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Photo-Isomerization and Photo-Induced Reactions in Liquid CCl₄ and CHCl₃

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Abstract

Transient absorption spectroscopy is used to follow the reactive intermediates involved in the first steps in the photochemistry initiated by ultraviolet (266-nm wavelength) excitation of solutions of 1,5-hexadiene, isoprene and 2,3-dimethylbut-2-ene in carbon tetrachloride or chloroform. Ultraviolet and visible bands centred close to 330 nm and 500 nm in both solvents are assigned respectively to a charge transfer band of Cl-solvent complexes, and the strong absorption band of a higher energy isomeric form of the solvent molecules (iso-CCl3-Cl or iso-CHCl2-Cl). These assignments are supported by calculations of electronic excitation energies. The isomeric forms have significant contributions to their structures from charge-separated resonance forms, and offer a re-interpretation of previous assignments of the carriers of the visible bands that were based on pulsed radiolysis experiments. Kinetic analysis demonstrates that the isomeric forms are produced via the Cl-solvent complexes. Addition of the unsaturated hydrocarbons provides a reactive loss channel for the Cl-solvent complexes, and reaction radii and bimolecular rate coefficients are derived from analysis using a Smoluchowski theory model. For reactions of Cl with 1,5-hexadiene, isoprene and 2,3-dimethylbut-2-ene in CCl4, rate coefficients at 294 K are, respectively, $(8.6 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{s}^{-1}$, $(9.5 \pm 1.6) \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ and $(1.7 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$. The larger reaction radius and rate coefficient for 2,3-dimethylbut-2-ene are interpreted as evidence for an H-atom abstraction channel that competes effectively with the channel involving addition of a Cl atom to a C=C bond. However, the addition mechanism appears to dominate the reactions of 1,5-hexadiene and isoprene. Two-photon excited CCl4 or CHCl3 can also ionize the diene or alkene solute.

Keywords: Smoluchowski model; geminate recombination; isomeric form; solvent complex; addition reaction.
1. Introduction

The kinetics and dynamics of reactions of chlorine atoms with organic molecules in the gas phase have been the subject of extensive experimental and theoretical investigation.\textsuperscript{1,2} For reactions with alkanes, H-atom abstraction occurs via a direct mechanism, either over a low energy barrier or via a barrierless process, and the reaction typically produces HCl that is vibrationally and rotationally cold. However, reactions of Cl atoms with unsaturated hydrocarbons exhibit addition pathways that compete with, or can dominate the direct abstraction pathway.\textsuperscript{3-9} The energized adduct may eliminate HCl under low pressure conditions, but at ambient pressures of a few Torr or more, collisional stabilization of the adduct can become favourable,\textsuperscript{10} with implications for atmospheric reaction pathways. The HCl may be produced vibrationally excited for unusually exothermic reactions of Cl atoms with alkenes such as propene, in which the H-atom abstraction pathway forms a resonance-stabilized allyl radical.\textsuperscript{5}

For free radical chlorination reactions in solution, Cl-atom complexes with the solvent play an important mechanistic role,\textsuperscript{11,12} and reactions of such complexes with various solutes are emerging as model systems for studying chemical kinetics and dynamics in organic solvents. For example, Hochstrasser and co-workers\textsuperscript{13} and Crim and coworkers\textsuperscript{14} used ultrafast transient infra-red (IR) absorption spectroscopy to follow the time dependence of production of HCl from reactions of Cl atoms with alkanes. Crim and coworkers\textsuperscript{14-16} also used a charge-transfer band in the ultraviolet (UV) region, previously assigned to Cl-solvent complexes,\textsuperscript{17,18} to follow the reaction kinetics on picosecond to nanosecond timescales, and applied this approach to reactions of Cl atoms with alkanes, alcohols and chloroalkanes. More recently, we monitored the HCl products of reactions of Cl atoms with 2,3-dimethylbut-2-ene in CCl\textsubscript{4} or CDCl\textsubscript{3} solutions using ultrafast transient IR absorption spectroscopy and observed that 15-25\% of the HCl is initially formed vibrationally excited in this exothermic abstraction reaction.\textsuperscript{19} Addition of a Cl atom followed by solvent stabilization of the adduct might be expected to dominate such reactions of unsaturated solutes, based on observations of the pressure dependence of the mechanisms of related gas-phase reactions. However, the reaction of Cl atoms with 2,3-dimethylbut-2-ene demonstrates that abstraction pathways can compete.
In the current work, we explore further the reactions of Cl atoms with unsaturated hydrocarbons in solution, using either CCl₄ or CHCl₃ as the solvent and as a photolytic source of Cl atoms. We adopt the method of Crim and co-workers¹⁴-¹⁶ to follow the kinetics of reactions using the near-UV charge-transfer bands characteristic of Cl atoms in these solvents. By probing the reaction products using a white-light continuum (WLC) spanning the near-UV and visible regions of the spectrum, we also observe the time evolution of a second spectral feature centred in the visible region that is a signature of another transient species in the solutions. The source of this visible band, which is also known from radiolysis experiments in CCl₄, has been the subject of prior debate. However, assignments derived from radiolysis and UV photolysis have converged to a solvent separated ion pair, denoted here by CCl₃⁺|Cl⁻,²⁰-²² or a charge-transfer complex CCl₅⁺−Cl⁻,²³ although the mechanisms of formation are suggested to differ for the two excitation methods. On the basis of evidence from the observed kinetics of growth of the spectral band, and with the support of electronic structure calculations, we propose an assignment to an isomeric form of CCl₄, denoted by iso-CCl₃-Cl. In chloroform, the visible band is assigned to the corresponding iso-CHCl₂-Cl species. Our assignments are similar in spirit to the earlier literature, but more consistent with recent experimental and computational studies of other halogenated methanes such as bromoform (CHBr₃).²⁴-²⁶ Iso species of this type are important as reactive agents in solution: for example, prior calculations indicated that iso-CH₂X-X (X= Cl, Br, I) species are the methylene transfer agents that produce cyclopropane in reactions of UV photo-excited CH₂X₂ with ethene.²⁷,²⁸ This cyclopropane production is accompanied by X₂ loss in a one-step process, and in the case of X = Cl, the barrier to reaction was computed to be 37 kJ mol⁻¹.

The alkenes we study here are 1,5-hexadiene, isoprene (2-methyl-1,3-butadiene), and 2,3-dimethylbut-2-ene, but to extract quantitative information for the rates and mechanisms of their reactions, spectroscopic measurements of the UV-induced photochemistry of the pure solvents, CCl₄ and CHCl₃ are also required. Time-resolved electronic absorption spectra of CCl₄ and CHCl₃ photoproducts are therefore presented and analysed to provide a framework for the photochemistry in the alkene solutions. We also undertook time-resolved vibrational spectroscopy studies of all the solutions, but these were less informative than the electronic spectroscopy data, with the exception of the 2,3-dimethylbut-2-ene system which was the focus of an earlier publication.¹⁹ The transient spectral features observed in infra-red absorption measurements for 1,5-hexadiene can all be assigned to radical cation pathways.²⁹
2. Experimental and Computational Details

2.1 Transient electronic absorption spectroscopy

Transient UV and visible absorption spectra were obtained using the ULTRA Laser Facility at the STFC Rutherford Appleton Laboratory, and full details of the laser system have been presented elsewhere. A titanium: sapphire oscillator (Femtolaser) generated pulses of 800 nm wavelength light at 65 MHz repetition rate which pumped a regenerative amplifier (Thales Optronique) operating at 10 kHz. The amplifier emitted ≤1 mJ pulses centred at 800 nm and of duration 40 – 80 fs. Third harmonic generation (THG) produced pulses of 266-nm light, and the current experiments typically used 1 μJ of this UV radiation. Focusing <10 μJ of the 800 nm output from the amplifier into a rastered 2-mm thick CaF$_2$ window generated a probe WLC which spanned wavelengths over the range 300 – 750 nm. After passage through the sample, the WLC was dispersed onto a 512-element silicon array (Quantum Detectors) to obtain UV-visible absorption spectra. A portion of the WLC bypassed the sample and was dispersed onto a second, equivalent array to provide a reference spectrum. However, for most of the results presented here, the reference spectrum was not required for data processing. Spectra were wavelength-calibrated using a series of narrow band-pass filters. The spectra were not corrected for the temporal chirp in the WLC: instead, data for time delays ≤ 1 ps were excluded from analysis.

The pump-pulse train was chopped at 5 kHz to facilitate collection of pump on – pump off difference spectra. The relative linear polarizations of the pump and probe pulses were set to the magic angle 54.7°. Spectra were obtained at about 50 selected, but randomly ordered, time delays between pump and probe pulses in the range 1 – 2000 ps. These delays were controlled using a motorised delay stage (Newport IMS600LM) on the pump beam path.

A peristaltic pump circulated samples through a Harrick cell fitted with CaF$_2$ windows spaced by 0.35 mm. The position of the cell was rastered in a plane perpendicular to the laser propagation direction, and the flow rate was chosen to ensure that successive laser pulses probed fresh portions of the sample. The samples probed were CCl$_4$, CHCl$_3$ (both solvents >99% purity, Sigma Aldrich), CDC$_3$ (Sigma Aldrich, >99.96 atom % D), and 0.25 – 0.75 M solutions of 1,5-hexadiene (97%, Sigma Aldrich), isoprene (≥99%, Sigma Aldrich) or 2,3-dimethylbut-2-ene (Sigma Aldrich, >99.9%) in these chlorinated solvents. Samples were
dried using molecular sieves (4Å) prior to use, and all glassware was stored in a drying oven between experiments. Measurements were made at an ambient temperature of 294 K.

2.2 Calculations of molecular structures and spectra

Electronic structure calculations used the Gaussian 09 software package\textsuperscript{31} on the Marquette University (MU) Pere high speed cluster. Full geometry optimizations were carried out using density functional theory (DFT) (with the meta-GGA hybrid functional M06-2X\textsuperscript{32} and post-Hartree-Fock (MP2) methods with an aug-cc-pVTZ basis set, either in vacuum or in neat solvent. Calculations in solvent used the Polarizable Continuum Model (PCM) as implemented in Gaussian 09. Characterization of the isomerization reaction coordinates started from relaxed redundant C-Cl-Cl bond angle scans. Structures corresponding to the energy maxima on these scans were then optimized as first-order saddle points, and intrinsic reaction coordinate (IRC) calculations were performed to verify that these saddle points correspond to transition states on the isomerization path. For the radical complexes, optimization used the same methods, with counterpoise correction for basis set superposition error (BSSE). All calculated binding energies were also corrected for zero-point energy. Natural Bond Orbital (NBO) calculations\textsuperscript{33,34} were carried out on the MU Pere cluster with NBO Version 5.9\textsuperscript{35}

Electronic spectra were calculated with time-dependent DFT (TDDFT) methods using the M06-2X and CAM-B3LYP\textsuperscript{36,37} functionals, with an aug-cc-pVTZ basis set. The performance of the M06-2X method has recently been benchmarked for electronic excitations, including Rydberg and charge-transfer transitions.\textsuperscript{38} TDDFT calculations in solvent also used the PCM method.

3. Results and Discussion

Measurements were made of transient absorption in the near-UV and visible regions for 266-nm photo-excited samples of CCl\textsubscript{4} and CHCl\textsubscript{3} (and CDCl\textsubscript{3}), and for dilute solutions of selected unsaturated hydrocarbons (1,5-hexadiene, isoprene and 2,3-dimethylbut-2-ene) in these chlorinated solvents. Results are presented first for the neat solvents, with analysis using a kinetic scheme based on the Smoluchowski model employed by Crim and co-workers
for Cl-atom reactions in solution. This analysis is then applied to the kinetics of reactions taking place in solutions containing the unsaturated hydrocarbons.

3.1 Photo-induced complexation and isomerization in CCl$_4$ and CHCl$_3$

Fig. 1 shows the time-evolution of the transient electronic absorption bands observed upon UV excitation of neat CCl$_4$ and CHCl$_3$, and recorded using the procedures described in section 2. One relatively sharp and short-lived band, centred near 330 nm, and a second, long-lived and very broad band centred close to 500 nm appear in CCl$_4$. These features were previously observed in experiments on picosecond and nanosecond timescales, and, in the case of photolytic production at 266 nm, shown to derive from 2-photon excitation of the solvent. Hereafter, these two bands will be referred to as the 330-nm (or UV) and 500-nm (or visible) features. Fig. 1 also shows time-resolved spectra for CHCl$_3$ and similar bands are observed centred at about the same wavelengths. CDCl$_3$ displayed almost identical behaviour to CHCl$_3$.

Figure 1: Time-resolved transient absorption spectra obtained following photoexcitation at 266 nm of samples of (a) CCl$_4$ and (b) CHCl$_3$. The inset key shows selected time delays, and vertical arrows indicate the directions of change of band intensities. Spectra are displayed up to time delays of 500 ps, and both UV and visible bands decline in intensity at later times.
3.1.1 UV and visible absorption band assignments

Two-photon excitation of CCl₄ at 266 nm results in fragmentation to CCl₃ radicals and Cl atoms, which then interact with the surrounding solvent molecules. The identities of the species that give rise to the transient UV-vis features have been the subject of prior debate,¹⁸,²⁰-²³ but the 330-nm feature is assigned to a charge-transfer band of Cl-CCl₄ complexes on the basis of careful arguments by Chateauneuf and further work by Crim and co-workers for related solvents.¹⁴,¹⁵,¹⁷,¹⁸ From the results of radiolysis experiments, Bühler argued that the species absorbing at 500 nm was ionic and assigned it to the ion pair CCl₃⁺||Cl⁻, where the symbol || denotes solvent separation.²⁰,³⁹ Washio et al. confirmed the spectral features in their picosecond and nanosecond pulsed radiolysis experiments, and proposed that geminate recombination of CCl₃⁺ and Cl⁻ ions produced the charge-transfer complex CCl₃δ⁺--Clδ⁻.²³ Miyasaki et al.,²¹ and more recently Zhang and Thomas,²² observed that two-photon photolysis of CCl₄ at 266 nm gave the same broad visible absorption band as radiolysis, and retained the assignment to the CCl₃⁺||Cl⁻ ion pair.²² In these experiments, it was recognized that the two-photon absorption at 266 nm corresponds to a total energy of 9.34 eV, which is significantly lower than the gas phase ionization energy (IE) of CCl₄ (11.47 eV).⁴⁰ This IE might be reduced in the liquid, with some reports arguing a reduction of as much as 1.5 eV.²²,⁴¹ However, the mechanism of formation of the solvent-separated ion pair following UV excitation required some degree of speculation in the absence of spectral signatures of postulated intermediate species.

Isomeric (iso) forms of the parent compound have been extensively characterised in several photolysis studies of halomethanes in matrices and in liquids,²⁴,²⁵,⁴²,⁴³ and shown to give rise to broad, strong visible absorption bands. A recent computational study of CHBr₃ isomerization showed significant charge-separation character in iso-CHBr₂-Br, which exhibits mixed covalent and ionic character, with (CHBr₂)⁺ Br⁻ contributing the major (62%) resonance structures.²⁶ We therefore undertook calculations of the electronic character of the iso-forms of CCl₄ and CHCl₃, following an NBO analysis similar to that reported by George et al.²⁶ and using the computational methods outlined in Section 2.2. Fig. 2 shows the derived contributions to the two isomeric forms and isomerization transition state from the principal covalent and charge-transfer resonance structures. For both iso-CCl₃-Cl and iso-CHCl₂-Cl, resonance structures with Cl⁻–CCl₃⁺ or Cl⁻–CHCl₂⁺ character constitute more than 50% of the molecular wavefunction. The outcomes of the TDDFT calculations for the iso
species are collected in Table 1 and show only modest dependence on the choice of functional. The calculations reveal very strong bands (with oscillator strengths close to 0.5) at wavelengths around 410 nm that are broadly consistent with the features we observe in Fig. 1 in the visible in our time-resolved transient absorption spectra.

Figure 2: Principal resonance form contributions to the molecular structures of the solvent, its iso form and the transition state for their inter-conversion. Dark blue represents the percentage of the covalent structure, and other colours correspond to charge-separated resonance structures, which are shown for the iso form at the right. Panel (a) is for CCl₄ and (b) is for CHCl₃. Results are shown for different computational methods described in the text.

<table>
<thead>
<tr>
<th></th>
<th>Cl-CCl₄</th>
<th>iso-CCl₃-Cl</th>
<th>Cl-CHCl₃</th>
<th>iso-CHCl₃-Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength / nm TDM06-2X</td>
<td>334</td>
<td>407</td>
<td>345</td>
<td>405</td>
</tr>
<tr>
<td>TDCAM-B3LYP</td>
<td>376</td>
<td>420</td>
<td>380</td>
<td>414</td>
</tr>
<tr>
<td>Oscillator strength TDM06-2X</td>
<td>0.07</td>
<td>0.51</td>
<td>0.08</td>
<td>0.46</td>
</tr>
<tr>
<td>TDCAM-B3LYP</td>
<td>0.11</td>
<td>0.49</td>
<td>0.13</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Table 1: Calculated wavelengths of the electronic absorptions of the Cl-solvent (Cl-CCl₄ and Cl-CHCl₃) complexes and iso forms (iso-CCl₃-Cl and iso-CHCl₃-Cl) considered to give rise to the transient UV and visible bands evident in Fig. 1. Calculations employed TDDFT methods, as described in the main text, with PCM model treatment of the solvent.
The calculations show that the ionic CCl$_3^+$||Cl$^-$ that is invoked in the literature as the carrier of the visible band in photolytically or radiolytically excited CCl$_4$ appears to be simply an alternative description of the iso-CCl$_3$-Cl form of CCl$_4$. For the above reasons, and because of arguments based on the time dependence of the 330-nm and 500-nm bands presented in section 3.1.2, the species giving rise to the broad absorption band at 500 nm is assigned here to iso-CCl$_3$-Cl, but it is recognised that this species exhibits significant ion pair (CCl$_3^+$ Cl$^-$) character. By analogy, and consistent with prior work, the UV band in chloroform is assigned to charge transfer in Cl-CHCl$_3$ (or Cl-CDCl$_3$) complexes, and the broad visible band to an isomeric form of chloroform, iso-CHCl$_2$-Cl (or iso-CDCl$_2$-Cl).

There is further persuasive evidence in support of the above assignments from our calculations and from other spectroscopic studies on related compounds. The computed wavelength ordering of the spectral bands for iso-forms and Cl-solvent complexes (Table 1) and the relative magnitudes of the oscillator strengths are consistent with the experimental observations. In particular, the very large oscillator strengths computed for the iso-forms, which are roughly 4–5 times larger than the Cl-solvent complex bands, are reflected in the wavelength-integrated intensities of the visible bands seen in Fig. 1. The calculations do place the strong absorption bands of the iso-forms of CCl$_4$ and CHCl$_3$ to shorter wavelength than the band centres observed experimentally, but these bands span a wide wavelength range, their exact positions are sensitive to the solvent environment and our choice of molecular geometry, and the calculations provide an incomplete description of solvation effects. Complementary to our observations, Preston et al. reported similar UV (around 400 nm) and visible (centred at 450 nm) absorption bands in time-resolved electronic absorption spectra of photolyzed bromoform dissolved in CCl$_4$ that were assigned to the CHBr$_3$-Br complex and iso-CHBr$_2$-Br, respectively, on the basis of time-resolved IR spectra. The bands share an isosbestic point at 420 nm, indicating that the CHBr$_3$-Br species is the precursor of iso-CHBr$_2$-Br.

3.1.2 Time dependence of the UV and visible bands

Our analysis of the observed time dependence of the spectral features is described in greater detail here for CCl$_4$ than for CHCl$_3$ (and CDCl$_3$), which follows a very similar path, but for which only the outcomes are presented. The 330-nm features for CCl$_4$ and CHCl$_3$ do not show pronounced evolution in their spectral shapes with time, but the visible bands shift to
shorter wavelength at early times. The shift indicates cooling of an iso species that is formed internally hot. We do not attempt to fit these changing band shapes, but instead sum the intensity across 10 nm of each absorption band around each band centre for every time delay. This integration gives the time-dependent intensity data shown in Fig. 3. We examined the effects of integrating over much wider portions of the visible band to incorporate the early time spectral shifts, but found it made no difference to the analysis that follows. The UV band of the Cl-solvent complexes has two decay components, the faster component being attributed to diffusive geminate recombination, while the slower loss is either by reaction or formation of the iso species.\textsuperscript{14,15} The visible band of the isomeric form exhibits a fast rise with a time constant that appears similar to that for the decay of the UV band, and a much slower decay. The slow component of the visible band decays on a timescale that is comparable to the previously reported time constant of 17 ns,\textsuperscript{18} but the decay of the UV band is much faster than the 170 ns time constant obtained in the earlier study. This discrepancy suggests two different decay processes are being observed in the two experiments that are optimized to observe kinetics on very different timescales.
The time dependences of the two bands were fitted using a model based on Smoluchowski theory that was previously used by Crim and co-workers\textsuperscript{14-16} and allows for geminate recombination of the radical photoproducts. The photoexcitation of CCl\textsubscript{4} is assumed to be followed by prompt dissociation to Cl + CCl\textsubscript{3}, and the model incorporates the distance, \(r_0\), at which the photofragment Cl and CCl\textsubscript{3} equilibrate in solution. As they equilibrate, the Cl atoms can form Cl-CCl\textsubscript{4} complexes. The subsequent random diffusive movement of these photo-produced radical pairs is described by a relative diffusion coefficient, \(D_r\), and CCl\textsubscript{3} and Cl-CCl\textsubscript{4} particles may recombine. The Smoluchowski model that describes the time-dependence of this behaviour is:

\[
[\text{Cl}]_t = [\text{Cl}]_0 \left\{ 1 - A \text{erfc} \left( \frac{B}{\sqrt{4D_r}} \right) \right\} \exp(-k_1 t)
\]  

(1)

where \([\text{Cl}]_t\) represents the time-dependent concentration of Cl-solvent complexes, with initial value \([\text{Cl}]_0\), and the final exponential term with rate coefficient \(k_1\) allows for reactive loss of these complexes. In Equation (1), \text{erfc} is the complementary error function, and:

\[
A = \frac{R_{\text{rec}}}{r_0}, \quad B = \frac{r_0 - R_{\text{rec}}}{\sqrt{4D_r}}
\]  

(2)

with \(R_{\text{rec}}\) the recombination radius within which radical recombination occurs with unit efficiency. The parameter \(A\) represents the asymptotic recombination yield describing the fraction of radical pairs that recombine. Values of \(R_{\text{rec}}\) and \(r_0\) obtained from data analysis using Equation (1) are somewhat qualitative because they depend on the choice of \(D_r\). This relative diffusion coefficient is the sum of the individual diffusion coefficients of the photofragments, \(D_{\text{Cl--CCl}_4}\) (for the Cl-CCl\textsubscript{4} complex) and \(D_{\text{CCl}_3}\), each of which is estimated using the Stokes-Einstein equation (with \(x\) denoting Cl-CCl\textsubscript{4} or CCl\textsubscript{3}):

\[
D_x = \frac{k_B T}{6\pi \eta \alpha_x}
\]  

(3)

Here \(k_B\) is the Boltzmann constant, \(T\) is the temperature of the solution, \(\alpha_x\) is the radius of species \(x\), and \(\eta\) is the viscosity of the solvent. The radius of a particular particle was obtained as the distance from its centre of mass to the centre of the furthest atom, using the Hartree-Fock 6-31G level of theory to compute geometries of Cl-CCl\textsubscript{4} and CCl\textsubscript{3}. This choice
of particle radius may be a slight underestimate, but we confirmed that taking the distance to
the outer edge of the furthest atom (as defined by its van der Waals radius) made little
difference to the outcomes of the subsequent analysis. The relative diffusion coefficient
describing the recombination of a CCl₃ radical with a Cl-solvent complex was then estimated
to be 2.23 nm² ns⁻¹.

In CCl₄, we do not expect the Cl-solvent complexes to react with the solvent, suggesting that
there should be no exponential decay term in Equation (1) unless they are removed by
another pathway. Nevertheless, this term was retained in the analysis of the data, and as will
be shown, results in a very small value of k₁ consistent with our expectation. The
concentration dependences in Equation (1) were re-expressed in terms of transient absorption
signals (S), to give the following functional form to describe the kinetics of the UV band:

\[
S_t(UV) = S_0(UV) \left\{ 1 - A \text{erfc} \left( \frac{B}{\sqrt{t-t_0}} \right) \right\} \exp \left( -k_1(t-t_0) \right)
\]

The value of the constant time offset, t₀, was fixed at 1.44 ps which corresponds to the first
data point used in the analysis, and is negligible compared to the 2000 ps interval over which
data are fitted. As Fig. 3 shows, the time dependence of the rise of the visible band appears
complementary to the decay of the UV band, and we see a clear isosbestic point between the
UV and visible bands in the CCl₄ spectra (Fig. 1), indicating the decay of the species
responsible for the 330-nm feature controls the rise of the species giving the 500-nm feature.
These observations encouraged simultaneous fitting of both bands to the same parameter set,
using the functional form:

\[
S_t(vis) = S_0(vis) \left\{ A \text{erfc} \left( \frac{B}{\sqrt{t-t_0}} \right) \right\} \exp \left( -k_2(t-t_0) \right)
\]

for the visible band. We fitted the data in Origin 8.5.1 software, using a non-linear least
squares fitting routine with custom functional form, and the outcomes successfully model the
data, as shown by the solid lines in Fig. 3. Best fit parameters and associated uncertainties are
displayed in Table 2, and values of parameters A and B are similar to those reported by Sheps
et al. The value of A suggests that approximately 1/3 of the photofragments undergo
recombination.

Table 2 also includes values for the analysis of spectra observed following CHCl₃ photolysis.
Simultaneous fits were again performed to the time-dependent intensities of the UV and

12
visible bands. The fits were not as robust as to the CCl₄ data and so we included spectral intensities for the two corresponding bands in CDCl₃, with the assumption that the kinetics would be identical in the two isotopologues of chloroform. This assumption is supported by the quality of the fits. The decay of the visible band is more rapid for chloroform than for CCl₄, suggesting either reactive loss of the iso-chloroform species, or faster isomerization back to the more energetically favourable CHCl₃ isomer. We return to this point later, and note that this faster decay prevents an isobestic point from developing in the spectra in Fig 1(b). The greater persistence of intensity in the UV band of CHCl₃ compared to CCl₄ at times approaching our measurement limit points to greater stability of the Cl-solvent complex in the former case. This deduction is supported by our calculations, as the binding energy of the Cl-CHCl₃ complex is roughly 50% larger than that of Cl-CCl₄ (-16 kJ mol⁻¹ vs. -11 kJ mol⁻¹ at the M06-2X/aug-cc-pVTZ level). Computed optimized structures of these complexes are shown in Supporting Information.

Table 2: Fit parameters from simultaneous analysis of the transient UV and visible bands for 266-nm photolysis of CCl₄ and CHCl₃. Uncertainties are 1 SD from the fits.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CCl₄</th>
<th>CHCl₃ and CDCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.339 ± 0.132</td>
<td>0.827 ± 0.068</td>
</tr>
<tr>
<td>B / ps¹/²</td>
<td>3.63 ± 0.17</td>
<td>0.277 ± 0.116</td>
</tr>
<tr>
<td></td>
<td>(0.115 ± 0.006)</td>
<td>(0.008 ± 0.004)</td>
</tr>
<tr>
<td>k₁ / ps⁻¹</td>
<td>0.0003 ± 0.0003</td>
<td>0.0008 ± 0.0002</td>
</tr>
<tr>
<td>k₂ / ps⁻¹</td>
<td>0.0006 ± 0.0004</td>
<td>0.0039 ± 0.0004</td>
</tr>
</tbody>
</table>

The upper bounds of the uncertainty ranges in the values of k₁ and k₂ for CCl₄ indicate lifetimes >1 ns for the decay of the UV and visible bands, but these lifetimes are ill-determined by our measurements which extend only to 2-ns delays. However, these rate coefficients suggest that reactive losses of the Cl-CCl₄ and iso-CCl₃-Cl species are modest on the timescales of our experiments in neat CCl₄. The parameter B takes a similar value in CCl₄ to the value reported by Sheps et al. for CH₂Cl₂,¹⁴,¹⁵ but the value obtained in CHCl₃ (and CDCl₃) is anomalously low and may be an artifact of our fitting.

Washio et al. observed the decay of a spectral feature in CCl₄ at 330 nm following pulsed radiolysis of the liquid sample, and measured lifetimes of ~60 ps and ~100 ns for two time components of the decay.²³ The latter time constant is broadly consistent with a value of 173
ns measured by Chateauneuf in UV excitation experiments,\textsuperscript{18} but is too slow for our experiments to confirm. Zhang and Thomas photoexcited CCl\textsubscript{4} at 266 nm and monitored the rise of absorption at a single wavelength of 532 nm: a single-exponential fit to their data gave a time constant of 46 ps.\textsuperscript{22} A similar analysis of the visible band growth from our measurements shown in Fig. 3, which benefit from superior time resolution and signal-to-noise ratio, gives an exponential rise time constant of 37 ± 2 ps. Confining our analysis to a probe wavelength of 532 nm does not alter the derived time constant. We therefore observe the same fast spectral evolution as in these radiolysis and photolysis experiments, but we are able to monitor the decay of the UV band and the associated growth of the visible band simultaneously.

Finally in this sub-section, we return to the decay rates of the visible bands in CCl\textsubscript{4} and CHCl\textsubscript{3}. In ultrafast studies of CHBr\textsubscript{3}, Tarnovsky and co-workers showed that the isomer lifetime is strongly solvent dependent,\textsuperscript{45} being shorter in weakly interacting polar solvents than in non-polar solvents. The origin of this effect lies in the differential solvation of the isomerization transition state compared to the isomer minimum, which lowers the effective barrier to isomerization back to the parent. Figure S2 of Supporting Information illustrates this behaviour in CCl\textsubscript{4} and CHCl\textsubscript{3} systems, with the outcomes of MP2/aug-cc-pVTZ intrinsic reaction coordinate scans obtained in vacuum and in liquid solvent using the PCM method. For CHCl\textsubscript{3}, the isomerization barrier from the \textit{iso} minimum decreases from 60 kJ mol\textsuperscript{-1} in vacuum to 16 kJ mol\textsuperscript{-1} in neat solvent. In contrast, the corresponding barrier for \textit{iso}-CCl\textsubscript{3}-Cl is computed to decrease from 64 kJ mol\textsuperscript{-1} to 34 kJ mol\textsuperscript{-1} in going from vacuum to neat solvent. These changes to barrier heights are consistent with faster return of \textit{iso}-CHCl\textsubscript{2}-Cl to CHCl\textsubscript{3} than for the related back-isomerization in CCl\textsubscript{4}.

\subsection*{3.1.3 Photochemical reaction scheme for CCl\textsubscript{4}}

The success of the simultaneous fit of the UV and visible bands to the same set of parameters using Equations (1) and (2) suggests that the rise of the visible band assigned to \textit{iso}-CCl\textsubscript{3}-Cl is a consequence of the decline in concentration of the Cl-CCl\textsubscript{4}. A reaction scheme is proposed in Fig. 4 to account for the experimental observations. Pal \textit{et al.}\textsuperscript{25} recently argued for a direct route to \textit{iso}-bromoform via a conical intersection from the S\textsubscript{1} state of photoexcited CHBr\textsubscript{3}, but we have no direct (experimental or theoretical) evidence for such a pathway in CCl\textsubscript{4} so have not included it in the scheme.
Figure 4: Chemical processes proposed to describe the production and loss of species giving rise to the absorption bands at 330 and 500 nm following UV photolysis of CCl₄. Processes A – E are described in the main text.

The mechanism in Fig. 4 is initiated by step A whereby UV excitation of CCl₄ forms energized neutral CCl₄* (as also proposed by Zhang and Thomas²²) which can either relax back to the ground state through solvent collisions, step -A, or dissociate to form CCl₃ and Cl. Promptly after the photodissociation, a fast interaction of Cl with CCl₄ forms the Cl-CCl₄ complex (step B), giving rise to the absorption band at 330 nm. The time constant for this process must be ≤ 2 ps to account for the fast rise observed experimentally. Proximity of a Cl atom to a CCl₄ molecule (i.e. a loosely solvated atom) may well be sufficient to give rise to the 300-nm CT band, without the need to relax to the minimum in the potential energy surface associated with a bound Cl-CCl₄ complex. The complex subsequently has two pathways for its fast removal. The first path involves recombination of the solvated Cl atom with CCl₃ either as a fast geminate recombination process, or after diffusion, which is suggested to take hundreds of nanoseconds¹⁸,²³,³⁹ and is therefore unlikely to be important on the timescale of this work. The two recombination pathways are collectively indicated as step C in Fig. 4. The second path transfers the Cl atom to a CCl₃ radical to form the metastable iso-CCl₃-Cl complex (step D), contributing to the growth of the absorption band at 500 nm as well as the loss of signal detected at 330 nm. This step will also be a combination of faster geminate and slower diffusive mechanisms. The conversion to the iso form is consistent with the coupled kinetics reported above and the observation of an isosbestic point at approx. 400 nm in the time-dependent spectra. The subsequent decay of iso-CCl₃-Cl (step E) by isomerization back to CCl₄ is slow, taking nanoseconds or longer.¹⁸,²³,⁴⁶ The decline of the absorption on the UV band to baseline within the timescale of our measurements indicates almost complete conversion of the Cl-CCl₄ complex back to two CCl₄ molecules or to iso-CCl₃-Cl (although we cannot discount removal of Cl-CCl₄ by reactions with impurities such as dissolved oxygen).
3.2 Photo-induced chemistry of alkenes and dienes in the chlorinated solvents

Having established the short-time UV photochemistry of neat CCl$_4$ and CHCl$_3$ solvents using broadband, time-resolved UV-vis absorption spectroscopy, the same experimental approach is applied to solutions of selected dienes and alkenes in these solvents. The unsaturated hydrocarbons provide an alternative pathway for removal of Cl-solvent complexes by chemical reaction, either by Cl-atom addition to a C=C bond, or by H-atom abstraction. The iso-forms of the solvent molecules may also prove reactive with these added solutes.$^{27,28}$

3.2.1 Photo-induced reaction of 1,5-hexadiene in CCl$_4$

Our most extensive studies were carried out for addition of 1,5-hexadiene to CCl$_4$, and the results of these experiments are the focus of the first part of this section. Solutions of 1,5-hexadiene in CCl$_4$ of concentrations 0.25, 0.50 and 0.75 M were examined in the same way as for the pure solvent. Fig. 5 Shows examples of time-resolved transient UV-vis absorption spectra of 0.5 M 1,5-hexadiene in CCl$_4$. 
Figure 5: Transient UV-visible absorption spectra of a solution of 0.5 M 1,5-hexadiene in CCl$_4$ following photoexcitation at 266 nm. The inset key shows selected time delays. Spectra are plotted up to a time delay of 300 ps and the vertical arrows indicate directions of change of the bands.

The absorption features for photo-excited solutions of 1,5-hexadiene in CCl$_4$ evident in Fig. 5 resemble closely those observed for neat CCl$_4$ (Fig. 1) and the time-dependences of the two bands were obtained in a similar way by wavelength-integration of 10-nm wide regions centred at 330 nm and 500 nm for each time delay. The results of this procedure are shown in Fig. 6 for a 0.25 M solution of 1,5-hexadiene in CCl$_4$, and are contrasted with the time-dependences for the neat solvent.
Addition of the solute accelerates the respective decay and growth of the UV and visible bands, and the modified scheme for the solution photochemistry shown in Fig. 7 accounts for these observations. In this scheme, the same processes argued to occur in neat CCl₄ are retained as steps A and B, leading to the formation of the Cl-CCl₄ complex that absorbs at 330 nm. However, the decay of the complex is now governed by chemical reaction between the diene and the Cl-CCl₄ complex (step F) in addition to formation of the *iso*-CCl₃-Cl species (step D, giving the absorption at 500 nm).
Calculations by Phillips and Fang suggested the *iso* species in dichloromethane, *iso*-CH$_2$Cl-Cl, might act as a carbenoid.\(^{27}\) Transfer of a methylene group to a C=C bond makes a cyclopropane species, with a computed energy barrier of 37 kJ mol$^{-1}$ in the case of ethene. Step G proposes a corresponding pathway for reactive loss of *iso*-CCl$_3$-Cl with 1,5-hexadiene, perhaps to form a dichlorocyclopropane species by CCl$_2$ transfer. However, the persistence of the 500-nm band in our data to time delays of 2 ns suggests that this type of reaction is at best slow, which is consistent with the aforementioned energy barrier.

Fig. 7 also incorporates formation of the radical cation of the 1,5-hexadiene, based on evidence from time-resolved IR absorption measurements\(^{29}\) that is summarized in Supporting Information. As noted earlier, the IE of CCl$_4$ (11.47 eV in the gas phase\(^{40}\)) is substantially above the energy of 2 photons of the 266-nm pump laser, but the IE of 1,5-hexadiene (likely to be similar to that of 1,3-trans-pentadiene which is 8.70 ± 0.02 eV\(^ {47}\)) is lower than the energy of 2-photon excited CCl$_4^*$. We therefore suggest excitation transfer from CCl$_4^*$ to the solute causes the observed ionization of the diene. Such ionization processes have been reported previously for solutes with IEs lower than the solvent excitation energy,\(^ {22}\) and must be fast to compete with dissociation step B. The Supporting Information contains an analysis of the time-dependent intensities of three transient IR bands centred at wavenumbers of 1260 cm$^{-1}$, 1350 cm$^{-1}$ and 1460 cm$^{-1}$ that we assign to 1,5-hexadiene$^+$. These bands reach their maximum intensity within a few picoseconds, consistent with the proposed mechanism, but are weak which may be indicative of a minor pathway.
3.2.2 Kinetic analysis of 1,5-hexadiene / CCl₄ and 1,5-hexadiene / CHCl₃ photochemistry

The experimental data for the time dependence of the UV band such as those shown in Fig. 6 were fitted to a model that is based on the Smoluchowski function of Equation (4) for reactions in neat CCl₄ with inclusion of a factor to account for reactive loss in the 1,5-hexadiene solutions. Following Crim and co-workers, we express the time-dependent Cl-CCl₄ absorption signal in the presence of 1,5-hexadiene, $S_t'(UV)$, as a combination of the recombination kinetics, governed by Equation (4) for $S_t(UV)$, and diffusion controlled reaction kinetics: ¹⁴⁻¹⁶

$$S_t'(UV) = S_t(UV) \exp \left\lbrace -4\pi R_{rxn} D_{rxn} C_{solute} \left( 1 + \frac{2R_{rxn}}{\sqrt{\pi D_{rxn}(t-t_0)}} \right) (t-t_0) \right\rbrace + S_\infty \quad (6)$$

Here, $R_{rxn}$ is the reaction radius, within which reaction between Cl-CCl₄ complex and 1,5-hexadiene occurs with unit probability. $C_{solute}$ denotes the concentration of the solute, which is fixed for any one experiment, $D_{rxn}$ is the sum of diffusion constants of the reacting Cl-CCl₄ complex and diene, and $S_\infty$ is a baseline offset evaluated at long time, which is generally found to be small. The value of $D_{rxn}$ is fixed to a value computed from the Stokes-Einstein equation, and depends only on the radii of the reactants. The parameters determining the form of $S_t(UV)$ were obtained for the neat solvent (Section 3.1.2) and we set $k_1 = k_2 = 0 \text{ ps}^{-1}$ hereafter, so the only free parameters in the fits to 1,5-hexadiene / CCl₄ or 1,5-hexadiene / CHCl₃ data are $R_{rxn}$ and the baseline offset.

In place of the definition of $R_{rxn}$ given above, and by analogy to the concept of a reaction cross section, it is also instructive to consider the ratio of $R_{rxn}$ to the sum of the molecular radii of the reactant pair as a measure of the ease of reaction. This ratio will be less than unity (i.e. not all encounters lead successfully to reaction) if reaction is impeded by factors such as an energy barrier, steric constraints, or a transition state that is late along the reaction coordinate. We will return to this point in the later discussion.

Two sets of time-resolved UV-vis absorption spectra were recorded for each concentration of 1,5-hexadiene in CCl₄, and the UV absorption bands in all these six resultant data sets were fitted simultaneously to Equation (6), with appropriate choices of $C_{solute}$. Representative data and a fit are shown in Fig. 6. The decline of the UV-band absorption to zero within 500 ps suggests the Cl-CCl₄ complexes are completely reactively removed if they do not convert to iso-CCl₃-Cl.
In the kinetic analysis of the diene solution data, only the time dependences of the UV bands were fitted for each solution. Table 3 lists the values of parameters derived from the fits, together with those constrained in the fitting process. The bimolecular rate coefficient for reaction of Cl-CCl4 with 1,5-hexadiene, $k_{bi}$, is derived using:\(^\text{(7)}\)

$$k_{bi} = 4\pi R_{rxn}D_{rxn} = (8.6 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

This reaction is likely to involve adduct formation, and in time-resolved IR absorption experiments with solutions of 1,5-hexadiene in CCl4 we were not able to observe production of HCl from either direct H-atom abstraction or an addition-elimination mechanism. The value for the bimolecular rate coefficient is similar to the $k = (9.9 \pm 1.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ reported by Chateauneuf for reaction of Cl with cyclohexene in solution in CCl4.\(^\text{18}\)

<table>
<thead>
<tr>
<th></th>
<th>1,5-hexadiene</th>
<th>isoprene</th>
<th>2,3-dimethylbut-2-ene</th>
<th>n-pentane a</th>
</tr>
</thead>
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<tr>
<td>$D_{ex} / \text{nm}^2 \text{ ns}^{-1}$</td>
<td>1.27</td>
<td>1.69</td>
<td>1.56</td>
<td>1.22</td>
</tr>
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<td>$k_1 / \text{ps}^{-1}$</td>
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<td>0</td>
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<tr>
<td>$A$</td>
<td>0.339</td>
<td>0.339</td>
<td>0.339</td>
<td>0.60 ± 0.04</td>
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<tr>
<td>$B / \text{ns}^{1/2}$</td>
<td>0.115</td>
<td>0.115</td>
<td>0.115</td>
<td>0.072 ± 0.025</td>
</tr>
<tr>
<td>$R_{ex} / \text{nm}$</td>
<td>0.89 ± 0.08</td>
<td>0.75 ± 0.13</td>
<td>1.46 ± 0.09</td>
<td>0.83 ± 0.23</td>
</tr>
<tr>
<td>$k_{ba} / \text{M}^{-1} \text{ s}^{-1}$</td>
<td>$(8.6 \pm 0.8) \times 10^9$</td>
<td>$(9.5 \pm 1.6) \times 10^9$</td>
<td>$(1.7 \pm 0.1) \times 10^{10}$</td>
<td>$(7.7 \pm 2.1) \times 10^9$</td>
</tr>
</tbody>
</table>

Table 3: Parameters derived from Smoluchowski model fits to time-dependent UV band intensities for Cl-CCl4 complexes in solutions of 1,5-hexadiene, isoprene and 2,3-dimethylbut-2-ene in CCl4. a previous work by Sheps et al.\(^\text{14}\) for n-pentane in CCl4. A and B were constrained to values obtained from analysis of data for neat CCl4 (see Table 1) and so uncertainties, which are not specified here, were not propagated into $R_{ex}$ and $k_{ba}$ values. $D_{ex}$ values were computed as described in the text.

The intensities of the UV and visible bands in Fig. 5 merit comparison with those in Fig. 1(a). We observe a decline in relative intensity of the UV band compared to the visible band in the presence of 1,5-hexadiene. The absolute absorbance of the visible band may also be smaller, and we note that Zhang and Thomas reported a reduction in the intensity of their 500-nm signal with increasing solute (cyclohexane) concentration.\(^\text{22}\) These effects can be understood by recalling that some of the Cl-CCl4, which generates signal at 500 nm by decaying to iso-CCl3-Cl, is now instead being consumed by reaction. Moreover, the ionization of the solute relaxes some fraction of the CCl4* precursor of the Cl-CCl4. However, the absolute reduction of the absorbances upon addition of the 1,5-hexadiene must be treated with some caution for
our transient spectra because conditions varied slightly between experiments with different solutions.

3.2.3 Photochemistry of Isoprene / CCl₄ and 2,3-dimethylbut-2-ene / CCl₄ solutions

The Smoluchowski model of Equation (6) was also used to examine the decay of the 330-nm UV absorption band in solutions of 2,3-dimethylbut-2-ene (0.25, 0.50 and 0.75 M, simultaneously fitted) and isoprene (0.64 M only) in CCl₄. The parameters constrained in, and obtained from, these fits are also shown in Table 3. The fit outcomes are compared to prior results from Sheps et al.¹⁴ for reaction of n-pentane in CCl₄, recalling that $R_{\text{rxn}}$ is the key parameter derived from our fits for the reactive removal of Cl-CCl₄.

3.2.4 Comparison of reaction rates and mechanisms

Isoprene and 1,5-hexadiene solutions give similar $R_{\text{rxn}}$ values, suggesting that both proceed via related mechanisms, which we propose involve nearly diffusion limited addition of a Cl atom across a C=C bond to form an adduct that is subsequently stabilized by solvent collisions. For reaction of isoprene with Cl atoms in the gas phase, >80% branching was reported for the adduct-forming channel.¹⁰ The $R_{\text{rxn}}$ value for n-pentane in CCl₄ (0.83 ± 0.23 nm)¹⁴ is similar to those for the two dienes although reaction of this alkane must occur by H-atom abstraction, and the similarities may simply reflect nearly barrierless processes for molecules of similar size. However, the value of $R_{\text{rxn}}$ for 2,3-dimethylbut-2-ene is larger than for the other reactions examined, despite the computed reactant-pair sizes being comparable. We previously reported time-resolved IR studies of this reaction in solution,¹⁹ for which we observed formation of HCl(v=0 and 1) products, indicative of direct abstraction dynamics. We argued that the steric bulk of the four -CH₃ groups might disfavour Cl atom addition to the central C=C bond in this solute, with the support of evidence from gas-phase studies with systematic variation of the substitution around the C=C bond.⁴ The larger $R_{\text{rxn}}$ value is consistent with this argument because it indicates a barrierless abstraction reaction at the periphery of the molecule. The value of $k_{\text{bi}}$ for the 2,3-dimethylbut-2-ene reaction agrees within uncertainties with a prior report by Chateauneuf of $(1.2 \pm 0.7) \times 10^{10}$ M⁻¹ s⁻¹.¹⁸
Contrary to the observations for 2,3-dimethylbut-2-ene, photochemical studies of both 1,5-hexadiene and isoprene solutions in CCl$_4$ using transient IR absorption spectroscopy showed no measurable HCl production.$^{29}$ 2,3-dimethylbut-2-ene has twelve equivalent H atoms, and abstraction of any one of them creates an allylic radical with resonance-stabilized forms. 1,5-hexadiene and isoprene only have four and three such labile H atoms, respectively. Abstraction of the remaining vinylic H atoms by a Cl atom is considerably less energetically favourable. For $n$-pentane there are also twelve H atoms accessible to an attacking Cl atom, and we and others have observed HCl production,$^{14,19}$ but the formation of a primary or secondary alkyl radical co-product by H-abstraction is significantly less exothermic than formation of an allylic radical. Hence, the transition state for abstraction is likely to be later along the reaction coordinate for $n$-pentane, which may account for the smaller value of $R_{rxn}$.

Values of the fit parameters obtained for photochemical reactions of 1,5-hexadiene and isoprene in the two different solvents CHCl$_3$ and in CCl$_4$ are compared in Table 4. The viscosity of chloroform is lower than that of CCl$_4$, giving larger diffusion coefficients for the former solvent. The smaller values of $R_{rxn}$ for reactions of 1,5-hexadiene and isoprene in CHCl$_3$ than in CCl$_4$ may indicate later or higher (but nevertheless modest) barriers to reaction than for the equivalent process in CCl$_4$, perhaps because of greater stability or lower reactivity of the Cl-CCl$_3$ complex than the analogous species in CCl$_4$ solution. Our computed binding energies at the M06-2X/aug-cc-pVTZ level for these two complexes support these suggestions: respective values for Cl-CCl$_4$ and Cl-CHCl$_3$ are -16 kJ mol$^{-1}$ and -11 kJ mol$^{-1}$. In a similar vein, Sheps et al. previously proposed that the Cl-CCl$_4$ complex was more reactive with $n$-pentane than the corresponding Cl-CH$_2$Cl$_2$ species invoked for reactions in dichloromethane,$^{15}$ and Chateauneuf reported significantly faster activation-controlled reaction of Cl-solvent complexes with CH$_2$Cl$_2$ in solution in CCl$_4$ than in neat CH$_2$Cl$_2$.$^{11}$ The smaller disparity between the bimolecular rate coefficients listed in Table 4 than between $R_{rxn}$ values for the two solvents is a result of compensation from the lower viscosity, and hence faster diffusion, in CHCl$_3$.

Table 4: Comparison of the values obtained from Smoluchowski model fits to the time-dependent UV band intensities of Cl-solvent complexes in solutions of 1,5-hexadiene and isoprene in CHCl$_3$ and CCl$_4$. $A$ and $B$ were constrained to values derived from neat solvents, and $D_{exa}$ was calculated as described in the main text. All other parameters were derived from fits to data for 0.5 M solutions.

<table>
<thead>
<tr>
<th></th>
<th>1,5-hexadiene / CHCl$_3$</th>
<th>1,5-hexadiene / CCl$_4$</th>
<th>Isoprene / CHCl$_3$</th>
<th>Isoprene / CCl$_4$</th>
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</thead>
<tbody>
<tr>
<td>$D_{exa}$/ nm$^2$ ns$^{-1}$</td>
<td>2.31</td>
<td>1.27</td>
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</tr>
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<td>$k_1 / \text{ps}^{-1}$</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>---------------------------</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$A$</td>
<td>0.828</td>
<td>0.339</td>
<td>0.828</td>
<td>0.339</td>
</tr>
<tr>
<td>$B / \text{ns}^{1/2}$</td>
<td>0.0087</td>
<td>0.115</td>
<td>0.0087</td>
<td>0.115</td>
</tr>
<tr>
<td>$R_{\text{rea}} / \text{nm}$</td>
<td>0.28 ± 0.14</td>
<td>0.89 ± 0.08</td>
<td>0.56 ± 0.16</td>
<td>0.75 ± 0.13</td>
</tr>
<tr>
<td>$k_{\text{bb}} / \text{M}^{-1} \text{s}^{-1}$</td>
<td>$(4.9 \pm 2.5) \times 10^9$</td>
<td>$(8.6 \pm 0.8) \times 10^9$</td>
<td>$(1.3 \pm 0.4) \times 10^{10}$</td>
<td>$(9.5 \pm 1.6) \times 10^9$</td>
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</table>

### 4. Conclusions

Transient absorption spectra were obtained with picosecond time resolution in the near-UV and visible regions following UV photoexcitation of liquid samples of CCl₄, CHCl₃ and solutions of 1,5-hexadiene, isoprene and 2,3-dimethylbut-2-ene in these chlorinated solvents. The transient absorption spectra show bands centred around 330 nm and 500 nm in both CCl₄ and CHCl₃ that have been reported previously in both 2-photon UV excitation and pulsed radiolysis experiments. The assignment of the UV band to charge-transfer within a Cl-solvent complex is well established, but the carrier of the visible band has been the subject of some debate. In CCl₄, we assign the visible band to $iso$-CCl₃-Cl based on evidence from the time-dependence of the absorption (which grows on a timescale commensurate with the decay of the UV band intensity), TDDFT calculations, and analogous studies in other halogenated solvents. Electronic structure calculations show the $iso$-CCl₃-Cl has >50% charge-separated resonance character, so our assignment is similar in spirit to previous attributions either to a solvent separated ion pair (CCl₃+$\|$Cl$^-$),$^{20,39}$ or a charge-transfer complex (CCl₃$^{5+}$-Cl$^{5-}$) resulting from geminate recombination of CCl₃$^+$ and Cl$^-$ ions.$^{23}$ However, our proposed mechanism for formation of the $iso$-CCl₃-Cl by recombination of neutral, solvated Cl and CCl₃ does not involve separated-ion recombination pathways. Analogous assignments are proposed for the carriers of the corresponding UV and visible bands observed in photoexcited chloroform. The time dependences of the bands were analysed using a model based on Smoluchowski theory, which also incorporates geminate recombination.

Addition of an unsaturated organic solute (1,5-hexadiene, isoprene or 2,3-dimethylbut-2-ene) provides alternative reactive pathways for removal of the Cl-solvent complex, and so the decay of the UV band becomes faster. The dominant reaction pathway involves Cl-adduct formation, with the exception of 2,3-dimethylbut-2-ene for which a direct abstraction
pathway to form HCl competes effectively. Our interpretation of the mechanism for HCl production from our earlier transient IR-absorption study\textsuperscript{19} is reinforced by the current data analysis: a significantly larger reaction radius for Cl-atom reaction with 2,3-dimethylbut-2-ene than for 1,5-hexadiene or isoprene is consistent with a barrierless abstraction reaction at the periphery of the $(\text{CH}_3)_2\text{C}=$C$(\text{CH}_3)_2$ molecule.

Bimolecular rate coefficients for the reactions of Cl atoms with 1,5-hexadiene, isoprene and 2,3-dimethylbut-2-ene in solution in CCl\textsubscript{4} at 294 K are, respectively, $(8.6 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $(9.5 \pm 1.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $(1.7 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, with the latter agreeing within uncertainties with a prior determination by Chateauneuf.\textsuperscript{18} The Cl-Cl\textsubscript{4} complex in CCl\textsubscript{4} solutions has a lower binding energy, and hence is more reactive towards 1,5-hexadiene than the corresponding complex, Cl-CHCl\textsubscript{3}, when CHCl\textsubscript{3} is used as the solvent. A further channel is observed by time-resolved IR spectroscopy that involves ionization of the organic solutes by energy transfer from photoexcited CCl\textsubscript{4}\textsuperscript{*}. However, we do not observe a possible pathway for removal of \textit{iso}-CCl\textsubscript{3}-Cl by addition of CCl\textsubscript{2} across a C=C bond in the 1,5-hexadiene on the timescale of our measurements.

\textbf{Acknowledgements}

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Supporting Information describes the computed structures of the Cl-solvent complexes and the energetics of the isomerisation pathways from CCl\textsubscript{4} to \textit{iso}-CCl\textsubscript{3}-Cl and from CHCl\textsubscript{3} to \textit{iso}-CHCl\textsubscript{2}-Cl. Analysis is reported of the transient infrared absorption bands observed following UV photoexcitation of 1,5-hexadiene solutions in CCl\textsubscript{4} and CDCl\textsubscript{3}. This material is available free of charge via the Internet at http://pubs.acs.org.

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