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Mechanistic Implications of the Intrahumic Dechlorination of Mirex

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The hydrophobic chlorocarbon mirex readily binds to aqueous humic acids (HAs). In HA solutions irradiated at sunlight wavelengths ($\lambda \geq 290$ nm), mirex molecules bound to HAs are transformed to photomirex by dechlorination. The mechanism of this intrahumic dechlorination was investigated both in HA solutions and in model systems simulating select photochemical capabilities of HAs. In HA solution, the reaction was unaffected by methanol and pentanol; was accelerated by hydroxide; and was inhibited by oxygen, 2-chloroethanol, nitrate, and hydrogen ion, all four of which can scavenge hydrated electron. Additional experiments probing for involvement of hydrated electron were consistent with it as the reactant. In irradiated *N*,*N*-dimethylaniline solution, a model system for generating hydrated electron, mirex was dechlorinated to form photomirex, the same product that is found in HA solution. Relative rate experiments in HA solution, while inconsistent with the reaction with hydrated electron in homogeneous solution, were consistent with reaction with a purely intrahumic hydrated electron. However, other humic-generated reductants cannot be eliminated as possible reactants. The potential confounding influence of hydrophobic partitioning to HAs on investigations using molecular probes is evaluated in terms of current data and previous reports.

Introduction

The chlorocarbon pesticide, mirex (Figure 1), is held to be a persistent, unreactive pollutant because it resists biodegradation (*1*) and partitions readily to sediment (*2*), natural dissolved organic matter (*3*, *4*) and biota (*5*). The lifetime of mirex in Lake Ontario, where mirex is a contaminant, is estimated at 10 years and is thought to be limited mostly by sediment burial (*6*). Mirex nevertheless is readily transformed in sunlit Lake Ontario water by dechlorination to form 8-monohydromirex (*7*), commonly called photomirex (Figure 1). The same reaction occurs in humic acid solutions irradiated at sunlight wavelengths (*7, 8*) with the transformation being a photochemical reaction that is mediated by natural dissolved organic matter (DOM) (*8*). This reaction is the source of photomirex found in Lake Ontario water, sediments, and biota (*9*).

Photochemical activity is observed both in native waters containing DOM and in aqueous solutions of isolated humic materials (*10*−*13*). These reactions include the formation of excited states capable of energy (*10*) and electron transfer (*14*) as well as the generation of short-lived reactants such as hydroxyl radical (*15*), hydrogen peroxide (*16*), and hydrated electron (*11*). While many organic contaminants undergo phototransformations mediated by DOM (*17*−*19*), mirex is unique because it is the first organic compound identified as transformed entirely via intrahumic reaction; that is, only mirex molecules bound to DOM undergo reaction (*8*). As the greatest fraction of mirex in Lake Ontario water (36−64%) is bound to DOM (*4*), this reaction has the potential to contribute significantly to the environmental fate of mirex.

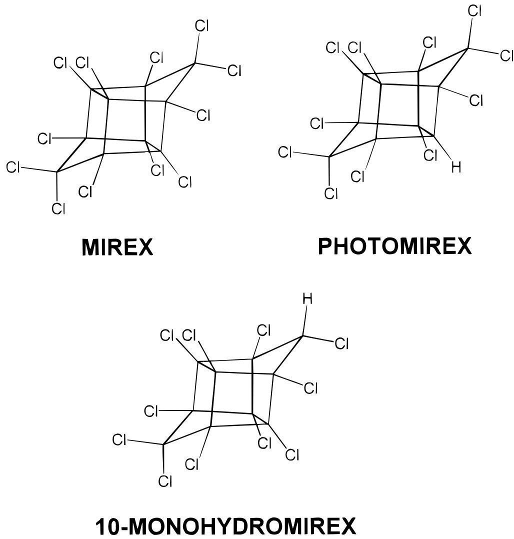

FIGURE 1. Structures of mirex, photomirex (8-monohydromirex), and 10-monohydromirex.

Several transient reactants produced by DOM may be capable of dechlorinating mirex, including carbon-centered radicals (*20*, *21*) and hydrated electron (*11*, *22*). DOM also could dechlorinate mirex through electron transfer or other reduction reactions (*14*, *23*, *24*). In this work, we report the results of experiments designed to elucidate the mechanism by which DOM transforms mirex to photomirex. Experiments were performed both in humic acid solution, looking at the effect of scavengers of various transient reactants on the reaction of mirex, and in model systems using compounds known to generate individual transient reactants.

Experimental Section

Materials. Humic acid was obtained from Aldrich Chemical Company as the sodium salt. Mirex (100%) was obtained from the U.S. EPA Pesticides and Industrial Chemical Repositories, and photomirex (97%) was from the Environmental Health Directorate of Health and Welfare Canada. Additives to humic acid solution were oxygen (UHP), argon (UHP), sodium or potassium nitrate (Fisher, certified), hydrochloric acid (EM, reagent), sodium hydroxide (Fisher, reagent), 2-chloroethanol (Kodak), methanol (Mallinckrodt Ultimar), and 1-pentanol (Aldrich). Additives to solutions of *N*,*N*-dimethylaniline (Aldrich) included nitrous oxide (Scott Specialty Gases, 10% in N_2) and trichloroacetic acid (Fisher, certified). Reference compounds used in relative rate experiments were chlorobenzene (Aldrich), lindane (Ultra Scientific, 99%+), and ortho- and meta-dichlorobenzene (Aldrich). Internal standards were octachlorostyrene and PCB congeners 14, 65, and 209 (99%+), all obtained from Ultra Scientific. All aqueous solutions were prepared using water purified with a Millipore four-bowl standard system (Milli-Q water), and all extraction solvents (hexane, isooctane) were pesticide grade (J. T. Baker Resi-Analyzed).

Mechanistic Experiments in Humic Acid (HA) Solution. HA solution preparation and DOC measurements are de-

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scribed elsewhere (*8*). Unless otherwise specified, all HA solutions were ~pH 6. Irradiations were performed using an Osram 150W/1 Xenon arc lamp in an Oriel uniform beam illuminator housing (Model 6148) powered by an Oriel universal power supply (Model 6240). Reaction vessels were 25 × 150 mm Kimax borosilicate culture tubes having Teflon-lined caps (Kimble 45066A-25150). The wavelength cutoff of the tubes was ~290 nm. HA solutions were amended with mirex in methanol (10-μL aliquots, final mirex concentration ~100 ng/L) and allowed to equilibrate 24 h prior to use. Aliquots (40 mL) of these solutions were amended with O_2, Ar, NO_3^-, 2-chloroethanol, methanol, or 1-pentanol after transfer to culture tubes. Gases (10 min bubbling at 0.1 L/min) and NO_3^- were added immediately prior to irradiation while the remaining compounds were added 24 h prior to irradiation. Irradiations were performed with the culture tubes placed in an inverted position directly against the condenser assembly of the lamp housing. Unless otherwise specified, solution temperatures during these and other irradiations were ~25 °C.

Mirex and photomirex were extracted from HA solution following a reported amended method (*8*) of Driscoll et al. (*25*). Analyses in these and all subsequent experiments were performed using methods and gas chromatography instrumentation described elsewhere (*8*).

Reactions in *N,N*-Dimethylaniline (DMA) Solution. Irradiations were performed using the lamp system described in the previous section. Reaction vessels were 110 × 285 mm (2 L) Wheaton-33 (borosilicate glass) roll bottles (wavelength cutoff ~295 nm). Roll bottle caps were customized with stainless steel disks having a through port (1/8-in. SS tubing) that was used both for sample withdrawal and gas introduction.

DMA solutions (~0.001 M) were prepared in roll bottles. DMA and analytes (mirex, chlorobenzene, lindane) dissolved in methanol were added to 1.7 L of water, and the solution was stirred in the dark with a glass-sealed magnetic stirbar for 24 h prior to use. Final analyte concentrations were 50−100 ng/L. Following the method of Kohler et al. (*26*), all DMA solutions were amended with methanol (final concentration 0.05 M) to suppress side reactions. Trichloroacetate and 2-chloroethanol were added to solutions at the same time as DMA. Gases (Ar, 10% N_2O in N_2) were added immediately prior to irradiation. Solutions in roll bottles were irradiated with stirring flush against the condenser assembly of the lamp housing. All experiments were replicated and matched with dark and light (irradiated solutions containing no DMA) controls.

Samples (40−50 mL) were withdrawn from roll bottles with a glass syringe and transferred to culture tubes containing 0.4 g of NaCl (Fisher certified). NaCl was heated to 600 °C overnight in a muffle furnace prior to use and was added to culture tubes to promote extraction of analytes. After sample transfer, the syringe was rinsed with 2 mL of methanol, and the methanol was added to the sample. Analytes were extracted from solution into hexane or isooctane (2−4 mL) by liquid−liquid extraction performed in the culture tubes.

Relative Rate Experiments in HA Solution. Most relative rate experiments were performed using roll bottles as reaction vessels. The light source was a Hanovia 450-W medium pressure Hg lamp housed in a reflector (Ace Glass 7883-02) and powered by an Ace Glass cased power supply (7830-60). HA solutions in roll bottles were amended as needed with mirex, lindane, DMA, and ortho- and meta-dichlorobenzene 24 h prior to irradiation. All solutions were bubbled with Ar immediately prior to irradiation. Solutions were irradiated with stirring ~20 cm in front of the lamp and were kept cool during irradiation with both a fan and a water-driven turbine stirrer (Fisherbrand 14511210). Samples (40 mL) were withdrawn from solutions with a glass syringe, transferred to culture tubes, and extracted as previously described for HA solutions.

Mirex and lindane relative rate experiments not involving DMA were performed in culture tubes with HA solution prepared as previously described. Culture tubes were irradiated in a photooxidation apparatus using an Oriel 350-W Hg arc lamp (Model 6286) powered by an Illumination Industries 350-W power supply. The distance between lamp and sample was 2 cm.

Quantum Yield. The wavelength dependence for the reaction of mirex in air-equilibrated Aldrich HA solution (10 mg/L DOC) was investigated over the region of 290−700 nm. Preliminary experiments performed using long wave pass filters indicated that the reaction did occur at wavelengths greater than 400 nm but not 500 nm. However, at wavelengths >310 nm, reaction of mirex was too slow to be measured when irradiations (<15 h) were performed using light from the Xe lamp that had passed through a high-intensity monochromator (19.2 nm band width, Bausch & Lomb Model 338679). A single reaction quantum yield was determined in a time series experiment performed at 300 nm using the monochromator and Xe lamp. The reaction vessel was a cylindrical quartz cell having a 10-cm path length and total volume of 20 mL. Solution temperature during irradiation was 22 °C. Light flux in the cell was measured using ferrioxalate actinometry (*27*). The preparation and extraction of the HA solution were performed as previously described, and each time series sample was matched with a dark control.

Kinetics. The transformation of mirex to photomirex in HA solution obeys rate laws for a consecutive, pseudo-first-order reaction (*7*, *8*). This reaction can be followed using photomirex (P) to mirex (M) concentration ratios and the integrated rate equation (*7*)

$$\mathrm{P/M} = \frac{k_{\mathrm{M}}'}{k_{\mathrm{M}}' - k_{\mathrm{P}}'}\left(e^{t(k_{\mathrm{M}}' - k_{\mathrm{P}}')} - 1\right) \tag{1}$$

where t is time and k_M' and k_P' are the respective reaction rate constants for mirex and photomirex. The alternate equation (*7*)

$$\ln\left(1 + \frac{\mathrm{P}}{\mathrm{M}}\right) = k_{\mathrm{M}}'t \tag{2}$$

applies when transformation of mirex to photomirex is <25% (*8*). Equation 1 was used to calculate k_M' in time series experiments, and eq 2 was used in single point irradiations.

Results

Humic Acid (HA) Solutions. The HA-mediated dechlorination of mirex follows apparent first-order kinetics according to

$$\mathrm{d[M]}/\mathrm{d}t = -k'[\mathrm{M}] \tag{3}$$

where [M] is the concentration of mirex and k' is the apparent first-order rate constant for the reaction of mirex. For reaction with a single transient reactant, this apparent rate constant is defined by (*12*)

$$k' = k_{\mathrm{M}}[\mathrm{X}]_{\mathrm{ss}} \tag{4}$$

where $[X]_{ss}$ is the steady-state concentration of the unknown DOM-photogenerated transient reactant X and k_M is the second-order rate constant for the reaction of mirex with X. Previously, we reported that k' in Aldrich HA solution decreased when select compounds were added to HA solution to scavenge X and thus reduce its steady-state concentration (*8*). These additives include oxygen (O_2), hydrogen ion (H^+), nitrate (NO_3^-), and 2-chloroethanol but not methanol or 1-pentanol (Figure 2).

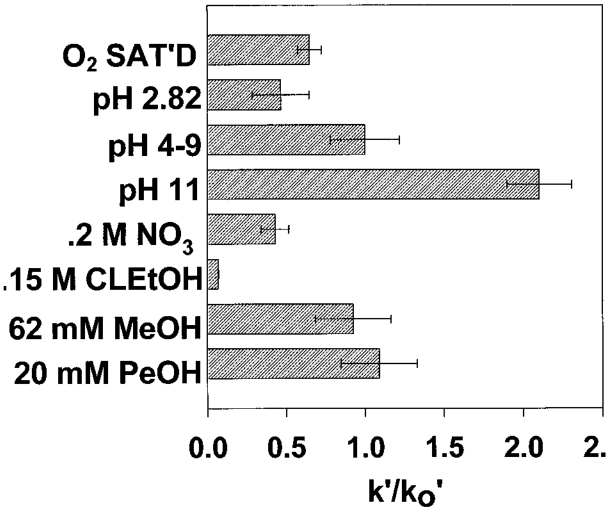

FIGURE 2. Effect of oxygenation (O_2 SAT'D), pH, nitrate (NO_3^-), 2-chloroethanol (ClEtOH), methanol (MeOH), and pentanol (PeOH) on the apparent rate constant (k') for the indirect photolysis of mirex in humic acid solution. Values of k' are reported relative to values in control solutions (k_0'). Error bars represent standard deviation.

O_2 is known or thought to be involved in the production and decay of various DOM-generated reactants. For example, O_2 can scavenge triplet energy to form singlet oxygen (*10*) and can scavenge hydrated electron (*11*) and reductants (*28*) to form superoxide anion (*12, 28*). Figure 2 shows that the mirex apparent reaction rate constant (k') decreased 40% in O_2 rich HA solution (33 mg/L DOC) relative to matching solution depleted in O_2. This precludes transient reactants such as superoxide anion or singlet oxygen from causing the reaction of mirex because O_2 is required for their production (*10, 28*). At the same time, this decrease implicates reactants for which O_2 is a scavenger, such as carbon-centered radicals (*20*), electron donors (*28*), or hydrated electron (*11*). Alternatively, O_2 could decrease k' by quenching excited states that are precursors to the reactant responsible for mirex transformation. However, involvement of energy transfer in the reaction is not likely because, even in systems with high enough energy to access the excited states of chlorocarbons and chlorinated aliphatic hydrocarbons, quenching of excited singlet and triplet states typically occurs through electron transfer (*29, 30*).

NO_3^- is a photochemical source of hydroxyl radical (*31*), is a scavenger of hydrated electron (*32*−*34*), and quenches some electron transfer reactions through what is thought to be an electron-exchange reaction initiated by NO_3^- on contact with excited electron donors (*35*). As reported previously, k' decreased with increasing NO_3^- concentration in O_2-depleted HA solution (33 mg/L DOC) (*8*). Figure 2 shows that at 0.2 M NO_3^-, k' decreased by ∼60%. This decrease in k' precludes the involvement of the hydroxyl radical as significant to the reaction of mirex. This was confirmed using Fenton's reagent following the method of Draper and Crosby (*36*), which did not cause an observable reaction of mirex.

The effect of pH on the reaction of mirex in O_2-depleted HA solution (33 mg/L DOC) is shown in Figure 3. Between pH 4 and pH 9, k' was relatively constant. However, k' decreased at low pH and increased at high pH. These trends are not likely to be due to pH-induced changes in solution absorbance because, while k' does not increase significantly between pH 6 and pH 9 (95% CI), the absorptivity of the HAs at any wavelength between 290 and 700 nm more than doubles when the pH is increased over the same range. These trends in k' also cannot be due to pH-induced changes in mirex HA−water partitioning because the reaction of mirex in HA solution is limited to mirex molecules that are bound to HA molecules (*8*) and hydrophobic binding to HAs decreases with increasing pH (*37*).

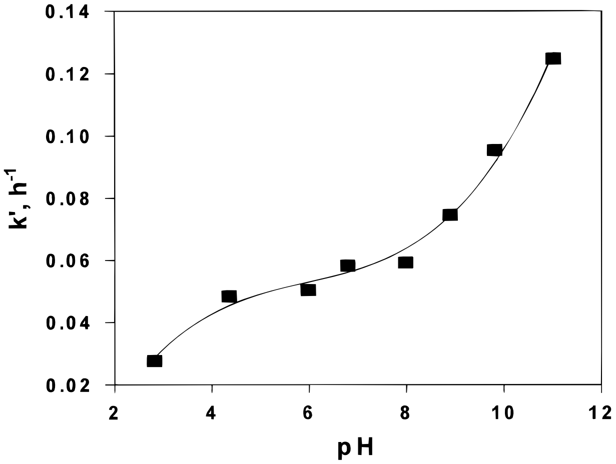

FIGURE 3. Effect of pH on the apparent rate constant (k') for the indirect photolysis of mirex in humic acid solution (33 mg/L DOC).

The increase in k' at high pH may be significant because hydroxide (HO^-) and NO_3^- quench electron transfer reactions with equal facility (*38, 39*). Quenching of electron transfer reactions by these and similar inorganic anions is thought to occur through electron exchange reactions that are initiated when an anion donates an electron to the ground-state "hole" in the excited electron donor (*35, 38, 39*). Supporting this mechanism, the quenching capabilities of these anions are correlated to the anion oxidation potentials rather than reduction potentials (*35, 38, 39*). The respective aqueous phase oxidation potentials of HO^- and NO_3^- are reported to be 2.29 and 2.3 eV vs the standard hydrogen electrode (*40*). Because NO_3^- and HO^- have opposite effects on the reaction of mirex in HA solution, these potentials mean that NO_3^- is likely to be interfering in the reaction by some mechanism other than quenching of excited electron donors. Consistent with this, fluorescence quenching commonly has been used to detect quenching of electron transfer reactions by NO_3^- (*35, 38*), but NO_3^- does not measurably decrease the fluorescence intensity of humic materials (*34*).

The decrease in k' at low pH is potentially significant because H^+, NO_3^-, and O_2 all are known to react with the hydrated electron (e_{aq}^-) at diffusion-controlled rates (*38*), suggesting that e_{aq}^- could participate in the transformation of mirex to photomirex in HA solution. In support of this, 2-chloroethanol decreased k' in O_2-depleted HA solution (10 mg/L DOC) (*8*). 2-Chloroethanol has been used as an e_{aq}^- probe in many systems, including HA solution (*11*), and has a reduction potential greater than that of water (*42*). At 0.15 M 2-chloroethanol, k' decreased by >90% (Figure 2). Methanol and pentanol had no effect on k' (Figure 2), indicating that 2-chloroethanol decreased k' not as an alcohol but as a chlorinated compound. This last result tends to preclude the involvement of carbon-centered radicals as significant to the reaction of mirex because carbon-centered radicals generally preferentially abstract hydrogen over chlorine (*43*).

Previous work has shown that mirex can be dechlorinated through electron transfer both from ground-state porphyrins (*24*) and in a charge-transfer complex with triethylamine (*23*). The dominant product of those reactions is 10-monohydromirex (Figure 1), with photomirex formed as only a minor product (*23*). The formation of 10-monohydromirex as the dominant product of electron transfer reactions is somewhat expected because these reactions have been shown to be largely controlled by redox potentials (*44*), and geminal dihalides typically are more easily reduced than isolated halides (*45, 46*). Nevertheless, the formation of photomirex as the product of the DOM-mediated reaction of mirex could be expected of an electron transfer reaction from DOM to mirex. In contrast, the reactivity of mirex toward e_{aq}^- and

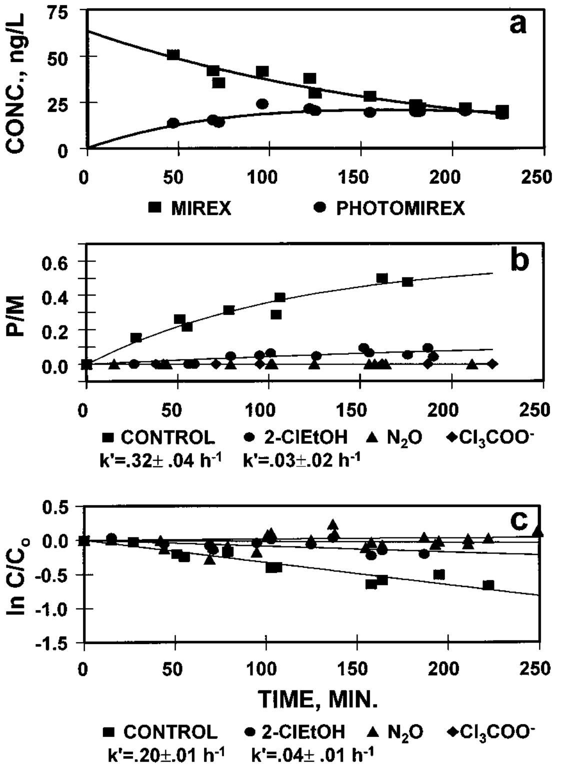

FIGURE 4. (a) Disappearance of mirex and appearance of photomirex in irradiated DMA solution. (b) Effect of 0.05 M 2-chloroethanol (2-ClEtOH), 0.005 M N_2O, and 0.05 M trichloroacetate on the apparent rate constant (*k'*) for transformation of mirex (M) to photomirex (P) in irradiated DMA solution. (c) Effect of 0.05 M 2-chloroethanol (2-ClEtOH), 0.005 M N_2O, and 0.05 M trichloroacetate (Cl_3COO^-) on the apparent rate constant (*k'*) for the reaction of lindane in irradiated ($\lambda \geq 290$ nm) DMA solution.

the product or products of the reaction of mirex with e_{aq}^- have not been reported.

Dimethylaniline Solution. To test whether e_{aq}^- could transform mirex to photomirex, the reaction of mirex was studied in irradiated ($\lambda \geq 290$ nm) aqueous solutions of *N*,*N*-dimethylaniline (DMA), which are known to produce e_{aq}^- (*26, 47*). Figure 4a shows the disappearance of mirex and the appearance of photomirex in DMA solution. Loss of mirex or formation of photomirex was not detected in dark or light controls. As with the reaction of mirex in HA solution, the reaction of mirex in DMA solution obeyed kinetics for a consecutive, pseudo-first-order reaction.

Figure 4b shows that the reaction of mirex in DMA solution was nearly quenched by 0.05 M 2-chloroethanol and was completely quenched by 0.05 M trichloroacetate (pH 8) and ~0.005 M N_2O, both of which are also e_{aq}^- scavengers (*11, 26*). These results are expected if mirex reacts with e_{aq}^- in DMA solution. Using chlorobenzene (CB, 50 μM) as a molecular probe for e_{aq}^- (*48, 49*), the measured steady-state concentration of e_{aq}^- ($[e_{aq}^-]_{ss}$) in DMA solution was 5.4×10^{-14} M. Assuming that measured residual oxygen (8.3×10^{-5} M) controls $[e_{aq}^-]_{ss}$ in DMA solution and given a rate constant of 2×10^{10} M^{-1} s^{-1} for the reaction of O_2 with e_{aq}^- (*41*), the calculated production rate of e_{aq}^- in these solutions was 8.9×10^{-8} M s^{-1}. Given a rate constant for reaction of 2-chloroethanol with e_{aq}^- of 2×10^8 M^{-1} s^{-1} (*50*), 0.05 M 2-chloroethanol should decrease $[e_{aq}^-]_{ss}$, and thus *k'*, by 86%, in good agreement with observation (85%). Furthermore, given the rate constants for the reaction of trichloroacetate and N_2O with e_{aq}^- (8.5×10^9 and 9.1×10^9 M^{-1} s^{-1}, respectively; *41*), 0.05 M trichloroacetate and ~0.005 M N_2O should completely quench (>97%) the reaction of mirex with e_{aq}^-. This is also in agreement with observation. Mirex therefore appears to react with e_{aq}^- to form photomirex, the same product formed in HA solution.

The second-order rate constant for the reaction of mirex with e_{aq}^- was determined in DMA solution using the method of relative rates with CB as the original reference compound. CB was chosen because its rate constant for reaction with e_{aq}^- is known (5×10^8 M^{-1} s^{-1}; *48, 49*) and is typical of rate constants for chlorinated, aliphatic hydrocarbons (10^8–10^9 M^{-1} s^{-1}; *41*). However, because of the low solubility of mirex (~100 ng/L; *3*) and the low relative response factor of CB in GC–ECD analysis, CB could not be detected when added to DMA solution at concentrations equal to that of mirex. Consequently, lindane was chosen as an intermediate reference compound for the relative rate experiments. Lindane has a GC–ECD response factor similar to mirex and, like mirex, is a chlorinated, aliphatic hydrocarbon. Lindane also is more soluble in water (~10 ppm; *51*) than mirex, and its rate constant with e_{aq}^- therefore could be determined using CB as the reference compound.

The relative rate method was tested using meta- and ortho-dichlorobenzene. The compounds have a relative reaction rate (meta-/ortho-) with e_{aq}^- of 1.1 (*48*), the same ratio found in this study. No loss of lindane occurred in light or dark controls, and quenching of the lindane reaction by 2-chloroethanol, trichloroacetate, and N_2O was similar to that of mirex (Figure 4c). On average, lindane reacted 1.25 times faster than CB in DMA solution, and mirex reacted 1.44 times faster than lindane. Given the rate constant for reaction of CB with e_{aq}^-, these results translate into second-order rate constants for reaction with e_{aq}^- of $8.71 \pm 0.11 \times 10^8$ M^{-1} s^{-1} for mirex and $6.05 \pm 0.77 \times 10^8$ M^{-1} s^{-1} for lindane.

Relative Rate in HA solution. As was found with mirex, the reaction of lindane in HA solution was quenched by 2-chloroethanol (0.05 M) but was unaffected by methanol (up to 0.1 M; *52*). Furthermore, when the concentration of lindane in HA solution was increased to 8 mg/L, near its solubility (~10 mg/L; *51*), the mirex *k'* decreased by 43% (*8*). These results suggest that lindane and mirex are competing for the same transient reactant in HA solution. However, while mirex reacted only 1.44 times faster than lindane in DMA solution, it reacted 31 ± 2.4 times faster in HA solution (10 mg/L DOC) (Figure 5a). If the reactions of mirex and lindane were occurring in a single-phase or homogeneous solution, then the relative rate results would rule out e_{aq}^- as the sole transient reactant responsible for the reactions.

However, HA solution is not homogeneous, at least not to molecules capable of associating with or partitioning to HAs. In the case of mirex, reaction is limited to mirex molecules that are bound to HA molecules (*8*). This indicates that the transient reactant responsible for the dechlorination occurs mostly in the HA phase. The DOC–water partition coefficient (K_{DOC}) of mirex in Aldrich HA solution is $10^{6.26}$ (*8*), meaning that 95% of mirex molecules are bound in HA solution containing 10 mg/L DOC. In contrast, approximately 2% of the lindane molecules would be expected to be bound in this solution (Table 1). As a consequence, even if lindane and mirex were reacting only with e_{aq}^- in the HA solution, the relative reaction rate of the two compounds in that solution would be expected to differ from the relative rate in homogeneous DMA solution.

For a compound that reacts only with e_{aq}^- in HA solution, if the intra- and extrahumic reaction rate constants are the same, the effect of binding on apparent reaction rate constant (*k'*) can be represented by (*8*)

$$k' = k[e_{aq}^-]_d f_d + k([e_{aq}^-]_b/[DOC])f_b \qquad (5)$$

where *k* is the rate constant for reaction of the compound with e_{aq}^-; $[e_{aq}^-]_d$ and $[e_{aq}^-]_b$ are the respective steady-state concentrations of e_{aq}^- in the dissolved (d) and bound (b) phases of HA solution, both expressed as molar concentrations

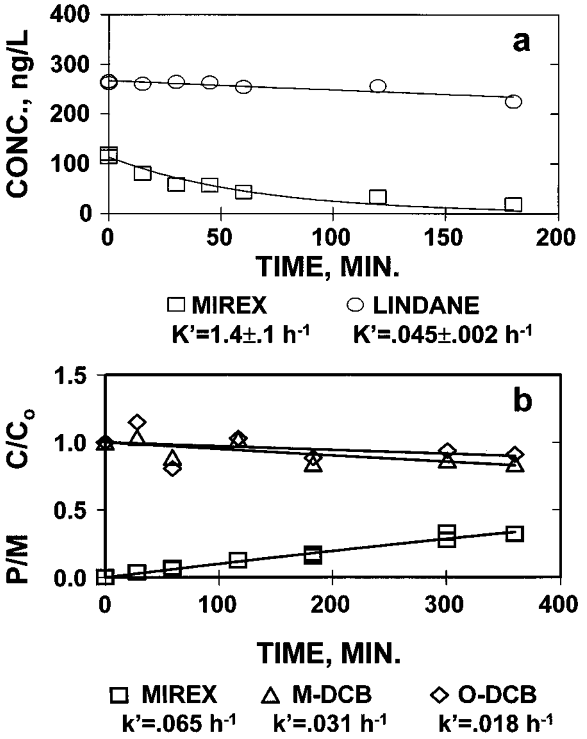

FIGURE 5. (a) Sample relative rate plot for the reactions of mirex and lindane in irradiated humic acid solution (10 mg of DOC/L). (b) Relative rate plot showing the transformation of mirex (M) to photomirex (P) and the disappearance of ortho- (O-DCB) and meta-dichlorobenzene (M-DCB) in irradiated humic acid solution (10 mg/L DOC).

TABLE 1. Comparison of Calculated and Apparent DOC-Bound Concentration Fractions (f_b) in HA Solution (10 mg/L DOC)

	log K_{DOC} [a]	calculated f_b [b]	apparent f_b [c]
lindane	3.22[d]	0.017	0.044
o-DCB	2.99[d]	0.010	0.023
m-DCB	3.21[d]	0.016	0.012

[a] DOC−water partition coefficient, L/kg. [b] Calculated using K_{DOC} values and eq 6. [c] Calculated from eq 7 assuming reaction with bound phase e_{aq}^- only. [d] Refs 51 and 54.

in the aqueous solution; [DOC] is the HA concentration (in kg/L); and f_d and f_b are the respective fractions of the compound in the dissolved phase and bound phases of HA solution. The value of $f_d = 1 - f_b$ and f_b is defined by (*53*)

$$f_b = \frac{K_{DOC}[DOC]}{1 + K_{DOC}[DOC]} \tag{6}$$

From eq 5, if e_{aq}^- were confined to the bound phase, then the ratio of the apparent reaction rate constants for two compounds (compounds 1 and 2) with e_{aq}^- in HA solution (k'_1/k'_2) would be

$$k'_1/k'_2 = \frac{k_1}{k_2}\frac{f_{b_1}}{f_{b_2}} \tag{7}$$

where k_1/k_2 is the ratio of their rate constants for reaction with e_{aq}^- and f_{b_1}/f_{b_2} is the ratio of the fractions of each compound bound. Note that eq 7 applies only when concentrations of the compounds are too low to significantly affect $[e_{aq}^-]_b$. For mirex and lindane in Aldrich HA solution having 10 mg/L DOC, if e_{aq}^- occurred only in the bound phase and mirex and lindane reacted only with e_{aq}^-, then a value of $k'_1/k'_2 = 31$ would mean that approximately 4% of the lindane molecules were in the bound phase of HA solution and therefore had access to e_{aq}^-. This value is in good agreement with expectation (~2%, Table 1). Similar good agreement between the expected and the observed binding of lindane in HA solution was reported previously and was based on the ability of lindane to quench the intrahumic reaction of mirex (*8*). Therefore, the relative rate results are quantitatively consistent with e_{aq}^- as the species responsible for the reaction of mirex in HA solution.

Results obtained using ortho-dichlorobenzene (o-DCB) and meta-dichlorobenzene (m-DCB) also are consistent with e_{aq}^-. The DCBs have second-order rate constants for reaction with e_{aq}^- nearly an order of magnitude greater than that of mirex (*48*) but, like lindane, have little affinity for HAs (Table 1). The relative rate of reaction of m-DCB to o-DCB in HA solution (1.73 ± 0.96) was not significantly different from the ratio of their rate constants (1.1; *48*), but mirex reacted 2−3.5 times faster than the DCBs (Figure 5b). Furthermore, at the DCB concentrations (~12 μg/L) needed to detect them simultaneously with mirex, the DCBs had the effect of decreasing the mirex k' by 73%. As with lindane, this result suggests that the DCBs and mirex are competing for the same transient reactant. Correcting for the decrease in $[e_{aq}^-]_b$ caused by the DCBs and assuming reaction of mirex and the DCBs only with intrahumic e_{aq}^-, 3.5% of the DCB molecules in this experiment apparently had access to intrahumic e_{aq}^- as compared with a prediction of 2.6% (Table 1).

These results illustrate one of the consequences of the effect of binding on DOM-mediated photoreactions: for compounds having different affinities for HAs, competition and relative rate results are expected to differ in HA solution vs homogeneous solution. This is true regardless of the relative contributions of the bound and dissolved phases to overall reaction rate constants (*8*). The reaction of mirex in HA solution represents one extreme, with the reactivity transforming mirex being restricted to the bound phase. At this extreme, compounds occurring primarily in the dissolved phase are expected to have both little access to bound-phase reactivity and little ability to compete for this reactivity. Reactivity restricted to the dissolved phase would be expected to give the opposite result, with bound-phase compounds being effectively protected from transformation. This is supported by a comparison of the reactions of lindane and mirex in HA solution (10 mg/L DOC) with and without added DMA (~0.001 M) (Figure 6). DMA has been used in previous work as a source of e_{aq}^- in HA solution supplementing that generated by HAs (*11*). Assuming the K_{DOC} of DMA is similar to that of other anilines (~100; *51, 55*), DMA has little affinity for HAs (f_b < 0.01). This means that DMA in HA solution constitutes a dissolved-phase source of e_{aq}^-. As Figure 6a illustrates, the loss of lindane was undetectable (95% CI) in the HA solution without added DMA even though the reaction of mirex went to ~75% completion. With added DMA (Figure 6b), the reaction of lindane was greatly accelerated but no change could be detected in the reaction of mirex (95% CI). The relative rate of reaction of mirex to lindane with added DMA was 1 ± 0.37, compared to 31 in HA solution having no DMA (Figure 5a). These results clearly indicate that the additional reactivity provided by DMA is unequally available to mirex and lindane. Assuming that DMA-photogenerated e_{aq}^- is available only to dissolved-phase compounds, the mirex k' in this solution would be predicted to increased by only 1.1%. This prediction agrees with the experimental result that DMA did not measurably affect the mirex reaction rate.

Quantum Yield. Quantum yields for e_{aq}^- production from humic materials in solution are reported to be as high as 0.22 when measured using flash photolysis (56). However, previous work generally has concluded that e_{aq}^- occurs in natural waters and solutions of humic materials at concentrations too low to transform pollutants (~10^{-17} M; *11*). The primary reason e_{aq}^- has been dismissed as an important intermediate

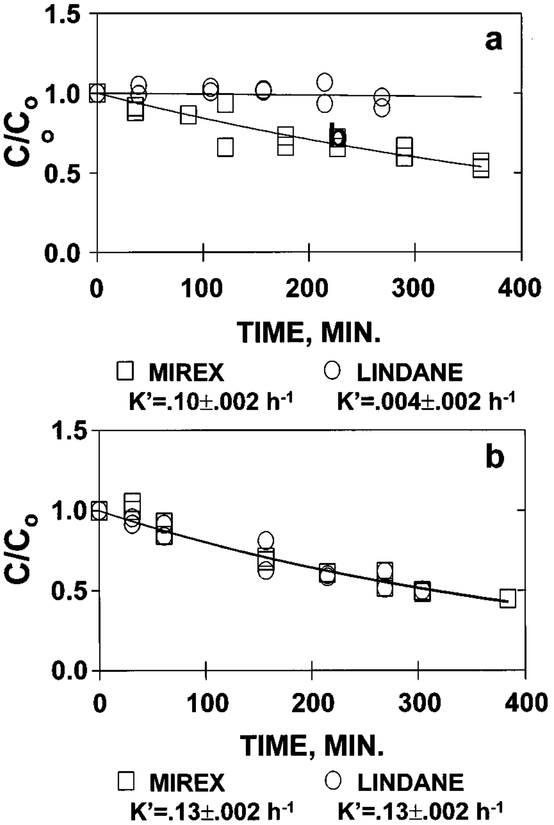

FIGURE 6. Relative rate plots showing the disappearance of mirex and lindane in Aldrich humic acid solution (10 mg of DOC/L) in the absence (a) and presence (b) of added DMA (0.001 M).

is the contrast between e_{aq}^- quantum yields measured using flash photolysis and those measured using 2-chloroethanol as a molecular probe for e_{aq}^- (*11*). Using the same solutions, the range of quantum yields determined by nanosecond flash photolysis was 0.0017–0.0076 while the range of quantum yields measured using 2-chloroethanol was <0.8–12 × 10^{-5}. It was originally hypothesized that this difference might be explained if some e_{aq}^- measured by flash photolysis existed in a kind of radical cage that collapsed before e_{aq}^- could escape to react with, and thus be measured by, 2-chloroethanol. Another explanation is that e_{aq}^- does not escape the HA matrix and that 2-chloroethanol, with an estimated K_{DOC} of 1.4 (*51, 54*), occurred in these solutions almost exclusively in the dissolved phase. The possibility of a purely intrahumic e_{aq}^- is supported by the work of Breugem et al. (*34*), who used NO_3^-, Zn^{2+}, and chloroform as molecular probes for e_{aq}^- to estimate the lifetime of e_{aq}^- generated in natural waters and HA solutions under steady-state conditions. Based on an estimated lifetime of 0.2 ns in HA solution and an average distance covered during that lifetime of 1.3 nm, the authors concluded that e_{aq}^- was confined to the humic matrix during its lifetime.

Assuming that reaction of mirex in HA solution is mediated solely by e_{aq}^- and is entirely intrahumic, eq 5 can be used to calculate the e_{aq}^- quantum yield if $[e_{aq}^-]_b$ is defined as

$$[e_{aq}^-]_b = \frac{I_{300}(1 - 10^{-\epsilon_{300}[DOC]l})\Phi_{300}}{k_r} \qquad (8)$$

where ϵ_{300} is the absorption coefficient for HA at 300 nm [in units of (kg/L DOC)$^{-1}$ cm^{-1}], Φ_{300} is the quantum yield for e_{aq}^- production at 300 nm, and k_r is the apparent rate constant (s^{-1}) for all processes removing e_{aq}^- from the humic matrix.

The apparent rate constant for reaction of mirex was 2.15 × 10^{-6} s^{-1} in air-equilibrated HA solution (10 mg/L DOC) at 300 nm. The light flux (I_{300}) in the solution was 1.1 × 10^{-9} Einsteins/L s^{-1}. Using the measured ϵ_{300} value of 2.1 × 10^4 (kg/L DOC)$^{-1}$ cm^{-1}, a path length of 10 cm, and the average apparent k_r value of 1.33 × 10^9 s^{-1} calculated by Breugem et al. (*34*) yields $\Phi_{300} = 0.03$ from eqs 5 and 8. This quantum yield falls within the range of values previously measured (0.22–0.0017; *11, 56*) using flash photolysis (355 nm) in both natural waters and solutions of humic materials. Therefore, the calculated quantum yield is consistent with the assumption that the intrahumic dechlorination of mirex is mediated by e_{aq}^-.

An intrahumic e_{aq}^- quantum yield measured by mirex in air-equilibrated HA solution (20 °C) would not be expected to differ significantly from one measured by mirex in deoxygenated solution. As previously demonstrated (*8*), the ability of scavengers to interfere in intrahumic reactions depends on the number of scavenger molecules present in individual HA molecules, with scavenger molecules being distributed in HA molecules according to a Poisson distribution. According to this distribution, the probability (Pr_n) of finding no scavenger molecules in an HA molecule ($n = 0$) is

$$Pr_n = e^{-N} \qquad (9)$$

where N in HA solution is the average number of humic-associated scavenger molecules per humic molecule. N is given by (*8*)

$$N = 10^{-3} f_c \mathrm{MW}_{HA} \frac{K_{DOC}}{1 + K_{DOC}[DOC]}[S] \qquad (10)$$

where f_c is the weight fraction of organic carbon in humic molecules, MW_{HA} is the gram molecular weight of the humic molecules, [S] is the truly dissolved (not bound) concentration of the scavenger, and K_{DOC} and [DOC] are expressed in units of L/kg and kg/L, respectively. Assuming $f_c = 0.5$ (*57*), $\mathrm{MW}_{HA} = 10^5$ g/mol (*58*), and $K_{DOC} = 1$ for O_2 then, given a bulk solution O_2 concentration of 2.84 × 10^{-4} M (20 °C), eqs 9 and 10 indicate that there is a >98% probability of finding no O_2 molecules in an HA molecule (10 mg of DOC/L). This means that >98% of all bound mirex molecules would be likely to react with e_{aq}^- without competition from O_2. This result illustrates another consequence of the effect of binding on DOM-mediated photoreactions: because it is possible for a hydrophilic scavenger to have little access to intrahumic transient reactants in spite of high bulk solution scavenger concentrations, it is also possible for transient reactant production rates and intrahumic steady-state concentrations to be substantially underestimated by molecular probes, such as 2-chloroethanol, that have little tendency to partition to HAs.

Environmental Significance

All of the experimental results are consistent with the assumption that e_{aq}^- is the transient reactant responsible for the intrahumic dechlorination of mirex to form photomirex. The results also eliminate oxidants such as hydroxyl radical and superoxide as being important to the reaction. However, they cannot rule out the possibility that some other photogenerated, humic-associated reductant is actually responsible for the reaction. Even though the actual reactant has not been firmly identified, the relative experiments with lindane and the DCBs indicate that reactivity with e_{aq}^- combined with DOM-binding affinity is a potentially useful predictor of photoreactivity of chlorinated compounds in natural water.

This reaction is potentially very significant for compounds that are associated with natural organic matter in sunlit water. This is exemplified by the photomirex to mirex concentration ratios (P/M ratios) found in the Lake Ontario system (*9*). Up to 65% of the mirex in the Lake Ontario water column is bound to DOM (*4*), but >99% of the incident sunlight is captured within only 15% of the lake volume (*59*, *60*). As a consequence, P/M ratios in lake surface sediments are approximately 0.1 (*5*, *9*). This ratio represents a time-integrated average for the entire lake water column and indicates that, on a whole lake basis, intrahumic reaction is relatively unimportant to the fate of mirex. However, P/M ratios peak at ~1 in Lake Ontario surface waters when the lake is stratified (*9*). In the St. Lawrence River, which receives only Lake Ontario surface waters, the average P/M ratio in sediments is 0.35 (*9*). This ratio is similar to those found in Lake Ontario biota, which include 0.34−0.42 in herring gull eggs (*61*, *62*), 0.37 in herring gulls (*62*), and 0.44−0.48 in fish (*63*). P/M ratios in the Lake Ontario food chain consequently reflect P/M ratios in Lake Ontario surface waters. On the basis of these ratios, the intrahumic reaction of mirex is significant. If this reaction is in fact mediated by e_{aq}^-, then e_{aq}^- acquires renewed environmental significance. Furthermore, because chlorinated aromatic hydrocarbons such as dichlorobenzenes react with e_{aq}^- about 20 times faster than does mirex, intrahumic e_{aq}^- could be even more significant to the environmental fate of hydrophobic halogenated aromatic hydrocarbons such as PCBs.

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