




Photoreduction of CCl_3F in aqueous solutions containing sulfonated poly(ether etherketone) and formate buffers

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Received: 15 March 2019 / Accepted: 19 May 2019 / Published online: 19 June 2019
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Abstract

Irradiation of aqueous solutions containing the sodium salt of sulfonated poly(ether etherketone) and $\text{HCO}_2\text{H}/\text{HCO}_2^-$ buffers with 350 nm photons induced photoreduction of CCl_3F to CHCl_2F and Cl^- . In situ determinations of chloride ion concentrations enabled evaluation of the quantum yield, $\phi(\text{Cl}^-)$, which amounted to 0.46 in air-free, neutral solutions. A delayed formation of F^- was noticed with a quantum yield of 0.18 probably due to a secondary transformation. High concentrations of the halide ions inhibited somewhat the photoreduction, whereas phase-separated CFC droplets increased the reaction rate. Despite the high quantum efficiencies obtained, no post-irradiation formation of Cl^- occurred. This observation together with other findings indicated that a chain process was not involved in the transformation. Most of the kinetic features of the photoreaction are explained in terms of a mechanism involving radicals of the reactants and of the polymer. Efficient photoreductions of CCl_3F also took place in sulfonated poly(ether etherketone) solutions containing air.

Keywords Photocatalysis · CFCs and HCFCs · Greenhouse gases · Polymeric sensitizer · Photoreduction

Introduction

Light-induced transformations constitute an elegant way to confront the challenges posed by the presence of undesirable chemicals in the environment. In principle these processes offer the possibility of utilizing electromagnetic radiation as the source of energy for the treatment of pollutants. A popular approach has used light-activated semiconducting or mineral particles dispersed in a fluid for the

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photochemical generation of free radicals that attack contaminants [1–4]. Most of the photocatalytic investigations have involved oxidations of organic chemicals in aqueous systems, whereas reductions have received sporadic attention [1, 5–8]. Reductions are appealing due to their ability to initiate the degradation of fully halogenated organic compounds, which resist oxidative pathways. Reductions of highly halogenated chemicals can also be driven in homogeneous systems by means of photoreactive molecules able to generate strongly reducing agents, such as α -hydroxy radicals and $\cdot\text{CO}_2^-$ [9–11]. Photosensitive macromolecular systems capable of inducing redox reactions of pollutants have resulted from incorporation of chromophores into natural and artificial polymers [12]. Systems able to photoinitiate reductions seem particularly attractive given that oxidation processes may compromise the integrity of the macrochains.

Achievement of photoreducing macromolecular systems seemed feasible via selection of polymer blends able to mimic the solution system comprising benzophenone (BP) and 2-propanol, which photogenerates reducing alcohol radicals with high efficiency [13]. Blends of the sodium salt of sulfonated poly(ether etherketone), SPEEK, and poly(vinyl alcohol), PVA, functioned in a similar fashion [14]. SPEEK consists of monomer units containing BP functions that under illumination abstracted H-atoms from PVA chains yielding α -hydroxy radicals of the polyketone called $\cdot\text{SPEEK}$ [15]. The estimated standard oxidation potential for this radical is about 1.3 V [15], enabling reduction of Ag(I), Au(III), Cu(II) and O_2 to take place [14–16]. Subsequent investigations showed that photolysis of SPEEK/PVA solutions induced the reduction of CCl_4 and CHCl_3 ; efficient chain reactions occurred when HCO_2^- ions served as H-atom donors instead of the polyol [17, 18]. The higher efficiencies obtained with formate ions seemed reasonable given that H-atom abstraction from HCO_2^- yields $\cdot\text{CO}_2^-$, a stronger reducing agent than $\cdot\text{SPEEK}$ with $E^0[\cdot\text{CO}_2^-, \text{CO}_2] = 1.9 \text{ V}$ [19].

The previous findings with CCl_4 and CHCl_3 prompted efforts to assess the feasibility of photoreducing CCl_3F (CFC 11) in a similar fashion. The long atmospheric lifetime of CCl_3F has made this CFC an important contributor to ozone depletion, and is also one of the greenhouse gases targeted for elimination from the atmosphere by means of photocatalytic solar updraft technologies [20]. Releases of CCl_3F into the atmosphere continue to occur via migration from underground sites of contamination [21], and more recently due to substantial illegal use of this CFC [22]. Earlier studies showed that illumination of TiO_2 suspensions containing formate buffers initiated chain reductions of CFC 11 [23–25]. Thus, a study was launched to assess the ability of SPEEK as a photocatalyst for the reduction of CCl_3F . Efforts were made to explore the possibility of attaining similar chain processes using solutions of the polymer; the present report is based on kinetic data gathered during the phototransformations of the CFC.

Experimental section

Samples of poly(ether etherketone), PEEK, were provided as gifts by Victrex (films consisting of polymer with an average molar mass of $M_n=4.5\times 10^4$ g mol⁻¹), and Evonik (VESTAKEEP L400P powder, $M_n=5\times 10^4$ g mol⁻¹). PEEK served as the precursor of the Na salt of sulfonated poly(ether etherketone), which was prepared via sulfonation of powders in H_2SO_4 as outlined previously [26]. CCl_3F was purchased from Aldrich, all other chemicals were obtained from VWR. Solutions were prepared from water purified by means of a Milli-Q Biocel system; unless otherwise stated, experiments took place at room temperature. Illuminations were carried out under conditions found previously to yield optimum reductions of CCl_4 and CHCl_3 , namely, using degassed aqueous solutions saturated with halomethane containing 0.018 M SPEEK (in terms of monomer units) and formate buffers with $[\text{HCO}_2^-] + [\text{HCO}_2\text{H}] = 0.38$ M [17, 18]. In these systems formate ions served both as H-atom donors and as an electrolyte required for the potentiometric determination of halide ions.

Given that CFC 11 boils at 23.8 °C, irradiations with 350 nm photons were conducted at 19 °C in a glass photoreactor equipped with a water jacket connected to a Fisher Isotemp 9000 bath circulator. Descriptions of the photoreactor, irradiation set-up and actinometry procedures, as well as of methods for determinations of $[\text{Cl}^-]$ and $[\text{H}^+]$ have been provided previously [17]; similar procedures allowed in situ potentiometric measurements of $[\text{F}^-]$ with a Thermo Scientific ion selective electrode (ISE). Photolytic experiments used 85 mL of solutions bubbled with Ar for 20 min inside sealed photoreactors. After injecting 1 mL of CFC-11, the solutions were equilibrated in the dark for about 5 min, followed by exposure to light under constant stirring. Each irradiation experiment was performed at least twice and the rate data exhibited systematic deviations of 20%. The solubility limit of CCl_3F in water is 8.1 mM (63 μL in 85 mL of H_2O) [27]; two separated liquid phases were noticed due to the excess CFC present in the aqueous SPEEK solutions. Under stirring the CFC was present mainly as small, spherical droplets dispersed throughout the aqueous phase.

Volatile products were detected by withdrawing headspace samples from illuminated solutions; a Shimadzu IR-Prestige-21 apparatus in conjunction with a 10 cm gas cell featuring KBr windows were utilized for FTIR measurements. CO_2 analysis employed a SRI 8610C GC instrument with a TCD detector, a Supelco 60/80 Carboxen 1000 column and He as carrier. Oxalate ions were quantified by means of a Shimadzu Prominence ion chromatograph equipped with a Dionex AS22 column, a Dionex AERS500 ion suppressor and a Shimadzu CCD10A conductivity detector. Runs were carried out under isocratic conditions using a mixture of 4 mM Na_2CO_3 and 1.5 mM NaHCO_3 as eluent.

Results and discussion

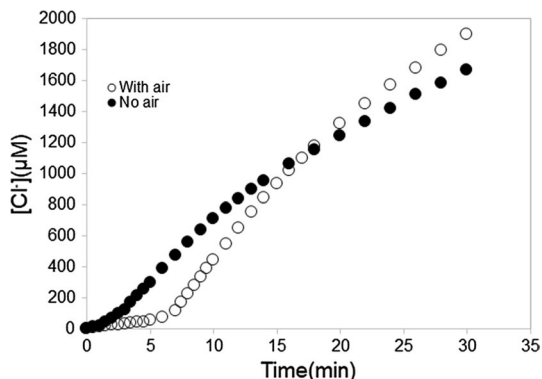
As shown in Fig. 1, exposure of solutions containing SPEEK, formate buffers and CCl_3F to 350 nm photons yielded Cl^- ions. Analogous results were obtained, within experimental error, upon utilization of SPEEK samples made via sulfonation of the

PEEK precursor provided by Evonik [17]. Control experiments performed without one of these components failed to generate halide ions. Excitation of ketones in the presence of chloromethanes is known to produce exciplexes that decay into Cl^- and radicals [28]. Obviously, formation of exciplexes via association of CCl_3F with excited BP groups from SPEEK was not a viable pathway given that no Cl^- was photogenerated in the absence of HCO_2^- . This means that the H-atom donor HCO_2^- was needed to photoreduce the CFC forming Cl^- , as in the cases of CCl_4 and CHCl_3 [17, 18].

The results from Fig. 1 indicate that the CCl_3F photoreduction was feasible in solutions initially with and without air. An important issue is that the degassed solutions also contained a small amount of O_2 given that the CFC injected into the photoreactor was saturated with air. Nevertheless, significant differences were noticed in both systems; for instance initially degassed systems exhibited a rather short initial step (1-2 min) called the induction period. During this period Cl^- generation was slow and irreproducible; because the results followed no simple rate law they were not further analyzed. The length of the induction period decreased with increasing light intensity (I_0), but became longer under conditions leading to slow reactions, such as low pH values. Similar findings were noted during the photoreductions of CCl_4 and CHCl_3 [17, 18], as well as of CCl_3F in TiO_2 suspensions [23, 24]. Induction periods are typical of these photoreactions in which O_2 present in the system can scavenge reducing radicals thereby interfering with the redox process.

Following the induction period, a linear $[\text{Cl}^-]$ increase ensued for 10 - 12 min, but the rate of concentration change decreased at longer times. Similar linear changes in product concentration during illumination have been noticed in prior studies [16–18, 26] and indicate that the CFC reduction was controlled by the fast zero-order photochemical formation of $\cdot\text{SPEEK}$. The slope of the linear concentration increase was equal to the reaction rate, $r(\text{Cl}^-) = d[\text{Cl}^-]/dt$, which then served to calculate the quantum yield of chloride ion formation, $\phi(\text{Cl}^-) = r(\text{Cl}^-)/I_0$. In analogy to the reductions of O_2 , CCl_4 and CHCl_3 [16–18], systematic quantum yields deviations of about 20% were noticed. These deviations can be partly attributed to the rather heterogeneous nature of the concentrated polymer solutions due to association of the macromolecules. Light scattering by the small CCl_3F droplets present in stirred solutions

Fig. 1 Evolution of the chloride ion concentration with time during photolysis of degassed (filled circle) and air-saturated (opened circle) solutions containing 0.018 M SPEEK, 0.36 M HCO_2^- and 1 mL of CCl_3F at pH = 7.3 with $I_0 = 2.2 \times 10^{-6} \text{ M}(\text{h}\nu) \text{ s}^{-1}$



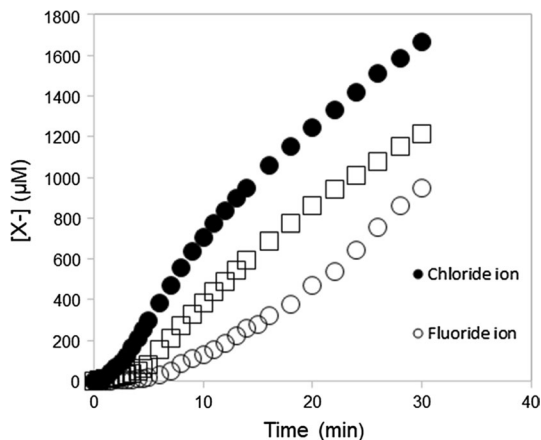
contributed as well to the error. Because the fraction of incident photons experiencing scattering was not accounted during actinometric determinations, the resulting $\phi(\text{Cl}^-)$ represent lower limits of the reduction efficiencies.

Analysis of the linear $[\text{Cl}^-]$ increase in Fig. 1 for degassed solutions yielded $\phi(\text{Cl}^-)=0.46$, which is higher than the efficiency (0.2) for CHCl_3 , but lower than the value (1.37) determined during photolysis of CCl_4 solutions [17, 18]. Such order of reactivity was not totally unexpected given the available thermodynamic data: $E^0[\text{CCl}_4, \cdot\text{CCl}_3, \text{Cl}^-]=-0.23$ V, $E^0[\text{CCl}_3\text{F}, \cdot\text{CCl}_2\text{F}, \text{Cl}^-]=-0.44$ V [29]; the reduction potential for CHCl_3 in ethanol has been estimated at -0.9 V and a similar value is anticipated for aqueous solutions [30]. However, the low $\phi(\text{Cl}^-)$ for the CFC (only 1/3 of the yield determined in the case of CCl_4) appeared odd given the strong reducing nature of both $\cdot\text{SPEEK}$ and $\cdot\text{CO}_2^-$ together with the small difference in reduction potential of the two halomethanes. Hence, the SPEEK-induced photoreduction of CFC 11 seemed to occur via a process different from the chain mechanism operating during the transformation of CCl_4 . The CCl_3F photodehalogenation was also dissimilar from the chain process of the CFC during photolysis of air-free TiO_2 dispersions that featured very large $\phi(\text{Cl}^-)$ values [23].

Illuminations were also conducted in the presence of air but in sealed photoreactors to avoid evaporative loss of the CFC. Typical results are included in Fig. 1 featuring a longer induction period of ~ 6 min as was noticed earlier for CHCl_3 . These observations further support the notion that the length of the induction period increases with increasing $[\text{O}_2]$ but is not a linear function of the amount of oxygen present in solution [16, 17, 23–25]. Evaluation of the subsequent linear increase of $[\text{Cl}^-]$ yielded $\phi(\text{Cl}^-)=0.74$, a value 50% higher than the quantum yield determined without air. Sub-linear $[\text{Cl}^-]$ changes were observed at longer irradiation times, which were still faster than those detected in air-free systems. Interestingly, the CCl_3F photoreduction in TiO_2 suspensions yielded analogous results, with $\phi(\text{Cl}^-)$ being twice as large in the presence than in the absence of air [24, 25]. Reduction of CFC 11 generates $\cdot\text{CCl}_2\text{F}$, a species known to form $\cdot\text{O}_2\text{CCl}_2\text{F}$ through reaction with oxygen [31]. As shown for isoflurane [32], alkylperoxyl radicals decay via reaction with $\cdot\text{O}_2^-/\cdot\text{HO}_2$ generating additional Cl^- ions. The higher dehalogenation yields of CCl_3F in O_2 -containing suspensions were partly rationalized on the basis of a similar $\cdot\text{O}_2\text{CCl}_2\text{F}$ decay [25], and can also account for the results with air-saturated solutions of Fig. 1. In contrast, the CHCl_3 photoreduction in air-saturated SPEEK solutions was slower than in the absence of O_2 , $\phi(\text{Cl}^-)=0.12$ [18]. Also, the CCl_4 photoreaction in air-saturated solutions featured a 30-min-long induction period and a subsequent retardation induced by O_2 that persisted for long times [17]. Hence, CCl_3F is the only halomethane tested so far exhibiting a more efficient reaction with than without air.

Fluoride ions were detected as well during the photoreduction of CCl_3F , Fig. 2 depicts a comparison of the kinetic data for the Cl^- and F^- generation in air-free solutions. Reproducible formation of F^- was noticed only at times ≥ 6 min of exposure and proceeded with a linear increase in $[\text{F}^-]$ for about 10 min with $\phi(\text{F}^-)=0.18$, but an accelerating change in concentration ensued thereafter. The data indicated that significant changes in $[\text{F}^-]$ were obtained only after about 0.4 mM Cl^- was already present. The accelerated $[\text{F}^-]$ increase at longer times also supports the

Fig. 2 Changes in the concentration of halide ions as a function of time during illumination of air-free solutions containing 0.018 M SPEEK, 0.36 M HCO_2^- and 1 mL of CCl_3F at $\text{pH}=7.3$ with $I_0=2.2\times 10^{-6}\text{ M}(\text{h}\nu)\text{ s}^{-1}$; (filled circle) Cl^- , (opened circle) $[\text{F}^-]$ and (opened square) when 0.6 mM F^- was initially present

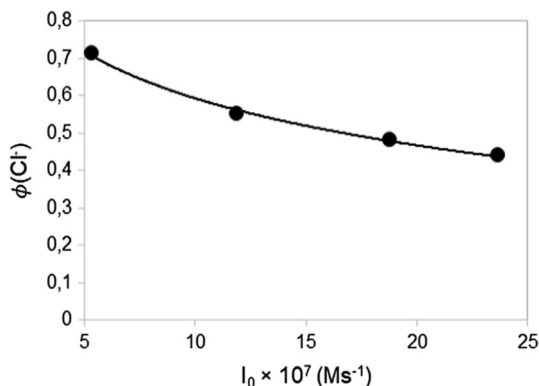


notion that fluoride was mainly a secondary product formed when the initial product of the CCl_3F photoreaction (CHCl_2F see below) experienced reduction by $\cdot\text{SPEEK}$. A close inspection of Fig. 2 revealed that $[\text{Cl}^-]$ ceased to increase linearly with time after $\sim 0.6\text{ mM}$ Cl^- was formed, suggesting that the halide ions inhibited the photoreaction. An analogous retardation effect was noticed for the slow photodechlorination of CHCl_3 [18], but not during the faster CCl_4 reduction [17].

To test the occurrence of an inhibiting effect, experiments were conducted in which degassed CFC-11 solutions initially containing 0.6 mM Cl^- , or F^- , were exposed to light. Included in Fig. 2 is the evolution of $[\text{Cl}^-]$ in the presence of F^- , nearly identical results were obtained when the solution contained initially chloride ions (data not shown). The results of Fig. 2 clearly demonstrated that partial inhibition of the CCl_3F reduction took place; the induction period increased to about 4 min, whereas $\phi(\text{Cl}^-)$ decreased to 0.36 when either Cl^- or F^- were initially present. Photochemical formation of α -hydroxy radicals involves H-atom abstraction from a donor by the triplet excited state of BP (${}^3\text{BP}^*$) [13]. Quenching ${}^3\text{BP}^*$ inhibits such process and Cl^- is a modest quencher with a quenching rate constant of $k_q=2.2\times 10^5\text{ M}^{-1}\text{ s}^{-1}$ [33]. An analogous process explains the CFC data in which Cl^- , and also F^- , quenched the excited BP groups from SPEEK and retarded the photoreduction. Inhibition became noticeable only after significant amounts of Cl^- and F^- were present, implying that the halide ions were moderate quenchers.

Depicted in Fig. 3 is the efficiency of photoreduction as a function of light intensity for degassed CCl_3F solutions. As anticipated for reactions involving free radicals, $\phi(\text{Cl}^-)$ increased with decreasing I_0 whereas the induction became shorter with larger photon fluxes. Higher light intensities favor radical combinations that decrease the rate of product formation. However, only a modest increase in $\phi(\text{Cl}^-)$ of 61% was observed when I_0 decreased from $2.4\times 10^{-6}\text{ M}(\text{h}\nu)\text{ s}^{-1}$ to $5.4\times 10^{-7}\text{ M}(\text{h}\nu)\text{ s}^{-1}$. As a comparison, a similar variation in photon flux increased $\phi(\text{Cl}^-)$ by 200% during the SPEEK-induced reduction of CHCl_3 , even though such reaction proceeded through a rather inefficient chain process [18]. The efficient free radical chain reduction of CCl_4 exhibited a linear dependence of quantum yield with $(I_0)^{-0.5}$ [17]. Such

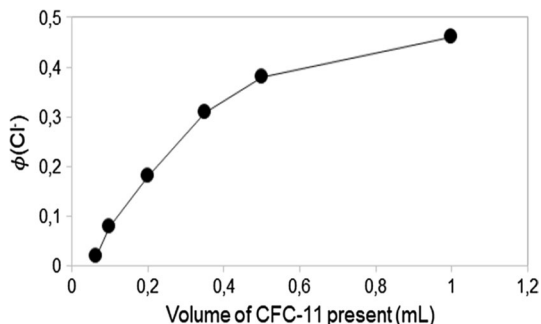
Fig. 3 Dependence of quantum yield of Cl^- formation with light intensity for Ar-saturated solutions at $\text{pH}=7.3$ containing 0.018 M SPEEK, 0.36 M HCO_2^- and 1 mL of CCl_3F



relationship is indicative of second-order terminations between chain carriers [34], but a plot of the $\phi(\text{Cl}^-)$ values displayed in Fig. 3 versus $(I_0)^{-0.5}$ was only approximately linear. Thus, the experiments based on light intensity effects provided no convincing evidence that CCl_3F was photoreduced by SPEEK through a chain process.

Portrayed in Fig. 4 is the evolution of $\phi(\text{Cl}^-)$ with increased volume of CFC 11 added to 85 mL of air-free SPEEK/ HCO_2^- solutions. The lowest volume of CCl_3F used (63 μL) corresponded to the solubility limit in water of 8.1 mM; above this quantity the excess CFC existed as a liquid phase-separated from the aqueous solutions. At the solubility limit $\phi(\text{Cl}^-)$ was only 0.02, but the quantum yield augmented smoothly with increasing CCl_3F excess up to 0.46 at the highest volume employed. Analogous trends were noticed in several chain photoreductions of halomethanes, such as the SPEEK-initiated chain reduction in solutions with excess CHCl_3 [18]. Another case was the photoreaction in illuminated TiO_2 suspensions containing CFC-11 amounts above the solubility limit [25]. In fact, the data of Fig. 4 was anticipated to parallel closely the results from photolyzed titania suspensions as both systems featured similar experimental conditions. However, divergent results were obtained as the SPEEK system always exhibited low $\phi(\text{Cl}^-)$ values, which increased 22 times when the volume of CCl_3F was incremented by a factor of 16. On the other hand, $\phi(\text{Cl}^-)$ values > 1 were always found for TiO_2 suspensions but the yields increased by a factor of only 4 upon incrementing the CFC excess [25].

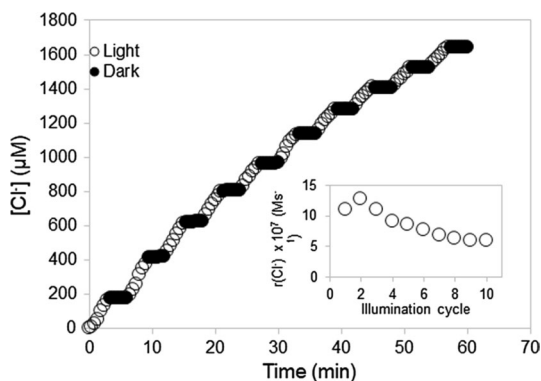
Fig. 4 Variation in the quantum yield of Cl^- formation with volume of CFC-11 added to 85 mL of degassed solutions at $\text{pH}=7.3$ containing 0.018 M SPEEK, 0.36 M HCO_2^- , $I_0=2.3 \times 10^{-6} \text{ M(h\nu)} \text{ s}^{-1}$



The earlier results from TiO_2 dispersions clearly showed that the CCl_3F droplets contributed to the chain photoreaction. Such observations were rationalized by means of a model for reactions between species confined to different liquid phases [35]. In this model, CFC molecules present within the interfacial region between organic phase and aqueous solution participated in a chain propagation reduction involving $\cdot\text{CO}_2^-$. Thus, augmenting the volume of excess CFC incremented the number (not the size) of the droplets, thereby increasing proportionally the interfacial area and enhancing the quantum yield of Cl^- . The model predicted a linear dependence of $1/\phi(\text{Cl}^-)$ and the reciprocal of the CFC volume, $(V_{\text{CFC}})^{-1}$, which was experimentally observed [25]. Interestingly, the findings of Fig. 4 implied that CCl_3F molecules within the droplets also participated in the SPEEK-initiated photoreaction. However, the data failed to follow the predicted linear relationship between $1/\phi(\text{Cl}^-)$ and $(V_{\text{CFC}})^{-1}$. This failure and the divergent results mentioned above were not consistent with a chain process operating during the photoreduction of CCl_3F induced by SPEEK.

Convincing evidence that photoreductions of several halomethanes involved free radical chain mechanisms was obtained from post-irradiation experiments, consisting of lengthy $[\text{Cl}^-]$ increases after photolysis was terminated due to chain propagations that persisted in the dark. [17, 18, 25]. Figure 5 illustrates results from a post-irradiation experiment on an Ar-saturated SPEEK/ HCO_2^- solution containing CCl_3F subjected to periodic illumination cycles each involving a 3-min light exposure followed by a dark period of the same length. While Cl^- was clearly formed during each light-exposure, halide ion generation was insignificant in the subsequent dark periods. These observations indicated that a chain process was not relevant for the SPEEK-initiated CFC 11 photoreduction. Presented in the inset of Fig. 5 is the evolution of $r(\text{Cl}^-)$ with increasing number of periodic illuminations; the rate decreased from $13 \mu\text{M s}^{-1}$ to about $1/2$ of this value after 10 cycles. Similar rates were determined for the CCl_3F reduction in TiO_2 dispersions, but production of Cl^- continued after illumination was interrupted [25]. The post-irradiation reaction occurred because radical chain carriers formed on the oxide surface were able to escape into the aqueous phase thereby avoiding fast recombination processes. This, in turn, enabled propagation of reductive chains in the solution bulk and dark formation of Cl^- .

Fig. 5 Evolution of $[\text{Cl}^-]$ during alternating illumination (opened circle) and dark periods (filled circle) of an air-free solution with 0.018 M SPEEK, 0.36 M HCO_2^- , 1 mL of CCl_3F at $\text{pH}=7.3$, $I_0=2.3 \times 10^{-6} \text{ M}(\text{h}\nu)^{-1} \text{ s}^{-1}$. The inset depicts the rate of Cl^- formation during the illumination period of each cycle

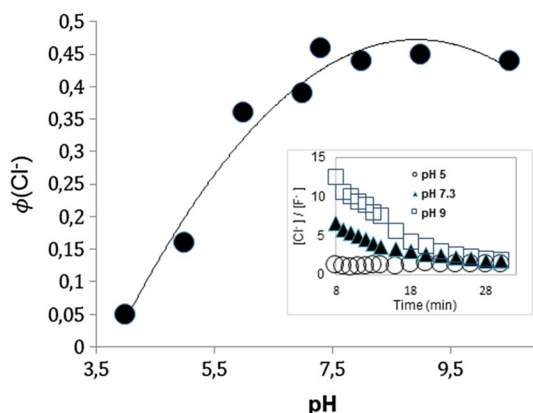


Hence, the data of Fig. 5 means that CCl_3F was reduced mainly in regions next to the SPEEK chains, where efficient chain propagation was restricted.

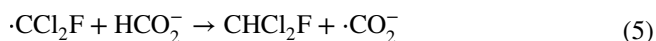
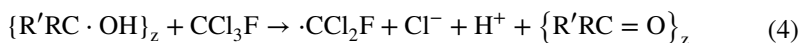
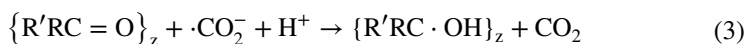
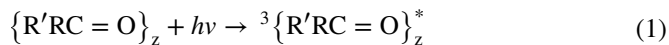
According to Fig. 6 systematic decreases in $[\text{H}_3\text{O}^+]$ induced a continuous increase in $\phi(\text{Cl}^-)$ until a value of 0.46 was attained in solutions that were neutral or slightly alkaline. The induction period followed the opposite trend, decreasing from about 22 min at $\text{pH}=4.1$ to 1–2 min at $\text{pH}>7$. Interestingly, the results of Fig. 6 are drastically different from the $\phi(\text{Cl}^-)$ evolution with pH noticed for the chain photoreductions of CCl_4 and CHCl_3 [17, 18]. Both photoreactions exhibited sharp $\phi(\text{Cl}^-)$ increases in near neutral solution leading to a maximum at $\text{pH}=7.3$, followed by a steep decrease thereafter. On the other hand, a trend analogous to that shown in Fig. 6 resulted for the efficiency of the O_2 photoreduction to H_2O_2 as a function of pH in SPEEK solutions containing air, which was not a chain process [16]. An apparent difference was that the CCl_3F reduction exhibited $\phi(\text{Cl}^-)$ values 20 times higher than the yields of peroxide formation, $\phi(\text{H}_2\text{O}_2)$. However, such difference was not unexpected since the solubility of CFC 11 is 31 times higher than that of O_2 , enabling CCl_3F to scavenge a higher fraction of the generated SPEEK. Also, reduction of oxygen required two polymer radicals whereas only one was needed to generate Cl^- from CCl_3F . Hence, the similar evolution of $\phi(\text{Cl}^-)$ and $\phi(\text{H}_2\text{O}_2)$ as a function of pH provided further support to the notion that CFC-11 was photoreduced via a non-chain process.

Additional analytical data were gathered from degassed CCl_3F solutions at $\text{pH}=7.3$ exposed to light for 30 min. IC determinations on such solutions revealed the presence of 0.65 mM oxalate ions with $\phi=0.16$. Headspace samples withdrawn from the illuminated solutions enabled detection of volatile products; GC analysis indicated formation of CO_2 during the photoreaction. FTIR data included signals at 3023 and 2123 cm^{-1} , which are characteristic of CHCl_2F (HCFC 21) [36]. These findings firmly established HCFC 21 as the main halomethane product given that such signals are absent in the spectrum of CCl_3F (<https://webbook.nist.gov/>). Air-free SPEEK/ HCO_2^- solutions containing CFC-11 turned yellow after extensive photolysis due to a uniform absorbance increase at $\lambda>360$ nm. Similar observations resulted during the photoreductions of CHCl_3 and CCl_4 due to formation of LAT

Fig. 6 Efficiencies of Cl^- formation as a function of pH for Ar-saturated solutions with 0.018 M SPEEK, 0.36 M HCO_2^- , 1 mL of CCl_3F and $I_0=2.3 \times 10^{-6} \text{ M}(\text{h}\nu) \text{ s}^{-1}$. Shown in the inset are ratios of $[\text{Cl}^-]$ to $[\text{F}^-]$ for solutions at (opened square) $\text{pH}=9$, (filled triangle) $\text{pH}=7.3$ and (opened circle) $\text{pH}=5$



(light absorbing transients) [18]. LAT were identified as products from combination of α -hydroxy radicals with the BP radical [37]. In the SPEEK/ HCO_2^- system LAT probably formed via reaction of $\cdot\text{CO}_2^-$ with SPEEK \cdot given that prior ESR results established these species as important intermediates generated by illumination [18]. The following mechanism accounts well for most of the observations:



Earlier attempts to understand the photochemistry of SPEEK systems using only fluid phase kinetics were unsuccessful as this polyelectrolyte forms complex structures via chain entanglement/aggregation [16–18]. Nonetheless, for ease of presentation, the mechanism was written as consisting of elementary reactions in homogeneous solution. In the simple notation used $\{\text{R}'\text{RC} = \text{O}\}_z$, ${}^3\{\text{R}'\text{RC} = \text{O}\}_z^*$ and $\{\text{R}'\text{RC} \cdot \text{OH}\}_z$ stand for SPEEK, a triple excited BP group of the polymer and $\cdot\text{SPEEK}$, respectively. In the radical formula, only one unpaired electron was anticipated to be present per polymer chain. The basic mechanistic features have been analyzed thoroughly before [17, 18]; the present discussion focuses exclusively on aspects relevant to the reduction of CFC-11. Step 6 summarizes three possible second-order processes that consume radicals: dimerization of $\cdot\text{CO}_2^-$ forming oxalate ions ($\text{R} = \text{R}' = \cdot\text{CO}_2^-$), formation of LAT ($\text{R} \cdot = \{\text{R}'\text{RC} \cdot \text{OH}\}_z$, $\text{R}' \cdot = \cdot\text{CO}_2^-$) and combination/disproportionation of $\cdot\text{SPEEK}$ ($\text{R} \cdot = \text{R}' \cdot = \{\text{R}'\text{RC} \cdot \text{OH}\}_z$).

As mentioned before, occurrence of step 2 has been corroborated by results from EPR experiments [18]. Step 3 or reduction of CFC-11 by $\cdot\text{CO}_2^-$ were possible routes for the CO_2 generation, but the latter reaction occurs with a rate constant of only $7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ [23]. In contrast, the rate constant for step 3 is likely to be similar to that for the reaction of 4-carboxybenzophenone with $\cdot\text{CO}_2^-$, $k = 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [38]. These rate constants together with the fact that the concentration of BP groups present in SPEEK is much larger than $[\text{CCl}_3\text{F}]$ suggested a preferential CO_2 formation through step 3, and not via reaction of $\cdot\text{CO}_2^-$ with CFC-11. Considering step 4 as the only reaction yielding Cl^- , the results obtained at different acidities implied that the quantum yield of $\cdot\text{SPEEK}$ generation, $\phi(\cdot\text{SPEEK})$, was a function of pH. Obviously, efficient $\cdot\text{SPEEK}$ formation accelerated the elimination of O_2 traces left after Ar-bubbling, and also increased $r(\text{Cl}^-)$. Such conclusion is fully supported by evidence indicating that $\phi(\cdot\text{SPEEK})$ diminished progressively as $[\text{H}_3\text{O}^+]$ increased

[16]. The observed trend was not surprising as H_3O^+ quenches $^3\text{BP}^*$ fast via energy transfer, $k_q = 6.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [39]. The findings of Fig. 6 imply that physical quenching of $^3\{\text{R}'\text{RC}=\text{O}\}_z^*$ by H_3O^+ was in competition with step 2. Quenching was probably assisted by electrostatic attractions between hydronium ions and SPEEK macromolecules, which possess an average of 156 SO_3^- anionic groups per chain.

Photolysis of neutral, air-free SPEEK solutions containing either PVA or HCO_2^- as H-atom donors resulted in a small fraction of polymer radicals that persisted for several min at room temperature in the absence of air [14, 17]. Detection of the persisting radicals by optical means is straightforward given that $\cdot\text{SPEEK}$ exhibits a strong absorption centered at 565 nm. However, the radical signal was not detected when air-free SPEEK/ HCO_2^- solutions containing CCl_3F were exposed to light, supporting the occurrence of step 4. The rate constant for step 4 remains unknown but is probably lower than the value for the CCl_4 reduction by $(\text{CH}_3)_2\text{C}\cdot\text{OH}$, $k = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [40]. A slower reduction of CCl_3F by $\cdot\text{SPEEK}$ seems reasonable since macromolecular α -hydroxy radicals (such as those of PVA) are less mobile than the prototypical molecular radical $(\text{CH}_3)_2\text{C}\cdot\text{OH}$ [41]. Detection of CHCl_2F supported the occurrence of step 5, which proceeds with a rate constant of only $2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ [23]. The presence of oxalate ions in irradiated solutions provided evidence that $\cdot\text{CO}_2^-$ was photogenerated and that dimerization of these species occurred; step 6 takes place in homogeneous solution with $k = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [40]. According to the data of Fig. 1, about 3.4 mM of halide ions were generated after 30 min of photolysis, whereas the $[\text{O}_2\text{C}\cdot\text{CO}_2^-]$ determined at that time implied that 1.3 mM $\cdot\text{CO}_2^-$ dimerized. Thus, the rest of the photogenerated $\cdot\text{CO}_2^-$ reduced SPEEK and/or reacted via step 6 producing LAT.

Further observations not explicitly addressed by the mechanism are those involving formation of fluoride ions. Interestingly, the linear increase of $[\text{F}^-]$ delayed from that of $[\text{Cl}^-]$ by several minutes (see Fig. 2) also occurred at all pH values. At $\text{pH} \geq 6$ the efficiency of Cl^- generation was between three and four times the value for F^- . Solutions with lower pH values yielded $\phi(\text{Cl}^-)/\phi(\text{F}^-)$ ratios closer to one because their extended induction periods, together with their low reaction rates, limited formation of the halide ions. The inset of Fig. 6 shows $[\text{Cl}^-]/[\text{F}^-]$ values plotted as a function of time for solutions at different pH values. Displayed are results obtained at $t \geq 8$ min of illumination, which according to Fig. 2 is the period at $\text{pH} = 7.3$ in which F^- was generated most efficiently. This procedure also eliminated most of the contribution due to the induction periods where reproducibility was an issue. In solutions at $\text{pH} = 5$ the initial $[\text{Cl}^-]/[\text{F}^-]$ ratio of about 1 increased abruptly to 1.4 after 18 min (the end of the induction period), and decreased thereafter. More pronounced changes were noticed at $\text{pH} = 7.3$ since $[\text{Cl}^-]/[\text{F}^-]$ decreased from about 7 at short times to 1.7 after 30 min of illumination. An even larger drop in $[\text{Cl}^-]/[\text{F}^-]$ occurred at $\text{pH} = 9$ from 13 to 1.9 at the end of the illumination.

Vastly different observations resulted from the chain photoreduction of CFC-11 in neutral TiO_2 suspensions containing HCO_2^- [23]. In such systems $[\text{Cl}^-]/[\text{F}^-]$ jumped abruptly from initial values of 3–7 to above 150 in 10 min, and continued to rise slowly thereafter. Efficient chain propagations operated in the suspensions that generated Cl^- fast while F^- was formed through the infrequent termination step. The divergent

findings of the CCl_3F photoreduction initiated by SPEEK confirmed that chain processes were not operative in the polymer system. Furthermore, the delayed F^- generation together with the higher formation efficiency at longer times suggested that a different phototransformation turned dominant under extended illumination. A similar change took place during the O_2 photoreduction in unstirred SPEEK solutions, where initially formed H_2O_2 was consumed efficiently upon further photolysis [16]. Given that α -hydroxy radicals reduce O_2 in water faster than H_2O_2 [40], these observations were inconsistent with processes governed by homogeneous kinetics.

In fact, SPEEK-initiated photoreductions of numerous oxidizers (including metal ions, oxygen as well as chloromethanes) exhibited some kinetic features divergent from those typical of reactions taking place in homogeneous solution [14, 16–18]. These differences were analyzed extensively and can be explained under the assumption that SPEEK solutions behave, to some extent, as heterogeneous systems. Heterogeneities are feasible for polymer solutions in the semidilute range of concentrations characterized by chain overlap and entanglement, which prevail above the overlap concentration (c^*) [42]. Evaluation of c^* for SPEEK yielded 0.19 wt% while the concentration of polymer used in photochemical experiments was 0.7 wt% [18]. Thus, formation of heterogeneous polymer structures via chain entanglement seemed reasonable for the highly concentrated SPEEK solutions. For polyelectrolytes, the presence of structures due to chain aggregation was inferred from observations from concentrated solutions but such interpretation remains controversial [43]. Nevertheless, involvement of SPEEK structures provides a simple way to account for the results of the O_2 photoreduction [16]. H_2O_2 formed with participation of O_2 and radicals present within a polymer structure. If exchange of the generated H_2O_2 by O_2 from the surrounding solution occurred slowly, then [peroxide] increased while [oxygen] decreased in the SPEEK structure. Under such conditions the reaction of H_2O_2 with $\cdot\text{SPEEK}$ became competitive with the oxygen reduction.

The delayed formation of F^- displayed in Fig. 2 and the decreasing $[\text{Cl}^-]/[\text{F}^-]$ values shown in the inset of Fig. 6 suggest that part of the CCl_3F photoreduction took place within structures of the polyelectrolyte. A slow exchange of CHCl_2F formed in an SPEEK structure with CCl_3F from the surrounding medium would have enabled [HCFC 21] to increase locally. This, in turn, allowed the reduction of CHCl_2F to compete with that of CFC-11. While such rationalization seems reasonable, the required slow exchange of chemicals between polyelectrolyte structures and surrounding solution is not easily justified. A more important question pertains the inability of the SPEEK system to induce a chain reduction of CCl_3F although such processes took place in the cases of CCl_4 and CHCl_3 . In contrast, a highly effective chain dehalogenation of CFC-11 was induced in illuminated TiO_2 suspensions containing HCO_2^- [23]. Obviously, the efficient chain propagations achieved in the titania suspensions were not sustainable in the polymer system.

Conclusions

An effective photoreduction of CCl₃F to form CHCl₂F took place in air-free, neutral aqueous solutions containing SPEEK as sensitizer and formate buffers as H-atom donors. The photodehalogenation yielded Cl⁻ ions in a continuous fashion whereas F⁻ formation was delayed, suggesting that fluoride resulted from a secondary process. Linear increases in the concentration of products with time were noticed at the early stages of the photoreactions. The zeroth-order kinetics indicated that the reaction was controlled by the initial photoprocess leading to ·SPEEK formation in a way analogous to the reductions of O₂, CCl₄ and CHCl₃ [16–18]. Kinetic results from a variety of experiments provided strong evidence that no chain process was involved in the photoreaction of CCl₃F. In fact, the photodehalogenation exhibited kinetic features that differed significantly from those of the chain reduction of the CFC in illuminated TiO₂ suspensions [23]. Nevertheless, a quantum yield of $\phi(\text{Cl}^-) = 0.46$ resulted in neutral solutions, which is the highest observed thus far for non-chain reductions initiated by SPEEK. Photoreduction of CCl₃F also took place in air-saturated solutions with $\phi(\text{Cl}^-) = 0.74$, that is 50% higher than in the absence of O₂. Thus, SPEEK-based materials may be useful in novel strategies for removal of undesired chemicals, such as CCl₃F, that contribute to atmospheric pollution [20].

Acknowledgements We were privileged to participate in this special issue honoring the career of Prof. Anna Eremenko and want to extend our best wishes of further success in her future endeavors. The authors are grateful to R. Leibfried (Victrex, USA) and to N. Negandhi (Evonik, USA) for generous gifts of PEEK samples, as well as to the Department of Chemistry & Biochemistry, Auburn University, for partial support of this work.

References

1. M.A. Henderson, *Surf. Sci. Rep.* **66**, 185 (2011)
2. R. Nguyen, P.E. Hoggard, *Curr. Catal.* **3**, 323 (2014)
3. J. Li, F. Wu, G. Mailhot, N. Deng, *J. Hazard Mater.* **174**, 368 (2010)
4. E.A. Ustinovich, D.G. Shchukin, D.V. Sviridov, *J. Photochem. Photobiol. A* **175**, 249 (2005)
5. M.A. Valenzuela, E. Albitzer, O. Ríos-Berny, I. Córdova, S.O. Flores, *J. Adv. Oxid. Technol.* **13**, 321 (2010)
6. P.E. Hoggard, A. Maldotti, *J. Catal.* **275**, 243 (2010)
7. B.A. Balko, P.G. Tratnyek, *J. Phys. Chem. B* **102**, 1459 (1998)
8. S.Y. Kuchmii, S.V. Kulik, A.V. Korzhak, A.I. Belous, A.I. Kryukov, *Theor. Exp. Chem.* **25**, 627 (1989)
9. H. Li, E.A. Betterton, R.G. Arnold, W.P. Ela, B. Barbaris, C. Grachane, *Environ. Sci. Technol.* **39**, 2266 (2005)
10. M. Maldotti, L. Andreotti, A. Molinari, G. Varani, G. Cerichelli, M. Chiarini, *Green Chem.* **3**, 42 (2001)
11. P.L. Huston, J.J. Pignatello, *Environ. Sci. Technol.* **30**, 3457 (1996)
12. M. Nowakowska, K. Szczubialka, *Polym. Degrad. Stab.* **145**, 120 (2017)
13. A. Gilbert, J. Baggott, *Essentials of Molecular Photochemistry* (CRC Press, Boca Raton, 1991), p. 287
14. A.S. Korchev, T.S. Shulyak, B.L. Slaten, W.F. Gale, G. Mills, *J. Phys. Chem. B* **109**, 7733 (2005)
15. A.S. Korchev, T. Konovalova, V. Cammarata, L. Kispert, B.L. Slaten, G. Mills, *Langmuir* **22**, 375 (2006)

16. B.K. Little, P. Lockhart, B.L. Slaten, G. Mills, *J. Phys. Chem. A* **117**, 4148 (2013)
17. J.R. Black, M.S. Islam, H.L. Carmichael, B.L. Slaten, B.K. Little, G. Mills, *J. Phys. Chem. A* **121**, 3918 (2017)
18. M.S. Islam, E.C. Duin, B.L. Slaten, G. Mills, *J. Phys. Chem. A* **122**, 7118 (2018)
19. H.A. Schwarz, R.W. Dobson, *J. Phys. Chem.* **93**, 409 (1989)
20. R. De Richter, T. Ming, S. Caillol, W. Liu, *Int. J. Greenh. Gas Control* **49**, 449 (2016)
21. P. Höhener, D. Werner, C. Balsinger, G. Pasteris, *Crit. Rev. Environ. Sci. Technol.* **33**, 1 (2003)
22. S.A. Montzka, G.S. Dutton, P. Yu, E. Ray, R.W. Portmann, J.S. Daniel, L. Kuijpers, B.D. Hall, D. Mondeel, C. Sisso, J.D. Nance, M. Rigby, A.J. Manning, L. Hu, F. Moore, B.R. Miller, J.W. Elkins, *Nature* **557**, 413 (2018)
23. R.L. Calhoun, K. Winkelmann, G. Mills, *J. Phys. Chem. B* **105**, 9739 (2001)
24. K. Winkelmann, R.L. Calhoun, G. Mills, *J. Phys. Chem. A* **110**, 13827 (2006)
25. K. Winkelmann, R.L. Calhoun, G. Mills, *J. Phys. Chem. C* **116**, 2829 (2012)
26. P. Lockhart, B.K. Little, B.L. Slaten, G. Mills, *J. Phys. Chem. A* **120**, 3867 (2016)
27. A.L. Horvath, *Halogenated Hydrocarbons: Solubility-Miscibility with Water* (Marcel Dekker, New York, 1982), p. 661
28. A. Gáplovsky, J. Donovalová, P. Hrcniar, P. Hrdlovic, *J. Photochem. Photobiol. A* **49**, 339 (1989)
29. D.M. Stanbury, *Adv. Inorg. Chem.* **33**, 69 (1989)
30. S.M. Bonesi, R. Erra-Balsells, *J. Chem. Soc. Perkin Trans.* **2**, 1583 (2000)
31. Z.B. Alfassi, S. Mosseri, P. Neta, *J. Phys. Chem.* **91**, 3383 (1987)
32. R. Flyunt, O. Makogon, S. Naumov, C. Schöneich, K.-D. Asmus, *J. Phys. Chem. A* **111**, 11618 (2007)
33. H. Shizuka, H. Obuchi, *J. Phys. Chem.* **86**, 1297 (1982)
34. E.S. Huysen, *Free-Radical Chain Reactions* (Wiley-Interscience, New York, 1970), p. 31
35. B.G. Cox, *Modern Liquid Phase Kinetics, Chapter 6*, vol. 21 (Oxford Press, New York, 1994)
36. H.B. Weissman, A.G. Meister, F.F. Cleveland, *J. Chem. Phys.* **19**, 72 (1958)
37. A. Demeter, T. Bérces, *J. Photochem. Photobiol. A* **46**, 27 (1989)
38. G.L. Hug, M. Bonifacic, K.-D. Asmus, D.A. Armstrong, *J. Phys. Chem. B* **104**, 6674 (2000)
39. M. Ramseier, P. Senn, J. Wirz, *J. Phys. Chem. A* **107**, 3305 (2003)
40. P. Neta, J. Grodkowski, A.B. Ross, *J. Phys. Chem. Ref. Data* **25**, 709 (1996)
41. P. Ulanski, K. Bothe, J.M. Rosiak, C. von Sonntag, *Makromol. Chem. Phys.* **159**, 1443 (1994)
42. I. Teraoka, *Polymer Solutions: An Introduction to Physical Properties, Chapters 1 and 4* (Wiley, New York, 2002)
43. M. Sedláč, in *Physical Chemistry of Polyelectrolytes*, ed. by T. Radeva (Marcel Dekker, New York, 2001), p. 1

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