Prometryne Oxidation by Sodium Hypochlorite in Aqueous Solution: Kinetics and Mechanism

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The reaction of the herbicide prometryne (C₉H₁₆N₅-S-CH₃) with sodium hypochlorite has been investigated from the kinetic and mechanistic stand point. Under the fixed experimental conditions: pH = 7, T = 25 $^{\circ}C$, [NaClO]/[substrate] = (10⁻³ M)/(10⁻⁵ M), prometryne oxidation takes place according to the following pathway: $R-S-CH_3$ (P) $\rightarrow R-SO-CH_3$ (a) $\rightarrow R-SO_2-CH_3$ (b) \rightarrow R-0-SO₂-CH₃ (x) \rightarrow R-OH (c), where R stands for $C_9H_{16}N_5$, i.e., the substituted triazine ring of prometryne and (x) is an unexpected intermediate never previously detected nor identified. After having synthesized the pure intermediates (a), (b), and (x), the values of the pseudo-first-order kinetic constants of the first three steps were experimentally obtained: $[k_1 = (0.64 \pm$ 0.03) s⁻¹, $k_2 = (1.81 \pm 0.05) \times 10^{-3}$ s⁻¹, $k_3 = (1.50 \pm 0.03)$ \times 10⁻⁴ s⁻¹]. As for k₄, its value [(2.5 ± 0.2) \times 10⁻⁵ s⁻¹] has been calculated indirectly on the basis of the kinetic theory concerning consecutive reactions. All the steps were pseudo-first-order reactions with respect to their specific substrate. The effect of pH on the hydrolysis of (b) $[(b) \rightarrow (c)]$, in the absence of NaClO, has been also assessed to better elucidate the mechanism of the overall pathway.

Introduction

In Italy, more than 70% of drinking water comes from groundwater resources where the occurrence of herbicides is very likely because of their intensive and prolonged use in agriculture (1). Concern about such an occurrence is growing, particularly in those areas characterized by permeable soils and where the local drinking water treatment plants (DWTP) have been designed without taking into account any option for herbicides removal. Among the currently available technologies for herbicides removal

from drinking water, many are not yet reliable [electrochemical (2), photocatalytic (3), microbiological (4)] while only a few [activated carbon adsorption (5), reverse osmosis (6), advanced oxidation processes (7)] are really effective at large scale facilities. These latter technologies, however, are rather expensive and often characterized by specific disadvantages. In particular, considering advanced oxidation processes, their main drawback is the incomplete mineralization of organic micropollutants with consequent formation of undesired byproducts (8). Significant efforts are currently under way all over the world to identify such byproducts with the aim of assessing their toxicity, which sometimes is greater than that of the parent compounds (9). At those DWTP where specific technologies are not available, the only treatment that could remove herbicides by oxidation is disinfection (10). However, although the use of chlorine and/or sodium hypochlorite as a disinfectant is widespread, relatively few efforts have been made to identify byproducts resulting from the reaction of such disinfectants with herbicides that could occurr in drinking water. In a previous study (11), by investigating the reactions of four sulfur-containing s-triazines (prometryne, terbutryne, ametryne, and desmetryne) with sodium hypochlorite, it was proposed that this class of herbicides [R-S-CH₃] was oxidized according to the following pathway:

$$\begin{array}{c} \text{R-S-CH}_3 \xrightarrow{(1)} \text{R-SO-CH}_3 \xrightarrow{(2)} \text{R-SO}_2\text{-CH}_3 \xrightarrow{(3)} \text{R-OH} \\ (a) \qquad (b) \qquad (c) \end{array}$$

where R stands for the specific substituted triazine ring. In other words, the oxidation of such herbicides gave rise to the consecutive formation of two intermediates, (a) and (b), and a single end byproduct (c). In that study, sulfurcontaining s-triazines were selected because they represent a class of herbicides that presumably is going to progressively replace the more toxic chlorine-containing homologous compounds for controlling broadleaf and grassy weeds in corn and other crops (12, 13). In Italy, for instance, since 1986 the use of atrazine, the most commercialized chlorinecontaining triazine, has been banned (14) in all areas where the occurrence of its residues exceeds 0.1 ppb, i.e., the maximum allowable concentration indicated by the European Economic Community (15). Interest in the environmental fate of sulfur-containing s-triazines has obviously grown soon after traces of such herbicides as well as that of their residues were found in soils and groundwater (16-18). During the present investigation, in order to kinetically characterize the three steps of the pathway reported above, after having synthesized the pure intermediates (a) and (b) of prometryne (P), reactions of each substrate [(P), (a), (b)] with an excess of NaClO have been carried out. The results of this kinetic investigation together with some unexpected experimental evidence concerning the actual pathway of prometryne oxidation are reported in the present paper.

Experimental Section

Chemicals. Prometryne (P) [2,4-bis(isopropylamino)-6-(methylthio)-*s*-triazine] 99% purity, (Polyscience, Niles, II) was used without further purification. Water and methanol used during liquid chromatography were HPLC-grade (Carlo Erba, Milan, Italy). Methanol and methylene chloride

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used for solid—liquid extractions were pesticide-grade from Carlo Erba. Sodium hypochlorite solutions were prepared from Carlo Erba stock solutions properly diluted and used after iodometric titration to check their exact concentration (19). All other chemicals were analytical-grade from Carlo Erba. Stock solutions were stored in dark bottles at 4 °C. Distilled water was used for preparing all aqueous solutions.

Synthesis of Intermediate (a) [2,4-(N,N'-Diisopropyl)diamino-6-methylsulfinyl-1,3,5-triazine]. A total of 0.482 g (2 mmol) of prometryne was dissolved in 25 mL of dichloromethane, and the solution was cooled to 0 °C. Within 10 min, 0.345 g (2 mmol) of dry *m*-chloroperoxybenzoic acid was added, in small portions and with continuous stirring. The reaction mixture was then stirred for 20 min and washed with 10 mL of a 10% sodium carbonate solution. After the two phases had been separated, the dichloromethane phase was dried over sodium sulfate, filtered, and then evaporated. The residue was suspended in 10 mL of diethyl ether and left at 0 °C overnight. The resulting white crystals, after filtration, were checked for purity by assessing their chemical structure using HPLC-MS and measuring their specific HPLC retention times.

Synthesis of Intermediate (b) [2,4-(N,N'-Diisopropyl)diamino-6-methylsulfonyl-1,3,5-triazine]. A total of 0.964 g (4 mmol) of prometryne was dissolved in 40 mL of HPLCgrade acetone. At 20 °C, 0.82 mL of 30% H₂O₂ (8 mmol) was added to the solution, which was stirred and refluxed over 22 h. Every 2 h, a further 0.2 mL of 30% H₂O₂ was added. The acetone was then evaporated, and the residue was redissolved in 20 mL of dichloromethane, which was sequentially dried over Na₂SO₄, filtered, and evaporated. The residue was then purified by chromatography on 25 g of oven-dried silica gel using chloroform as the eluant. After chloroform evaporation, the residue was dissolved in a mixture of diethyl ether (2.5 mL) and n-hexane (1 mL), and left at 0 °C overnight. The resulting white crystals were filtered and checked for purity as reported for the intermediate (a).

Synthesis of Intermediate (x): [2,4-(N,N-Diisopropyl)diamino-6-methanesulfonate ester 1,3,5-triazine]. A total of 1.05 mg (5 μ mol) of compound (c) was dissolved in 2 mL of pyridine, and at 0 °C, 39 μ L (0.5 mmol) of methanesulfonyl chloride was added under stirring. After 5 min, the temperature was raised to 27 °C.

Kinetics Experiments. A 1-mL sample of the substrate [(P), (a), or (b)] in methanolic solution (1 mM) was placed in a 100-mL reaction flask. After methanol evaporation, a 50 mM phosphate buffer (pH = 7) solution (99 mL) was added at 25 °C. The solution was stirred to dissolve the substrate, and an appropiate amount of sodium hypochlorite (1 mL) was added. In the resulting solution, the sodium hypochlorite concentration was 10^{-3} M while that of the substrate was 10^{-5} M. At scheduled times, 1 mL of the reaction mixture was withdrawn, quenched with $10 \,\mu$ L of 10% sodium thiosulfate solution, and analyzed by HPLC-UV. In the case of prometryne, as it reacted very quickly with sodium hypochlorite, it was necessary to prepare several reaction flasks, each one quenched at scheduled times.

HPLC Conditions. A 1050-Ti series HPLC chromatograph (Hewlett-Packard, Palo Alto, CA) equipped with a $5-\mu$ m C-18 silica solid phase (150 \times 4.6 mm i.d.) from Supelco (Bellefonte, PA) and a 1050 series variable wavelenght detector, set at 224 nm, was used. Samples, injected



FIGURE 1. Decay rates, by reacting with NaClO, of prometryne (P), prometryne's sulfoxide (a), and prometryne sulfone (b) at pH = 7. Experimental conditions in the text.

via a $10-\mu$ L Rheodyne loop, were eluted with a (methanol)/ (50 mM ammonium acetate) 55/45 v/v solution at a flow rate of 1 mL/min. For samples containing prometryne, the mobile-phase composition was (methanol)/(50 mM ammonium acetate) 65/35 v/v.

Mass Spectrometric Analysis. AVG (Manchester, U.K.) TS-250 trisector mass spectrometer operating in plasmaspray mode and equipped with a thermospray interface and a PDP-11 microcomputer (Digital, Maynard, MA) for data acquisition was used (20, 21). The sample to be analyzed was concentrated according to the following solid-liquid extraction procedure: after conditioning a 500mg ENVI-18 solid-phase cartridge (Supelco, Bellefonte, PA) by loading sequentially (methylene chloride)/(methanol) 1/1 v/v solution, methanol, and water (12 mL each), 100 mL of the quenched sample was allowed to flow through the conditioned cartridge. After a 5-min drying step, the cartridge was eluted with methanol (5 mL). The volume of the methanol extract was reduced to 1 mL by a gentle stream of purified air. The plasmaspray conditions (positive ions) were as follows: source temperature = 250 °C, vapor temperature = $130 \degree C$, scan speed = 1 s, resolution = 500, and mass range from 100 to 400 amu.

Results and Discussion

The experimental conditions under which each step of the proposed prometryne (P) oxidation pathway $[(P) \rightarrow (a) \rightarrow (b) \rightarrow (c)]$ was kinetically characterized were: [NaClO]/ [substrate] = $(10^{-3} \text{ M})/(10^{-5} \text{ M})$, pH = 7, T = 25 °C. The kinetic constants relative to each step were determined by monitoring, with respect to time, the decreasing concentration of each substrate [(P), (a), (b)] by HPLC. Each substrate was identified by its specific HPLC retention time: (P) = 9.8, (a) = 9.0, and (b) = 7.9 min. As shown in Figure 1, for each substrate by plotting the values of its concentration (on a ln scale) versus time, a straight line is always obtained. This means that each investigated step can be considered a pseudo-first-order reaction with respect to its specific substrate. The corresponding pseudo-first-order kinetic constant values (k_1, k_2, k_3) , easily obtained for



FIGURE 2. Prometryne's sulfone oxidation by NaClO: HPLC chromatograms of reaction mixture samples quenched at successive times (A = 0, B = 60, C = 180, and D = 480 min). Experimental conditions in the text.



FIGURE 3. Plasmaspray mass spectra of the unknown intermediate (x). Instrumental conditions in the text.

each step from the slope of the straight lines in Figure 1, are $k_1 = (0.64 \pm 0.03)s^{-1}$, $k_2 = (1.81 \pm 0.05) \times 10^{-3} s^{-1}$, $k_3 = (1.50 \pm 0.03) \times 10^{-4} s^{-1}$.

From the mechanistic point of view, an unexpected result was obtained when investigating the decay of (b). As shown by the consecutive HPLC chromatograms in Figure 2, decay of (b) gave rise to two byproducts: an unknown intermediate (x) [retention time = 8.6 min] and the expected hydrolysis product (c) [retention time = 5.8 min]. Furthermore, looking at Figure 2D, it is also evident that the only end byproduct of the decay of (b) is (c). This proves that, in the investigated system, the transformation (x) \rightarrow (c) occurs.

In order to assess the chemical structure of this unknown intermediate, the sample giving HPLC chromatograms shown in Figure 2C was concentrated and analyzed by HPLC-MS according to the conditions reported in the Experimental Section.

As indicated in Figure 3, the mass spectrum of the intermediate (x) shows a $[M + H]^+$ molecular ion at 290 amu that is presumably consistent with a structure of 2,4-(N,N'-diisopropyl)-diamino-6-methyl sulfonate ester-1,3,5-triazine [R-O-SO₂-CH₃] whose molecular weight is 289 amu. In addition to the 290 amu peak, the presence of the -O-SO₂-CH₃ group in the chemical structure of the intermediate (x) is supported by the presence of a peak at 212 amu. This peak can be reasonably associated with the ion [R-O + 2H]⁺ which could result from (x) after the loss of the -SO₂-CH₃ group. The same peak, in fact, is also present in the MS spectra of the intermediate (c) whose molecular ion [M + H]⁺ corresponds to a [R-OH + H]⁺ ion. In any case, in

order to better support the proposed structure [R-O-SO2-CH₃] for the intermediate (x), a reaction between (c) and methanesulfonyl chloride has been carried out under the conditions reported in the Experimental Section. The expected reaction product of such a reaction should have the same structure of the compound proposed for intermediate (x). In fact, HPLC chromatogram of a reaction mixture sample taken after 45 min showed two peaks: the first at the same retention time (5.8 min) of the starting hydroxylated triazine and the second at the same retention time (8.8 min) recorded for the intermediate (x). In addition, HPLC-MS spectrum of such a reaction product was the same as the intermediate (x). The conclusion that the chemical structure of the intermediate (x) is R-O-SO₂-CH₃ (i.e., the expected oxidation product of intermediate (b) = $R-SO_2-CH_3$) proves that in the investigated system the transformation (b) \rightarrow (x) occurs.

From the results so far discussed, however, it is not possible to determine whether the formation of (x) and (c) is consecutive or simultaneous. In other words, the decay of (b) could occur according to one of the two following pathways:

$$(b) \rightarrow (x) \rightarrow (c)$$
 or $(x) \rightarrow (c)$

With the aim of assessing which one is the actual pathway, considering that the reaction (b) \rightarrow (c) is a simple hydrolysis that can occur in the absence of oxidant, the decay of (b) was investigated in the absence of NaClO at pH = 7 [initial concentration of (b): 10^{-5} M]. Under such experimental conditions, after 48 h, no decrease in the initial concentration of (b) was observed. This result proves that, at least at pH = 7, the reaction (b) \rightarrow (c) does not occur and that the actual pathway is: (b) \rightarrow (c).

Taking into account that the transformations R-O-SO₂-CH₃ \rightarrow R-OH, i.e., (x) \rightarrow (c), and R-SO₂-CH₃ \rightarrow R-OH, i.e., (b) \rightarrow (c), are both hydrolysis reactions; the fact that, at pH = 7, only the first one occurs could be explained by considering that as a nucleophilic substituent -O-SO₂-CH₃ is a better leaving group than -SO₂-CH₃. On the basis of the actual pathway of the decay of (b), it is possible to conclude that the formation of (x) and (c) must be consecutive and not simultaneous. Accordingly, the actual prometryne (P) hypochlorination pathway is:

$$(\mathbf{P}) \xrightarrow{k_1} (\mathbf{a}) \xrightarrow{k_2} (\mathbf{b}) \xrightarrow{k_3} (\mathbf{x}) \xrightarrow{k_4} (\mathbf{c})$$

The previously obtained k_3 value $[(1.50 \pm 0.03) \times 10^{-4} \text{ s}^{-1}]$, then, refers to the transformation (b) \rightarrow (x) and not to (b) \rightarrow (c).

At this point, to characterize the whole pathway, the kinetic constant (k_4) of the step $(x) \rightarrow (c)$ had to be evaluated. In this case, as the pure intermediate (x) was not available, the evaluation was undertaken indirectly using the following equation applicable to pseudo-first-order consecutive reactions (22):

$$[\mathbf{x}] = [\mathbf{b}]_{o} \frac{k_{3}}{k_{4} - k_{3}} [\mathbf{e}^{-k_{3}t} - \mathbf{e}^{-k_{4}t}]$$

where $[b]_0$ is the initial concentration of the intermediate (b) and [x] is the concentration of the intermediate (x) at the time *t*. Differentiating this equation with respect to the time and equalizing the result to zero, the time (t_{max}) when



FIGURE 4. Decay rate of prometryne's sulfone during its hydrolysis at pH = 11.

TABLE 1

Pseudo-First-Order Kinetic Constants (s^{-1}) for Each Step of Prometryne Oxidation Pathway Reported in Figure 5

$K_1 (pH = 7)^a$	0.64 ± 0.03
$K_2 (pH = 7)^a$	$(1.81 \pm 0.05) imes 10^{-3}$
$K_{3}(pH = 7)^{a}$	$(1.50 \pm 0.03) imes 10^{-4}$
$K_4 (pH = 7)^b$	$(2.5 \pm 0.2) imes 10^{-5}$
$K_5 (pH = 11)^a$	$(2.67 \pm 0.07) imes 10^{-4}$

^a Evaluated experimentally. ^b Evaluated indirectly.

[x] is maximum can be obtained, i.e.

$$t_{\max} = \frac{\ln (k_3/k_4)}{k_3 - k_4}$$

Introducing in this latter equation the experimental k_3 and $t_{\rm max}$ values, respectively $(1.50 \pm 0.03) \times 10^{-4} \, {\rm s}^{-1}$ and 240 min, a value of $(2.5 \pm 0.2) \times 10^{-5} \, {\rm s}^{-1}$ has been calculated for k_4 , and this means that $k_4 < k_3$. Such a result is consistent with the trend of the chromatograms shown in Figures 2B,C which, on the basis of peaks height, indicate that after 180 min the amount of (x) is greater than that resulting after 60 min. Such a temporary increase of (x) amount, in fact, is possible only if $k_4 < k_3$.

As for the previously discussed experimental result, which indicated that at pH = 7 ([OH⁻] = 10⁻⁷) after 48 h the prometryne sulfone intermediate (b) does not undergo hydrolysis, it could be ascribed to the fact that the replacement of the -SO₂-CH₃ group by OH⁻ ions does not occur at all or to the extremely slow kinetics of such replacement due to the very low hydroxyl ions concentration. In order to clear up this point, an experiment was carried out monitoring the decay of (b) in the absence of NaClO at pH = 11 ([OH⁻] = 10^{-3} M). As shown in Figure 4, the obtained results prove that, using such a high hydroxyl ions concentration, the hydrolysis (b) \rightarrow (c) occurs easily and that even this step can be considered a pseudo-firstorder reaction $[k_5 = (2.67 \pm 0.07) \times 10^{-4} \text{ s}^{-1}]$. In Table 1, all the pseudo-first-order kinetic constants values, obtained experimentally as well as calculated indirectly, have been summarized.

The fact that during a previous investigation (11) the intermediate (x) was not detected even in samples whose HPLC chromatograms showed the simultaneous presence



FIGURE 5. Proposed degradation pathway for prometryne oxidation by NaClO: i-Pr = isopropyl, i.e., $-CH(CH_3)_2$.

of (b) and (c) peaks can be explained only by assuming that the actual concentration of (x) in those samples was too low to be analytically detected. Such a very low concentration value was presumably due to the fact that during that investigation the decay of (b) was monitored in a single batch where (1) all the transformations (P) \rightarrow (a) \rightarrow (b) \rightarrow $(x) \rightarrow (c)$ occurred simultaneously; (2) the sum of the molar concentrations of all substrates ([P] + [a] + [b] + [x] + [c])was 10^{-5} M; and (3) the concentration of (b), when it began to decay, was unknown. The actual concentration of (x) in such a batch was a fraction of 10^{-5} whose numerical value depended on the degree of conversion of each step of the overall pathway. Conversely, during the present study, as pure intermediate (b) was available, it has been possible to investigate its decay in a specific batch where the starting concentration of such an intermediate was known, i.e., 10⁻⁵ M. The results discussed in the present paper prove that in such a batch the actual concentration of (x) was high enough to be detected by HPLC as well as by MS. On the basis of the experimental evidences acquired during the present investigation, it is possible to propose, as shown in Figure 5, a definitive pathway for prometryne oxidation by NaClO.

Conclusion

The results of the present investigation allow us to better clear up the mechanism of prometryne (P) oxidation by an excess of NaClO. In fact, after having identified by HPLC-MS an unexpected intermediate (x), a three-step oxidation pathway $[(P) \rightarrow (a) \rightarrow (b) \rightarrow (c)]$ previously proposed for

such a herbicide has been consequently modified as

$$\begin{array}{ccc} \text{R-S-CH}_3 \xrightarrow{(1)} \text{R-SO-CH}_3 \xrightarrow{(2)} \text{R-SO}_2\text{-CH}_3 \xrightarrow{(3)} \\ (P) & (a) & (b) \\ & & \text{R-O-SO}_2\text{-CH}_3 \xrightarrow{(4)} \text{R-OH} \\ & & & (c) \end{array}$$

where R stands for $C_9H_{16}N_5$, i.e., the substituted triazine ring of prometryne. Once synthetized, the pure intermediates (a) and (b), the kinetic constants of the first three steps of such pathway have been experimentally evaluated. The resulting values are respectively $k_1 = (0.64 \pm 0.03) \text{ s}^{-1}$, k_2 = $(1.81 \pm 0.05) \times 10^{-3} \text{ s}^{-1}$, $k_3 = (1.50 \pm 0.03) \times 10^{-4} \text{ s}^{-1}$. As for k_4 , because the pure intermediate (x) was not available, its value [$(2.5 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$] has been calculated indirectly on the basis of theoretical considerations concerning consecutive reactions.

Under the fixed experimental conditions, pH = 7, T = 25 °C, $[NaClO]/[substrate] = <math>(10^{-3} \text{ M})/(10^{-5} \text{ M})$, each step is resulted to be a pseudo-first-order reaction with respect to its specific substrate. Furthermore, it has been proved that the direct hydrolysis (b) \rightarrow (c) takes place only at very high pH values. Whether the toxicity of the intermediates (a), (b), and (x) and the end byproduct (c) are lesser or greater than that of prometryne is a question still to be assessed. From the technological viewpoint, it is interesting to notice that in spite of the concern over its potential toxicity, water chlorination by sodium hypochlorite together with pathogens inactivation could provide also some side benefits such as sulfur-containing *s*-triazines degradation.

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