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Kinetic Study of the Reactions of Chlorine Atoms and $Cl_2^{\bullet-}$ Radical Anions in Aqueous Solutions. II. Toluene, Benzoic Acid, and Chlorobenzene[†]

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Laser and conventional flash photolysis of $Na_2S_2O_8$ aqueous solutions containing Cl^- ions were employed to investigate the reactions of chlorine atoms and $Cl_2^{\bullet-}$ radical ions with toluene, benzoic acid, and chlorobenzene. A mechanism is proposed which accounts for the faster decay of $Cl_2^{\bullet-}$ in aqueous solutions containing increasing concentrations of the organic substrates. Interpretation of the experimental data is supported by kinetic computer simulations. Chlorine atoms react with the three substituted aromatics studied here almost with diffusion-controlled rate constants, $k = (1.8 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1}. The high reactivity observed for Cl atoms contrasts with that of the $Cl_2^{\bullet-}$ radical ions, for which the rate constant for its reactions with the substituted benzenes is $\leq 1 \times 10^6$ M^{-1} s^{-1}. The organic radicals produced from these reactions, as well as the nature of the reaction products are discussed. The observed results seem to support an addition mechanism yielding chlorocyclohexadienyl radicals (Cl−CHD) as the most significant reaction channel following reaction of Cl atoms and the organic compounds. In air-saturated solutions, subsequent thermal reactions of Cl−CHD radicals lead both to chlorination and oxidation of the aromatics.

Introduction

Chloride is one of the most abundant anions in the tropospheric aqueous phase.[1] Chlorine atoms, which in the presence of chloride ions reversibly yield $Cl_2^{\bullet-}$ radical ions,[2,3] may be formed in cloud droplets by the reaction of chloride with strongly oxidizing radicals such as $NO_3^{\bullet}$, $SO_4^{\bullet-}$, and $HO^{\bullet}$. Therefore, oxidation of chloride may represent an important sink of strong oxidants in tropospheric multiphase systems, depending on the final fate of the $Cl^{\bullet}$ atoms and $Cl_2^{\bullet-}$ radicals.

$Cl^{\bullet}$ and $Cl_2^{\bullet-}$ radicals are strong oxidants ($E(Cl_2^{\bullet-}/2Cl^-) =$ 2.0 V and $E(Cl^{\bullet}/Cl^-) = 2.4$ V vs NHE)[4,5] and may react with many organic compounds.[6] Cl atoms react rapidly with many species[7−9] and can contribute to the loss of $Cl_2^{\bullet-}$ under atmospheric conditions. In a previous paper on the reactions of $Cl^{\bullet}/Cl_2^{\bullet-}$ with benzene in water,[9] we have shown that the high reactivity of Cl atoms toward benzene contrasts that of the $Cl_2^{\bullet-}$ radical anions.

The determination of the reactivity of $Cl^{\bullet}$ and $Cl_2^{\bullet-}$ radicals toward aromatic compounds is of environmental importance, as these reactions may both lead to the formation of undesired chlorinated derivatives and/or promote their oxidation as observed for benzene.[9] Here we report a kinetic and mechanistic study on the aqueous phase reactions of $Cl_2^{\bullet-}$ and $Cl^{\bullet}$ with toluene, benzoic acid, and chlorobenzene.

The reactions of $Cl^{\bullet}$ and $Cl_2^{\bullet-}$ are studied by laser and conventional flash photolysis as well as by steady-state photolysis of $S_2O_8^{2-}$ solutions containing various concentrations of Cl^- in the presence of substituted benzenes.

Results and Discussion

$SO_4^{\bullet-}$ radical ions, absorbing in the wavelength range from 300 to 550 nm, were generated by photolysis of aqueous peroxodisulfate solutions[9−11] in the pH range 3−4 (reaction 1). In the presence of chloride ions at concentrations $>10^{-4}$ M,[9] $SO_4^{\bullet-}$ radicals are readily depleted due to the high efficiency of reaction 2 yielding chlorine atoms. The reverse reaction (reaction −2) is of no significance under our experimental conditions, where SO_4^{2-} ions of very low concentration are formed only after reaction 2. Reaction of $Cl^{\bullet}$ with Cl^- ions reversibly yields $Cl_2^{\bullet-}$ radical ions, reactions 3 and 4.

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\bullet-} \qquad \text{(R,1)}$$

$$SO_4^{\bullet-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\bullet} \qquad \log k = 8.43 + 1.018 \times I^{1/2\ 2,9} \qquad \text{(R,2)}$$

$$Cl^{\bullet} + SO_4^{2-} \rightarrow Cl^- + SO_4^{\bullet-} \qquad 2.1 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}\ ^{7b} \qquad \text{(R−2)}$$

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-} \qquad 8.5 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}\ ^{7} \qquad \text{(R,3)}$$

$$Cl_2^{\bullet-} \rightarrow Cl^{\bullet} + Cl^- \qquad 6.0 \times 10^4\ \mathrm{s^{-1}}\ ^{2} \qquad \text{(R,4)}$$

Time-resolved experiments with $[Cl^-] > 10^{-3}$ M and $[S_2O_8^{2-}]$ = 25 mM (laser experiments) or 5 mM (conventional flash experiments) show a transient species with an absorption maximum at $\lambda \sim 340$ nm, whose spectrum is in agreement with that reported for the $Cl_2^{\bullet-}$ radical ions.[12] In the $[Cl^-]$ range used

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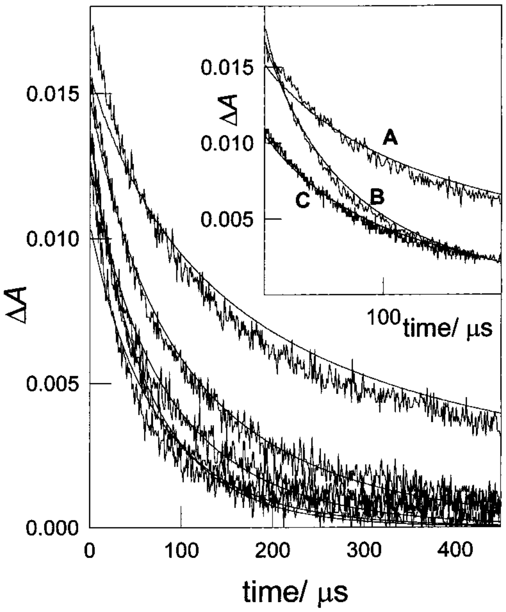


Figure 1. Signals obtained at $\lambda_{obs} = 340$ nm by laser flash photolysis experiments with 25 mM $K_2S_2O_8$ and 49.2 mM NaCl solutions containing variable concentrations of chlorobenzene from up to down: 0, 1.3, 2.17, 2.82, and 3.47 mM. *Inset*: Idem for solutions containing 25 mM $K_2S_2O_8$ and (a) [ClBz] = 0 M, $[Cl^-] = 0.069$ M; (b) [ClBz] = 2.8 mM, $[Cl^-] = 69$ mM; and (*c*) [ClBz] = 2.8 mM, $[Cl^-] = 96.2$ mM. The solid lines represent computer simulations (refer to text).

in the present study and taking $K_{3,4} = 1.4 \times 10^5\ M^{-1}$ for the stability constant for the reversible reactions 3 and 4,[7] and $\epsilon(Cl^{\bullet}, 350\ nm) = 3800\ M^{-1}\ cm^{-1}$,[13] any contribution of chlorine atoms to the observed absorption traces can be neglected.

The transient decay follows a complex kinetics strongly depending on $[Cl^-]$. A complete description of the mechanism can be found in refs 7 and 9. The most significant reactions accounting for the observed experimental decay of $Cl_2^{\bullet-}$ are the reversible reactions 3 and 4, the recombination of the $Cl_2^{\bullet-}$ radical ions (reaction 5), and the complex reversible reaction system of $Cl^{\bullet}/Cl_2^{\bullet-}$ with water schematized by reactions 6, −6, 7, −7, and 8.

$$\mathrm{Cl_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow Cl_2 + 2Cl^-}$$

$$\log k = 8.8 + 1.6 \times I^{1/2}/(I^{1/2}+1)\ ^{2,9} \tag{R,5}$$

$$\mathrm{Cl_2^{\bullet-} + H_2O \rightarrow (HOClH)^{\bullet} + Cl-}\quad 1300\ \mathrm{s^{-1}}\ ^{2,7} \tag{R,6}$$

$$\mathrm{(HOClH)^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-} + H_2O}\ ^{2,9} \tag{R,-6}$$

$$\mathrm{Cl^{\bullet} + H_2O \rightarrow (HOClH)^{\bullet}}\quad 2.5 \times 10^5\ \mathrm{s^{-1}}\ ^{2,7} \tag{R,7}$$

$$\mathrm{(HOClH) \rightarrow Cl^{\bullet} + H_2O}\ ^{2,9} \tag{R,-7}$$

$$\mathrm{(HOClH)^{\bullet} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} (HOCl)^{\bullet-} \rightleftarrows Cl^- + HO^{\bullet}}\ ^{2,9} \tag{R,8}$$

Photolysis of air-saturated aqueous peroxodisulfate solutions containing chloride ions in the range 0.03 M to 0.6 M and [XPh] $< 2 \times 10^{-3}$ M where XPh stands for the substituted benzenes, leads to the formation of a transient species whose spectrum agrees with that of the $Cl_2^{\bullet-}$ radical ion.

For a given $[Cl^-]$, faster decay rates of $Cl_2^{\bullet-}$ are observed by addition of increasing amounts of XPh, as shown in Figure 1 for chlorobenzene. The experimental absorption traces at a given wavelength of analysis, *A(λ)*, could be fitted according to eq 1.[9] The calculated constant *g* is independent of *λ* but linearly depends on [XPh], as shown in Figure 2 for toluene. The small absorption term *h*(*λ*) [< 5% of the initial absorption of $Cl_2^{\bullet-}$, *f*(*λ*)] may be associated with a longer lived species formed after $Cl_2^{\bullet-}$ depletion.

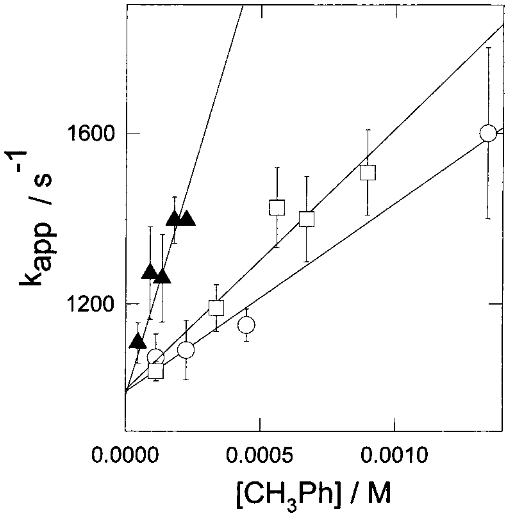


Figure 2. Linear dependence of the first-order decay component (k_{app}) of $Cl_2^{\bullet-}$ on $[CH_3Ph]$ for experiments with $[Cl^-] = 0.1$ M (▲), 0.2 M (□), and 0.4 M (○).

$$A(\lambda) = f(\lambda) \times e^{-g \times t} + h(\lambda) \tag{E,1}$$

The effect of XPh on the decay rate of $Cl_2^{\bullet-}$ may be understood if reactions 9 and 10 efficiently compete with the decay reactions of $Cl_2^{\bullet-}$ and $Cl^{\bullet}$, reactions 5 to 8.

$$\mathrm{Cl_2^{\bullet-} + XPh \rightarrow Cl^- + organic\ radical} \tag{R,9}$$

$$\mathrm{Cl^{\bullet} + XPh \rightarrow organic\ radical} \tag{R,10}$$

The total concentration of the organic radicals $R^{\bullet}$ formed from the reaction of XPh with $Cl^{\bullet}$ and $Cl_2^{\bullet-}$ cannot exceed the initial concentration of sulfate radicals $[SO_4^{\bullet-}]_o$, therefore $[R^{\bullet}] < 10^{-6}$ M (laser experiments) or $< 3 \times 10^{-5}$ M (conventional flash experiments). Consequently, a diffusion-controlled reaction between $R^{\bullet}$ and $Cl_2^{\bullet-}$, reaction 11, may accelerate the decay kinetics of $Cl_2^{\bullet-}$ radical ions. However, in a first approximation, the contribution of reaction 11 will not be considered.

$$\mathrm{Cl_2^{\bullet-} + R^{\bullet} \rightarrow products} \tag{R,11}$$

The efficient removal of $HO^{\bullet}$ radicals by the substituted benzenes[14] does not allow the attainment of equilibrium conditions for reactions 6 to 8, and reactions of $Cl_2^{\bullet-}$ and $Cl^{\bullet}$ with water may be considered as simple first-order reactions[9] with rate constants k_6 and k_7, respectively. Under these conditions, reactions 6, 7, 9, and 10 are the main reactions depleting $Cl_2^{\bullet-}$ which are in equilibrium with $Cl^{\bullet}$.[9] As $K_{3,4} \times [Cl^-] > 1$ and $k_7/K_{3,4}[Cl^-] \ll k_6$,[9] the apparent first-order decay rate constant of $Cl_2^{\bullet-}$, k_{app}, is given by eq 2.

$$k_{app} = k_6 + \left[\frac{k_{10}}{K_{3,4} \times [Cl^-]} + k_9\right] \times [XPh] \tag{E,2}$$

In fact, plots of k_{app} (factor *g* in eq 1) vs [XPh] fit to eq 2, as shown in Figure 2 for toluene. The intercepts of the straight lines in Figure 2 are (939 ± 245), (976 ± 260), and (949 ± 243) s^{-1} for $[Cl^-] = 0.1$, 0.2, and 0.4 M, respectively. In this

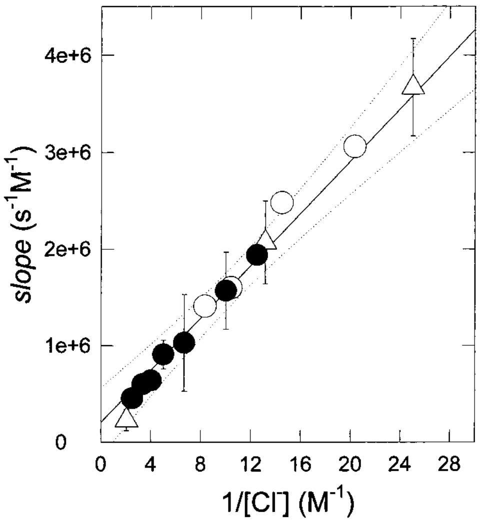


Figure 3. Dependence of the slopes of the plots of k_{app} vs [XPh] on $[Cl^-]^{-1}$ for (●) toluene, (△) benzoic acid, and (○) chlorobenzene. Since the organic radical ($R^\bullet$) formed from benzoic acid shows significant absorption at 340 nm (vide infra), the observation wavelength for the experiments done with this substrate was 360 nm.

work the error bars stand for a Student's distribution taking a 99% confidence level. Similar results for the intercept values of the curves of k_{app} vs [XPh] are obtained for benzoic acid and chlorobenzene (data not shown). The intercept values agree, within the experimental error, with reported values for k_6.[9] The slopes of the straight lines obtained by plotting k_{app} vs [XPh] linearly depend on $[Cl^-]^{-1}$ as expected from eq 2 (see Figure 3).

Figure 3 shows that, within the experimental error, data obtained for the three aromatics fall in the same straight line. From the slope of the linear function in Figure 3 obtained for all the substrates, the bimolecular rate constant $k_{10} = (1.8 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1} is obtained. From the intercept k_9 is estimated to be $(2 \pm 4) \times 10^5$ M^{-1} s^{-1}.

To validate the simplified kinetic analysis (vide supra) and to evaluate the contribution of reaction 11 to the concentration profiles of $Cl_2^{\bullet-}$, a detailed kinetic analysis was performed with the aid of computer simulations (for details of the program see Experimental section). For this purpose, the set of reactions depicted in Table 1 of ref 9 along with reactions 9 to 11 and the reactions of ClPh with $HO^\bullet$ and $SO_4^{\bullet-}$ radicals[15] were used. No equilibrium conditions were assumed a priori for the reversible reactions 3 and 4 and those involving the reactions of $Cl_2^{\bullet-}$/ $Cl^\bullet$ with water, reactions 6 to 8. The program considers the flash emission as a delta function producing $SO_4^{\bullet-}$ radicals. Simulated $Cl_2^{\bullet-}$, $Cl^\bullet$, Cl_2, and Cl_3^- concentration profiles were converted into the corresponding absorption curves and then added and compared with the experimental data to fit the complete set of experiments with the substrate chlorobenzene in a global analysis.

Initial $[SO_4^{\bullet-}]_o$ and the reaction rate constants k_9, k_{10}, and k_{11} were allowed to vary to fit the experimental absorption profiles. Figure 1 shows the excellent agreement observed between simulated and experimental profiles. The adjusted $[SO_4^{\bullet-}]_o$ agree, within the 15% experimental error, with the values measured in corresponding experiments in the absence of Cl^- and ClPh. The rate constants $k_{10} = (1.7 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1} and $k_{11} = (0.003 \pm 16) \times 10^6$ M^{-1} s^{-1} are obtained in agreement with the values calculated from the simplified kinetic analysis also considering a negligible rate for k_{11}. For k_9 the value $(9 \pm 3) \times 10^5$ M^{-1} s^{-1} is obtained. However, constricting k_9 to a value $\leq 2 \times 10^5$ M^{-1} s^{-1}, the goodness of the fitting and the values of k_{10} and k_{11} are not changed, also in agreement with the simplified kinetic analysis. If k_{11} is fixed to a value of 1×10^{10} M^{-1} s^{-1}, the optimal $k_{10} = (8.2 \pm 1.6) \times 10^9$ M^{-1} s^{-1} is retrieved though the agreement between simulated and experimental curves is not good, thus further indicating that reaction 11 does not significantly contribute to the $Cl_2^{\bullet-}$ decay. When the program considers a moderate absorption coefficient of $R^\bullet$ ($\epsilon_{(340\ nm)} \leq 1500$ M^{-1} cm^{-1}) and the decay reactions observed in oxygen-saturated solution (vide infra), the same values for k_9 and k_{10} are obtained, within the error bars. Consequently, the small absorbance of $R^\bullet$ has no effect on the simplified kinetic analysis.

TABLE 1: Main Products Obtained after Reaction of $Cl^\bullet$ Atoms with XPh after Four Minutes Irradiation

substrate	identified products[a]	experimental conditions
benzoic acid	3-chlorobenzoic acid, 4-chlorobenzoic acid, and chlorobenzene	$[CO_2HPh] = 7.2$ mM $[S_2O_8^{2-}] = 5$ mM $[Cl^-] = 0.5$ M
toluene	1-chloro-2-methylbenzene, benzaldehyde, benzyl alcohol, benzyl chloride, 1-chloro-4-methylbenzene, and bibenzyl	$[S_2O_8^{2-}] = 5$ mM $[Cl^-] = 0.5$ M $[CH_3Ph] = 0.8$ mM
chlorobenzene	phenol, 2 chlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, and 2,3,6-trichlorophenol[b]	$[S_2O_8^{2-}] = 5$ mM $[Cl^-] = 0.5$ M $[ClPh] = 0.56$ mM

[a] Chromatographic peaks with mass spectra corresponding to C_4–C_5 fragmentation products containing carbonyl functions, but no Cl atoms were detected for all the substrates. [b] 2,3,4,6-Tetrachlorophenol, 2,3,5,6-tetrachlorophenol, hydroxyquinone tetrachloro, and phenol pentachloro were also detected after irradiation for 8 min .

Organic Transient Detection. Information on the pathways involved in the reaction of XPh with $Cl^\bullet$ may be gained if the nature of the organic transients ($R^\bullet$) formed after reaction 10 is established. For this purpose, time-resolved experiments were performed with high concentrations of organic substrates ([XPh] $> 10^{-3}$ M), such that reaction 10 is so efficient that Cl atoms are readily scavenged and the $R^\bullet$ radical products may be observed. Due to the very low reactivity of $Cl_2^{\bullet-}$ radical ions toward XPh, the contribution of reaction 9 to the observed transients is expected to be of no significance.

The experimental conditions were carefully chosen. On one hand, high $[Cl^-]$ to [XPh] ratios guarantee a negligible contribution of the reactions of XPh with $SO_4^{\bullet-}$ radicals competing with reaction 2. On the other hand, low $[Cl^-]$ yield $Cl_2^{\bullet-}$ lifetimes < 300 μs (see eq 2) necessary for detecting $R^\bullet$ and obtaining information on its decay reactions.

Photolysis of XPh was minimized using a XPh saturated aqueous solution as filter. Blank experiments performed under identical experimental conditions used for detecting the organic transients but in the absence of $S_2O_8^{2-}$ showed no signal, indicating that any contribution of XPh photolysis is negligible and that the observed transients are mainly formed after reaction 10.

Similar considerations were taken in steady irradiation experiments of air-saturated solutions performed to identify the reaction products. In all cases the experiments showed depletion of XPh and the simultaneous formation of the products depicted in Table 1. Due to the particular behavior observed for the organic transients and reaction products generated from the reaction of $Cl^\bullet$ with the different XPh, these will be discussed separately.

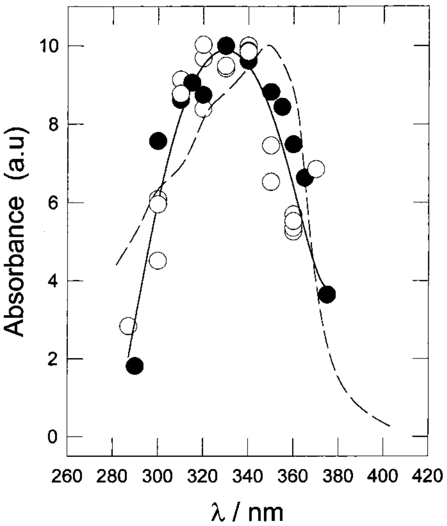


Figure 4. Absorption spectrum of the organic transients obtained 200 μs after irradiation with a conventional flash lamp, of nitrogen-saturated solutions containing 5 mM $K_2S_2O_8$ and 0.05 M (○) or 0.1 M (●) NaCl in the presence of 7.2 mM benzoic acid. The dashed line corresponds to the normalized reported spectrum of the HO−CHD radicals of benzoic acid.[16]

Benzoic Acid. Preliminary experiments showed that the transient species formed after reaction of $Cl^\bullet$ with benzoic acid (HCO_2Ph) presents an absorption maximum close to that of $Cl_2^{\bullet-}$. Thus, for the optimal experimental conditions $[Cl^-] = 0.05$ or 0.1 M, $[S_2O_8^{2-}] = 5$ mM and $[HCO_2Ph] = 7.2$ mM, $Cl_2^{\bullet-}$ lifetime is $\leq 120\ \mu$s, and consequently, the transient spectra were taken 200 μs after the pulse of light in order to minimize any contribution of $Cl_2^{\bullet-}$.

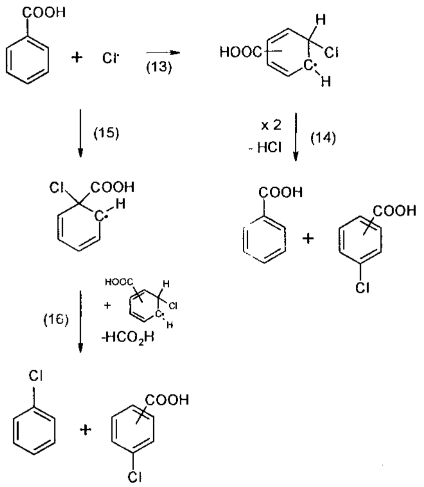
The observed transient absorbs in the wavelength region from 280 to 460 nm with maximum at around 330 nm, as depicted in Figure 4. In N_2-saturated solutions a second-order decay kinetics is observed with a bimolecular decay rate of $2k/\epsilon_{max}$(330 nm) of $1 \times 10^5\ s^{-1}$ cm. Experiments performed under identical conditions but in the presence of molecular oxygen show the same transient spectrum, although with lower absorbance.

The spectrum and kinetic behavior of the organic transient is typical of cyclohexadyenyl radicals (CHD). In fact, the hydroxycyclohexadienyl radical (HO−CHD) of benzoic acid, also shown in Figure 4, shows a single absorption maximum at 350 nm ($\epsilon = 3600-3800\ M^{-1}\ cm^{-1}$) and a bimolecular decay rate $2k/\epsilon_{max}$(350 nm) of $1 \times 10^5\ s^{-1}$ cm.[16] The cyclohexadienyl radical of benzoic acid (H−CHD) shows an absorption maximum at around 320−330 nm.[16,17] Moreover, HO−CHD radicals of various substituted benzenes[18] and the chlorocyclohexadienyl radical (Cl−CHD) of benzene[11] are known to rapidly and reversibly react with molecular oxygen, yielding peroxyl radicals (reaction 12). Peroxyl radicals (PR) typically exhibit broad absorption only at $\lambda < 280$ nm.[19,20] Consequently, after a few microseconds the equilibrium condition for reaction 12 is established and the main effect of oxygen on the CHD spectrum taken 200 μs after the pulse of light is that of lowering the absorption.

$$\text{HO−CHD} + O_2 \rightleftarrows \text{PR} \qquad (\text{R},12)$$

Addition of $Cl^\bullet$ to the aromatic ring of benzoic acid yielding chlorocyclohexadienyl radicals (ClCHD), reaction 13 in Scheme 1, in a reaction similar to that observed for benzene[9] is a possible reaction pathway. On the basis of comparison of the kinetic and spectroscopic patterns of the observed transient with those of the H−CHD and HO−CHD radicals of benzoic acid, it may be assigned to a mixture of the three possible isomers of Cl−CHD radicals of benzoic acid. Cl−CHD radical formation is further supported by the nature of the observed reaction products, as shown in Scheme 1.

SCHEME 1: Reactions of Benzoic Acid



Disproportionation of the 3- and 4-Cl−CHD radicals of benzoic acid with loss of HCl leads to the formation of the isomers 3- and 4-chlorobenzoic acid, respectively, supporting an addition/elimination route (reactions 13 and 14). Formation of 3- and 4-chlorobenzoic acid was not quantified, however, assuming that their chloroform/water partition coefficients and GC detector sensitivities are similar to those of benzoic acid, the total yield of the chlorobenzoic acids accounts for a 30% the amount of benzoic acid depleted.

A further reaction pathway for the reaction of $Cl^\bullet$ with benzoic acid is H-abstraction from the carboxylic group yielding benzoylperoxyl radicals. The latter radical shows an absorption maximum at $\lambda > 800$ nm and is known to decarboxylate in organic solvents yielding phenyl radicals and carbon dioxide with a first-order oxygen-independent rate constant of the order of $6 \times 10^6\ s^{-1}$.[21,22] Assuming that benzoylperoxyl radicals decarboxylate with similar rates in aqueous solutions, their lifetime should be of fractions of microseconds. The phenyl radicals thus formed efficiently react with molecular oxygen (phenyl lifetime $< 3\ \mu$s in air saturated solutions)[23b] yielding arylperoxyl radicals which absorb in the wavelength range from 400 to 500 nm and decay by bimolecular recombination with second-order rate constants $< 10^7\ M^{-1}\ s^{-1}$.[23,24] The observed transient does not show absorption in this wavelength range, and we may conclude that the H-abstraction route is of no significance. This is also supported by the fact that germinate products resulting from cage recombination of the phenyl/benzoyloxyl radical pairs (vide infra) were not formed.[25] For the same reasons, an H-abstraction pathway from the aromatic ring yielding phenyl radicals and HCl should also be of no significance.

Chlorobenzene also observed as a reaction product though in very small yields (<0.4%), may be formed from the reaction of phenyl radicals with $Cl_2^{\bullet-}/Cl^\bullet$. However, under our experimental conditions, $[O_2]/[Cl_2^{\bullet-}] > 10^3$, the reaction with O_2 is expected to be an important reaction depleting phenyl radicals. Since benzoyloxyl radical formation is not supported by our time-resolved experiments (vide supra), we suggest chlorobenzene may be formed after an *ipso* addition of $Cl^\bullet$ to benzoic acid yielding an *ipso* Cl−CHD radical, reaction 15. Subsequent bimolecular reaction with the other isomers of Cl−CHD radicals

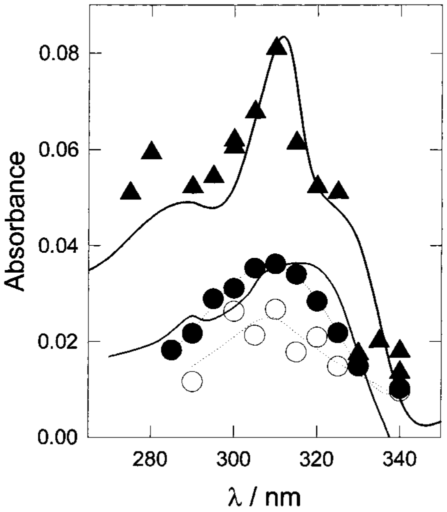
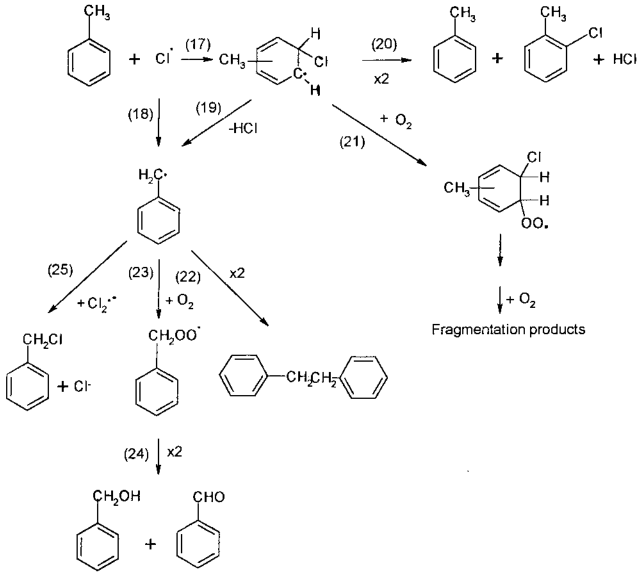


Figure 5. Absorption spectrum of the organic transients obtained 250 μs after irradiation with a conventional flash lamp for N_2 (▲), air (●) and O_2 (○)-saturated 5 mM $K_2S_2O_8$ solutions containing 0.5 M NaCl in the presence of 5.6 mM toluene. The solid line corresponds to the normalized published spectrum of the HO−CHD radicals of toluene from refs 27 (upper spectrum) and 26, 28] (lower spectrum).

SCHEME 2: Reactions of Toluene



yields either chlorobenzene upon elimination of formic acid, as shown in reaction 16, or benzoic acid when HCl is eliminated (not shown).

Reaction of Cl−CHD radicals with molecular oxygen leads to oxidized fragmentation products, as will be discussed for the other substrates (vide infra).

Toluene. The absorption spectra of the transient obtained at 250 μs after the flash of light in N_2-, air-, and O_2-saturated solutions containing 7.3 mM $S_2O_8{}^{2-}$, 0.5 M Cl^-, and 5.6 mM CH_3Ph is shown in Figure 5. In N_2-saturated solutions the spectrum shows a sharp peak at about 310−315 nm and a shoulder below 290 nm. In the presence of molecular oxygen but otherwise identical experimental conditions, the transient spectrum shows lower absorbance and a less structured band with a maximum at around 305−315 nm.

The reaction of Cl• with toluene may proceed either by addition to the aromatic ring yielding Cl−CHD radicals, reaction 17 in Scheme 2, or by H-abstraction from the CH_3 group yielding benzyl radicals, reaction 18. The observed spectrum in air- and O_2-saturated solutions and the band at 315 nm under N_2 saturation present similar patterns to that of the HO−CHD radical of toluene[26−28] (see Figure 5). The shoulder observed at $\lambda > 290$ nm in N_2-saturated solutions may be due to the contribution of benzyl radicals which were reported to present absorption in the 290−250 nm range in aqueous solutions.[27] Benzyl radicals irreversibly react with molecular oxygen with a rate constant of 2.8×10^9 M^{-1} s^{-1} to yield peroxyl radicals absorbing at $\lambda < 280$ nm and thus should not be observed in air- and O_2-saturated solutions. Note that benzyl radicals in MTHF matrixes show an absorption maximum at 308 and 319 nm.[29] If such absorption is also present in aqueous solutions, its contribution to the visible absorption band observed in N_2-saturated solutions cannot be discarded.

Similar absorption spectra were observed for the Cl−CHD and HO−CHD radicals of benzene[9] and also for those of benzoic acid (vide supra), consequently, the observed transient in the presence of oxygen may be assigned to Cl−CHD radicals of toluene. The lower absorbance observed with increasing $[O_2]$ may be explained by a reversible reaction with O_2 as observed for the Cl−CHD radicals of benzene[9] and benzoic acid (vide supra) and for most HO−CHD.[20]

An addition reaction yielding Cl−CHD, reaction 17, and a subsequent loss of HCl catalyzed by acids, reaction 19, may also explain the formation of benzyl radicals. The latter reaction pathway resembles the addition of HO• radicals to toluene, where benzyl radicals are formed from the acid-catalyzed elimination of water from the HO−CHD radical.[30,31] Therefore, formation of benzyl radicals does not unambiguously support an H-abstraction reaction from the CH_3 group. In fact, kinetic isotope studies of the reactions of toluene with Cl atoms in CCl_4 shows that the isotope effect on the rates of the reaction of Cl atoms with $CH_2DC_6H_5$ is very small, thus further supporting an addition mechanism.[32]

Disproportionation of the Cl−CHD radicals of toluene yields toluene and chlorotoluene, reaction 20. Mainly 2- and 4-chlorotoluene were detected as reaction products, in agreement with free radical substitutions at an aromatic carbon.[33] Reaction of Cl−CHD radicals with O_2 yields PR which upon subsequent addition of O_2, reaction 21, leads to fragmentation products as reported for most CHD radicals.[9,20]

Formation of bibenzyl can be explained from the recombination of benzyl radicals, reaction 22.[34] Reaction of benzyl radicals with O_2 yields peroxyl radicals[35] which undergo subsequent disproportionation yielding benzyl alcohol and benzaldehyde, reactions 23 and 24. Reaction of benzyl radicals with $Cl_2^{\bullet-}$ leads to the formation of benzyl chloride and chloride ions, reaction 25.

Photochlorination of toluene by chlorine in organic solvents at low temperatures and high chlorine concentrations is also reported to undergo an attack of Cl•, both, on the ring and on the side-chain C−H bonds, with the former being highly reversible.[36]

Chlorobenzene. The absorption traces of the organic intermediate of chlorobenzene were obtained in experiments with $[S_2O_8{}^{2-}] = 0.01$ M, $[Cl^-] = 0.05$ M, and $[ClPh] = 4.46 \times 10^{-3}$ M. The transient spectrum taken 150 and 500 μs after the flash pulse shows an absorption maximum around 310−320 nm, both for N_2- and air-saturated solutions, as shown in Figure 6. In N_2-saturated solutions a second-order decay kinetics is observed with a bimolecular decay rate of $2k/\epsilon_{max}$(320 nm) of 4×10^5 s^{-1} cm. Experiments performed under identical conditions but in the presence of molecular oxygen show the same transient spectrum although with lower absorbance and

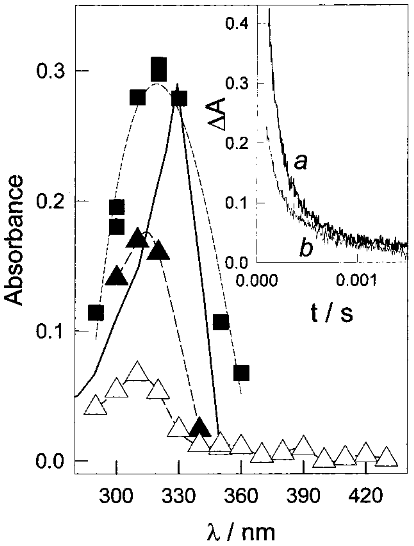
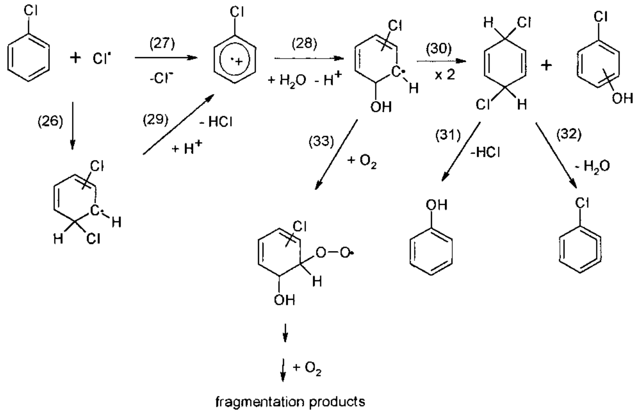


Figure 6. Absorption spectrum of the organic transients obtained 150 μs and 500 μs (black and white symbols, respectively) after irradiation with a conventional flash lamp for N_2- (squares) and air- (triangles) saturated 5 mM $K_2S_2O_8$ and 0.05 M NaCl solutions in the presence of 4.5 mM chlorobenzene. The dashed line corresponds to the normalized reported spectrum of the HO−CHD radicals of chlorobenzene. *Inset*: Absorption traces obtained at 320 nm in (a) N_2- and (b) air-saturated solutions.

SCHEME 3: Reactions of Chlorobenzene



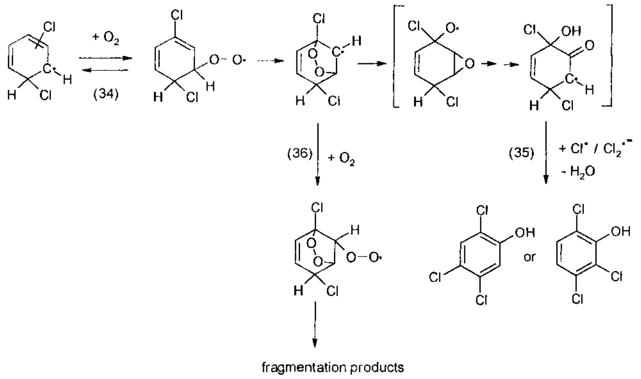
faster decay kinetics (shown in Figure 6 *inset*), as expected from a reversible reaction with O_2 yielding peroxyl radicals (vide infra).[18,19]

The transient absorption spectrum, its bimolecular decay and the reversible reaction with O_2, are characteristic of the CHD radicals and resemble those of the HO−CHD radical of chlorobenzene,[37] except for the higher absorption observed at shorter wavelengths, as shown in Figure 6. The polychlorinated phenols detected as reaction products (depicted in Table 1) indicate a complex reaction system where both, the Cl−CHD and HO−CHD radicals of chlorobenzene are involved. Consequently, the observed transient may be assigned to the contribution of all the isomeric forms of both CHD radicals.

The CHD radicals may be formed from two different reaction channels: addition of Cl$^\bullet$ to the aromatic ring of ClPh yields a Cl−CHD, reaction 26 in Scheme 3, and a charge transfer from the aromatic ring to Cl$^\bullet$ yielding an unstable radical cation which subsequently hydrolyses to a HO−CHD radical, as shown in reactions 27 and 28.

Dichlorobenzene formed from the disproportionation of the Cl−CHD radicals of ClPh[38] is not observed. Thus, under our experimental conditions for product detection, Cl−CHD radicals readily decay by reactions other than disproportionation.

SCHEME 4: Reactions Leading to the Formation of Trichlorophenol



Cl−CHD radicals may lose HCl to yield an unstable chlorobenzene radical cation which efficiently adds water to yield HO−CHD radicals (reactions 29 and 28). The latter radicals undergo subsequent disproportionation to chlorophenol (an observed minor reaction product) and chlorohydroxycyclohexadienes, which may either eliminate HCl yielding phenol or eliminate water leading to chlorobenzene (reactions 31 and 32, respectively). Otherwise, the reaction of HO−CHD with O_2 leads to the formation of oxidized open chain products (vide supra). HO−CHD radical disproportionation reactions in O_2-containing solutions were reported not to contribute significantly to product formation,[38] in agreement with the relatively small peaks of chlorophenol observed.

As HO−CHD radicals may be formed both, from the addition and electron tranfer pathways (vide supra), the contribution of the electron-transfer route cannot be discarded for this substrate.

Formation of tri- and tetrachlorophenols may occur from the subsequent diffusion-controlled H-abstraction reactions by Cl atoms from the HO group of chlorophenol yielding chlorophenoxyl radicals which upon subsequent Cl addition leads to an increased chlorination of the phenol.[39,40] The latter reaction path seems unlikely since dichlorophenol, an intermediate product in the chlorination pathway to trichlorophenol, is not formed in detectable yields and high ratios of trichlorophenols to chlorophenol are already observed at short irradiation times. These observations suggest that trichlorophenols are most probably formed during the primary steps of the reaction. A possible reaction pathway, shown in Scheme 4 for the para Cl−CHD isomer, involves a reversible reaction of Cl−CHD radicals with molecular oxygen yielding endoperoxides, which are stabilized by subsequent rearrangement, intramolecular H-abstraction and reaction with Cl$^\bullet$/$Cl_2^{\bullet-}$ to yield trichlorophenols, reaction 35. Otherwise, subsequent addition of O_2 to the endoperoxides leads to the rupture of the cycle yielding oxidized fragmentation products,[38] reaction 36.

Conclusions

The rate constants k_{10} determined here in aqueous solution for XPh: toluene, benzoic acid, and chlorobenzene and that of benzene,[9] as well as those reported in the literature in CH_2Cl_2 for phenol, aniline, dimethylaniline, dimethoxybenzene, and hexamethylbenzene[39] all fall within the experimental error in the range from 1.2×10^{10} to 2.5×10^{10} M^{-1} s^{-1}. The reaction rate constants being diffusion-controlled, show no dependence on the σ-Hammett parameter of the substituent in the aromatic ring. The high reactivity of Cl atoms contrasts with that of $Cl_2^{\bullet-}$

radical ions, for which the rate constants for the reactions with the substituted benzenes are $< 1 \times 10^6$ M^{-1} s^{-1}. This observation is in agreement with studies involving aliphatic organic compounds reported by Gilbert[6] and Buxton.[12] Comparison of the reactivity of $Cl^{\bullet}$ with some reported rate constants for the reactions of $Cl_2^{\bullet-}$ indicates that, in many cases, these rate constants are largely accounted for by the fraction of Cl atoms present in equilibrium with $Cl_2^{\bullet-}$, as already discussed in refs 7 and 12.

No evidence for the formation of a π-complex,[41−43] absorbing at 490 nm with a lifetime of 1 to 10 μs was found. We may therefore conclude that a π-complex between the aromatics and Cl atoms is either not formed or decomposes in aqueous solutions in less than 50 ns to yield Cl−CHD radicals. The same behavior was observed for the substrate benzene.[9] Very low bond energies (<12 kJ) were calculated for the π-complex of benzene,[44] thus indicating that, unless highly stabilized by the solvent, it cannot survive to play any role in a sequence of chemical reactions. Further evidence supporting the formation of adducts with Cl atoms other than a loosely bound π-complex are the formation of a three-electron complex, $Me_2S\therefore Cl$[46] and Cl−CHD radicals of pyridine and azarenes.[4,48]

Chlorine atom addition to the aromatic ring of the XPh studied here and to benzene[9] yielding a Cl−CHD radical, seems to be an important reaction channel for reaction 10. However, neither the contribution of an H-abstraction reaction pathway from the CH_3 group of toluene nor an electron transfer from the aromatic ring of ClPh to Cl atoms can be unambiguously neglected. An electron-transfer reaction pathway is of no significance for the substrates benzene,[9] toluene and benzoic acid, since phenolic derivatives formed from the disproportionation of HO−CHD radicals were not observed as reaction products. An electron-transfer mechanism was also proposed for *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine and dimethoxy benzene in dichloromethane.[39]

Cl−CHD adduct formation in the photochemical chlorination of benzene was already postulated in the fifties supported by trapping experiments with maleic anhydride.[45] Cl−CHD formation is also a contributing pathway in the reaction of $Cl^{\bullet}$ with benzene in the gas phase though its main fate is decomposition to reform the reactants.[44]

Formation of Cl−CHD radicals was proposed to be the main species responsible for the increased selectivity in the abstraction of tertiary with respect to primary hydrogen observed in the chlorination of alkanes in aromatic solvents.[45−47] Moreover, the apparent reactivity of such Cl-adducts toward 2,3-dimethylbutane, as observed in time-resolved experiments, was reported to reflect the extent of their reversible dissociation to free $Cl^{\bullet}$.[49]

The difference in the behavior of the Cl−CHD radicals in the gas phase and in organic solvents compared with that in the aqueous phase seems to be the lack of dissociation of Cl−CHD in aqueous solutions. A possible explanation for the apparent mechanistic differences is that Cl−CHD is always formed in each phase but it does not significantly dissociate on the time scale of our observations (see ref 9). This indicates that the role of the aqueous medium is that of stabilizing the Cl−CHD radicals.

The contribution of H-atom abstraction from the aromatic ring yielding reactive phenyl radicals is not supported by our studies, since aryl peroxyl radical formation from the reaction of phenyl with O_2 (vide supra), neither its reaction products were observed. The fact that H-abstraction from the aromatic ring is not an important reaction channel is in line with the reported behavior of Cl atoms showing a strong preference for H-abstraction from OH groups and/or to undergo electron transfer with the anions of aliphatic alcohols, rather than abstracting hydrogen from C−H bonds.[8]

Experimental Section

Materials. Potassium peroxodisulfate (Merck), sodium chloride (Merck p.a.), chlorobenzene (Merck p.a.), toluene (Merck p.a.), and benzoic acid (Merck p.a.) were used as received. Distilled water (>18Ω cm^{-1}, < 20 ppb of organic carbon) was obtained from a Millipore system.

Time-Resolved Experiments. Flash photolysis experiments were carried out using a conventional equipment (Xenon Co. model 720C) with modified optics and electronics (optical path length 11 cm). Laser experiments were performed with a Spectron SL400 Nd:YAG system generating 266 nm pulses (∼8 ns pulse width, optical path length 1 cm).

Preparative Experiments. A cylindrical low-pressure Hg lamp (Heraeus, MNNI 35/20, Germany) emitting at 254 nm was used. The photochemical reactor was of annular geometry (volume: 400 mL, annular optical path of 1 cm). The whole reactor was immersed in a thermostat controlling the temperature at 25 ± 1 °C.

A more complete description of the experimental setup for time-resolved and preparative experiments can be found in refs 9 and 50.

Methods. Unless otherwise indicated, typical $S_2O_8^{2-}$ concentrations were 5.0×10^{-3} M for conventional flash photolysis and 2.5×10^{-2} M for laser experiments. The pH of the samples was controlled with a Methrom-Herisau pH meter model E512. The pH of the peroxodisulfate solutions was approximately 4 due to the acid content incorporated with the $K_2S_2O_8$, containing water and acid as impurities. The ionic strength of the solutions was within the range of 0.005 to 0.2 M.

Solutions of the aromatics were prepared by dilution of their saturated aqueous solution at 25 °C. For experiments performed in the absence of molecular oxygen, the saturated solutions of the organic substrates and the water used for dilution were bubbled with N_2.

Organic products were extracted from the aqueous solutions with a fixed volume of chloroform and the extracts stored in glass vials with PTFE/silicone septum-lined screw caps and minimized headspace. Analysis of the extracts was performed by gas chromatography with a HP 6890 chromatograph equipped with a fused silica HP5-MS GC capillary column and coupled to an HP 5973 mass selective detector. The analysis was performed by using a temperature program starting at 80 °C and ending at 200 °C at a rate of 10 °C/min and held at 200 °C for 5 min. Helium was used as carrier gas with a flow rate of 29 cm^3/s. Injection volumes were of 20 μL.

Kinetic Computer Simulations. The model is based on component balances and equilibrium equations that are formulated in terms of a differential algebraic equations system (DAE). The DAE system is solved by a modified version of the LSODI routine[51] based on Gear's Stiff method.[52] The version implemented performs the solution of the DAE system concomitantly to the evaluation of the parametric sensitivities based on the decoupled direct method.[53] In consequence, the simulation of the system is robust, such that it can be carried out with success for very different parameter values, while the sensitivities obtained are accurate and obtained without much computational effort. The estimation criterion used to solve this problem is the least squares. The algorithm for minimization of the criterion is based on the rotational discrimination[54] and provides additional features for assessing the identifiability of the problem.[55]

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