

# Ion Chromatographic Determination of the Decomposition Products of Tecnazene Solution Irradiated by Ultraviolet Light. Inorganic and Organic Anions

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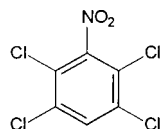
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Ion chromatographic (IC) methods using sodium hydroxide and methanol gradients were used for the determination of small inorganic and organic anions as decomposition products of a tecnazene solution in water irradiated by UV light. After 60 min of UV irradiation, >99% of the tecnazene was decomposed, and 11 organic and 3 inorganic anions were identified and quantified. A fourth inorganic anion, carbonate, was not quantified due to likely losses as carbon dioxide. The final content of chloride, total nitrogen, and total carbon released from the saturated tecnazene solution after 60 min of UV irradiation were 108, 85, and 38%, respectively. These results suggest that other products rich in carbon and/or nitrogen (such as phenolic compounds and nitrobenzenes) were formed during the UV irradiation of the tecnazene solution. The results obtained indicate several decomposition pathways of tecnazene in water solutions, for example, ring opening reactions, dechlorination, and replacement of the ring nitro group. The determination of nonionic decomposition products from the latter two possibilities is the subject of further study.

**Keywords:** Photodecomposition; tecnazene; 1,2,4,5-tetrachloro-3-nitrobenzene; UV irradiation; ion chromatography; anions

## INTRODUCTION

Tecnazene (1,2,4,5-tetrachloro-3-nitrobenzene)



is a fungicide used on potatoes for the purpose of sprout suppression and dry rot control. It has been used mainly in the United Kingdom and applied at the time of store loading at a rate of ~0.1 g/kg of potatoes (1). The United Kingdom banned its usage in January 2000 with the concession that the remaining stocks could be used over the next 2 years.

Despite the fact that it has been used commercially since 1947, the behavior of tecnazene in the environment is not well understood. Little is known beyond that it has limited water solubility, is volatile, and is susceptible to UV irradiation (1) as well as to microbial breakdown. However, as tecnazene is a nitroderivative of organochlorine pesticide the expectation is that it will persist in the environment for some time. Potato washing and processing plants use large quantities of water, and as the tecnazene is concentrated in the soil and potato skin this leads to a buildup of the chemical downstream of the effluent outfall. Tecnazene has been found to be highly toxic to several aquatic species

including fish (2). The fact that tecnazene and its metabolites have been identified in sediments and fish downstream of potato washing and processing plants was a major factor leading to its withdrawal from use.

As UV irradiation has become a recognized treatment method for the removal of pesticides from both waste and drinking water (3–6), it was decided to examine the effects of UV light on tecnazene decomposition and attempt to identify and quantify the decomposition products. In terms of toxicity, studying pesticide decomposition pathways is of great concern, because there is a possibility of the production of undesirable byproducts.

The ultimate goal of this study is to identify and quantify tecnazene decomposition products released during UV irradiation treatment of a tecnazene solution in water, so that a full picture of the decomposition pathway can be obtained. This paper reports on the formation of inorganic and organic anions.

## EXPERIMENTAL PROCEDURES

**Reagents.** All of the chemicals were of analytical grade purity and were supplied by BDH, Sigma-Aldrich, and Fluka. Acetonitrile (Fischer Scientific) of HPLC grade was used for the preparation of the mobile phase for the HPLC determination of tecnazene. Standard stock solutions and standard solutions were prepared using ultrapure deionized water (Purite Select, Purite Ltd.).

Stock solutions (1000 mg/L) of inorganic anions were prepared from the corresponding potassium or sodium salts, and 100 or 10 mM (in the case of the less soluble chemicals) stock solutions of organic anions were prepared from the corresponding ammonium or sodium salts or from organic acids. Working standard solutions were freshly prepared every

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**Table 1. Concentration of Anions in Calibration Standards**

stand-ard	all organics ( $\mu\text{M}$ )	$\text{Cl}^-$ (ppb)	$\text{NO}_2^-$ (ppb)	$\text{NO}_3^-$ (ppb)	$\text{ClO}_2^-$ (ppb)	$\text{ClO}_3^-$ (ppb)	$\text{SO}_4^{2-}$ (ppb)	$\text{ClO}_4^-$ (ppb)
1	2	1000	100	100	100	100	50	100
2	1	500	50	50	50	50	25	50
3	0.5	250	25	25	25	25	12.5	25

day, and the standard solutions prepared from the acidic stock solutions were neutralized by the addition of 1 mM NaOH (Vickers Laboratories Ltd.). Stock solutions were stored at 4 °C to minimize microbial breakdown.

Tecnazene (1,2,4,5-tetrachloro-3-nitrobenzene, Sigma-Aldrich) was recrystallized in acetonitrile before use. Saturated tecnazene solution was prepared by ultrasonication of 0.01 g of tecnazene in 500 mL of water in a 1.0 L beaker for 30 min. After an hour of standing, the solution was filtered through a Gelman Sciences Supor-200, 47 mm, 0.2  $\mu\text{m}$  filter. The solution was kept at a constant room temperature of  $20 \pm 2$  °C in darkness.

**Apparatus.** HPLC determination and quantification of tecnazene were carried out using a C18 Hypersil column (250  $\times$  4.6 mm, Jones Chromatography), SA103 isocratic pump (Speck Analytical), LC spectrophotometer (Knauer), and SP4290 Integrator (Spectra Physics) using an injection volume of 20  $\mu\text{L}$ , 70% acetonitrile/30% 20 mM phosphate buffer at pH 2.5 as a mobile phase at a flow rate of 0.8 mL/min and UV detection at 225 nm. The calibration standards for the quantification of tecnazene in the original saturated and irradiated solutions were prepared in a 10% v/v acetonitrile/water mixture.

Determination of inorganic and organic anions was carried out using a Dionex DX-500 ion chromatography system equipped with an AS40 autosampler, a GP40 gradient pump, an AS11 analytical column (250  $\times$  4 mm) with an AG11 guard column (50  $\times$  4 mm), an ASRS-Ultra self-regenerating suppressor in external water flow mode using a high pressurized reservoir containing ultrapure deionized water, and an ED40 conductivity detector (all parts from Dionex Corp.).

The sodium hydroxide eluents for the IC determinations were prepared under a helium atmosphere using 50% w/v solution of NaOH (Vickers Laboratories Ltd.). The mobile phase consisted of NaOH eluent(s), ultrapure deionized water, and methanol (BDH) of HPLC grade.

**UV Apparatus.** A 1 L reaction vessel was wrapped in aluminum foil and filled with saturated tecnazene solution, and the contents were stirred using a magnetic stirrer (IKA-MAG, Janke & Kunkel Laborotechniek). UV irradiation of the solution was carried out using an Engelhard Hanovia medium-pressure mercury vapor photochemical reactor lamp jacketed with a water-cooled quartz sleeve.

**Data Evaluation and Calibration.** Data evaluation and peak identification were carried out using PeakNet 4.30 software (Dionex Corp.). Calibration standards of organic and inorganic anions at three different concentration levels (see Table 1) were used for the quantification of the decomposition products in UV-irradiated tecnazene solution. Statistical evaluation was carried out using Excel 97 spreadsheet software (Microsoft).

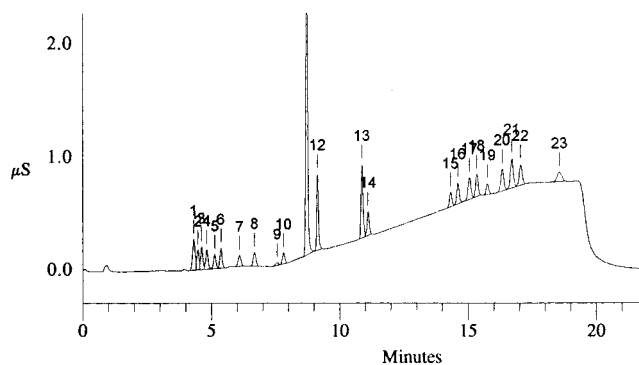
## RESULTS AND DISCUSSION

Tecnazene is rather insoluble in water (7). The solubility in water at 20 °C is 0.9 mg/L (7). With five independent batches of saturated tecnazene solution in water a mean value of 0.87 mg/L and an RSD of 8.3% were obtained. However, after vial-to-vial transfer of the saturated tecnazene solution, a significant decrease in the tecnazene concentration ( $\sim 20\%$ ) was observed. This decrease in the concentration can be explained by the adsorption of tecnazene onto the glass walls of the vials. Therefore, each tecnazene solution was equilibrated

**Table 2. IC Conditions for the Simultaneous Separation of 23 Organic and Inorganic Anions<sup>a</sup>**

sodium hydroxide gradient
0.2–0.5 mM in 6 min
0.5–8.5 mM in 10 min
8.5 mM for 2 min
0.2 mM for 6 min
methanol gradient
10–12% in 6 min
12–14% in 4 min
14% for 8 min
10% for 6 min

<sup>a</sup> Flow rate, 2 mL/min; injection volume, 100  $\mu\text{L}$ ; suppressor current, 100 mA.



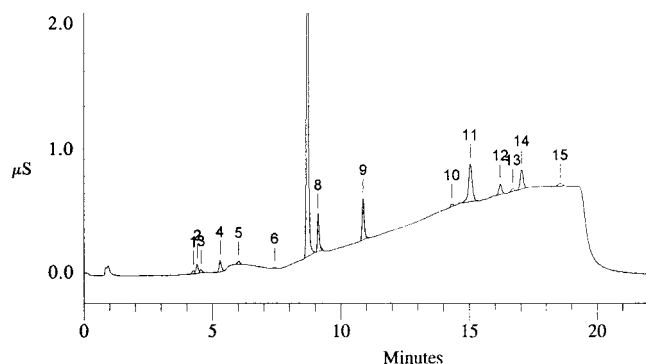
**Figure 1.** Simultaneous determination of 23 organic and inorganic anions at calibration level 2 (for IC conditions, see Table 2). Peaks: 1, lactate; 2, acetate; 3, glycolate; 4, propionate; 5, butyrate; 6, formate; 7, pyruvate; 8, chlorite; 9, glyoxylate; 10, chloroacetate; 11, chloride; 12, nitrite; 13, nitrate; 14, chlorate; 15, succinate; 16, malate; 17, carbonate (impurity not quantified); 18, tartrate; 19, maleate; 20, tartronate; 21, sulfate; 22, oxalate; 23, ketomalonate.

before any quantitative analysis was carried out. The equilibration time of an hour appeared to be sufficient as after this period no further decrease in the tecnazene concentration was observed.

An IC method was developed for the simultaneous determination of small inorganic and organic anions using sodium hydroxide and methanol gradients (see Table 2 for details). With this method full baseline separation of 23 possible tecnazene decomposition products was achieved (see Figure 1). For the determination of two further unresolved potential decomposition products, malonate and perchlorate, individual separations had to be developed due to the coelution with carbonate and the high affinity for the column packing, respectively.

For malonate, a sodium hydroxide gradient separation was used: 0.1–0.5 mM in 6 min, 0.5–6 mM in 10 min, 6 mM for 2 min, and 0.1 mM for 6 min at 2 mL/min and ASRS current of 100 mA. For perchlorate, an isocratic separation was used: 100 mM NaOH for 10 min at 1 mL/min and an ASRS current of 300 mA.

For the quantification of the resulting decomposition products of the irradiated tecnazene solution, three-level calibration curves for all anions except for carbonate were measured (concentration versus peak area). The calibration curves were linear in the whole calibration range for all of the anions with values of  $r^2$  ranging from 0.996 (acetate) to 0.9999 (chloride). The RSD values ( $n = 10$ ) for the calibration standard 2 (see Table 1 for details) were in the ranges from 0.2% (chloride) to 1.0% (lactate) and from 0.9% (chloride) to 5.5% (succinate) for the retention times and peak areas, respectively.



**Figure 2.** Determination of UV irradiation products of tecnazene solution, irradiation time of 60 min (for IC conditions, see Table 2). Peaks: 1, lactate; 2, acetate; 3, glycolate; 4, formate; 5, pyruvate; 6, glyoxylate; 7, chloride; 8, nitrite; 9, nitrate; 10, succinate; 11, carbonate; 12, tartronate; 13, sulfate; 14, oxalate; 15, ketomalonnate.

**Table 3.** LODs of All Anions Determined by IC<sup>a</sup>

anion	LOD	anion	LOD
lactate	20 nM	nitrate	1 ppb
acetate	40 nM	chlorate	3 ppb
glycolate	40 nM	succinate	40 nM
propionate	40 nM	malate	40 nM
butyrate	40 nM	tartrate	40 nM
formate	20 nM	maleate	40 nM
pyruvate	40 nM	tartronate	40 nM
chlorite	3 ppb	sulfate	3 ppb
glyoxylate	80 nM	oxalate	40 nM
chloroacetate	40 nM	ketomalonnate	40 nM
chloride	3 ppb	malonnate	40 nM
nitrite	1 ppb	perchlorate	6 ppb

<sup>a</sup> Injection volume, 100  $\mu$ L. Calculated as 3 times noise level (3 *S/N*).

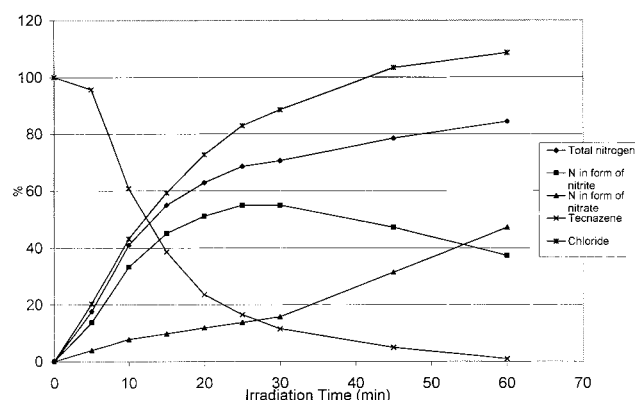
LODs for all anions calculated as 3 *S/N* are summarized in Table 3.

Carbonate was present in every standard solution and sample as a result of dissolution of atmospheric carbon dioxide and the formation of carbon dioxide during UV irradiation and therefore had to be taken in account when the IC methods were developed. Also, this meant that carbonate was excluded from the final quantification (and excluded from the carbon atoms balance of the decomposition products of tecnazene).

Samples were prepared by UV irradiation of the tecnazene solution in water. The reaction vessel was filled with the tecnazene solution and left to equilibrate. After 1 h, the first sample was withdrawn and the UV irradiation was started. The total irradiation time chosen was 60 min as after an hour >99% of tecnazene was decomposed. In addition to the first sample, eight other samples were withdrawn at irradiation times of 5, 10, 15, 20, 25, 30, 45, and 60 min and analyzed to determine and quantify the UV irradiation products. At the same time the quantitative HPLC determination of the tecnazene remaining was carried out.

As a result of the UV irradiation, 11 organic anions, namely, lactate, acetate, glycolate, formate, pyruvate, glyoxylate, succinate, malonnate, tartronate, oxalate, and ketomalonnate, and 3 inorganic anions, namely, chloride, nitrite, and nitrate, were identified (see Figure 2) and quantified. Final concentrations of all decomposition products after 60 min of irradiation are summarized in Table 4.

Figure 3 shows the percentages of chloride, nitrite, nitrate, and total nitrogen released by the UV irradiation



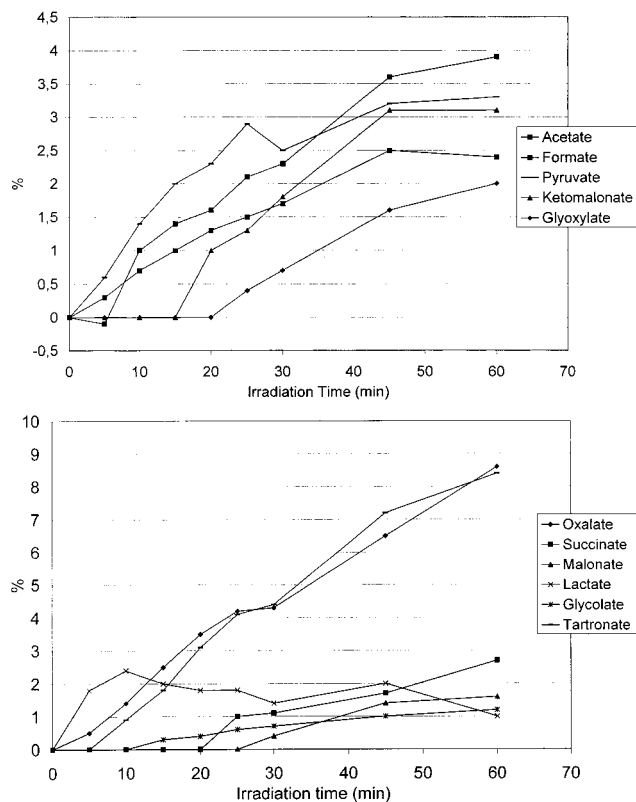
**Figure 3.** Quantitative determination of inorganic anions released by the UV irradiation of tecnazene solution.

**Table 4.** Final Concentrations of the Organic and Inorganic Anions as the Decomposition Products of the Tecnazene Solution Irradiated for 60 min

% of tecnazene remaining	0.9
% of Cl <sup>-</sup> released	108.5
% of N released in the form of NO <sub>2</sub> <sup>-</sup>	37.3
% of N released in the form of NO <sub>3</sub> <sup>-</sup>	47.1
% of total N released	84.4
% of C released from tecnazene in the form of corresponding organic anion	
lactate	1.0
acetate	3.9
glycolate	1.2
formate	2.4
pyruvate	3.3
glyoxylate	2.0
succinate	2.7
malonnate	1.6
tartronate	8.4
oxalate	8.6
ketomalonnate	3.1
% of total C released	38.2

tion of the tecnazene solution and the percentage of remaining tecnazene. In the first stage (0–5 min) of UV irradiation the decomposition of tecnazene was rather slow. In the later stages of irradiation (5–30 min) the decomposition rate of tecnazene increased, and after 60 min, 99.1% of tecnazene was decomposed. The content of nitrite rapidly increased in the first 25 min, reached a maximum at 25–30 min, and then slowly decreased, whereas the content of nitrate continuously increased up to 60 min. This is probably due to the initial liberation of NO<sub>2</sub><sup>-</sup> from the nitro group of the tecnazene and by nitrite oxidation in the second step. Chlorine liberation is probably a first-order reaction producing chloride anion directly by breaking the C–Cl bond. Further oxidation of chloride anions to oxoanions was investigated by determining different oxoanions in irradiated solution, but no trace of these compounds has been detected in the real samples. It suggests that no further oxidation of chloride took place after the C–Cl bond had been broken.

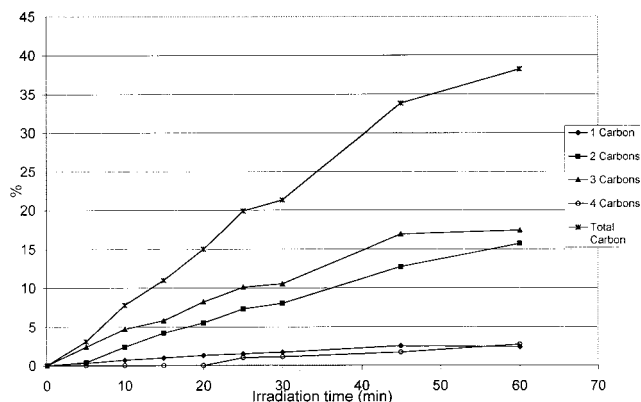
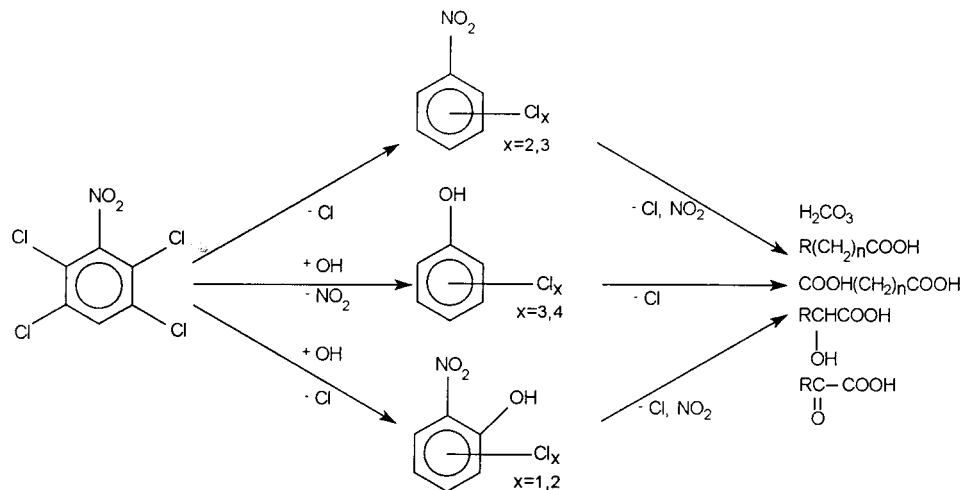
Figure 4 shows the values for all of the organic anions. In addition to the monocarboxylic nonsubstituted organic anions, dicarboxylic, hydroxycarboxylic, and ketocarboxylic organic anions were formed, among which dicarboxylic and hydroxycarboxylic were the most frequent. The concentration of some compounds, that is, lactate, showed maxima at 10 min, whereas the formation of others (glycolate, glyoxalate, succinate, malonnate, and ketomalonnate) was observed first after 15–30 min of irradiation.



**Figure 4.** Quantitative determination of (a) monocarboxylic and ketocarboxylic and (b) dicarboxylic and hydroxycarboxylic organic anions released by the UV irradiation of tecnazene solution.

In Figure 5 the values for total carbon and organic anions containing one, two, three, and four carbon atoms in the chain are depicted for convenience. The formation of decomposition products containing three carbon atoms is preferred through the whole irradiation process of tecnazene, whereas two-carbon-atom products prevail in the second stage, and the contents of one- and four-carbon molecules are negligible throughout the whole process. According to the results obtained in the experiment, it can be suggested that the symmetrical halving of the benzene ring into  $C_3$  molecules and the symmetrical formation of the  $C_2$  molecules (probably after nitro group and chlorine substituents are released) is more likely, whereas the nonsymmetrical opening of the benzene ring to form  $C_4$  and/or  $C_1$  molecules is less

#### Scheme 1



**Figure 5.** Summary of the quantitative determination of carbon-containing organic anions according to the number of carbon atoms in their chains.

probable. A simplified schematic drawing of the proposed decomposition pathway of tecnazene during UV irradiation is depicted in Scheme 1. The calculation of the total carbon released during the photolytic decomposition is influenced by the omission of carbon dioxide from the balance but suggests that substituted benzene compounds, that is, chlorophenols ( $\beta$ ), nitrobenzenes, nitrophenols, etc., are significant intermediates.

#### CONCLUSIONS

IC methods were developed for the separation of the possible anionic decomposition products of a saturated tecnazene solution irradiated by UV light. In a tecnazene solution UV-irradiated for 60 min, 11 organic anions and 3 inorganic anions were identified and quantified. Carbonate could not be quantified reliably. The higher content of chloride anions determined (103 and 108% in the samples of tecnazene solution irradiated for 45 and 60 min, respectively) compared to the calculated content of chlorine in the saturated tecnazene solution was likely to be caused by the sorption of tecnazene onto the glass walls of the reaction vessel, leading to an underestimate of the initial tecnazene concentration. The recoveries of the total nitrogen and total carbon after 60 min of UV irradiation were 85 and 38%, respectively. These results suggest that in addition to the wide variety of small inorganic and organic anions some other decomposition products rich in carbon and/or nitrogen (such as phenolic compounds and nitrobenzenes) can be formed.



In terms of the study of decomposition products of tecnazene, the results obtained by IC indicate several possible decomposition pathways. The early release of chloride is evidence of a dechlorination pathway of tecnazene decomposition. The formation of organic anions is evidence of the ring-opening reaction of tecnazene decomposition. The formation of nitrite and nitrate anions could indicate the replacement of the ring nitro group by another group, probably hydroxyl, or just the release of the nitro group and subsequent replacement by a proton. The determination of these compounds is the subject of further study.

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