Environ. Sci. Technol. **2004**, *38,* 4134−4139

Odorous Products of the Chlorination of Phenylalanine in Water: Formation, Evolution, and Quantification

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To explain some of the possible origins of an odor episode which took place in a drinking water supply in the region of Paris (France), the chlorination reaction in water of phenylalanine was studied. This amino acid was chosen for first experiments because of its physical and chemical particular properties. Changes in the different byproducts formed were followed by high-performance liquid chromatography (HPLC) over a period of time. *N*-chlorophenylalanine (mono-*N*-chlorinated amino acid) and then phenylacetaldehyde were the major products formed for the lower chlorine to nitrogen molar ratios. For Cl/N molar ratios of 1 and beyond, phenylacetonitrile and *N*-chlorophenylacetaldimine appeared and increased with the chlorination level. *N*-chlorophenylacetaldimine was quantified by using its difference of stability in various organic solvents. Our attention was first directed to the monochlorinated derivative but further examination indicated that it could not be responsible for odor troubles: it dissociated before reaching the consumer's tap and it was produced at consistently low yields under conditions relevant to drinking water treatment. On the contrary, chloroaldimine appeared to be a very odorous and water-stable product: it strongly smells of swimming pool with a floral background. The odor detection threshold is about 3 $\mu g \cdot L^{-1}$ and it can persist for more than one week at 18 °C. It is now suspected of being a source of off-flavor concerns among consumers.

Introduction

Drinking water disinfection is necessary for eliminating pathogenic organisms. Indeed, it must be without adverse effect on any form of life. Chlorine is one of the most important products used for chemical disinfection of drinking water because it is effective, cheap, and readily available. Moreover, it is one of the only disinfectants to have retentive power. But as an oxidizing disinfectant, chlorine can also react with natural organic matter (NOM) present in drinking water (*1*). The organic compounds composing NOM (polysaccharides, amino sugars and amino acids, proteins, and polyhydroxyaromatic compounds) can produce undesirable disinfection byproducts. Great concern has been focused on the health risks of drinking water because some of the disinfection byproducts have been linked to cancer in animals or are suspected to have possible reproductive and development effects (*2*), but little attention has been paid to off-flavor properties of treated water. However, drinking water also needs to have good organoleptic properties. It should not present any odor, color, or taste because the consumer often uses sensory evaluation for judging water quality, assuming, most often wrongly, that water with an unpleasant smell is unsafe for consumption (*3*). A better understanding of the chemical causes of drinking water odor is by this fact necessary for water operators. The composition of water before chlorine addition has a great incidence on the formation of disinfection byproducts. Our study was financially supported by the Mery-sur-Oise treatment plant, located in the north suburbs of Paris. The study was based on an isolated odor episode following the implantation of a new membrane process. Part of the water (70%) from this plant has been nanofiltered since 1999 (*4*). So only very little organic matter is able to pass the membrane barrier. Only low-molecular-weight compounds such as amino acids (*5*) and short peptides can pass through the membrane.

Now odorous chlorinated products, for example, are formed especially with the amino acids encountered at low concentration in water, under a dissolved free form or even more as little peptides. The major amino acids present in treated water are alanine, glycine, valine, phenylalanine, serine, threonine, isoleucine, aspartic acid, tyrosine, proline, glutamic acid, and leucine (*6*). Amino acid concentrations in drinking water range from 0.33 to 1.05 $\mu g \cdot L^{-1}$ (*7*). According to Dossier Berne (*8*), free amino acid concentrations determined in several drinking water factories of western France would vary between 0 and 30 $\mu g \cdot L^{-1}$. It is well-known that the reaction of aqueous chlorine with amino acids leads to the formation of *N*-chloramines, nitriles, and aldehydes (*9*), which are most often odorous products and can cause some odor problems in distributed water (*10*). Indeed, amino acid chlorination is always a subject of great concern and has received attention for different reasons: chloramines are believed to be toxic to some fishes (*11*, *12*) and are also strongly suspected of interfering with the disinfectant concentration measurements in water (*13*−*15*).

Several studies (*16*−*20*) presented a new scheme for the pathway of amino acids chlorination. They demonstrated that *N*-chloroaldimines can be produced during this reaction but no information was available for their odor properties. The aim of this work was to identify the byproducts formed during the chlorination reaction of amino acids, which are suspected of being odorous. It has been known for a long time that aldehydes have weak odor detection thresholds, closed to $\mu g \cdot L^{-1}$ concentration (*21*). The kind of odor presented by these aldehydes is related to their molecular weight: low-molecular-weight aldehydes present unpleasant odors and high-molecular-weight aldehydes present floral or fruity odors (*22*). Our study focused on the chloroaldimine, for which no odor description was available in the literature but which rapidly appeared odorous at low concentrations. In this way, the amino acid chlorination reaction was studied to determine the odor-producing potential of this product in the drinking water industry.

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10.1021/es035021i CCC: $27.50

Published on Web 06/22/2004

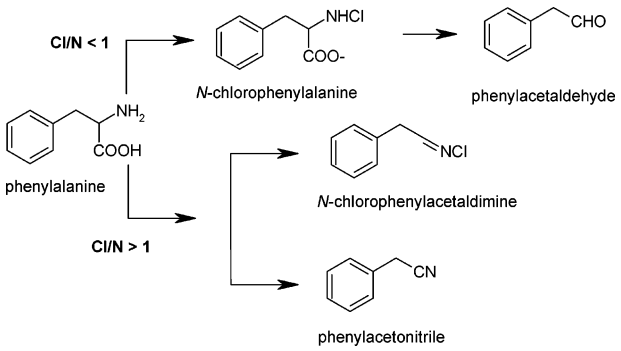

FIGURE 1. Simplified scheme for chlorination of phenylalanine, adaptedfrom Conyers and Scully (*18*). Principal byproducts formed.

Even if it is not the most abundant amino acid in water, phenylalanine was chosen for its UV-absorbing properties. This enabled us to follow the chlorination reactions and the appearance of byproducts easily. Moreover, this product has only one nitrogen atom, which restricts its reactivity with chlorine and thus the complexity of the reaction mixtures obtained. Various Cl/N molar ratios and various reaction times were studied (Figure 1). Other amino acids will be studied to extend the results.

Materials and Methods

Reagents and Apparatus. D,L-Phenylalanine (99%) was obtained from Jansen Chimica, phenylacetonitrile (98−99%) was from EGA Chemie, and phenylacetaldehyde (90%) was purchased from Aldrich. The sodium hypochlorite solution (2 mol·L^{-1} minimum) was purchased from Prolabo and its concentration in active chlorine was regularly checked by thiosulfate titration (*23*) to record the decay rate of the solution in consideration. All the buffers and solutions were prepared in demineralized Millipore water with no chlorine demand (*24*). The free and combined chlorine were determined by reaction with *N*,*N*-diethyl-*p*-phenylenediamine (DPD) in absence or presence of iodide (*24*). Indeed, DPD gives a specific pink color in the presence of chlorine, the intensity of which can be measured by spectrophotometry (λ = 515 nm). Addition of potassium iodide crystals is necessary to reveal combined chlorine but this method cannot differentiate organic and mineral chloramines. Dechlorination was realized by addition of 3 equiv (with regards to the quantity of chlorine introduced) of sodium thiosulfate 0.1 mol·L^{-1} and 15 min of good stirring.

Measurements of the optical density for the determination of free and combined chlorine with DPD titration were made with a spectrofluorimeter Seconam S.750. This titration was available for chlorine concentrations between 0.05 and 4 mg Cl_2·L^{-1}. The equation of the curve was OD (optical density) = 0.1806*C* (*C* was the chlorine concentration in mg Cl_2·L^{-1}) with a correlation coefficient of 0.9939. Nuclear magnetic resonance (NMR) data were obtained with a Brucker FT ARX (^{1}H 400.13 MHz and ^{13}C 100.61 MHz). HPLC was performed using an Alliance Waters 2690 separation module with a Waters 2487 UV detector (λ = 254 nm). A Waters fraction collector II was added at the outlet of the HPLC apparatus. The majority of the analyses were first performed after 30 min of contact time and then at various intervals during the week with an injection volume of 250 μL. Separations were carried out on a C18 Symmetry column (4.6 × 250 mm) maintained at 30 °C, with a dual solvent system. Solvent A was 90% water (pH 4 adjusted with acetic acid) and 10% acetonitrile and solvent B was 90% acetonitrile and 10% water (pH 4 adjusted with acetic acid). The solvent program (flow rate of 1 mL·min^{-1}) consisted of a 5-min isocratic elution with 85% A/15% B followed by a linear gradient to 55% A/45% B over 20 min. Then a second linear gradient was applied to 10% A/90% B over 15 min and a 5-min isocratic elution with 10% A/90% B. These conditions were determined by Nweke and Scully (*16*).

Chlorination and Identification of the Byproducts Formed. Chlorinations of phenylalanine were first conducted in both phosphate buffer (pH 7) and water for Cl/N molar ratios of 1 and 2. Results obtained were similar. The same final products were formed and reached the same levels of concentration. So all experiments were then carried out in water to simplify the procedure. These conditions were also chosen to ensure that the pH conditions were quite similar to industrial conditions. Model solutions of phenylalanine (50 mL, 10^{-3} mol·L^{-1}) were chlorinated to different chlorine to nitrogen molar ratios by addition of micro volumes of the hypochlorite solution, incubated in the dark at room temperature, and regularly analyzed by HPLC−UV. Cl/N molar ratios of 0.5, 1, 1.5, and 2 will be presented here. All the compounds formed were collected with the fraction collector. Once the compounds were isolated, their flavor characteristics were determined and their oxidizing ability was tested to determine if they were *N*-chlorinated products: fractions obtained were mixed with various quantities of DPD, phosphate buffer (0.5 mol·L^{-1}, pH 6.3), and potassium iodide (*24*).

The *N*-chlorophenylacetaldimine was synthesized. A sodium hypochlorite solution (50 mL, Cl/N molar ratio of 2.4, providing the best conditions for chloroaldimine formation, as indicated below) was cooled in an ice bath, and phenylalanine (0.01 mol·L^{-1}, 1.65 g) was added while the mixture was stirred. After 10 min, the reaction mixture, which became cloudy, was extracted with 3 mL of $CDCl_3$, dried over anhydrous Na_2SO_4, and analyzed by both NMR and HPLC. The stability of chloroaldimine in various solvents was studied to establish an extraction method for this product and furthermore to quantify it. A solution of phenylalanine (50 mL, 0.2 mol·L^{-1}) was chlorinated with a Cl/N molar ratio of 2.8 and fractionated. Solvent (100 mL ofwater, hexane, methanol, acetonitrile, or dichloromethane) was added to 10 mL of the reaction mixture. After 24 h, the solution was analyzed by HPLC (injection of the organic phase for hexane and dichloromethane).

Because *N*-chlorophenylacetaldimine is not commercially available, a quantification method was investigated. Syntheses with different initial concentrations in phenylalanine (0.01, 0.02, 0.05, 0.1, and 0.2 mol·L^{-1}) were realized, with a Cl/N molar ratio of 2.4. Once the reaction stabilized, the solutions were shared out into two equal parts and each of them was percolated on a SepPak Cartridge C18, washed with equal quantities of water, and eluted with the same volume of solvent (5 mL approximately), hexane for one sample and acetonitrile for the other. To confirm the validity of the extraction protocol, the one in acetonitrile was injected immediately after concentration: it showed exactly the same quantity of aldehyde, nitrile, and chloroaldimine as the hexane extract.

The synthesis of imine was realized by an organic way. Phenylacetaldehyde (46 mg, 0.38 × 10^{-3} mol·L^{-1}) was introduced into 50 mL of anhydrous methanol. This solution was added to a solution of 5 equiv of ammonium chloride (NH_4Cl, 95 mg) in an additional 50 mL of methanol. Molecular sieves were used to absorb the water formed during the reaction. The solution was mixed with a magnetic stirrer for 1 h, then the reaction mixture was injected on HPLC.

Olfaction Tests. The olfaction tests were realized with standard compounds for aldehyde and nitrile and with chlorinated amino acid solutions (Cl/N 2.4) for the chloroaldimine. In these conditions, *N*-chloroaldimine concentration was considered to be 35% of the initial amino acid concentration. The following laboratory-made protocol was employed. First, all the glass was washed with an odorless

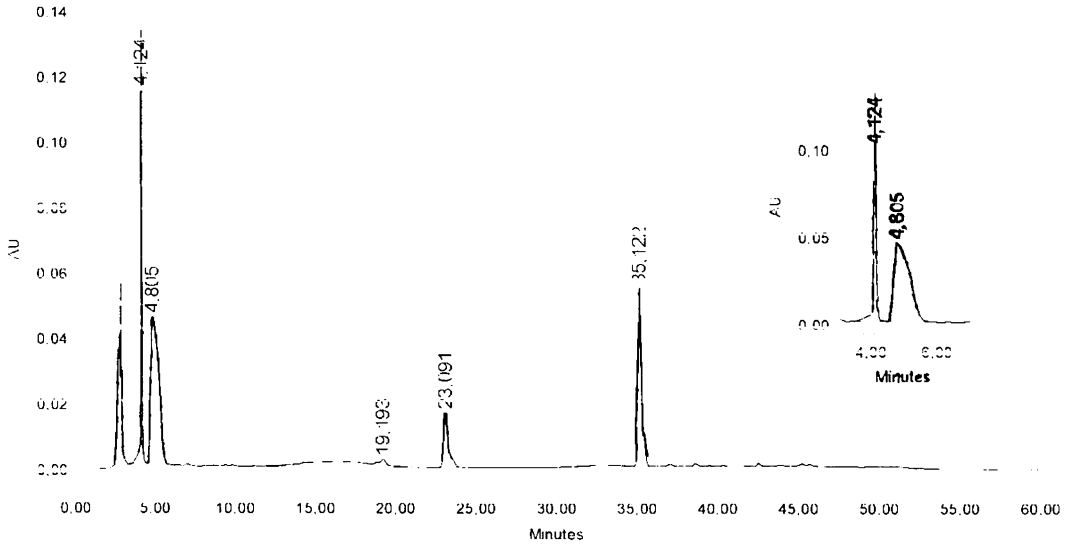

FIGURE 2. High-performance liquid chromatogram on C18 column with UV detection of a solution of phenylalanine (1 mM) Cl/N = 1.5 after 30 min chlorination. For chlorination rates close to 1 and for reaction times of several hours, another product was observed with a retention time of 39 min.

TABLE 1. Stable Levels Reached by Phenylalanine, Phenylacetaldehyde, and Phenylacetonitrile for Different Cl/N Molar Ratios of a Phenylalanine Solution (10^{-3} mol·L^{-1}) at 22 °C

	Cl/N = 0.5	Cl/N = 1	Cl/N = 1.5	Cl/N = 2
[Phe] (10^{-3}mol·L^{-1})	0.5	<0.05	<0.05	<0.05
[Ald] (10^{-3}mol·L^{-1})	0.42	0.88	0.45	0.14
[Nit] (10^{-3}mol·L^{-1})	undetected	0.02	0.18	0.45

detergent, rinsed 10× with hot tap water, and then rinsed 3× with unodorous water. Solutions at various concentrations ranging from 10^{-10} mol·L^{-1} to 10^{-3} mol·L^{-1} in each product were prepared and one blank of the water used for the dilution was added. Scent-bottles (250 mL) were totally filled with each solution and incubated for 1 h at 45 °C. Heated solutions were then placed in Erlenmeyer flasks and presented randomly to a panel of testers who had to indicate if they detected an odor or not. The panel was composed of 4 men and 3 women, randomly chosen, from 22 to 45 years old. First, solutions of a wide range of concentrations were used in order to situate the limit. Then the value was stated precisely by presenting several times the solutions of concentrations closest to the pre-estimated limit. The test took place in a well ventilated place. The odor detection threshold was determined when the average of positive answers was lower than 50%.

Results and Discussion

Identification of the Products Formed. Samples of phenylalanine (10^{-3} mol·L^{-1}) chlorinated at different levels were periodically injected (250 μL) during a week. The results obtained were on the whole in agreement with Conyers and Scully's proposed scheme of pathways (*18*). The chromatogram of a solution chlorinated to a Cl/N ratio of 1.5 is shown in Figure 2, as an example of the results obtained. The compounds that eluted with retention times of 4.8 and 35 min possessed oxidizing ability that indicated they were chlorinated products. The compounds with retention times of 4.8, 19, 23, and 35 min presented odors of respectively chlorine/swimming-pool, flowers, "white glue", and swimming-pool/flowers. Reference materials were used to identify and quantify phenylalanine (4.16 min), phenylacetaldehyde (19 min), and phenylacetonitrile (23 min). Indeed, standards chromatographed under identical analysis conditions allowed us to establish calibration curves for a concentration range between 0.05 × 10^{-3} and 10^{-3} mol·L^{-1}. Whatever the chlorination rate was, phenylalanine (Phe), -acetaldehyde (Ald), and -acetonitrile (Nit) levels reached a plateau in about 4 h (Table 1).

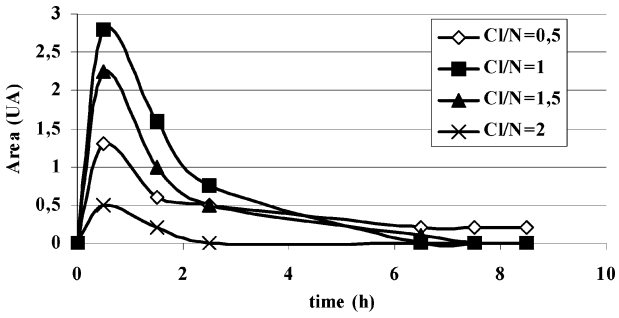

FIGURE 3. Evolution over time of *N*-chlorophenylalanine for different levels of chlorination of a model solution of phenylalanine (1 mM) at 25 °C.

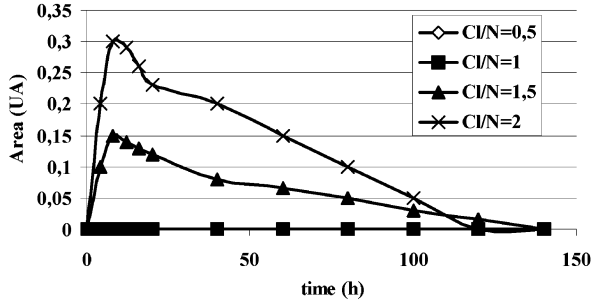

FIGURE 4. Evolution over time of *N*-chlorophenylacetaldimine for different levels of chlorination of a model solution of phenylalanine (1 mM) at 25 °C.

The compound with reaction time of 4.8 min appeared in a broad peak; it was formed quasi instantaneously for the majority of chlorination rates close to 1 and then it quickly decreased with time and had totally disappeared after 10 h (Figure 3). It showed oxidizing ability and was transformed into phenylalanine by the addition of thiosulfate. The peak was, for all these reasons, attributed to *N*-chlorophenylalanine. However, in contrast with findings of previous authors, it should be emphasized that the *N*-chlorophenyl-

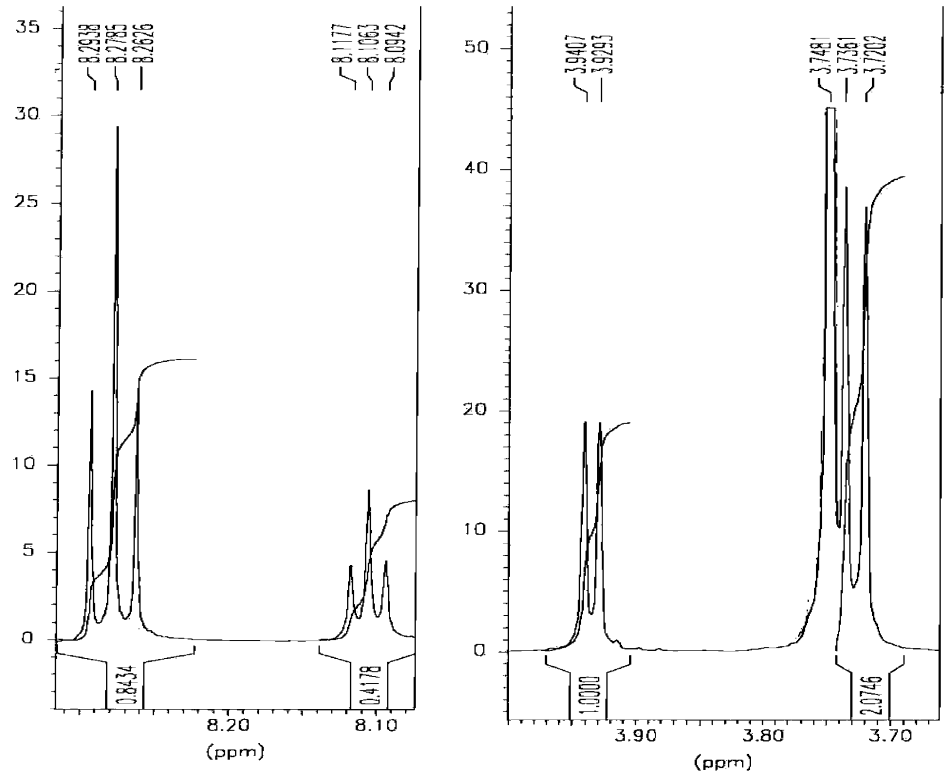

FIGURE 5. Parts of the proton NMR spectrum of *N*-chlorophenylacetaldimine in $CDCl_3$ contaminated by phenylacetonitrile.

alanine was observed even for a chlorination ratio close to 2, yet to a lesser extent and present only during the first 2 h after chlorination. We noticed, in agreement with the literature, that dichloramine (which should have been revealed by a different reaction with DPD) was never observed. Indeed, this observation might be partially explained by a very quick degradation of the compound, thus we were unable to analyze it.

The compound with retention time of 35 min increased for a chlorination rate greater than 1 (it appeared for Cl/N molar ratio of 1 and then, the higher the chlorination rate, the higher the quantity) and decreased with time (Figure 4). The greatest yields were observed for chlorination rates greater than 2. It also possessed an oxidizing ability. It was believed to be *N*-chlorophenylacetaldimine, and this structure was proved by synthesis immediately followed by NMR analysis. The proton spectrum (Figure 5) is consistent with a mixture of the two stereoisomers of *N*-chlorophenylacetaldimine, anti and syn, contaminated by phenylacetonitrile (40/20/40). This has already been described elsewhere (*18*).

RMN^{1}H ($CDCl_3$): 8.28 (t, 0.66 H, HC═N, $J = 6.36$ Hz), 8.10 (t, 0.33 H, HC═N, $J = 4.56$ Hz), 7.37 (m, 5H, C_6H_5), 3.93 (d, 0.66H, CH_2C═N), 3.74 (d, 1.32H, CH_2C═N).

RMN^{13}C ($CDCl_3$): 175 (C═NCl), 173 (C═NCl), 133−127 (aromatic C), 41 (CH_2), 40 (CH_2).

The chloroaldimine was previously thought to be unstable in all the organic solvents. Indeed it was entirely decayed in only aldehyde and nitrile in acetonitrile, but it remained stable in hexane. This allowed us afterward to relate the peak area of chloroaldimine, observed for the hexane-stable fraction, and the concentrations of aldehyde and nitrile obtained for the acetonitrile fraction injected after 2 h: chloroaldimine concentrations were deduced from mass balance. A calibration curve was obtained (area (UA) $= 5.63 \times 10^6$ C (10^{-3} mol·L^{-1})) in the range 0.005 to 0.1 mol·L^{-1} with a correlation coefficient of 0.9976 for an injection volume of 250 μL. For the lower concentrations, one of the previous solutions of known concentration was used as a standard. It was diluted to determine the analytical detection limit of the product, which was found to be 5×10^{-5} mol·L^{-1} by this method. This quantification method gave us the same proportions of chloroaldimine formed during the chlorination reactions as those of Conyers and Scully (*18*) based on the use of radioactive chlorine. This enforced the validity of our titration method. Previously it was believed that *N*-chloraldimines were precursors of nitriles (*9*). Our results suggest, in agreement with Conyers and Scully (*18*), that the nitrile and the chloraldimine are formed by competitive pathways. Indeed, nitrile was always and only present in water with chloroaldimine but did not increase when chloroaldimine decreased.

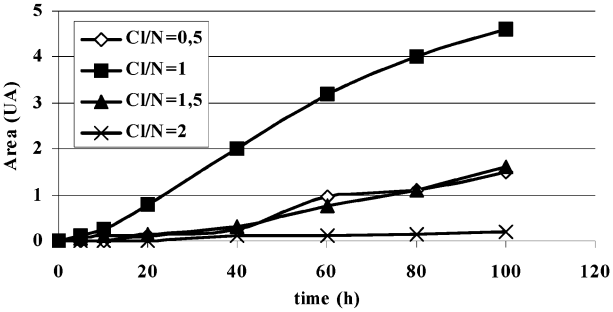

FIGURE 6. Evolution over time of peak with retention time of 39 min thought to be imine or derivative for different levels of chlorination of a model solution of phenylalanine (1 mM) at 25 °C.

The compound with a reaction time of 39 min appeared when *N*-chlorophenylacetaldimine was treated by a large excess of thiosulfate, but the reaction was not instantaneous. This was observed also for chlorination levels close to 1 as well as the *N*-chlorophenylalanine but appeared later (Figure 6). It revealed a lot in UV analysis that is consistent with the presence of a double bond. At first sight it was thus believed to be the imine. This hypothesis was supported by the fact that the action of ammonia on phenylacetaldehyde leads to

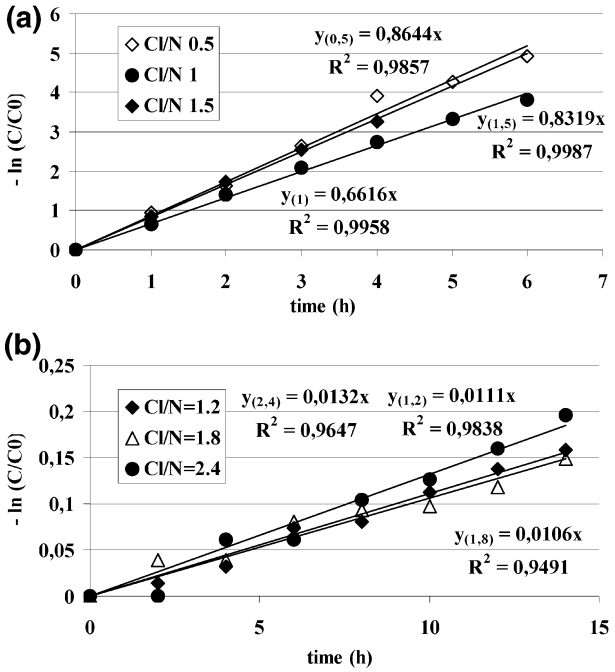

FIGURE 7. (a) *N*-chlorophenylalanine kinetics of decomposition at 22 °C for various chlorination rates. (b) *N*-chlorophenylacetaldimine kinetics of decomposition at 22 °C for various chlorination rates.

the formation of a compound with the same reaction time. Indeed, it is widely known that the action of ammonium chloride on aldehyde classically leads to the formation of an imine. In this way a reaction of ammonium chloride on phenylacetaldehyde was carried out. A regular analysis of the reaction mixture showed a decrease in the quantity of aldehyde while the resulting product had a retention time of 39 min. This partially confirmed our assumption, nevertheless we came up against an impossibility: as the reaction is a mole per mole one, the amount of disappeared aldehyde should be equal to the amount of alleged imine present. However, the detector response attributed to imine was unsuitable. We tried to use it to quantify the imine in the chlorination reactions but the quantity of alleged imine obtained was highly overestimated with regard to the amounts of introduced phenylalanine and identified and quantified byproducts. For these reasons, the 39-min compound may be now assumed to be a polymer of imine. Further studies are needed to address these issues. This compound concentration seemed to reach a plateau for all the chlorination rates. This partially questions the scheme of pathway proposed (*18*) where the degradation of imine in aldehyde is announced as quantitative. These results suggest that there may be an equilibrium. However, by considering the total amount of quantifiable products obtained, the quantity which could be attributed to the imine or derivative cannot be very large. For Cl/N ratio of 1 the imine reached is maximum area while the total of unreacted phenylalanine, aldehyde, and nitrile was more than 95% of the initial phenylalanine. Moreover, this compound is not odorous, so we did not follow our investigations on it.

Odorous Byproducts. Previously, the odor complaints were attributed to the organic monochloramines, but they are not formed in large proportions considering the high chlorination ratios applied during water treatment. In addition their odors do not persist enough to affect the consumer. Indeed, decays of chlorinated derivatives were studied. The decomposition of the two compounds followed first-order kinetics whatever the initial product concentration was (i.e., whatever the chlorination rate was). This is shown in Figure 7a and b. The average first-order coefficients were

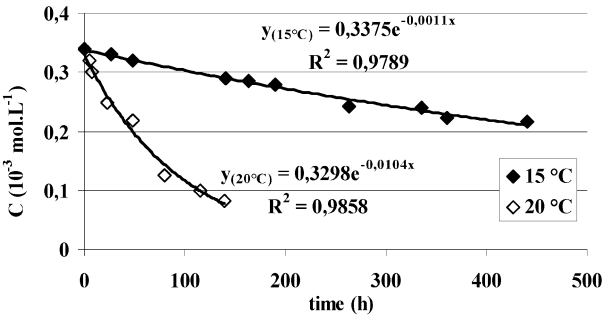

FIGURE 8. Decay rates of *N*-chlorophenylacetaldimine for 2 different temperatures.

3.2×10^{-6} s^{-1} for the chloroaldimine and 2.1×10^{-4} s^{-1} for the monochlorinated derivative. For the same temperature, the latter decayed 60 times quicker than the chloroaldimine. Consequently, it must be stressed that if the *N*-chlorophenylalanine is not stable enough to be involved in water odor problems, the *N*-chlorophenylacetaldimine has a sufficient lifetime to remain several days in the distribution network.

The odor detection thresholds determined with our olfaction test for phenylacetaldehyde, phenylacetonitrile, and *N*-chlorophenylacetaldimine were respectively 30, 1200, and 3 $\mu g \cdot L^{-1}$. It should be emphasized that not only the well-known aldehyde, but above all the chloroaldimine, for which no odor characteristic was available, exhibited really low odor detection thresholds in water. According to amino acid concentrations in drinking water process, these products could be involved in odor problems. In contrast, the nitrile cannot be implicated.

Moreover, Buttery and co-workers (*25*) announced an odor detection threshold for phenylacetaldehyde of 4 $\mu g \cdot L^{-1}$ which led us to suppose that with their protocol the chloroaldimine could be detected at even lower concentrations. Chloroaldimine decay for 2 temperatures (15 and 20 °C) were also performed (Figure 8). The decomposition kinetics were still first-order reactions. The half longer lifetimes observed at 15 and 20 °C were respectively about 500 and 50 h. These results highlight a very significant difference of stability for a variation in temperature of only 5 °C. No data are available to confirm our results, yet in winter chloroaldimine may remain in the distribution network for a long time. This study will now be extended to other amino acids, such as alanine, leucine, or valine. They are susceptible to be present in water at higher concentrations than phenylalanine, and as they have lower molecular weight, their chloroaldimines will probably be even more odorous than *N*-chlorophenylacetaldimine.

Acknowledgments

We are grateful to the Syndicat des Eaux d'Ile-de-France (SEDIF) for financially supporting this project.

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Received for review September 16, 2003. Revised manuscript received March 17, 2004. Accepted May 18, 2004.

ES035021I