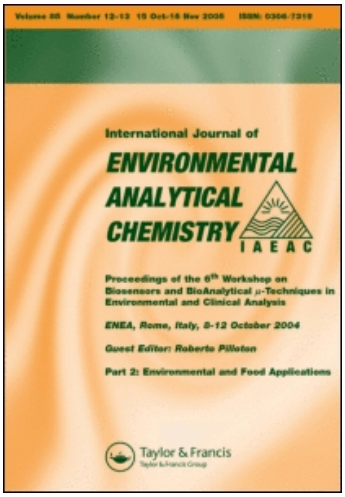

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ATRAZINE DEGRADATION BY OZONATION IN THE PRESENCE OF METHANOL AS SCAVENGER

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Studies on atrazine ozonation performed in methanol containing solutions showed a strong influence of the methanol content which might favour direct O_3 reactions as compared to processes induced by $OH^{\cdot}$ radicals. The importance of the slackening effect on the degradation rate of atrazine (which demonstrates a scavenger activity) was evaluated in various solvent compositions and pseudo-kinetic constants k' were found to be in the 10^{-3}–10^{-2} s^{-1} range. The appearence rate of deethylatrazine as major oxidation product was thus also modified (k' values between 10^{-4} and 10^{-3} s^{-1}). Several by-products were detected which are either related to deethylatrazine (intermediates or oxidation products) or belong to competitive pathways. Among them, a number of formamides (a new class of atrazine ozonation products) were identified using MS and MS-MS techniques. These compounds are produced by oxidation of the N-ethylamino group likely through a non radicalar process. *Deschloro*-triazines were also characterized as structures whose formation specifically depends on the presence of methanol.

KEY WORDS: Atrazine, ozonation, methanolic solution, scavenger, formamide, *deschloro*-triazine.

INTRODUCTION

Contamination of surface and ground waters by organic micropollutants such as pesticide residues constitutes one of the major problems encountered in drinking water production[1]. Among the pesticides present in water, atrazine (CIET)**, a herbicide of the *s*-triazine group which is extensively used, persistent and mobile, is the most often detected. Its concentration frequently exceeds the µg/l level, whereas in European Community the maximum concentration allowed is 0.1 µg/l for one pesticide, and 0.5 µg/l for the sum of all pesticides present and thus the necessary treatment will have to proceed with at least a 90% efficacy. The major methods of elimination include adsorption on activated carbon and oxidation with ozone. During the last decade, a growing interest has been paid to ozone (being used alone or in association with hydrogen peroxide or UV) reactivity towards pesticide residues in order to define optimal processes[4–9].

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** The nomenclature developed by A. M. Cook and R. Hütter[2] is used herein to identify *s*-triazine compounds: A amino, C chloro, E ethylamino, I isopropylamino, O hydroxy and T triazine ring. According to Ref. [3], D is used for acetamido, and we introduced F for formamido and H for unsubstituted carbon.

Oxidation reactions of ozone in water are complex: only a part of dissolved O_3 reacts directly (E° = 2.07 V) and selectively (but slowly) with solutes. The other part decomposes by radical chain reactions to generate secondary oxidants such as $OH^\cdot$ radicals, which are more reactive (E° = 3.06 V) and less selective[4]. Reactions of $OH^\cdot$ with organic compounds are very rapid, the kinetic constants being generally in the 10^7 -10^{10} l mol^{-1} s^{-1} range while being only 10^{-1}–10^4 l mol^{-1} s^{-1} for direct O_3 reaction[5]. A kinetic characterization of the direct and radical reactions with atrazine has been reported which showed second order reactions (first order with respect to atrazine and to O_3 or $OH^\cdot$ concentrations), the kinetic constants being 6 l mol^{-1} s^{-1} [6] and ~ 2 10^9 l mol^{-1} s^{-1} [7,8] respectively for O_3 and $OH^\cdot$. Some species present in natural waters are known to act either as initiators (OH^-, Fe^{2+}, HO_2^-, formates, ...), promoters (aryls, sugars, ...) or scavengers (carbonates, bicarbonates, acetates, ...) of ozone decomposition[9]. The oxidation rate of a specified micropollutant is thus limited by the rates of the processes which produce radicals (i.e. by coupling H_2O_2 or UV treatment to O_3) and by the competitive decomposition of other compounds (rather than by the inherent reactivity with the oxidant).

A number of degradation products of atrazine (ADPs) obtained after ozone treatment of aqueous solutions has already been reported[3,10–13]. Deethylatrazine (CEAT) and deisopropylatrazine (CIAT) are commonly identified and/or quantified through a classical procedure which generally includes liquid/liquid extraction and gas chromatography (GC) with thermoionic or mass spectrometric detection. The other ADPs are less accessible owing to their higher polarity which requires the search for specific methods of extraction (i.e. solid-phase extraction[14–16]) and/or analysis (i.e. GC after derivatization[17] or high performance liquid chromatography[18,19]).

In fact, in the ozonation studies methanol is often used as additional solvent for the initial dissolution of atrazine (solubility *ca* 18 g/l instead of 33 mg/l in water) to be performed before the O_3 treatment. Even though the amount of methanol is generally small, it would be of interest to determine the importance of its effects (kinetically and/or qualitatively) since it has often be suspected to act as a scavenger.

The aim of this work was then to study the influence of methanol (under various compositions with water) on the disappearence rate of atrazine or appearence rates of the major ADPs. Since quite high concentrations may be reached in the starting solutions allowing a simplified procedure for analysis, this will also give the opportunity to study extensively the by-products formed under such conditions including the minor ones.

EXPERIMENTAL

Chemicals

Atrazine (> 98%, CIET, 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine), deethylatrazine (99.9%, CIAT, 6-amino-2-chloro-4-(isopropylamino)-*s*-triazine), deisopropylatrazine (99.8%, CEAT, 6-amino-2-chloro-4-(ethylamino)-*s*-triazine), 2-chloro-4,6-diamino-*s*-triazine (96.9%, CAAT), hydroxyatrazine (99.9%, OIET, 2-(ethylamino)-4-hydroxy-6-(isopropylamino)-*s*-triazine), hydroxydeethylatrazine (99.9%, OIAT, 2-amino-4-hydroxy-6-(isopropylamino)-*s*-triazine), hydroxydeisopropylatrazine (99.9%, OEAT, 2-amino-4-(ethylamino)-6-hydroxy-*s*-triazine) and ammeline (99.6%, OAAT, 2,4-diamino-6-hydroxy-*s*-triazine) were obtained from Promochem (Strasbourg, France). Ammelide (OOAT, 2-amino-4,6-dihydroxy-*s*-triazine) was a gift from Ciba-

Geigy (Basel, Switzerland). Cyanuric acid (98%, OOOT, 2,4,6-trihydroxy-*s*-triazine) was purchased from Janssen (Geel, Belgium).

Methanol (Prolabo, Paris, France) was purex grade, and "pure" water was prepared by purification of osmosed water in an Elgastat UHP System (Elga, High Wycombe, UK). Diazomethane for methylation was prepared from N-methyl-N-nitrosotoluene-4-sulfonamide (analysis grade, Prolabo) in diethyl ether.

Ozonation procedure

Ozone was generated by corona discharge in nitrogen/oxygen 80/20 (U grade, Alphagaz, Paris, France) using a Degremont ozonizer (Rueil Malmaison, France). The stream of air and ozone (7.5 mg O_3/l) was introduced continuously (200 ml/min for 3 hr) through a stainless steel capillary placed at the bottom of a 21 cm × 1.6 cm ø (i.e. 40 ml) glass tube (thermostated at 21 ± 2°C) containing 25 ml of atrazine solution. The solutions being used were made at 100 µg/ml in 100/0, 95/5, 50/50, 20/80 and 5/95 (v/v) methanol/water mixtures respectively. The concentration being used is equivalent to 3 times the solubility limit in water, thus no 0/100 (water alone) experiment is presented herein. Furthermore, experiments in 100% water can practically only be performed at much lower concentrations[3,10–13]. Samples of 30 µl were taken with a syringe every 15 or 30 min, and dissolved O_3 was eliminated by a nitrogen stream to stop the reaction. Residual O_3 in the outlet gas stream was directed (*via* a stainless steel capillary at the top of the reaction tube) to traps containing 0.2 M solutions of potassium iodide (99%, Janssen, Geel, Belgium). Ozone consumed represented less than 8% (minimum detectable) of the amount applied so that the treated solution could be considered as saturated in O_3.

Analysis procedure

Solvent of the 30 µl samples to be analyzed was evaporated until dryness either under nitrogen stream or vacuum (Speed Vac concentrator, Savant, New York). The residues obtained were redissolved in 300 µl methanol, directly or after derivatization with diazomethane. The latter was achieved to analyze hydroxylated compounds using 300 µl of CH_2N_2 in diethyl ether. The yellow solution was sonicated during 30 min.

Quantitations were performed (within the 72 hour-period following ozonation) by gas chromatography on a Varian 3700 apparatus (Harbor City, CA) equipped with a Ross injector (240°C) and a thermoionic detector (310°C). The column was a CP-Sil 5-CB 25 m × 0.32 mm i.d. (film thickness 0.22 µm). Column temperature was: isothermal at 165°C for 8 min, followed by temperature programming to 200°C at 2°C/min and 200°C maintained for 5 min. The 4 µl injections were equivalent to 40 ng of initial atrazine (the limit of detection being 10 pg). Integration of the GC chromatograms was done with a Varian 4400 integrator and calibration was made using an external standard method with a mixture of CIET, CIAT, CEAT, CAAT and methylated cyanuric acid (met-OOOT). The quantitation of the other compounds being found was done taking atrazine as standard. Results are expressed in molar percentages relatively to initial atrazine.

Identifications were realized using a triple quadrupole mass spectrometer Nermag R-30–10 C (Quad Service, Poissy, France). Sample introduction was done *via* a gas chromatograph Delsi Di 200 (Perkin Elmer, St Quentin en Yvelines, France). The chromatographic conditions were similar to those mentioned above (except that helium was used as carrier gas instead of nitrogen). Ionization was performed by electron impact

(EI, 70 eV) or chemical ionization (CI, 95 eV), using NH_3 or ND_3 as reagent gas (10^{-4} torr in the source housing). The CAD daughter ion spectra were obtained with a 15–25 eV collision energy and a 7 10^{-2} torr argon pressure.

RESULTS

Atrazine degradation

In all our experiments, and even after 3 hr ozonation, some residual atrazine was found unchanged. Its amount depended on the solvent composition. For solutions containing 50 to 100% methanol, the final atrazine concentration corresponded to 30–40% of the initial one (Table 1). When the percentage of methanol was < 50%, then residual atrazine reached much lower levels (7.1% with 5% of methanol). The importance of the slackening effect of methanol on the degradation rate of atrazine can be seen from the pseudo-kinetic constant calculation according to eq. (1), obtained after integration of $-d[CIET]/dt = k' [CIET]$.

$$[CIET]/[CIET]_o = e^{-k't} \quad (1)$$

with $k' = k_{OH^\cdot} [OH^\cdot]$ and/or $k_{O3} [O_3]$, since $[OH^\cdot]$ is assumed to be constant, radicals reacting rapidly after their formation, as well as $[O_3]$ since operating with large O_3 excess.

The determined k' are in the 5 10^{-3} to 16 10^{-3} s^{-1} range (from 50–100% to 5% methanol). These values are approximately 10 times higher than that measured by Kearney *et al.*[11] in water alone (7.2 10^{-4} s^{-1}). This is however consistent since in the latter study the same (formulated) atrazine concentration was used, but with a much lower introduction rate of ozone.

It has to be noted that CIET degradation starts slowly (Figure 1) which could correspond to the time necessary for the solvent saturation with O_3.

Atrazine degradation products

ADPs can be classified into 3 groups according to their substituent in position 2 in the triazinic ring: chlorotriazines, hydroxytriazines (analyzed after derivatization) and dehalogenated triazines.

Table 1 Parameters characterizing atrazine degradation as a function of solvent composition.

Solvent (Methanol/water, v/v)	*% of residual atrazine after 3 hr of ozonation*	*Kinetic pseudo-constant k' (s^{-1})*	*Correlation coefficient R*
100–0	37%	$5.6\,10^{-3}$	0.974
95–5	33%	$6.2\,10^{-3}$	0.998
50–50	40%	$5.3\,10^{-3}$	0.998
20–80	20%	$8.8\,10^{-3}$	0.987
5–95	7%	$16.2\,10^{-3}$	0.989

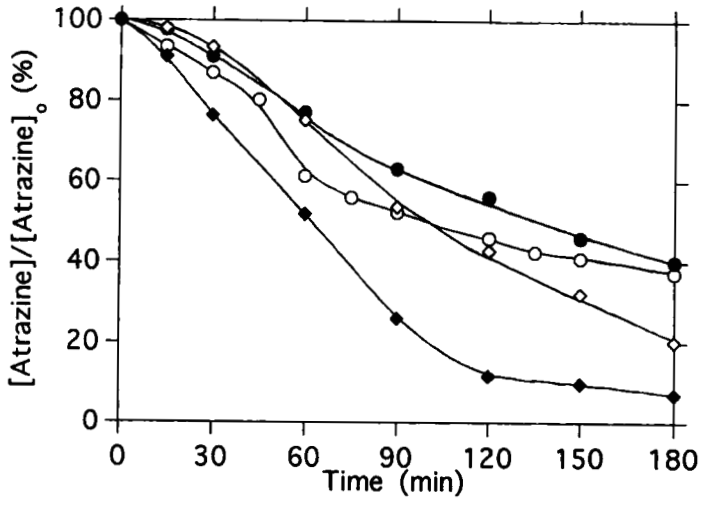


Figure 1 Atrazine degradation curves during ozonation in water/methanol mixtures, respectively (v/v): ○ 0/100, ● 50/50, ◊ 80/20, ◆ 95/5.

Chlorinated degradation products

Dealkylated compounds These compounds were identified by comparison with standards (retention times and mass spectra).

Deethylatrazine (CIAT) was the major degradation product. Its concentration increased continuously during the O_3 treatment (Figure 2) and the final yield clearly depended on the solvent composition: 39%, 32%, 23% and 11% in 5/95, 20/80, 50/50 and 100/0 (v/v) methanol/water respectively. CIAT accumulation was thus favoured by the lower percentages of methanol.

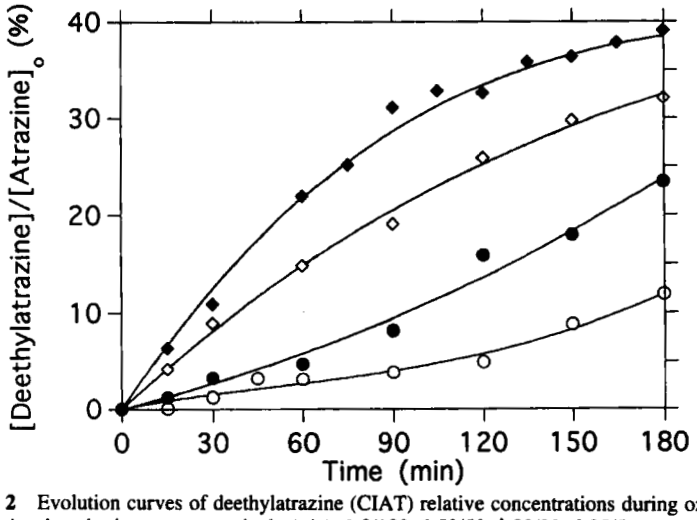
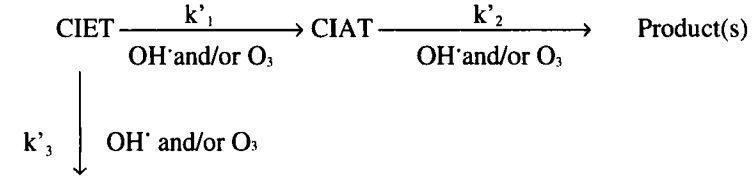


Figure 2 Evolution curves of deethylatrazine (CIAT) relative concentrations during ozonation in water/methanol mixtures, respectively (v/v): ○ 0/100, ● 50/50, ◊ 80/20, ◆ 95/5.

Our data could be used to determine the CIAT pseudo-kinetic constants using the following model:



$d[CIET]/dt = -(k'_1 + k'_3)[CIET]$
$d[CIAT]/dt = k'_1\,[CIET] - k'_2[CIAT]$

After integration, equations (2) and (3) are obtained:

$$[CIET]/[CIET]_0 = e^{-(k'_1 + k'_3)t} \quad (2)$$

$$[CIAT]/[CIET]_0 = (k'_1/(k'_2 - k'_1 - k'_3)) * (e^{-(k'_1 + k'_3)t} - e^{-k'_2 t}) \quad (3)$$

The constants k'_1, k'_2 and k'_3 were determined using eq. (3) by iterative calculations for all compositions of solvent. Except in the case of the 100% and 50% methanol experiments, results were found consistent and the logical order $k'_2 < k'_1 < k'_3$ was obtained, all the values being in the 10^{-3} to 10^{-4} s^{-1} range (correlation coefficient ≥ 0.99). Furthermore, as expected from eq. (1) and (2), the sums $k'_1 + k'_3$ were approximately equal to the k' values previously determined.

Deisopropylatrazine (CEAT) was always present, but at low concentrations (< 3% of initial atrazine). At this level, uncertainties regarding measurements were important (variation coefficient between 3 and 25%, with 2 replications). Evolutions curves (Figure 3) were thus only indicative and the differences due to the solvent composition were less appreciable than for CIAT. For instance, there was no significant difference after 2 hr reaction between the 50/50, 20/80 and 5/95 (v/v) methanol/water conditions. After 3 hr ozonation in pure methanol, the yield of CEAT obtained was, however, significantly higher. The application of the previous kinetic model to CEAT led to unprecise values, but still in the 10^{-3} to 10^{-4} s^{-1} range. Interestingly, it can be noted that the final [CIAT]/[CEAT] ratio decreased with an increase of the methanol percentage (*ca* 28 to 5 between 5 and 100% methanol).

Deethyl-deisopropylatrazine (CAAT) was detected in all experiments after 60 min of reaction, but its concentration remained low (< 2% of initial atrazine). As for CEAT, uncertainties were large and did not allow any study of the evolution curves.

Amides

Among the chlorinated degradation products, some contained an amide group: acetamide (symbolized by letter D) or formamide (letter F).

CDIT and CDAT can reach up to 8 and 1% of initial atrazine respectively.

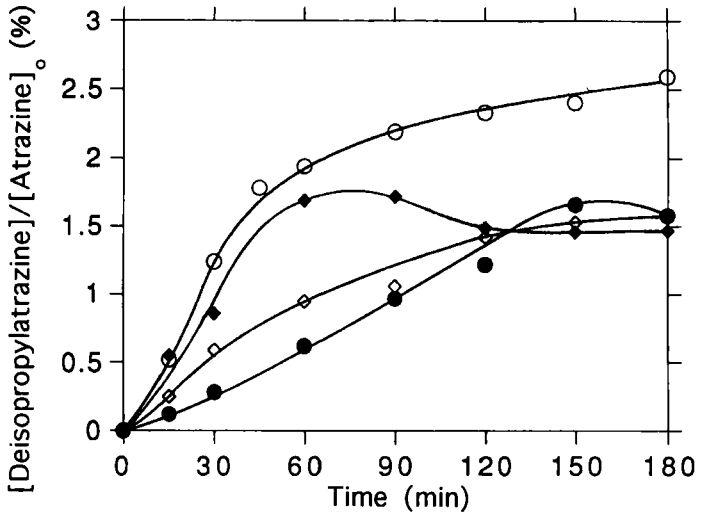


Figure 3 Evolution curves of deisopropylatrazine (CEAT) relative concentrations during ozonation in water/methanol mixtures, respectively (v/v): ○ 0/100, ● 50/50, ◊ 80/20, ◆ 95/5.

Quantification of these compounds was not precise enough to establish evolution curves. This was apparently due to a lack of reproducibility and/or consistency during the concentration steps of the sample preparation: i) the yields measured after derivatization (which includes an evaporation step) were systematically lower by ~ 90% than those obtained directly and ii) concentrations performed under vacuum (*cf* "Speed Vac") gave rise to better results as compared to the use of a nitrogen stream.

CDIT and CDAT were identified by mass spectrometry (MS and MS-MS). The molecular weights were confirmed by CI-NH_3 whereas the number of mobile hydrogens could be deduced from CI-ND_3 (2 and 3 respectively for CDIT and CDAT according to the m/z values found for M_DD^+ at m/z 233 and 192). Furthermore, EI spectra were similar to those published previously[3,11]. Finally, these structures perfectly agreed with the daughter ion spectra of MH^+ (either ^{35}Cl or ^{37}Cl) on the basis of previous studies[20]. For CDIT, the following ions were observed at m/z: 230/232 MH^+ (parent ion), 188/190 $[MH\text{-}C_3H_6]^+$ or $[MH\text{-}CH_2CO]^+$, 146/148 $[MH\text{-}C_3H_6\text{-}CH_2CO]^+$, 110 $[MH\text{-}C_3H_6\text{-}CH_2CO\text{-}HCl]^+$, 104/106 $[ClC{=}N\text{-}C(=NH)NH_2]^+$, 79/81 $[HN{=}CCl\text{-}NH_3]^+$, 68 $[104/106\text{-}HCl]^+$, 43 $[C_3H_7]^+$ or $[H_3N\text{-}CN]^+$ or $[CH_3CO]^+$. Consistently, in the CAD spectrum of M_DD^+, the two initial transitions (MH^+-42u-42u) remained unchanged.

For CDAT, similar (or common) ions were produced: 188/190 MH^+ (parent ion),146/148 $[MH\text{-}H_2N\text{-}CN]^+$ or $[MH\text{-}CH_2CO]^+$, 110 $[MH\text{-}H_2N\text{-}CN\text{-}HCl]^+$ or $[MH\text{-}CH_2CO\text{-}HCl]^+$, 104/106, 79/81 and 68 (see above), 43 $[H_3N\text{-}CN]^+$ or $[CH_3CO]^+$.

CDDT and CDET although present at trace levels were identified from their molecular weights (determined by CI–NH_3 respectively as 229 and 215) and from their EI spectra interpreted accordingly to Hapeman-Somich *et al.*[3]. For CDDT the characteristic ions were at m/z: 229/231 $M^{+\cdot}$, 201/203 $[M\text{-}CO]^{+\cdot}$, 187/189 $[M\text{-}H_2C{=}CO]^+$,186/188 $[M\text{-}{}^{\cdot}COCH_3]^+$, 172/174 [M-cyclo $(HNCOCH^{\cdot})]^+$, 145/147 $CAAT^{+\cdot}$, 110 $[CAAT\text{-}Cl]^+$, 68 $[NC\text{-}N{=}C{=}NH_2]^+$. In the case of CDET the following ions were considered: 215/217 $M^{+\cdot}$, 200/202 $[M\text{-}{}^{\cdot}CH_3]^+$, 187/189 $[M\text{-}C_2H_4]^{+\cdot}$ or $[M\text{-}CO]^{+\cdot}$, 173/175 $[M\text{-}H_2C{=}CO]^{+\cdot}$, 172/174 $[M\text{-}HN{=}CHCH_3{}^{\cdot}]^+$ or $[M\text{-}{}^{\cdot}COCH_3]^+$, 158/160 [M-cyclo $(HNCOCH^{\cdot})]^+$, 145/147, 110 and 68 as for CDDT.

Two trace compounds of MW 215 (e.g. isomeric for CIET and CDET) were new. Their structures were established by GC-EI-MS and from criteria suggested by Hapeman-Somich *et al.*[3] to differentiate between N-ethyl, N-isopropyl and N-acetyl groups as substituents on *s*-triazines: i) ion $[M-15]^+$ ($^{\cdot}CH_3$ loss) is obtained from compounds containing a secondary amine but not from amides, ii) in the case of acetamides, ions $[M-28]^+$, $[M-42]^+$, $[M-43]^+$, $[M-57]^+$ due to losses of CO, $COCH_2$, $^{\cdot}COCH_3$, cyclo($HNCOCH_2$) respectively, are generally observed and iii) the N-ethyl group can eliminate C_2H_4 but not $^{\cdot}C_2H_5$ although the N-isopropyl may lose C_3H_6 and $^{\cdot}CH(CH_3)_2$ as well. On this basis and examining spectra (Figure 4), we propose structures containing a N-formyl group (not considered previously) CIFT and CDFT.

Indeed, the CIFT spectrum exhibited a $[M-15]^+$ ion (m/z 200/202) which indicated the presence of a secondary amine but did not contain a $[M-57]^+$ ion (*cf* acetamide). The $[M-43]^+$ ion (m/z 172/174) could then be attributed to a N-isopropyl group. The second N-substituent e.g. 29 u would consequently lead to assign the $[M-28]^+$ and $[M-29]^+$ ions to $[M-CO]^+$ and $[M-HCO^{\cdot}]^+$ ions thus generated by N-CHO. For this compound, the obtained quantitative data were enough significant to demonstrate the influence of the

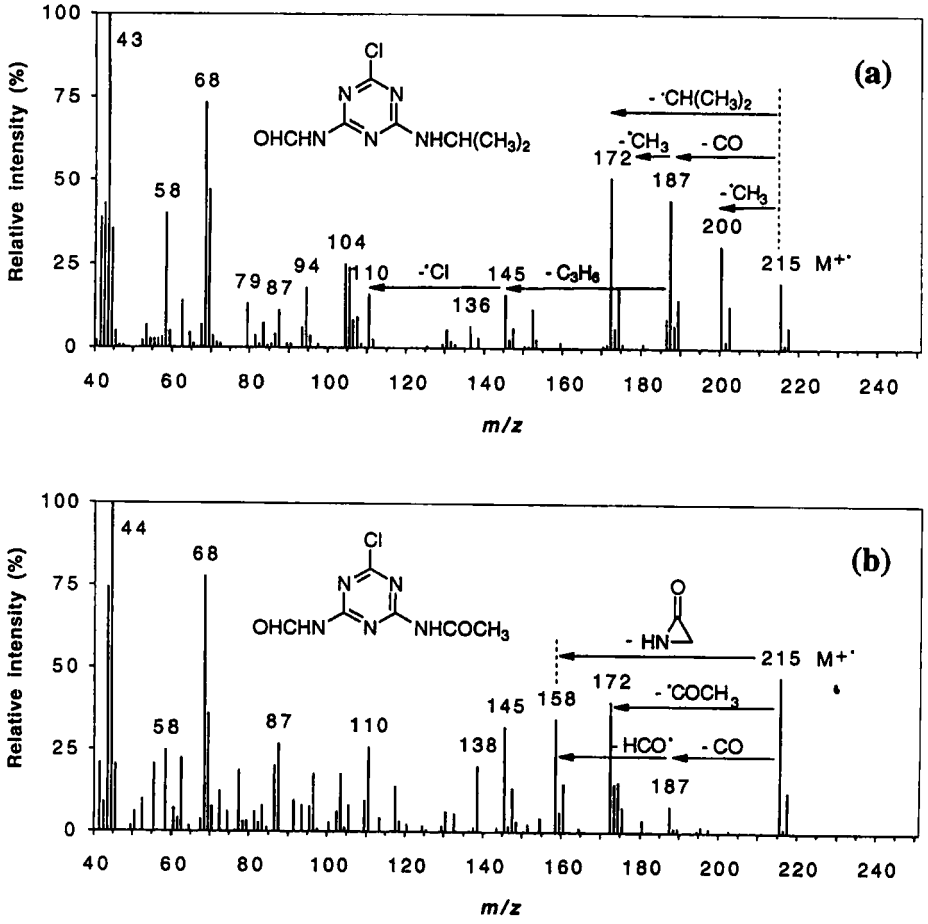


Figure 4 GC-MS spectra (electron impact) of (a) CIFT and (b) CDFT obtained by ozonation of atrazine.

methanol content on its formation during ozonation. After 90 min, the yields were respectively 0.01, 0.1, 0.2 and 0.5% when increasing the percentage of methanol (e.g. 5, 20, 50 and 100%). CIFT could reach a 1% yield after 3 hr in the 100% methanol medium whereas less than 0.2% was finally obtained in the other mixtures.

Concerning CDFT, all ions relevant to an acetamide were present. Further, the second substituent was not an ethyl (*cf* CDET whose spectrum and retention time are different) and then ions at m/z 187/189 and 158/160 should be interpreted as $[M\text{-}CO]^{+\cdot}$ and $[M\text{-}CO\text{-}HCO^{\cdot}]^{+}$ (second contribution).

Hydroxylated degradation products

Hydroxytriazines were analyzed after methylation. Derivatization of such compounds is known to be not quantitative owing to tautomerization[17,21]. In fact, our procedure was tested using standard OIET as model and yields (5 repetitions) were estimated as 90 ± 10%.

Under ozonation OIET was produced with a maximum of concentration near 90 min (4% of initial atrazine for the 100% methanol experiment *vs* 1.6% for 20% methanol). OIAT, ODIT and OIFT were detected in the 100% methanolic solution at low concentrations until 120 min (≤ 0.5%) but reached 1.6%, 5% and 1.8% respectively at 180 min. In methanol/water mixtures, they did not exceed 1%. OEAT (*ca* 0.5%) appeared in all experiments after 60 min and traces of cyanuric acid (OOOT) were sometimes detected.

OIET, OIAT, OEAT and OOOT were identified by comparison with O-methylated standard compounds (retention times and spectra, Table 2). Amide ODIT was characterized by MS (EI and CI-NH_3) as O-methylated derivative. Its fragmentation (EI conditions) was similar to that of CDIT. OIFT structure was assigned by comparison to CIFT.

Dehalogenated degradation products

Five ADPs were detected which correspond to dehalogenated forms of CIET, CIAT, CEAT, CAAT and CDIT. Present at trace levels (< 0.5% for HEAT, HAAT and HDIT, < 1% for HIAT and < 2% for HEIT) in mixtures of methanol/water, they became more abundant when ozonation was conducted in methanol alone (9% HIET and 3% HIAT after 3 hr). As an example, Figure 5 shows the evolution of the HIET yield in function of time and its dependence on the methanol content.

HIET, HIAT, HEAT, HAAT and HDIT structures were unambiguously identified by GC-MS performed under EI (see Table 3) and CI conditions. The two former compounds were also suspected to be formed by photolysis of atrazine in aqueous solution spiked with methanol[22].

DISCUSSION

The slackening effect of the presence of methanol in aqueous solutions of O_3-treated atrazine was clearly demonstrated. It could be attributed to a lower implication of $OH^{\cdot}$ radicals as compared to direct O_3 reactions. Indeed, $OH^{\cdot}$ radicals are known to react with

Table 2 Characteristic mass ions of the O-methoxylated hydroxytriazines obtained by GC-MS (EI) and their relative abundances (in italic).

Ions	*met-OIET*	*met-OIAT*	*met-OEAT*	*met-ODIT*	*met-OIFT*	*met-OOOT*
$M^{+\cdot}$	211 (*26*)	183 (*39*)	169 (*79*)	225 (*61*)	211 (*18*)	171(*100*)
M-15 ($^{\cdot}CH_3$)	196 (*34*)	168 (*60*)	154 (*43*)	210 (*41*)	196 (*16*)	
M-28 ($H_2C{=}CH_2$, CO)	183 (*2*)	155 (*1*)	141 (*45*)		183 (*41*)	143 (*40*)
M-29($H^{\cdot}$+CO/C_2H_4)[a]	182 (*3*)					142 (*15*)
M-42($H_2C{=}CHCH_3$, $H_2C{=}C{=}O$)	169 (*23*)	141 (*36*)		183 (*16*)	169 (*17*)	
M-43($^{\cdot}CH(CH_3)_2$, $^{\cdot}COCH_3$, $HN{=}CHCH_3$, etc)	168 (*20*)		126 (*50*)	182 (*9*)	168 (*47*)	
M-57($HN{=}C(CH_3)_2$, $HNC(O)CH_2$, etc)	154 (*19*)			168 (*98*)		
met-OAAT$^{+\cdot}$	141 (*11*)	141 (*36*)	141 (*45*)	141 (*28*)	141 (*20*)	
[met-OAAT-$^{\cdot}OCH_3$]$^+$	111 (*18*)	111 (*19*)	111 (*43*)	111 (*23*)	111 (*11*)	111 (*4*)
$NC{-}N{=}C{=}NH_2^+$	68 (*15*)	68 (*30*)	68 (*44*)	68 (*23*)	68 (*41*)	
$(CH_3)_2C{=}NH_2^+$, $H_2CC(O)NH_2^+$, etc	58 (*100*)	58 (*100*)	58 (*51*)	58 (*100*)	58 (*39*)	58 (*97*)
$CH_3CH{=}NH_2^+$, H_2NCO^+	44 (*45*)	44 (*20*)	44 (*100*)	44 (*24*)	44 (*100*)	
$NC{-}NH_3^+$, CH_3CO^+	43 (*51*)	43 (*40*)	43 (*85*)	43 (*78*)		

[a] : M–1 ($H^{\cdot}$) also detected.

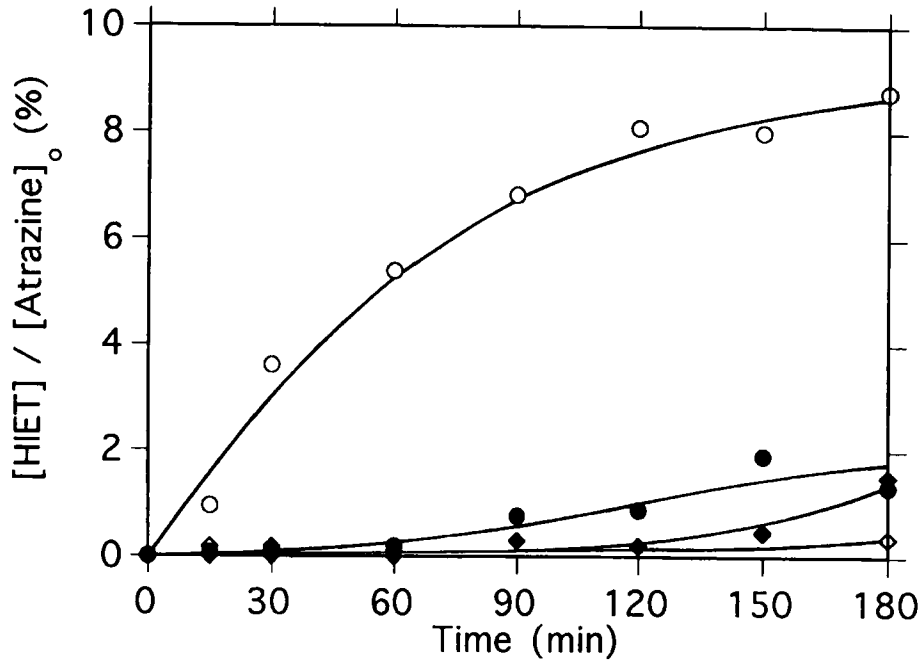


Figure 5 Evolution curves of HIET relative concentrations during ozonation in water/methanol mixtures, respectively (v/v): ○ 0/100, ● 50/50, ◊ 80/20, ◆ 95/5.

Table 3 Characteristic mass ions of the dehalogenated ADPs obtained by GC-MS (EI) and their relative abundances (in italic).

Ions	*HIET*	*HIAT*	*HEAT*	*HAAT*	*HDIT*
$M^{+\cdot}$	181 (*40*)	153 (*72*)	139 (*97*)	111(*100*)	195 (*49*)
M-15 ($^{\cdot}CH_3$)	166 (*89*)	138 (*100*)	124 (*54*)		180 (*16*)
M-28 ($H_2C{=}CH_2$, CO)	153 (*4*)		111 (*57*)		
M-29($H^{\cdot}$+ C_2H_4)[a]	152 (*3*)				
M-42($H_2C{=}\dot{C}HCH_3$, $H_2C{=}C{=}O$)		111 (*53*)			153 (*9*)
M-43($^{\cdot}CH(CH_3)_2$,$COCH_3$, $HN{=}CHCH_3$, etc)	139 (*5*)		96 (*25*)		152 (*16*)
M-57($HN{=}C(CH_3)_2$, $HNC(O)CH_2$, etc)	124 (*15*)	96 (*13*)			138 (*100*)
$HAAT^{+\cdot}$	111 (*15*)	111 (*53*)	111 (*57*)	111(*100*)	111 (*33*)
$NC{-}N{=}C{=}NH_2^+$	68 (*57*)	68 (*40*)	68 (*26*)	68 (*5*)	68 (*29*)
$(CH_3)_2C{=}NH_2^+$, $H_2CC(O)NH_2^+$	58 (*86*)	58 (*51*)			58 (*49*)
$NC{-}NH_3^+$, CH_3CO^+	43 (*100*)	43 (*80*)	43 (*100*)	43 (*42*)	43 (*76*)

[a] : M–1 ($H^{\cdot}$) also detected.

alcohols by hydrogen abstraction. In the case of methanol, this can yield (k = 7 10^8 l mol^{-1} s^{-1}) $HOCH_2^{\cdot}$ as new species[9] which may act thereafter as a scavenger to stop the radical process through reactions with another radical.

Under our conditions, CIAT was by far the major degradation product in any composition of solvent (*cf* % of methanol). Several by-products were identified which were either related to CIAT (intermediates or oxidation products) or belonged to

competitive pathways (*cf* Figures 6 and 7 showing formulas of the identified ADPs and typical GC chromatogram).

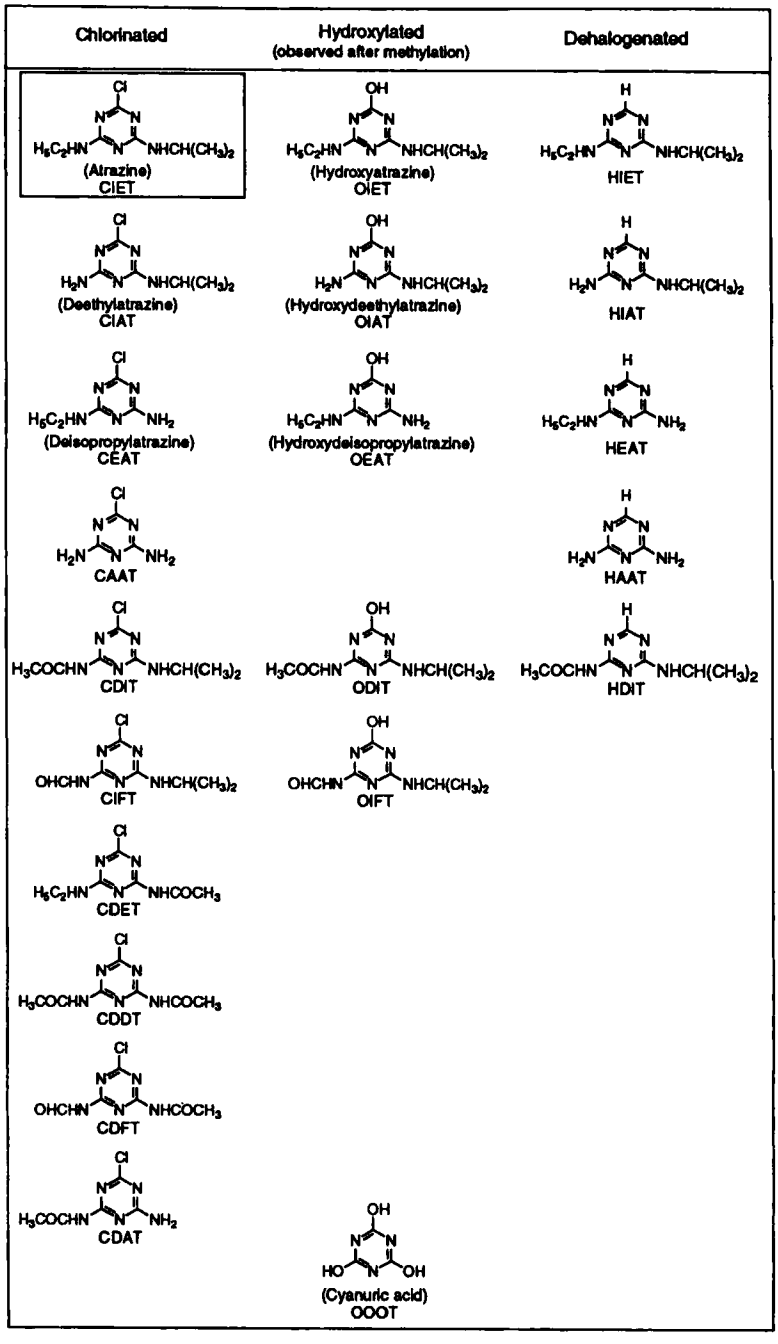


Figure 6 Atrazine ozonation products obtained in methanolic solution.

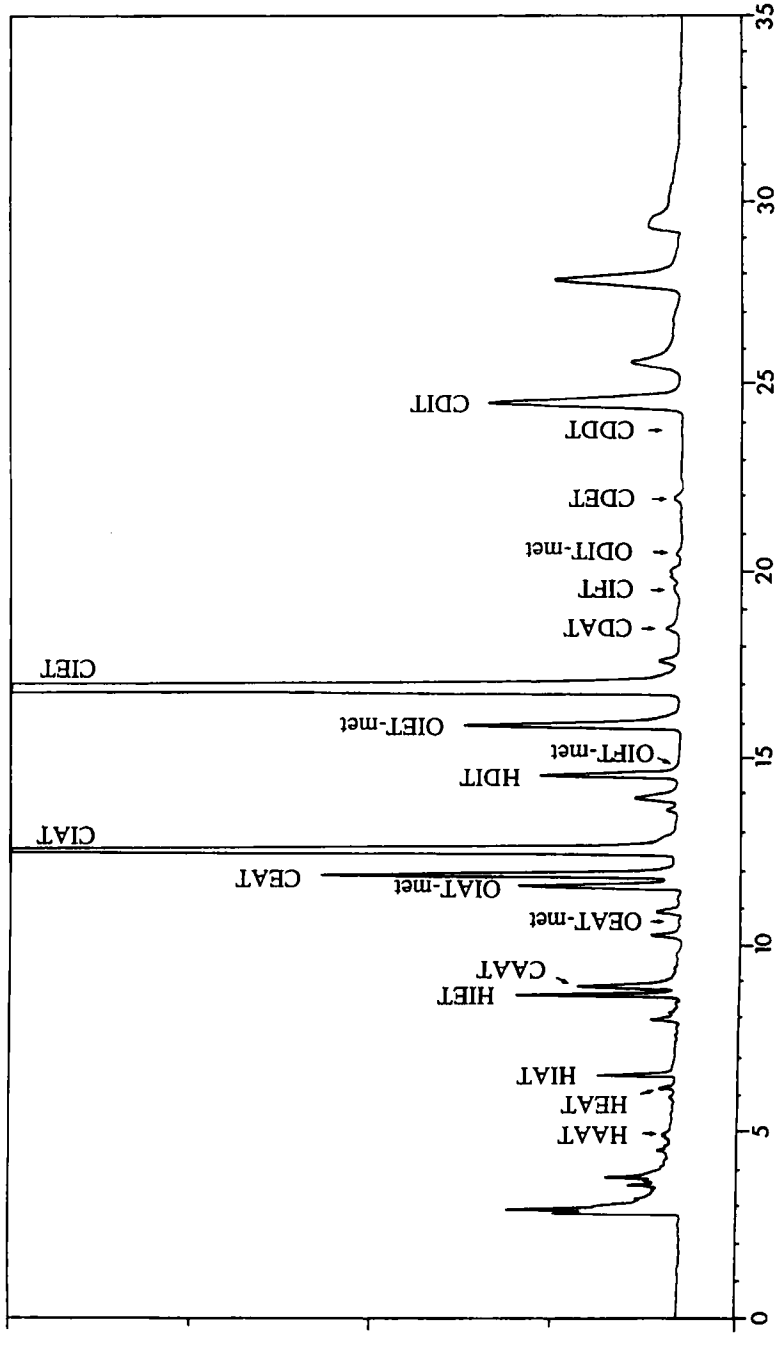


Figure 7 GC-thermoionic detection chromatogram obtained after 60 min ozonation of atrazine in 100% methanol and derivatization with diazomethane.

The main degradation pathways of atrazine observed herein include N-dealkylation (*via* amide formation) and hydroxylation (by substitution of the chloro- or amino-substituent) which classically also occur in 100% aqueous solutions[3,10–13]. The formation of *deschloro*-triazines seems, however, to be specific of the methanol containing solutions as it has never been observed in 100% aqueous solutions[3,12,13]. Dehalogenation could result from a reaction with $HOCH_2^{\cdot}$ (liberating HCl and formaldehyde) since its behaviour may not be limited to the scavenger activity mentioned above.

The N-formylamino group present in 3 by-products (Figure 6) is also original in this context and must be considered as resulting from a competitive (although minor) pathway of the decomposition of the N-ethylamino group. Such a process could be initiated by O_3 oxidation to give a carbinolamine (Figure 8 adapted from Bailey[23]) that would give rise after further O_3/H_2O reactions to either of the following groups: $NCOCH_3$, NHCHO and NH_2. Under the same conditions, the N-isopropylamino group would yield only $NCOCH_3$ and NH_2.

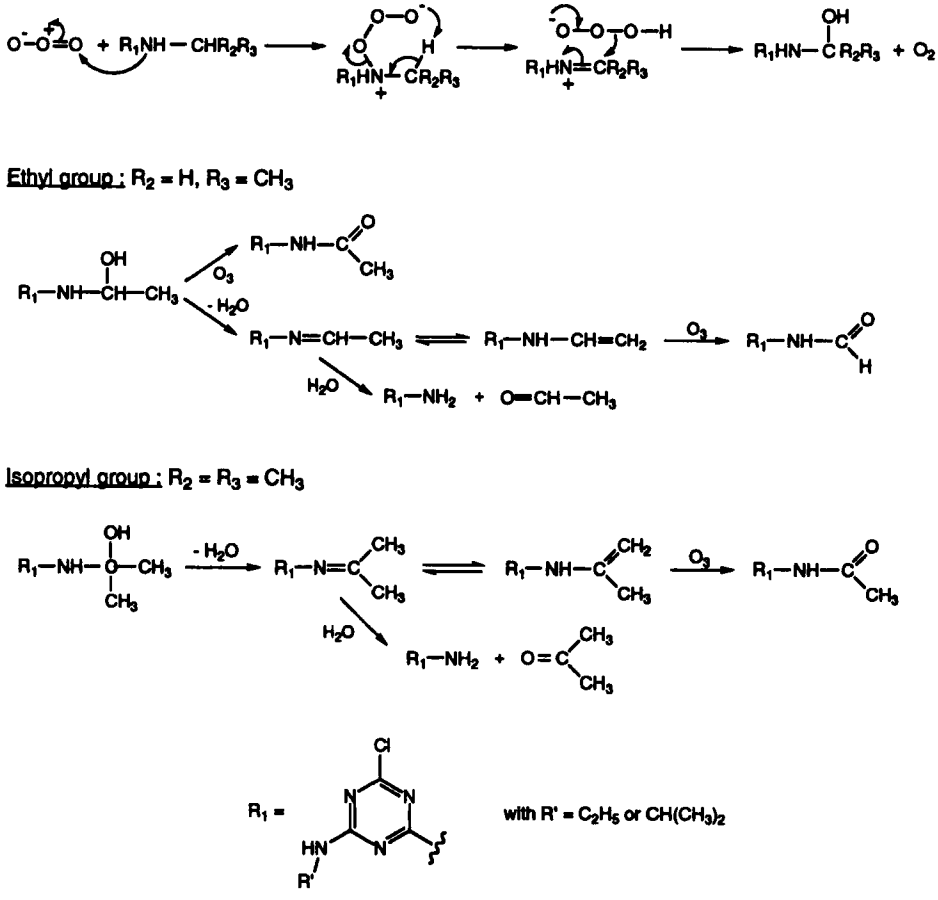


Figure 8 Secondary amine reactions with ozone, *via* a carbinolamine (adapted from Bailey[23]).

CONCLUSION

Studies performed on the ozonation of atrazine are widely influenced by the methanol content even though this additional solvent (frequently used as co-solvent for the initial dissolution of the pesticide) is present in small amounts.

The main consequences not only concern the disappearence rate of the pesticide and the appearence rate (e.g. slackening effect) of the major degradation product(s) but also the processes through which the by-products will be formed.

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