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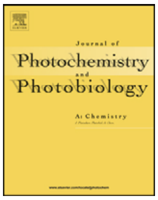

Participation of a heterolytic path in the photochemistry of chlorobenzene

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ABSTRACT

The photochemistry of chlorobenzene in different media has been studied in the presence of oxygen as well as of allyltrimethylsilane and benzene. These are selective traps of the phenyl radical and of the phenyl cation, respectively. Photo-homolysis is a primary process, under most conditions the main processes. However, in an acidic alcohol such as 2,2,2-trifluoroethanol (TFE), this is substituted by photoheterolysis, though with a lower efficiency.

1. Introduction

Haloaromatics are among the most ubiquitous and persistent pollutants [1–5] and their fate in the environment is a matter of concern. Photochemistry appears to contribute significantly to abiotic degradation paths and this has favored research in the field. In particular, the photochemistry of the simplest haloaromatic, chlorobenzene (**1**) has been repeatedly investigated during the last decades [6–12] and indeed has originated intriguing mechanistic issues.

To summarize, the irradiation of **1** under various conditions causes mainly two processes, reduction to benzene and, in nucleophilic solvents (e.g. alcohols), solvolysis. Notice that both of these involve the labilization of the C–Cl bond, not an expected reaction from the initially formed $\pi\pi^*$ states. This point has been investigated in depth by experimental [13–16] and computational studies [17–21]. In this way, the viability of homolytic fragmentation (Scheme 1, path *a*), finally resulting in overall reductive dehalogenation via the phenyl radical, has been demonstrated [12]. As for solvolysis, various hypotheses (highlighted in Scheme 1) have been considered. These differ for the key intermediate involved, viz. a radical cation formed by photoionization (path *b*), a polar exciplex (see below), or the cation resulting from photoheterolysis (path *c*) [2,12,22–25]. The competition between the above mechanisms may then change according to conditions.

While homolytic fragmentation appears to be well established, its heterolytic counterpart has not often been favored, although it has been early proposed [26]. On the other hand, such a mechanism (path *c*) has been shown to be favored for electron-donating substituted chlorobenzenes [27,28]. Indeed, the triplet state of these compounds cleaves, at least in polar solvents, to give triplet phenyl cations, which are synthetically useful intermediates. One may wonder whether such a path has some role also with parent **1** under suitable conditions.

In view of the above, we decided to study the photochemical behaviour of chlorobenzene in various solvents as well as in the presence of diagnostic traps in an attempt to distinguish the contributions of different mechanisms to the photochemistry of this important molecule and whether selectivity could be induced.

2. Experimental

Photolyses were carried out on 15 mL samples of 5×10^{-2} M solutions of chlorobenzene (**1**) in a 1 cm optical path quartz tube. After flushing with nitrogen or oxygen, the tube was stoppered and irradiated by means of four 15 W low pressure mercury lamps (emission at 254 nm) for 4 h. The irradiated solution was examined by gas chromatography and products **2**–**5** (for a previous characterization of ether **3** see Ref. [29]), as well as of bicyclohexyl and phenylcyclohexane were identified by comparison of the GC/MS data with authentic samples. Their amount was assessed on the basis of calibration curves with authentic samples. Quantum yields were measured with the same set up, by using 3 mL samples of 1×10^{-2} M solutions. The light flux was measured by ferrioxalate actinometry.

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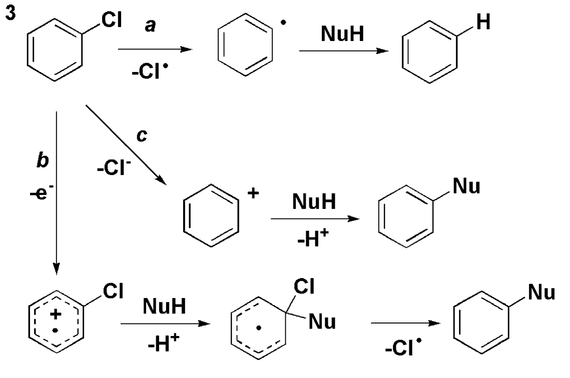


Scheme 1. Photochemistry of **1**.

Fluorescence spectra were measured by means of a LS-55 PerkinElmer spectrofluorimeter and the fluorescence intensity (area of the corrected spectrum) compared with that in cyclohexane (for which the quantum yield has been determined as 0.007) [30]. The difference was within 20%.

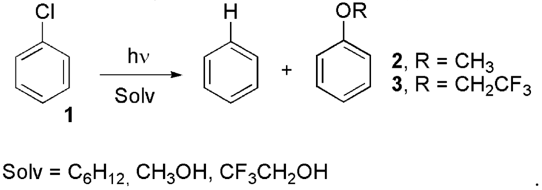
Flash photolysis experiments were carried out by means of an Applied Photophysics instrument fitted with a Lumonics Nd YAG laser operating on the fourth harmonic (266 nm) and delivering about 2 mJ per pulse.

3. Results

3.1. Photochemistry

In this work, the photochemistry of **1** has been explored in neat solvent as well as in the presence of typical π nucleophiles, allyltrimethylsilane (ATMS) and benzene, known as specific traps of triplet phenyl cations. The effect of oxygen as a trap of phenyl radicals has been also observed and compared with previous results reported in literature [12,31]. The experiments were carried out in media of different polarity and nucleophilicity, cyclohexane, methanol and 2,2,2-trifluoroethanol (TFE). Since one of the aims of the work was to detect a potential selectivity, the experiments were carried out at a relatively high starting concentration of **1** (5×10^{-2} M) and high conversion (>50%), so that it could be judged whether the results had some preparative significance. The effect of experimental parameters was assessed by comparing the results of irradiations at a fixed time. Under all conditions, reductive dehalogenation to benzene occurred to a large extent. The other products formed and the corresponding yields with respect to consumed **1** are reported in Tables 1–3.

Table 1
Products formed by irradiation of chlorobenzene (**1**), 5×10^{-2} M.

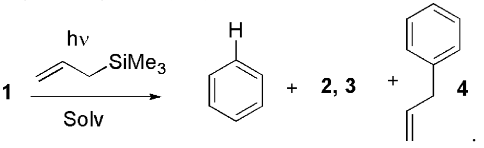


Solvent	ε	Substitution, %	
		Neat solvent	0.05 M Et_3N
C_6H_{12}	2.0	[a]	
MeOH	32.6	**2** (20)	**2** (12)[b]
CF_3CH_2OH	26.5	**3** (31)	**3** (42)
CF_3CH_2OH/O_2		**3** (tr)	**3** (10)

[a] Bicyclohexyl and phenylcyclohexane formed.

[b] Under this condition the photochemical consumption of **1** increases by 84%.

Table 2
Products formed by irradiation of chlorobenzene (**1**, 5×10^{-2} M) in the presence of allyltrimethylsilane (1 M).



Solvent	Substitution, %	Arylation, %
C_6H_{12}		**4** (7)
MeOH		**4** (55)
CF_3CH_2OH	**3** (8)	**4** (8), (43)[a]
CF_3CH_2OH/O_2	**3** (tr)	**4** (tr), (53)[a]

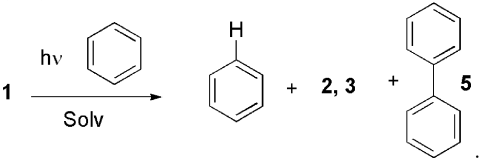
[a] In the presence of Et_3N, 5×10^{-2} M.

The reaction was first examined in some neat solvents (see Table 1). In cyclohexane reduction was accompanied by the formation of bicyclohexyl and phenylcyclohexane as radical coupling products. In alcohols, substitution of the carbon–chloro with a carbon–oxygen bond atom took place to some degree, giving anisole (**2**) in methanol and 2,2,2-trifluoroethoxybenzene (**3**) in trifluoroethanol. The reactions were then repeated in the presence of triethylamine (Et_3N) equimolecular with **1**, in order to buffer hydrogen chloride potentially formed in the reaction. As a matter of fact, this addition had virtually no effect on the photoreaction in cyclohexane. On the other hand, it increased the consumption of **1** in methanol (as shown in Table 1), where however the amount of anisole formed did not significantly change. In the case of TFE, the consumption of **1** remained unchanged while the yield of ether **3** considerably increased. Since the substitution pathway was the most significant in this case, the effect of oxygen saturation was tested, finding that the consumption of **1** increased, while the formation of the ether was strongly inhibited.

Further irradiations were carried out in the presence of ATMS (1 M, see Table 2). Under these conditions, a small amount of allylbenzene (**4**) was formed in cyclohexane and much more (around 50%) in methanol (see Table 2). The yield of **4** was lower in TFE (8%), where a comparable amount of ether **3** was formed. However, the presence of triethylamine levelled the yield of alkene arylation to *ca.* 50% also in this instance. In alcohols, formation of **4** was accompanied by partial or complete quenching of the ethers formation. Furthermore, oxygen saturation had only little effect on the yield of **4** in the presence of Et_3N, whereas in the absence of the amine both the ether and allylbenzene were no more formed.

Irradiations in the presence of 1 M benzene led, except for the irradiations in cyclohexane, to the formation of biphenyl, in a modest amount (12–19%) and again at the expenses of the ethers (see Table 3).

Table 3
Products formed by irradiation of chlorobenzene (**1**) in the presence of benzene (1 M).



Solvent	Substitution, %	Arylation, %
C_6H_{12}		None
MeOH	**2** (6)[a]	**5** (12)
CF_3CH_2OH	**3** (19)[a]	**5** (19)

[a] No significant change in the presence of Et_3N, 5×10^{-2} M.

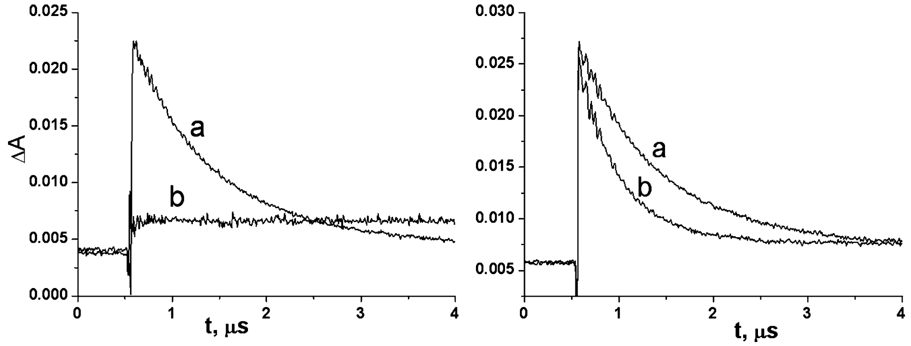


Fig. 1. (left) (a) Profile of the transient absorption at 320 nm observed upon flashing a nitrogen flushed solution 5×10^{-3} M of **1** in cyclohexane; (b) the same in an oxygen flushed solution. (right) **2** (a) as before; (b) the same in the presence of 10^{-2} M ATMS.

Table 4
Quantum yield of reaction [Φ_R, Φ_R (O_2) is the value in oxygen saturated solution] of chlorobenzene (**1**), as well as triplet lifetime (τ_T) and rate of reaction of the latter intermediate with ATMS (k_q).

Solvent	Φ_R	Φ_R (O_2)	τ_T, s	k_q, mol^{-1} s^{-1}
C_6H_{12}	.27	.065	1.1×10^{-6}	1×10^8
CF_3CH_2OH	.065	.033	3.0×10^{-7}	2×10^8

3.2. *Mechanistic investigations*

A series of photophysical experiments were carried out with the aim of obtaining further evidence on the mechanisms involved in the photodegradation of **1** (see Table 4). The fluorescence of **1** was found to be little affected by the medium characteristics, with the intensity varying by no more than 20% in methanol and trifluoroethanol in comparison to cyclohexane (for which the value Φ_F 0.007 has been determined) [30].

The quantum yield of reaction was then measured on 1×10^{-2} M solutions at a conversion lower than 20% and was found to be larger in cyclohexane than in trifluoroethanol. However, in the first case Φ_R was reduced to 1/4 upon saturation of the solution by oxygen, in the latter to 1/2.

A flash photolysis investigation in cyclohexane revealed a conspicuous transient at 300, 320 nm. This was fully quenched in oxygen-equilibrated solution, where it gave place to a different transient with a weak absorption at 300–330 and 470 nm with a rise time of *ca.* 100 ns (see Fig. 1). This observation confirmed previous results, which had led to the identification of the first species as the chlorobenzene triplet and the latter one as the phenylperoxy radical [12]. Under our conditions (low-energy pulses) no significant ionization was observed (compare [32]). The exploration was then extended to TFE, where the triplet was well apparent, indeed with the same initial intensity as in cyclohexane, but was *ca.* 3 times shorter lived (see Fig. 2). Quenching by oxygen was likewise observed, but the long-lived transient absorbance in the visible was absent in this case.

Furthermore, experiments were carried out in the presence of ATMS in the range 0.01–0.05 M. Under these conditions, a pseudo first-order decay was observed and from the experimental value $k_{obs} = k_q \times [ATMS]$ the rate of quenching of the triplet was determined and found to be in the order of 10^8 mol^{-1} s^{-1}, with a larger value in TFE than in cyclohexane (see Fig. 1, Table 4).

4. Discussion

The observed behaviour for **1** in neat solvents can be explained through the different pathways described in Scheme 2, the key points of which are briefly indicated in the following. A first remark is that the fluorescence little changes in going from cyclohexane to ionic media while both reaction quantum yield and product distribution undergo marked changes (e.g. Φ_R is reduced to 1/4 and the triplet lifetime to 1/3 in going to trifluoroethanol). This supports the notion that the singlet is scarcely affected by the solvent polarity, the main process remaining ISC ($\Phi_{ISC} = 0.7$) [32], and that the photoreactions essentially proceed from the triplet state.

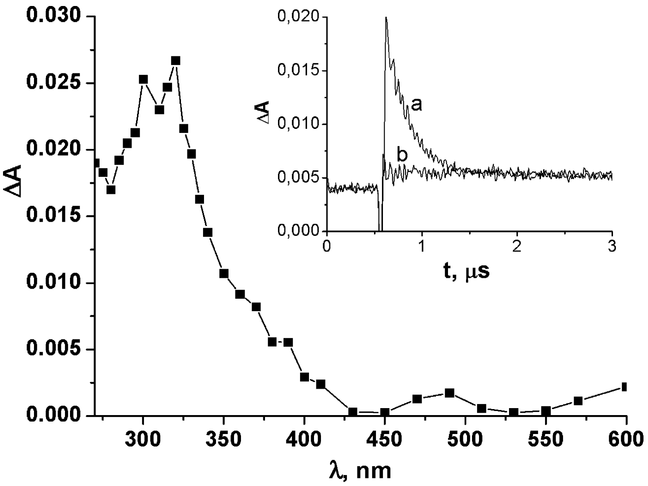
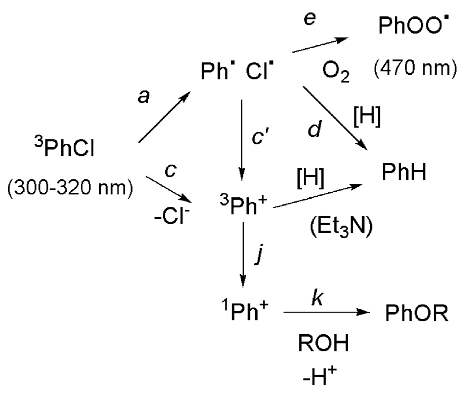
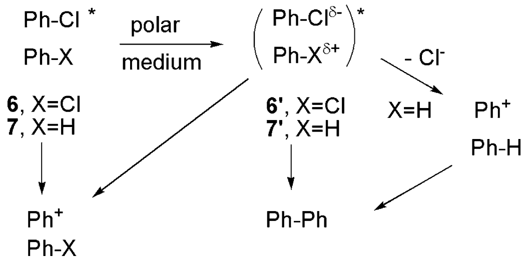


Fig. 2. Transient absorption observed 1 μs after flashing a nitrogen-flushed solution 5×10^{-3} M of **1** in TFE. Inset (a) Profile of the above transient absorption at 320 nm; (b) the same in an oxygen flushed solution.

There is no doubt that homolytic fragmentation of the C–Cl bond (path *a* in Schemes 1 and 2) is the main reaction in cyclohexane as indicated by the observed hydrogen abstraction (path *d*), as sup-



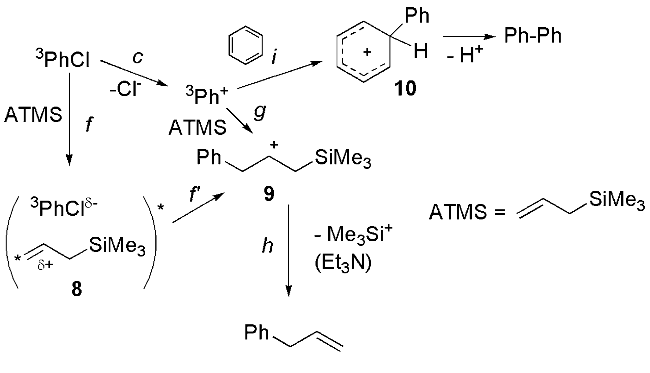
Scheme 2. Photoreactions of **1** in neat solvent. The absorption maxima of the intermediates revealed by flash photolysis are indicated.



Scheme 3. Possible excimer/exciplex path in the photochemistry of **1**.

ported by the formation of bicyclohexyl and phenylcyclohexane, as well as by oxygen trapping (path *e*). The latter reaction is known to occur at a rate $>1 \times 10^{10}\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$ [33] and leads to the peroxyl radical, identified by the absorption extended in the visible [12,33,34]. The efficiency of homolytic cleavage depends on the starting concentration of **1**, with a significant decrease at 1×10^{-2} M and above, known to be due to the formation of an excimer (6, see Scheme 3) that is less reactive than the monomer excited state [10]. Et_3N has only little effect with **1** as noticed in previous work [3]. π donors, on the other hand, do affect the reaction. Thus, irradiation of **1** in neat benzene had been previously found to give biphenyl [35] and in the present work it has been found that phenylation occurs also with an alkene, ATMS. These are minor reactions in cyclohexane. By analogy with the above, these reactions might be explained through the intermediacy of exciplexes with such π donors (7 with benzene, see Scheme 3, and 8 with ATMS, see Scheme 4, path *f*). Indeed, the data in Table 4 suggest that *ca.* 80% of triplet chlorobenzene is quenched by ATMS under preparative conditions (0.05 M). This leads to exciplexes that, contrary to the case of 6, arise from different components and thus have an asymmetric electronic distribution. This gives some chance to chemical reaction as opposed to unproductive decay. What would be the result of such interaction is doubtful, either reduction or alkylation. The former may be more likely, because there is abundant evidence in the literature of reductive dechlorination of aryl halides via an exciplex with a π donor [36], but it is possible to explain the formation of the small amount of allylbenzene found in cyclohexane to path *f*. In principle, one may extend this rationalization and attribute the larger yield of product 4 in polar media to the same path, by taking into account the increased charge separation in the exciplex.

However, the changes occurring in going to polar media, or at least in TFE, seem to us better rationalized through the intervention of triplet phenyl cation from the heterolytic fragmentation of ^{3}**1** (probably assisted by the donor, path *f*'). In fact, arylated product **4** *substitutes* solvolysis product **3** in TFE and the data in Table 2 show that ATMS traps the intermediate 70 times more efficiently than the solvent (43% **4** vs. 8% 3 yield, 0.075 ATMS/TFE molar ratio). This is exactly what happens with bona fide triplet phenyl cation (e.g. as obtained from the triplet sensitized decomposition of phenyldiazonium salts) [37] that smoothly add to ATMS (and to benzene) to give arylated products as in the present case (paths *h*, *i*), while it does not add to nucleophiles centered on a non-bonding orbital, such as are alcohols. Notice that the yield of **4** is high only in the presence of Et_3N. This is again diagnostic and is due to the base catalyzed elimination of the trimethylsilyl cation from adduct **9**, a phenomenon previously noted in related allyl and benzyl cations [38,39]. In addition, since acidity is liberated during the reaction, triethylamine preserve from degradation acid sensitive ATMS. As one may expect, the base has no effect on the easy deprotonation of Wheland adduct **10**, nor on the desilylation of **9** in a nucleophilic solvent such as MeOH.



Scheme 4. Photoreactions of **1** in the presence of allyltrimethylsilane (ATMS) or benzene as π nucleophile.

As mentioned above, while solvolysis poorly competes with addition to the alkene, product **3** is formed in a rather high yield in the absence of ATMS. This fits with the proposed mechanism since the cation is initially formed from triplet ^{3}**1** and thus in the triplet multiplicity, but ISC to the much more stable singlet then occurs (path *j*, Scheme 2) [40]. Thus, in the presence of a good trap for such species such as a π nucleophile (reaction rate $>10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) [41], the cation is trapped as in the triplet state as soon as formed, independently of whether it is formed via unimolecular cleavage or via exciplex. In the contrary case, there is time for ISC to the singlet cation, an unselective electrophile that mainly reacts with the solvent (path *k*).

It should be further distinguished whether the phenyl cation is the primary product from ^{3}**1** (path *c*), or the photochemical cleavage is in any case homolytic, but in polar solvents electron transfer between the radical and the chlorine atom produces the cation (path *c*′ in Scheme 2). Should the latter hypothesis apply, the reaction would be in every case subject to quenching by oxygen that efficiently traps phenyl radicals. However, flash photolysis experiments show that no phenylperoxy radical is formed in TFE. Furthermore, a comparison of the reactions in TFE/O_2 in the presence and absence of ATMS (see Tables 1 and 2) evidences that solvolysis is quenched, while alkene arylation is not. This supports that in this solvent the latter process involves fast trapping either of triplet ^{1}**1** or of the first formed intermediate $^3Ph^+$ by a π trap, with no oxygen interference. In contrast, the latter process requires ISC to $^1Ph^+$ and is more easily perturbed. At any rate, notice that path *c*′ would give the cation in the singlet state, reacting indiscriminately with n and π nucleophiles, contrary to what observed.

Summing up the various pieces of evidence, the homolytic fragmentation of the chlorobenzene triplet (^{3}**1**), characterized in previous work [3,6,10–12], is identified by oxygen trapping of phenyl radicals. Shifting to a polar solvent does not affect the singlet (^{1}**1**), but shortens the lifetime of triplet. The reaction quantum yield decreases under these condition, indicating a favored ISC back to the ground state. Donor-assisted heterolytic cleavage has some role, though, and gives the triplet phenyl cation, efficiently quenched by π nucleophiles, not by oxygen. More precisely, this path appears to be favored by acidity rather than polarity (compare acidic TFE, $pK_a = 12.37$, with MeOH, $pK_a = 15.49$, while the latter solvent is more polar). Solvent co-operation to heterolytic cleavage could involve some stabilization of the charge on the leaving chloride. Hydrogen bonding to chlorobenzene is notoriously scarce, but there is some indication of it in the ground state [42] and it appears conceivable that an acidic alcohol has a serious role in facilitating heterolysis from the excited state via a complex $Ph{-}Cl\cdots HOCH_2CF_3$. The rate of non-assisted heterolysis under these conditions is around $1 \times 10^6\,\mathrm{s}^{-1}$ or somewhat below (see Fig. 1), in the same region as the homolysis of **1** [32], but much below heterolysis of electron-donating substituted chlorobenzenes ($>10^8\,\mathrm{s}^{-1}$) [38].

5. Conclusion

The parallel exploration of trapping by nucleophiles (n and π) and by oxygen suggests that the homolytic fragmentation typical of triplet chlorobenzene in apolar media shifts to heterolysis in trifluoroethanol (the results are less clear cut in methanol [12], where an homolytic cleavage followed by electron transfer cannot be excluded). Heterolysis is inefficient, but is accelerated by π donors and leads to triplet phenyl cation, in turn be trapped by an alkene and by benzene to give phenylated products.

It is instructive to compare the photochemistry of chlorobenzene and chloroaniline. In the latter case, stabilization by the substituent makes homolysis of the triplet thermodynamically inaccessible, but on the other hand stabilizes the cation. As a result, 4-chloroaniline is next to photostable in cyclohexane and reacts efficiently (via heterolysis) in polar solvents. On the contrary, the high energy triplet of chlorobenzene makes homolysis efficient in apolar media, while polarity (and more than that hydrogen bonding) disfavors homolysis and makes heterolysis viable, though inefficiently. Thus, the easy homolysis of chlorobenzene is quenched both by passing to a polar medium and by introducing a donating group, to be substituted by ionic chemistry. Although in the cases examined, the reactions are not sufficiently clean for making the reactions preparatively appealing, chlorobenzene could play an interesting role as photochemical model for the study of photodegradative pathways in the dehalogenation of haloaromatics.

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References

[1] N.J. Bunce, J.P. Landers, J.A. Lanshaw, J.S. Nakai, Environ. Sci. Technol. 23 (1989) 213.

[2] D. Dulin, H. Drossman, T. Mill, Environ. Sci. Technol. 20 (1986) 72.

[3] N.J. Bunce, J. Org. Chem. 47 (1982) 1948.

[4] M. Julliard, M. Chanon, A. Galadi, J. Photochem. Photobiol. A: Chem. 83 (1994) 107.

[5] L. Sanchez-Prado, S. Risticevic, J. Pawliszyn, E. Psillakis, J. Photochem. Photobiol. A: Chem. 206 (2009) 227.

[6] N.J. Bunce, in: W.M. Horspool, P.S. Song (Eds.), CRC Handbook of Organic Photochemistry and Photobiology, CRC Press, Boca Raton, 1995, p. 1181.

[7] J. Cornelisse, in: W.M. Horspool, P.S. Song (Eds.), CRC Handbook of Organic Photochemistry and Photobiology, CRC Press, Boca Raton, 1995, p. 250.

[8] K.S. Içli, in: W.M. Horspool, F. Lenci (Eds.), CRC Handbook of Organic Photochemistry and Photobiology, 2nd ed., CRC Press, Boca Raton, 1995, p. 37/1.

[9] M. Fagnoni, A. Albini, in: V. Ramamurthy, K. Schanze (Eds.), Organic Photochemistry and Photophysics, Taylor & Francis, Boca Raton, 2006, p. 131.

[10] N.J. Bunce, J.P. Bergsma, M.D. Bergsma, W. De Graaf, Y. Kumar, L. Ravanal, J. Org. Chem. 45 (1980) 3708.

[11] K.-L. Han, G.-Z. He, J. Photochem. Photobiol. C: Photochem. Rev. 8 (2007) 55.

[12] J.P. Da Silva, S. Jockusch, N.J. Turro, Photochem. Photobiol. Sci. 8 (2009) 210.

[13] A. Freedman, S.C. Yang, M. Kawasaki, R. Bersohn, J. Chem. Phys. 72 (1980) 1028.

[14] T. Ichimura, Y. Mori, H. Shinohara, N. Nishi, Chem. Phys. 189 (1994) 117.

[15] T. Ichimura, Y. Mori, J. Chem. Phys. 58 (1973) 288.

[16] M. Kadi, J. Davidsson, A.N. Tarnovsky, M. Rasmusson, E. Åkesson, Chem. Phys. Lett. 350 (2001) 93.

[17] Y.-J. Liu, P. Persson, S. Lunell, J. Phys. Chem. A 108 (2004) 2339.

[18] O. Rubio-Pons, O. Loboda, B. Minaev, B. Schimmelpfenning, O. Vahtras, H. Aigren, Mol. Phys. 101 (2003) 2103.

[19] S. Nagaoka, T. Takemura, H. Baba, N. Koga, K. Morokuma, J. Phys. Chem. 90 (1986) 759.

[20] M.S. Park, K.W. Lee, K.H. Jung, J. Chem. Phys. 114 (2001) 10368.

[21] G.-J. Wang, R.-S. Zhu, H. Zhang, K.-L. Han, G.-Z. He, N.-Q. Lou, Chem. Phys. Lett. 288 (1998) 429.

[22] T. Moore, R.M. Pagni, J. Org. Chem. 52 (1987) 770.

[23] J. Orvis, J. Weiss, R.M. Pagni, J. Org. Chem. 56 (1991) 1851.

[24] T. Ichimura, M. Iwai, Y. Mori, J. Phys. Chem. 92 (1988) 4047.

[25] J.P. Soumillon, B. DeWolf, J. Chem. Soc., Chem. Commun. (1981) 436.

[26] G.C. Miller, M.J. Mille, D.G. Crosby, Tetrahedron 35 (1979) 1797.

[27] S. Protti, M. Fagnoni, M. Mella, A. Albini, J. Org. Chem. 69 (2004) 3465.

[28] I. Manet, S. Monti, G. Grabner, S. Protti, D. Dondi, V. Dichiarante, M. Fagnoni, A. Albini, Chem. Eur. J. 14 (2008) 1029.

[29] M.A. Keegstra, T.H.A. Peters, L. Brandsma, Tetrahedron 48 (1992) 3633.

[30] C.M. Previtali, W. Ebbesen, J. Photochem. 27 (1984) 9.

[31] V. Avila, H.E. Gsponer, C.M. Previtali, J. Photochem. 27 (1984) 163.

[32] C.M. Previtali, T.W. Ebbesen, J. Photochem. 30 (1985) 259.

[33] X. Fang, R. Mertens, C. von Sonntag, J. Chem. Soc., Perkin Trans. 2 (1995) 1033.

[34] K. Tonokura, Y. Norikane, M. Koshi, Y. Nakano, S. Nakamichi, M. Goto, S. Hashimoto, M. Kawasaki, M.P. Sulbaek Andersen, M.D. Hurley, T.J. Wallington, J. Phys. Chem. A 106 (2002) 5908.

[35] G.M. Robinson, J.M. Vernon, J. Chem. Soc. C (1971) 3363.

[36] J. Saltiel, W.K. Smothers, K.S. Schanze, S.A. Charman, R. Bonneau, Photochem. Photobiol. Sci. 8 (2009) 856.

[37] S. Milanesi, M. Fagnoni, A. Albini, J. Org. Chem. 70 (2005) 603.

[38] I. Manet, S. Monti, M. Fagnoni, S. Protti, A. Albini, Chem. Eur. J. 11 (2005) 140.

[39] M. Freccero, A. Pratt, C. Long, A. Albini, J. Am. Chem. Soc. 120 (1998) 284.

[40] V. Dichiarante, D. Dondi, S. Protti, M. Fagnoni, A. Albini, J. Am. Chem. Soc. 129 (2007) 5605, correction, 11662.

[41] V. Dichiarante, M. Fagnoni, A. Albini, J. Org. Chem. 73 (2008) 1282.

[42] C. Jimenez-Rodriguez, R.G. Eastham, D.J. Cole-Hamilton, Dalton Trans. (2005) 1826.