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DEGRADATION OF ATRAZINE BY HYDROLYSIS AND BY HYDROXYL RADICALS

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Rates of degradation of the triazine herbicide atrazine are reported, together with an analysis of the sequence of stages involved, using hydroxyl radicals generated by hydrogen peroxide in the presence of UV light and by the pure photochemical reaction. These conditions bring about the displacement of chlorine by hydroxyl, dealkylation of the alkylamino groups and finally deamination of the triazine ring. The significance of these results to water purification is discussed.

INTRODUCTION

The herbicide atrazine, 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine (**1**), together with other related triazines used in agriculture, has become a priority pollutant in many natural waters of Europe.[1-3] The natural degradation of these compounds is slow and their removal is a major problem for suppliers of potable water. Acid and alkaline hydrolysis will displace the chlorine[4,5] slowly, but a rapid, safe and inexpensive route to the removal of the triazine nucleus is an important goal for water-purification research. Oxidative degradation by powerful oxidants such as ozone[6,7] and the hydroxyl radical[8,9] seem to be the most promising techniques and the aim of this work was to elucidate the pathways by which these herbicides are degraded. This paper reports the rates of hydrolysis of atrazine as a function of pH and the sequence of intermediates which is obtained when it is subjected to attack by hydroxyl radicals generated by the ultraviolet irradiation of hydrogen peroxide over a range of pH and by the effect of the radiation alone.

EXPERIMENTAL

Commercial atrazine (Ciba-Geigy) was purified by recrystallization from ethanol, m.p. 175–177 °C. Aqueous solutions of atrazine, up to a maximum concentration of 100 mg l^{-1}, were prepared and their concentrations were determined by high-performance liquid chromatography (HPLC).

N,N-Diethyl-1,4-phenylenediamine (DPD) solution was made by dissolving DPD (0·1 g) in 0·05 M sulphuric acid (10 ml). The solution was freshly prepared each week and stored in the dark.

Peroxidase (POD) solution was prepared by dissolving the solid enzyme (0·017 g) in water (10 ml) and the solution was freshly prepared weekly.

Hydrogen peroxide was assayed as follows:[10] to 25·0 ml of a sample of water containing hydrogen peroxide (between 0·085 and 0·85 mg l^{-1}) were added 5·0 ml of phosphate buffer (pH 6), 50 μl of DPD reagent and 50 μl POD solution. After allowing the mixture to stand for 2 min, the absorbance at 550 nm (A) was measured in a 1 cm cell against a blank of pure water containing the reagents. Then the relationship $[H_2O_2]$ (mg l^{-1}) = 1·944 A was used.

Kinetic procedure

Atrazine solution was added to an equal volume of buffer solution to give final pH values between 1·4 and 10 at 65 °C. Aliquots were withdrawn at intervals and the residual atrazine concentration was determined. First-order kinetics were observed. Rates of degradation at pH 1·4 over a range of temperature between 48 and 65 °C were measured and the Arrhenius parameters were determined (Table 2).

Reaction of atrazine with hydrogen peroxide under ultraviolet irradiation

To water containing atrazine at various concentrations was added hydrogen peroxide [0·06 g l^{-1} of 30% (w/v) H_2O_2]. The solution was placed in a water-cooled photoreactor (Applied Photophysics, Model RQ125), a

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quartz vessel fitted with a centrally located medium-pressure mercury lamp, and was irradiated for various time intervals. Periodically, samples were withdrawn for analysis by HPLC. The UV intensity was determined by ferrioxalate actinometry[11] and was found to be 0·70 W l^{-1} at 254 nm.

Photochemical degradation

Atrazine and its deisopropyl degradation product, (4) were separately dissolved in water (concentrations 50–80 ppm) and irradiated as described above, analysing the product by HPLC.

Separation and identification of products

Atrazine and its degradation products were separated and determined by HPLC using the following isocratic (i.e. constant solvent) method; column, LiChrosorb RP-18, 10 μm 25 cm × 5 mm i.d.; mobile phase, 65% (w/w) methanol–water; pressure, 1900 psi; flow-rate, 1·0 ml min^{-1}; UV detection at 220 nm; temperature, ambient; injection volume, 0·1 ml.

Products were identified by comparison of their retention times with those of authentic samples which were either purchased or synthesized.

2-Ethylamino-4-hydroxy-6-isopropylamino-1,3,5-triazine (**2**) was prepared by the alkaline hydrolysis of atrazine.[5]

2-Amino-4-chloro-6-isopropylamino-1,3,5-triazine (**3**) cyanuric chloride (5 g, 27 mmol) was dissolved in hot acetone (200 ml) and the solution cooled to −30 °C. Anhydrous ammonia was rapidly passed into the solution, whereupon the temperature initially rose but was maintained below −10 °C. When the temperature began to fall, the contents of the vessel were poured on to ice and the solid product, 2-amino-4,6-dichloro-1,3,5-triazine, was immediately treated with isopropylamine (10 g, an excess), stirring the ice slurry. A white precipitate of **3** formed and the mixture was heated in order to melt the ice. The solid was filtered, washed, dried and recrystallized from hexane; m.p. 98 °C (lit.[12] m.p. 98 °C)

2-Amino-4-chloro-6-ethylamino-1,3,5-triazine (**4**) was prepared analogously to **3**, replacing isopropylamine with ethylamine, and had m.p. 174–176 °C (lit.[12] m.p. 177 °C).

2-Amino-4-ethylamino-6-hydroxy-1,3,5-triazine (**5**) and 2-amino-4-hydroxy-6-isopropylamino-1,3,5-triazine (**6**) were prepared by the irradiation at 254 nm for 1 h of aqueous solutions of **4** and **3**, respectively.[13] They were identified by the appearance of new chromatographic peaks and by their mass spectra obtained using combined HPLC and mass spectrometry (MPLC–MS). M^+ for **5** had m/z 169 and **6** 155.

2-Chloro-4,6-diamino-1,3,5-triazine (**7**) was obtained from Aldrich.

Table 1. HPLC retention times of products

Compound	t_R (min)	Compound	t_R (min)
1	9·00	**8**	–
2	5·30	**9**	2·85
3	4·50	**10**	2·60
4	3·90	**11**	3·50
5	3·00	**12**	6·10
6	3·20	**13**	2·80
7	3·10	**14**	15·10

2,4-Diamino-6-hydroxy-1,3,5-triazine (**9**) was prepared by the alkaline hydrolysis of **7** (2 g, 13·7 mmol) by 2 M sodium hydroxide (20 ml). The mixture was heated under reflux until the solid dissolved, then was cooled and neutralized with HCl. Compound **9** separated out and was filtered and recrystallized from 2 M potassium carbonate solution; yield, 1·2 g (70%).

2-Amino-4,6-dihydroxy-1-3-5-triazine (**10**) was supplied by WRC (Medmenham). 2,4,6-Trihydroxy-1,3,5-triazine (cyanuric acid) (**13**) was obtained from Aldrich.

2,4-Bis(*tert*-butylamino)-6-chloro-1,3,5-triazine (**14**) was prepared by the treatment of cyanuric chloride (5 g, 27 mmol) with *tert*-butylamine (7.3 g, 100 mmol) in acetone (200 ml). The solution was heated under reflux for 3 h and was then cooled and poured on to ice. The solid product of crude **13** was filtered and recrystallized from hexane, m.p. 165 °C. Found, C 51·26, H 7·82, N 27·16; $C_{11}H_{20}N_5Cl$ requires C 50·46, H 7·72, N 26·59%. M.W. = 201·73.

2-Acetylamino-4-chloro-6-isopropylamino-1,3,5-triazine (**11**), (M^+, m/z 229/231), 2-amino-4-chloro-6-hydroxy-1,3,5-triazine (**8**) (M^+, m/z 146/148) and 2-acetylamino-4-hydroxy-6-isopropylamino-1,3,5-triazine (**12**) (M^+, m/z 211) were inferred to be formed by the appearance of novel product peaks in the chromatogram whose molecular masses matched these structures (HPLC–MS using chemical ionization) and whose retention times agreed with literature values. They were very minor products.

HPLC retention times of compounds **1**–**14** are given in Table 1.

Methods for degradation of atrazine

Hydrolytic methods

A solution of atrazine (100 mg l^{-1}) was prepared in an appropriate aqueous buffer solution and was maintained at a fixed temperature between 60 and 90 °C. Samples were withdrawn at intervals and analysed by HPLC. On standing, the sole product of the hydrolysis crystallized out and was identified as **2**. The buffers used were prepared by mixing 0·1 M potassium dihydrogenphosphate solution (50 ml) with the requisite

Table 2. Rate data for acid and alkaline hydrolysis of atrazine[a]

T (°C)	pH	$10^{-5}k$ (s^{-1})[b]
48·0	1·4	1·8
58·0	1·4	4·27
65·0	1·4	6·07
65·0	1·9	2·00
65·0	2·12	1·55
65·0	12·38	4·87
65·0	12·92	9·02

[a] At pH 1·4, $E_a = 67·7$ kJ mol^{-1}, $\log A = 9·60$.
[b] Relative standard deviation 5%, $n = 5$

amount of 0·1 M sodium hydroxide solution to give the desired pH.

Rate constants were calculated using the Guggenheim procedure and linear plots were established by a least-squares methods (Table 2).

Hydrogen peroxide and UV irradiation

To a solution of atrazine (500 ml at a concentration 50 mg l^{-1}) in water was added '100 volume' hydrogen peroxide (1 ml). A portion of the solution was retained for analysis as detailed above and the remainder was placed in the immersion cell and irradiated. Samples were removed periodically for analysis of atrazine and its degradation products. Plots of progress of the reaction for the products were constituted from which the sequence of events could be inferred (Figure 2).

RESULTS AND DISCUSSION

Rates of hydrolysis of atrazine to the corresponding hydroxy compound, **2**, and Arrhenius parameters are given in Table 2. The hydrolysis rates show a first-order dependence on both $[H_3O^+]$ and $[OH^-]$ and were found to be too slow to measure near neutral pH. The mechanism of alkaline hydrolysis is presumed to be a two-step nucleophilic displacement of chlorine (S_NAr) (Scheme 1) by OH^- but the acidic hydrolysis must be assumed to proceed via protonated triazine. Protonation at one or other of the side-chain nitrogens, which are the more basic centres, would then activate the ring to attack by H_2O.

Ultraviolet irradiation of atrazine and of its de-isopropyl derivative, **4**, led to a relatively slow conversion to the corresponding hydroxylated products, **2** and **5**, respectively. This is presumed to occur by attack of water on the excited species and contributes a minor pathway to the degradation. By comparison, these conversions were considerably faster in the presence of

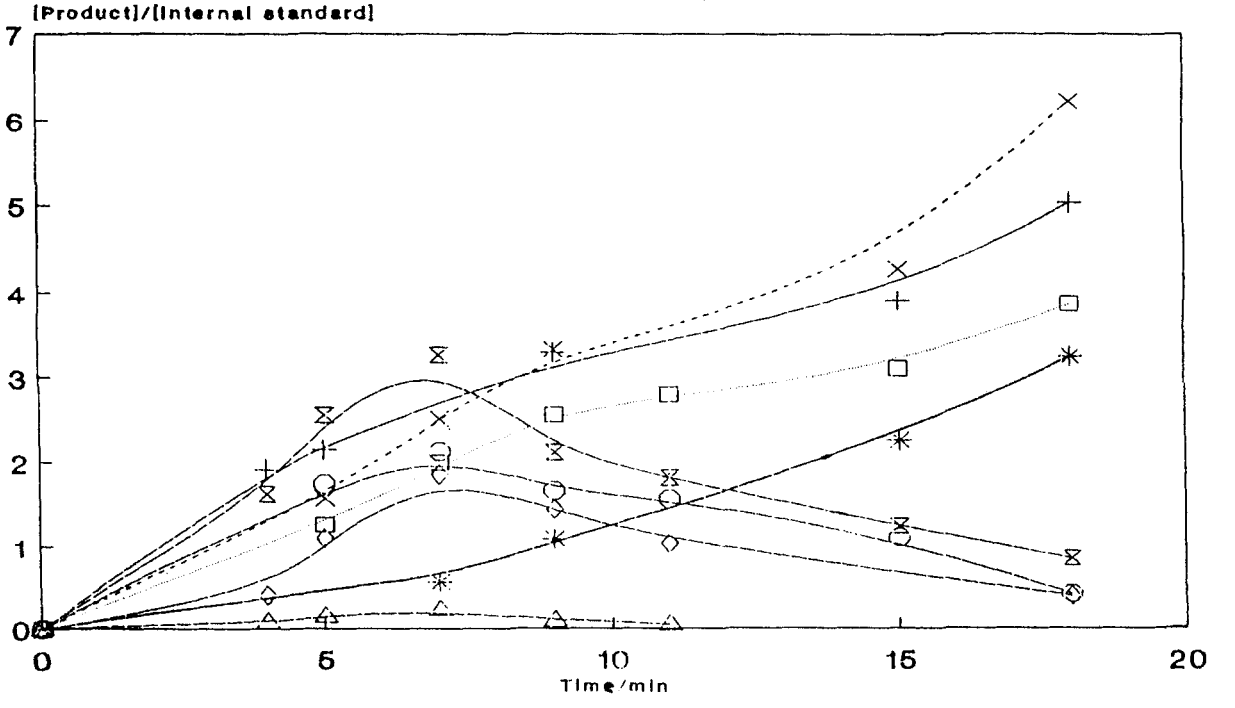


Figure 1. Degradation of atrazine by hydrogen peroxide and UV radiation at pH 4·7 (1); (13) + (10) + (9); (7) + (5); (6); (12); (4); (3); (2); (11)

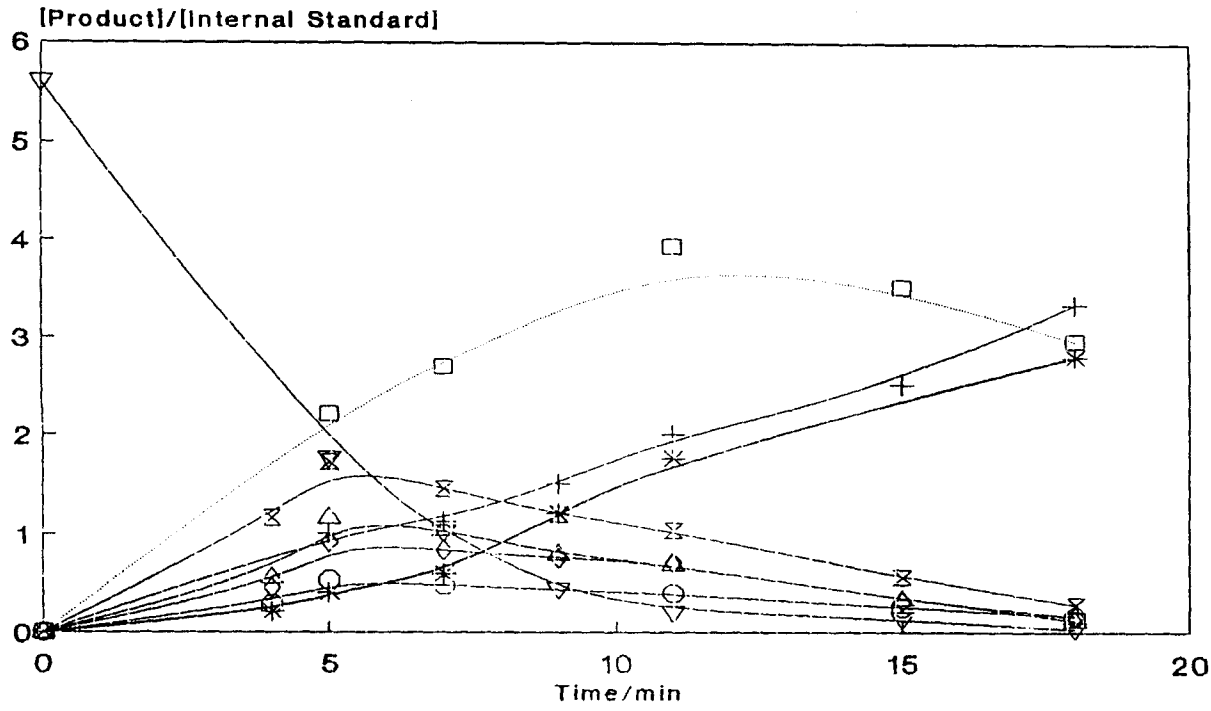
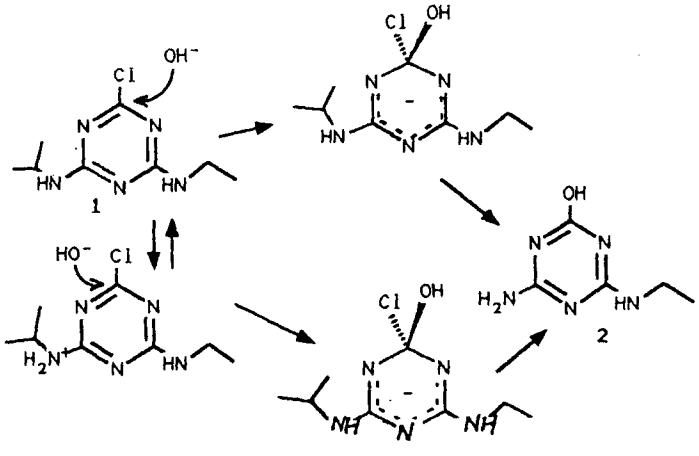


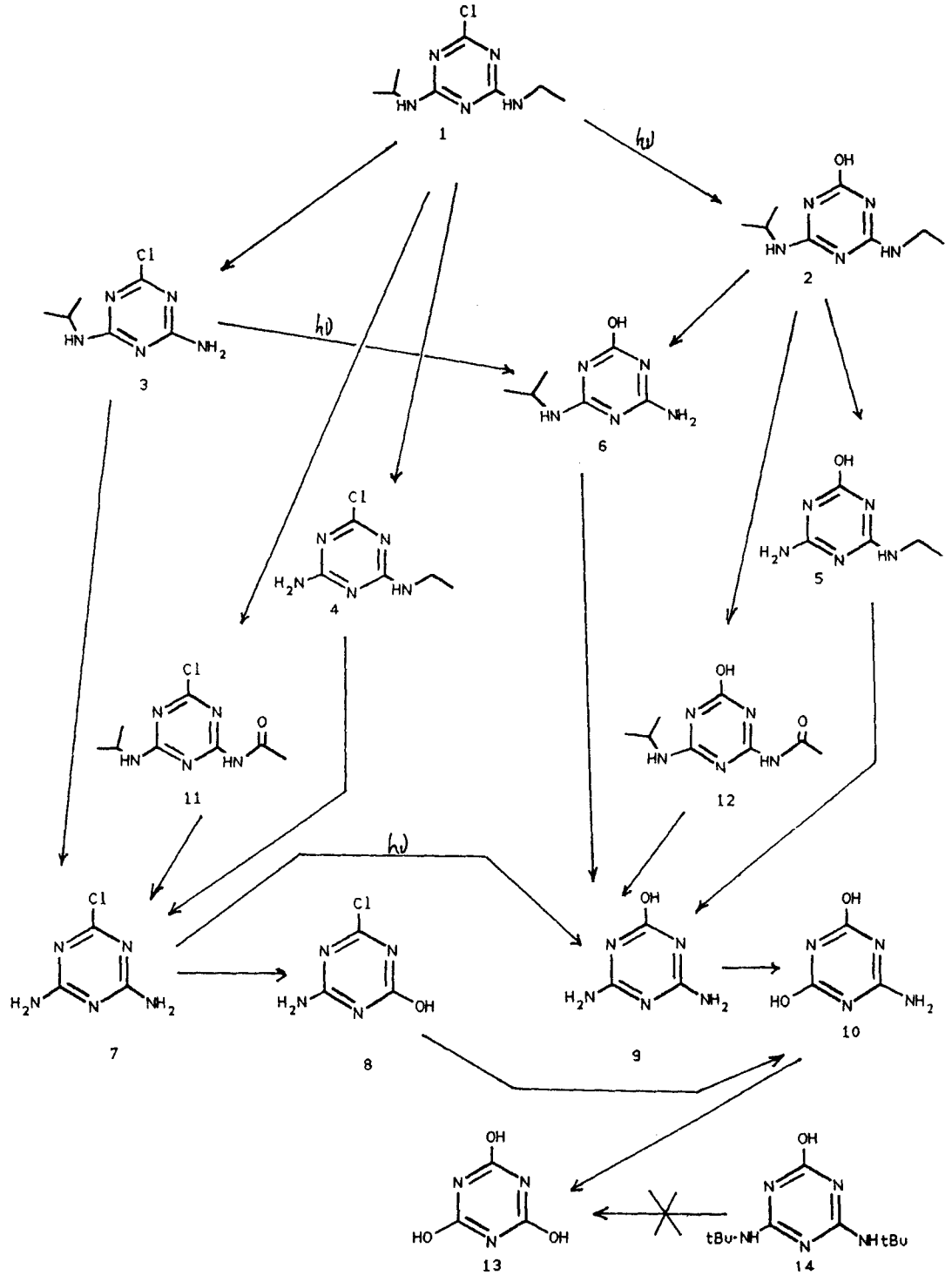
Figure 2. Degradation of atrazine by hydrogen peroxide and UV radiation at pH 6·9 (1); (13) + (10) + (9); (7) + (5); (6); (12); (4); (3); (2); (11)

hydrogen peroxide (under our conditions, about 12 min for 90% completion compared with 60 min in the absence of the hydrogen peroxide).

When treated with hydrogen peroxide and ultraviolet radiation, atrazine degrades by stages eventually to form cyanuric acid. The reactive species is undoubtedly the hydroxyl radical formed by photolysis of H_2O_2 and is involved in three types of reaction: (a) displacement of the chlorine by OH·, (b) fission of the alky–nitrogen bonds and (c) fission of the aryl–nitrogen bonds, to which we may add (d) photochemical hydrolysis of the aryl–chlorine bond. Reactions of types a and b occur in parallel while type c occurs subsequently to b. From **1** are obtained sequentially **3**, **4** and **7**, whereas from **2** are



Scheme 1



Scheme 2

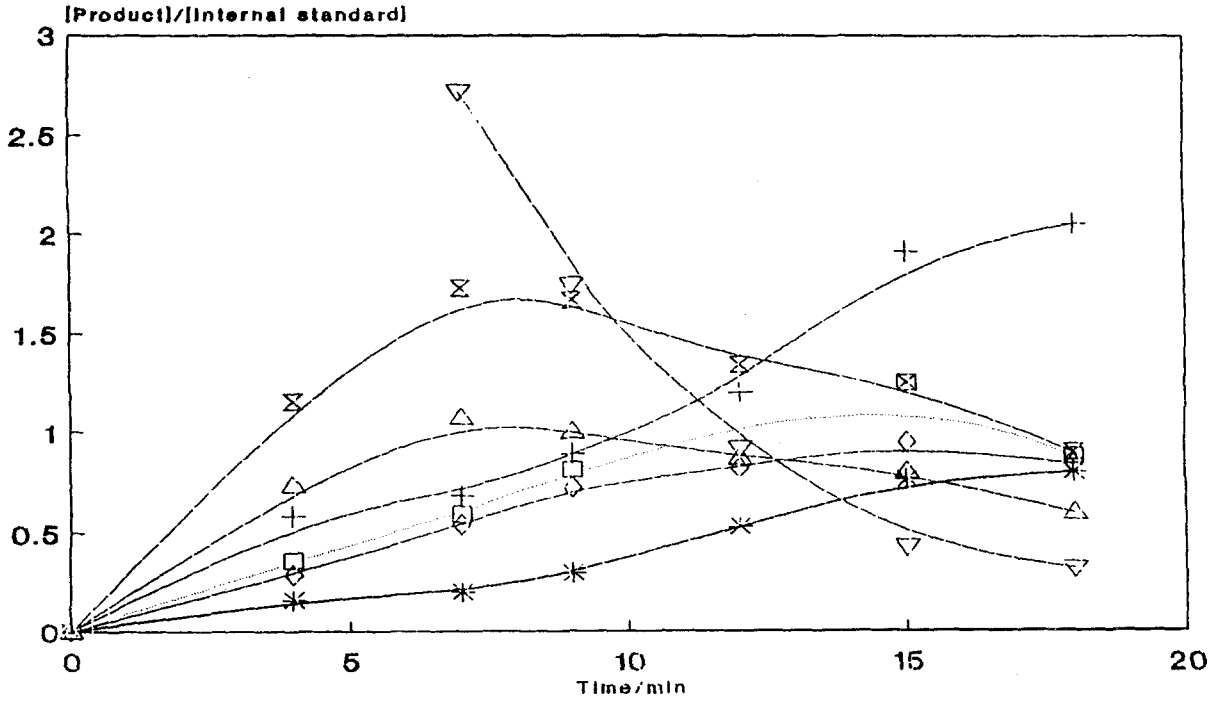
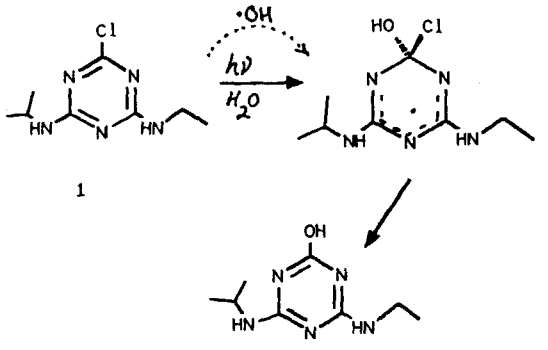


Figure 3. Degradation of atrazine by hydrogen peroxide and UV radiation at pH 9·0 (1); (13) + (10) + (9); (7) + (5); (6); (12); (4); (3); (2); (11)

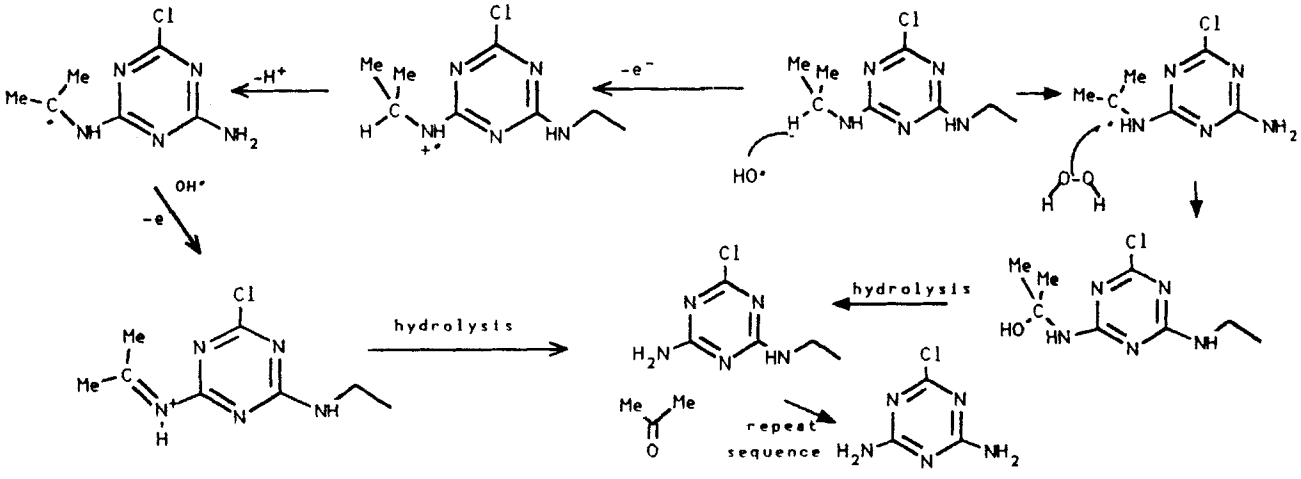
formed **5**, **6** and **9** (Scheme 2, Figures 1–3). Hydrolysis of **1** to form **2** under these conditions is mainly photochemical and presumably occurs by attack of water on excited atrazine, although there is also a contribution to this reaction of *ca* 10% by the added hydrogen peroxide, which may be by a radical displacement of chlorine (Scheme 3).

The fission of the *N*-alkyl groups is believed to occur by one-electron oxidation followed by loss of an α-proton to yield an iminium ion, which undergoes hydrolysis releasing the alkyl group as a carbonyl compounds (Scheme 4) and leaving an aminotriazine,[14] although α-hydrogen abstraction and subsequent formation of an *O,N*-acetal is an alternative route to the same products. As support for this scheme we note that, at low pH at least, the isopropyl group is removed faster than is ethyl, as would be expected for a group that can form a tertiary radical. Further, *N-tert*-butyl groups do not degrade at all under these conditions; **14** was synthesized and subjected to the degradation procedure but survived intact the conditions which completely destroyed atrazine. The microbial degradation of atrazine by *Pseudomonas* species[15] shows a similar sequence of products; removal of the isopropyl group is faster than removal of ethyl while displacement of chlorine is very slow.



Scheme 3

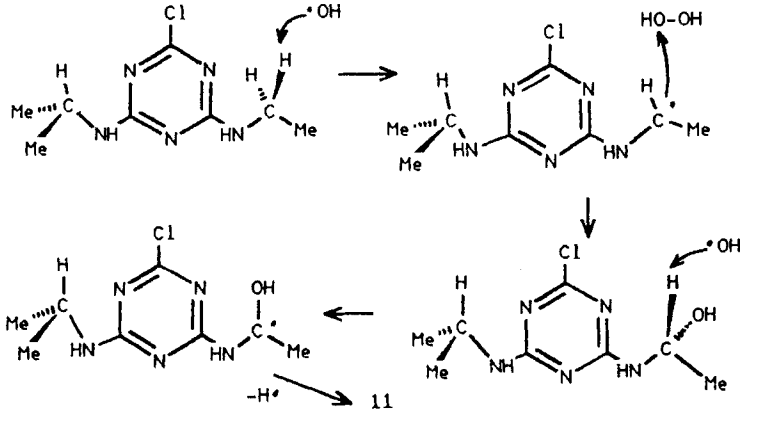
Additional evidence for the involvement of the hydroxyl radical comes from the observation that an identical sequence of degradation products, (**1** → **3**, **4** → **7**) formed in the same order and proportions, is obtained when atrazine is treated with Fenton's reagent (hydrogen peroxide in the presence of Fe^{2+}), which is known to generate OH·.[16] The corresponding series of hydroxylated products (**2**, **5**, **6**, **9**) are not obtained under these conditions since the hydroxyl radicals are available for only a short duration as compared with the photolytic method, and chlorine displacement is unable to compete with amine attack.



Scheme 4

A further pathway for oxidation of an *N*-ethyl group results in conversion to the *N*-acetyltriazine. Both 2-acetyl-4-chloro-6-isopropylaminotriazine (**11**) and the 4-hydroxy analogue (**12**), were detected during the course of the reaction as minor intermediates. It is proposed that these arise from **1** and **2**, respectively, by hydroxylation and further hydrogen abstraction at the α-carbon (Scheme 5). There are marked differences in the rate and product profiles for the reactions carried out at different pH values, analogously to the anodic oxidation of *p*-aminodiphenylamine.[17] At pH 4·7, the loss of the *N*-isopropyl group is faster than that of the *N*-ethyl group and the products are 3 and 4. The rates of formation of these two become more equal at pH 7, whereas at pH 9 oxidation of the ethyl side-chain to the amide, **11**, is fastest. Further, the overall rates of degradation of atrazine increase with increasing acidity of the medium (Figure 4). These observations suggest that rates and products are affected by protonation and that protonated atrazine is a more reactive species towards the hydroxyl radical than is the neutral species. They further suggest that protonation occurs preferentially on one nitrogen, presumably the *N*-isopropyl group rather than the *N*-ethyl group, and that this renders the α-hydrogen more susceptible to radical attack. At higher pH an increasing proportion of attack at the *N*-ethyl group can be attributed to a combination of steric and statistical factors and results also in the further oxidation of the intermediate to the amide, **11**. The situation with regard to the degradation of hydroxyatrazine (**2**) is less clear, but here a small peak tentatively identified as **12** is seen under alkaline but not acidic conditions.

We conclude that atrazine and analogous triazine



Scheme 5

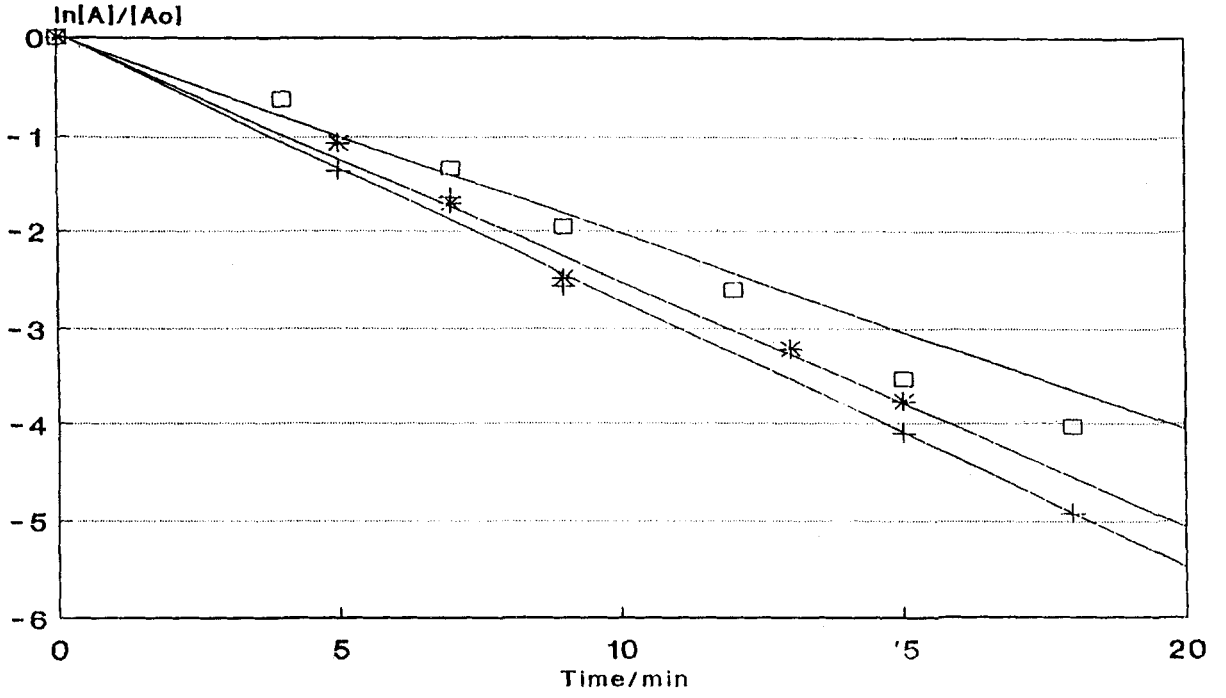


Figure 4. Integrated first-order rate plots for the hydrolysis of atrazine at pH 4·7 (+), 6·9 (*) and 9·4 (□) by H_2O_2 under UV irradiation

herbicides can be destroyed by hydrogen peroxide in the presence of UV radiation, although the end product seems to be cyanuric acid. Assessment of the published toxicological data indicate that cyanuric acid is less toxic than atrazine and that compounds intermediate between the two are likely to have intermediate toxicities.[18] Further, initial studies[19] have shown that, if required, cyanuric acid can be removed from water by charcoal treatment. It therefore seems possible that this could be a process adaptable to large-scale treatment of waters whereas hydrolysis under nearly neutral conditions is too slow to be effective.

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REFERENCES

1. R. M. Harrison, *Pollution: Causes, Effects and Control*, 2nd ed. Royal Society of Chemistry, London (1990).
2. Environmental Data Services Report No. 161, Environmental Data Services, London (1988).
3. EEC Directive No. 80/778, July 15th, 1988 EEC, Brussel.
4. S. Horrobin, *J. Chem. Soc.* 4130 (1963).
5. S. J. Plust, J. R. Loeha, F. J. Feher, J. H. Benedict and H. F. Herbrandson, *J. Org. Chem.* **46**, 3661 (1981).
6. P. C. Kearney, M. T. Muldoon, C. J. Somich, J. M. Ruth and D. J. Voaden, *J. Agric. Food Chem.* **36**, 1301 (1988).
7. C. D. Adams, S. J. Randtke, E. M. Thurman and R. A. Hulsey, paper presented at the American Water Works Association, 109th Annual Conference, June, 1990.
8. D. G. Hager and C. E. Smith, Haz Mat. West, Conf. Proc. Dec. 3, 1985, Long Beach CA, 252–265.
9. D. Peterson, D. Watson and W. Winterlin, *J. Environ. Sci. Health* **B23**, 587; D. Bader, *Water Res.* **22a**, 1109.
10. D. Bader, *Water Res.* **22**, 1109 (1988).
11. American Public Health Association, American Water Works Association and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 15th ed., p. 1134 APHA, Washington, DC (1980).
12. W. M. Pearlman and C. K. Banks, *J. Am. Chem. Soc.* **70**, 3726 (1948).
13. G. Durand and D. Barcels, *J. Chromatogr.* **502**, 275 (1990).
14. Y. L. Chow, in *Reactive Intermediates*, edited by R. A. Abramovitch, Vol. I, p. 151. Plenum Press, New York (1980).
15. R. M. Behki, *J. Agric. Food Chem.* **34**, 746 (1986).
16. J. R. Plimmer and P. C. Kearney, *J. Agric. Food Chem.*

19, 572 (1971); J. R. Plimmer, P. C. Kearney, D. D. Kaufman and F. S. Guardia, *J. Agric. Food Chem.* **15**, 996 (1967).
17. R. Male and R. D. Allendoerfer, *J. Phys. Chem.* **92**, (1988).
18. P. J. Jackson, WRC, personal communication (1991).
19. Water Research Centre, Medmenham, unpublished results (1991).