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Free-Radical Oxidants in Natural Waters

Abstract. *Photooxidation of cumene (isopropylbenzene) and pyridine in dilute solution in natural waters gives products characteristic of reactions with alkylperoxy* ($RO_2\cdot$) *and hydroxyl* ($HO\cdot$) *radicals. On the basis of the rates of formation of the products, the average concentrations of* $RO_2\cdot$ *and* $HO\cdot$ *are estimated to be about* 10^{-9} *and* 10^{-17} *mole per liter, respectively. The concentration of* $RO_2\cdot$ *is large enough that, for some classes of reactive chemicals, oxidation can be an important process in natural waters.*

An amazing variety of synthetic organic chemicals are found in the waterways of the United States, many in significant concentrations (*1*). Their fates are largely unknown, although dilution, biodegradation, volatilization, hydrolysis, and photooxidation processes have all been implicated in their loss (*2*). Several investigators have reported evidence of free-radical oxidations of chemicals exposed to sunlight (or light of wavelength above 300 nm) in natural waters but not in pure water (*2*). The implication is that when the natural organics present in many water bodies undergo photolysis, they generate free radicals such as alkylperoxy ($RO_2\cdot$) or hydroxyl ($HO\cdot$) and other oxidants such as singlet oxygen ($^1O_2$) (*3*) and that these oxidants contribute to the transformation of some synthetic chemicals in water. We have investigated the importance of free radicals as oxidants for organic chemicals in a variety of natural waters, using cumene (isopropylbenzene) and pyridine (C_5H_5N) to probe quantitatively for $RO_2\cdot$ and $HO\cdot$.

In our laboratory experiments only one kind of radical was generated in pure water; we used azo-bis(2-carbomethoxypropane) (MAB) as a thermal source of $RO_2\cdot$ (*4*) and $10^{-3}M$ H_2O_2 in water, photolyzed with > 290-nm light, as a source of $HO\cdot$ (*4a*). All the significant oxidation products from each kind of experiment were measured and identified.

Table 1 summarizes the experimental results and shows that cumene (CuH) at $10^{-4}M$ in pure water oxidizes readily in the presence of $RO_2\cdot$ and O_2 to give only products from side-chain oxidation: cumyl hydroperoxide (CuOOH), cumyl alcohol (CuOH), and acetophenone ($C_6H_5COCH_3$). However, $HO\cdot$ oxidizes CuH in water to form both side-chain and ring oxidation products, including 2- and 4-isopropylphenols in a 30:70 ratio (*5*). The following reactions summarize the radical oxidation of CuH:

$$RO_2\cdot + CuH \rightarrow RO_2H + Cu\cdot$$

$$Cu\cdot + O_2 \rightarrow CuO_2\cdot$$

$$CuO_2\cdot + CuH \rightarrow CuO_2H + Cu\cdot$$

$$CuO_2\cdot + RO_2\cdot \rightarrow CuO\cdot + RO\cdot + O_2$$

$$CuO\cdot \rightarrow C_6H_5COCH_3 + CH_3\cdot$$

$$CH_3\cdot + O_2 + CuO_2\cdot \rightarrow CH_2O + CuOH + O_2 \text{ (two steps)}$$

$$HO\cdot + CuH \rightarrow H_2O + Cu\cdot$$

$$HO\cdot + O_2 + CuH \rightarrow HOC_6H_4\text{-}i\text{-}C_3H_7 + HO_2\cdot \text{ (two steps)}$$

where $HOC_6H_4\text{-}i\text{-}C_3H_7$ is hydroxyisopropylbenzene.

These experiments provide the basis for interpreting results from experiments with CuH dissolved in natural waters and exposed to light. Photolyses of CuH dissolved in filter-sterilized natural waters and then exposed to either sunlight or to a xenon lamp (*6*) gave mixtures of the same side-chain and ring oxidation products found in radical-initiated reactions (Table 1). Table 2 summarizes these results. In all cases except for pure water, the proportions of side-chain and ring oxidation products were such that participation by both $RO_2\cdot$ and $HO\cdot$ is required to account for the results.

The ratio of products from side-chain and ring oxidation (*S*/*R*) evidently does not vary widely either in the same water source sampled at different times or in difference sources; the Aucilla River, a highly eutrophic river in northern Florida, showed somewhat greater activity than Coyote Creek or Boronda Lake and also exhibits much higher absorptivity in the solar region. The different relative proportions of oxidation products of $RO_2\cdot$ or $HO\cdot$ found may be due to different secondary reactions as well as different spectral, photochemical, and chemical properties of the waters (*7*).

We measured the products and the *S*/*R* ratio from CuH at several times in one experiment with photolyzing Aucilla River water containing $1 \times 10^{-4}M$ CuH. No significant change in *S*/*R* was found over a 144-hour period (measured at 24, 72, and 144 hours); this result indicates that phenols did not arise from the photolysis of initially formed CuOOH.

Table 1. Distribution of oxidation products from CuH oxidized in pure water at 50°C (concentrations are in $M \times 10^{-6}$).

Radical (source)	$[CuH]_0$	[Products]*		
		Side chain† (*S*)	Ring‡ (*R*)	*S*/*R*
$RO_2\cdot$ (MAB)§	303	9.27 ± 0.5	< 0.02	> 500
$RO_2\cdot$ (MAB)‖	245	7.65 ± 0.4	< 0.01	> 800
$RO_2\cdot$ (MAB)¶	23	3.44 ± 0.2	< 0.01	> 300
$HO\cdot$ (H_2O_2)#	~ 220	2.85 ± 0.2	6.68 ± 0.4	0.43

*Values averaged from three or more analyses; we analyzed the products by using an hplc C_{18} μ-Bondapak column (4 mm by 30 cm) and gradient elution of an acetonitrile-water mixture from 10 to 100 percent in acetonitrile in 30 minutes with 2 ml min^{-1} throughput. An ultraviolet detector set at 254 nm was used to measure products by comparison with peak areas for known mixtures. †Sum of CuOH, CuOOH, and $C_6H_5COCH_3$. ‡Sum of 2- and 4-hydroxyisopropylbenzenes; identity of these products was confirmed by gas chromatography-mass spectroscopy. §$[MAB]_0 = 1.45 \times 10^{-4}M$; 24-hour experiment. ‖$[MAB]_0 = 1.00 \times 10^{-4}M$; 24-hour experiment. ¶$[MAB]_0 = 1.03 \times 10^{-4}M$; 72 hour experiment. #$[H_2O_2]_0 = 1.0 \times 10^{-3}M$; experiments were carried out at 30°C with a xenon light source (*6*).

We also used C_5H_5N as a probe for natural radical oxidants when we discovered that RO_2 reacts slowly with C_5H_5N in water to give only pyridine *N*-oxide (C_5H_5NO), whereas $HO\cdot$ (from H_2O_2) gives hydroxypyridines and more polar products but no *N*-oxide:

$$C_5H_5N + RO_2\cdot \rightarrow C_5H_5NO + RO\cdot$$

$$C_5H_5N + HO\cdot \rightarrow \text{2-, 3-, and}$$

$$\text{4-}HOC_5H_4N + \text{unidentified products}$$

We also found that, although C_5H_5N does not photolyze in pure water at wavelengths above 300 nm, it undergoes significant loss when it photolyzes in natural waters, both in the absence and in the presence of oxygen to give very polar (hplc) unidentified products, possibly by way of the Dewar-C_5H_5N form (*8*). In aerated, photolyzed natural waters under conditions similar to those described in Table 2, both C_5H_5NO and hydroxypyridines were formed in small amounts together with the larger amounts of polar products.

Kinetic analysis of the experiments with CuH and C_5H_5N is straightforward. The rates of formation of oxidation products of $HO\cdot$ or $RO_2\cdot$ with CuH or C_5H_5N follow from the assumption that each radical is in a steady-state concentration and that each radical produces a unique set of oxidation products. Thus, the CuH oxidation follows the relations

$$dS/dt + dR/dt = -(d\text{CuH}/dt) = (k_p[RO_2\cdot] + k_A[HO\cdot])[\text{CuH}] \quad (1)$$

$$k_T = k_p[RO_2\cdot] + k_A[HO\cdot] \quad (2)$$

where k_p and k_A are the specific rate constants for H atom transfer or addition by $RO_2\cdot$ and $HO\cdot$, respectively (*9*). Integration of Eq. 1 between time limits of $t = 0$ and $t = t$ gives expressions for the averaged concentrations of $RO_2\cdot$ and $HO\cdot$ in natural waters exposed to sunlight or simulated sunlight (*10*):

$$[RO_2\cdot]_{av} = [S]_t k_T/[\text{CuH}]_0 k_P(1 - e) \quad (3)$$

$$[HO\cdot]_{av} = [R]_t k_T/[\text{CuH}]_0 k_A(1 - e) \quad (4)$$

A similar relation holds for the formation of C_5H_5NO in two natural waters by reaction of $RO_2\cdot$ with C_5H_5N. Hydroxypyridines could not be measured reliably; therefore, C_5H_5N was not used to estimate the concentration of $HO\cdot$:

$$[RO_2\cdot] = [C_5H_5NO]_t k^1_T/[C_5H_5N]_0 \times k_{ox}(1 - e) \quad (5)$$

where, in this case, k^1_T is the rate constant for the loss of C_5H_5N by all processes known or otherwise. Table 3 summarizes the concentrations of $RO_2\cdot$ and $HO\cdot$ in natural waters as calculated from these experiments. The fair agreement between values of $[RO_2\cdot]$ found when CuH was used as a probe and those found when C_5H_5N was used gives some confidence that the true value is larger or smaller by less than a factor of 5 than the estimated value.

Table 2. Distribution of oxidation products from CuH photolyzed in natural waters (concentrations are in $M \times 10^{-6}$). Water samples were filter-sterilized through 0.22-μm Micropore filters and photolyzed for 5 days with a xenon source (*6*) (light > 290 nm).

Water source	$[\text{CuH}]_0$	[Products]* Side chain† (*S*)	Ring‡ (*R*)	*S/R*
Boronda Lake§	246	5.8	5.8	1.0
Coyote Creek‖	208	9.1	4.2	2.2
	74	1.97	0.61	3.2
Aucilla River¶	274	13	6.9	1.9
Pure water#	229	0.09	0.5	0.18

*See asterisked footnote in Table 1. †Sum of CuOH, CuOOH, and $C_6H_5COCH_3$. ‡Sum of 2- and 4-hydroxyisopropylbenzenes. §Eutrophic lake, Palo Alto, California. ‖Eutrophic creek, San Jose, California. ¶Eutrophic river, northern Florida. #Purified with the Milli-O water purification unit (Millipore Corporation).

Because many natural eutrophic water bodies contain particulates which will scatter light and dissolved organics which will absorb light, the estimated $[RO_2\cdot]_{av}$ and $[HO\cdot]_{av}$ values reported here for filtered water, photolyzed in thin layers, are upper bounds on the concentrations expected to be present in eutrophic water bodies more than 1 or 2 m in depth (*10*). Half-lives estimated from these concentrations will be minimum values.

From the $[RO_2\cdot]$ measured in this way, coupled with the values of k_p for a range of organic structures (*11*), we can estimate minimum half-lives for these structures in reactions with $RO_2\cdot$ in aquatic systems. In general, only the most reactive chemicals will be transformed by $RO_2\cdot$, with half-lives of a few days or less; these include phenols, aromatic amines, hydroxylamines, and hydroquinones.

Table 3. Averaged steady-state concentrations of radicals in photolyzed natural waters. Concentrations are based on experiments with a xenon lamp adjusted to closely resemble the sunlight in brightness and spectral distribution (*6*); values of $[RO_2\cdot]$ and $[HO\cdot]$ are applicable only to near-surface photolysis conditions in natural waters (see text).

Water	Probe	Average radical concentration (*M*)* $[RO_2\cdot] \times 10^9$	$[HO\cdot] \times 10^{17}$
Aucilla River	CuH	2.8	1.8
Boronda Lake	CuH	9.5	0.15
Boronda Lake	C_5H_5N	0.45	
Coyote Creek	CuH	9.1	1.6
Coyote Creek	C_5H_5N	5.0	

*Calculated from Eqs. 3, 4, or 5; $k^1_T = 1.7 \times 10^{-7}$ sec^{-1}; $k_p = 10M^{-1}\ sec^{-1}$; and $k_{ox} = 0.67M^{-1}sec^{-1}$.

Despite the very high reactivity of $HO\cdot$, its very low concentrations found here make it unlikely that oxidation by $HO\cdot$ will be an important pathway in aquatic systems for most organic compounds; the half-life for oxidation by $HO\cdot$ of even the most reactive structure will be at least 80 days (*12*).

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