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Kinetics of the chemical degradation of diuron

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Abstract

The influence of pH and buffer concentration on the chemical degradation of diuron in water has been analysed over a wide temperature range. The process irreversibly gives 3,4-dichloroaniline as the only product containing the phenyl ring. H⁺, OH⁻ and phosphate buffer are efficient catalysts of the reaction. The rate constant first increases rapidly at low buffer concentrations and then gradually levels off at higher ones. At 40 °C and high phosphate concentration (>0.01 M), or in the extreme pH regions, the half-life is approximately 4 months and the activation energy is 127 ± 2 kJ mol⁻¹. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

This paper presents the results of a study regarding the spontaneous chemical degradation in aqueous solution of diuron (CAS 330-54-1), N'-(3,4-dichlorophenyl)-N,N-dimethylurea (Fig. 1), a neutral herbicide used as soil sterilant (Tomlin, 1997).

Our purpose was to acquire information about the kinetics of the spontaneous chemical degradation of diuron that can be useful in estimating its half-life in the environment.

Since the commercialisation of diuron, numerous studies have investigated its microbial degradation (Esposito et al., 1998). The main metabolites are the monoand the di-demethylated derivatives at the terminal nitrogen atom (Attaway et al., 1982; Ellis and Camper, 1982; Gustafson, 1989). Recent studies have evidenced that these metabolites have higher toxic effects than parent diuron (Tixier et al., 2000). 3,4-dichloroaniline has been identified as a minor degradation product of diuron. Berger (1999) has reported the half-lives of some phenylurea herbicides in native and sterile soil.

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However, despite the interest in this herbicide, apart from qualitative data on its hydrolysis at elevated temperature and in acid and basic medium (Tomlin, 1997), there is no detailed description of the exogenous parameters affecting its abiotic degradation. In this study, we have investigated the kinetics in aqueous homogeneous phase.

2. Materials and methods

2.1. Chemicals

Diuron and its degradation products, N'-(3,4-dichlorophenyl)-*N*-methylurea, N'-(3,4-dichlorophenyl)urea and 3,4-dichloroaniline, were supplied by Dr. Ehrenstorfer GmbH. 3,4-Dichlorophenyl isocyanate was supplied by Fluka. All the other chemicals were from Carlo Erba.

2.2. HPLC analyses

HPLC analyses were performed on a chromatographic Waters system, consisting of a 515 HPLC pump and a 2487 dual λ absorbance detector, equipped with a C₁₈ reversed-phase column (3.9 × 150 mm). Diuron and/

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Fig. 1. Diuron.

or its degradation product were eluted by a linear gradient 35–42% of acetonitrile in water in 15 min, flow rate 1 ml/min, $\lambda = 248$ nm.

2.3. Kinetic measurements

Aqueous solutions of diuron, 30 mg/l, at the desired pH, phosphate buffer concentrations and fractions of the buffer in the free base form (α) were stored in a thermostated bath (30, 40, 50, 60 and 70 ± 0.1 °C) in the dark: total concentration of phosphate buffer = 0.05, 0.10, 0.15 and 0.20 M, α = 0.2, 0.4, 0.6 and 0.8. Kinetic runs at 70 °C were also made in non-buffered solutions, adjusting the pH with dilute solution of KOH or NaOH, pH range 1–13. In these last experiments, the pH values were periodically checked, and, if required (at neutral pH), adjusted with a few drops of acid or base. In all samples, a constant ionic strength of 1 M was maintained by the addition of KCl.

At pre-selected times the reacting mixtures were analysed by HPLC. The rate constants were calculated by least-squares analysis, assuming the rate of the reaction to be first-order in [diuron]. The fitting of the experimental data was satisfactory for all the samples. The values of rate constants, obtained from different runs carried out under the same experimental conditions, were reproducible to within 7%, except in kinetic runs carried out at neutral pH without buffer where the lower value of the reaction rate ($t_{1/2}$ being of the order a few months) resulted in a lower reproducibility.

The limiting maximum values of the rate constant obtained at high buffer concentrations were computed by least-squares fits of the *observed rate constant* (k_{obs}) -*total buffer concentration* data to the equation

$$k_{\text{obs}} = k_0 + k_{\text{Max}} [\text{buffer}]/(a + [\text{buffer}]),$$

where k_0 is the rate constant at zero buffer concentration, k_{Max}/a is the slope at zero buffer concentration and k_{Max} is the limiting value of the rate constant.

The lines in Fig. 3 were computed using the above equation and the constants obtained by the fits.

The temperature effect on k_{Max} was analysed by calculating the pre-exponential factor and the activation energy from the linear regression of $\ln(k_{\text{Max}})$ versus 1/T by least-squares method. The entropy and enthalpy of activation were calculated by the standard formulae derived from the absolute theory of reaction rate (Connors, 1990).

2.4. Stability in water of 3,4-dichlorophenyl isocyanate

A saturated solution of 3,4-dichlorophenyl isocyanate, obtained by stirring a suspension of the solid in water for half an hour, was filtered on 0.20 μ m membrane filter and analysed by HPLC carried out as reported above. The chromatogram revealed the presence in solution only of 3,4-dichloroaniline.

3. Results

The degradation reaction of diuron was studied incubating homogeneous aqueous solutions in thermostated baths and monitoring the course of the reaction by HPLC analyses.

Under all the experimental conditions, diuron underwent spontaneous irreversible hydrolysis (hydrolysis of the ureide group) with an appreciable rate giving a single derivative with an aromatic ring, which, by HPLC co-injection of pure compounds and mass spectrometry techniques, was identified as 3,4-dichloroaniline. The demethylated diuron derivatives, produced by biotic degradations, were not found in any of the samples. The sum of the area of the diuron peak plus the 3,4-dichloroaniline one, corrected by the different absorbance at the wavelength of the spectrometer detector, was constant during the kinetic runs, indicating the absence of reaction intermediate in an appreciable amount. Fig. 2 reports a typical time–concentration curve. The rate



Fig. 2. Typical time profiles for the chemical degradation of diuron. T = 70 °C, pH 7.2, 0.38 M phosphate buffer, ionic strength 1 M (KCl): diuron (\blacktriangle), 3,4-dichloroaniline (\blacktriangledown).

constants were calculated from the time dependence of diuron and/or 3,4-dichloroaniline concentration by least-squares analysis, assuming the rate to be first-order in the diuron concentration. The fitting of the experimental data was satisfactory for all the samples.

3.1. Buffer dependence of the pseudo-first-order rate constant

Under all the experimental conditions, the pseudofirst-order rate constant (k_{obs}), determined at constant pH by varying the total concentration of phosphate buffer, increased rapidly at low concentrations of buffer and then gradually levelled off at higher concentrations. Fig. 3 reports the experimental data obtained at 70 °C for various values of the fraction (α) of the buffer in the free base form. Similarly shaped curves were observed at the other temperature values checked. At constant temperature, the slope of the curves at low phosphate concentration depends markedly on the value of α , while the limiting rate, reached at high phosphate concentration, is not dependent on α .

3.2. pH dependence of the pseudo-first-order rate constant

Fig. 4 shows a plot of k_0 versus pH, where k_0 is the pseudo-first-order rate constant determined in non-buffered solutions. In the pH range 4–9, the rate constant is substantially pH independent, while at lower and higher pH values the curve markedly increases, suggesting an efficient catalysis by hydronium ion at low pH and by hydroxide ion at high pH. At extreme pH values (<2 or >12), the k_0 value is again constant. It is worth noting



Fig. 3. Dependence of the observed first-order rate constant (k_{obs}) for the degradation reaction of diuron on the total phosphate buffer concentration: fraction of the free base in the buffer 0.2 (\blacktriangle), 0.4 (\triangledown), 0.6 (\blacksquare), 0.8 (\blacklozenge); T = 70 °C, ionic strength 1 M (KCl).



Fig. 4. pH dependence of the first-order rate constant (k_0) for the degradation reaction of diuron: T = 70 °C, ionic strength 1 M (KCl).

that the k_0 value reached in these pH extreme regions is equal, within the experimental errors, to that reached at high phosphate concentration.

3.3. Temperature dependence of reaction rate

The Arrhenius plot for the limiting rate-constants reached at high buffer concentrations (computed as reported in Section 2) is linear in the temperature range studied (Fig. 5). The pre-exponential factor and the apparent activation parameters are respectively: $\ln A = 43 \pm 1 \text{ day}^{-1}$; $E_a = 127 \pm 2 \text{ kJ mol}^{-1}$; $\Delta H^{\ddagger} = 124 \pm 2 \text{ kJ mol}^{-1}$; $\Delta S^{\ddagger} = 14 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$.



Fig. 5. Arrhenius plot for the step that is rate-limiting at high concentration of H^+ , OH^- or buffers; ionic strength 1 M (KCl).



4. Discussion

The results here reported show that the abiotic degradation of diuron in water solution is an irreversible reaction and gives 3,4-dichloroaniline as the only product in detectable amount containing the phenyl ring. Moreover, the reaction is markedly catalysed by H⁺, OH⁻ and buffers. The hyperbolical shape of the curve describing the dependence of the rate constant on the buffer concentration is a clear indication that the degradation reaction of phenylureas is a multi-step process, which proceeds through the formation of an intermediate (Hand and Jencks, 1975; Capasso et al., 1998). At low buffer concentrations the formation of the intermediate (or its breakdown) is buffer catalysed and rate limiting. As the buffer concentration increases, rate limiting is the non-catalysed breakdown of the intermediate (or its formation). The pH-rate profile shows, as expected from literature data (Tomlin, 1997), the catalytic effect of hydronium and hydroxide ions. The constant value of k_0 in the two extreme pH regions gives an additional indication that the degradation reaction of diuron proceeds through two (or more) steps, one of which is not catalysed by acids and bases. It should be noted that the k_0 value in the extreme pH regions is identical to that measured for high values of phosphate concentration buffer. The low value of the entropy of activation ($\Delta S^{\ddagger} = 14 \text{ J K}^{-1} \text{ mol}^{-1}$) indicates that there is not a marked change in the disorder or motional modes in the formation of the transition state in this reaction step. It is unlikely that the addition of a water molecule to the substrate occurs in this step (Schaleger and Long, 1963).

Earlier reports (Frost and Pearson, 1963) have indicated that the most likely mechanism for the chemical decomposition of ureas involves formation of isocyanic acid, or of isocyanates, which, subsequently, hydrolyses to amine and carbon dioxide. Moreover kinetic evidences indicated that the isocyanic acid, or isocyanate, formation from ureas occurs through a stepwise mechanism with the formation of an intermediate zwitterion (Williams and Jencks, 1974). On this basis, our experimental kinetic data can be rationalised in terms of the reaction pathway depicted in Scheme 1.

The reaction starts by the formation of the zwitterion 1 by general acid-base catalysis, which gives the phenyl isocyanate derivative 2 and dimethylamine by an uncatalysed step. At low catalyst concentrations (pH range 3–11 and low buffer concentrations), the breakdown of 1 to 2 is rate limiting, whereas at high catalyst concentrations, its formation becomes rate limiting.

The hydrolysis rate constant of **2** is much higher than the rate constant for its formation; consequently the concentration of **2** is always very small, less than the sensitivity of the HPLC used for this study. Castro et al. (1985) reported a half-life value of 20 s for the non-acidcatalysed hydrolysis of phenyl isocyanate in aqueous solution at 25 °C. Coherently, it was not possible to detect 3,4-dichlorophenyl isocyanate in water solution by HPLC in any of the pH values considered, because of its very fast degradation to 3,4-dichloroaniline.

5. Conclusion

The study of pH, buffer, and temperature effects on the chemical hydrolysis of the ureide group in diuron has produced a detailed description of the kinetics of this reaction and provided evidences that the reaction is a multi-step process that proceeds through the formation of intermediates. The hydroxide and hydrogen ions, and the buffers are efficient catalysts of the reaction. The rate constant increases with their concentrations up to a limiting value depending on the temperature. The hydrolysis of dichlorophenyl isocyanate, a relatively stable intermediate of the degradation process, is very fast; therefore it cannot be detected by the usual analytical methods.

Finally, we wish to underline the environmental aspect of the kinetics here reported. It is reasonable to suppose that the organic and inorganic matter of soils, as well as the chemicals dissolved in ground aqueous phases, can catalyse the chemical degradation of diuron, increasing the reaction rate up to the limiting value. This value can be computed for each temperature in the interval examined, and by reasonable extrapolation also outside the experimental range, by the Arrhenius parameters reported above. It should be taken into account for the prediction of the fate of diuron after its dispersal in a field (Gustafson, 1993).

It is worth noting that the biotic degradation has not been considered in this work. However, its occurrence in a field should have the effect of further increasing the degradation rate, and then of decreasing the permanence of diuron in the environment.

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