Photochemical & Photobiological Sciences

Cite this: Photochem. Photobiol. Sci., 2011, 10, 123

www.rsc.org/pps

Cationic and radical intermediates in the acid photorelease from aryl sulfonates and phosphates[†]

Marco Terpolilli,^{*a*} Daniele Merli,^{*b*} Stefano Protti,^{*a*} Valentina Dichiarante,^{*a*} Maurizio Fagnoni^{**a*} and Angelo Albini^{*a*}

Received 20th September 2010, Accepted 15th October 2010 DOI: 10.1039/c0pp00284d

The irradiation of a series of phenyl sulfonates and phosphates leads to the quantitative release of acidity with a reasonable quantum yield (≈ 0.2). Products characterization, ion chromatography analysis and potentiometric titration are consistent with the intervening of two different paths in this reaction, *viz*. cationic with phosphates and (mainly) radical with sulfonates.

Introduction

Molecules capable of generating acidity upon irradiation (Photo Acid Generators, PAGs), are used as initiators in cationic polymerization, in chemically amplified photoresists, 1a-c as well as in bioorganic synthesis.1d-e The most widely used class of these compounds is that of aromatic onium salts Ar_nX⁺MY_m⁻, such as iodonium and sulfonium salts.² These are a convenient choice because of their thermal stability (>200 °C) and the easy chemical modification that allows tuning the absorption characteristics. Some drawbacks, such as the limited solubility in organic solvents that may cause phase separation from spun-on resist polymer matrices, make the development of new "caged protons" desirable, with particular regard to non-ionic molecules. The most important example of the latter class are the diazonaphthoquinone derivatives (DNQ), where a carboxylic acid is liberated after a photo-Wolff rearrangement.^{1a} The photorelease of other acids (e.g. sulfonic) has been more elusive and involves substituted esters. Mechanisms that have been considered include the photoinduced intramolecular hydrogen abstraction in 2-nitrobenzyl sulfonates³ and the homolytic photocleavage of the ArO-S bond in aryl sulfonates. In the latter

^aDepartment of Organic Chemistry, University of Pavia, Pavia, 27100, Italy. E-mail: fagnoni@unipv.it

^bDepartment of General Chemistry, University of Pavia, Pavia, 27100, Italy † Electronic supplementary information (ESI) available: Potentiometric titration of **1b-1e** irradiated solutions and ¹H and ¹³C NMR spectra of compounds **1d–f**. See DOI: 10.1039/c0pp00284d case, the initial step leads either to (non-acid-generating) photo-Fries rearrangement or to hydrogen abstraction from the solvent, depending on the structure.⁴ Polysulfonates, *e.g.* the tris(mesylate) of pyrogallol (MeSB), release more acidity than monosulfonates,⁵ and indeed MeSB-based resists were found to be more photosensitive than those incorporating a sulfonium salt.⁶ In recent years, our own and other groups have been studying the photochemistry of electron-rich aromatic halides and esters (**1** in Scheme 1) in polar solvents and found that heterolysis of the Ar–X bond occurs, most effectively under acetone sensitization, and leads to triplet phenyl cations.⁷⁻⁹ These are synthetically useful intermediates that have been exploited for a variety of arylation reactions.

Organic preparations by this method are usually carried out under buffered conditions, because otherwise the solution pH strongly decreases (Scheme 1). The latter characteristics is appealing because, if the reaction occurs according to Scheme 1, it should be possible not only to generate acidity from such compounds, but also to tune the strength of the photogenerated acid by changing the group X in the precursor.

As an example, triflic ($pK_a = -13$), hydrochloric ($pK_a = -6$), methanesulfonic ($pK_a = -1.54$), diethylphosphoric ($pK_a = 0.71$) and hydrofluoric acid ($pK_a = 3.18$) could be photoreleased as preferred from compounds of formula **1**.

In the following, a study aimed to explore the potentialities of this class of compounds for the photorelease of acids is reported. Some families of aromatic derivatives were examined, of which the amount and nature of the acid liberated had not been previously



Scheme 1 Photo acid generation via phenyl cations.

determined. In the choice of the potential PAGs to explore this issue, those liberating volatile acids such as HF and HCl that can cause pinholes in the resist films were excluded. Sulfonates were thus preferred, on the basis of the potential release of strong acids, including triflic acid, a somewhat volatile but strong acid¹⁰ that is known for inducing acid amplification in photoresists.¹¹ It was appealing also to investigate phosphate esters, at they are presently scarcely considered.^{12,13}

Materials and methods

Previous studies have shown that phenyl cations are conveniently photogenerated starting from various electron-donating substituted aromatics.¹⁰ However, aminophenol and hydroxyphenol esters were not considered for this work due to their poor thermal stability and easy oxidation. Thus, sulfonate and phosphate esters of *p*-methoxy (**1a**,**c**) and *p*-*t*-butylphenol (**1d**,**f**) were chosen.

Experimental details: general

Unless otherwise stated, all reagents were commercially available and used without purification. ¹H and ¹³C NMR spectra were recorded on a 300 MHz (Bruker) spectrometer. The attributions were made on the basis of ¹H and ¹³C NMR; chemical shifts are reported in ppm downfield from TMS. GC-MS analyses have been carried out with a Thermo Scientific DSQ II Single Quadrupole instrument (Column Rtx-5 MS (Restek), Detection mode: Electronic Impact).

Synthesis of esters 1a-f

p-Methoxy esters 1a-c were obtained as previously described.⁸ Mesylate 1d, triflate 1e and phosphate 1f were obtained by known procedures from the corresponding phenols. 4-tert-Butylphenylmethanesulfonate (1d) was obtained from the corresponding phenol by a known procedure¹⁴ in 56% yield as a colorless solid, mp 49-50 °C (from ethanol, lit: 50-52 °C¹⁵). Spectroscopic data of 1d in accordance with literature data.¹⁵ Anal. calcd for C₁₁H₁₆O₃S: C, 57.87; H, 7.06%. Found: C, 57.9; H, 7.1%. 4-tert-Butylphenyltrifluoromethanesulfonate (1e) was synthesized from p-(t-butyl)phenol in 43% yield as an oil.¹⁶ Spectroscopic data of 1e in accordance with literature data.¹⁷ Anal. calcd for C11H13F3O3S: C, 46.80; H, 4.64%. Found: C, 46.9; H, 4.6%. 4tert-Butylphenyldiethylphosphate (1f) was obtained by a known procedure¹⁸ in 69% yield as an oil. ¹H NMR (δ, CDCl₃):¹⁹ 1.30 (s, 9H), 1.35-1.40 (t, 6H, J = 6 Hz), 4.20-4.30 (qui, J = 6 Hz), 7.10-7.35 (AA'BB', 4H). ¹³C NMR (δ, CDCl₃): 15.9 (CH₃), 31.3 (CH₃), 34.2, 64.3 (CH₂), 119.2 (CH), 126.4 (CH), 147.7, 148.3. IR (neat, v/cm⁻¹: 2965, 1513, 1272, 1031, 964, 840. Anal. calcd for C₁₄H₁₃O₄P: C, 58.73; H, 8.10%. Found: C, 58.7; H, 8.0%.

Photolysis of esters 1a-f

The photochemical reactions were performed by using nitrogenpurged solutions (except where indicated) of the chosen ester (0.01 M) in quartz tubes. HPLC grade purity methanol (0.05% water content as determined by Karl-Fischer titration) was used as solvent for all the photolysis experiments. Irradiations were performed in a multilamp reactor fitted with 4 low pressure Hg lamps (emission maximum: $\lambda = 254$ nm), and the reaction course was followed by GC analysis. As described below, organic photoproducts from **1a**,**f** have been quantified on the basis of calibration curves from commercial samples. The presence of gaseous fluoroform in the photolyzed solution has been revealed by means of GC-MS and IR analysis (gas, v/cm^{-1} 3035, 1374, 1158²⁰). In the last case, the analysis was performed on the gas released in a 10 cm cell by using sodium chloride windows, internal volume 100 ml, purged with nitrogen before the introduction of the sample.

The acidity liberated has been determined on 10 mL of the photolysed solutions by dilution with water (50 mL) and titration with aqueous 0.1 M NaOH. Potentiometric acid titrations (NaOH 0.1 M) of **1b–e** have been followed by using an Orion mod. 250 potentiometer equipped with an Orion pH glass combined electrode mod 91–56. The titrations by using 0.1 M NaOH have been performed on 10 mL photolyzed solutions in MeOH diluted with 100 mL water.

Ion chromatography analyses have been performed by means of a Dionex GP40 instrument equipped with a conductimetric detector (Dionex 20 CD20) and an electrochemical suppressor (ASRS Ultra II, 4 mm) by using the following conditions: chromatographic column IONPAC AS23 (4 mm × 250 mm), guard column IONPAC AG12 (4 mm × 50 mm), eluent: NaHCO₃ 0.8 mM + Na₂CO₃ 4.5 mM, flux: 1 mL min⁻¹; current imposed at detector: 50 mA. Commercially available tetrabutylammonium mesylate, trifluoromethanesulfonic acid and diethyl phosphate were used as standards.

Results and discussion

Photophysical and photochemical properties of esters **1a**,**f** have been resumed in Table 1. Methoxyphenyl esters **1a**–**c** exhibited two absorption maxima in the UV around 276 ($\varepsilon > 10^3$ L cm⁻¹ mol⁻¹) and 224 nm ($\varepsilon \approx 10^4$ L cm⁻¹ mol⁻¹), while *t*-butylphenyl esters **1d**–**f** absorbed somewhat blue-shifted and less intensively (260, $\varepsilon > 10^2$ L cm⁻¹ mol⁻¹, and 212 nm, $\varepsilon \approx 10^4$ L cm⁻¹ mol⁻¹ as the maxima, see Table 1 and Fig. 1).

In this study, 0.01 M methanol solutions of esters **1a–f** were deaerated and irradiated, resulting in complete consumption after 6 h in almost all cases. The quantum yield of disappearance of **1** (Φ_R), at 254 nm ranged from 0.11 to 0.2, except for the case of less reactive phosphate **1f** ($\Phi_R = 0.02$).

The percent yield of organic products and the mmol of inorganic products formed upon 6 h irradiation (24 h for **1f**) of solutions containing 0.3 mmol of starting compound **1**, as well as the acidity generated are reported in Table 1.

The pH of the photolyzed solutions was around 1 and we were happy to find that the amount of acid released was close to quantitative (>90%) as titrated by NaOH.

More precisely, potentiometric titrations evidenced a single pK_a value for **1c** and **1d**, but two for **1b** and **1e** (ratio between the stronger and the weaker acid 4 : 1 and 2 : 1 respectively, see Fig. 2).

As for the organic moiety, the photoprocesses occurring are reduction (giving 2), formal hydrolysis (forming deprotected 3) and solvolysis (4), since no photo-Fries adducts were detected by GC analysis. Triflates 1b, 1e gave the corresponding phenol 3 as the exclusive (from 1b) or the main photoproduct (1e gave also a 5% amount of *t*-butylbenzene 2b). In the case of *p*-methoxyphenyl mesylate (1a), deprotection and reduction took place in a comparable yield (25% vs. 19%), but some dimethoxybenzene was formed too (4, 9%), while the other mesylate (1e) was exclusively deprotected to give *p*-*t*-butylphenol 3b.



^{*a*} 0.01 M solution of **1a–f** in degassed methanol, irradiated at 254 nm until complete consumption of the ester. ^{*b*} GC yield. ^{*c*} The analysis is based on a 0.03 mmol amount of starting **1**. ^{*d*} Variable amounts of formate anion have been detected in all the photolyzed solutions. ^{*e*} Fluoroform was detected by IR analysis. ^{*f*} Reaction carried out in oxygen saturated solution. ^{*s*} See ref. 14. ^{*b*} Fluoroform was detected by GC-MS analysis.



Fig. 1 Absorption spectra of (a) 1×10^{-4} M MeOH solution of **1a** (dotted line), **1b** (dashed line), **1c** (solid line) and (b) 5×10^{-4} M MeOH solution of **1d** (dotted line), **1e** (dashed line) and **1f** (solid line).

With phosphates 1c and 1f photoreduction was the main process giving anisole 2a (58%, along with ether 4 in 25% yield) and alkylbenzene 2b (36%), respectively.

According to ion chromatography analyses, phosphates and mesylates (except 1a) released the *O*,*O*-diethylphosphate and



Fig. 2 Potentiometric titration of a 10^{-2} M solution of 1c (\bigcirc , 0.1 mmol) and 1e (\square , 0.1 mmol) after irradiation in MeOH.

the mesylate anion, respectively in a close to quantitative yield (>92%). On the contrary, only traces of triflate anion were present in photolyzed solutions of **1b,1e**, where the main anion was fluoride (up to 56% yield). In this case, a gas was liberated, as apparent from the fizz on opening the reaction tubes, that was shown to be fluoroform, CHF₃ by IR²⁰ and GC-MS analysis.

It is noteworthy that, when the photolysis of **1b,1e** was performed in oxygen saturated methanol, triflate anion was formed in a good yield at the expense of fluoride (Table 1).

In the case of **1e**, small amounts of sulfur dioxide, sulfurous acid dimethyl ester as well as dimethoxymethane, ethandiol and 4-*t*-butylanisole were also detected. Moreover, variable amounts of formate anion have been detected in all of the irradiated solutions.

The data above demonstrate that all of the aryl esters release acidity with a reasonable quantum yields (except for 1f). The thermal stability, good miscibility with resins and convenient (and

Published on 09 November 2010. Downloaded on 26/10/2014 03:14:35

tunable) absorption in the UV-C make these compounds suitable candidates as PAGs. It is noteworthy that two different mechanisms operate involving a cationic and a radical intermediates, as shown in Schemes 2 and 3. With phosphates **1c**,**f**, intersystem crossing (ISC) is efficient,²¹ and product analysis supports that the reaction proceeds from the *triplet* state and involves *heterolysis* of the aryl-oxygen bond (cleavage **a**, Scheme 2). Triplet phenyl cation $(^{3}1^{+})$ and the corresponding counterion $(EtO)_{2}PO_{2}^{-}$ are formed. As previously demonstrated,²² the cation abstracts a hydrogen atom from the medium and gives anisole (**2a**) or *t*-butylbenzene (**2b**) *via* radical cation **5** along with formaldehyde that under acidic conditions is transformed into dimethoxymethane or (photo)oxidized²³ to formic acid (Scheme 2).



Scheme 2 Cationic intermediates in the photolysis of 1.

In part, the triplet cation intersystem crosses to the singlet $({}^{1}1^{+}, R = OMe)^{9}$ that in turn adds the solvent and gives *p*-dimethoxybenzene (4).²⁴ The last pathway scarcely contributes in the case of triplet 4-*t*-butylphenyl cation, which rather abstracts hydrogen and thus gives **2b** with only a trace of the solvolysis product, 4-*t*-butylanisole.²³ The heterolytic path accounts also for part of the reaction of mesylate **1a**, as witnessed by the formation of products **2a** and **4**.

In the aim of confirming the proposed mechanism, irradiations experiments in deuterated solvents have been carried out. Thus, photolysis of phosphate 1c in CH₃OD afforded non-deuterated anisole 2a exclusively. On the contrary, in CD₃OD complete monodeuterated anisole 2a-d₁, was formed along with trideuterated 4-d₃.[‡] On the other hand, among sulfonates *homolytic* cleavage of the oxygen-sulfur bond competes (in the case of 1a) or becomes the exclusive path (with mesylate 1d and triflates 1b,e). Since heterolytic cleavage is the exclusive reaction in the acetone sensitized irradiation of 1a and 1b,⁸ homolytic cleavage proceeds from the *singlet*. A phenoxyl (6) and a sulfonyl radical are formed (cleavage b, Scheme 3)²⁵ and escape from the solvent cage (no photo-Fries products are detected). Radical 6 abstracts hydrogen



Scheme 3 Radical intermediates in the photolysis of 1.

and gives the corresponding phenol 3 along with a 'CH₂OH radical that ultimately is converted into formic acid or dimerized to form ethandiol. As for the sulfonyl radical CR'₃SO₂, its fate depends on the nature of group CR'_3 . The CH_3SO_2 radical gives methanesulfonic acid,²⁶ while in the case of trifluoromethanesulfonyl radical such a path is overcome by the known α cleavage to trifluoromethyl radical CF₃ and SO₂.^{27,28} The sulfur dioxide formed is either liberated as a gas or reacts with the solvent giving MeOSO₂H²⁹ (and in part the dimethyl ester³⁰). This accounts for the formation of a certain amount of weak sulfurous acid, as evidenced in the potentiometric titration. The acid is formed upon dilution of the photolyzed solution with water (see ESI \dagger). As for the CF₃ radical, this abstracts hydrogen from the solvent giving inert fluoroform as the final product³¹ or CF₃OH.^{31,32} The last compound is known to fragment thermally to HF and COF₂³³ that liberates a further amount of HF by reaction with MeOH.34

The case with oxygenated solutions is different, where the radical $CF_3SO_2^{\bullet}$ is trapped by O_2^{35} and gives triflic acid *via* the peroxidic intermediate $CF_3SO_2-O_2^{\bullet}$.

Conclusions

The promising characteristics of a number of aryl esters for acid photorelease have been demonstrated. Besides the homolytic cleavage of the oxygen-sulfur bond, presumably operating also in some known PAGs as pyrogallol trimesylate, heterolytic cleavage of the aryl-oxygen bond has been demonstrated to contribute. The latter path had not been previously invoked among PAGs and its participation depends on the nature of the leaving group and of the aromatic moiety. Such a path can be made more important,

[‡] Compound **2a**, MS (*m*/*z*): 108 (M⁺, 100), 79 (15), 78 (60), 77 (20), 65 (35), 51 (10); **2a**-d₁, MS (*m*/*z*): 109 (M⁺), 80 (20), 79 (65), 78 (25), 66 (45), 52 (10); **4**-d₃, MS (*m*/*z*): 141 (M⁺), 126 (60), 123 (55), 98 (20), 95 (15).

View Article Online

at least with methoxyphenyl sulfonate esters, by passing to triplet sensitized conditions.⁸ In contrast, the heterolytic path is exclusive with phosphates and does not require sensitization. When the homolytic path is followed with triflates, the role of oxygen is determining for forming a strong acid and avoiding the release of volatile substances (HF and CHF₃) that can have an adverse effect in a photoresist.

Acknowledgements

We are grateful to Dr Barbara Mannucci and Dr Federica Corana of Centro Grandi Strumenti (University of Pavia) for technical support.

Notes and references

- (a) S.-Y. Moon and J.-M. Kim, Chemistry of photolithographic imaging materials based on the chemical amplification concept, J. Photochem. Photobiol. C, 2007, 8, 157–173; (b) J. M. Frechét, The photogeneration of acid and base within polymer coatings: Approaches to polymer curing and imaging, Pure Appl. Chem., 1992, 64, 1239–1248; (c) M. Shirai and M. Tsunooka, Photoacid and photobase generators: Chemistry and applications to polymeric materials, Prog. Polym. Sci., 1996, 21, 1–45; (d) P. J. Serafinowski and P. B. Garland, Novel photoacid generators for photodirected oligonucleotide synthesis, J. Am. Chem. Soc., 2003, 125, 962–965; (e) X. Gao, E. Gulari and X. Zhou, In situ synthesis of oligonucleotide microarrays, Biopolymers, 2004, 73, 579– 596.
- 2 J. V. Crivello, The discovery and development of onium salt cationic photoinitiators, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 4241–4254.
- 3 F. M. Houlihan, O. Nalamasu, J. Kometani and E. Reichmanis, A retrospective on 2-nitrobenzyl sulfonate photoacid generators, *J. Imag. Sci. Technol.*, 1997, **41**, 35–40.
- 4 Y.-S. Chang, J.-S. Jang and M.-L. Deinzer, Photochemistry of irgasantriflate: A simple conversion of an aromatic hydroxyl group to chlorine in the synthesis of polychlorinated diphenyl ethers and polychlorinated dibenzofurans, *Tetrahedron*, 1990, **46**, 4161–4164.
- 5 (a) T. Ueno, L. Schlegel, N. Hayashi, H. Shiraishi and T. Iwayanagi, Acid formation from various sulfonates in a chemical amplification positive resist, *Polym. Eng. Sci.*, 1992, **32**, 1511–1515; (b) L. Schlegel, T. Ueno, H. Shiraishi, N. Hayashi and T. Iwayanagi, Acid formation and deprotection reaction by novel sulfonates in a chemical amplification positive photoresist, *Chem. Mater.*, 1990, **2**, 299–305.
- 6 L. Schlegel, T. Ueno, H. Shiraishi, N. Hayashi and T. Iwayanagi, Highly sensitive positive deep UV resist utilizing a sulfonate acid generator and a tetrahydropyranyl inhibitor, *Microelectron. Eng.*, 1991, 13, 33–36.
- 7 (a) V. Dichiarante and M. Fagnoni, Aryl cation chemistry as an emerging versatile tool for metal-free arylations, *Synlett*, 2008, 787–800; (b) M. Fagnoni and A. Albini, Arylation reactions: the photo-S_N1 path *via* phenyl cation as an alternative to metal catalysis, *Acc. Chem. Res.*, 2005, **38**, 713–721; (c) M. Slegt, S. Hermen, H. S. Overkleeft and G. Lodder, Fingerprints of singlet and triplet phenyl cations, *Eur. J. Org. Chem.*, 2007, 5364–5375.
- 8 M. De Carolis, S. Protti, M. Fagnoni and A. Albini, Metal-free cross-coupling reactions of aryl sulfonates and phosphates through photoeterolysis of aryl-oxygen bonds, *Angew. Chem., Int. Ed.*, 2005, **44**, 1232–1236.
- 9 S. Lazzaroni, D. Dondi, M. Fagnoni and A. Albini, Geometry and energy of substituted phenyl cations, J. Org. Chem., 2008, 73, 206–211.
- 10 R. D. Allen, J. Opitz, C. E. Larson, T. I. Wallow, R. A. DiPietro, G. Breyta, R. Sooriyakumaran and D. C. Hofer, The influence of photoacid structure on the design and performance of 193 nm resists, *J. Photopolym. Sci. Technol.*, 1997, **10**, 503–510.
- 11 (a) S. Lee, K. Arimitsu, S.-W. Park and K. Ichimura, Synthesis and evaluation of novel acid amplifiers liberating fluoroalkanesulfonic acids, J. Photopolym. Sci. Technol., 2000, 13, 215–216; (b) S. Kruger, S. Revuru, C. Higgins, S. Gibbons, D. A. Freedman, W. Yueh, T. R. Younkin and R. L. Brainard, Fluorinated acid amplifiers for EUV lithography, J. Am. Chem. Soc., 2009, 131, 9862–9863.
- 12 S. Protti and M. Fagnoni, Phosphate esters as "tunable" reagents in organic synthesis, *Chem. Commun.*, 2008, 3611–3621.

- 13 M. Shi, K. Yamamoto, Y. Okamoto and S. Takamuku, Photolysis of aryl esters of tri- and tetracoordinate phosphorus compounds, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1991, **60**, 1–14.
- 14 R. K. Crossland and K. L. Servis, Facile synthesis of methanesulfonate esters, J. Org. Chem., 1970, 35, 3195–3196.
- 15 R. H. Munday, J. R. Martinelli and S. L. Buchwald, Palladiumcatalyzed carbonylation of aryl tosylates and mesylates, J. Am. Chem. Soc., 2008, 130, 2754–2755.
- 16 D. E. Frantz, D. G. Weaver, J. P. Carey, M. H. Kress and U. H. Dolling, Practical synthesis of aryl triflates under aqueous conditions, *Org. Lett.*, 2002, 4, 4717–4718.
- 17 (a) F. Y. Kwong, C. W. Lai, M. Yu, Y. Tian and K. S. Chan, Palladiumcatalyzed phosphination of functionalized aryl triflates, *Tetrahedron*, 2003, **59**, 10295–10305; (b) W. M. Seganish and P. DeShong, Preparation and palladium-catalyzed cross-coupling of aryl triethylammonium bis(catechol) silicates with aryl triflates, *J. Org. Chem.*, 2004, **69**, 1137– 1143.
- 18 K. Genkina, A. E. Shipov, T. A. Mastryukova and M. I. Kabachnik, Synthesis of unsymmetrical triaryl phosphates under phase-transfer catalysis, *Russ. J. Gen. Chem.*, 1996, 66, 1742–1744.
- 19 R. Tacke, M. Strecker and R. Niedner, Sila-Pharmaka, 22. Cholinesterase-hemmende organophosphorsäureester und ihre silaanaloga, *Liebigs Ann. Chem.*, 1981, 1981, 387–395.
- 20 R. A. Levine and W. B. Person, Absolute infrared intensity measurements of fluoroform (CHF₃) fundamentals, J. Phys. Chem., 1977, 81, 1118–1119.
- 21 V. Dichiarante, D. Dondi, S. Protti, M. Fagnoni and A. Albini, A meta effect in organic photochemistry? The case of S_N1 reactions in methoxyphenyl derivatives, *J. Am. Chem. Soc.*, 2007, **129**, 5605–5611, correction: 11662.
- 22 V. Dichiarante, M. Fagnoni and A. Albini, Eco-friendly hydrodehalogenation of electron-rich aryl chlorides and fluorides by photochemical reaction, *Green Chem.*, 2009, **11**, 942–945.
- 23 O. A. Snytnikova, A. N. Simonov, O. P. Pestunova, V. N. Parnom and Y. P. Tsentalovich, Study of the photoinduced formose reaction by flash and stationary photolysis, *Mendeleev Commun.*, 2006, 16, 9–11.
- 24 Studies on the photodecomposition of phenyldiazonium ions demonstrated that singet phenyl cations add non-selectively even to weak nucleophiles. See: S. Milanesi, M. Fagnoni and A. Albini, Cationic arylation through photo(sensitised) decomposition of diazonium salts. Chemoselectivity of triplet phenyl cations, *Chem. Commun.*, 2003, 216– 217.
- 25 See, for example: J. Andraos, G. G. Barclay, D. R. Medeiros, M. V. Baldovi, J. C. Scaiano and R. Sinta, Model studies on the photochemistry of phenolic sulfonate photoacid generators, *Chem. Mater.*, 1998, **10**, 1694–1699.
- 26 E. Robert-Banchereau, S. Lacombe and J. Ollivier, Unsensitized photooxidation of sulfur compounds with molecular oxygen in solution, *Tetrahedron*, 1997, 53, 2087–2102.
- 27 F. Bertrand, F. Leguyader, L. Liguori, G. Ouvry, B. Quiclet-Sire, S. Seguin and S. Z. Zard, α-Scission of sulfonyl radicals: a versatile process for organic synthesis, C. R. Acad. Sci. II C, 2001, 4, 547–555.
- 28 D. Gonbeau, M. F. Guimon, S. Duplantier, J. Ollivier and G. Pfister-Guillouzo, Sulfochloration of trifluoromethane. Theoretical study of the trifluoromethane sulfonyl radical, *Chem. Phys.*, 1989, **135**, 85–89.
- 29 L. S. Guss and I. M. Kolthoff, The behavior of sulfur dioxide as an acid in methanol, J. Am. Chem. Soc., 1944, 66, 1484–1488.
- 30 A. Seubert and G. Wünsch, Nebenreaktionen in Karl-Fischerreagentien, *Fresenius' Z. Anal. Chem.*, 1989, **334**, 256–260.
- 31 E. R. Morris and J. C. J. Thynne, Reactions of radicals containing fluorine. Part 1. Hydrogen and deuterium atom abstraction from trideuteromethanol by trifluoromethyl radicals, *Trans. Faraday Soc.*, 1968, 64, 414–421.
- 32 J. Lillie, D. Behar, R. J. Sujdak and R. H. Schuler, Lifetime of trifluoromethyl radical in aqueous solution, J. Phys. Chem., 1972, 76, 2517–2520.
- 33 K. Seppelt, Trifluoromethanol, CF₃OH, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 322–323.
- 34 M. Avataneo, U. De Patto, M. Galimberti and G. Marchionni, Synthesis of α,ω-dimethoxyfluoropolyethers: reaction mechanism and kinetics, *J. Fluorine Chem.*, 2005, **126**, 631–637.
- 35 R. Flyunt, O. Makogon, M. N. Schuchmann, K.-D. Asmus and C. von Sonntag, OH-Radical-induced oxidation of methanesulfinic acid. The reactions of the methanesulfonyl radical in the absence and presence of dioxygen, J. Chem. Soc., Perkin Trans. 2, 2001, 787–792.