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Binding Effects on Humic-Mediated Photoreaction: Intrahumic Dechlorination of Mirex in Water

SUSAN E. BURNS,*
JOHN P. HASSETT, AND
MAURA V. ROSSI†

Department of Chemistry, State University of New York College of Environmental Science & Forestry, Syracuse, New York 13210

A kinetic model was developed describing the effects of hydrophobic partitioning to humics on second-order humic-mediated photoreactions in aqueous solution. Model development and evaluation were in terms of the humic-mediated dechlorination of the hydrophobic chlorocarbon, mirex. Mirex dechlorination in irradiated ($\lambda \geq 290$ nm) Aldrich humic acid (HA) solution was examined as a function of humic acid and scavenger concentration. Kinetic models in which HA solution is described as a homogeneous or single-phase solution were not able to describe the effects of HA and scavenger concentrations on mirex dechlorination rates. However, these effects were successfully described by including partitioning in the models to characterize the bound phase and dissolved phase mirex reactions separately. The resulting model uses homogeneous phase kinetics to describe reaction in the dissolved phase. Bound phase reaction is described as occurring within individual HA molecules with the distribution of scavengers within HA molecules following a Poisson distribution. Used to assess the relative reactivities of the bound and dissolved phases, the model indicated that the reaction of mirex in HA solution is confined to the humic phase. The general predictions and utility of the model are evaluated both in terms of experimental data and pollutant photodegradation.

Introduction

Sorption of organic pollutants to humic materials or natural organic matter affects pollutant reactivity. Reported effects of sorption on reactivity include acceleration of acid-catalyzed hydrolysis and retardation of base-catalyzed hydrolysis (*1*, *2*), acceleration and inhibition of photolysis rates (*3*−*5*), and changes in reaction products and product ratios (*3*, *6*). In some cases, reactivity is altered because sorbed pollutants appear to encounter a solution microenvironment that is different from the bulk solution. For example, the buffer-catalyzed hydrolysis of humic-bound molecules apparently is analogous to intramicellar hydrolysis, with the environment of the sorbed molecules being buffered by the humic materials (*7*). In other cases, the reactivity of sorbed pollutants is altered because humic materials are themselves reactive. The contribution of humic reactivity to the transformation of sorbed pollutants is most apparent in reports of pollutant photochemistry.

In sunlit surface waters, humic materials either directly or through secondary photoreactions appear to be capable of initiating photosensitization reactions, photooxidations, photoreductions, and radical reactions (*8*−*10*). Some pollutants, such as ethylenethiourea, are resistant to direct photoreaction in sunlight but nevertheless undergo phototransformations in the presence of humic materials (*11*). The ability of molecules to be transformed by humic-mediated photoreactions can be influenced by binding or other interactions that bring molecules into close proximity with humic materials. For example, Blough (*12*) demonstrated that EPR signal loss in nitroxide probes was a function of electrostatic interactions between the probes and humic materials in solution, with cationic probes apparently encountering a greater number of humic-generated reductants or carbon-centered radicals than neutral and anionic probes. Similarly, Green et al. (*13*) found both that cationic nitroxides were more efficient than neutral nitroxides at quenching the fluorescence of humic materials and that the quenching of humic fluorescence by anionic nitroxides was undetectable. These results indicate that at least some humic reactivity is not homogeneously distributed in solution. They also indicate that this inhomogeneity in reactivity is a function of the ability of molecules to approach or come into contact with humic materials. This raises the possibility that pollutants sorbed to humic materials in water can undergo reactions not readily available to molecules restricted to the bulk solution.

The previously reported photodechlorination of the hydrophobic pesticide mirex in humic acid solution (*14*, *15*) appears to exemplify the ability of humic materials to act as a distinct reactive phase in water. In this work, we develop a kinetic model describing the effects of sorption on second-order humic-mediated photoreactions. Application of this model to the photodechlorination of mirex indicates that only sorbed mirex undergoes photodechlorination in humic acid solution and that the reaction can be described as occurring wholly within humic acid molecules.

Experimental Section

Materials. Solvents used were hexane (Resi-Analyzed, J. T. Baker Inc.) and methanol (Optima, Fisher Scientific). Commercial humic acid was obtained from Aldrich Chemical Company as the sodium salt. Mirex (dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane, 100%) was obtained from the U.S. EPA Pesticides & Industrial Chemical Repository, and photomirex (1,2,3,4,5,5,6,7,9,10,10-undecachloropenta-

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* Corresponding author present address: Department of Chemistry, Western Michigan University, Kalamazoo, MI, 49008; phone: (616) 387-2846; fax: (616) 387-2909.

† Present address: Instituto de Quimica, Universidade de Sao Paulo, Sao Paulo, Brazil.

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cyclo[$5.3.0.0^{2,6}.0^{3,9}.0^{4,8}$]decane, 97%) was obtained from the Environmental Health Directorate of Health and Welfare Canada. Compounds used in competition experiments included 2-chloroethanol (99%, Eastman Kodak), lindane (99%, Ultra Scientific), pentanol (Aldrich Chemical Co.), and potassium nitrate (Fisher Scientific). Argon and oxygen gases were UHP grade. Internal standards used were octachlorostyrene and PCB congeners (99%+) obtained from Ultra Scientific.

Humic Acid Solutions. Humic acid (HA) stock solutions were prepared using a variation on the method of Zepp et al. (*16*) by extracting 2 g of solid humic material with 2 L of 0.1 N sodium hydroxide solution and pressure-filtering it through a 0.2-μm capsule filter (Gelman Sciences no. 12117) at 4−6 psi. The filtrate was adjusted to pH 6 with HCl and filtered again. HA working solutions (~pH 6) were made by diluting stock with water. All solutions were made using water purified with a Millipore 4-bowl standard system (Milli-Q water). Dissolved organic carbon (DOC) was routinely measured by absorbance at 355 nm using a Perkin Elmer Lambda 5 spectrophotometer, following the method of Zepp et al. (*16*). This method was calibrated against potassium persulfate digestion (*17*) performed in screw-cap vials, using a Beckman 215A infrared analyzer to measure evolved carbon dioxide.

Photolysis. Irradiations were performed using Osram XBO 150W/1 xenon or 200 W Hg arc lamps housed in an Oriel uniform beam illuminator lamp housing (Model 6148) powered by either an Oriel (Model 6240) or Spectral Energy universal power supply (Model LPS 251HR). Reaction vessels were 25 × 150 mm Kimax borosilicate culture tubes having Teflon-lined caps (Kimble 45066A-25150). Tubes were filled with 40 mL of solution. Mirex in methanol was added to these solutions in 5−10-μL aliquots. Final mirex concentrations in all HA solutions were ~100 ng/L, and all solutions were allowed to equilibrate a minimum of 24 h before use. HA solutions for competition experiments were prepared in 4 L batches and amended with mirex in methanol (~10-μL aliquots). Aliquots (40 mL) of these solutions were transferred to culture tubes and other organic compounds (methanol, 2-chloroethanol, lindane, pentane) were added and allowed to equilibrate for 24 h. Gases (10 min bubbling at ~0.1 L/min) and potassium nitrate were added immediately prior to irradiation. Culture tubes were inverted and placed against the condensing lens assembly of the lamp housing for irradiation. Replicates and dark and other controls were included in all experiments.

Mirex K_{DOC}. The dynamic headspace method of Yin and Hassett (*19*) was used to measure binding of mirex in humic acid solution. In this method, K_{DOC} is calculated from measurements of Henry's law in pure water and apparent Henry's law in HA solution. Measurements were made using 1.7-L solutions contained in 110 × 285 mm borosilicate roll bottles (Wheaton-33). HA solutions had ~10 mg/L DOC. Gas phase mirex sparged out of solution was trapped on Tenax and eluted from the Tenax using acetone and hexane.

Analyses. Mirex was extracted from HA solution by an adaptation of the method of Driscoll et al. (*20*). Chromic acid cleaning solution (2 mL) and hexane (3 mL) were added to 40 mL of the sample in a screw-top culture tube. The solution was heated for 2 h at 100 °C. After the solution was cooled, the hexane extract was siphoned off for analysis. Solutions in Milli-Q water were extracted using liquid−liquid extraction into hexane. Extracts were analyzed using capillary column GC-ECD, and compounds were quantified by comparison to internal standards. Blanks and mirex and photomirex standards with internal standards were included in each GC sample run to establish retention times and response factors.

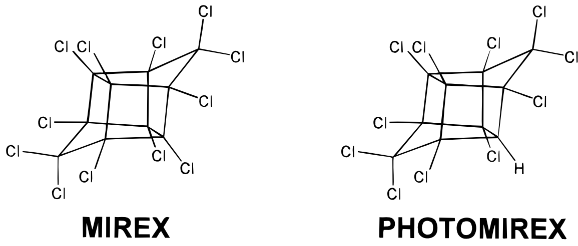

FIGURE 1. Structures of mirex and photomirex.

Two gas chromatographs were used: a Hewlett Packard 5890 and a Varian 3400. Detector signal output on both instruments was collected on a computer. Both poly(dimethylsiloxane) and poly(5% diphenyl−95% dimethylsiloxane) capillary columns were used (30 m × 0.25 mm i.d., 0.25 μm film). All injections were splitless, and various temperature programs were used.

Rate Constants and Curve Fitting. The transformation of mirex to photomirex in HA solution has been demonstrated to follow rate laws for a consecutive, apparent first-order reaction according to the scheme (*14*):

$$\mathrm{M} \xrightarrow{k_{\mathrm{M}}'} \mathrm{P} \xrightarrow{k_{\mathrm{P}}'} \mathrm{D} \tag{1}$$

where k_M' and k_P' are the apparent first-order rate constants for the reactions of mirex (M) and photomirex (P), respectively, and D is a dihydro derivative of mirex tentatively identified elsewhere as 2,8-dihydromirex (*14*, *18*). Structures of mirex and photomirex are given in Figure 1. Mirex apparent reaction rate constants in this work were determined from single-point irradiations using photomirex (P) to mirex (M) concentration ratios and the integrated rate expression:

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

This expression has been used previously (*14*, *15*) and was found to be valid for mirex phototransformations of less than ~25%. Data reported here are for experiments meeting that criterion.

Curve fitting was performed using Scientist Version 2.0, a MicroMath Scientific Software data fitting program. Ratios and products of unknown constant terms in models (eqs 8, 17, 19, and 27) were combined into single parameters. Boundary conditions for parameter estimates were specified when necessary to force parameter estimates to assume the appropriate sign (e.g., parameter > 0). Additional boundary conditions were imposed when model outcomes were unchanged by parameter values outside the boundary conditions.

Results and Discussion

Previous work (*14*, *15*) has demonstrated that mirex is transformed to photomirex (8-monohydromirex) in Aldrich humic acid (HA) solution irradiated at sunlight wavelengths. The same reaction occurs in Fluka HA solution (*21*) and in Lake Ontario water (*14*, *22*), where mirex is a pollutant. In the current work, the transformation of mirex to photomirex was studied in irradiated (λ > 290 nm) Aldrich HA solutions. While Aldrich humic acids are not fully representative of natural aquatic organic matter, mirex and photomirex have similar physical behavior in HA solutions and natural waters (*19, 23*), and several studies have demonstrated that natural waters and solutions of dissolved humic materials represent similar photochemical environments (cf. refs 24 and 25).

Consistent with previous work (*14*), dark reaction of mirex in HA solution was not observed. Reaction of mirex also was not observed in irradiated control solutions (Milli-Q water) containing no HAs. This result contrasts with previous work in which mirex transformation was reported to occur in sunlit glass-distilled water (*14*). The contradictory findings may reflect the different waters used, with Milli-Q water presumably being cleaner than distilled water.

HA Concentration Effects. In the absence of direct photolysis, phototransformation of mirex in HA solutions must be mediated by HAs. Reports of humic-mediated photoreactions are numerous (cf. refs, 26 and 27). These reactions are described as involving intermediate reactive species or excited states generated when humic materials absorb light. The reaction of mirex with such an intermediate can be formulated as

$$d[\mathrm{M}]/dt = -k_x[\mathrm{X}][\mathrm{M}] \qquad (3)$$

where k_x is the second-order rate constant for reaction of mirex with generalized or unknown intermediate X. Under conditions of constant irradiation, humic-generated intermediates typically have been found to occur at steady-state concentrations, resulting in humic-mediated reactions that follow first-order kinetics (*8*, *9*). Steady-state concentrations of HA-generated intermediates occur when intermediate production and loss processes are balanced. The homogeneous solution description for these processes in HA solution irradiated with monochromatic light of wavelength λ is (*24*, *28*)

$$d[\mathrm{X}]/dt = I_\lambda(1 - 10^{-\epsilon_\lambda[\mathrm{DOC}]l})\Phi_{\lambda,x} - k_r[\mathrm{X}] \qquad (4)$$

which gives the steady-state concentration of X as

$$[\mathrm{X}] = [I_\lambda(1 - 10^{-\epsilon_\lambda[\mathrm{DOC}]l})\Phi_{\lambda,x}]/k_r \qquad (5)$$

where I_λ is the light flux per unit volume of solution (e.g., Einsteins min^{-1} L^{-1}), ϵ_λ is the extinction coefficient of humic acids expressed in terms of dissolved organic carbon concentration ([DOC], kg/L), l is the light path length, $\Phi_{\lambda,x}$ is the quantum efficiency for production of X, and k_r is the combined rate constant for all processes that remove X.

The production rate of X ($P_{\lambda,x}$) is

$$P_{\lambda,x} = A_\lambda\Phi_{\lambda,x} \qquad (6)$$

where A_λ is the rate of light absorption by HA solution and is given by:

$$A_\lambda = I_\lambda(1 - 10^{-\epsilon_\lambda[\mathrm{DOC}]l}) \qquad (7)$$

Substituting eqs 5 and 6 into eq 3 yields an expression for the system-specific, pseudo-first-order, homogeneous solution rate constant for reaction of mirex with X:

$$k_x' = k_x P_x(\lambda)/k_r = \frac{k_x\left[\sum_\lambda I_\lambda\left(1 - 10^{-\epsilon_\lambda[\mathrm{DOC}]l}\right)\right]}{k_r} \qquad (8)$$

where $P_x(\lambda)$ is the result of integration of eq 6 across the spectrum.

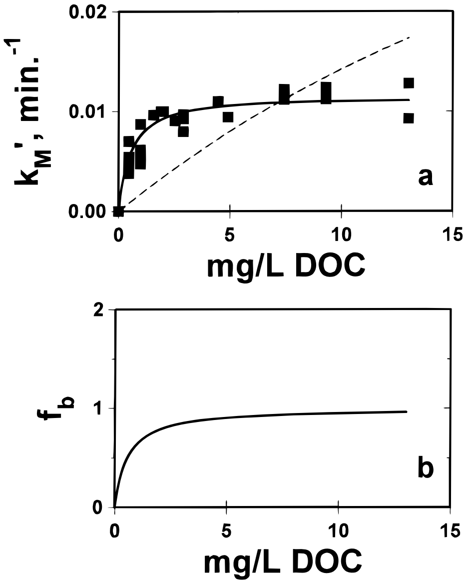

FIGURE 2. (a) Change in mirex apparent reaction rate constant (k_M') with DOC (■) in irradiated Aldrich HA solution ($\lambda \geq 290$ nm). The dotted and solid lines are the respective curve fits of eqs 8 and 17 to the data. (b) Calculated fraction of mirex bound (f_b) in Aldrich HA solution.

Equation 8 predicts that k_x' will increase with [DOC] and approach a limiting value. This is qualitatively what is observed in a plot of k_M' vs [DOC] (Figure 2a), where k_M' is the overall apparent first-order rate constant for mirex photoreaction. However, as eq 8 indicates, k_M' will approach a limiting value fastest at the wavelength of greatest ϵ_λ. Under the experimental conditions used, this wavelength can be no less than ~290 nm because HA absorbance increases with decreasing wavelength, and the lower wavelength cutoff imposed by the borosilicate reaction vessels is ~290 nm. Figure 2a shows the fit of eq 8 (dotted line) to experimental data using a path length of 1 cm and the measured value of $\epsilon_{290} = 2 \times 10^4$ (kg of DOC/L)$^{-1}$ cm^{-1}. This fit represents an extreme case, with the curvature in the fit being the maximum possible given the [DOC] range (<15 mg/L) and minimum wavelength (290 nm) used. Figure 2a demonstrates that, even at maximum curvature, eq 8 is a poor model of the dependence of k_M' on [DOC]. The experimental results consequently are inconsistent with a reaction in which photoproduction of X and reaction of it with mirex occur in a homogeneous solution.

Dependencies on [DOC] similar to the results in Figure 2a have been observed for the humic-mediated reductive dissolution of metal oxides complexed to HAs (*29*) and postulated for the HA-photosensitized reactions of pollutants bound to HAs (*24*, *29*). What distinguishes these reactions from the description in eq 8 is binding. Implicit in eq 8 is the assumption that all X entities have equal access to all mirex molecules in solution (i.e., solution homogeneity). That reactions of bound molecules have been found to deviate from this description indicates that the HA matrix may represent a separate reactive environment where bound molecules are exposed to activities of reactive species different from those experienced by compounds in the bulk solution. This phenomenon has been postulated previously (*16, 25*) and is supported by the work of Blough (*12*) and Green et al. (*13*) showing that electrostatic interactions influence the access molecules have to humic-generated excited states and reactive species.

Previous work in our laboratory has shown that mirex is bound by dissolved HA and aquatic organic matter (*19*, *23*). The DOC−water partition coefficient (K_{DOC}) for the humic acid used in this study was determined to be 1.82 ($\pm$0.38) $\times$ 10^6 L/kg, in good agreement with previous work (*19*). The fraction of mirex bound by humic acid (f_b) was calculated as (*30*)

$$f_b = K_{DOC}[DOC]/(1 + K_{DOC}[DOC]) \tag{9}$$

with (DOC) expressed in kg/L. A plot of f_b vs [DOC] (Figure 2b) follows the same trend as the data for k_M' vs [DOC]. This similarity indicates that photochemical transformation of mirex is strongly influenced by binding to humic material.

An alternative to a homogeneous solution reaction of mirex is a reaction in which the transformation of mirex molecules bound to HAs must be considered separately from the transformation of mirex molecules not bound to HAs. If bound mirex molecules are considered to reside within the aqueous matrix of individual humic molecules, then the reaction of mirex with an intermediate within the humic matrix can be expressed in terms of the concentrations of mirex ($[M]_b/[DOC]$) and X ($[X]_b/[DOC]$) in the humic matrix

$$\left(\frac{d([M]_b/[DOC])}{dt}\right)_{rxn} = -k_{x_b}([X]_b/[DOC])([M]_b/[DOC]) \tag{10}$$

where $[M]_b$ is humic-bound mirex and $[X]_b$ is an intermediate species associated with the humic matrix, both expressed as molar concentrations in the aqueous solution. Note that eq 10 describes mirex loss from the humic matrix due to reaction (rxn) only. Equation 10 simplifies to

$$(d[M]_b/dt)_{rxn} = -k_{x_b}([X]_b/[DOC])[M]_b \tag{11}$$

The expression for the steady-state value of $[X]_b$ is similar to eq 5

$$[X]_b = \frac{[I_\lambda(1 - 10^{-\epsilon_\lambda[DOC]l})\,\Phi_{\lambda,x_b}]}{k_{r_b}} \tag{12}$$

where Φ_{λ,x_b} is the quantum efficiency for production of X in the humic matrix and k_{r_b} applies to reactions removing X from the humic matrix. Combining eqs 10 and 12 gives an expression for the system-specific pseudo-first-order rate constant for reaction of bound mirex with X inside the humic matrix:

$$k_{x_b}' = k_{x_b}\,(P_{x_b}(\lambda)/[DOC])/k_{r_b} \tag{13}$$

where $P_{x_b}(\lambda)$ is the wavelength-integrated photochemical production rate of X in the humic matrix, similar to $P_x(\lambda)$ in eqs 6 and 7.

If eq 8 applies to truly dissolved (not bound) mirex, and eq 13 applies to bound mirex, then the overall loss of mirex from the system can be expressed as

$$d[M]_T/dt = -k_x'f_d[M]_T - k_{x_b}'f_b[M]_T \tag{14}$$

to give an overall rate constant of

$$k_M' = k_x'f_d + k_{x_b}'f_b \tag{15}$$

where $[M]_T$ is the total mirex concentration in the system and f_d is the fraction of mirex that is truly dissolved. An implicit assumption built into eqs 14 and 15 is that sorption equilibrium is maintained during mirex phototransformation. Combining eqs 8, 9, and 13 with eq 15 and recognizing that

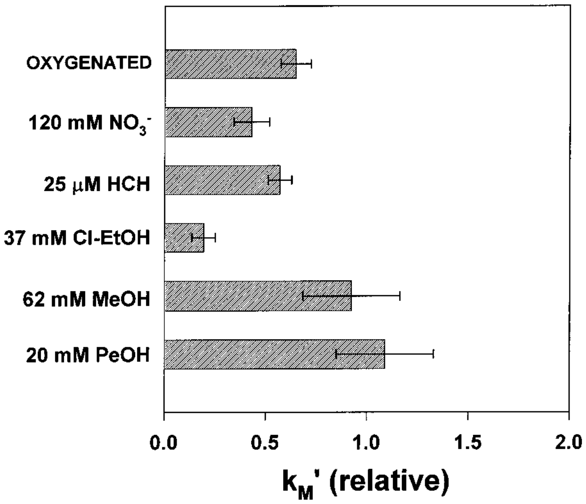

FIGURE 3. Effect of added oxygen (oxygenated), nitrate (NO_3^-), lindane (HCH), 2-chloroethanol (Cl-EtOH), methanol (MeOH), and pentanol (PeOH) on the mirex (∼100 ng/L) apparent rate constant (k_M') in Aldrich HA solution (30 mg/L DOC). Values of k_M' are relative to argon-purged controls containing no additives. Each bar is the average of replicates and error bars represent standard error.

$$f_d = \frac{1}{1 + K_{DOC}[DOC]} \tag{16}$$

yields the overall rate constant as a function of [DOC]:

$$k_M' = \frac{1}{1 + K_{DOC}[DOC]}[(k_xP_x(\lambda)/k_r) + (k_{x_b}K_{DOC}\,P_{x_b}(\lambda)/k_{r_b})] \tag{17}$$

$P_x(\lambda)$ and $P_{x_b}(\lambda)$ are not simple functions of [DOC] except when the product $\epsilon_\lambda[DOC]l$ is $\leq$0.02 (*28*). When this is true, $P_x(\lambda)$ and $P_{x_b}(\lambda)$ are linear functions of [DOC] because the rate of light absorption, A_λ (eq 7), reduces to a linear function of [DOC] (*31*). Under these conditions, eq 17 predicts that k_M' will be proportional to the product [DOC] $\times$ f_d (eq 16) as all other terms in eq 17 are constants. Equation 17 further predicts that the proportionality will hold regardless of the relative contributions of the dissolved and bound phases to overall reaction rate constant.

Equation 17 was fit to experimental data using $K_{DOC} = 1.82 \times 10^6$ L/kg and assuming that $P_x(\lambda)$ and $P_{x_b}(\lambda)$ were linear functions of [DOC]. The resulting curve fit is shown using a solid line in Figure 2a. This fit demonstrates that eq 17 is a better predictor of mirex photochemical behavior than eq 8 ($R^2 = 0.97$ for eq 17 vs $R^2 = 0.7$ for eq 8) and indicates that the reaction of mirex in HA solution is more accurately described as occurring in separate bound and dissolved photochemical environments.

Scavenger Effects. Some compounds added to HA solution in competition experiments decreased k_M' relative to controls. These compounds included oxygen, nitrate, lindane, and 2-chloroethanol but not methanol or pentanol (Figure 3). The ability of some additives to decrease apparent reaction rate constants is typical of HA-mediated photoreactions. This is because HA-mediated photore-

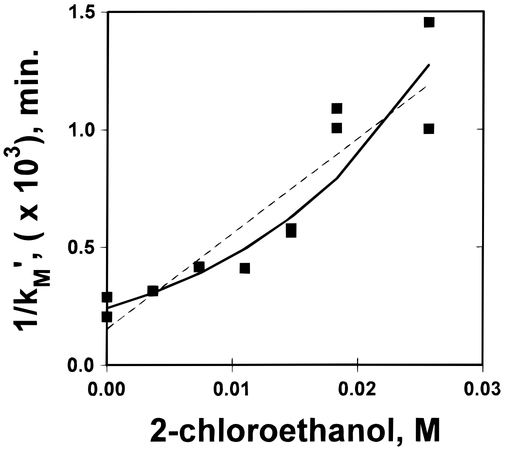

FIGURE 4. Comparison between the observed (■) and predicted (dotted line, eq 19; solid line, eq 27) effect of 2-chloroethanol concentration on the mirex (~100 ng/L) apparent photoreaction rate constant (k_M') in Aldrich HA solution (10 mg/L DOC).

actions commonly involve scavengable, short-lived excited states or reactive species that occur at steady-state concentrations in HA solution under conditions of constant irradiation. For example, Zepp et al. (*25*) used the cis-trans isomerization of 1,3-pentadiene as a probe for reactive triplet states in HA solution. Under conditions of constant irradiation, the isomerization followed first-order kinetics. However, the addition of oxygen to HA solution reduced, through competition, the number of reactive triplet states available to 1,3-pentadiene. Isomerization of 1,3-pentadiene consequently was described by different apparent first-order rate constants in HA solutions containing different oxygen concentrations. Scavenger-induced decreases in apparent reaction rate constant consequently indicate that mirex is transformed in HA solution by a second-order reaction with some intermediate *X* that is photochemically generated by HAs, as assumed in the derivations of eqs 8 and 17. Further, since mirex photoreaction follows apparent first-order kinetics both in the presence and absence of scavengers, *X* must occur in HA solution at steady-state concentrations.

The quantitative effects of adding scavengers to HA solution support the hypothesis that dissolved and bound mirex exist in different photochemical environments. If mirex reacted in a homogeneous solution, eq 8 would apply. For solutions with added scavenger, eq 8 becomes

$$k_{x,s}' = k_x P_x(\lambda)/(k_r + k_s[S]_T) \qquad (18)$$

where $[S]_T$ is the total concentration of added scavenger and k_s is the second-order rate constant for reaction of the scavenger with the reactive intermediate, *X*. Equation 18 can be rearranged into a linear form

$$1/k_{x,s}' = (k_s/k_x P_x(\lambda))[S]_T + (k_r/k_x P_x(\lambda)) \qquad (19)$$

Figure 4 shows a sample plot of the fit of eq 19 (dotted line) to experimental data assuming that $k_{x,s}' = k_{M_s}'$, where k_{M_s}' is the overall apparent first-order rate constant for mirex photoreaction in HA solution containing an added scavenger. In these experiments, [DOC] was held constant so that $P_x(\lambda)$ was constant. The experimental data were found to be nonlinear by ANOVA ($p < 0.05$) using the method of Peterson (*32*). The scavenger effects are therefore inconsistant with a homogeneus phase reaction between mirex and the single reactive intermediate *X*.

Equation 13 describes the rate constant for mirex reaction in the humic matrix in the absence of added scavengers. If scavenger molecules must be in the humic matrix to interfere in the reaction of bound mirex, then the description for scavenging in the humic phase can be assumed to be analogous to that for scavenging in micellar systems (*33*, *34*); that is, the number of reactive intermediates available to mirex in a humic molecule depends on the number of scavenger molecules present in that humic molecule. Under these conditions, the presence of an added scavenger changes eq 13 to yield

$$k_{x_b,s_b}' = (k_{x_b} P_{x_b}(\lambda)/[DOC])[1/(k_{r_b} + n k_{s_b})] \qquad (20)$$

where k_{s_b} is the rate constant for the reaction of the added scavenger with the reactive intermediate inside a humic molecule and *n* is the number of scavenger molecules present in that humic molecule. In considering the humic phase as a whole, since *n* is an integer, there must be a distribution of humic molecules with different values of *n*. Expansion of eq 20 to include all values of *n* yields

$$k_{x_b,s_b}' = (k_{x_b} P_{x_b}(\lambda)/[DOC]) \sum_{n=0}^{\infty} [Pr_n/(k_{r_b} + n k_{s_b})] \qquad (21)$$

where Pr_n is the probability of finding *n* scavenger molecules in a humic molecule. Atik and Singer (*33*) and Atik and Thomas (*34*) have shown that the distribution of scavengers among micelles is described by a Poisson distribution:

$$Pr_n = e^{-N} N^n/n! \qquad (22)$$

where *N* in HA solution is the average number of humic-associated scavenger molecules per humic molecule.

The value of *N* can be related to the bulk solution concentration of scavenger through a partition coefficient, K_p:

$$N = K_p[S] \qquad (23)$$

where [S] is the truly dissolved (not bound) molar concentration of the scavenger. For scavenger molecules that follow linear partitioning as described by K_{DOC}, *N* can be described by

$$N = 10^{-3} f_c MW_{HA} \frac{K_{DOC}}{1 + K_{DOC}[DOC]}[S] \qquad (24)$$

where f_c is the weight fraction of organic carbon in humic molecules, MW_{HA} is the gram molecular weight of the humic material, and K_{DOC} and [DOC] are expressed in units of L/kg and kg/L, respectively. In this study, [DOC] was 10^{-5} Kg/L, and the scavengers had $K_{DOC} < 10^4$ L/kg. Therefore, K_{DOC}[DOC] for the scavengers was $\ll 1$, meaning that the fraction of scavenger dissolved (f_d, eq 16) ≈ 1.

Equation 24 can be used to estimate values of *N*. For example, K_{DOC} for lindane and 2-chloroethanol are 1670 (*35*, *36*) and 1.4, respectively (*36*, *37*). Assuming $f_c = 0.5$ (*38*) and $MW_{HA} = 10^5$ g/mol (*39*), *N* is 0−3 for lindane and 0−2 for 2-chloroethanol over the concentration ranges used. Since *N* is predicted to be small, the probability that reaction will continue unquenched in some humic molecules ($n = 0$) remains significant even in the presence of high concentrations of scavenger (e.g., 0.025 M 2-chloroethanol).

Equation 24 implies that it may not be possible to quench completely the reaction of bound molecules since solubility (maximum $[S]_T$) tends to decrease with increasing K_{DOC}.

Equations 21–23 combine to give a general equation for humic-bound mirex reaction in the presence of added scavenger:

$$k_{x_b,s_b}' = \frac{k_{x_b}P_{x_b}(\lambda)}{[DOC]}\left(\frac{e^{-K_P[S]}}{k_{r_b}} + \frac{e^{-K_P[S]}K_P[S]}{k_{r_b}+k_{s_b}} + \frac{e^{-K_P[S]}(K_P[S])^2}{k_{r_b}+2k_{s_b}} + ... + \frac{e^{-K_P[S]}(K_P[S])^n}{k_{r_b}+nk_{s_b}}\right) \quad (25)$$

This equation indicates that when N is <0.1, >90% of the humic molecules contain no added scavenger. It also indicates that if k_{s_b} is sufficiently large, reaction in a humic molecule will be completely quenched by the presence of one scavenger molecule.

Equations 18 and 25 were substituted into eq 15 to give an equation that describes the overall rate constant for mirex phototransformation as a function of concentration of added scavenger. Preliminary curve fitting of experimental data to that equation indicated that the terms for bound mirex where Pr_n was >0 were insignificant, meaning that a single scavenger molecule in the humic matrix was sufficient to quench all reaction of mirex. Therefore, the combined equation can be simplified to

$$k_{M_s}' = \frac{k_x P_x(\lambda)}{k_r + k_s[S]} f_d + \frac{k_{x_b}P_{x_b}(\lambda)}{k_{r_b}[DOC]} e^{-K_P[S]} f_b \quad (26)$$

where the total solution concentration of scavenger ($[S]_T$) in eq 18 has been changed to [S], the dissolved concentration of scavenger, in order to restrict this description to the dissolved phase.

When $[S]_T = 0$, eq 26 reduces to eq 17, the overall rate constant for mirex in the absence of added scavengers. Dividing eq 26 by eq 17 and combining with eqs 8 and 13 gives

$$\frac{k_{M_s}'}{k_M'} = \frac{\dfrac{k_x'/k_{x_b}'}{1+(k_s/k_r)[S]} f_d + e^{-K_P[S]} f_b}{[(k_x'/k_{x_b}')f_d] + f_b} \quad (27)$$

Using measured values of f_d (0.05) and f_b (0.95), eq 27 was applied simultaneously to observed effects of three scavengers to determine the relative reactivities of mirex in the dissolved and bound phases (i.e., $k_x'/k_{x_b'}$). Figure 5 illustrates the resulting curve fits using 2-chloroethanol, nitrate, and lindane as scavengers. While values of the parameters K_P and k_s/k_r were allowed to vary for each scavenger, the parameter k_x'/k_{x_b}' was held to be the same for the three scavengers because experiments were performed in HA solution having a constant [DOC] of 10 mg/L. The curve fitting results indicate that reactivity of mirex in HA solution is restricted to the bound phase (e.g., $k_x'/k_{x_b}' \approx 0$). An additional curve fit of eq 27 (solid line) to the 2-chloroethanol data appears in Figure 4. This curve fit was performed using a rearranged form of the equation assuming $k_x'/k_{x_b}' = 0$. In conjunction with Figure 5a, this fit demonstrates that eq 27 better describes the data than eq 19. Therefore, the scavenger effects support the reaction of mirex wholly within the bound phase over reaction of mirex in homogeneous solution.

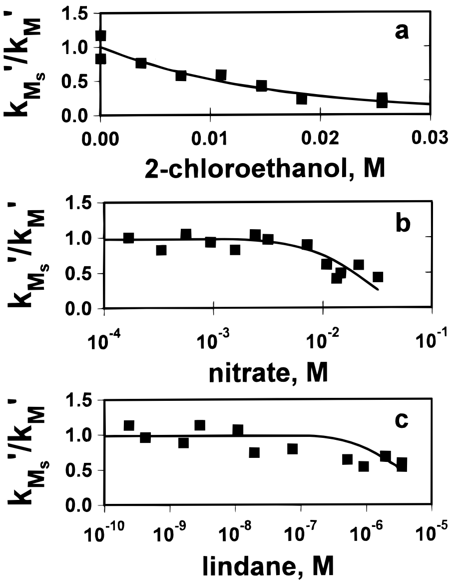

FIGURE 5. Effect of 2-chloroethanol (a), nitrate (b), and lindane (c) on the apparent rate constant for mirex photoreaction (k_{M_s}') relative to solutions containing no additives (k_M'). Lines through data points (■) are curve fits to eq 27.

TABLE 1

Comparison of Estimated and Calculated Values of the Humic Acid–Water Partition Coefficient K_P

	est $K_P{}^a$ (L/M_{HA})	SD	calcd $K_P{}^b$
lindane	2.3×10^4	5×10^3	8.4×10^4
2-chloroethanol	65	6	70
nitrate	6.3	1	NA[c]

[a] Parameter estimates and standard deviations are from curve fits of eq 27 to individual scavenger data sets assuming bound phase reaction only. [b] Calculated from K_{DOC} using eqs 23 and 24 and assuming $f_c = 0.5$ and $MW_{HA} = 10^5$ g/mol. [c] K_{DOC} unknown.

Parameter estimates for K_P obtained from the curve fits in Figure 5 are compared in Table 1 with values calculated from K_{DOC} and eqs 23 and 24. A calculated value of K_P is not included for nitrate because its K_{DOC} is not known. The values for K_P in both cases reflect the expected relative affinities of the scavengers for humic acids in water, decreasing in the series lindane > 2-chloroethanol > nitrate. This supports the view that the ability of a scavenger to interfere in bound phase reactions depends on the affinity of the scavenger for the bound phase. Furthermore, the good agreement between the calculated and curve fit estimates of K_P corroborates the overall accuracy of eq 21 in representing the effects of binding on HA-mediated photoreactions. Consequently, as has been observed by Blough (*12*), not only can bound phase molecules encounter different activities of reactive intermediates, but they also can encounter different activities of scavengers.

The reaction of mirex in the bound phase might appropriately be called an intrahumic reaction. The description in eqs 20–23 for scavenger effects in the bound phase is based on a kinetic model developed by Atik and Singer (*33*) and Atik and Thomas (*34*) to predict the ability of scavengers to quench intramicellar reactions. A key feature distinguishing this model from that used for homogeneous solutions is the dependence of intramicellar quenching on the number of scavenger molecules in micelles, not the bulk solution scavenger concentration. The associated rate constant for intramicellar quenching is specific for reaction in a micelle containing one scavenger molecule and has units of time^{-1}. The model consequently operates on a molecular level, using the Poisson distribution to sum the molecular level kinetics into an overall rate constant. The successful application of this model in describing the photoreaction of mirex in the bound phase of HA solution suggests that this reaction, like intramicellar reactions, occurs within discrete microenvironments. The aqueous matrix of individual HA molecules may constitute such a microenvironment, as suggested in recent work by Engebretson and von Wandruszka (*40, 41*) on the behavior of fluorescence molecules bound to HAs. Therefore, the appellation of "intrahumic" may be appropriate for bound phase reactions.

Implications

The success of eqs 17 and 27 in describing mirex photochemical behavior corroborates their use in predicting the effect of binding on humic-mediated photoreaction. Based on these equations, the description for the second-order reaction of any compound C with any single HA-photogenerated reactive intermediate X is provided by

$$-\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = [\mathrm{C}]_{\mathrm{T}}\left(f_{\mathrm{d}}\frac{k_x \mathrm{P}_x(\lambda)}{k_{\mathrm{r}} + k_{\mathrm{s}}[\mathrm{S}]} + f_{\mathrm{b}}\frac{k_{x_{\mathrm{b}}}\mathrm{P}_{x_{\mathrm{b}}}(\lambda)}{[\mathrm{DOC}]}\sum_{n=0}^{\infty}\frac{\mathrm{Pr}_n}{k_{\mathrm{r_b}} + nk_{\mathrm{s_b}}}\right) \quad (28)$$

Equation 28 represents a simplified model applicable only to reactions involving a single reactive intermediate and only when certain assumptions hold true. The first of these assumptions is that sorption equilibrium is maintained during photoreaction and that the bound and dissolved fractions of a compound in HA solution are therefore constant. A second, less apparent assumption is that the partitioning of scavenger molecules to HAs can be described using an average molecular weight for HAs (eq 24). A related assumption is that this average molecular weight does not change with HA concentration (e.g., due to aggregation). It is also assumed that scavenger molecules in one phase of HA solution do not affect the steady-state concentration of reactive intermediates in the other phase. Equation 28 nevertheless can be expanded to describe more than one reactive intermediate, to include descriptions of how f_{b} and f_{d} vary with time, and to provide more complex descriptions of HA molecular weight distributions and scavenger effects.

In spite of the specific limitations of the model, the description of HA-mediated photoreaction as a homogeneous phase phenomenon (eq 8) is demonstrated to be a special case of eq 28, one that is applicable only when $f_{\mathrm{d}} \approx 1$. Additionally, provided that the assumptions behind the model are true, eq 28 permits the reactivities of the bound and dissolved phases of HA solution to be assessed by looking at scavengers effects. This is possible because the effects of scavengers in the two phases depend on different distributions. Scavengers molecules are distributed according to a normal distribution in the dissolved phase and according to a Poisson distribution in the bound phase. The result is that bound and dissolved phase reaction rates are predicted to have detectably different dependencies on scavenger concentration. It should be noted, however, that scavenger effects observed to deviate from the homogeneous solution description in eqs 18 and 19 are not in themselves sufficient to invoke intrahumic reaction. The same deviation potentially could arise in a purely homogeneous phase reaction if, for example, that reaction was mediated by multiple reactive intermediates having different rates of reaction with a given scavenger. However, the homogeneous solution model failed to describe the reaction of mirex in the absence of scavengers, making necessary an alternate description for that reaction. Taken together, the HA concentration effects and scavenger effects support intrahumic reaction but not homogeneous phase reaction.

The different dependencies that intra- and extrahumic reactions are predicted to have on scavenger concentrations ultimately are derived from scavenger effects on the steady-state activities of reactive intermediates in the two phases. As a consequence, these different dependencies may mean that bound phase molecules encounter activities of HA-generated reactive intermediates that are much higher than currently thought. Intrahumic reactions nevertheless complicate using model compounds and solutions to make predictions about pollutant behavior in the environment. Such predictions require measurements of reactive intermediate quantum yields, production rates, or steady-state concentrations. To measure the production rates of quantum yields, probe molecules must successfully outcompete all other loss processes. The bulk solution probe concentration necessary to accomplish this within the humic matrix may not be possible without changing the solvent properties of water. An additional complication is that numerous studies have demonstrated that the relative magnitudes of different rate constants in homogeneous solution do not necessarily agree with the relative magnitudes of rate constants for the same reactions in micelles (*42*). This means that it may not be possible to use the intrahumic reaction rates of model compounds in conjunction with homogeneous phase reaction rate constants to draw conclusions about other intrahumic reaction rates.

Reported elsewhere (*21, 43*) are complete results of work investigating the identity of the transient reactant responsible for the transformation of mirex in HA solution. These results suggest that the hydrated electron is the reactive intermediate responsible for the transformation of mirex in HA solution. Photoproduction of hydrated electron from humic materials and natural organic matter has been demonstrated previously (*16*), and the ability of hydrated electron to initiate dechlorination reactions is well known (cf. ref 44). However, because the hydrated electron reacts with oxygen at diffusion-controlled rates, steady-state hydrated electron concentrations in sunlit natural waters generally are believed to be too low ($\sim 10^{-17}$ M; *16*) to contribute significantly to the transformation of most aquatic pollutants. Zepp et al. (*16*) excluded from this conclusion pollutants in the bound phase. Supporting this conclusion, the reaction of mirex in sunlit, air-equilibrated HA solution, or natural water has a demonstrated $t_{1/2} = 7$ days (*14*, *15*).

Regardless of the identity of the reactive intermediate responsible for mirex transformation, a mirex half-life on the order of 7 days means that intrahumic reaction can contribute significantly to the environmental fate of pollutants. In Lake Ontario, where mirex is a pollutant, phototransformation of mirex has been identified as the source of photomirex to the lake (*15*). Concentration ratios of photomirex to mirex in lake sediments are on the order of 0.1 (*15, 45*), while ratios in biota from the lake (e.g., fish and benthic invertebrates) are as high as 0.93 (*45*). These ratios reflect the efficiency of natural dissolved organic matter in transforming mirex in this system. As a consequence, these ratios also exemplify the potential significance of intrahumic reactions in the aquatic environment.

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