Aqueous Ozonation of Atrazine. Product Identification and Description of the Degradation Pathway

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The aqueous ozonation of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine] at pH 6 afforded four primary products: 6-amino-2-chloro-4-(isopropylamino)-*s*-triazine, 6-amino-2-chloro-4-(ethylamino)-*s*-triazine, 4-acetamido-2-chloro-6-(ethylamino)-*s*-triazine, and 4-acetamido-2-chloro-6-(isopropylamino)-*s*-triazine. These compounds were subsequently degraded to 2-chloro-4,6-diacetamido-*s*-triazine, 4-acetamido-6-amino-2-chloro-*s*-triazine, and 2-chloro-4,6-diamino-*s*-triazine. The amino alkyl groups are the first site of attack and are either removed or converted to the acetamide but not to the aldehyde. The *s*-triazine ring remains intact, and the chlorine is not removed. Studies also demonstrated that the alkyl group is far more reactive than the amide moiety, which in turn is oxidized more rapidly than the amino group.

INTRODUCTION

The disposal of pesticide waste and unusable equipment rinsate is of great concern to pesticide applicators and farmers. In some cases improper disposal has been directly linked to point source contamination of groundwater and farm wells (Aharonson, 1987; Parsons and Witt, 1988). Pesticide waste and rinsate typically consists of a variety of pesticides at concentrations less than 200 ppm, formulating agents, surfactants, emulsifiers, and fertilizers (Somich et al., 1990). We recently presented the results of an on-site study demonstrating the potential of a two-stage process to treat pesticide wastes involving ozonation followed by microbial mineralization, i.e., breakdown to CO_2, H_2O, NH_3 or NO_3^-, and inorganic salts (Somich et al., 1990). The *s*-triazine herbicides, such as atrazine, which is the most widely used *s*-triazine, were found to be somewhat recalcitrant to this treatment compared to the other pesticides. Optimization of the first stage of this scheme requires that the ozonation products be identified, the ozonation mechanism elucidated, and the variables defined.

Ozonation studies of dilute solutions of organic compounds in water have generally focused on total organic carbon loss or disappearance of parent material (Glaze, 1987; Hoigne, 1988; Hoigne and Bader, 1983a,b). In some studies products have been identified (Glaze, 1986; Peyton et al., 1989). Other studies have clearly demonstrated that ozone is not the only oxidizing species present under most aqueous ozonation conditions (Glaze and Kang, 1988; Peyton and Glaze, 1987; Staehelin and Hoigne, 1982, 1985). However, the fate of the organic species is critical to understanding of the overall process and in determining the active species and their respective roles in the degradation of the organic compound. This demands isolation and characterization of the major products and the fate of these compounds. Thus, the purpose of the present study was to examine the aqueous ozonation of pure atrazine more thoroughly, emphasizing the fate and chemistry of the *s*-triazine rather than the ozone chemistry. The information obtained will be used in subsequent studies to further develop and optimize pesticide waste remediation processes.

MATERIALS AND METHODS

Equipment and Instrumentation. HPLC data were obtained from one of the following: (1) two Waters Model 6000 pumps equipped with a Waters Model 990 photodiode array detector and accompanying NEC APC-III controller and software; (2) a Gilson Model 42 HPLC system equipped with a Gilson Model 116 UV detector (210 and 230 nm monitored) and IBM PC/AT controller and accompanying Gilson/Windows software. Waters Nova-Pak 4-μm C-18, 8 mm × 10 cm, radial compression module columns were used on the Waters HPLC system, and a standard Beckman C-18 (ODS, 5 μm) end-capped, 4.6 mm × 25 cm, steel jacketed column was used with the Gilson system. Semipreparative HPLC was carried out on the Gilson system with a standard Beckman C-18 (ODS, 5 μm) end-capped, 10 mm × 25 cm, steel jacketed semipreparative column.

Mass spectra were obtained on a Finnigan MAT Model 4510 mass spectrometer equipped with a direct exposure probe. Samples of ca. 100 ng were placed onto the probe tip, and a current increasing from 0 to 1000 mA was applied at a rate of 20 mA/s. Electron impact spectra were collected at a source temperature of 150 °C. ^{1}H NMR spectra were obtained on a General Electric QE-300 spectrometer using ca. 3 mg of sample in DMSO-d_6 and tetramethylsilane (TMS) as an internal standard.

General Ozonation Procedure. Initial ozonation studies of atrazine were carried out in a previously described reactor (Somich et al., 1988). Subsequent isolation of intermediates and mechanistic studies were conducted using a custom-designed glass reactor (Figure 1) in which ozone/oxygen gas was passed over the top of the solution to decrease the ozone contact time with the solution, decreasing the rate of reaction. The reactor consisted of a 400-mL beaker with a sampling valve attached to the bottom and a 600-mL beaker inverted over the smaller beaker serving as a top to the reactor. An inverted funnel was inserted through the opening in the top and was placed at a level ca. 1 cm above the reaction solution. The reaction was magnetically stirred. Ozone was generated using a PCI ozone generator Model GL-1B (PCI Ozone Corp., West Caldwell, NJ 07006) with oxygen feed. Ozone concentration in reactor feed gas did not exceed 10 mg/L as determined by iodometric titration (Flamm, 1977).

Isolation studies involved ozonation of a 100-mL solution of 0.15–10 mM starting material buffered at pH 6 (0.175 g of K_2HPO_4; 1.052 g of KH_2PO_4) to prevent the reaction from becoming more acidic. Ozonation continued until all starting material was depleted or the maximum concentration of product was achieved

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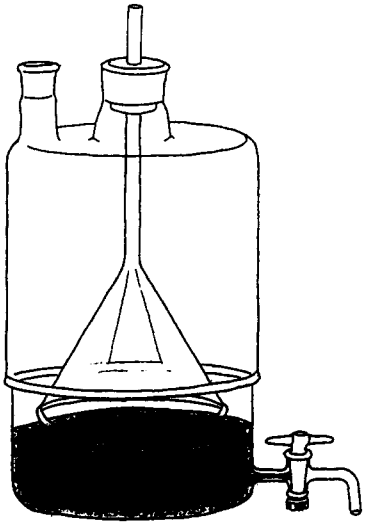


Figure 1. Ozonation reactor with minimal mass contact time.

as determined by HPLC. The reaction mixture was extracted three times with 50 mL of ethyl acetate, concentrated to ca. 5 mL in vacuo and then to dryness using nitrogen, and redissolved in acetonitrile. Separation of the reaction mixture was achieved by semipreparative HPLC (0–20% acetonitrile/water linear gradient in 8 min, 6 mL/min).

Mechanistic studies were conducted using a 100-mL solution of 0.153 mM starting material buffered at pH 6 (0.175 g of K_2HPO_4; 1.052 g of KH_2PO_4). Samples were taken at appropriate time intervals and analyzed directly (i.e., no extraction procedures were carried out) by HPLC using one of the following: (1) 0–50% acetonitrile/phosphoric acid buffer (pH 2) gradient (Waters curve no. 8) in 5 min at a flow rate of 2 mL/min or (2) 0–5% acetonitrile/phosphoric acid buffer (pH 2) at 2 min, to 20% at 5 min, and to 60% at 7 min (all linear transitions) at a flow rate of 1.5 mL/min.

For convenience the nomenclature system used by Cook (1987) is used here: A, amino; C, chloro; E, ethylamino; I, isopropylamino; O, hydroxy; and T, triazine ring. Several ozonation products contain an acetamido group, and in keeping with this nomenclature, D has been added to denote this moiety. Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine], 6-amino-2-chloro-4-(isopropylamino)-*s*-triazine (CIAT), 6-amino-2-chloro-4-(ethylamino)-*s*-triazine (CEAT), and 2-chloro-4,6-diamino-*s*-triazine (CAAT) were gifts from Ciba-Geigy.

Synthesis of 4-Acetamido-2-chloro-6-(ethylamino)-*s*-triazine (CDET). Two hundred milligrams (1.16 mmol) of CEAT and 50 mL of acetic anhydride (0.53 mol) in 50 mL of ethyl acetate were refluxed for 6 h. The reaction mixture was concentrated in vacuo to near dryness and the resultant powder recrystallized twice from acetone, affording 74 mg (30% yield) of CDET (white crystals): mp 180–181 °C.

Synthesis of 4-Acetamido-2-chloro-6-(isopropylamino)-*s*-triazine (CDIT). One hundred milligrams (0.46 mM) of CIAT and 25 mL of acetic anhydride (0.26 mol) in 25 mL of ethyl acetate were refluxed for 7 h. The reaction mixture was concentrated in vacuo to near dryness and the resultant powder recrystallized twice from acetone, affording 35 mg (28% yield) of CDIT (white crystals): mp 177–178 °C [lit. mp 187–188 °C (Rejto et al., 1983)].

Synthesis of 6-Amino-4-acetamido-2-chloro-*s*-triazine (CDAT) and 2-Chloro-4,6-diacetamido-*s*-triazine (CDDT). Two hundred milligrams (1.38 mmol) of CAAT and 50 mL of acetic anhydride (0.53 mol) in 50 mL of ethyl acetate were refluxed gently for 7 h. The reaction was allowed to cool and precipitate filtered and recrystallized from ethyl acetate to give 47 mg (18% yield) of CDAT (white crystals): mp 225 °C (dec). The filtrate was concentrated in vacuo to near dryness and reconstituted in 30 mL of acetonitrile. Separation of CDDT from CDAT and CAAT was achieved by semipreparative HPLC using the following gradient scheme of acetonitrile/water at 4 mL/min: 0–20% in 8 min, 20% 8–9 min, 20–80% from 9 to 10 min, 80% 10–13 min. Ten milligrams (8% yield) of CDDT was obtained: mp 197–198 °C.

Synthesis of 2-[[3′-Chloro-5′-(isopropylamino)-*s*-triazyl]-amino]acetaldehyde. An excess (15 mL) of chloroacetaldehyde diethyl acetal (Aldrich Chemical Co.) in 20 mL of aqueous HCl (pH 1.5) was heated at 80 °C for several hours to obtain free aldehyde. The solution was cooled and made alkaline with aqueous KOH (pH 9.5). Twenty-five milliliters of this solution (60 mmol of chloroacetaldehyde) was added to 50 mg (0.23 mmol) of CIAT and heated at 80 °C for 1.5 h. The mixture was extracted with 50 mL of ethyl acetate (three times) and concentrated in vacuo and the residue recrystallized from acetone.

RESULTS

Ozonation of Atrazine. Initial laboratory studies involving the treatment of an aqueous solution of pure atrazine with ozone revealed that degradation of atrazine and its products proceeded too rapidly, which limited isolation of sufficient material for analysis. This necessitated the use of a less efficient reactor (Figure 1). Ozonation of atrazine afforded a complex mixture consisting of four primary products, 6-amino-2-chloro-4-(isopropylamino)-*s*-triazine (CIAT), 6-amino-2-chloro-4-(ethylamino)-*s*-triazine (CEAT), 4-acetamido-2-chloro-6-(isopropylamino)-*s*-triazine (CDIT), and 4-acetamido-2-chloro-6-(ethylamino)-*s*-triazine (CDET); three secondary products, 2-chloro-4,6-diacetamido-*s*-triazine (CDDT), 6-amino-4-acetamido-2-chloro-*s*-triazine (CDAT), and 2-chloro-4,6-diamino-*s*-triazine (CAAT); and two transient products, X and Y. All products isolated at this stage of ozonation contained a chlorine.

The ratio of these products changed as the reaction proceeded because their relative degradation rates were not the same. A more useful indication of the importance of these compounds is their relative ratio with respect to the disappearance of parent material, atrazine. For instance, at 35% loss of atrazine (initial concentration of 0.153 mM), the following percentages relative to the total amount of product material were observed: CDIT, 19%; CIAT, 51%; CDET, 1%; CEAT, 12%; CDDT, 2%; CDAT, 4%; and CAAT, 11%. Accordingly, as the reaction continued, the concentration of the primary products decreased and that of the secondary products increased. At 90% depletion of atrazine (153 μM initial concentration), the following concentrations were observed: CIET, 15 μM; CDIT, 22 μM; CIAT, 30 μM; CDET, 0.6 μM; CEAT, 3.2 μM; CDDT, 1.4 μM; CDAT, 11 μM; and CAAT, 17 μM.

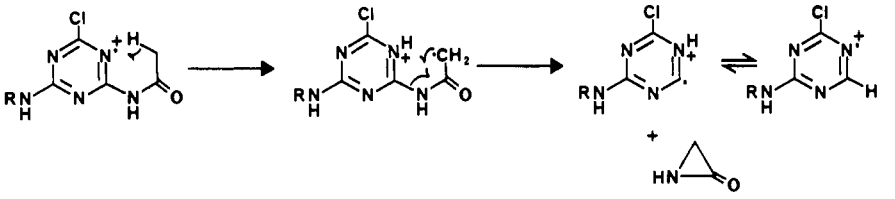
Product Analysis. Identification of CAAT, CEAT, and CIAT was established by comparison with authentic samples. Synthesis and mass spectrometry provided structural verification of the remaining products (CDAT, CDDT, CDET, and CDIT). Incomplete amidization of CAAT using acetic anhydride afforded a mixture of CAAT, CDAT, and CDDT in ca. 1:2:1 ratio, which was separated by HPLC. In a similar fashion CDET and CDIT were synthesized by amidization of CEAT and CIAT, respectively. Mass spectral analyses are shown in Table I.

Loss of $HNCH_2C(O)$, m/z $(M - 57)^+$, was observed in the mass spectra of all four amides (eq 1). The amide moiety can also undergo a McLafferty-type rearrangement affording ketene loss (McLafferty, 1980). Ion peaks corresponding to CO loss were observed in CDAT, CDDT, and CDET but not in CDIT. Loss of $^{\bullet}C(O)CH_3$ was not observed in CDAT but was in CDDT, CDET, and CDIT. Methyl cleavage $(M-15)^+$ was not observed in mass spectra of CDAT or CDDT but was seen in CDIT and CDET, which implies that $^{\bullet}CH_3$ loss is from the alkyl moiety, not the amide. Under similar conditions, the mass spectrum of atrazine showed a base peak at m/z 200 (202, ^{37}Cl) $(M - 15)^+$ corresponding to loss of $^{\bullet}CH_3$. Loss of $^{\bullet}CH(CH_3)_2$ occurred in CDIT, but $^{\bullet}CH_2CH_3$ loss was not observed in

Table I. Fragmentation in Mass Spectra of Amide Ozonation Products

fragment lost	CDAT	CDDT	CDET	CDIT
parent^{+a}	187 (189)	229 (231)	215 (217)	229 (231)
$\cdot CH_3$			200 (202)	214 (216)
$CH_2{=}CH_2$			187 (189)	
CO	159 (161)	201 (203)	187 (189)	
$CH_2{=}C{=}O$		187 (189)	173 (175)	187 (189)
$CH_3CH{=}CH_2$				187 (189)
$\cdot CH(CH_3)_2$				186 (188)
$\cdot C(O)CH_3$			172 (174)	186 (188)
$\cdot CH_3$ and $CH_2{=}C{=}O$		172 (174)	158 (160)	172 (174)
$\cdot CH_2CH_3$ and CO			158 (160)	
$HNC(O)CH_2$		172 (174)	158 (160)	172 (174)
$\cdot C(O)CH_3$ and CO		159 (161)		
$CAAT^{+a}$	145 (147)	145 (147)	145 (147)	145 (147)
$CAAT - Cl^{+a}$	110	110	110	110
$NCN{=}C{=}NH_2{}^{+a}$	68	68	68	68

[a] Ion, not fragment.



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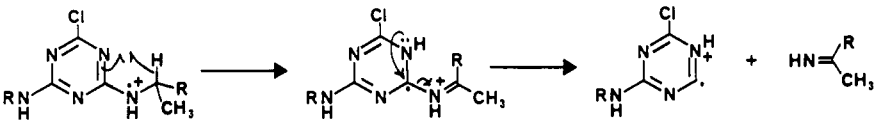

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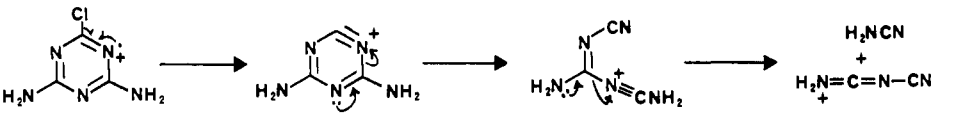


(3)

CDET. Interestingly, a peak in the fragmentation pattern of atrazine exists at m/z 172 (174) corresponding to $\cdot CH(CH_3)_2$ cleavage, but virtually no loss of $\cdot CH_2CH_3$ at m/z 186 (188) was observed. The alkylamino groups can also undergo a McLafferty-type rearrangement giving rise to alkene loss, ethene, or propene (McLafferty, 1980). The $(M-57)^+$ ion in the spectrum of CDIT can be rationalized as a rearrangement with loss of $HN{=}C(CH_3)_2$, and in a similar fashion the $(M-43)^+$ ion in the CDET spectrum corresponds to loss of $HN{=}CH(CH_3)$ (eq 2). Elimination of the alkyl and amido substituents on the amine nitrogens affords $CAAT^+$, which is followed by loss of $Cl^\cdot$ to give m/z 110. Further fragmentation gives rise to an ion at m/z 68 (eq 3).

The ^1H NMR signals for the atrazine ozonation products are listed in Table II. There are apparently several intramolecular hydrogen-bonding arrangements between the hydrogen on the alkylamino nitrogens and the ring nitrogens which complicate relatively simple spectra. For example, the two triplets at 1.07 and 1.06 ppm observed in the spectrum of CEAT must be due to two different isomeric forms. In contrast, the hydrogen of the amide nitrogen must be involved overwhelmingly in only one hydrogen-bonding arrangement, if at all, since only one signal was seen for each hydrogen in CDDT and CDAT. This observation has not been discussed in NMR studies concerning s-triazines heretofore in the literature as most involved data collection on low-field spectrometers (Haque and Lilley, 1972; Russel et al., 1968).

2-[[3′-Chloro-5′-(isopropylamino)-s-triazyl]amino]-acetaldehyde was also synthesized to verify that this compound was not among the atrazine ozonation products. Mass spectral analysis showed a parent peak and a base peak at m/z 229 (231) and 145, respectively. None of this compound could be detected by HPLC in atrazine ozonation.

Ozonation of Atrazine Degradation Products. Ozonation of CDET gave rise to CDAT and CDDT in an initial 9:1 ratio; these compounds subsequently decomposed to CAAT and CDAT, respectively. No CEAT was formed during this reaction. CEAT ozonation afforded CAAT and CDAT in a 9:1 ratio. Treatment of CDIT with ozone also yielded CDAT and CDDT initially in a 60:40 ratio, which then gave rise to formation of CAAT and more CDAT. CDET, CIAT, or CEAT was not detected during this reaction. Ozonation of CIAT afforded CDAT and CAAT in nearly equivalent amounts; formation of CEAT was not observed.

Ozonation of CDAT afforded a transient intermediate, X, and then CAAT. Attempts to isolate X were unsuccessful as it decomposed with time to form CAAT and was sensitive to heat (>40 °C), to acid, and to base. There was some marginal evidence that X is a carbamic acid with a presumed molecular weight of 189. A mass spectrum of a quick isolation of X showed peaks at m/z 171 (173) $(M - H_2O)^+$, 145 (base peak) (147), 129 (131), 110, and 68.

Table II. ^{1}H NMR Spectra of Atrazine and Its Ozonation Products[a]

compd	$HNC(O)CH_3$	HNR[b]	$CH(CH_3)_2$	CH_2CH_3
CIET		7.83–7.62 (m, 2 H)	4.05–3.97 (m, 1 H) 1.13–1.03 (m, 6 H)	3.29–3.17 (m, 2 H) 1.13–1.03 (m, 3 H)
CEAT		7.29 (s, 1.5 H) 7.16, 7.08 [2 s (b), 0.5 H] 7.74, 7.59 (2 t, 1 H, J = 5 Hz)		3.28–3.18 (m, 2 H) 1.07, 1.06 (2 t, 3 H, J = 7 Hz)
CIAT		7.28 (s, 1.5 H) 7.16, 7.02 [2 s (b), 0.5 H] 7.69, 7.52 (2 d, 1 H, J = 8 Hz)	4.02 (septet, 1 H, J = 7 Hz) 1.15 (d, 6 H, J = 7 Hz)	
CDET	10.60, 10.56 (2 s, 1 H) 2.27, 2.20 (2 s, 3 H)	8.54, 8.41 (2 t, 1 H, J = 6 Hz)		3.34, 3.37 (2 q, 2 H, J = 7 Hz) 1.11, 1.10 (2 t, 3 H, J = 7 Hz)
CDIT	10.59, 10.55 (2 s, 1 H) 2.27, 2.20 (2 s, 3 H)	8.42, 8.34 (2 d, 1 H, J = 8 Hz)	4.11–3.99 (m, 1 H) 1.14, 1.13 (2 d, 6 H, J = 7 Hz)	
CDDT	11.09 (s, 2 H) 2.31 (s, 6 H)			
CDAT	10.59 (s, 1 H) 2.20 (s, 3 H)	7.91 (d, 2 H, J = 5 Hz)		

[a] Samples dissolved in DMSO-d_6; 300 MHz spectrometer. [b] R = ethyl, isopropyl, or H.

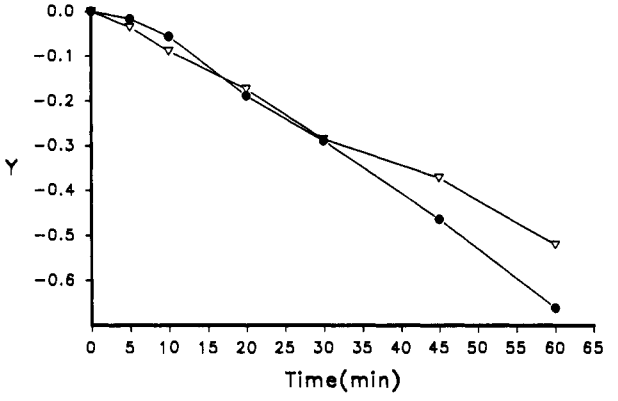


Figure 2. Degradation of CDAT (●), $y = \ln([CDAT]/[CDAT]_0)$, and formation of X (▽), $y = \ln\{1 - ([X]/[CDAT]_0)\}$.

Examination of CDDT ozonation also revealed a transient intermediate Y, but no attempts to isolate Y were carried out.

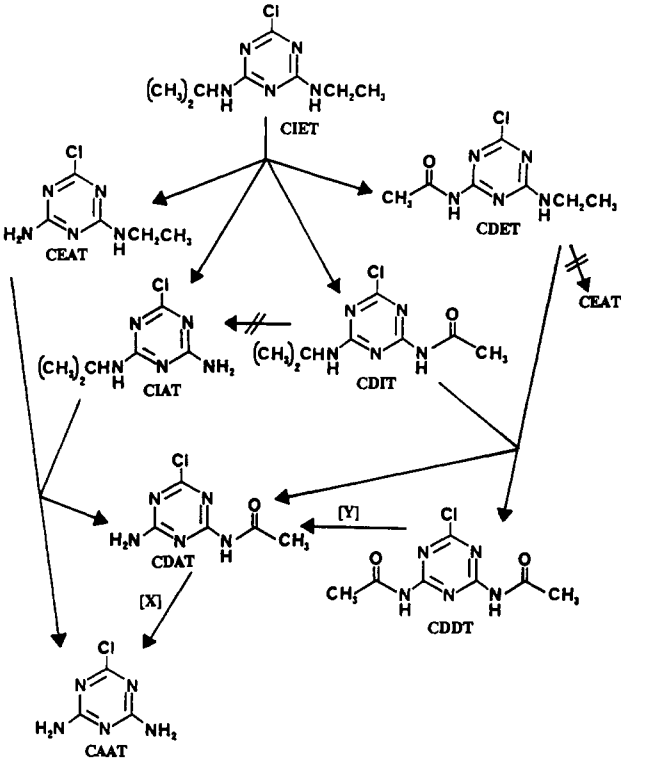
In previous work the aqueous ozonation rate of pesticides was observed to be pseudo first order (Kearney et al., 1988; Somich et al., 1988). Presumably, the concentration of ozone and other oxidants remains constant once steady state is achieved. A plot of the first-order formation of X ($\ln\{1 - [X]/[CDAT]_0\}$) and first-order degradation of CDAT ($\ln\{[CDAT]_t/[CDAT]_0\}$) vs time demonstrated that for the first 30 min the two lines overlapped, suggesting that X was indeed an intermediate (Figure 2). After 30 min, the X line became nonlinear because a significant portion of X degraded to CAAT. It is unclear whether the degradation of X is due strictly to its inherent instability or if further participation of ozone is involved. Also, the HPLC detector response factor for CDAT and X were presumed to be similar since X could not be isolated, nor was it stable long enough to run standard curves.

Prolonged ozonation (>3 h) of CAAT eventually gave rise to COAT and nitrate but no OAAT (ammeline) as determined by comparison of the HPLC retention times and the UV spectra (200–350 nm) with standards. When AAtrex Nine-O (formulated atrazine) was ozonated, a mixture of CDDT, CDAT, and CAAT was formed. Further oxidation beyond CAAT did not occur under similar conditions.

DISCUSSION AND CONCLUSION

Analysis of the aqueous ozonation of atrazine and its degradation products demonstrated that amino alkyl groups are the first site of attack. The alkyl group is either removed or converted to the acetamide, and the *s*-triazine ring remains intact. Furthermore, the isopropyl group is not converted to the ethyl group, nor are the ethyl or isopropyl moieties converted to the aldehyde as has been previously proposed (Kearney et al., 1988). The ozonation reactions of CDET and CDIT clearly demonstrate that the alkyl group is far more reactive than the amide moiety. These results are summarized in Scheme I. Additionally, oxidation of the amino group was shown to occur after long ozonation times to afford nitrate and the corresponding hydroxy-*s*-triazine. The chlorine is not removed until it is made somewhat more reactive as it is with COAT.

Scheme I



Legube et al. (1987) have examined the ozonation of nitrogen heterocycles under slightly acidic conditions and found that atrazine was poorly reactive and that the triazine ring remained intact. They isolated two products, one of which was CDAT and the other could not be

identified. Reanalysis of their mass spectral data [m/z 229 (231), 214 (216), 187, 172 (174), 145, 85, 71, 58, 43] shows a good match with CDIT isolated in this paper. NMR data were also presented for this second compound: 1.2–1.3 (d, 3 H) and 2.6 ppm (s, 1 H). More likely the ratio of these two signals was closer to 2:1, corresponding to the two isopropyl methyls and the amide methyl, respectively. Furthermore, the signal for isopropyl methyls would be a doublet since they are coupled to the methyne hydrogen, and the amide, which is not adjacent to any hydrogens, would give rise to a singlet. The multiplet for the methyne may not have been seen if the conditions for the NMR analysis were less than desirable and sample size was small. They also tentatively identified three other compounds, which were characterized by derivatization of the reaction mixture and subsequent GC/MS analysis, as OAIT [4-amino-2-hydroxy-6-(isopropylamino)-s-triazine], OOIT [2,4-dihydroxy-6-(isopropylamino)-s-triazine], and OOOT. Interestingly, these compounds, including the two retaining the amino alkyl moiety, were dechlorinated, whereas in the present paper all alkylated products (CIAT, CEAT, CDIT, and CDET) retained chlorine.

CDIT has also been observed in the sensitized photooxidation of atrazine as were CIAT and CAAT (Rejto et al., 1983). NMR and mass spectral data obtained for CDIT were similar to data from this study. More recently, the photocatalytic degradation of atrazine using TiO_2 was found to give rise to CDIT, CIAT, and CAAT in addition to OIET (hydroxyatrazine), OAAT, OOAT, and OOOT (Pelizzetti et al., 1990). Presumably, oxidation involved hydroxy radicals, although the extent of a photooxidation vs hydroxy radical mechanism was unclear. In both studies neither CDET nor CEAT was detected.

In summary, the results have demonstrated the fate of s-triazine moiety and the alkyl groups and will provide the necessary details to proceed in the optimization of s-triazine remediation. Investigations are continuing to discern the extent of hydroxy radical involvement and the role of other oxidizing species in the ozonation of atrazine and to quantitate the preference of oxidation and/or removal of the ethyl, isopropyl, and acetyl nitrogen substituents. With the appearance of s-triazine residues not only in agricultural sites but in groundwater and surface waters as well, these results will certainly be useful to waste remediation investigators and may also be helpful to those developing methods for triazine residue removal in water treatment.

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Registry No. CIAT, 6190-65-4; CEAT, 1007-28-9; CDIT, 83364-15-2; CDET, 142179-76-8; CDDT, 143593-21-9; CDAT, 115339-34-9; CAAT, 3397-62-4; $ClCH_2CH(OEt)_2$, 621-62-5; atrazine, 1912-24-9; 2-[[3′-chloro-5′-(isopropylamino)-S-triazyl]amino]acetaldehyde, 115339-35-0.