

Talekar, N. S.; Sun, L. T.; Lee, E. M.; Chen, J. S. "Persistence of Some Insecticides in Subtropical Soil". *J. Agric. Food Chem.* 1977, 25, 348-352.

Venkateswarlu, K.; Sethunathan, N. "Degradation of Carbofuran in Rice Soils as Influenced by Repeated Applications and Exposure to Aerobic Conditions following Anaerobiosis". *J. Agric. Food Chem.* 1978, 26, 1148-1151.

Venkateswarlu, K.; Gowda, T. K. S.; Sethunathan, N. "Persistence

and Biodegradation of Carbofuran in Soils. *J. Agric. Food Chem.* 1977, 25, 533-536.

Received for review October 27, 1986. Revised manuscript received August 14, 1987. Accepted September 21, 1987. This research was financed, in part, by the Department of Environment and Forests, Government of India, New Delhi (Contract No. 33(2)/84-EN.I).

Photochemistry of Pesticides. 8.¹ Photodegradation of 2,4,5-Trihaloimidazoles in the Presence of Singlet Oxygen

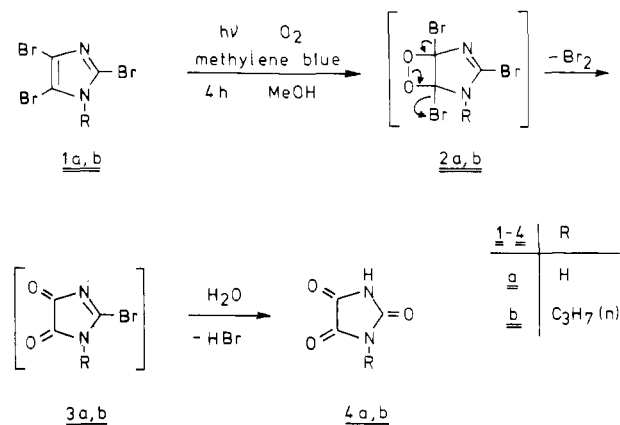
Heinrich Wamhoff,* Wafaa M. Abdou,² and Magdy Zahran

Sensitized photooxidation of 2,4,5-tribromoimidazoles **1a,b** leads in a rapid degradation reaction to parabanic acid derivatives **4a,b**. Similarly, 2,4,5-tribromo-1-(4-chlorobenzoyl)imidazole (**1c**) affords parabanic acid (**4a**). However, photolysis of 2,4,5-trichloroimidazoles **7a-d** results in a ring cleavage to give dimethyl oxalate (**8**), ammonium chloride, and alkylureas **11a,b**.

In recent years, there has been an increased interest in the environmental photochemistry and photodegradation of heterocyclic herbicides, pesticides, and insecticides (Gunther and Gunther, 1971; Kearney and Kaufman, 1975, 1976; Meallier and Coste, 1981; Ruzo, 1983; Chen, 1985; Moorman et al., 1985; Mukerjee, 1985). Following our current studies on the photochemistry of pesticides (Mahran et al., 1983; Abdou et al., 1985, 1986; Wamhoff et al., 1985), we have become interested in the photochemical behavior and decomposition of 2,4,5-tribromoimidazole (**1a**), 2,4,5-trichloroimidazole (**7a**) (Lutz and De Lorenzo, 1967, 1969; Wade and Landram, 1968; Wasco, 1969; Draber et al., 1970; Martin and Pissiotas, 1971; Pissiotas, 1971, 1972; Steimig and Fischer, 1971; Steimig and Adolphi, 1973; Stensio et al., 1973; Büchel and Erdmann, 1976; Schulze and Klein, 1977, and their N-substituted derivatives **1b,c** and **7b-d** (Boots Pure Drug Co., Ltd., 1967; Rutz and Gubler, 1968; Martin and Pissiotas, 1970; Drabek and Pissiotas, 1972; Büchel, 1976; Takahashi and Ando, 1978) under various conditions.

Compounds **1a** and **7a** as well as the related N-substituted derivatives **1b,c** and **7b-d** have been recognized as potent biocides with special application as herbicides, pesticides, bactericides, miticides, and insecticides (cf. aforementioned literature). However, up to now no investigations have been carried out on the photolysis of **1a-c** and **7a-d**. It has been shown that the parent compound imidazole is capable of slow photooxidation in methanol and in the presence of singlet oxygen to give dimethoxyhydantoin (Wasserman et al., 1968; Wasserman and Lipshutz, 1979), whereas 4,5-diphenylimidazole gives a mixture of 4,5-dimethoxy-4,5-diphenylhydantoin and 5-methoxy-4,5-diphenylhydantoin (Wasserman et al., 1968). In addition, it has been reported that sensitized or direct photooxidation of lophin (2,4,5-triphenylimidazole) gives di-

Scheme I



benzoylbenzamidine (Dufraisse et al., 1957, 1964). Other substituted imidazoles, such as 2-methyl- or 1,2-dimethylimidazoles (Matsuura and Ikari, 1969), histidine (Ochiai et al., 1968), 4-phenyl- and tetraphenylimidazole (Wasserman et al., 1968; Wasserman and Lipshutz, 1979) have been studied as well.

RESULTS AND DISCUSSION

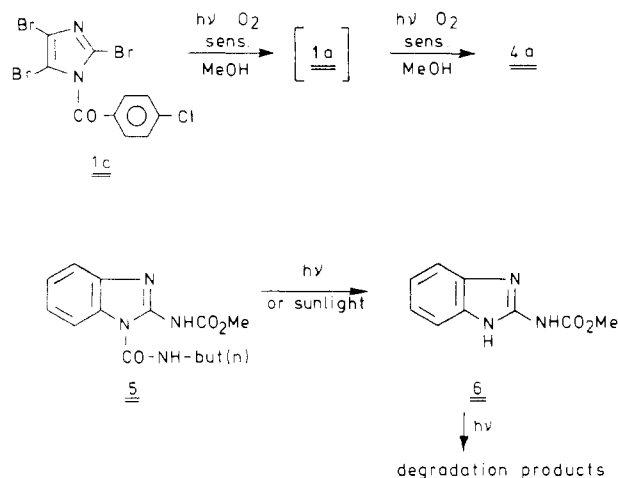
In our investigation, we have found that singlet oxygen photolysis of a 1% solution of 2,4,5-tribromoimidazole (**1a**) in methanol and in a Pyrex vessel using methylene blue as sensitizer affords parabanic acid (**4a**) as the only reaction product in 80-85% yield after a considerably short irradiation time (4 h). The identity of **4a** was established by comparison with an authentic specimen (Biltz and Schiemann, 1926). Br₂ and HBr were also identified as decomposition products during the irradiation. Similarly, upon photosensitized oxidation of 1-propyltribromoimidazole (**1b**) propyl parabanate (**4b**) was obtained in ca. 80% yield and its constitution confirmed (Baerlicher and Ebert, 1972). **4a,b** were also isolated and identified when the irradiation was carried out in dry toluene or chloroform; furthermore, photolysis of **1a** with UV light as well as in the presence of visible light, without sensitizer, and with continuous circulation of dry air, leads after 35 h to parabanic acid (**4a**). No reaction was, however, observed in a comparative experiment without exposure to UV irradiation. This indicates that both oxygen and light are

Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, FRG.

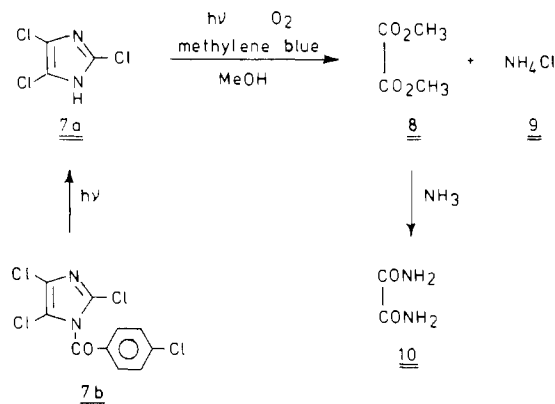
¹Part 7: Abdou, W. M.; Born, L.; Hulpke, H.; Mahran, M. R.; Sidky, M. M.; Wamhoff, H. *Phosphorus Sulfur* 1987, 29, 179.

²Research Fellow from National Research Centre, Cairo, A.R. Egypt.

Scheme II



Scheme III



essential conditions for the rapid photodegradation found.

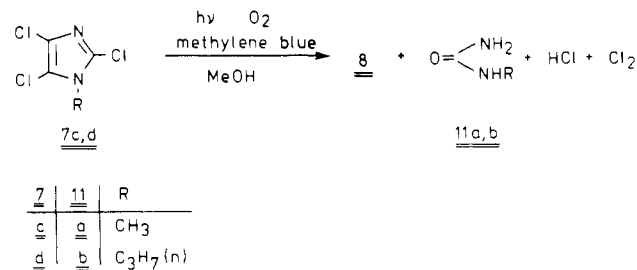
On the basis of the isolated products, the conditions applied, and several leading mechanisms discussed in the literature for photooxidation with singlet oxygen (Foote, 1968; Bartlett and Schaap, 1970; Wasserman and Lipshutz, 1979; Wamhoff et al., 1981; Wamhoff and Kleimann, 1981), and the photoinduced substitution of hydroxyl for halogen groups (Crosby and Tutass, 1966; Munakata and Kuwahara, 1969), we discuss for the degradation $1a,b \rightarrow 4a,b$ the mechanism shown in Scheme I.

Following this, $1a,b$ add 1O_2 in a [2 + 2] manner to give an elusive 1,2-dioxetane species **2**, which cleaves metathetically under bromine elimination to afford **3**, in turn undergoing a displacement reaction to afford $4a,b$.

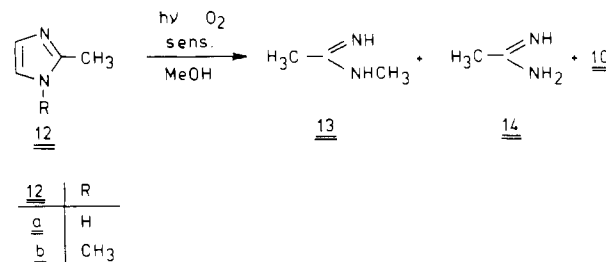
Remarkably, when 1-(4-chlorobenzoyl)-2,4,5-tribromoimidazole (**1c**) was irradiated under the same conditions, again parabanic acid (**4a**) was obtained in ca. 85% yield. In this case, initial photodebenzoylation (e.g., by α -cleavage) may occur to give **1a** followed by photooxidation into **4a** (Scheme II). Otherwise, the benzoyl group could be simply saponified by HBr originated during the reaction. This conversion $1c \rightarrow 4a$ is paralleled by the known fact that the fungicide Benlate (**5**) is photochemically smoothly converted into the parent methyl benzimidazol-2-yl-carbamate **6** and subsequent degradation products (Watkins, 1974; Abdou et al., 1986).

In contrast to the behavior of **1**, which undergoes direct and simple photooxidation, an extensive decomposition occurs when 2,4,5-trichloroimidazole (**7a**) or 1-(4-chlorobenzoyl)-2,4,5-trichloroimidazole (**7b**) is photolyzed in methanol under the prevailing conditions. Dimethyl oxalate (**8**), identified as oxamide (**10**), and ammonium chloride (**9**) are the isolated and characterized products (Scheme III).

Scheme IV



Scheme V



Furthermore, upon photooxidation, 2,4,5-trichloro-1-methylimidazole (**7c**) and 2,4,5-trichloro-1-*n*-propylimidazole (**7d**) afford dimethyl oxalate (**8**; 39 and 32% yields, respectively) and the substituted ureas **11a,b** in 42 and 35% yields, respectively; chlorine and HCl can be easily detected during the irradiation. **11a,b** were confirmed by comparing melting point, IR, MS, and 1H NMR with authentic specimens (Biltz and Topp, 1913; Boivin and Boivin, 1951). When the photooxidation of **7c,d** is carried out in toluene or chloroform, oxamide (**10**) is isolated along with the main products (Scheme IV).

The photodegradation of related imidazoles is known: thus, dye-sensitized photooxidation of 2-methyl- and 1,2-dimethylimidazoles **12a,b** gives analogously degradation products **10**, **13**, and **14** (Matsuura and Ikari, 1969) (Scheme V).

The nature of the excited states and the degradation mechanisms are currently being investigated.

EXPERIMENTAL SECTION

Melting points are uncorrected. Analyses were carried out by Mikroanalytisches Laboratorium by Dr. F. Pascher, Bonn. IR spectra were recorded on a Perkin-Elmer Model 157-G. 1H NMR spectra were taken in $CDCl_3$ on a Bruker WH-90 spectrometer with TMS as internal standard. Mass spectra were recorded on a AEI (Kratos) MS-50. Photolyses were carried out in a Pyrex photoreactor equipped with a Hg high-pressure lamp (Philips HPK 125). The TLC system used was toluene/ethyl acetate/ethanol (6:3:1, v/v/v).

2,4,5-Tribromo- (**1a**), 2,4,5-trichloro- (**7a**), and 2,4,5-trichloro-1-methylimidazole (**7c**) have been supplied by Bayer AG, Leverkusen.

Photooxidation of the 2,4,5-Tribromoimidazoles 1a,b. General Procedure. A solution of **1a** (2.5 g, 8 mmol) or **1b** (2.5 g, 7 mmol) in dry MeOH (250 mL) containing 50 mg of methylene blue was irradiated for 4–6 h, while a steady stream of oxygen was circulated into the mixture. After evaporation of the solvent in vacuo, **4a,b** were obtained by column chromatography (silica gel/EtOH with increasing amounts of Et_2O).

4a (parabanic acid): 0.8 g (85%) from EtOH, colorless crystals; mp 242 °C (lit. mp 241–243 °C; Murray, 1957); MS, m/e 114 (M^+).

4b (*n*-propyl parabanate): 0.85 g (80%) from EtOH, colorless crystals; mp 110–112 °C (lit. mp 109–112 °C;

Baerlicher and Ebert, 1972); MS, m/e 156 (M^+).

When the photooxidation of **1a,b** was carried out in toluene or CHCl_3 , TLC monitoring indicated the disappearance of **1a,b** after 10 h. Working up the photolysate as described above resulted in the isolation of **4a,b** in 85 and 80% yields, respectively. Employing a 250-W tungsten lamp gave **4a,b** in ca. 65% yield after 35-h irradiation time.

Photooxidation of 1-(4-Chlorobenzoyl)-2,4,5-trichloroimidazole (1c). Photodegradation of **1c** (2.5 g, 6 mmol) in MeOH (250 mL) was carried out as described for **1a,b**, and parabanic acid (**4a**) was obtained; 0.5 g (85%) (melting point, mixed melting point, comparative IR).

Photooxidation of 2,4,5-Trichloroimidazoles 7a,b. A solution of **7a** (2.5 g, 14.6 mmol) or **7b** (2.5 g, 8.1 mmol) in MeOH (250 mL) containing methylene blue (50 mg) was irradiated for 10 h, while oxygen was circulated in a steady stream. Concentration of the reaction mixture in vacuo gave a white material identified to be NH_4Cl , 0.55 g (70%). The MeOH distillate, which had a distinctive odor, produced a white precipitate upon treatment with gaseous NH_3 and was recrystallized from MeOH to give colorless needles that proved to be oxamide **10**: 0.6 g (50%); mp $>300^\circ\text{C}$ (melting point, mixed melting point, comparative IR spectra); MS, m/e 88 (M^+). This yield of **10** corresponds to 0.85 g (50%) of dimethyl oxalate (**8**).

1-n-Propyl-2,4,5-trichloroimidazole (7d). **7d** was prepared according to Pissiotas (1971) as follows: A mixture of 2,4,5-trichloroimidazole (20 g, 117 mmol), *n*-propyl bromide (18.5 mL, 150 mmol), K_2CO_3 (29 g), and acetone (200 mL) was refluxed for 18 h. After cooling, the mixture was filtered and the filtrate concentrated in vacuo. Distillation of the residue gave 15 g (75%) of **7d**: bp 135°C (0.05 mmHg); $^1\text{H NMR}$ δ 0.91 (2 H, t, $J = 6$, CH_2), 1.87 (3 H, q, $J = 6$, CH_3), 2.14 (2 H, t, $J = 6$, CH_2); MS, m/e (%) 213 (100), 211 (33). Anal. Calcd for $\text{C}_8\text{H}_7\text{Cl}_3\text{N}_2$: C, 33.73; H, 3.30; Cl, 49.84; N, 13.12. Found: C, 33.52; H, 3.29; Cl, 49.75; N, 12.89.

Photooxidation of 2,4,5-Trichloroimidazoles 7c,d. **7c** (2.5 g, 13 mmol) or **7d** (2.5 g, 10 mmol) was irradiated in MeOH (250 mL) containing methylene blue (50 mg) for 24 h in the way described above. Concentration of the solution in vacuo afforded a yellow oil; the MeOH distillate produced a white precipitate upon treatment with gaseous NH_3 and was recrystallized from MeOH to give colorless needles proving to be oxamide **10**: 462 and 326 mg, respectively (corresponding to 620 (39%) and 438 mg (32%) of **8**, respectively): mp $>300^\circ\text{C}$. The oily residue was worked up and separated in a manner similar to the general procedure to afford the alkylureas **11a,b**.

11a (*N*-methylurea): 428 mg (42%); mp $92\text{--}94^\circ\text{C}$ (lit. mp 95°C ; Biltz and Topp, 1913); MS, m/e 74 (M^+).

11b (*N*-(*n*-propyl)urea): 415 mg (35%); mp $105\text{--}107^\circ\text{C}$ (lit. mp 107°C ; Boivin and Boivin, 1951); MS, m/e 102 (M^+).

When the photodegradation of **7a-d** was carried out in toluene or CHCl_3 similar to the manner described above the following was isolated: **7a,b**, 526 mg (75%) of **9**; **7c**, 550 mg (55%) of **11a**; **7d**, 510 mg (51%) of **11b**; oxamide always in ca. 20% yield.

ACKNOWLEDGMENT

This work was supported by the Fonds der Chemischen Industrie and the Bayer AG. W.M.A. thanks the Heinrich-Hertz-Stiftung for granting a research fellowship. We are indebted to Dr. G. Jäger and Prof. Dr. H. Hulpke (Bayer AG, Leverkusen and Monheim), for supplying samples and for valuable discussions.

Registry No. **1a**, 2034-22-2; **1b**, 31250-78-9; **1c**, 15287-32-8; **4a**, 120-89-8; **4b**, 40408-38-6; **7a**, 7682-38-4; **7b**, 111160-99-7; **7c**,

873-25-6; **7d**, 111161-00-3; O_2 , 7782-44-7; *n*-propyl bromide, 106-94-5; 2,4,5-trichloroimidazole, 7682-38-4.

LITERATURE CITED

- Abdou, W. M.; Mahran, M. R.; Wamhoff, H. *Chemosphere* **1985**, *14*, 1343; **1986**, *15*, 1063.
- Abdou, W. M.; Born, L.; Hulpke, H.; Mahran, M. R.; Sidky, M. M.; Wamhoff, H. *Phosphorus Sulfur* **1987**, *29*, 179.
- Baerlicher, T.; Ebert, E. Ger. Offen. 2214 448, 1972; *Chem. Abstr.* **1973**, *78*, 4249.
- Bartlett, P. D.; Schaap, A. P. *J. Am. Chem. Soc.* **1970**, *92*, 3223.
- Biltz, H.; Topp, E. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 1404.
- Biltz, H.; Schiemann, G. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 721.
- Boivin, J. L.; Boivin, A. *Can. J. Chem.* **1951**, *29*, 478.
- Boots Pure Drug Co. Ltd. Neth. Patent 6 609 596, 1967; *Chem. Abstr.* **1967**, *67*, 64.398b.
- Büchel, K. H. Ger. Offen. 2 441 820, 1976; *Chem. Abstr.* **1976**, *84*, 180.223r.
- Büchel, K. H.; Erdmann, H. *Chem. Ber.* **1976**, *109*, 1625.
- Chen, Z.-m. *Huanying Kexue Xuebao* **1985**, *5*, 70; *Chem. Abstr.* **1985**, *103*, 83.496k.
- Crosby, D. G.; Tutass, H. O. *J. Agric. Food Chem.* **1966**, *14*, 596.
- Drabek, J.; Pissiotas, G. Ger. Offen. 2 133 571, 1972; *Chem. Abstr.* **1972**, *76*, 140.806m.
- Draber, W.; Falbe, J.; Büchel, K. H.; Korte, F. U.S. Patent 3 501 286, 1970; *Chem. Abstr.* **1970**, *72*, 120.399q.
- Dufraisse, C.; White, D. M. *J. Am. Chem. Soc.* **1964**, *86*, 5685.
- Dufraisse, C.; Etienne, A.; Martel, J. *Compt. Rend.* **1957**, *244*, 970, 3106.
- Foot, C. S. *Acc. Chem. Res.* **1968**, *1*, 104.
- Gunther, F. A., Gunther, J. O., Eds. *Chemistry of Pesticides*; Springer: New York, 1971.
- Kearney, P. C., Kaufman, D. D., Eds. *Herbicides Chemistry, Degradation and Mode of Action*, 2nd. ed.; Marcel Dekker: New York: Vol. 1, 1975; Vol. 2, 1976.
- Lutz, A. W.; De Lorenzo, S. A. *J. Heterocycl. Chem.* **1967**, *4*, 399.
- Lutz, A. W.; De Lorenzo, S. A. U.S. Patent 3 409 606, 1968; *Chem. Abstr.* **1969**, *70*, 37.814q.
- Mahran, M. R.; Sidky, M. M.; Wamhoff, H. *Chemosphere* **1983**, *12*, 1611, 1653.
- Martin, H.; Pissiotas, G. Ger. Offen. 1 950 991, 1970; *Chem. Abstr.* **1970**, *73*, 35.378p.
- Martin, H.; Pissiotas, G. Ger. Offen. 2 347 766, 1971; *Chem. Abstr.* **1971**, *75*, 34.500b.
- Matsuura, T.; Ikari, M. *Kogyo Kagaku Zasshi Japan* **1969**, *72*, 179; *Chem. Abstr.* **1969**, *70*, 96.256e.
- Meallier, P.; Coste, C. M. *Trav. Soc. Pharm. Montpellier* **1981**, *41*, 19; *Chem. Abstr.* **1981**, *96*, 99.256e.
- Moorman, A. R.; Findak, D. C.; Ku, H. S. *J. Heterocycl. Chem.* **1985**, *22*, 915.
- Mukejee, S. K. *Indian Agric. Chem.* **1985**, *18*, 1; *Chem. Abstr.* **1985**, *104*, 220.622k.
- Munakata, K.; Kuwahara, M. *Residue Rev.* **1969**, *25*, 13; *Chem. Abstr.* **1970**, *72*, 42.083w.
- Murray, J. I. *Org. Synth.* **1957**, *37*, 71.
- Ochiai, M.; Mizuta, E.; Asahi, Y.; Morita, K. *Tetrahedron* **1968**, *24*, 5861.
- Pissiotas, G. Ger. Offen. 2 031 400, 1971; *Chem. Abstr.* **1971**, *74*, 100.059x.
- Pissiotas, G. Swiss Patent 527 560, 1972; *Chem. Abstr.* **1973**, *78*, 25.379d.
- Rutz, H.; Gubler, K. S. African Patent 68 02 643, 1968; *Chem. Abstr.* **1969**, *71*, 38.964w.
- Rutz, H.; Gubler, K. S. African Patent 68 02 644, 1968; *Chem. Abstr.* **1969**, *71*, 70.601u.
- Ruzo, L. O. *Proceedings of the International Congress of Pesticides Chemistry*; Miyamoto, J. Kearney, P. C., Eds.; Pergamon: Oxford, 1983; *Chem. Abstr.* **1983**, *99*, 34.374j.
- Schulze, H.; Klein, H. P. U.S. Patent 4 032 484, 1977; *Chem. Abstr.* **1977**, *87*, 69.244q.
- Steimig, A.; Fischer, A. Ger. Offen. 2 005 325, 1971; *Chem. Abstr.* **1972**, *76*, 95.743q.
- Steimig, A.; Adolphi, H. Ger. Offen. 2 146 707, 1973; *Chem. Abstr.* **1973**, *79*, 14.452s.
- Stensio, K.; Wahlberg, K.; Wahren, R. *Acta Chem. Scand* **1973**, *27*, 2179.

- Takahashi, S.; Ando, M. Japan Kokai Tokkyo Koho 78 124 266, 1978; *Chem. Abstr.* 1979, 90, 186.944x.
 Wade, L. L.; Landram, J. F. U.S. Patent 3 565 992, 1968; *Chem. Abstr.* 1971, 75, 4621z.
 Wamhoff, H.; Kleimann, W. *J. Chem. Soc., Chem. Commun.* 1981, 743.
 Wamhoff, H.; Kleimann, W.; Kunz, G.; Theis, C. H. *Angew. Chem.* 1981, 93, 601; *Angew. Chem., Int. Ed. Engl.* 1981, 20, 612.
 Wamhoff, H.; Abdou, W. M.; Kunz, H.; Mahran, M. R.; Schupp, W.; Sidky, M. M.; Zahran, M. *Proceedings of the Beijing International Congress of Photochemistry (BICP), Abstracts of*

- Papers*; Academia Sinica: Beijing, PRC, 1985; p 144.
 Wasco, J. L. U.S. Patent 3 435 050, 1969; *Chem. Abstr.* 1969, 70, 115.154r.
 Wasserman, H. H.; Lipshutz, B. H. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic: New York, 1979; p 481.
 Wasserman, H. H.; Stiller, K.; Floyd, M. B. *Tetrahedron Lett.* 1968, 3277.
 Watkins, D. A. M. *Chemosphere* 1974, 5, 239.

Received for review January 20, 1987. Accepted August 10, 1987.

Metal Complexes of Picloram

Hope Heaster Michaud and Patrick E. Hoggard*

Insoluble complexes of picloram with nickel(II) and iron(II) are formed at near-neutral pH. This presents a mechanism for the possible removal of picloram from contaminated ground water, naturally or intentionally.

Picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid = Hpcl) is a widely used herbicide for control of perennial weeds and shrubs. It has been the herbicide of choice in some statewide leafy spurge control programs. Although its mammalian toxicity is relatively low, it is not easily degraded microbially (Foy, 1976), and therefore its persistence in the soil is of some concern. In surface waters photochemical degradation pathways do exist (Hedlund and Youngson, 1972; Skurlatov, 1983). Its solubility in water is moderate, 430 ppm (Weed Science Society of America, 1970). It is, however, usually applied as the much more water-soluble potassium salt, and in any case the free acid is converted to the anion in near-neutral or alkaline soils with even modest buffering capacity. Picloram should thus be highly mobile, and experimental studies have confirmed this (Baur et al., 1972). The obvious problems that can result if substantial amounts reach the ground water have spurred studies in geographic areas subject to intensive spraying (Glatt, 1985; Lym and Messersmith, 1986).

The pyridine-2-carboxylic acid functionality is well-known to coordinate metal ions strongly (Anderegg, 1960; Yuen et al., 1983). The consequences of metal ion coordination by picloram, aside from the biochemical implications for herbicidal activity, are not obvious a priori. Mobility may be increased or decreased. Depending on the lability of the complex formed, toxicity might be increased, decreased, or unaffected.

An earlier study showed relatively weak complex formation in solution between picloram and Fe(III) or Cu(II) (Chang and Foy, 1982). We report here the much stronger interaction with Fe(II) and Ni(II) ions under pH conditions closer to those in soils, and we discuss the implications for ground water contamination.

EXPERIMENTAL SECTION

Technical-grade picloram (free acid) was provided by Dow Chemical Co. It was recrystallized prior to use by

Table I. Infrared Data on Metal-Picloram Complexes

| | $\nu_a(\text{COO})$ | $\nu(\text{py})^a$ | $\nu(\text{py})^b$ |
|----------------------|-------------------------|--------------------|--------------------|
| HPcl | 1705 vs | 642 m | 431 m |
| Ni(pcl) ₂ | 1626 vs | 658 w | 484 w |
| Fe(pcl) ₂ | 1611 vs, 1640 w, 1674 w | 654 w | 459 w |

^a In-plane ring deformation. ^b Out-of-plane ring deformation.

slowly dissolving in warm (50 °C) methanol to saturation. Decolorizing charcoal was added and heating continued for 15 min. After filtration the solution was cooled and half the solvent was allowed to evaporate. The cream-colored crystalline picloram was filtered off and dried in a vacuum desiccator.

Ni(pcl)₂·4.5H₂O. Ni(NO₃)₂·6H₂O (2.9 g, 0.010 mol) was dissolved in 25 mL of H₂O. Picloram (4.8 g, 0.020 mol) and 0.80 g (0.020 mol) of NaOH were dissolved in warm absolute ethanol. The two solutions were combined. Upon cooling, a lime green crystalline precipitate was collected. It was soluble in EtOH and in water. Upon recrystallization twice from water and air-drying, the yield was 0.5 g. After air-drying for several days, the compound was no longer soluble in water or alcohols. Anal. Calcd for Ni(C₆H₂Cl₃N₂O₂)₂·4.5H₂O: C, 23.20; H, 2.09; N, 9.02; Cl, 34.31; Ni, 9.46. Found: C, 23.79; H, 2.21; N, 8.94; Cl, 34.48; Ni, 9.24.

Fe(pcl)₂·H₂O. FeSO₄·7H₂O (3.1 g, 0.010 mol) was dissolved in 25 mL of H₂O. Picloram (4.8 g, 0.020 mol) and 0.80 g (0.020 mol) of NaOH were dissolved in 25 mL of warm EtOH. When the two solutions were mixed, a burnt orange precipitate formed. This was insoluble in water, alcohols, CH₃CO₂H, CH₃CN, and DMSO. After the precipitate was washed with MeOH and air-dried, the yield was 4.5 g. Anal. Calcd for Fe(C₆H₂Cl₃N₂O₂)₂·H₂O: C, 25.95; N, 10.09; Cl, 38.39; H, 1.08; Fe, 10.07. Found: C, 26.05; N, 10.05; Cl, 38.49; H, 1.25; Fe, 10.03.

Instrumentation. X-ray powder diffraction spectra (Philips APD-3600) were recorded to confirm the crystallinity of the two complexes. Infrared spectra were measured on a Mattson Cygnus FTIR spectrometer and UV-visible spectra on a Hewlett-Packard 8451 diode array spectrometer.

* Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105.