

Degradation of some triazine herbicides by UV radiation such as used in the UV disinfection of drinking water

K. Nick, H.F. Schöler, G. Mark*, T. Söylemez*, M.S. Akhlaq*, H.-P. Schuchmann* and C. von Sonntag*, *Hygiene-Institut der Universität Bonn Sigmund-Freud-Straße 25, D-5300 Bonn and *Max-Planck-Institut für Strahlenchemie Stiftstraße 34–36, D-4330 Mülheim a.d. Ruhr, Germany*

ABSTRACT: The UV ($\lambda = 254$ nm) photolysis, in aqueous solution, of some common herbicides of the s-triazine family (atrazines) has been studied. The main products (accounting for *c.* 90% of the degraded educts) are hydroxyl compounds which arise through dechlorination at the heteroaromatic ring. Quantum yields of chlorinated-triazine destruction and of hydroxytriazine formation have been determined. It has been established that with UV doses at present considered sufficient for drinking-water disinfection (fluences of 250 J/m^2), less than 5% of the triazines are transformed.

La dégradation de quelques herbicides triaziniques dans la lumière UV, sous les conditions de la désinfection de l'eau potable par irradiation UV

RESUME: La photolyse UV ($\lambda = 254$ nm), en solution aqueuse, de quelques herbicides appartenant à la famille des s-traizines (des atrazines) a été étudiée. Les produits majeurs, qui répondent à 90% environ des triazines chlorinés dégradés, sont des composés hydroxylés créés après perte d'un atome de chlore auprès de l'anneau hétéroaromatique. Des rendements quantiques de la destruction des triazines chlorinés et de la production des hydroxytriazines ont été déterminés. Il a été établi que moins de 5% des triazines sont transformés par des doses UV à présent considérées comme suffisant à la désinfection des eaux potables (fluences de 250 J/m^2).

INTRODUCTION

There is increasing interest in substituting chemical disinfection of drinking water, e.g. treatment with chlorine or chlorine dioxide, by disinfection using UV radiation. Because of the high effectivity of UV radiation in the inactivation of bacteria and viruses, very little by-product formation from trace constituents is expected at the low doses required for adequate disinfection. In those cases where studies have been carried out in some detail this expectation has proved to be correct [1–5].

Some of the herbicides currently in use are not readily biodegradable. Hence they persist in the soil and in the water run-off, and even reach groundwater. The amount allowed in drinking-water is very low; German regulations (TVO) set the maximum legally permissible level of total herbicide concentration at $0.5 \mu\text{g/l}$, subject to the further restriction that the concentration of any single herbicide must not surpass $0.1 \mu\text{g/l}$.

Because many herbicides absorb in the UV, and because the problem of water contamination by these compounds is very widely discussed among the general public, questions

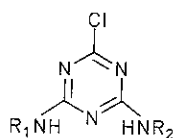
posed regarding the extent to which UV photolysis of herbicides gives rise to new anthropogenic compounds, have to be answered; i.e. to what extent are herbicides degraded during UV processing of drinking water. In addition, one would like to know the chemical nature of the major photodegradation products in order to evaluate whether or not there is an additional risk from such products. However, some of the herbicides at present in use do not show very significant absorption coefficients in the UV above a wavelength λ of 240 nm at which drinking water disinfection by UV light takes place, and only those that possess an aromatic ring or a similar chromophore may be noticeably degraded under these conditions.

A considerable number of studies has dealt with the photodegradation of herbicides [6–15], but in none of them have the quantum yields (dimension: molecules per absorbed quanta; unit: mol/einstein), or the fluences (J/m^2) required for their degradation by one or more decades, been determined. (For a glossary of photochemical terms see [16]). Hence, up to the present time it has not been

possible to view the extent of their photochemical degradation in the perspective of the UV-induced inactivation of bacteria. It has recently been shown that about 65 J/m² of 254 nm radiation are required to reduce the count of *E. coli* by one decade [17].

In the present work we have studied the photodegradation of some herbicides (1–4) of the triazine family. Included in this investigation are the corresponding dealkylated derivatives (5–7), because these are the major biodegradation products of those herbicides and are found in ground- and surface waters alongside their parent compounds. All of these have significant absorption coefficients at 254 nm (cf. Table 1), the characteristic wavelength (90%) emitted by the low-pressure mercury arc. Their formulae are shown in Fig. 1. The photodegradation products have been identified and their quantum yields determined. A mechanism for their formation is put forward.

In this work for the first time, the UV (254-nm) fluences to achieve one decadic reduction of some triazine herbicides have been established. It will be shown that their photolysis is not a cause for concern in drinking-water processing involving UV disinfection.



| | R ₁ | R ₂ |
|---------------------------------------|------------------------------------|------------------------------------|
| 1 Atrazine | -C ₂ H ₅ | -iso-C ₃ H ₇ |
| 2 Simazine | -C ₂ H ₅ | -C ₂ H ₅ |
| 3 Propazine | -iso-C ₃ H ₇ | -iso-C ₃ H ₇ |
| 4 Terbutylazine | -C ₂ H ₅ | -t-C ₄ H ₉ |
| 5 Desethylatrazine | -H | -iso-C ₃ H ₇ |
| 6 Desisopropylatrazine | -C ₂ H ₅ | -H |
| 7 Desethyldeisopropylatrazine | -H | -H |
| 8 Hydroxyatrazine | -C ₂ H ₅ | -iso-C ₃ H ₇ |
| 9 Hydroxysimazine | -C ₂ H ₅ | -C ₂ H ₅ |
| 10 Hydroxypropazine | -iso-C ₃ H ₇ | -iso-C ₃ H ₇ |
| 11 Hydroxyterbutylazine | -t-C ₄ H ₉ | -C ₂ H ₅ |
| 12 Hydroxydesethylatrazine | -H | -iso-C ₃ H ₇ |
| 13 Hydroxydesisopropylatrazine | -C ₂ H ₅ | -H |
| 14 Hydroxydesethyldeisopropylatrazine | -H | -H |

Fig. 1. Chemical formulae of atrazine and some other triazine derivatives.

EXPERIMENTAL PROCEDURE

The herbicides were obtained from Fa. Ehrenstorfer, Augsburg. Solutions were made up either in water directly, or else methanolic stock solutions (1000 p.p.m. \approx 10 mmol/l) were diluted to the desired concentration with water. The water was purified with a Millipore-Q filter system.

UV irradiations were done in 4 \times 20-cm² quartz cells, with an internal pathlength of 6 mm, made from rectangular quartz tubing supplied by Heraeus Quarzschmelze, Hanau. The cells were placed at a distance of about 16 cm from a Heraeus Original Hanau Sterisol N30/89 low-pressure mercury lamp that does not emit light with wavelengths shorter than the 254-nm line. The light intensity at 254 nm was determined using the oxygen-saturated peroxydisulphate-*t*-butanol actinometer, $\Phi(\text{H}^+) = 1.8$ [18,19] or the ferrioxalate actinometer [20]. The absorbance at 254 nm of the herbicide solutions in these cells was kept below 0.03. Under such conditions the concentration of the herbicides is still several orders of magnitude higher than in any drinking-water feedstock. The advantage of this procedure lies in that, on one hand the absorbance is sufficiently high so as to allow easy subsequent educt quantification by HPLC without the need to concentrate the solution, yet on the other hand is sufficiently low to treat the data according to a rate law which is only strictly fulfilled at 'vanishing absorbance' [21] (in the present study, the transmittance always surpasses 97%).

Absorption spectra were taken on a Pye Unicam SP 1750 spectrophotometer. Merck/Hitachi, Knauer, and ERC equipment was used for HPLC. Analyses of the degradation of herbicides 1–4 were done on a 20-cm Hypersil ODS (5- μ m) column using water:acetonitrile (1:1). For the measurement of the degradation of derivatives 5 and 6 and of the formation of 8 and 9, a 10-cm Inertsil C-8 (5- μ m) column was used with water:acetonitrile (4:1) as the eluent. After each run the column had to be purged for 10 min with water:acetonitrile (1:9). For the determination of 10 and 11, water:acetonitrile (7:3) was adequate, while 12 and 13 were determined using water:acetonitrile (20:1). 7 and 14 were determined on a 20-cm Inertsil C₈ (5- μ m) column with water:acetonitrile (20:1) as eluent.

For GC-MS, a Carlo Erba gas chromatograph (Mega 5100), directly coupled to a Finnigan mass spectrometer (ITD 700), was used. For example, 20 ml of a 2-mg/l aqueous atrazine solution were irradiated for 1 h to a fluence of 24 kJ/m², then evaporated to dryness in a rotary evaporator. Methanol (0.5 ml) was added, followed by 1 ml of 0.1-mol/l ether-diazomethane. After a 1-h reaction time the solution was concentrated to 0.5 ml under reduced pressure (15 mmHg, 20°C) [22]. A 2- μ l aliquot of this solution was injected into the gas chromatograph with a temperature program of 60°C (3 min), 25°C/min, 180°C (0 min), 5°C/min, 240°C (0 min), 40°C/min, 280°C (10 min). Retention time

and characteristic fragments of the main methylation product agreed with those of atratone (methoxyatrazine).

RESULTS AND DISCUSSION

The UV-absorption spectra of the triazine herbicides 1–4 and their bio- and photodegradation products 5–14 have been measured and the decadic molar absorption coefficients at $\lambda = 254$ nm determined (Table 1).

Solutions of the herbicides were photolysed as described. From time to time a sample was withdrawn from the irradiated solution and analysed for the remaining herbicide and the photoproducts. Because of the low absorptions at 254 nm encountered in these experiments the case of 'vanishing absorption' is approximated, and a representation of the decrease of the herbicide concentration $[H]$ should be linear when $\log([H]/[H]_0)$ is plotted vs. the irradiation time. This is immediately understood considering

$$-\frac{d[H]}{dt} = E\sigma_a\Gamma[H], \quad (1)$$

and its integrated form

$$2.3 \log([H]/[H]_0) = -E\sigma_a\Gamma t, \quad (1a)$$

where t is irradiation time, E is irradiance (W/m^2) or fluence rate (radiant power incident upon the surface), σ_a is the absorption cross-section (m^2/mol), Γ is the energy yield of herbicide degradation (mol/J) and $[H]_0$ is the herbicide concentration before irradiation. H , fluence (J/m^2), can be substituted for Et ; $\sigma_a = 0.23|\epsilon|$, where $|\epsilon|$ is the numerical value of the molar decadic absorption coefficient $\epsilon(254 \text{ nm})$ given in Table 1; and Γ is related to the more

familiar entity Φ , quantum yield ($\text{mol}/\text{einstein}$), through Einstein's equation $E_q = h\nu N_L(\text{J}/\text{einstein})$. In the case of 254-nm quanta, the numerical relationship is $\Phi = 4.71 \times 10^5 \Gamma$ (for details see [21]). Hence,

$$2.3 \log([H]/[H]_0) = 0.23|\epsilon|H\Phi/4.71 \times 10^5. \quad (2)$$

The condition of 'vanishing absorption' requires that light intensity (irradiance) is not significantly attenuated by the solution. In our case this requirement is fulfilled, because the transmittance is greater than 97%. Data plotted according to Eqn 2 are shown in Fig. 2 for atrazine H_1 . Similar linear plots were obtained for the other herbicides and their bio- and photodegradation products investigated.

A logarithmic dependence of the surviving fraction on photolysis time is also found when bacteria are inactivated by UV radiation. Hence, the same rate law is followed in herbicide degradation and the inactivation of microorganisms. Thus, by comparing in these two systems the fluence required for the reduction of the concentration of the trace constituent by, for example, one decade (H_{90} , 90% decomposition), we arrive at the effectivity of herbicide degradation relative to the UV inactivation of *E. coli* for which $65 \text{ J}/\text{m}^2/\text{decade}$ may be typical [17]. In drinking-water processing, this is a more relevant parameter than the quantum yield Φ or energy yield Γ alone. A UV fluence of $250 \text{ J}/\text{m}^2$ has generally been considered sufficient for the disinfection of drinking water (cf. [23]). For instance, a reduction of the *E. coli* count by about four decades is effected by this fluence. If this value is substituted in Eqn 2, the percentage of the herbicide degraded under such conditions can be calculated. These values are included in Table 1.

Table 1. Spectral and photochemical data of herbicides and derivatives investigated in the present study

| Nr | Herbicide* | ϵ_{254} (l/mol/cm) | H (90% decomp.) (kJ/m ²) | Fraction decomposed at 250 J m ² (%) | Φ (decomposition) (mmol/einstein) |
|----|------------------------------------|--------------------------------|--|--|--|
| 1 | Atrazine | 3860 | 24 | 2.4 | 50 |
| 2 | Simazine | 3330 | 17 | 3.4 | 83 |
| 3 | Propazine | 3370 | 14 | 4.1 | 99 |
| 4 | Terbutylazine | 3830 | 13 | 4.4 | 94 |
| 5 | Desethylatrazine | 3440 | 23 | 2.5 | 59 |
| 6 | Desisopropylatrazine | 3600 | 22 | 2.6 | 59 |
| 7 | Desethyldeisopropylatrazine | 2200 | 116 | 0.5 | 18 |
| 8 | Hydroxyatrazine | 940 | ** | | |
| 9 | Hydroxysimazine | 1340 | ** | | |
| 10 | Hydroxypropazine | 2160 | ** | | |
| 11 | Hydroxyterbutylazine | 2720 | ** | | |
| 12 | Hydroxydesethylatrazine | 610 | *** | | |
| 13 | Hydroxydeisopropylatrazine | 560 | *** | | |
| 14 | Hydroxydesethyldeisopropylatrazine | 460 | *** | | |

*Nomenclature as defined in [30], ** > 300 kJ/m² for 10% decomposition, *** > 500 kJ/m² for 10% decomposition

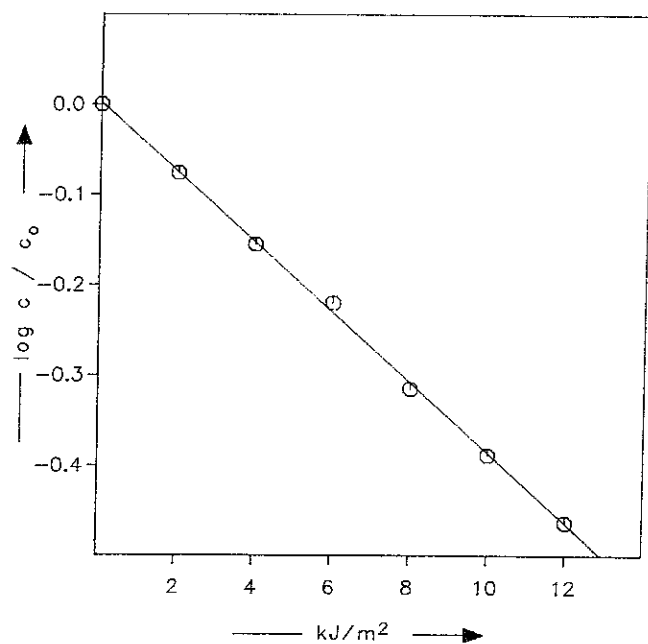


Fig. 2. Degradation of atrazine by UV (254-nm) light. $\log([atrazine]/[atrazine]_0)$ is plotted vs. the fluence.

For the compounds studied here, they are seen to stay below 5%, i.e. under UV-disinfection conditions the triazines are barely degraded. Following Eqn 2 and the relationship between Φ and Γ (see above), quantum yields of decomposition (last column in Table 1) can be calculated from the measured ϵ and H_{90} values.

Mechanistic aspects

It can be seen from Fig. 3 that in the photolysis of atrazine there is only one major product; this is hydroxyatrazine (8). It accounts for about 90% of the atrazine degraded. A similar situation holds for all of the other triazines investigated (data not shown).

Photosubstitution of aromatic chlorinated compounds (ACl) is a well-known process [24,25]. It has been considered that this process may in fact have three steps: the homolytic scission of the C-Cl bond (Reaction 4) followed by an electron transfer of the two resulting radicals within the solvent cage (Reaction 5) and reaction of the carbocation with water (Reaction 6):

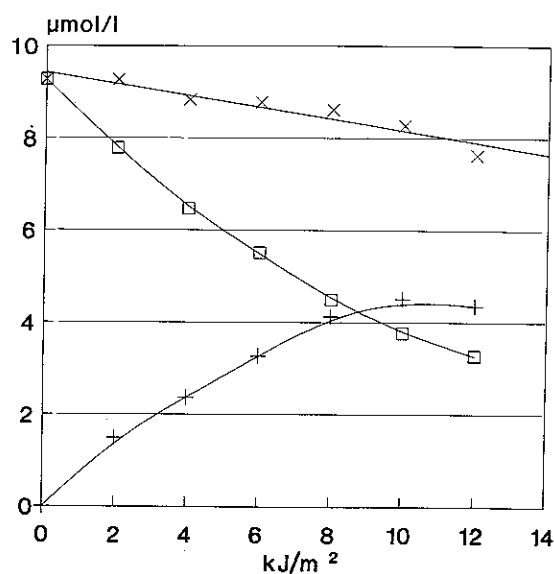
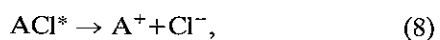
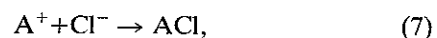
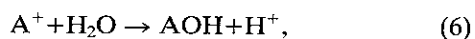
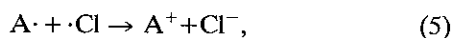
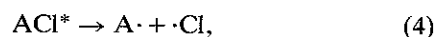
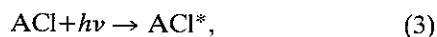
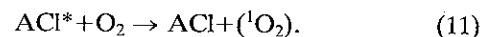
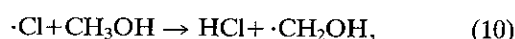
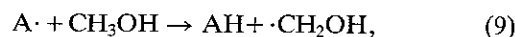


Fig. 3. Degradation of atrazine by UV (254-nm) light. Degradation of atrazine (\square), build-up of hydroxyatrazine (+), and the sum of the amounts of these two compounds as a function of the fluence (\times).



In competition with Reaction 6 the chloride ion may react within the cage with the carbon cation (Reaction 7), a reaction which reduces the quantum yield of product formation.

An alternative to the homolytic scission (Reaction 4) is the heterolytic cleavage in the excited state (Reaction 8) (cf. [26]); this reaction path is favoured in polar solvents, especially water. Productwise, the two alternatives are indistinguishable in the absence of scavengers. However, when methanol is added, measurable amounts of the radicals should be scavenged as both $A\cdot$ and $\cdot Cl$ are expected to react with the alcohol with diffusion-controlled rate constants [27,28]. Hence, any $A\cdot$ and $\cdot Cl$ radicals escaping the cage should be scavenged according to Reactions 9 and 10. As a result of this, the dehalogenated triazine (AH) should become a noticeable product [29]. In the event, in an aqueous 2-mg/l atrazine solution containing 30 vol% methanol irradiated for 1 h, corresponding to a fluence of 24 kJ/m^2 , i.e. at a degradation of atrazine of 90%, a yield of only 0.5% of the dechlorinated triazine was observed by GC-MS, perhaps indicating some participation of Reaction 4 in the mechanism.

It is noted that saturation of the atrazine solutions with oxygen reduces the quantum yield of atrazine destruction by 30% as compared to the photolysis of oxygen-free solutions. This indicates that oxygen quenches an excited state (Reaction 11). Because the effect is not very pronounced,

oxygen may either interfere with a long-lived singlet or a short-lived triplet state. At present, a distinction cannot be made.

The yields of the hydroxy compounds do not completely match the consumption of the chlorinated educts (Fig. 3). The absence of a full material balance is not due to the concomitant photolysis of the hydroxytriazines, because these compounds are relatively photostable (see Table 1). Rather, there must be minor products that have escaped identification. This is by no means unlikely if the missing 10% are made up of a multitude of compounds.

It is worth mentioning that with the herbicides 1-4 irradiated to a conversion of more than 10%, no mutagenicity was detected by the Ames test even when the irradiated material was applied in high concentrations (H.-J. Moriske and M. Wiese, in preparation). In this respect the behaviour of the hydroxytriazines parallels that of their chlorinated parent compounds.

CONCLUSION

At a UV fluence of 250 J/m² the photodegradation of the triazine herbicides studied remains below 5% (see Table 1). Hence, it is concluded that the hygienic properties of drinking water regarding its triazine content are not materially affected when it is disinfected with UV radiation. Some preliminary data from our laboratories indicate that this is also true for other herbicides currently in agricultural use.

ACKNOWLEDGMENTS

This work has been supported by the Bundesministerium für Forschung und Technologie, Project 02-WT 8720 (initiator, Prof. G.O. Schenck; coordinator, Prof. H. Bernhardt). We thank the summer students A. von Sonntag and J. Reddig for their technical assistance.

BIBLIOGRAPHY

1. von Sonntag, C. Disinfection with UV-radiation. In: *Process Technologies for Water Treatment* (ed. Stucki, S.), pp. 159-179. Plenum Press, New York (1988).
2. von Sonntag, C. The chemistry behind the upgrading of water with uv light. An overview. In: *Ozone+UV in the Treatment of Water and Other Liquids* (ed. Masschelein, W.), pp. V-1-1-V-1-11. International Ozone Association, European Committee (Wasser Berlin '89) (1989).
3. Akhlaq, M.S., Schuchmann, H.-P. and von Sonntag, C. Degradation of the polysaccharide alginic acid: a comparison of the effects of UV light and ozone. *Environmental Science and Technology* **24**, 379-383 (1990).
4. Deeble, D.J., Randall, R.C., Williams, P.A., Phillips, G.O., Akhlag, M.S., Puramshetty, J.P.R., Bothe, E., Steffen, H. and von Sonntag, C. The treatment of aqueous gum arabic solutions with ultraviolet radiation. *Food Hydrocolloids* **4**, 313-321 (1990).
5. von Sonntag, C. Untersuchungen zur hygienischen Sicherheit der Trinkwasserdesinfektion mit UV-Strahlen. Photochemische und aktinometrische Untersuchungen. *DVGW-Schriftenreihe Wasser* **108**, 47-60 (1990).
6. Pape, B.E. and Zabik, M.J. Photochemistry of bioactive compounds. Solution phase photochemistry of symmetrical triazines. *Journal of Agriculture and Food Chemistry* **20**, 316-320 (1972).
7. Ruzo, L.O., Zabik, M.J. and Schuetz, R.D. Photochemistry of bioactive compounds. Kinetics of selected s-triazines in solution. *Journal of Agriculture and Food Chemistry* **21**, 1047-1049 (1973).
8. Burkhard, N. and Guth, J.A. Photodegradation of atrazine, atraton and ametryne in aqueous solution with acetone as a photosensitizer. *Pesticide Science* **7**, 65-71 (1976).
9. Sakriß, W., Gäb, S. and Korte, F. Beiträge zur ökologischen Chemie CXXVIII. Photooxidationsreaktionen von Metabenzthiazuron in Lösung. *Chemosphere* **5**, 339-348 (1976).
10. Khan, S.U. and Schnitzer, M. UV Irradiation of atrazine in aqueous fulvic acid solution. *Journal of Environmental Science and Health* **13B**, 299-310 (1978).
11. Gabel, B., Stachel, B. and Thiemann, W. Möglichkeiten der technischen Anwendung einer Kombination von Ultraviolett-Bestrahlung und H₂O₂-Behandlung zur Desinfektion von Trinkwasser und Oxidation von Inhaltsstoffen. *Fachliche Berichte HWW* **2**, 37-42 (1982).
12. Stachel, B., Gabel, B., Cetinkaya, M., von Düszein, J., Kozicki, R., Lahl, U., Podbielski, A. and Thiemann, W. Abbau von Organochlorverbindungen durch UV-Bestrahlung bei gleichzeitiger Wasserstoffperoxid-Zugabe unter Wasserwerksbedingungen. *gwf-wasser/abwasser* **123**, 190-194 (1982).
13. Bandemer, T. and Thiemann, W. Abbau chlororganischer Schadstoffe im Wasser durch Ultraviolettbestrahlung und Zusatz von Wasserstoffperoxid. *Brunnenbau, Bau von Wasserwerken, Rohrleitungsbau (bbr)* **37**, 413-417 (1986).
14. Kearney, P.C., Muldoon, M.T. and Somich, C.J. UV-Ozonation of eleven major pesticides as a waste disposal pretreatment. *Chemosphere* **16**, 2321-2330 (1987).
15. Thiemann, W. and Bandemer, T. Kombination von UV-Bestrahlung und Wasserstoffperoxid-Zusatz zur Beseitigung organischer Substanzen aus Rohwasser. *DVGW-Schriftenreihe Wasser* **107**, 129-145 (1988).
16. Braslavsky, S.E. and Houk, K.N. Glossary of terms used in photochemistry. *Pure and Applied Chemistry* **60**, 1055-1106 (1988).
17. Zemke, V. and Schoenen, D. UV disinfection experiments with *E. coli* and actinometric determination of the irradiation intensity. *Zentralblatt für Hygiene* **188**, 380-384 (1989).
18. Mark, G., Schuchmann, M.N., Schuchmann, H.-P. and von Sonntag, C. A chemical actinometer for use in connection with UV treatment in drinking-water processing. *Journal of Water Supply Research and Technology—Aqua* **39**, 309-313 (1990).

19. Mark, G., Schuchmann, M.N., Schuchmann, H.-P. and von Sonntag, C. The photolysis of potassium peroxodisulphate in aqueous solution in the presence of tert-butanol: a simple actinometer for 254 nm radiation. *Journal of Photochemistry and Photobiology A: Chemistry* **55**, 157–168 (1990).
20. Calvert, J.G. and Pitts, J.N., Jr. *Photochemistry*. Wiley, New York (1966).
21. von Sonntag, C. and Schuchmann, H.-P. UV-disinfection of Drinking-water and by-product formation: some basic considerations. *Journal of Water Supply Research and Technology—Aqua* **41**, 67–74 (1992).
22. Färber, H. and Nick, K. Determination of hydroxy-s-triazines in water using HPLC and GC-MS. *Forsenius' Zeitschrift für Analytische Chemie*, (in press).
23. Martiny, H., Wlodavezyk, K., Harms, G. and Rüden, H. Anwendung von UV-Strahlen zur Desinfektion von Wasser I. Mitt.: Mikrobiologische Untersuchungen in Trinkwasser. *Zentralblatt für Bakteriologie und Hygiene* **B185**, 350–367 (1988).
24. Grimshaw, J. and de Silva, A.P. Photochemistry and photocyclization of aryl halides. *Chemistry Society Review* **10**, 181–203 (1981).
25. Choudry, G.G., Webster, G.R.B. and Hutzinger, O. Environmentally significant photochemistry of chlorinated benzenes and their derivatives in aquatic systems. *Toxicology and Environmental Chemistry* **13**, 27–83 (1986).
26. McClelland, R.A., Kanagasabapathy, V.M., Banait, N.S. and Steenken, S. Flash photolysis generation as reactivities of triarylmethyl and diarylmethyl cations in aqueous solution. *Journal of the American Chemical Society* **111**, 3966–3972 (1989).
27. Madhavan, V., Schuler, R.H. and Fessenden, R.W. Absolute rate constants for reactions of phenyl radicals. *Journal of the American Chemical Society* **100**, 888–893 (1978).
28. Ingold, K.U., Luszyk, J. and Raner, K.D. The unusual and the unexpected in an old reaction. The photochlorination of alkanes with molecular chlorine in solution. *Archives of Chemical Research* **23**, 219–225 (1990).
29. Campbell, J.M., von Sonntag, C. and Schulte-Frohlinde, D. Photolysis of 5-bromouracil and some related compounds in solution. *Zeitschrift für Naturforschung* **29b**, 750–757 (1974).
30. Worthing, R. and Hance, R.J. (eds) *The Pesticide Manual*, 9th edn. The British Crop Protection Council, London (1991).