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Reactions of phenylurea compounds with aqueous chlorine: Implications for herbicide transformation during drinking water disinfection

Sarinma Chusaksri[a], Somyote Sutthivaiyakit[b], David L. Sedlak[c,*], Pakawadee Sutthivaiyakit[a,**]

[a] Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University, Kasetsart, Bangkok 10900, Thailand
[b] Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Ramkhamhaeng University, Bangkok 10240, Thailand
[c] Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720, USA

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ABSTRACT

Phenylurea herbicides have been known to contaminate surface waters serving as potable supplies. To access the potential for transformation of these compounds during drinking water treatment, reactions of phenylurea compounds with aqueous chlorine at different pHs were investigated. The effect of substitution at the amino-N on the rate of transformation depends upon pH. Under acidic conditions, all of the phenylurea studied except 3,4-dichloro-3′-*N*-methylphenylurea (3,4-DCMPU) exhibited third-order kinetics, second order with respect to chlorine and first order with respect to phenylurea, while the reactions of 3,4-DCMPU were first order with respect to both chlorine and the organic compound. Under neutral and alkaline conditions, all compounds exhibited second-order kinetics that was first order with respect to chlorine and the organic compound. Apparent second-order rate constants at 25 °C and pH 7 were 0.76 ± 0.16, 0.52 ± 0.11, 0.39 ± 0.02, 0.27 ± 0.04 and $0.23 \pm 0.05\ M^{-1}\ s^{-1}$ for phenylurea, 3, 4-dichlorophenylurea, 3, 4-DCMPU, metoxuron and monuron, respectively. Studies of the chlorination products, monitored by LC/MS/MS, under different pH values indicated the reaction to take place at both N atoms and also at *ortho*- and *para*- positions of the phenylurea aromatic group. The main chlorinating species were found to be different in different pH ranges. Under conditions typically encountered in drinking water treatment systems, transformation of these compounds by chlorine will be incomplete.

1. Introduction

Phenylurea herbicides (Fig. 1) are widely used in agriculture for weed control of non-crop areas for pre-emergent treatment of fruit crops [1]. As a result of their resistance to biotransformation and low affinity for soil, some phenylurea compounds may be present in drinking water supplies. Moreover, due to their toxicity and possible carcinogenic properties, they have received special attention recently [2,3].

Chlorine, an oxidant that is widely used for drinking water disinfection, can transform a variety of organic compounds [4–8]. Previous investigators have studied the kinetics of chlorine reactions and product formation for phenylurea compounds [9–16]. Irrespective of the site of reaction, the reaction rate was found to vary with solution conditions. In particular, rates of transformation were reported to increase with decreasing pH in the presence of bromide ions [12,13]. Apparent second-order rate constants for chlorine reactions with diuron were insensitive to the presence of bromide whereas for isoproturon reactions in the presence of bromide were much faster than in its absence [13].

There are several moieties on phenylurea compounds that are susceptible to attack by chlorine. For example, the transformation for chlortoluron was proposed to involve chlorine substitution and hydroxylation of the aromatic ring [15]. For fenuron, reactions with chlorine resulted in the formation of N-chloro derivatives [16].

On the basis of previous results, it is apparent that the reactions of chlorine with phenylurea compounds are affected by locations of substituents and chlorine speciation. However, the reaction mechanism and products are still unclear. The objective of this study was to investigate the mechanism of chlorine reaction with phenylurea compounds and determine the role of substituents on the reactivity of the compounds and product formation.

2. Materials and methods

2.1. Materials

N-Phenylurea (97%) and metoxuron (99.5%) were obtained from Aldrich and Riedel-de Hähn, respectively. Monuron (99.0%), 3,4-dichloro-3′-*N*-methylphenylurea (3,4-DCMPU) (97.5%), and

* Corresponding author. Tel.: +1 5106430256; fax: +1 510642748.
** Corresponding author. Tel.: +66 25625555x2237; fax: +66 25625555x2207.
E-mail addresses: sedlak@ce.berkeley.edu (D.L. Sedlak), fscipws@ku.ac.th, plumeria1108@yahoo.com (P. Sutthivaiyakit).

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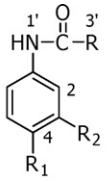


	R	R_1	R_2
Phenylurea (PU)	NH_2	H	H
3,4-dichlorophenylurea (3,4-DCPU)	NH_2	Cl	Cl
3,4-dichloro-3′-*N*-methylphenylurea (3,4-DCMPU)	$NHCH_3$	Cl	Cl
Monuron	$N(CH_3)_2$	Cl	H
Metoxuron	$N(CH_3)_2$	Cl	OCH_3

Fig. 1. Chemical structures of investigated phenylureas.

3,4-dichlorophenylurea (3,4-DCPU) (99.0%) were obtained from Dr. Ehrenstofer GmbH. 4-Chlorophenylurea (97.1%) and 3-hydroxyphenylurea were obtained from Chem Service, Inc. Sodium hypochlorite solution (NaOCl, 4–6% active chlorine) was purchased from Merck. High purity water was obtained from a Maxima water purification system (USF-Elga, High Wycombe, U. K.). Other chemicals were of analytical reagent grade.

Buffers used for various pH ranges included: a 10 mM mixture of sodium acetate and acetic acid for pH 5, a 10 mM mixture of sodium phosphate monobasic and potassium phosphate dibasic for pH 6, 7 and 8, and a mixture of disodium tetraborate and boric acid for pH 9. Solution pH values were further adjusted by addition of 1 N sulfuric acid and 1 N sodium hydroxide. The ionic strength was maintained at 100 mM using sodium nitrate.

Stock solutions of phenylurea compounds were prepared in water at concentrations ranging from 0.3 to 8.0 mM. The solutions were diluted from the concentrated stock to obtain an initial concentration of 10 μM in the pH-buffered solutions.

The stock solutions of NaOCl (~5 mM) was prepared daily by diluting a commercial solution of sodium hypochlorite into the buffered solution after standardization by iodometry [17]. To initiate reactions, the stock chlorine solutions were diluted to obtain a concentration between 150 and 300 μM. The DPD-FAS titrimetry method [17] was used to determine the initial chlorine concentration. New stock solutions of free chlorine and phenylurea compounds were prepared daily. All experiments were performed at 25 ± 2 °C. Measurements of pH were carried out with a Sartaurius pH meter, model PB 11 using a glass combination electrode.

3′-*N*-Chlorophenylurea and 2-chlorophenylurea were synthesized using the modified method of Chatway and Chaney [18].

2.2. Kinetic experiments

Chlorination experiments were carried out under conditions of excess chlorine to yield pseudo-first order kinetics (≥30:1 ratio of chlorine to phenylureas on a molar basis). Experiments were performed in the presence of 100 mM sodium nitrate and 10 mM buffer in 1 mL amber glass vials with PTFE septa. Experiments were initiated by adding 500 μL aliquots containing (300–600 μM) chlorine, 20 mM buffer and 200 mM sodium nitrate to 500 μL of a 10 μM solution of the phenylurea compounds in separate vials. Vials were immediately capped, shaken and incubated for various time periods. At fixed time interval, one vial was taken out from the incubator and analyzed immediately by HPLC. To verify the stability of chlorine, separate experiments were run in parallel before and after each kinetic experiment chlorine was measured using a 200 mL volumetric flask as a reactor and DPD-FAS titrimetry for chorine analysis. Control samples containing only the phenylurea compound (5 μM) were also used to ensure that no hydrolysis occurred during the experiments.

HPLC with a diode array detector (An 1100 LC binary pump, Agilent Technology, Waldbronn, Germany) was used to monitor loss of parent compounds and formation of phenylurea chlorination products. Phenylurea compounds and their transformation products were separated using a Synergi MAX-RP C-12 column (250 mm × 4.6 mm, 4 μm) and detected with a UV detector. *N*-Phenylurea, metoxuron, monuron, 3, 4-DCMPU, and 3,4-DCPU were monitored at 237, 244, 246, 250, and 248 nm, respectively. Gradient elution was carried out with methanol and 1 mM ammonium formate, which was acidified to pH 3.5 with 0.01% formic acid, the program used was as follows: from 43.5% methanol to 55% in 5 min, to 85% in 15 min, to 100% in 5 min and held for a further 5 min at a flow rate of 0.6 mL/min for *N*-phenylurea, metoxuron, monuron. The gradient program used for 3,4-DCMPU, and 3,4-DCPU was as follows: from 45% methanol to 80% in 20 min, to 90% in 1 min, to 100% in 5 min at a flow rate of 0.7 mL/min. Concentrations of phenylureas were determined by comparing peak areas with an external standard calibration curve.

2.3. Identification of chlorination products of N-phenylurea using LC/ESI-MS/MS

The products of the N-phenylurea/hypochlorite reaction at pH values of 5, 7 and 9 were identified from a reaction of a 100 mL solution containing 5 μM of each phenylurea buffered at pHs 5, 7, and 9, after addition of 200 μM chlorine. Samples were collected after one hour and immediately extracted twice with 20 mL of ethyl acetate. The combined extracts were evaporated to dryness and the residue was redissolved in 500 μL of a water:methanol (1:1) mixture and injected into a LC/ESI-MS/MS system (Applied Biosystem API 2000 triple quadrupole mass spectrometer, Thornhill, Toronto, Canada). Identification of reaction products was carried out by interpretation of fragment ions and by comparison with authentic standards. The optimized parameters for MS/MS transitions of *N*-phenylurea and its products are shown in Tables S1–S3.

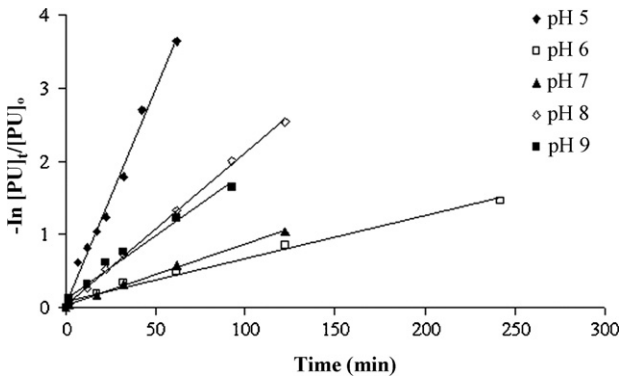


Fig. 2. Pseudo-first-order kinetic plots of the chlorination of phenylurea in the pH range of 5–9 and at 25 °C, [PU] = 5 μM, $[Cl(I)]_{TOTAL}$ = 200 μM. r^2 values range from 0.98 to 0.99.

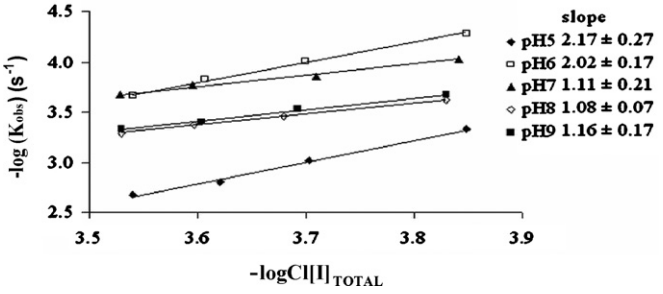


Fig. 3. Reaction order of free chlorine with PU between pHs 5 and 9.

3. Results and discussion

3.1. Reaction orders and apparent rate constants for N-phenylurea

With a large excess of free chlorine (150–300 μM) relative to *N*-phenylurea (5 μM) in the pH range of 5 to 9, the reaction exhibited pseudo-first order kinetic as shown by the linear plots of $\ln([PU]_t/[PU]_o)$ versus time (Fig. 2). From these plots, pseudo-first order rate constants (k_{obs}) values were obtained at each pH and free chlorine concentration.

For control samples incubated in the absence of chlorine, no change in concentration was observed indicating that the acid- and base-catalyzed hydrolysis transformation of phenylurea was negligible over the pH range studied (pHs 5–9) and at 25 ± 2 °C. The hydrolysis of urea compounds was, however, observed under vigorous conditions, i.e. higher concentration of acid and base and at high temperature [19–21].

The reaction order with respect to chlorine was obtained from the relationship between the initial total chlorine concentration and k_{obs} at each pH value (Fig. 3, Table 1). The disappearance of phenylurea compounds under acidic conditions was second order with respect to chlorine while the kinetics were first order kinetics with respect to chlorine and the phenylurea at pH values 7, 8 and 9 [22].

Table 1
Apparent rate constants for the chlorination of *N*-phenylurea at different pH values.

pH	Apparent rate constant	r^2	Unit
5	$(2.67 \pm 0.44) \times 10^4$	0.99	$M^{-2}\,s^{-1}$
6	$(2.64 \pm 0.29) \times 10^3$	0.99	$M^{-2}\,s^{-1}$
7	0.76 ± 0.16	0.98	$M^{-1}\,s^{-1}$
8	1.83 ± 0.16	0.99	$M^{-1}\,s^{-1}$
9	1.78 ± 0.26	0.99	$M^{-1}\,s^{-1}$

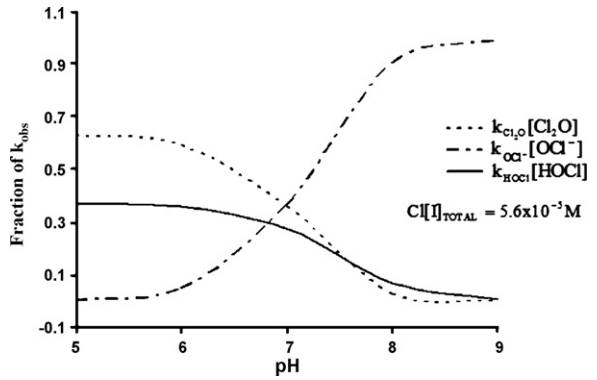


Fig. 4. Fraction of the observed rate constant (k_{obs}) contributed by reaction of the phenylurea compound with Cl_2O, OCl^-, and HOCl as a function of pH at $[Cl(I)]_{TOTAL} = 5.6 \times 10^{-5}$ M.

The effect of pH on the apparent reaction order and rate constant can be explained by the pH-dependent speciation of chlorine as indicated below:

$$HOCl \rightarrow ClO^- + H^+ \quad K_{a1} \tag{1}$$

$$2HOCl \rightarrow Cl_2O + H_2O \quad K_2 \tag{2}$$

$$Cl_2O + PU \rightarrow \text{products} \quad k_1 \tag{3}$$

$$OCl^- + PU \rightarrow \text{products} \quad k_2 \tag{4}$$

$$HOCl + PU \rightarrow \text{products} \quad k_3 \tag{5}$$

The values for K_{a1} and K_2 are 2.9×10^{-8} and 8.74×10^{-3}, respectively [6].

From this set of reactions it is possible to predict the rate of phenylurea transformation over the entire pH range [22,23], as follows:

$$-\frac{d[PU]}{dt} = (k_1[Cl_2O] + k_2[OCl^-] + k_3[HOCl])[PU] \tag{6}$$

and

$$Cl[I]_{TOTAL} = [HOCl] + [OCl^-] + 2[Cl_2O] \tag{7}$$

Taking into account of the speciation of free chlorine (reactions (1) and (2)), Eq. (6) is transformed into Eq. (8)

$$-\frac{d[PU]}{dt} = \left(k_1K_2[HOCl]^2 + k_2K_{a1}\frac{[HOCl]}{[H^+]} + k_3[HOCl]\right)[PU] \tag{8}$$

Finally, k_{obs} at each pH and FAC is given by Eq. (9):

$$k_{obs} = k_1K_2[HOCl]^2 + k_2K_{a1}\frac{[HOCl]}{[H^+]} + k_3[HOCl] \tag{9}$$

Nonlinear regression analysis using Microsoft Excel Solver was used for the k_{obs} data at each pH value to estimate k_1, k_2, and k_3. These results were used to calculate the contributions of Cl_2O, OCl^-, and HOCl to phenylurea transformation as a function of pH at total chlorine concentration of 5.6×10^{-5} M (Fig. 4).

The chlorine species responsible for phenylurea transformation depends upon solution pH. Under acidic conditions, the minor species Cl_2O is responsible for over half of the transformation reactions. The high reactivity of Cl_2O is consistent with findings reported previously [22–24]. Under neutral and basic conditions, Cl_2O becomes less important and OCl^- becomes the predominant reactive chlorine species responsible for phenylurea transformation. Hypochlorite (OCl^-) has been previously observed to react with cyclopeptides to yield chloroamides [25].

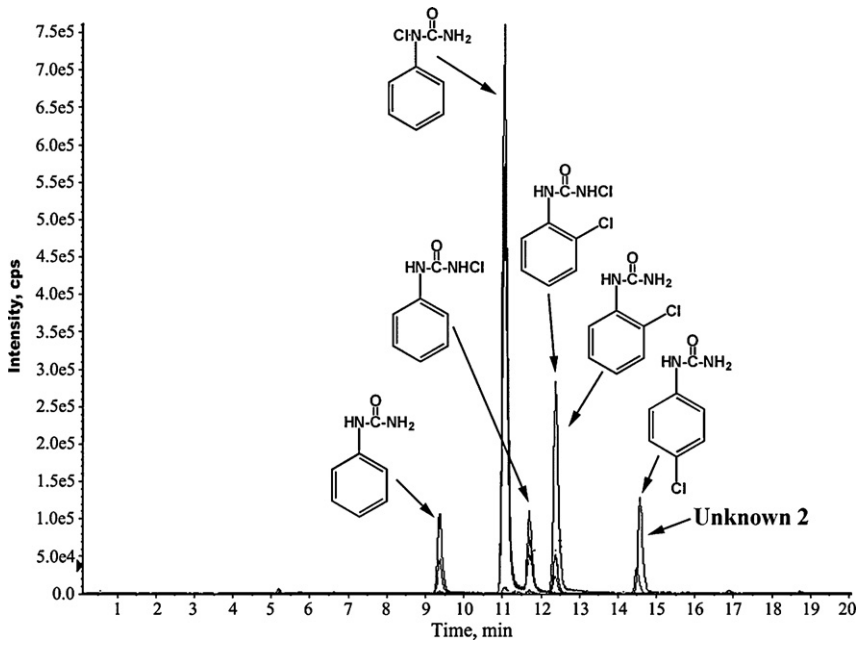


Fig. 5. MRM chromatogram obtained from LC-ESI (PI)–MS/MS analysis of the extract obtained from chlorination of *N*-phenylurea after 1 h at pH 7.

3.2. Identification of products from the chlorination of N-phenylurea

Identification of products from the chlorine reactions was based on the interpretation of fragment ions. In cases where authentic standards were available, retention times and MS spectra were also used for identification (Table S4 and Figures S1–S10). The LC/ESI-MS chromatograms were first acquired in the full scan mode (60–400 amu). The protonated and deprotonated molecular ions were then confirmed by a product ion scan. Additionally, one or two of the most abundant daughter ions were chosen for multireaction monitoring mode (MRM) to acquire the MRM chromatograms of the extract of product formation as illustrated in Figs. 5 and 6 and Figures S11–14.

Under acidic conditions, seven main products, (i.e. 3′-*N*-chlorophenylurea, 2-chlorophenylurea, 1′-*N*-chlorophenylurea, 2,3′-*N*-dichlorophenylurea, 4-chlorophenylurea, 4,3′-*N*-dichlorophenylurea, and 2,4-dichlorophenylurea) and an unidentified peak at a retention time of 14.54 min were detected (Figures S11, S12). Under neutral conditions, apart from those seven compounds observed in acid solution, an unidentified compound peak at a retention time of 5.20 min (*m*/*z* 151) and 1′-*N*-chlorophenylurea were also observed (Figs. 5 and 6). In basic solutions, products were identical to those detected in the neutral

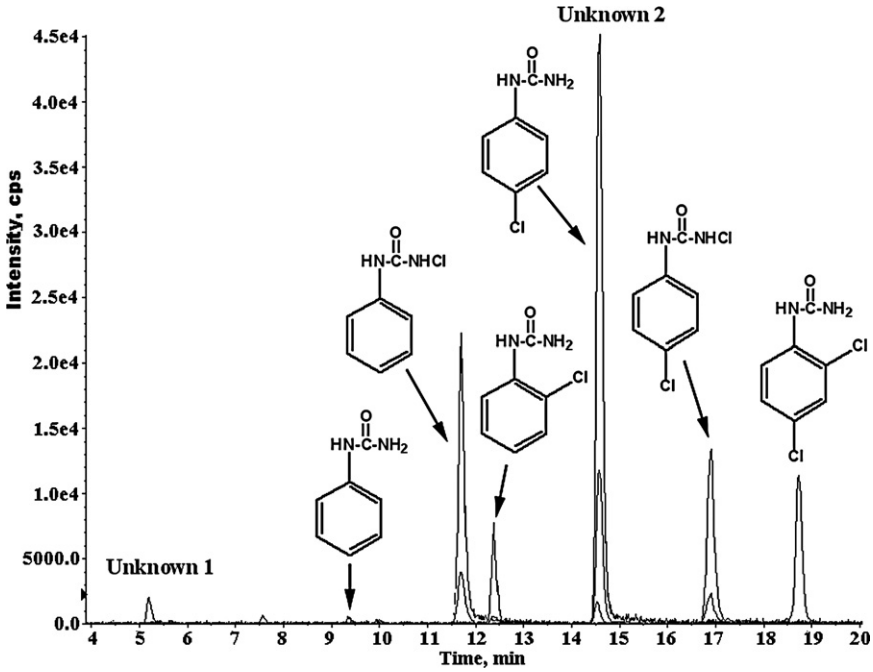


Fig. 6. MRM chromatogram obtained from LC-ESI (NI)–MS/MS analysis of the extract obtained from chlorination obtained from *N*-phenylurea after 1 h at pH 7.

Table 2
Apparent rate constants for the chlorination of *N*-phenylurea and its derivatives at different pH values.

Compounds	k_{app}		
	pH 5	pH 7	pH 9
N-phenylurea	26,700 ± 4450 M^{-2} s^{-1}	0.76 ± 0.16 M^{-1} s^{-1}	1.78 ± 0.26 $M^{-1}s^{-1}$
3,4-DCPU	17,000 ± 246 M^{-2} s^{-1}	0.52 ± 0.11 M^{-1} s^{-1}	1.84 ± 0.42 M^{-1} s^{-1}
3,4-DCMPU	19.70 ± 3.96 M^{-1} s^{-1}	0.39 ± 0.02 M^{-1} s^{-1}	0.53 ± 0.14 M^{-1} s^{-1}
Metoxuron	2.07 ± 0.30 M^{-2} s^{-1}	0.27 ± 0.04 M^{-1} s^{-1}	0.88 ± 0.15 M^{-1} s^{-1}
Monuron	0.33 ± 0.05 M^{-2} s^{-1}	0.23 ± 0.05 M^{-1} s^{-1}	0.72 ± 0.14 M^{-1} s^{-1}

solution but with the absence of an unidentified peak at 14.54 min (Figures S13, S14).

3.3. Transformation kinetics for other phenylurea compound

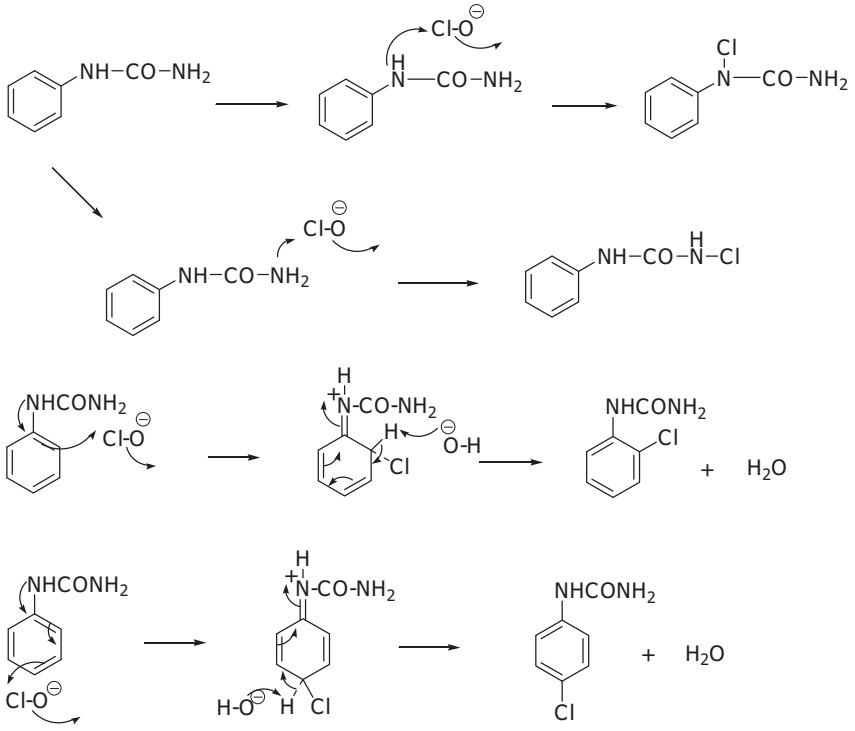
On the basis of previous research and the data collected as part of this study, we propose a reaction scheme for the phenylureas. Under neutral conditions, the initial step in the reaction involves the attack of hypochlorite at both N atoms giving the N chlorinated products. Aromatic electrophilic substitutions by a chlorine atom at the *ortho*- and *para* positions were also detected (Scheme 1). This step is supported by the observed second-order kinetics (i.e. first-order with respect to both phenylurea and chlorine) and the detection of 1′-N-chlorophenylurea, 3′-N-chlorophenylurea, 2-chlorophenylurea and 4-chlorophenylurea as products.

Chlorination of phenylurea derivatives was studied at pH 5, 7 and 9 (Table 2). In all cases except for 3,4-DCMPU, second order reaction kinetics with respect to chlorine were observed under acidic conditions, suggesting that Cl_2O or a related species was involved. However, for 3,4-DCMPU, which exhibited first order kinetics with respect to chlorine, HOCl was suggested as a predominant species under acidic condition as observed for diuron and isoproturon [13].

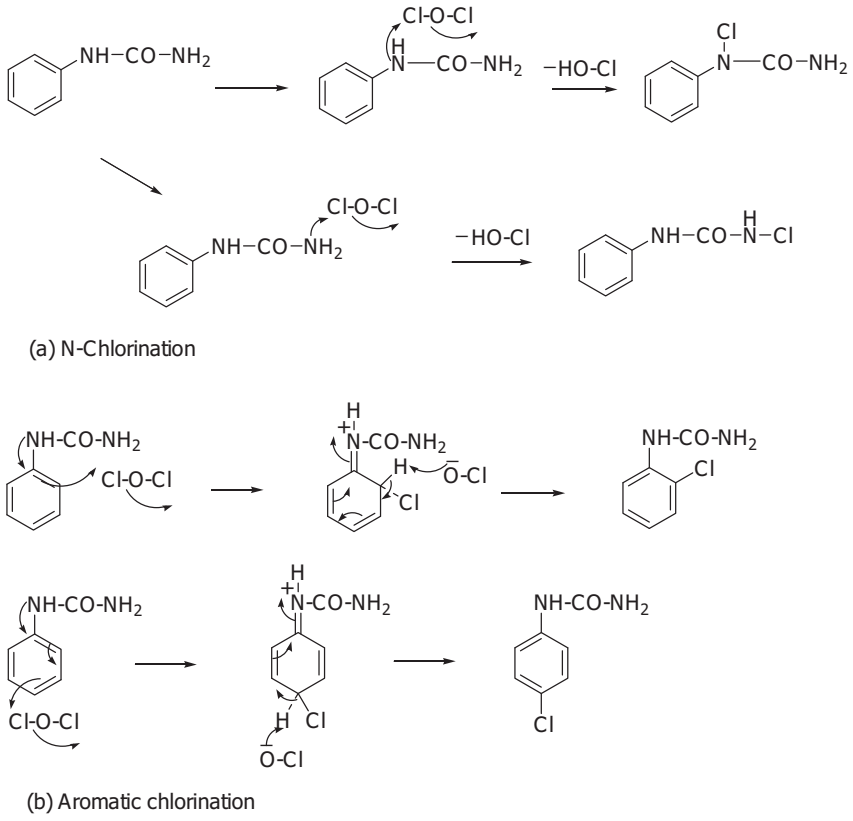
Substitution of the hydrogen atom at 3′-N with the methyl group decreased the reactivity of the compound under acidic and neutral pH conditions (i.e. compare apparent rate constants of 3,4-DCPU and 3,4-DCMPU). Substitution of hydrogen atoms with two electron withdrawing substituents on the aromatic ring (i.e. 3,4-DCPU) decreased the reactivity of the compound under acidic conditions indicating that the nucleophilicity of the aromatic ring was important. A similar phenomenon was also observed with metoxuron which has an electron donating OMe group and exhibited faster kinetic than that of monuron at pH 5.

Under acidic conditions, products of chlorination at the 2- and 4-positions were less abundant. This result may be partly due to the formation of $ArNH(C{=}O^{+}H)NH_2$ species, an intermediate that has an aromatic ring which is less nucleophilic [26,27]. As a result, the subsequent electrophilic aromatic chlorination reactions were slower (Scheme 2). Replacement of a hydrogen atom at 3′-N with a methyl group as in 3,4-DCMPU slowed down the reaction rate indicating less availability of replaceable hydrogen atom and steric bulk at 3′-N atom to play a role in this conversion.

The rate of transformation of phenylurea under basic conditions (pH 9) was found to be faster than under neutral condition (pH 7), despite the fact that the proposed form of chlorine was OCl^{-} in both cases. This result implies that under basic conditions the reaction involves the removal of the acidic proton on the nitrogen adjacent to the conjugated ring by base, while under neutral condition the 1′-NH and 3′-NH_2 groups acted as the nucleophile (Scheme 3). At pH 9, reaction of phenylurea when compare to that of 3,4-DCPU was found to be slower, this result also supported the intervention of conjugated base as nucleophile, particularly at 1′-*N* atom, since



Scheme 1. Proposed reaction pathways under neutral condition.



Scheme 2. Proposed reaction pathways under acidic condition. (a) N-chlorination and (b) aromatic chlorination.

the presence of electron-withdrawing chloro group giving rise to the more acidic 1′-N*H* group which led to fast N-chlorination and gave rise to a higher reaction rate.

Under basic conditions, the formation of the 2-chlorinated product was greater than that of the 4-chloro product. This finding is consistent with a reaction pathway in which the intramolecular rearrangement of 1′-*N*-chlorophenylurea to 2-chloro product occurs in parallel with normal aromatic electrophilic chlorination as in Scheme 3 (c) [18].

3.4. Kinetics of phenylurea transformation during chlorination

To predict the apparent rate constant at other pH values (Table 3), Eq. (9) was also used for 3,4-DCPU, metoxuron and monuron. As the chlorination kinetics of 3,4-DCMPU exhibits first order in both chlorine and 3,4-DCMPU, Eqs. (10) and (11) were used for 3,4-DCMPU as follows

$$k_{obs} = k_2 K_{a1} \frac{[HOCl]}{[H^+]} + k_3[HOCl] + k_4[H^+][HOCl] \quad (10)$$

$$[Cl(I)]_{TOTAL} = [HOCl] + [OCl^-] \quad (11)$$

In Eq. (10), k_4 represents the contribution to the observed reaction rate involving acid catalysis according to Eq. (12) below:

$$HOCl + H^+ + PU \rightarrow \text{products} \quad k_4 \quad (12)$$

The final term in Eq. (10) was needed due to the possible participation of the strong electrophile of H_2OCl^+ [23].

Table 3 shows rate constants for the chlorination of phenylurea and its derivatives obtained by fitting the data in Tables 1 and 2.

Fig. 7 depicts the plot of half-life values as a function of pH for *N*-phenylurea and its derivative at $[Cl(I)]_{TOTAL} = 5.6 \times 10^{-5}$ M. Substitution at the ring and at the amino functional group affects the rates of reaction at each site. In particular, the presence of replaceable hydrogen atom at the amino N greatly enhances the rate of chlorination of these pesticides. Under these conditions, the half-lives of phenylurea herbicide will range between 100 and 1000 min. For contact times typical of water treatment plants (e.g., contact times around 1 h) negligible transformation of the phenylureas is expected. However, transformation of phenylureas to the products described previously could be significant in water distribution system where chlorine contact times up to 10,000 min are encountered. Under such conditions, phenylureas will be removed and the main products observed here, namely 1′-N-chlorophenylurea, 3′-N-chlorophenylurea, 2-chlorophenylurea and 4-chlorophenylurea compounds will be present.

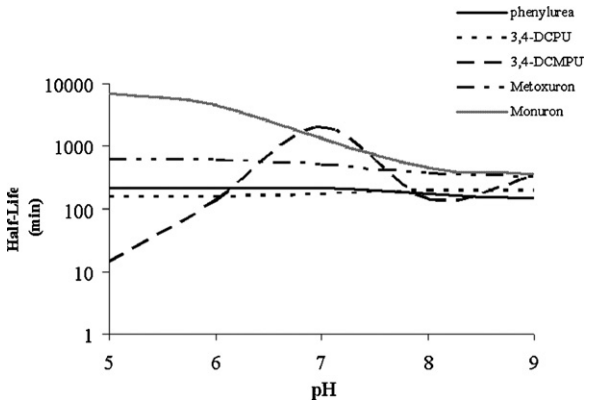
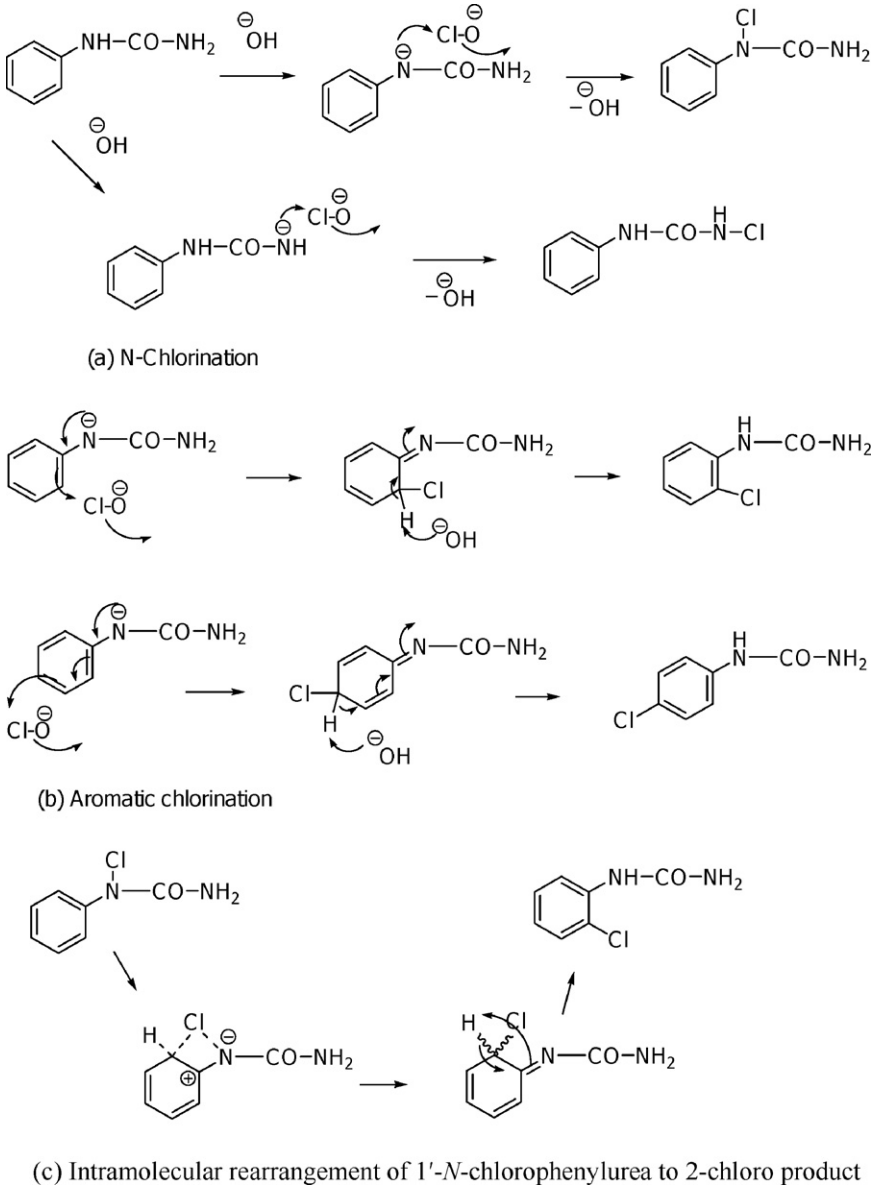


Fig. 7. Half life values for chlorination of phenylurea and its derivatives at different pHs. $[Cl(I)]_{TOTAL} = 5.6 \times 10^{-5}$ M was assumed to be constant.



Scheme 3. Proposed reaction pathways under basic condition. (a) N-chlorination, (b) aromatic chlorination and (c) intramolecular rearrangement of 1′-*N*-chlorophenylurea to 2-chloro product.

Table 3
Rate constants for the chlorination reaction of phenylurea and its derivatives.

Compounds	k_1 ($M^{-2}\,s^{-1}$)	k_2 ($M^{-1}\,s^{-1}$)	k_3 ($M^{-1}\,s^{-1}$)	k_4 ($M^{-2}\,s^{-1}$)
N-Phenylurea	1.36×10^6 (4.84×10^{-6})	1.49 (0.15)	0.36 (0.54)	–
3,4-DCPU	1.00×10^6 (6.17×10^{-6})	1.07 (0.29)	0.90 (0.61)	–
Metoxuron	8.20×10^3 (7.41×10^{-7})	0.67 (0.05)	0.34 (0.069)	–
Monuron	2.55×10^4 (4.16×10^{-7})	0.62 (0.02)	0.02 (0.004)	–
3,4-DCMPU	–	0.63 (0.08)	0.07 (0.39)	1.46×10^6 (9.35×10^{-6})

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.01.063.

References

[1] M.A. Kamrin, Pesticide Profiles: Toxicity, Environmental Impact, and Fate, Lewis Publishers, New York, 1997.

[2] H. Měšt, ánková, G. Mailhot, J.F. Pilichowski, J. Krýsa, J. Jirkovský, M. Bolte, Mineralisation of monuron photoinduced by Fe(III) in aqueous solution, Chemosphere 57 (2004) 1307–1315.
[3] A. Kotrikla, G. Gatidou, T.D. Lekkas, Monitoring of triazine and phenylurea herbicides in the surface waters of Greece, J. Environ. Sci. Health B 41 (2006) 135–144.
[4] B. Xu, N.-Y Gao, H. Cheng, C.-Y. Hu, S.-J. Xia, X.-F. Sun, X. Wang, S. Yang, Ametryn degradation by aqueous chlorine: kinetics and reaction influences, J. Hazard. Mater. 169 (2009) 586–592.
[5] P. Wang, Y.-L. He, C.-H. Huang, Reactions of tetracycline antibiotics with chlorine dioxide and free chlorine, Water Res. 45 (2011) 1838–1846.
[6] M. Deborde, U.V. Gunten, Reactions of chlorine with inorganic and organic compounds during water treatment—kinetics and mechanisms. A critical review, Water Res. 42 (2008) 13–51.
[7] B. Panyapinyopol, T.F. Marhaba, V. Kanokkantapong, P. Pavasant, Characterization of precursors to triholomethanes formation in Bangkok source water, J. Hazard. Mater. B 120 (2005) 229–236.
[8] J.L. Acero, F. Javier Beńtez, F.J. Real, M. González, Chlorination of organophosphorus pesticides in natural waters, J. Hazard. Mater. 153 (2008) 320–328.
[9] A. Lopez, G. Mascolo, R. Földényi, R. Passino, Disinfection by-products formation during hypochlorination of isoproturon contamination groundwater, Water Sci. Technol. 34 (1996) 351–358.
[10] A. Lopez, G. Mascolo, G. Tiravanti, R. Passino, Degradation of herbicides (ametryn and isoproturon) during water disinfection by means of two oxidants (hypochlorite and chlorine dioxide), Water Sci. Technol. 35 (1997) 129–136.
[11] A. Lopez, G. Mascolo, R. Ciannarella, G. Tiravanti, Formation of volatile halogenated by-products during chlorination of isoproturon aqueous solutions, Chemosphere 45 (2001) 269–274.
[12] G. Mascolo, A. Lopez, H. James, M. Fielding, By-products formation during degradation of isoproturon in aqueous solution. II: chlorination, Water Res. 35 (2001) 1705–1713.
[13] J.L. Acero, F.J. Real, F.J. Benitez, M. Gonzalez, Kinetics of reactions between chlorine or bromine and the herbicides diuron and isoproturon, J. Chem. Technol. Biotechnol. 82 (2007) 214–222.
[14] C.G. Zambonin, I. Losito, F. Palmisano, Liquid chromatography/electrospray ionization sequential mass spectrometric identification of the main chlortoluron by-products during water disinfection using chlorine, Rapid Commun. Mass Spectrom. 14 (2000) 824–828.
[15] I. Losito, C.G. Zambonin, F. Palmisano, Degradation of chlortoluron in water disinfection processes: a kinetic study, J. Environ. Monit. 2 (2000) 582–586.
[16] L.V. Rak, P.N. Taran, M.A. Shevchenko, Interaction of available chlorine with fenuron in dilute aqueous solutions, Khim. I Tekhnologiya Vody. 3 (1981) 224–226.
[17] Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, American Water Works Association, Water Environment Control Federation, Washington, DC, 2005.
[18] F.D. Chattaway, N.K. Chaney, Action of chlorine on phenylcarbamide, J. Chem. Soc. Trans. 97 (1910) 292–299.
[19] J.C. Giffney, C.J. O'Connor, Hydrolysis of phenylureas. Part II. Hydrolysis in acid and aqueous solution, J. Chem. Soc. Perkin Trans. 2 (1976) 362–368.
[20] R. Laudien, R. Mitzner, Phenylureas. Part 1. Mechanism of the basic hydrolysis of phenylureas, J. Chem. Soc. Perkin Trans. 2 (2001) 2226–2229.
[21] R. Laudien, R. Mitzner, Phenylureas. Part 2. Mechanism of the acid hydrolysis of phenylureas, J. Chem. Soc. Perkin Trans. 2 (2001) 2230–2232.
[22] J.D. Sivey, C.E. McCullough, A.L. Roberts, Chlorine monoxide (Cl_2O) and molecular chlorine (Cl_2) as active chlorinating agents in reaction of dimethamid with aqueous free chlorine, Environ. Sci. Technol. 44 (2010) 3357–3362.
[23] C.G. Swain, D.R. Crist, Mechanism of chlorination by hypochlorous acid. The last of chlorinium ion, Cl^{+1}, J. Am. Chem. Soc. 94 (1972) 3195–3200.
[24] E.A. Voudrias, M. Reinhard, Reactivities of hypochlorous and hypobromous acid, chlorine monoxide, hypobromous acidium ion. Chlorine, bromine, and bromine chloride in elctrophilic aromatic substitution reactions with *p*-xylene in water, Environ. Sci. Technol. 22 (1988) 1049–1056.
[25] W.A. Prütz, Consecutive halogen transfer between various functional groups induced by reaction of hypohalous acids: NADH oxidation by halogenated amide groups, Arch. Biochem. Biophys. 371 (1999) 107–114.
[26] P. Sykes, A Guidebook to Mechanism in Organic Chemistry, forth ed., Longman, Bristol, 1975.
[27] M.B. Smith, J. March, March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, sixth ed., Wiley-Interscience, New Jersey, 2007.