

# Rate Constants for Reaction of Hydroxyl Radicals with Several Drinking Water Contaminants

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■ Rate constants for reactions of the hydroxyl radical with 25 potential organic drinking water contaminants, including solvents, haloalkanes, esters, aromatics, and pesticides (for example, aldicarb, atrazine, 1,2-dibromo-3-chloropropane, endrin, glyphosate, haloforms, lindane, picloram, etc.), have been measured in water using relative rate methods. A variety of HO<sup>•</sup>-generating techniques were used, including ozone decomposition, Fenton's reaction, and a convenient new method employing photo-Fenton's chemistry. In addition, rate constants for 19 other compounds were estimated using structure-activity relationships. The present results are consistent with previous work that demonstrated that HO<sup>•</sup> is a relatively nonselective radical toward C-H bonds, but is least reactive with aliphatic polyhalogenated compounds. Olefins and aromatics all react at nearly diffusion-controlled rates in water, unlike the case in the gas phase where these compounds react more selectively. The rate constants are useful in estimating HO<sup>•</sup>-induced oxidation rates of organic compounds in a variety of aqueous systems including atmospheric water droplets, sunlit surface waters, supercritical and near-critical water reactors, and room temperature radical oxidation processes.

## Introduction

Reactions of aqueous hydroxyl radicals with organic compounds are important in many systems of environmental interest including atmospheric water droplets (1), sunlit surface waters (2), supercritical and near-critical water reactors (3), and nuclear reactor cooling systems (4), and radical oxidation processes (ROPs) including simple ozonation (5), ozone photolysis (6), ozone with H<sub>2</sub>O<sub>2</sub> (7), H<sub>2</sub>O<sub>2</sub> photolysis (8), semiconductor irradiation (9), electron beams (10), and  $\gamma$ -radiolysis (11). [The term "advanced oxidation processes" (AOPs) was originally coined to refer to those processes that employ the hydroxyl radical as the main oxidant. We prefer the terms "radical oxidation processes" (ROPs) as more specific or "radical treatment processes" (RTPs) to include those like  $\gamma$ - or e<sup>-</sup>-beam irradiation and semiconductor photocatalysis in which other radical processes can also be important. "Advanced" has transitory applicability.] In contrast to most other oxidants, reactions of HO<sup>•</sup> radicals with organics containing C-H or C-C multiple bonds generally proceed with rate constants approaching the diffusion-controlled limit (10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>) (12), and therefore oxidation rates are usually limited by the rates of HO<sup>•</sup> generation and competition by other HO<sup>•</sup> scavengers in solution rather than by inherent reactivity with the oxidant. Competing scavengers are usually the dissolved organic carbon (DOC) with minor contributions from HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>, Fe<sup>II</sup>, and the HO<sup>•</sup>-generating reagents themselves (e.g., O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>) (13). Some compounds, particularly those containing multiple halogens or oxygen atoms and few hydrogen atoms, react with HO<sup>•</sup> relatively slowly (10<sup>7</sup>-10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>) or, in the case of perhalogenated compounds, not at all (12, 14). In such

cases, oxidation rates and efficiencies can be low even in clean waters containing low levels of natural scavengers because competition by the HO<sup>•</sup>-generating reagents becomes significant. Therefore, knowledge of HO<sup>•</sup> reaction rate constants is useful in predicting oxidation rates and efficiencies in a variety of systems.

Extensive kinetic data are available on the reactions of HO<sup>•</sup> with organic substrates in water (12, 14); however, there is a dearth of data for potential environmental pollutants, especially those with low rate constants. The 1986 Amendments to the Safe Drinking Water Act call for regulation of 50 organic contaminants in drinking water supplies to limit human exposure (15). The compounds encompass those that are toxic to some degree and have been shown to be present in, or have the potential for leaching into, groundwaters or surface waters; they include halogenated solvents, pesticides, phthalate esters, polycyclic aromatics (PAHs), dioxins, polychlorinated biphenyls (PCBs), etc. As part of a study of the feasibility of using ozone to treat the regulated contaminants (16), we determined the HO<sup>•</sup> reaction rate constants (*k*<sub>HO<sup>•</sup></sub>) of all of the regulated contaminants for which no literature data were available. A variety of HO<sup>•</sup>-generating techniques were used, including a convenient new method employing photo-Fenton's chemistry, and some rate constants were estimated using structure-activity relationships. A subsequent paper compares the rates of direct ozone reactions vs HO<sup>•</sup> reactions and assesses the differences in products from the two processes.

## Experimental Methods

**Stock Solutions.** Water used to prepare all solutions was from a Milli-Q purification system (Millipore Corp.) featuring reverse osmosis, activated carbon, ion exchange, and 0.2- $\mu$ m membrane filters.

**Ozone and H<sub>2</sub>O<sub>2</sub>.** Stock solutions of aqueous ozone were prepared using a 0.5-L min<sup>-1</sup> oxygen feed into a Welsbach Model T-408 ozone generator and allowing the gas stream to first pass through a wash bottle containing pH 6 phosphate buffer (to remove nitrogen oxides) and then into a flask containing distilled water and cooled in an ice-water bath. Continuous gas flow maintained an ozone concentration of about 800  $\mu$ M (38 ppm).

The 35% w/w H<sub>2</sub>O<sub>2</sub> solution was Albione 35 from Du Pont. Stabilizers were not removed before use.

**Organic Compounds.** Solutions of organic compounds were prepared by weight by rapidly stirring with Milli-Q water an amount calculated to give at most half their water solubility. Stock solutions were used within 2 days. All compounds were reagent grade or better and were used as received except lindane which was sublimed, endothall which was recrystallized from toluene/acetone, and diquat which was converted to the nitrate salt by precipitation of Br<sup>-</sup> with AgNO<sub>3</sub>. Estimates of hydrolysis rate constants from the literature (17) indicated that none of the compounds hydrolyzed significantly under the conditions used.

**Instruments.** Polar and semipolar organic compounds were determined on an HP1090 HPLC equipped with a (100  $\times$  2.1) mm 5- $\mu$ m Hypersil octadecylsilyl column and a photodiode array detector. An HP5880 GC with a J&W

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DB-5 capillary column [poly(diphenyldimethylsiloxane), 0.25  $\mu\text{m}$  film thickness, 15 m length, 0.33 mm i.d.] and an electron capture detector was used for measuring halogenated hydrocarbons. Chlordane was characterized using a Ribermag R 10-10C GC/MS system also equipped with a DB-5 column. Ionic compounds were determined on a Dionex 2000i ion chromatograph equipped with AG4A and AS4A columns and a conductivity detector. An HP8452A diode array spectrophotometer with an HP89500A UV/vis ChemStation was used for absorption measurements of iron-phenanthroline complexes.

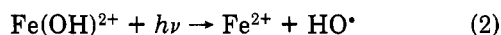
**Experimental Measurements of  $k_{\text{HO}\cdot}$ .** All experimental hydroxyl radical rate constants were determined using competition kinetics, and all except those employing Walling's method were evaluated according to eq (1), where

$$k_{\text{HO}\cdot}^{\text{M}} = \frac{\ln ([\text{M}]_0/[\text{M}]_{\infty})}{\ln ([\text{C}]_0/[\text{C}]_{\infty})} k_{\text{HO}\cdot}^{\text{C}} \quad (1)$$

$k_{\text{HO}\cdot}^{\text{C}}$  and  $k_{\text{HO}\cdot}^{\text{M}}$  are the rate constants for the reference compound and substrate, respectively. The two compounds were mixed and their concentrations measured by GC or HPLC before and after exposure to hydroxyl radicals. The extent of oxidation was varied in a series of batch experiments by changing the initial concentration of the  $\text{HO}\cdot$ -generating oxidant, which decomposed nearly to completion. In a few cases, more than one substrate was mixed with the reference compound and oxidized simultaneously. Chlordane and toxaphene were complex mixtures; they were used as received and the GC traces examined for decrease of any peaks following oxidation. Different methods of generating hydroxyl radicals ( $\text{HO}\cdot$ ) were used depending on the reactivity and light stability of the compound.

**Ozone Decomposition.** In this method, developed by Hoigné and Bader (5,13),  $\text{HO}\cdot$  is generated in batch reactors by allowing ozone to decompose for some hours at  $\text{pH} > 8$  (50 mM phosphate buffer) in the presence of the organic compounds. For compounds like alcohols and aromatics that generate the  $\text{O}_2\cdot^-$  radical upon reaction with  $\text{HO}\cdot$  in aerated water (18), we found the reaction to be complete in seconds to minutes in the absence of other scavengers. The method is relatively unambiguous and convenient if an ozone generator is accessible, but it has the drawbacks that it can only be used for compounds that do not react with ozone directly and that the limited solubility of ozone in water results in low conversions for compounds that react slowly with  $\text{HO}\cdot$  because ozone itself becomes a competitor for the  $\text{HO}\cdot$  produced. Extensive relative rate measurements (5) have demonstrated that  $\text{HO}\cdot$  is the dominant oxidant in this system and that contributions by other radicals present in solution such as  $\text{O}_2\cdot^-$  and  $\text{O}_3\cdot^-$  are nearly always negligible.

**Photo-Fenton's System.** Because of the low conversions for slowly reacting halogenated alkanes found by ozone decomposition, we developed the photo-Fenton's system to produce greater amounts of  $\text{HO}\cdot$ . In this method,  $\text{HO}\cdot$  is formed both by photolysis of  $\text{Fe}(\text{OH})_2^{2+}$  or  $\text{Fe}(\text{OH})_2^+$  (1) and by dark reaction of  $\text{Fe}^{\text{II}}$  with  $\text{H}_2\text{O}_2$ , e.g.



The principal advantages over the ozone decomposition method are that ozone-reactive substrates can be studied and much higher doses of oxidant ( $\text{H}_2\text{O}_2$ ) can be added without significantly diluting the aqueous organic solution. This method is also much more rapid than direct photolysis of  $\text{H}_2\text{O}_2$  at long wavelengths ( $> 300 \text{ nm}$ ), which are

often desirable to minimize photolysis of the organic substrate. However, caution must be exercised for compounds that complex iron and can be photooxidized directly as an  $\text{Fe}^{\text{III}}$  complex.

A typical procedure involved adding  $\text{Fe}(\text{ClO}_4)_3$  to an unbuffered aqueous solution of substrate and reference compound to yield 170  $\mu\text{M}$   $\text{Fe}^{\text{III}}$  and  $\text{pH} \sim 3$ . The sum of the substrate and reference compound concentrations was kept less than the dissolved oxygen concentration ( $\sim 250 \mu\text{M}$  under air). The sample was divided into several subsamples, and aliquots of 0.1 M  $\text{H}_2\text{O}_2$  were added to yield concentrations increasing from 0.1 to 1 mM  $\text{H}_2\text{O}_2$ . Each sample was photolyzed in a borosilicate glass tube at 30 cm from a Varian Eimac R300-3 (300 W) xenon lamp. The light intensity reaching the solutions as measured by a LI-COR Model LI-1800/12 spectroradiometer was about 700  $\text{W}\cdot\text{m}^{-2}$  in the range 300–500 nm, or about 4 times the intensity of spring, noon sunlight at 38° N. After being exposed for 1–2 min, most of the  $\text{H}_2\text{O}_2$  was consumed, as measured by  $\text{Ti}^{\text{IV}}$  complexation (19). The sample was removed from the light and an aliquot analyzed for substrate and reference compound as described above. Observed losses were corrected for any direct photolysis occurring in the absence of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{\text{III}}$ ; such corrections were small.

No acid or buffers were added to stabilize the iron solutions, in order to minimize the protonation of substrates and to simulate water treatment conditions where it would be desirable to avoid such additions. No precipitation occurred at  $\text{pH} \leq 3.6$ , although we did notice a moderate increase in absorbance following irradiation, suggesting that the light sped the rate of iron oxyhydroxide polymerization. In one experiment with 1 mM  $\text{Fe}^{\text{III}}$  at pH 4.3, precipitation became detectable and the oxidation became less efficient. Iron precipitation should be avoided both for rate constant measurements and for treatment processes, in the former case because selective sorption to the precipitate could affect relative rates of removal for some compound pairs.

To verify that  $\text{HO}\cdot$  radicals are generated in the photo-Fenton's method, we measured the relative rate of oxidation of tetrachloroethylene versus trichloroethylene, two compounds having known values of  $k_{\text{HO}\cdot}$ . The measured ratio of rate constants was 0.54, compared to a value of 0.62 calculated from literature data (12), consistent with  $\text{HO}\cdot$  as the dominant oxidant in this system. Further verification was obtained from the 1,1,2-trichloroethane/methanol pair, which gave a rate constant ratio of 0.13 (measured indirectly via 2-bromomethanol, see below) compared to a literature ratio of 0.11 (12, 14). Also,  $k_{\text{HO}\cdot}$  values for  $\text{CH}_2\text{Br}_2$  and  $\text{CHCl}_3$  determined by the photo-Fenton's method gave excellent agreement with data resulting from ozone decomposition (see Table I).

**Fenton's System.** For compounds that react slowly with  $\text{HO}\cdot$  and were light-sensitive, the dark Fenton's system was most appropriate. This approach involved adding small but increasing volumes of  $\text{H}_2\text{O}_2$  to a series of solutions containing a fixed, excess concentration of  $\text{Fe}(\text{ClO}_4)_2$  (freshly prepared in the range 0.2–2 mM) in the presence of the substrate and a reference compound. After waiting 10 min for the reaction to come to completion, the substrate and reference compounds were analyzed. This method was slightly slower than the photo-Fenton's method but was suitable for compounds that are subject to direct photolysis, such as hexachlorocyclopentadiene and picloram.

**Walling's Method.** This procedure was used for two compounds that we had difficulty analyzing in water. This

method, developed by Walling and Kato (20) and Walling and El-Taliawi (21), offers the advantage that it is not necessary to analyze for the compound of interest, but rather involves simple spectrophotometric measurement of  $\text{Fe}^{\text{II}}$  regardless of the substrate tested. It is therefore suitable for polar, nonchromophoric compounds or those lacking precise size definition, such as polymeric materials. The method is limited by the requirement of a solubility greater than a few mM and it operates only at  $\text{pH} < 2$ , so that the effect of ionization of some test compounds cannot be determined. Furthermore, the need to measure rather small absorbance differences limits the method's accuracy. It should also be cautioned that the reaction stoichiometry can vary with the type of organic radical formed (20, 22).  $\text{Cu}^{\text{II}}$  ion can be added as a catalyst to allow measurement of nearly all types of carbon radicals except those that can form stabilized anions on reduction, such as carbonyl-conjugated radicals (20, 22). Because the method determines the sum of reactivities of nearly all organic compounds present, impurities may interfere. Methods involving analytical separation of the substrate, such as the competitive ozone and Fenton's methods described above, are not subject to interference by impurities.

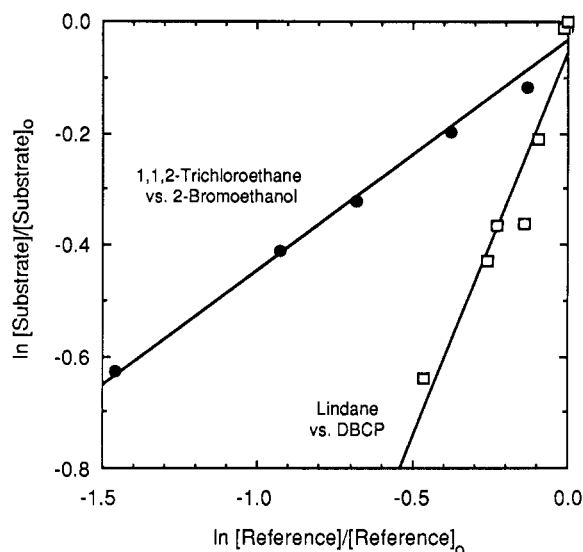
The details and theory of the method were described previously (20, 21). We added small concentrations of  $\text{H}_2\text{O}_2$  to deoxygenated mixtures of 5 mM  $\text{Fe}(\text{ClO}_4)_2$ , 2 mM  $\text{Cu}(\text{ClO}_4)_2$  catalyst, and the organic in 0.1 M  $\text{HClO}_4$  and determined the concentration of  $\text{Fe}^{\text{II}}$  remaining by its absorbance at 410 nm after complexation with excess 1,10-phenanthroline in pH 4 acetate buffer. By varying the concentration ratio of  $\text{Fe}^{\text{II}}$  to organic substrate (RH), one affects their competition for  $\text{HO}^\bullet$ . Conversion was kept to  $< 20\%$  so that initial rate assumptions could be made. Under these conditions, a plot of  $R$  vs  $2r(1 - R)$ , where  $R = \Delta[\text{Fe}^{\text{II}}]/2\Delta[\text{H}_2\text{O}_2]$  and  $r = [\text{Fe}^{\text{II}}]_0/2[\text{RH}]_0$ , gave a slope equal to  $k_{\text{HO}^\bullet}^{\text{Fe}^{2+}}/k_{\text{HO}^\bullet}^{\text{RH}}$ . Using the slope and the known value for  $k_{\text{HO}^\bullet}^{\text{Fe}^{2+}}$  of  $3.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (12), we calculated  $k_{\text{HO}^\bullet}^{\text{RH}}$ , the rate constant for reaction of the organic with  $\text{HO}^\bullet$ . We tested Walling's method using isopropanol as a substrate in the presence of  $\text{Cu}^{\text{II}}$ . We determined a rate constant of  $(1.4 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , in reasonable agreement with the literature value of  $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (12), demonstrating that we were applying the method correctly.

**Predictive Correlations for  $k_{\text{HO}^\bullet}$ .** Predictive equations based on literature values were determined by correlating sets of aqueous-phase data with either gas-phase data or  $\sigma$  constants for the same compounds. Data for the aqueous phase were taken from Buxton et al. (12) and Lal et al. (14) and for the gas phase from Atkinson (23).  $\sigma$  and  $\sigma^+$  constants were taken from Perrin et al. (24). Correlations were performed on a personal computer using the Statworks statistical program.

### Results and Discussion

A summary of all hydroxyl radical rate constants is given in Table I. The error limits are given as 95% confidence intervals on the slopes of relative rate plots. However, analytical precision was usually somewhat better than overall accuracy, which was more difficult to assess because it was sometimes affected by chemical processes that were not well defined. From radiation chemistry results (12) we expected errors of  $\pm 50\%$ . We found that agreement between different methods was often better than this, although we consider a range of a factor of 2 acceptable for the purposes of estimating oxidation rates during treatment processes.

**Experimental Rate Constants.** Figure 1 is a typical plot of a relative rate experiment. The scatter in the data was somewhat less for the heterocyclic aromatics, some-



**Figure 1.** Examples of relative rate data obtained using photo-Fenton's method (circles) and dark Fenton's method (squares).

what greater for the halomethanes, and about the same as in Figure 1 for most of the other compounds.

As one reviewer pointed out, methods employing Fe or Cu ions may result in complexation with the organic substrate. The extent of complexation was estimated from the stability constants given by Perrin (25) and references therein. Compounds that could have formed complexes but were present mostly as free ligand under the conditions used include adipic acid monoethyl ester, dalapon, propionic acid, and glycolic acid. Insufficient data were found to evaluate complexation by atrazine, simazine, picloram, endothall, aldicarb, and vydate, although except for picloram and endothall their structures and small protonation constants suggest that metal binding constants should not be large. By chemical analogy to iminodiacetate, glyphosate was probably present mostly in complexed form. Complexation may affect relative rates of oxidation, and therefore methods and conditions should preferably be chosen that avoid complex formation. However, while reduced metals often have higher rates of oxidation upon complexation, the rate constants for oxidized metal complexes are often similar to those found for the ligand with a proton substituted for the metal (12).

The photo-Fenton's method proved particularly useful. The results for dibromomethane (1) and chloroform (3) showed that the photo-Fenton's and ozone decomposition methods gave similar results but the former had considerably narrower confidence intervals for these slowly reacting compounds. The data for lindane (21) and endrin (22) show good agreement between the photo-Fenton's and Fenton's methods when the same standards were used, with slightly better precision for the photo-Fenton's system.

**Halogenated Alkanes and Alkenes.** Our rate constant for chloroform (3) ( $5.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) is a factor of 5 higher than that given in the literature [ $1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (12)]. We prefer the higher value because excellent agreement was obtained using 1,1,1-trichloroethane and 1,1,2-trichloroethane as reference compounds and because these substances have rate constants much closer to that of chloroform than the reference compounds used in the older studies (12). The higher value also places  $\text{CHCl}_3$  much nearer to the predictive correlation line for saturated compounds (see below).

The heavily chlorinated compounds gave the most experimental difficulties because they react slowly and few

Table I. Summary of Hydroxyl Radical Rate Constants in Aqueous Solution<sup>a</sup>

compd	structure	pK <sub>a</sub> <sup>b</sup>	concn, mM	pH range	method <sup>c</sup>	k <sub>HO•</sub> <sup>d</sup> M <sup>-1</sup> s <sup>-1</sup>	ref compd	ref k <sub>HO•</sub> <sup>e</sup>	N/
dibromomethane (1)	CH <sub>2</sub> Br <sub>2</sub>	NR	0.42	8.5	O <sub>3</sub> decomp	(9.0 ± 3.0) × 10 <sup>7</sup>	CH <sub>3</sub> CCl <sub>3</sub>	4.0 × 10 <sup>7</sup>	2
dichloromethane (2)	CH <sub>2</sub> Cl <sub>2</sub>	NR	0.34	3	photo-Fenton	(9.9 ± 0.2) × 10 <sup>7</sup> 2.2 × 10 <sup>7g</sup> 5.8 × 10 <sup>7e</sup>	CH <sub>2</sub> ClCHCl <sub>2</sub>	1.1 × 10 <sup>8</sup>	1
trichloromethane (3)	CHCl <sub>3</sub>	NR	0.16	8.5	O <sub>3</sub> decomp calc air <sup>c</sup>	(9 ± 6) × 10 <sup>7</sup> 1.2 × 10 <sup>8</sup> 1.1 × 10 <sup>7e</sup>	CH <sub>3</sub> CCl <sub>3</sub> self in air	4.0 × 10 <sup>7</sup> (8.5 × 10 <sup>7</sup> )	2
tribromomethane (4)	CHBr <sub>3</sub>	NR	0.1	8.5	O <sub>3</sub> decomp	(5.4 ± 3.0) × 10 <sup>7</sup>	CH <sub>3</sub> CCl <sub>3</sub>	4.0 × 10 <sup>7</sup>	2
carbon tetrachloride (5)	CCl <sub>4</sub>	NR	0.34	3	photo-Fenton	(5.0 ± 0.3) × 10 <sup>7</sup>	CH <sub>2</sub> ClCHCl <sub>2</sub>	1.1 × 10 <sup>8</sup>	1
1,1,2-trichloroethane (6)		NR	0.11	8.5	O <sub>3</sub> decomp calc air	(1.3 ± 0.6) × 10 <sup>8</sup> <2 × 10 <sup>6</sup> 1.1 × 10 <sup>8e</sup>	CH <sub>3</sub> CCl <sub>3</sub> self in air	4.0 × 10 <sup>7</sup> (<6 × 10 <sup>6</sup> )	2
1,2-dichloropropane (7)		NR	0.22	2.8	photo-Fenton calc air	(1.3 ± 0.4) × 10 <sup>8</sup> 2 × 10 <sup>8</sup>	CH <sub>2</sub> BrCH <sub>2</sub> OH self in air	3.5 × 10 <sup>8</sup> (2 × 10 <sup>8</sup> )	1
1,2-dibromo-3-chloropropane (8)		NR	0.12	2.8	photo-Fenton	(3.8 ± 1.9) × 10 <sup>8</sup>	DBCP	4.2 × 10 <sup>8</sup>	1
epichlorohydrin (9)		NR	0.045	2.7	photo-Fenton	(3.2 ± 0.4) × 10 <sup>8</sup>	CH <sub>2</sub> BrCH <sub>2</sub> OH	3.5 × 10 <sup>8</sup>	2
2-bromoethanol (10)	BrCH <sub>2</sub> CH <sub>2</sub> OH	NR	0.045	2.7	photo-Fenton	(4.2 ± 0.9) × 10 <sup>8</sup>	CCl <sub>2</sub> =CCl <sub>2</sub>	2.6 × 10 <sup>9</sup>	1
1,1,1-trichloro-2-methyl-2-propanol (11)		NR	NR		calc air calc air	2.9 × 10 <sup>8</sup> 2.9 × 10 <sup>8</sup>	self in air self in air	(2.6 × 10 <sup>8</sup> ) (2.6 × 10 <sup>8</sup> )	
adipic acid monoethyl ester (12)		NR	0.5	2.7	photo-Fenton	(3.5 ± 2.3) × 10 <sup>8</sup>	CH <sub>3</sub> OH	9.7 × 10 <sup>8</sup>	1
phthalates (13)		NR	NR	3	Fenton	(2.7 ± 0.5) × 10 <sup>8</sup>	CH <sub>2</sub> ClCHClCH <sub>3</sub>	3.3 × 10 <sup>8</sup>	1
dimethyl (13a)									
diethyl (13b)									
trichlorobenzenes (14)		NR	4.4	3-30	1	Walling	(3.0 ± 0.8) × 10 <sup>9</sup>	Fe <sup>2+</sup>	1
1,2,4- (14a)									
1,2,3- (14b)									
dichlorobenzenes (15)		NR	NR						
para- (15a)									
meta- (15b)									
ortho- (15c)									
PCBs (16)		NR	0.17-0.23	8.7	O <sub>3</sub> decomp calc σ	4 × 10 <sup>9</sup> (5.0 ± 1.0) × 10 <sup>9</sup> 4 × 10 <sup>9</sup>	chlorobenzene	5.5 × 10 <sup>9</sup>	2
2,3,3',5,6- (16a)									
2,2',4,4',5,5'- (16b)									
PAHs (17)		NR	NR						
	etc.								

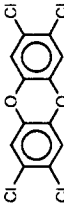
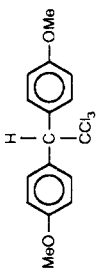
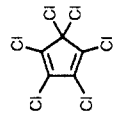
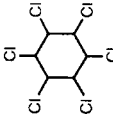
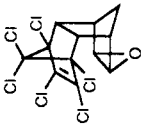
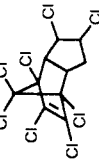
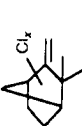
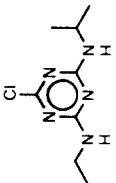
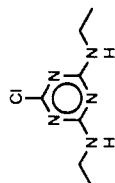
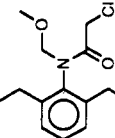
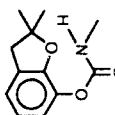
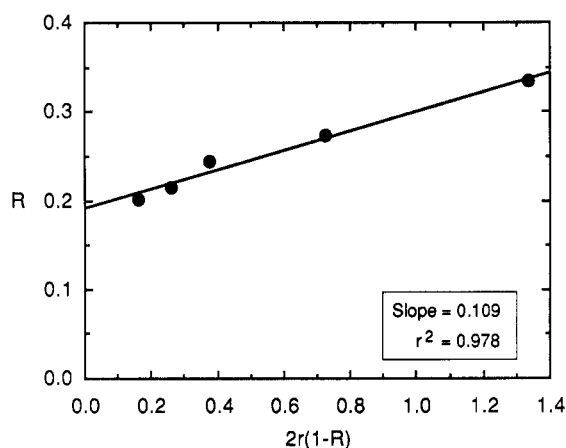
2,3,7,8-tetrachlorodibenzo- dioxin (18)		NR	calc $\sigma$	$4 \times 10^9$		
methoxychlor (19)		NR	calc $\sigma$	$2 \times 10^{10}$		
hexachlorocyclopentadiene (20)		NR	0.0054 0.020–0.029 0.014 0.006	3.4 2.8 3.4 3.4	Fenton Fenton Fenton Fenton	$(8.8 \pm 3.7) \times 10^8$ DBCP $(2.2 \pm 0.6) \times 10^9$ $\text{CCl}_2=\text{CCl}_2$ $(3.4 \pm 0.7) \times 10^9$ $\text{CCl}_2=\text{CCl}_2$ (70 $\mu\text{M Br}^-$ ) lindane $4.2 \times 10^8$ 2 $2.6 \times 10^9$ 1 $2.6 \times 10^9$ 1 $8 \times 10^8$ 1
lindane (21)		NR	0.007 0.004 0.004–0.005	2.9 2.9 2.8	Fenton photo-Fenton Fenton	$(5.8 \pm 1.9) \times 10^8$ DBCP $(5.2 \pm 0.9) \times 10^8$ DBCP $(1.1 \pm 0.2) \times 10^9$ $\text{CCl}_2=\text{CCl}_2$ (70 $\mu\text{M Br}^-$ ) $4.2 \times 10^8$ 1 $4.2 \times 10^8$ 1 $2.6 \times 10^9$ 2
endrin (22)		NR	0.012 0.0009 0.0010 0.0005	2.8 2.8 3.4 2.8	Fenton Fenton photo-Fenton Fenton	$(9.2 \pm 0.4) \times 10^8$ $\text{CCl}_2=\text{CCl}_2$ $(2.7 \pm 0.7) \times 10^8$ DBCP $(1.1 \pm 0.2) \times 10^9$ lindane $(1.3 \pm 0.4) \times 10^9$ lindane $2.6 \times 10^9$ 1 $4.2 \times 10^8$ 1 $8 \times 10^8$ 1 $8 \times 10^8$ 1
chlordane (23)		NR	0.0009	3.3	photo-Fenton	$(6\text{--}170) \times 10^8$ lindane $8 \times 10^8$ 1
toxaphene (24)		NR	0.003 $1.9 \pm 0.1$	$1.9 \pm 0.1$	Fenton	$(1.2\text{--}8.1) \times 10^8$ lindane $8 \times 10^8$ 1
atrazine (25)		1.6	0.020	3.6	photo-Fenton	$(2.6 \pm 0.4) \times 10^9$ acetophenone $5.9 \times 10^9$ 1
simazine (26)		2.0	0.020	3.5	photo-Fenton	$(2.8 \pm 0.2) \times 10^9$ acetophenone $5.9 \times 10^9$ 1
alachlor (27)		NR			calc $\sigma$	$7 \times 10^9$
carbofuran (28)		NR			calc $\sigma$	$7 \times 10^9$

Table I (Continued)

compd	structure	pK <sub>a</sub> <sup>b</sup>	concn, mM	pH range	method <sup>c</sup>	k <sub>HO•</sub> <sup>d</sup> M <sup>-1</sup> s <sup>-1</sup>	ref compd	ref k <sub>HO•</sub> <sup>e</sup>	N/ <sup>f</sup>
pentachlorophenol (29)		4.7			calc σ	4 × 10 <sup>9</sup>			
dinoseb (30)		4.5			calc σ	4 × 10 <sup>9</sup>			
picloram (31)		3.6	0.021	2.1–3.7	Fenton	(3.4 ± 0.3) × 10 <sup>9</sup>	acetophenone	5.9 × 10 <sup>9</sup>	2
2,4-D (32)		2.64			calc σ	5 × 10 <sup>9</sup>			
2,4,5-TP (33)		2.7			calc σ	4 × 10 <sup>9</sup>			
aldicarb (34)		NR	0.038	3.5	Fenton	(8.1 ± 1.1) × 10 <sup>9</sup>	acetophenone	5.9 × 10 <sup>9</sup>	1
vydate (oxamyl) (35)		NR	0.013	3.4	Fenton	(2.0 ± 0.2) × 10 <sup>9</sup>	acetophenone	5.9 × 10 <sup>9</sup>	1
dalapon (36)		2.06	0.10	3.4	photo-Fenton	(7.3 ± 0.3) × 10 <sup>7</sup>	propionic acid	4.6 × 10 <sup>8</sup>	1
endothall (37)		4.2, 6.3	3–30	1	Walling	(1.5 ± 0.6) × 10 <sup>9</sup>	Fe <sup>2+</sup>	3.3 × 10 <sup>8</sup>	1
glyphosate (38)		2.6, 5.9, 10.4	0.16	3.8	photo-Fenton	(1.8 ± 0.5) × 10 <sup>8</sup>	glycolic acid	7.3 × 10 <sup>8</sup>	1
diquat (39)		NR	0.064	3.1	Fenton	(8.0 ± 1.8) × 10 <sup>8</sup>	acetophenone	5.9 × 10 <sup>9</sup>	1

<sup>a</sup> All data at 24 ± 1 °C except *m*-dichlorobenzene, which was at 22 ± 2 °C. <sup>b</sup> See Yao and Haag (16) for sources of data; NR, not relevant (compound does not ionize to a kinetically significant extent). <sup>c</sup> Calc air, calculated from gas-phase measurements using log k<sub>HO•(water)</sub> = 1.682 + 0.805 [log k<sub>HO•(air)</sub>], with both in units of M<sup>-1</sup> s<sup>-1</sup>. Calc σ, calculated using log k<sub>HO•</sub> = 9.829–0.318 Σσ. <sup>d</sup> Error limits are 95% confidence intervals on the slopes. <sup>e</sup> All data from Buxton et al. (12) or Lal et al. (14) except 2-bromoethanol and chloroform which were determined in this work. Data for the gas phase are given in parentheses and are from Atkinson (23). <sup>f</sup> N, number of measurements. <sup>g</sup> Klöpffer et al. (30).



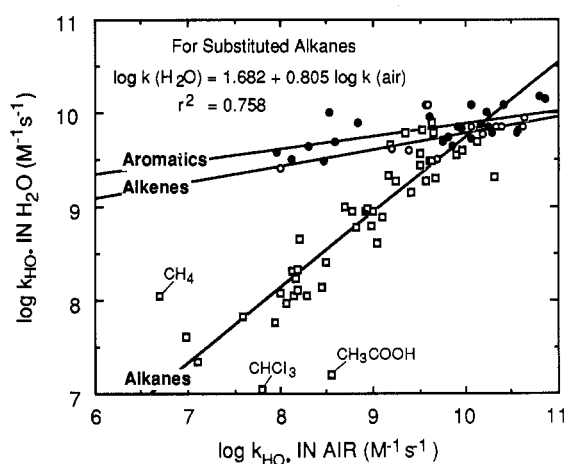
**Figure 2.** Determination of  $k_{\text{HO}\cdot}$  for ethyl adipate using Walling's method.

appropriate reference compounds were available for which hydroxyl radical rate constants were accurately known. For example, the results for hexachlorocyclopentadiene (20), lindane (21), and endrin (22) gave some discrepancies. The values obtained using 1,2-dibromo-3-chloropropane (8) (DBCP) as a reference compound were 2–5 times smaller than those obtained using tetrachloroethylene or lindane as standards, even though the value for DBCP was itself determined relative to tetrachloroethylene. This discrepancy was not a result of differences between the Fenton's and photo-Fenton's methods because the two systems gave consistent results as discussed above. We considered the possibility that oxidation of DBCP produced  $\text{Br}\cdot$ , which was inhibiting further oxidation of the substrates, but addition of  $70\ \mu\text{M}$   $\text{Br}^-$  had little effect. An interfering process for these substrates is the involvement of chlorine atom chain reactions that become more severe with increasing chlorine substitution (26) and are difficult to suppress without also suppressing  $\text{HO}\cdot$  reactions.  $\text{Cl}\cdot$  reactions may explain the lack of effect of bromide, because the  $\text{Cl}_2\cdot^-$  or  $\text{Br}_2\cdot^-$  radical ions formed in these systems have similar selectivities to each other (27). The average rate constants, if assigned to  $\text{HO}\cdot$  reactions, were  $2.3 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$  for hexachlorocyclopentadiene (20),  $7.5 \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$  for lindane (21), and  $7.5 \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$  for endrin (22).

**Chlordane and Toxaphene.** Chlordane (23) exhibited a range of rate constants. Some components oxidized rapidly, notably heptachlor and chlordene, which have two double bonds, while others were less reactive, such as the chlordane isomers, which have only one (hindered) double bond. Similarly, toxaphene (24) exhibited a range of rate constants, although the range was not as great as with chlordane, possibly because toxaphene contains fewer double bonds.

**Triazines.** The data for atrazine (25) and simazine (26) are the first measurements we are aware of for triazines. Reaction can occur by addition to the ring or H abstraction from the side-chain NH or CH groups. The rate constants are similar to those for  $\text{HO}\cdot$  addition to carbon homocyclic aromatics but somewhat lower than for H abstraction from NH of anilines. This result could be interpreted as an attack at either of these two sites, modified by the electron-withdrawing effect of the ring nitrogens (24), that is, the amine groups behave more like amidines than anilines. The data are also consistent with attack at the side-chain CH groups, and oxidation there has been noted during ozonation (28), presumably via  $\text{HO}\cdot$ .

**Picloram (31)** gave a rate constant that was independent of pH from pH 2.1 to 3.7; reaction probably occurs by addition to the ring or H abstraction from the amine,

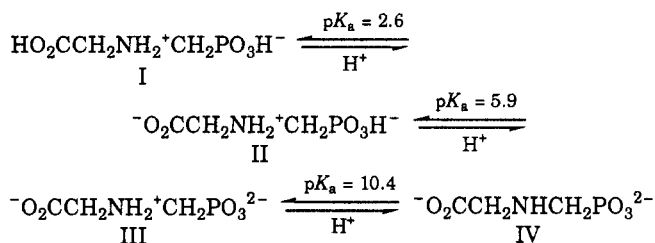


**Figure 3.** Correlation of hydroxyl radical rate constants for un-ionized forms of the compounds in water versus air. Substituted alkanes, open squares; alkenes, open circles; aromatics, solid circles.

neither of which should be greatly affected by ionization of the carboxyl group. Although amine-H reactivity is greatly decreased by protonation (12), the amine group in picloram is protonated only in concentrated acid (16).

**Carboxylic Acids.** Figure 2 gives an example of the type of plot obtained by Walling's method. The slope yields a value of  $(3.0 \pm 0.8) \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$  for ethyl adipate (12), similar to the value of  $2.0 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$  for adipic acid (12). Endothall (37) gave a rate constant of  $1.5 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$ , also in the expected range. Because the experiments were conducted in 0.1 M acid, these rate constants refer to the undissociated forms of the compounds. However, we expect the values for the dissociated forms to be the same because hydroxyl radical rate constants for long-chain fatty acids are hardly effected by ionization of the carboxyl group (12). By analogy to succinate, endothall would have expected complex  $\text{Fe}^{\text{III}}$ , although in the Walling method used iron is present mostly as  $\text{Fe}^{\text{II}}$ , which has much lower stability constants than  $\text{Fe}^{\text{III}}$  (25). The value for dalapon (36) corresponds to the anion, because the pH is well above the  $\text{pK}_a$ .

**Glyphosate (38)** at pH 3.8 in the absence of metals is present mainly as the zwitterion II with negative charges on the carboxyl and one phosphonate oxygen, and a positive charge on the nitrogen. It is not likely that form III,



which dominates at neutral pH and has both phosphonate oxygens ionized, has a significantly greater rate constant. However, it should be cautioned that the rate constant may have been affected by complexation with iron, as discussed above. The value for the reference compound, glycolic acid, was taken as the average of the values for the acidic and basic forms ( $6.0 \times 10^8$  and  $8.6 \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$ , respectively), because the experimental pH was equal to its  $\text{pK}_a$  of 3.8 (29).

**Predictive Correlations.** Figure 3 shows a correlation of hydroxyl radical H-atom abstraction rate constants for substituted alkanes in water versus the gas phase using literature data (12, 14, 23). The correlation included nine haloalkanes, seven alcohols, seven unsubstituted alkanes,

five esters, five epoxides and ethers, four acids, three ketones, two nitriles, one amine, and two difunctional compounds. The compounds were predominantly (82%) straight chained containing four or less carbon atoms; 18% were C<sub>5</sub>-C<sub>8</sub>, and a few were cyclic or branched hydrocarbons. Sulfides and aldehydes deviated noticeably from the best-fit line and were then omitted from the correlation because sulfides can react by addition to S rather than H-atom abstraction, and aldehydes hydrate in water resulting in possibly different reactivity than the unhydrated forms present in air. Deviations for some of the small compounds (CH<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>3</sub>COOH) were as large as an order of magnitude, but most of the rate constants lie within a factor of 3 of the regression line given by

$$\log k_{\text{HO}\cdot}(\text{water}) = 1.682 + 0.805 \log k_{\text{HO}\cdot}(\text{air}) \quad (4)$$

where both rate constants are in units of molar<sup>-1</sup> second<sup>-1</sup>. Klöpffer et al. (30) and Güsten et al. (31) reported somewhat different correlations, for example, the equivalents of

$$\log k_{\text{HO}\cdot}(\text{water}) = -1.45 + 1.12 \log k_{\text{HO}\cdot}(\text{air}) \quad (5)$$

$$\log k_{\text{HO}\cdot}(\text{water}) = 0.98 + 0.88 \log k_{\text{HO}\cdot}(\text{air}) \quad (6)$$

respectively. Our correlation uses mostly the same data as that of Klöpffer et al. (30) but is improved by the use of a few updated rate constants (especially acetonitrile), addition of some new rate constants, and removal of compounds that ionize or hydrate in water and those for which H-atom abstraction is not the only pathway. Experimental data for 1,1,2-trichloroethane (6) and 1,2-dibromo-3-chloropropane (8) gave good agreement with the values calculated from the gas-phase data (see Table I), and therefore the correlation could be used with reasonable confidence for other alkanes as well.

Aromatics and alkenes do not fall on the same correlation line as alkanes, apparently because they can react rapidly by addition to double bonds rather than H-atom abstraction (31). We therefore correlated rate constants for aromatics in water with Hammett  $\sigma$  constants (24), as shown in Figure 2, because this can be done for more compounds without the need for a gas-phase value:

$$\log k_{\text{HO}\cdot}(\text{water}) = 9.829 - 0.318 \sum \sigma \quad (7)$$

This correlation includes seven methyl- and four halo-substituted benzenes, three heterocyclic compounds, two phenols, along with benzene, naphthalene, and -NH<sub>2</sub>, -OCH<sub>3</sub>, -CN, -NO<sub>2</sub>, -CHO, vinyl, and phenyl-substituted benzene. Regression versus  $\sigma^+$  constants as recommended by Atkinson (23) for gas-phase data gave only a small improvement in correlation coefficient that did not justify the difficulties resulting from the lesser availability of  $\sigma^+$  constants. Figure 4 shows that, contrary to results in the gas phase (23), addition of HO $\cdot$  to olefins is so facile in water that the rate constants are almost independent of the substituents on the double bond. The same conclusion was drawn by Güsten et al. (31).

**Aromatic Compounds.** For aromatics the range of values was only a factor of 5 (including those for aniline and nitrobenzene), and all data are within a factor of 1.6 of the correlation line. Therefore simple calculations were likely to give data of about the same accuracy as experimental measurements. The experimental value for *m*-dichlorobenzene (15b) verified the correlation equation given in Figure 4, and all other rate constants for aromatics were calculated using this equation. Rate constants for PAHs (17) and 2,3,7,8-tetrachlorodibenzodioxin (18) (TCDD) were also calculated from  $\sigma$  values. Because the rate constants for benzene and naphthalene are nearly the same

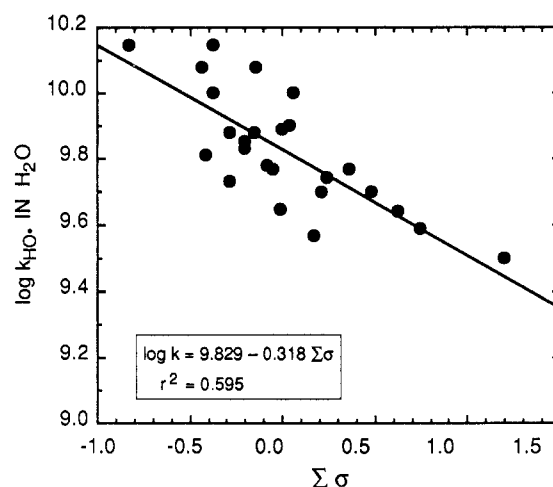


Figure 4. Correlation of hydroxyl radical rate constants for aromatics in water versus Hammett  $\sigma$  constants.

[the  $\sigma$  value is near zero for an annulated ring (19)], we estimated that the values for PAHs are also essentially the same. The calculation for TCDD assumes no rate-promoting effect of the oxygen atoms because the inductive effects of the *o*- and *m*-phenoxy groups balance each other, and no statistical factor because the rings are fused; therefore, the value is about the same as for the dichlorobenzenes.

### Conclusions

Rate constants for reactions of the hydroxyl radical with 39 compounds or classes of compounds were measured or estimated using structure-activity relationships. The photo-Fenton's system proved to be a convenient HO $\cdot$  source, especially for slowly reacting substrates, and it has less interference by direct photolysis of substrates than the use of H<sub>2</sub>O<sub>2</sub> photolysis in the absence of iron.

The present results are consistent with previous work (12) that demonstrated that HO $\cdot$  is a relatively nonselective radical toward C-H bonds, but is least reactive with aliphatic polyhalogenated compounds. Olefins and aromatics react with HO $\cdot$  in water with rate constants that vary by less than a factor of 10, whereas in the gas phase the values for these same compounds vary by a factor of nearly 500. In both cases the fastest reactions proceed at near the diffusion-controlled limit.

During water treatment the rate of substrate oxidation by HO $\cdot$  will depend on the type of radical oxidation process, which determines the HO $\cdot$  concentration. For simple ozonation of surface waters containing low concentrations (<10<sup>-5</sup> M) of organic contaminants, we calculate half-lives ranging from 30 s to 2 h for HO $\cdot$  oxidation of the compounds listed in Table I except CCl<sub>4</sub>, assuming an HO $\cdot$  concentration of 2 × 10<sup>-12</sup> M at 1 ppm ozone (Haag and Yao, unpublished). These rates may be modified in real treatment systems by sorption of hydrophilic compounds to particulate matter or in waters containing very high amounts of carbonate and therefore lower HO $\cdot$  concentrations.

### Acknowledgments

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**Registry No.** 2,4-D, 94-75-7; 2,4,5-TP, 93-72-1; dibromomethane, 74-95-3; dichloromethane, 75-09-2; trichloromethane, 67-66-3; tribromomethane, 75-25-2; carbon tetrachloride, 56-23-5; 1,1,2-trichloroethane, 79-00-5; 1,2-dichloropropane, 78-87-5; 1,2-



dibromo-3-chloropropane, 96-12-8; epichlorohydrin, 106-89-8; 2-bromoethanol, 540-51-2; 1,1,1-trichloro-2-methyl-2-propanol, 57-15-8; adipic acid monoethyl ester, 626-86-8; dimethyl phthalate, 131-11-3; diethyl phthalate, 84-66-2; 1,2,4-trichlorobenzene, 120-82-1; 1,2,3-trichlorobenzene, 87-61-6; *para*-dichlorobenzene, 106-46-7; *meta*-dichlorobenzene, 541-73-1; *ortho*-dichlorobenzene, 95-50-1; 2,3,3',5,6-pentachlorodiphenyl, 74472-36-9; 2,2',4',4,5,5'-hexachlorobiphenyl, 35065-27-1; 2,3,7,8-tetrachlorodibenzodioxin, 1746-01-6; methoxychlor, 72-43-5; hexachlorocyclopentadiene, 77-47-4; lindane, 58-89-9; endin, 72-20-8; chlordane, 12789-03-6; toxaphene, 8001-35-2; atrazine, 1912-24-9; simazine, 122-34-9; alachlor, 15972-60-8; carbofuran, 1563-66-2; pentachlorophenol, 87-86-5; dinoseb, 88-85-7; picloram, 1918-02-1; aldicarb, 116-06-3; vydate (oxamyl), 23135-22-0; dalapon, 75-99-0; endothall, 145-73-3; glyphosate, 1071-83-6; diquat, 2764-72-9; hydroxyl radical, 3352-57-6.

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