) and Fukuzumi et al. (1999)	1.3±0.1		0.4±0.1	<0.02
Triethylamine	1.02	Mann and Barnes (1970)	1.1±0.1	2.6±0.1	2.6±0.2	0.43
Perylene	1.00[e]	Mann and Barnes (1970)	1.4±0.1	4.0±0.1	2.5±0.5	0.42
Triphenylamine	0.92	Mann and Barnes (1970)	1.2±0.1	-[f]	2.5±0.4	0.42
Terthiophene	0.91[d]	Meerholz and Heinze (1996)	1.7±0.1	5.0±0.2	2.6±0.1	0.43
Quaterthiophene	0.76[d]	Meerholz and Heinze (1996)	-[e]	4.1±0.2	2.6±0.5	0.42

A second, slower process provides enhanced yields of cations for solutes with sufficiently low oxidation potentials.

[a] Potential vs. SCE in acetonitrile with 0.1 M electrolyte.

[b] Fraction of Cl•:toluene complex that oxidizes the solute to produce the cation; the remainder is assumed to react via hydrogen abstraction or addition.

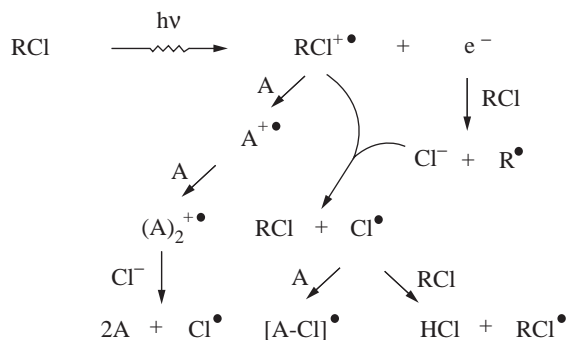[c] In 0.5 M NaOAc.
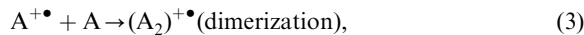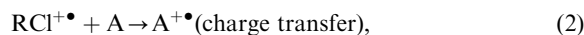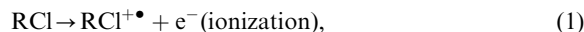
[d] In CH_2Cl_2.

[e] 0.5 M NaOAc in acetic acid.

[f] Not determined due to unfavorable absorption.

tions were observed in DCE/benzene solutions (1.86 M) for anthracene and triethylamine. For the solutes whose yield was observed to increase, the kinetics of growth of the cation was biphasic (see inset to Fig. 1). The rates of reaction of the solutes with the oxidizing species formed in the DCE/toluene solution are collected in Table 1. The increase in yield occurred only for solutes with potential, $E°_{red} \leqslant 1.1$ V vs. SCE for the $S^{+•}/S$ couple. For those solutes, the average increase was by a factor of 2.6 with some variation.

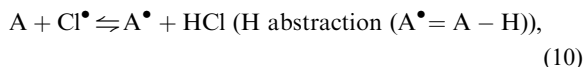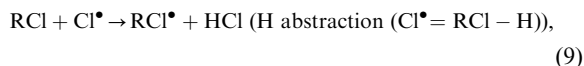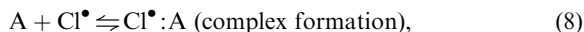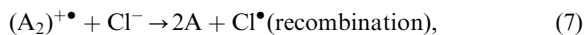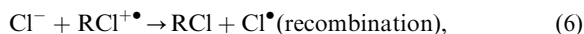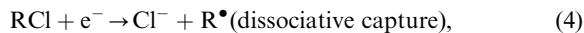The initial, faster growth of cations ($k = 1$–2×10^{10} M^{-1} s^{-1}) is accompanied by decay of the toluene dimer cation at 900–1000 nm at the same rate (see below); it is clearly due to hole transfer from that species. The second, slower process is due to another, less powerful, oxidizing species formed only when large concentrations of toluene or benzene have been added to the solution. One purpose of this paper is to delineate the mechanism leading to the increased yields that arise from this slower step. A plausible explanation is that an additional oxidizing species is formed in the DCE/toluene solutions that has an oxidizing potential near 1.1 V.

Understanding of this chemistry requires inclusion of a number of reactions (2–17), which will be discussed below. This set of reactions includes the known radiation chemistry of halocarbon liquids (Arai et al., 1969; Shank and Dorfman, 1970; Sumiyoshi et al., 1988; Wang et al., 1979) with additional reactions that occur with addition of an arene (A) such as toluene. Scheme 1 provides a schematic summary without the added solute (S) of lower potential.
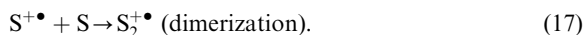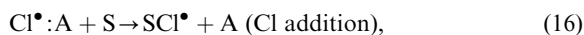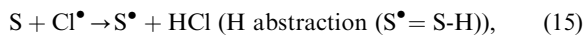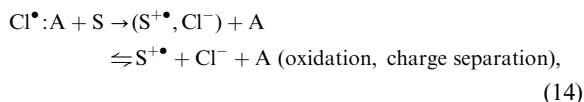
Radiolysis events in DCE/Arene (A = e.g. toluene):

$$RCl \rightarrow RCl^{+•} + e^- \text{ (ionization),} \tag{1}$$

$$RCl^{+•} + A \rightarrow A^{+•} \text{ (charge transfer),} \tag{2}$$

$$A^{+•} + A \rightarrow (A_2)^{+•} \text{ (dimerization),} \tag{3}$$

Scheme 1. Radiation chemistry of halocarbons (where RCl$^•$ is the halocarbon following hydrogen abstraction) and a halocarbon/arene binary solution where the arene (A) is present in large concentrations.

$$RCl + e^- \rightarrow Cl^- + R^• \text{ (dissociative capture),} \tag{4}$$

$$(A_2)^{+•} + e^- \rightarrow 2A_2^* \leftrightharpoons A + A^* \text{ (recombination),} \tag{5}$$

$$Cl^- + RCl^{+•} \rightarrow RCl + Cl^• \text{ (recombination),} \tag{6}$$

$$(A_2)^{+•} + Cl^- \rightarrow 2A + Cl^• \text{ (recombination),} \tag{7}$$

$$A + Cl^• \leftrightharpoons Cl^•:A \text{ (complex formation),} \tag{8}$$

$$RCl + Cl^• \rightarrow RCl^• + HCl \text{ (H abstraction (Cl}^• = RCl - H)),} \tag{9}$$

$$A + Cl^• \leftrightharpoons A^• + HCl \text{ (H abstraction (A}^• = A - H)),} \tag{10}$$

In the presence of an added solute, S:

$$(A_2)^{+•} + S \rightarrow S^{+•} + 2A \text{ (charge transfer),} \tag{11}$$

$$S^{+•} + Cl^- \rightarrow S + Cl^• \text{ (recombination),} \tag{12}$$

$$S^{+•} + Cl^- \rightarrow (S^{+•}, Cl^-) \text{ (recombination non-reactive),} \tag{13}$$

$$Cl^•:A + S \rightarrow (S^{+•}, Cl^-) + A \leftrightharpoons S^{+•} + Cl^- + A \text{ (oxidation, charge separation),} \tag{14}$$

$$S + Cl^• \rightarrow S^• + HCl \text{ (H abstraction (S}^• = S-H)),} \tag{15}$$

$$Cl^•:A + S \rightarrow SCl^• + A \text{ (Cl addition),} \tag{16}$$

$$S^{+•} + S \rightarrow S_2^{+•} \text{ (dimerization).} \tag{17}$$
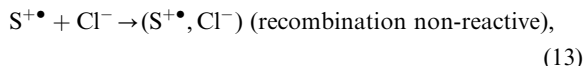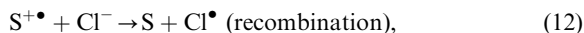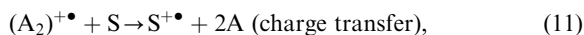
In this sequence, the interaction of high-energy radiation with the solvent results in the ejection of an electron from the halocarbon (reaction 1) that undergoes rapid dissociative capture (reaction 4) by other solvent molecules to form Cl$^-$ and a smaller yield of excited species. Published reports (Sumiyoshi et al., 1988; Wang et al., 1979) indicate that two radical cations, ClCH$_2$CH$_2$Cl$^{+•}$ and possibly vinylchloride cation, are formed with a total yield at $G = 0.68$ molecules 100 eV^{-1}. The solvent radical cations are collectively referred to below as DCE$^{+•}$ (or RCl$^{+•}$). A second ion, possibly ClCH$_2$CH$_2^+$ had a yield of $G = 0.20$ and was reported not to transfer charge to aromatic molecules (Wang et al., 1979), while both may both contribute to the broad absorption band in the visible and both are known (Sumiyoshi et al., 1988; Wang et al., 1979) to transfer charge to some solutes. The present work assumes Wang's reported $G = 0.68$ molecules 100 eV^{-1} of radical cations. Other reactions will be discussed below.

3.2. Radiation products of DCE–arene binary solutions and their rates of formation

The enhancement of cation yield occurs in DCE solutions containing large (~ 1 M) concentrations of toluene. Absorption spectra observed following pulse radiolysis of a DCE solution containing 1.57 M toluene are shown in Fig. 2. Instead of the broad absorption band(s) of $DCE^{+\bullet}$ at 550 nm (Sumiyoshi et al., 1988), absorption peaks at 460 and 1000 nm are formed within 2 ns following the electron pulse. $DCE^{+\bullet}$ is rapidly captured by toluene ($1.5 \pm 0.8 \times 10^{10}\,M^{-1}\,s^{-1}$) as expected based upon the ionization potentials of DCE and toluene (11.05 eV (Berman et al., 1979) and 8.83 eV (Howell et al., 1984; Lu et al., 1992), respectively) to form a toluene radical cation. Radical cations, of toluene and many other aryls, are known to form dimers in the presence of appreciable concentrations of the corresponding neutral (Badger and Brocklehurst, 1969; Fukuzumi et al., 1999; Kira et al., 1971, 1972; Nakai et al., 1997; Ohashi et al., 1998; Rodgers, 1971; Sumiyoshi, 1995) (reaction 3). The 1000 nm band is due to the toluene dimer cation, $(PhMe)_2^{+\bullet}$, reported to absorb with $\lambda_{max} = 980$ nm. (Badger and Brocklehurst, 1969; Ohashi et al., 1998). The kinetics of the 460 nm band are different indicating that this absorption peak is due to a different species (see inset to Fig. 2). The identity of this second species will be discussed later.

The 12 ps time resolution of the pulse–probe system resolved the rate of formation of the toluene cation dimer at 1000 nm (Fig. 3) and the decay of $DCE^{+\bullet}$ at 520 nm (not shown), close to the known maximum absorption of these species (Sumiyoshi et al., 1988). The pseudo-first-order growth at 1000 nm is linear (Fig. 3 inset) in toluene concentration yielding a bimolecular rate constant $k = (2.2 \pm 0.7) \times 10^{10}\,M^{-1}\,s^{-1}$ for the formation of the toluene cation dimer. The addition of
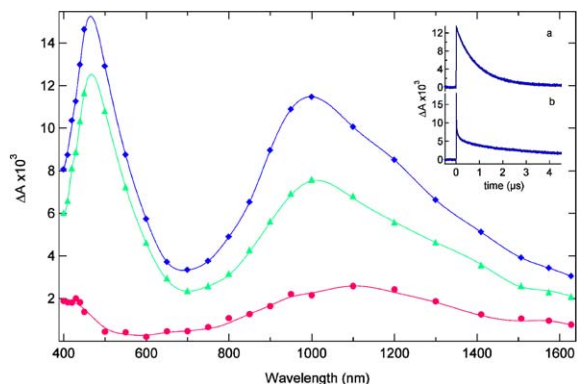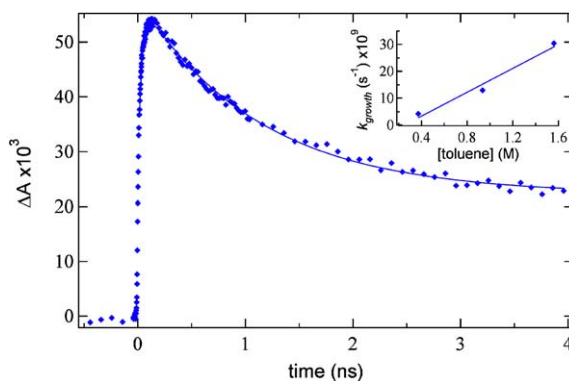

Fig. 3. Kinetics of growth and subsequent geminate decay of the toluene cation dimer at 1000 nm in a DCE solution containing 1.57 M toluene. Inset shows the dependence of the rate of growth of the toluene cation dimer on the concentration of toluene.

toluene causes $DCE^{+\bullet}$ at 520 nm to decay with $k = (1.5 \pm 1.0) \times 10^{10} \times M^{-1} \times s^{-1}$, in reasonable agreement with the rate of toluene cation dimer growth. The large uncertainty arises from uncertain corrections for the 460 nm species, which overlaps the 520 nm band. The growth at 1000 nm requires two steps (reactions 2 and 3), both of which are expected to have pseudo-first-order rates proportional to the concentration of toluene. The similarity of the rates observed at 1000 and 520 nm suggests that the rate of second step (dimerization of $toluene^{+\bullet}$) is fast, possibly even faster than the rate of hole transfer from $DCE^{+\bullet}$ to toluene monomer. An alternative possibility that some holes are captured directly by pre-existing neutral toluene dimers or incipient dimmers seems less likely given the linearity of Fig. 3. Toluene monomer cation, known to absorb weakly at 550 nm (Badger and Brocklehurst, 1969) was not observed, probably because its small absorption is obscured by absorption of both $DCE^{+\bullet}$ and the transient formed at 460 nm. The rate of dimerization of the toluene monomer cation at room temperature has not been reported previously; however, the rate of dimerization of the structurally related naphthalene has been reported at lower temperatures (Rodgers, 1972). Extrapolation of that data to 20 °C gives a rate constant of $1.4 \times 10^{10}\,M^{-1}\,s^{-1}$. These rate constants are in reasonable accord with diffusion-controlled hole transfer from the solvent cation to toluene, which may be estimated using the modified Debye equation (Backstrom and Sandros, 1960; Debye, 1942) (Eq. (18)).

$$k_{diff} = (2RT/3000\eta)(2 + r_1/r_2 + r_2/r_1). \qquad (18)$$

Using a ratio of the radii of toluene (r_1) to the DCE radical cation (r_2) of 1.3, and a viscosity of 8.87×10^{-3} P at 25 °C for DCE, Eq. (18) gives $7.6 \times 10^9\,M^{-1}\,s^{-1}$ at 25 °C. This is a factor of 2 slower than the observed rate

Fig. 2. Absorption spectrum of DCE containing 1.57 M toluene at ♦ $t = 20$ ns, ▲ $t = 180$ ns and ● $t = 4.5\,\mu s$ following the electron pulse. Insets are the time-resolved decays at (a) 500 nm and (b) 900 nm. $D = 12$ Gy.

of toluene dimer cation growth, which may indicate that Eq. (18) underestimates diffusion constants. Charge transfer reactions which occur more rapidly than the diffusion-controlled rate have been reported previously in DCE and were attributed to migration of the hole in DCE via a resonance charge transfer (Arai et al., 1969; Shank and Dorfman, 1970). A lower limit of $k \geqslant 2.2 \times 10^{10}\,\mathrm{M^{-1}\,s^{-1}}$ may thus be placed on the rate of dimerization of the toluene cation, comparable to the previously determined dimerization rate of naphthalene.

Following its rapid formation, decay of the 1000 nm band of the toluene dimer cation from 100 ps to 5 µs can be described as the sum of three exponentials with rate constants $(7.7 \pm 2) \times 10^8$, $(8.6 \pm 2) \times 10^7$ and $(4.3 \pm 1) \times 10^5\,\mathrm{s^{-1}}$, with fractions of 0.39, 0.49 and 0.12. The two fast components are due to geminate recombination in which cations are drawn to combine with Cl^- by Coulomb attractions; the slower is due to homogenous cations that have escaped the Coulomb field. Escape is probable for charge pairs at a distance longer than the Onsager radius, (Onsager, 1934), $r_c = 5.4$ nm in DCE, where the Coulomb energy equals thermal energy, $e^2/\varepsilon r_c = kT$. Extrapolation of the modeled decay curve to $t = 0$ gives an initial yield at $G = 4.3 \pm 0.9$ $(PhMe)_2^{+\bullet}$ ions $100\,\mathrm{eV^{-1}}$ of absorbed energy, compared to a homogeneous yield of $G = 0.5$ (see below), allowing $\varepsilon_{1000\,\mathrm{nm}}$ of $(PhMe)_2^{+\bullet}$ to be determined as $(5.2 \pm 1.0) \times 10^3\,\mathrm{M^{-1}\,cm^{-1}}$. The present data thus show that most (88%) of the observed $(PhMe)_2^{+\bullet}$ ions decay geminately and only 12% survive to become free ions. The 88% geminate fraction would be higher if there are very fast decaying components not observed here.

Observation of the growth of the species with $\lambda_{max} = 460$ nm is obscured by overlapping absorptions of $DCE^{+\bullet}$ and $(PhMe)_2^{+\bullet}$. In contrast to $(PhMe)_2^{+\bullet}$ or $DCE^{+\bullet}$ in neat DCE, the decay of the 460 nm species is first order, so there is no geminate recombination suggesting that it may be uncharged. At low concentrations, the decay depends slightly on [toluene], but above 0.4 M $k = (1.12 \pm 0.08) \times 10^6\,\mathrm{s^{-1}}$, independent of the concentration of toluene. The yield of the 460 nm species increases with concentration, reaching a plateau for [toluene] > 0.4 M. Neither the yield nor decay of the species is affected by the presence of oxygen.

A neutral complex of $Cl^\bullet$ atom with toluene is a plausible candidate for the 460 nm species. $Cl^\bullet$ atoms are formed by ion recombination of Cl^- with radical cations, such as $(PhMe)_2^{+\bullet}$, and are known to form complexes with many molecules (Buhler and Ebert, 1967; Buhler, 1968; Bunce et al., 1985; Chateauneuf, 1993; McGimpsey and Scaiano, 1988; Raner et al., 1989a,b; Sumiyoshi, 1997; Sumiyoshi et al., 1993). Absorption bands having similar lifetimes and positions are observed for π-halogen atom charge transfer complexes, including the $Cl^\bullet$:toluene complex (Buhler and Ebert, 1967; Buhler, 1968; Bunce et al., 1985;

Chateauneuf, 1993; McGimpsey and Scaiano, 1988; Raner et al., 1989a,b; Sumiyoshi, 1997; Sumiyoshi et al., 1993). The $Cl^\bullet$:benzene charge transfer complex has been extensively studied (Buhler and Ebert, 1967; Buhler, 1968; Bunce et al., 1985; Chateauneuf, 1993; McGimpsey and Scaiano, 1988; Raner et al., 1989a,b; Sumiyoshi, 1997). The transient absorption spectrum of pulse radiolyzed DCE containing 1.86 M benzene is almost identical to that of the DCE/toluene solution and also displays two peaks, one centered around 950 nm and the other around 470 nm (data not shown). The 950 nm absorption is due to the formation of the benzene cation dimer (Badger and Brocklehurst, 1969; Nakai et al., 1997; Ohashi et al., 1998). The 470 nm band is characteristic of the $Cl^\bullet$:benzene charge transfer complex (Buhler and Ebert, 1967; Buhler, 1968; Raner et al., 1989b); the λ_{max} of the $Cl^\bullet$:toluene π-transfer complex in CCl_4 has been reported as 479 nm (Buhler and Ebert, 1967; Raner et al., 1989b).

Identifying the 460 nm species as a $Cl^\bullet$:toluene charge transfer complex, the origin of the additional oxidizing equivalents is clear. Millimolar concentrations of solutes such as those employed in Table 2 capture only ~12% of the $DCE^{+\bullet}$ in DCE or $(PhMe)_2^{+\bullet}$ ions in DCE/ toluene formed at $t = 110$ ps. The geminate recombination (reactions 5–7) of the remaining ~88% converts those oxidizing equivalents to $Cl^\bullet$ and for these ions the recombination is complete within ~20 ns. In DCE, $Cl^\bullet$ disappears quickly ($\tau \sim 7$ ns) (Sumiyoshi et al., 1993) by abstraction of hydrogen from the solvent (reaction 9), but with 1.6 M toluene (or other arene) the chlorine atoms are complexed efficiently by the arene (reaction 10). The high concentration of the arene, necessary for competition with fast hydrogen abstraction from the solvent, also suppresses dissociation of the charge transfer complex. Indeed, based on the lowest reported value of K_{eq} (200 M^{-1}) (Chateauneuf, 1993), the concentration of free chlorine atoms in solution is small (~0.017 µM). Thus the yield of charge transfer complex formed reflects the yield of chlorine atoms produced by radiolysis in the DCE solutions. The role of the aromatic in the binary solutions is to reduce the tendency of the Cl atom to abstract hydrogen from the solvent or to add to aromatic hydrocarbons, while retaining substantial oxidizing power. The potential of this more stable species is lowered with respect to that of the free chlorine atom and the complex is able to react much more selectively (Bunce et al., 1985; Ingold et al., 1990; Raner et al., 1989a) with species in solution.

3.3. Properties and yield of Cl$^\bullet$:arene complexes

From the reported molar absorption coefficient of the $Cl^\bullet$:benzene complex, $\varepsilon = 1800\,\mathrm{M^{-1}\,cm^{-1}}$ at 490 nm (McGimpsey and Scaiano, 1988), the limiting yield of $Cl^\bullet$:benzene complex at high benzene concentration in

Table 2
Oxidizing species formed in 1,2-dichloroethane (DCE) with and without toluene (1.57 M)

Species	E_{red} (V vs. SCE)	Yield, G 100 eV^{-1} [a]
DCE$^{\bullet+}$ in DCE	> 2.5	0.68 ± 0.1 [b] (free)
(PhMe)$_2^{\bullet+}$ in DCE/PhMe [c]	> 2.0	4.3 ± 0.9 (total)
		0.5 ± 0.07 (free)
		3.8 ± 0.9 (geminate)
Cl$^{\bullet}$:toluene in DCE/PhMe	$\geq 1.1 \pm 0.1$	3.0 [d]
		1.3 ± 0.3 [e]

[a] Yield in molecules 100 eV^{-1} of absorbed energy. For ions these are homogeneous yields at times > 100 ns; larger yields of geminate ions may occur at earlier times.

[b] Wang et al. (1979).

[c] The free ion yield was calculated from measured absorbance of biphenyl cation and dose along with the reported extinction coefficient of biphenyl at 690 nm (Sehested and Hart, 1975; Shank and Dorfman, 1970). Total and geminate yields $G_{tot} = G_{free} + G_{gem}$ were obtained from the observed decays of (PhMe)$_2^{\bullet+}$. G_{tot} may be larger if fast decaying (< 50 ps) components exist (see text).

[d] From direct measurement of absorbance of PhMe:Cl$^{\bullet}$ using the reported extinction coefficient (McGimpsey and Scaiano, 1988).

[e] From yields measured for positive ions (Table 1) less the yield $G = 0.5$ from (PhMe)$_2^{\bullet+}$.

the present work may be calculated as $G = 3.0 \pm 0.2$ molecules 100 eV^{-1}, which is also an estimate for the yield of chlorine atoms. Assuming the same ε for the Cl$^{\bullet}$:toluene complex, which has a similar λ_{max} and width, leads to a yield $G = 3.0$ for that complex also. This value is consistent with the $G = 3.8 \pm 0.9$ yield (Table 2) of geminate ions, which are the source of the Cl$^{\bullet}$:toluene complexes. Therefore, conversion of Cl$^{\bullet}$ to the complex (reaction 8) may suffer little competition from hydrogen abstraction (reaction 9), although the errors on the difference are large. When CCl$_4$/benzene solutions were pulse radiolyzed, an identical procedure led to $G = 1.9 \pm 0.2$, which is similar within experimental error to the value of $G = 1.6$ previously reported for the yield of the Cl$^{\bullet}$:benzene complex in CCl$_4$/benzene (Sumiyoshi et al., 1993), but smaller than the yield of chlorine atoms in radiolyzed CCl$_4$ determined via scavenging experiments ($G = 2.34$) (Collinson et al., 1961). It is striking that the yield of chlorine atom formed by radiolysis is significantly larger in DCE ($G = 3.0 \pm 0.2$) than in CCl$_4$ ($G = 1.9 \pm 0.2$). The origin of this difference is unclear, but may be due to fast geminate recombination of CCl$_4^{+\bullet}$ and CCl$_4^{-\bullet}$ that may not yield Cl$^{\bullet}$.

The observed half life of the π:Cl$^{\bullet}$ complexes in DCE are slightly shorter in this study than found in CCl$_4$ (Buhler and Ebert, 1967; Raner et al., 1989a). This is expected because in CCl$_4$ hydrogen abstraction from the solvent (reactions 9–10) is not possible. A previous study found the rate of Cl$^{\bullet}$:benzene complex decay to decrease with increasing benzene concentration in the range 1.4×10^{-3}–5.6×10^{-1} M in CCl$_4$ (Sumiyoshi, 1997). This was attributed to rapid reaction of the chlorine atom with solvent following dissociation of the complex. The higher concentration of aromatic used here suppresses the formation of free chlorine atoms.

3.4. Oxidation of aromatic solutes by Cl$^{\bullet}$:toluene complex

The spectra obtained upon radiolysis of DCE/toluene solutions of 2,2'-bithiophene, terthiophene and quaterthiophene solutions were of identical form to those in DCE (see Fig. 1 for terthiophene) and are typical of the radical cations of these molecules (Emmi et al., 1999a,b; Keszthelyi et al., 2000; Wintgens et al., 1994). The spectra formed in the fast kinetic step (reaction with (PhMe)$_2^{+\bullet}$) and slow kinetic step (oxidation via Cl$^{\bullet}$:toluene complex) are indistinguishable. Complete spectra were not recorded for all solutes but peaks observed for triphenylamine (Oyama et al., 1991; Shida, 1988; Sumiyoshi, 1995; Zador et al., 1974) and other solutes were typical of the radical cations (Shida, 1988). The Cl$^{\bullet}$:toluene complex therefore has E_{red} near, probably slightly above, 1.1 V vs. SCE and provides an increased yield of cations upon radiolysis. It is of interest to note that bithiophene, which has a reported oxidation potential above 1.1 V, also experiences a slight increase in yield upon addition of toluene when compared to the yield in DCE only. For 9,10-dimethylanthracene, a slower oxidation step is also observed although this step contributes less than 12% to the total cation yield.

For a number of solutes (9-methylanthracene, 9,10-dimethylanthracene, perylene, and terthiophene) in the DCE/toluene solutions, an absorption band with a maximum below 500 nm was observed attributed to the formation of the triplet state due to their rapid formation and long lifetime (significantly different from the lifetime of the ions). The triplet states may be formed by absorption of Cerenkov radiation or by energy transfer from solute-excited states produced in the radiolysis in reaction 5.

While the chemistry of Cl$^\bullet$:arene complexes has been investigated, the focus of previous work was centered upon the ability of this complex to selectively abstract hydrogen from alkanes such as 2,3-dimethylbutane in a photochemically initiated reaction (Bunce et al., 1985; Chateauneuf, 1993; Ingold et al., 1990; Raner et al., 1989a). The present measurements indicate (Table 2) that the yield $G = 3.0$ of Cl$^\bullet$:toluene complexes provides an additional yield $G = 1.3$ of cations. This is only $1.3/3.0 = \sim 40\%$ efficient. The low efficiency and fluctuations among the different solutes may be due to competition from hydrogen abstraction or chlorine addition (reverse of reaction 8 followed by reaction 9 or reaction 16). The sum of the rate constants for those two processes may be estimated as $k = (2.2 \pm 0.8) \times 10^9 \, M^{-1} s^{-1}$ from reactions with solutes for which oxidation is an insignificant reaction pathway. The rate of the kinetically slower process reported in Table 1 thus is the total rate constant for reaction of each solute with the Cl$^\bullet$:toluene complex.

The yield of cation was measured at high concentrations (0.2 M) of biphenyl and triphenylamine, the cations of which have known molar absorption coefficients at 690 nm ($\varepsilon = 1.05 \times 10^4 \times M^{-1} cm^{-1}$) (Sehested and Hart, 1975; Shank and Dorfman, 1970) and 560 nm ($\varepsilon = 1.40 \times 10^4 \, M^{-1} cm^{-1}$) (Oyama et al., 1991; Zador et al., 1974), respectively. These two compounds are useful for measurements because both have high solubility and their cations are resistant to dimerization. The potential of biphenyl$^{+\bullet}$ is above the potential of the Cl$^\bullet$:toluene complex whereas the potential of triphenylamine$^{+\bullet}$ is below, so that only the toluene cation dimer transfers holes to biphenyl while triphenylamine may be oxidized by both the toluene cation dimer and the Cl$^\bullet$:toluene complex.

Biphenyl$^{+\bullet}$ ions decay both geminately and homogeneously with kinetics similar to those for $(PhMe)_2^{+\bullet}$. The concentration of free ions formed was determined by modeling the latter part of the geminate recombination ($t > 10 \, ns$) and subsequent absorbance as two first-order processes. The initial absorbance due to the free biphenyl ions was obtained by extrapolation of the second process back to $t = 0$ to obtain $G = 0.5 \pm 0.1$ molecules $100 \, eV^{-1}$ in the DCE/toluene solution. This is lower than the reported yield ($G = 0.68$) for the formation of solvent radical cations in DCE (Wang et al., 1979). The difference between the yield in the two solutions is likely to be due in part to the slightly larger Onsager radius in the DCE/toluene solution (assuming that the dielectric constant of the binary solution is equal to a weighted average of the DCE and toluene), $R_c = 5.8 \, nm$, compared to that of neat DCE, $R_c = 5.4 \, nm$, leading to a slightly lower free ion yield in the DCE/toluene solution.

TPA$^{+\bullet}$ is formed in a 0.2 M solution of TPA in DCE/toluene with a yield $G = (3.7 \pm 0.2)$ molecules $100 \, eV^{-1}$ at

3 ns following the electron pulse and does not show geminate decay. TPA is one of the solutes having $E_{red} < 1.1 \, V$ and is oxidized by Cl$^\bullet$:toluene, so TPA cations should clearly not oxidize Cl$^-$ to Cl$^\bullet$ (reaction 12). Geminate pairs of TPA$^{+\bullet}$ with Cl$^-$ would instead drift together to form stable ion pairs, (TPA$^{+\bullet}$,Cl$^-$), (reaction 13). The yield ($G = 3.7$) is consistent with the yield $G = 4.3$ for $(PhMe)_2^{+\bullet}$ cations formed at $t = 110 \, ps$ (Table 2). Competition between geminate decay of those $(PhMe)_2^{+\bullet}$ ions, described with three exponentials as mentioned earlier, and hole transfer to TPA predicts that 89% of those holes will be captured giving $G = 4.3 \times 0.89 = 3.8$. Hence a large yield of TPA$^{+\bullet}$ is formed, preventing formation of Cl$^\bullet$:toluene complexes: when reaction 13 does not occur, Cl$^\bullet$ and hence Cl$^\bullet$:toluene are not formed.

Dimerization of TPA$^{+\bullet}$ occurred with $k = (1.9 \pm 0.5) \times 10^6 \, M^{-1} s^{-1}$ as determined by the growth of the dimer TPA$_2^{+\bullet}$ at 1000 nm where the monomer TPA$^{+\bullet}$ has negligible absorbance (Oyama et al., 1991; Sumiyoshi, 1995). This is slower than the reported rate $k = 1.3 \times 10^8 \, M^{-1} s^{-1}$ (Oyama et al., 1991; Sumiyoshi, 1995), perhaps due to ion pair formation with Cl$^-$ or formation of a weak complex between the triphenylamine radical cation and toluene.

Hence, the origin of the increased yield can be understood with reference to scheme 1. In solvents like DCE that are not highly polar, most ions decay by geminate recombination (e.g. the fast spike shown in inset b of Fig. 2) so an initial yield $G \sim 4$ is reduced in DCE to ~ 0.7, or to 0.5 in DCE/toluene, within several ns. As indicated in scheme 1 the recombination produces Cl$^\bullet$ atom in DCE, which decays rapidly by hydrogen abstraction from the solvent. Sufficient concentrations of an arene such as toluene leads to formation of Cl$^\bullet$:toluene complexes, preventing hydrogen abstraction by the Cl$^\bullet$ atom while preserving part of the oxidizing power of Cl$^\bullet$. Increased yields (Brede et al., 1980) of cations in CCl$_4$ occurred upon addition of alkanes, although the absolute yields may still be much smaller than in the present case.

The rate of oxidation of solutes by the charge transfer complex deserves further dicussion. Oxidation of a solute molecule, S, to a radical cation by Cl$^\bullet$:toluene or similar Cl$^\bullet$:arene complexes (reaction 14) is a charge separation reaction and is expected to initially create ion pairs, $(S^{+\bullet}, Cl^-)$. In a solvent having a moderate dielectric constant such as DCE, $\varepsilon = 10.4$ (Lide, 1994), the Coulomb attraction can be substantial and contribute to the energetics of reaction 2. The energetic benefit from the Coulomb potential, illustrated in Fig. 4, will be larger for a smaller solute due to a smaller effective M$^{+\bullet}$,Cl$^-$ distance in the ion pair. As that separation distance becomes larger, the volume available to it becomes larger adding a term $R \ln (4\pi R^2)$ to the entropy to modify the free energy as shown in curve b of
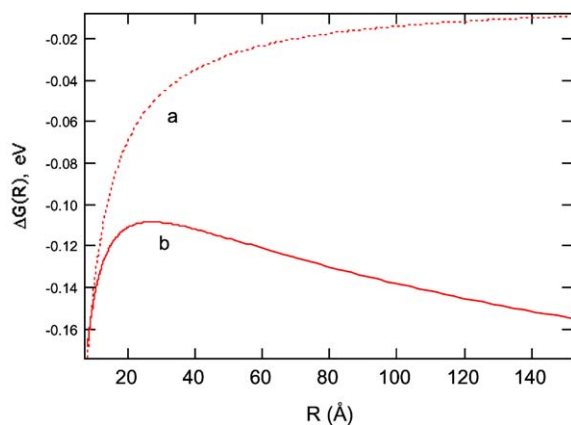
Fig. 4. Energy for separation of two opposite charges to a distance R against the Coulomb potential in a solvent with a dielectric constant of 10.36 without (a) and with (b) the R^2 entropic term.

Fig. 4, facilitating separation of the ion pairs. For ion pairs $(Na^+, Ar^{-\bullet})$ in THF, $\varepsilon = 7.6$ (Lide, 1994), the dissociation constant K_d is in the range $10^{-6\pm2}$ $dm^3\,mole^{-1}$ for two and three ring aromatics (Slates and Szwarc, 1965). Since the present experiments create just a few μM of ion pairs, they are likely to dissociate after passing over a barrier like that shown in curve b of Fig. 4. For K_d's in the range mentioned above, the dissociation rates can be estimated from $K_d = k_d/k_a$ to be $(10^{-6\pm2}\,dm^3\,mole^{-1})$ $(10^{11}\,M^{-1}\,s^{-1}) = 10^{5\pm2}\,s^{-1}$, after which the ions will behave as free ions. Here $k_a = \sim 10^{11}\,M^{-1}\,s^{-1}$ is the diffusion-controlled rate for association of oppositely charged ions. While stronger Coulomb attraction in the ion-pair favors oxidation of small molecules to form $(M^{+\bullet}, Cl^-)$, free $M^{+\bullet}$ ions will be formed having reactivities that are not diminished by the ion-pairing energy that helped to form them. It is just necessary to wait a time in the ns to μs region. Thus, the rates of reaction of the $Cl^\bullet$:arene complex with the organic molecules investigated do not vary significantly as might be expected as the free energy for the transfer changes.

4. Conclusions

Addition of toluene or other molecules that can complex the chlorine atom to 1,2-dichloroethane leads to formation of a long-lived complex that can oxidize molecules having redox potentials <1.1 V vs. SCE to their radical cations. Thus the addition of molecules like toluene more than doubles the yields of radical cations formed by radiolysis of DCE and is likely to be general for chloroalkanes. The source of the increased yield, the $Cl^\bullet$:toluene complex, decays with a rate of

$1.12 \times 10^6\,s^{-1}$, probably by hydrogen abstraction, so it is an effective source of cations only for molecules at millimolar concentrations. The $Cl^\bullet$:toluene complex is produced with a yield $G = 3.0$, but reaction with solutes produces cations with $\sim 40\%$ efficiency.

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