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Reactions of carbon dioxide radical anion with substituted benzenes

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ABSTRACT: We report mechanistic studies on the reactivity of $CO_2^{\cdot -}$ radicals towards substituted benzenes, XPh, with X = NO_2, COOH, COH, CH_3, H, Cl and HO. Vacuum ultraviolet (VUV, 172 nm) irradiation of aqueous solutions containing formate was used as a method of $CO_2^{\cdot -}$ radical generation for the study of the reaction products, which were determined by gas chromatography–mass spectrometry and high-performance liquid chromatography. The nature of some of the reaction intermediates was studied by laser flash photolysis of aqueous solutions of peroxodisulfate in the presence of formate. The observed products and intermediates of reaction are discussed and rationalized by a dual reactivity of the $CO_2^{\cdot -}$ radical anion with substituted benzenes: a one-electron reduction and radical addition to the aromatic ring. For substituted benzenes with X = NO_2, COOH and COH, the observed products support an electron transfer from $CO_2^{\cdot -}$ to the substrates as the primary reaction channel, while the reactions with toluene follow the channel of radical addition. Benzene and chlorobenzene react with $CO_2^{\cdot -}$ by both routes, electron transfer and radical addition. Our experimental results indicate that H abstraction by the $CO_2^{\cdot -}$ radical is negligible under the chosen experimental conditions. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: carbon dioxide radical anion; vacuum ultraviolet irradiation; electron transfer; radical addition; phenol; toluene; benzene; chlorobenzene; benzaldehyde; benzoic acid

INTRODUCTION

Carbon dioxide radical anions, $CO_2^{\cdot -}$, are commonly used in aqueous chemistry as a reducing agent for metalloporphyrins or as intermediate in the formation of superoxide anion. $CO_2^{\cdot -}$ has been reported to undergo efficient electron transfer reactions with methyl viologen,[1] quinones,[2] alkyl halides,[3] fumarates,[4] nitro and nitrosobenzenes[5,6] and chlorinated benzaldehydes.[7] With nitrobenzenes and chlorinated benzaldehydes, electron attachment occurs on the nitro and aldehyde groups, respectively. $CO_2^{\cdot -}$ radicals have also been reported to add to some unsaturated compounds such as acrylamide[8] and pyridin-3-ol.[9] Efficient hydrogen abstraction from mercaptobenzenes have also been reported.[10,11]

The exact determination of the reduction potential, $E°$, of the couple $CO_2/CO_2^{\cdot -}$ was difficult because of the irreversibility of the electron transfer process due to the change in structure from linear to bent.[12] Results of different approximations and experimental methods agree in a value of $E°$ $(CO_2/CO_2^{\cdot -}) \approx -1.9$ V.[12,13] Despite the fact that the $CO_2^{\cdot -}$ radical is characterized by a more negative reduction potential than $O_2^{\cdot -}$ radicals $[E°(O_2/O_2^{\cdot -}) \approx -0.16$ V], in agreement with its efficient reaction with oxygen,[2] the reaction of $CO_2^{\cdot -}$ with sulfur radical cation complexes[14] is slower by a factor of 2.6. The trend observed in reactivity is in line with theoretical calculations[15] predicting a high internal reorganization energy ($\lambda = 447$ kJ mol^{-1}) for the couple $CO_2/CO_2^{\cdot -}$ than for the couple $O_2/O_2^{\cdot -}$ ($\lambda = 88.6$ kJ mol^{-1}).

The estimated value for the reduction potential of the couple $CO_2^{\cdot -}$, H^+/HCO_2^- is 1.07 V at pH 7.[12] The fact that $CO_2^{\cdot -}$ is also able to oxidize hydrogencarbonate to $CO_3^{\cdot -}$ ($k = 2 \times 10^3$ l mol^{-1} s^{-1})[16a] although the reduction potential for the couple $CO_3^{\cdot -}/CO_3^{2-}$ is $E° = 1.5$ V,[16b] is an indication that $CO_2^{\cdot -}$ radicals may oxidize some classes of substrates by hydrogen abstraction and/or by an addition–elimination pathway.

Dimerization to oxalate, reaction (R1), seems to be the

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main reaction of $CO_2^{\cdot -}$ in the absence of added substrates.[5]

$$CO_2^{\cdot -} + CO_2^{\cdot -} \rightarrow C_2O_4^{2-} \qquad (R1)$$

The reaction channels of $CO_2^{\cdot -}$ radicals in the presence of organic substrates depend strongly on the particular substrate and need still to be investigated in detail. In this paper we report mechanistic studies on the reactivity of $CO_2^{\cdot -}$ radicals towards substituted benzenes, XPh, with X = HO, CH_3, H, Cl, COH, COOH and NO_2.

$CO_2^{\cdot -}$ radicals show absorption in the UV ($\lambda_{max} = 235$ nm) with a relatively high extinction coefficient [ε (235 nm) = 3000 l mol^{-1} cm^{-1}], independent of pH between pH 3 and 13.[17] The conjugate acid of $CO_2^{\cdot -}$, i.e., $HCO_2^{\cdot}$, has a pK_a value of 1.4.[2]

For our investigations, $CO_2^{\cdot -}$ radicals were generated in aqueous systems by two different ways:

(i) by reaction of $HO^{\cdot}$ radicals and H atoms with formic acid (pK_a = 3.75) or formate ions, reactions (R2–R5):[2]

$$HO^{\cdot} + HCO_2^{-} \rightarrow H_2O + CO_2^{\cdot -} \qquad k_1 = 3.2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1} \qquad (R2)$$

$$HO^{\cdot} + HCO_2H \rightarrow H_2O + HCO_2^{\cdot} \qquad k_2 = 1.3 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1} \qquad (R3)$$

$$H^{\cdot} + HCO_2^{-} \rightarrow H_2 + CO_2^{\cdot -} \qquad k_3 = 2.1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1} \qquad (R4)$$

$$H^{\cdot} + HCO_2H \rightarrow H_2 + HCO_2^{\cdot} \qquad k_4 = 6.1 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1} \qquad (R5)$$

Vacuum ultraviolet (VUV) photolysis of liquid water (λ_{exc} <185 nm) provides a clean source of $HO^{\cdot}$ radicals and H atoms and, with much lower efficiency, hydrated electrons (e_{aq}^{-}).[18] Formate reacts efficiently with $HO^{\cdot}$ and $H^{\cdot}$, as shown in reactions (R2–R5). The quantum yields of hydrated electron formation, $\phi(e_{aq}^{-})$, are very low, and in acidic solutions of pH $\leq$4 the concentration of e_{aq}^{-} is further decreased owing to the efficient scavenging of e_{aq}^{-} by H_3O^+ to yield H atoms ($k = 2.4 \times 10^{10}$ l mol^{-1} s^{-1})[19] (see below). Consequently, VUV irradiation (λ_{exc} = 172 nm) of N_2-saturated aqueous solutions (pH $\approx$ 4) containing formic acid/formate ions yields mainly $CO_2^{\cdot -}$ radicals and this generation method was used for experiments under steady-state conditions.

(*ii*) Sulfate radicals ($SO_4^{\cdot -}$) efficiently react with formate ions yielding $CO_2^{\cdot -}$ radicals,[20] reaction (R6). The photolysis of peroxodisulfate, $S_2O_8^{2-}$, providing a clean source of $SO_4^{\cdot -}$ radical anions with high pH-independent quantum yields,[21] laser flash photolysis (λ_{exc} = 266 nm) of Ar-saturated peroxodisulfate solutions of pH 5 in the presence of formate ions was used as a convenient method for time-resolved studies involving $CO_2^{\cdot -}$ radicals. Reaction of $CO_2^{\cdot -}$ radicals with $S_2O_8^{2-}$ ions,[22] reaction (R7), yields again $SO_4^{\cdot -}$ radicals as reaction products, and its main effect is that of depleting formate and peroxodisulfate from the reaction system.

$$SO_4^{\cdot -} + HCO_2^{-} \rightarrow SO_4^{2-} + CO_2^{\cdot -} + H^+ \qquad k_6 = 1.1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1} \qquad (R6)$$

$$S_2O_8^{2-} + CO_2^{\cdot -} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + CO_2 \qquad k_7 = 1 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1} \qquad (R7)$$

The reaction products obtained from the reaction of $CO_2^{\cdot -}$ with the aromatic substrates with reaction (R8) were determined by gas chromatography–mass spectrometry (GC–MS) and high-performance liquid chromatography (HPLC). The nature of some of the reaction intermediates was studied by laser flash photolysis.

$$CO_2^{\cdot -} + XPh \rightarrow \text{products} \qquad (R8)$$

RESULTS AND DISCUSSION

Generation of $CO_2^{\cdot -}$ by VUV irradiation of aqueous solutions requires efficient scavenging by formic acid and formate ions [reactions (R2–R5)] of $HO^{\cdot}$ and $H^{\cdot}$ which are primarily formed by photolysis. Under the chosen experimental conditions, e_{aq}^{-} are efficiently quenched by H_3O^+. Other reactions of $H^{\cdot}$, $HO^{\cdot}$ and e^{-}_{aq}, such as recombination reactions leading to H_2 and H_2O_2, respectively, and with the substituted benzenes should be negligible.

The high absorbance of water ($k_{H_2O,\ 172\ nm}$ = 550 cm^{-1}), the quantum yield of water homolysis ($\Phi_{H_2O,\ 172\ nm} = 0.42 \pm 0.04$ mol einstein^{-1})[23] and the short lifetime of H atoms and HO radicals lead to strong heterogeneity in the macroscopically homogeneous reaction system. A volume of primary reactions close to the surface of the lamp, in which the rates of reactions (R2–R5) are controlled by the diffusion of formic acid/formate ions into this layer, and a large volume of secondary reactions in which slower thermal reactions dominate, may be differentiated. To avoid undesirable competing reactions as those already mentioned (see above), high local concentrations of formic acid/formate ions in the proximity of the surface of the light source are needed. Taking into account that $HO^{\cdot}$ radicals and H atoms react mainly with formate, the minimum average concentration of formate in the reaction system, $[CO_2H^{-}]_{min}$, which ensures that its concentration on the surface of the lamp remains above zero, may be estimated according to Eqn. (1),[23] assuming steady-state conditions in the volume of primary reactions and, hence, involving equal rates of formate depletion [reactions (R2–R5)] and diffusion. In a first approximation, formate/formic acid

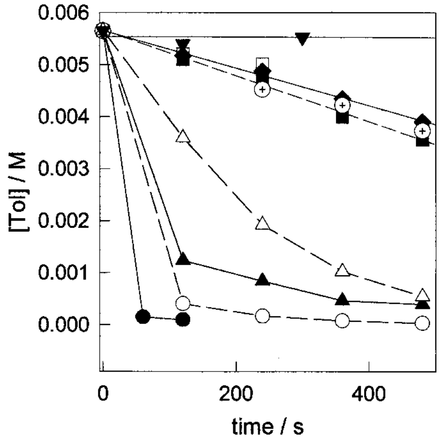


Figure 1. Depletion of toluene during VUV irradiation of saturated aqueous solutions of toluene containing different analytical concentrations of formate ion: 0 (●); 0.01 (○); 0.02 (▲); 0.1 (△); 0.2 (■); 0.5 (□); 1 (◆); and 1.78 M (⊕). The effect of synthetic air bubbling on the concentration of toluene (▼) is also shown

photolysis may be neglected (see below).

$$[\mathrm{HCO_2}^-]_{\min} = \frac{2\times 10^3 \times \Phi_{\mathrm{H_2O}} \times P_0}{D_{\mathrm{HCO_2}^-} \times k_{\mathrm{H_2O,172\,nm}} \times \ln 10} \qquad (1)$$

Taking the incident photon rate per unit area $P_0 = 8.5 \times 10^{-8}$ einstein $\mathrm{s^{-1}\,cm^{-2}}$,[18,23] and for the diffusion coefficient, $D_{\mathrm{HCO_2}^-}$, its value at infinite dilution ($1.45 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$),[24] $[\mathrm{HCO_2}^-]_{\min}$ is estimated to be 4×10^{-3} M. It has been shown in studies using methanol as a quencher of $\mathrm{HO^{\bullet}}$ radicals, that an excess factor $n = [\mathrm{MeOH}]_0/[\mathrm{MeOH}]_{\min} > 70$ is required for a scavenging reaction of $\mathrm{HO^{\bullet}}$ radicals.[23] If a similar ratio is expected for formate, the required concentration of formate ion in the reaction system should be >0.3 M.

In order to check the validity of this estimation, and to establish the experimental conditions under which the added organic substrate, XPh, will not react with $\mathrm{HO^{\bullet}}$ radicals and H atoms, a series of experiments were performed to investigate the depletion rate of XPh as a function of the analytical initial concentration of formate $[\mathrm{HCO_2}^-]_0$. Toluene was used as the organic probe, since it efficiently reacts with $\mathrm{HO^{\bullet}}$ ($k = 5.1 \times 10^9\ \mathrm{l\,mol^{-1}\,s^{-1}}$)[25] and $\mathrm{H^{\bullet}}$ ($k = 2.6 \times 10^9\ \mathrm{l\,mol^{-1}\ s^{-1}}$)[26] and is expected to show relatively low reactivity towards the electron-rich $\mathrm{CO_2^{\bullet -}}$ radicals.

In the absence of formate, mainly reactions with $\mathrm{HO^{\bullet}}$ radicals and H atoms deplete toluene. In the presence of formate, both toluene and formate compete for $\mathrm{HO^{\bullet}}$ and $\mathrm{H^{\bullet}}$. Under conditions of high formate to toluene molar ratios, the reactive intermediates are quantitatively scavenged by formate and toluene reacts primarily with $\mathrm{CO_2^{\bullet -}}$. Figure 1 shows the depletion of toluene obtained from saturated aqueous solutions of pH 4 containing different $[\mathrm{HCO_2}^-]_0$.

The depletion rates of toluene observed for $[\mathrm{HCO_2}^-]_0 \geq 0.2$ M are coincident, within experimental error. This observation indicates that under these conditions, the $\mathrm{CO_2^{\bullet -}}$ formation rates are independent of $[\mathrm{HCO_2}^-]_0$, and $\mathrm{HO^{\bullet}}$ and $\mathrm{H^{\bullet}}$ formed by water homolysis are quantitatively scavenged by formic acid/formate ions, in agreement with our previous discussion (see above).

The choice of $[\mathrm{HCO_2}^-]_0 = 1$ M then guarantees that $\mathrm{HO^{\bullet}}$ and H atoms are quantitatively scavenged by $\mathrm{HCO_2H/HCO_2}^-$, even in the presence of efficient $\mathrm{HO^{\bullet}}$ and $\mathrm{H^{\bullet}}$ scavengers and for long irradiation periods, where even after a 50% consumption of $[\mathrm{HCO_2}^-]_0$ the depletion rates of toluene are not affected.

Owing to the high concentrations of formic acid/formate ions used, VUV absorption by these substances may be suspected to compete with that of water. In fact, formic acid is known to absorb in the gas phase at wavelengths >180 nm, e.g. $\varepsilon_{200\ \mathrm{nm}} = 40\ \mathrm{l\,mol^{-1}\ cm^{-1}}$, and below 180 nm several Rydberg transitions have been found leading to an ionization potential of 11.33 eV (corresponding in energy to light of 109 nm).[27–29] Photolysis of formic acid in the gas phase has been reported to undergo two main reaction channels [e.g. reactions (R9–R11)], of which reaction (R9) is the most important process for irradiation wavelengths from 190 to 234 nm.[28,29]

$$\mathrm{HCO_2H} + h\nu \rightarrow \mathrm{HO^{\bullet}} + \mathrm{H^{\bullet}CO} \qquad (\mathrm{R9}a)$$

$$\mathrm{H^{\bullet}CO} \rightarrow \mathrm{CO} + \mathrm{H^{\bullet}} \qquad (\mathrm{R9}b)$$

$$\mathrm{HCO_2H} + h\nu \rightarrow \mathrm{H^{\bullet}} + {}^{\bullet}\mathrm{CO_2H} \qquad (\mathrm{R10})$$

$$^{\bullet}\mathrm{CO_2H} \rightarrow \mathrm{CO_2^{\bullet -}} + \mathrm{H^+} \qquad (\mathrm{R11})$$

Photolysis at 253.7 nm of formate/formic acid in aqueous solutions has been reported to lead to dissociation producing $\mathrm{HO^{\bullet}}$ and $\mathrm{H^{\bullet}CO}$, reaction (R9a). Formyl radicals, $\mathrm{H^{\bullet}CO}$, efficiently dissociate to CO and H atoms, reaction (R9b).[30] Thus, electronic excitation of formic acid/formate results in the final formation of $\mathrm{CO_2^{\bullet -}}$ also involving reactions (R2–R5).

Our experiments show no effect on the decay rate of toluene when $[\mathrm{HCOO}^-]_0$ is increased to >0.2 M. This result indicates that similar $\mathrm{CO_2^{\bullet -}}$ concentrations are formed. If photolysis of formate/formic acid were to contribute significantly to the formation of $\mathrm{CO_2^{\bullet -}}$, light should be quantitatively absorbed by formic acid already at $[\mathrm{HCO_2}^-]_0 = 0.2$ M and, consequently, the formate/formic acid absorption coefficient at 172 nm should be much higher than $2.7 \times 10^4\ \mathrm{l\,mol^{-1}\,cm^{-1}}$ owing to the even lower local concentrations of formate/formic acid near the surface of the lamp. We therefore conclude that formate/formic acid photolysis is not a significant process under our experimental conditions.

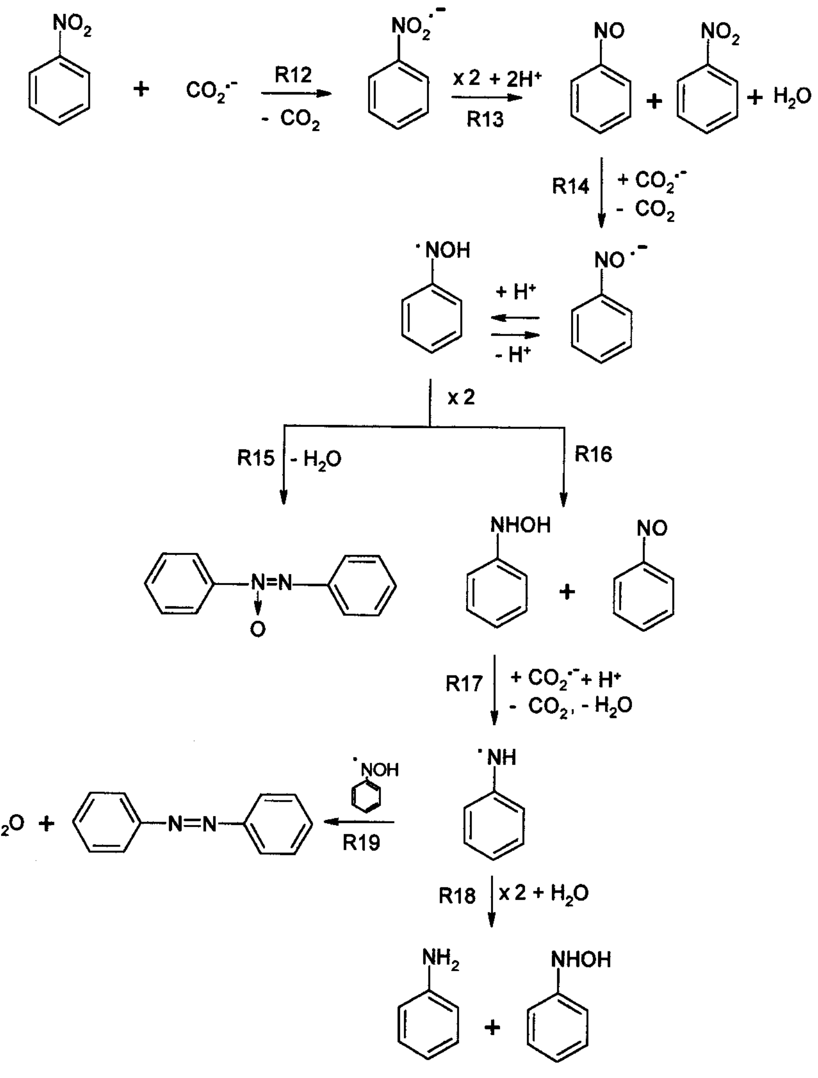
Table 1. Reaction products

Substrate	Reaction products
Nitrobenzene	Nitrosobenzene, aniline, *N*-phenylformamide, azoxybenzene, azobenzene
Benzaldehyde	Benzyl alcohol
Benzoic acid	Benzaldehyde
Benzene	Benzaldehyde, 1,4-cyclohexadiene, phenol, benzoic acid[a], biphenyl
Toluene	2-Methylphenol, 3,3′-dimethylbiphenyl
Chlorobenzene	Phenol, 2-chlorophenol, benzaldehyde
Phenol	–[b]

[a] Determined by HPLC. Identified by its retention time and UV absorption spectrum.
[b] No products were detected by GC. One unidentified product was detected by HPLC.

In the absence of aromatic substrates and for $[HCO_2^-]_0 = 1$ M, diminution of $[HCO_2^-]$ follows a zero-order decay of $(8 \pm 3) \times 10^{-5}$ mol l^{-1} s^{-1} for experiments made with 400 ml of solution. Consequently, $\sim 3 \times 10^{-5}$ mol s^{-1} of formate are consumed by its reactions with $HO^{\cdot}$ and H atoms near the surface of the lamp. Taking into account that 2 mol of formate are consumed per mole of water homolysed and that $\Phi_{H_2O} = 0.42$ mol einstein^{-1} at 172 nm, P_0 is estimated to be $(1.7 \pm 0.7) \times 10^{-7}$ einstein s^{-1} cm^{-2}, as expected for Xe lamps of this type (see above).

As $CO_2^{\cdot -}$ radicals are formed from formate/formic acid due to reactions (R2–R5), $\sim 1.4 \times 10^{-7}$ mol cm^{-2} s^{-1} of $CO_2^{\cdot -}$ radicals are produced near the surface of the lamp. Depletion of $CO_2^{\cdot -}$ in the primary volume of reactions is governed by their second-order recombina-



Scheme 1

tion, reaction (R1),[31] and by reaction with the organic matter, reaction (R8), hence severely reducing the steady concentration of $CO_2^{\cdot -}$ which under such conditions cannot diffuse far out of this primary volume. In order to understand the complex kinetic process taking place in the primary (irradiated) volume of reactions, a differential equation system should take into account the diffusion of $CO_2^{\cdot -}$ and of the organic matter to and from the bulk solution (secondary volume), the rate of $CO_2^{\cdot -}$ formation and reactions (R1) and (R8). Assuming the steady-state condition for $CO_2^{\cdot -}$ radicals and the organic matter in the primary volume of reactions, the product $k_8 \times [CO_2^{\cdot -}]_{ss}$ is estimated to be of the order of 6×10^{-2} s^{-1} for $10^9 > k_8$ ($l\,mol^{-1}\,s^{-1}$) $> 10^6$. The macroscopic depletion rate of aromatic substrates is then controlled by the rate of reaction (R8) in the primary volume of reaction and diffusion of the organic substrates from the bulk solution to the neighbourhood of the lamp surface. Under such conditions, substrate depletion rates of the order of 10^{-6} mol s^{-1} are expected, as observed experimentally for all the substrates investigated, except for phenol, for which an even lower depletion rate is found.

The reaction products formed after the reaction of $CO_2^{\cdot -}$ with the substituted benzenes were determined either by GC–MS or HPLC under the described experimental conditions. Products were analysed for different irradiation times up to 10 min and for <10% reactant consumption in order to avoid secondary reactions of the reaction products. The products formed from the substrates investigated and properly identified are listed in Table 1. Aliphatic compounds of low molecular weight, i.e. containing four carbon atoms or less, are eluted with the solvent and could not be detected with our chromatographic set-up.

NITROBENZENE

Concerning our investigations with nitrobenzene, the formation of products involving a reduction process (Table 1), can be explained if an electron transfer from $CO_2^{\cdot -}$ to nitrobenzene, reaction (R12), is the primary reaction (Scheme 1)

Flash photolysis experiments with Ar-saturated peroxodisulfate solutions containing formate and nitrobenzene showed the formation of a transient species in the microsecond time range with an absorption maximum of 290–280 nm. Under the conditions of our experiments, $SO_4^{\cdot -}$ radicals generated from the photolysis of peroxodisulfate readily react with formate ions according to reaction (R6) (with a lifetime $\tau_{SO_4^{\cdot -}} = 15$ ns) yielding $CO_2^{\cdot -}$ radical anions. Absorption of $CO_2^{\cdot -}$ radicals is not observed in our experiments owing to the high absorption of the solutions at $\lambda < 250$ nm. $CO_2^{\cdot -}$ radicals further react with nitrobenzene according to reaction (R12) ($\tau_{CO_2^{\cdot -}} = 1$ μs) leading to the observed transient. Figure 2 shows the transient absorption spectrum with a maximum at ~285 nm, in agreement with the reported spectrum of the radical anion of nitrobenzene.[6] The observed transient formed by reaction (R12) is therefore assigned to the radical anion of nitrobenzene.

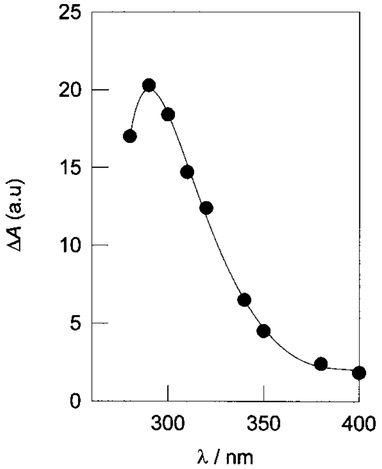


Figure 2. Absorption spectrum of the transient observed 3 μs after laser excitation of an Ar-saturated 2.25×10^{-2} M $S_2O_8^{2-}$ acid solution (pH 5) containing 0.4 M formate ion and 3 mM nitrobenzene

Formation of nitrosobenzene may be explained by disproportionation of the radical anion of nitrobenzene to nitrobenzene and nitrosobenzene,[32] reaction (R13).

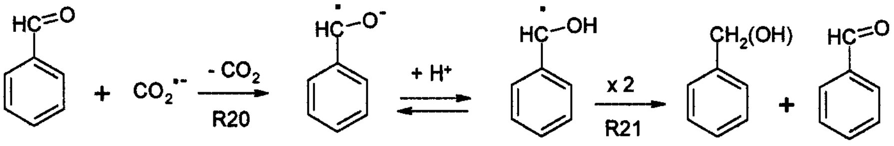
Nitrosobenzene is known to react with $CO_2^{\cdot -}$ radical anions with $k = 4 \times 10^9$ $l\,mol^{-1}$ s^{-1},[6] yielding the nitrosobenzene radical, reaction (R14), which under our experimental conditions is present in its acid form ($pK_a = 11.7$[6]). Further condensation of the acid form of the nitrosobenzene radical with loss of water yields azoxybenzene, reaction (R15). Disproportionation of the conjugate acid of nitrosobenzene radical, reaction (R16), may yield nitrosobenzene and phenylhydroxylamine. The latter product was not observed, however, it may have been further reduced by $CO_2^{\cdot -}$ to the intermediate amine radical, $C_6H_5N^{\cdot}H$, which subsequently disproportionates to phenylhydroxylamine and aniline, reactions (R17) and (R18), respectively.

Formation of *N*-phenylformamide at longer irradiation times may arise, either from addition of $CO_2^{\cdot -}$ to the nitrogen atom of the amine radical followed by reduction, or by a condensation reaction between aniline and formic acid.

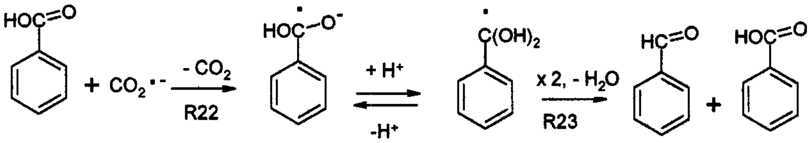
Formation of azobenzene, which is observed after 5 min of photolysis, may be explained by condensation of the amine radical with the nitrosobenzene radical, reaction (R19), or by the reaction of the amine radical with nitrosobenzene and further reduction.[33]

BENZALDEHYDE

For benzaldehyde as a substrate, benzyl alcohol is the only observed reaction product. Reaction of $CO_2^{\cdot -}$



Scheme 2



Scheme 3

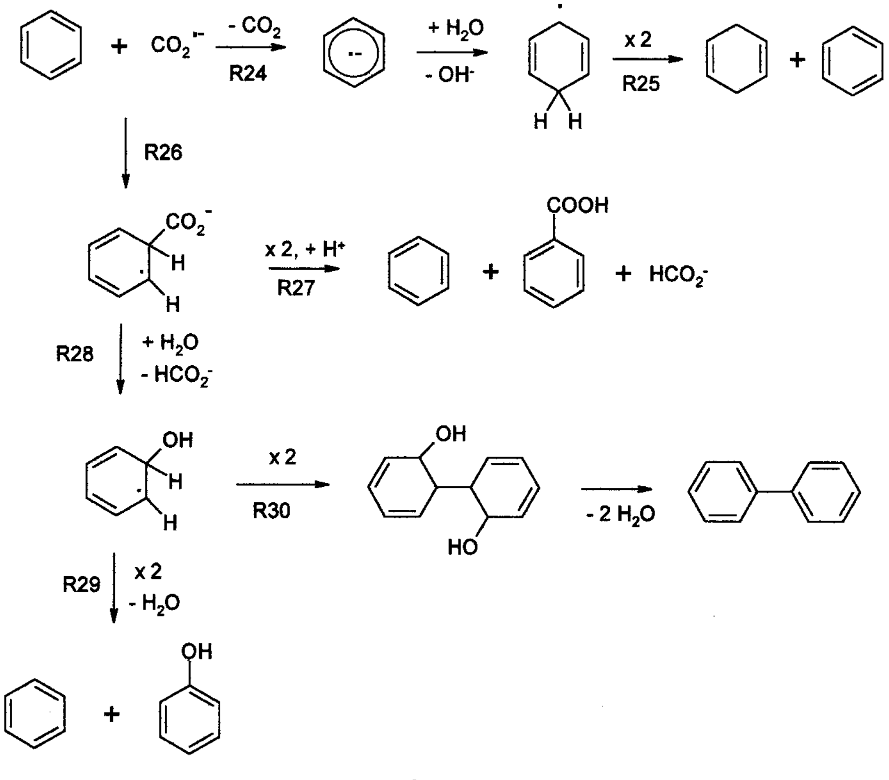
radicals with benzaldehyde, reaction (R20) (Scheme 2), was reported to proceed by electron attachment on the CHO group, yielding the carbonyl radical anion.[7] Reversible protonation of the carbonyl radical anion yields the carbonyl radical showing a pK_a of 8.4.[7] Further disproportionation of the carbonyl radical yields benzyl alcohol and benzaldehyde, reaction (R21).

BENZOIC ACID

The reaction of $CO_2^{\cdot -}$ with benzoic acid leads to benzaldehyde. The electron transfer from the $CO_2^{\cdot -}$ radical to the carboxyl group yields the benzoyl radical, reaction (R22) (Scheme 3), as already observed with the hydrated electron.[34] Further disproportionation of the benzoyl radical produces benzoic acid and benzaldehyde as shown in reaction (R23).

Benzene

The reaction of benzene with $CO_2^{\cdot -}$ leads to both reduced and oxidized products. Formation of 1,4-cyclohexadiene may be explained by an electron transfer from $CO_2^{\cdot -}$ to the aromatic ring leading to the radical anion of benzene, reaction (R24) (Scheme 4). Subsequent reaction with water leads to the intermediate formation of cyclohexa-



Scheme 4

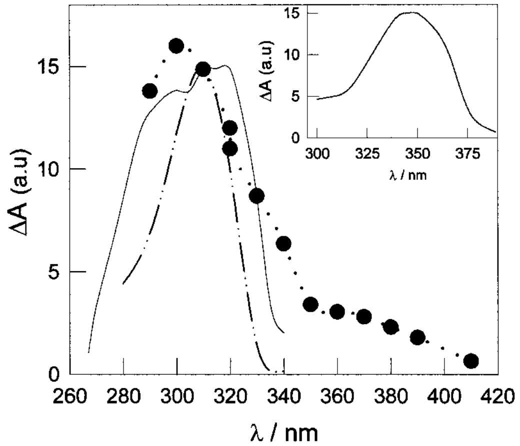


Figure 3. Absorption spectrum of the transient observed 3 μs after laser excitation of an Ar-saturated 2.25×10^{-2} M $S_2O_8^{2-}$ acid solution (pH 5) containing 0.4 M formate ion and 1×10^{-2} M benzene. The solid and dashed (—..—) lines show the literature absorption spectra of the HO–CHD[43] and H–CHD[42] radicals of benzene, respectively. The inset shows the literature spectrum of the H–CHD of benzoic acid.[34]

dienyl radicals, H–CHD, which undergo subsequent disproportionation to benzene and 1,4-cyclohexadiene, reaction (R25). A similar reaction sequence was proposed for the reaction of benzene with hydrated electrons.[27]

The formation of benzoic acid, benzaldehyde, biphenyl and phenol may be explained by an addition of $CO_2^{\cdot -}$ to benzene, reaction (R26). Disproportionation of the adduct, CO_2^{-}–CHD, yields benzene with elimination of formate, and benzoic acid, reaction (R27). Benzaldehyde would then be formed by the subsequent reduction of benzoic acid (see above). Alternatively, the CO_2^{-}–CHD adduct may eliminate formate and add water, hence producing a hydroxycyclohexadienyl radical (HO–CHD), reaction (R28), in agreement with the observed reactivity of sulfate and phosphate radical adducts of aromatic substrates in aqueous solution[35] and as expected for the relatively good leaving group HCO_2^{-}.[35d] HO–CHD can either disproportionate to yield phenol and benzene with elimination of water, reaction (R29), or recombine yielding biphenyl[36–38] as shown in reaction (R30).

H-abstraction by $CO_2^{\cdot -}$ from the aromatic ring could also lead to the formation of benzoic acid, if the intermediate phenyl radical were subsequently to react with $CO_2^{\cdot -}$. However, phenyl radicals are highly reactive and may alternatively react with benzene ($k = 4.5 \times 10^5$ l mol^{-1} s^{-1}) to yield a phenylcyclohexadienyl radical (Ph–CHD), which upon disproportionation would lead to biphenyl (observed as a reaction product, see above) and phenylcyclohexadiene.[38,39] The latter product not being detected in our experiments, we conclude that biphenyl is formed by an addition mechanism rather than by an H-abstraction.

In order to obtain information on the intermediates of the reaction of $CO_2^{\cdot -}$ with benzene, flash photolysis experiments with Ar-saturated peroxodisulfate solutions containing formate and benzene were performed. Formation of a transient species with an absorption maximum at ∼300 nm was observed, as shown in Fig. 3.

The radical anion of benzene is reported to present an absorption maximum at 290 nm in aqueous solution and two absorption maxima at approx. 285 and 385 nm in a matrix at 77 K.[40,41] Since the radical anion of benzene is known to protonate to H–CHD on a microsecond timescale,[42] the latter radical may be detected with our laser equipment. Figure 3 shows the spectrum of the transient species obtained, along with that of the H–CHD and HO–CHD radicals of benzene[42,43] whose participation in the overall reaction has already been discussed (see above). The observed transient shows important contributions of the H–CHD and HO–CHD radicals; however, absorption at wavelengths higher than 340 nm cannot entirely be attributed to these radicals.

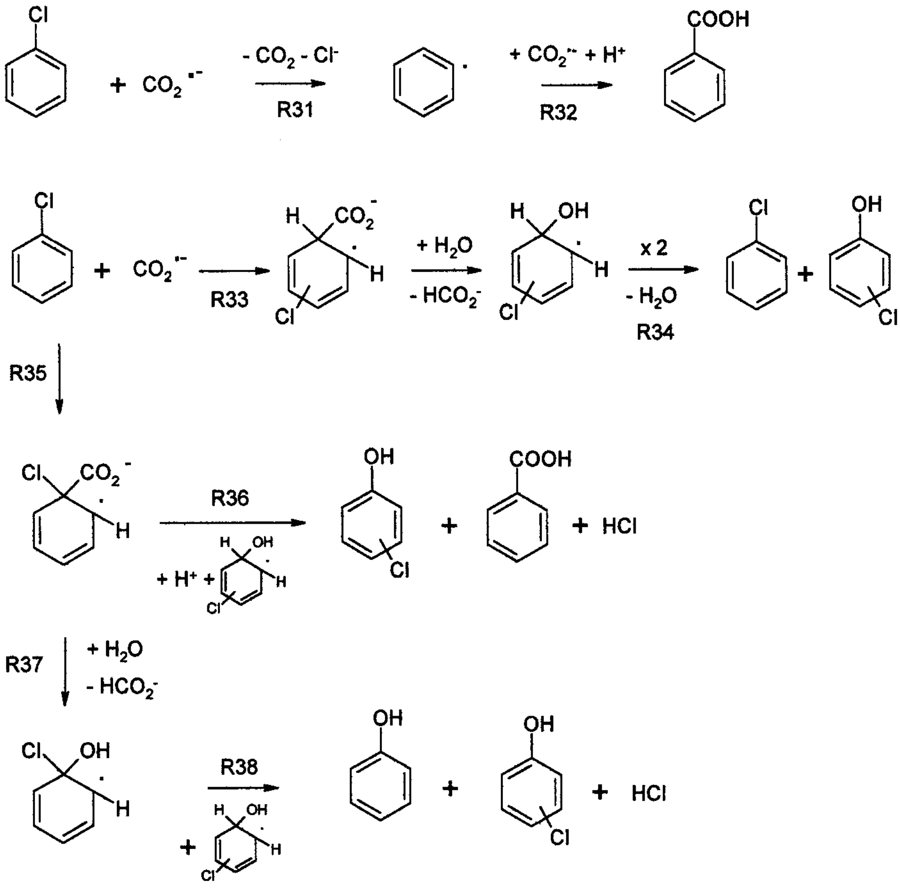
The formation of CO_2^{-}–CHD has been postulated in order to account for the generation of benzoic acid as a reaction product (see above). We expect that the lifetime of this radical is longer than 50 μs in order to be able to undergo disproportionation to benzoic acid. The observed absorption at $\lambda > 340$ nm may in fact be attributed to the CO_2^{-}–CHD radical, because of the agreement of its absorption spectrum with that of the structurally related H adduct of benzoic acid showing, both, absorption maxima at around 350 nm.[34] Despite the fact that Ph–CHD phenylcyclohexadienyl radicals also show an absorption with a maximum between 330 and 340 nm,[39] its contribution to the observed spectrum is neglected, because the recombination product, phenylcyclohexadiene, was not found (see above). Consequently, the time-resolved experiments with benzene support both the addition and electron transfer pathways of reaction.

Toluene

The reaction of $CO_2^{\cdot -}$ with toluene leads to 2-methylphenol and 3,3′-dimethylbiphenyl. Both products may be formed by an addition – elimination reaction channel leading to the HO–CHD radical of toluene, which may either disproportionate to 2-methylphenol and toluene with elimination of water or recombine to dimethylbiphenyl, as observed for benzene in reactions (R26), (R28), (R29) and (R30).

Chlorobenzene

The reaction of $CO_2^{\cdot -}$ with chlorobenzene leads to 2-chlorophenol, benzaldehyde and phenol. An electron transfer from $CO_2^{\cdot -}$ to the aromatic ring is expected to lead to the dehalogenation of the aromatic substrate, as



Scheme 5

observed for the reaction of chlorobenzene with the hydrated electrons.[44] The dehalogenation of chlorobenzene yields reactive phenyl radicals, reaction (R31), which upon further reaction with $CO_2^{\cdot-}$ radicals generates benzoic acid, reaction (R32) (Scheme 5). Further reduction of benzoic acid by $CO_2^{\cdot-}$ leads to the formation of benzaldehyde, an observed reaction product (see above).

Formation of chlorophenol may be explained by an addition–elimination reaction leading to an HO–CHD adduct of chlorobenzene which disproportionates to chlorophenol and chlorobenzene, as shown in reactions (R33) and (R34).

Formation of phenol very likely requires an *ipso* addition of $CO_2^{\cdot-}$ to chlorobenzene, as shown in reaction (R35). The *ipso* position was also reported to be the preferred site for hydroxyl radical addition to chlorobenzene.[45] The bimolecular reaction of the *ipso* adduct CO_2^-CHD with HO–CHD radicals of chlorobenzene is an alternative reaction channel yielding benzoic acid, HCl and chlorophenol, reaction (R36). Elimination of HCO_2^- from the *ipso* adduct, reaction (R37), and subsequent reaction with HO–CHD radicals leads to the formation of phenol, HCl and chlorophenol,[46] reaction (R38).

Phenol

The reaction of $CO_2^{\cdot-}$ with phenol resulted in a surprisingly small substrate depletion. No products were found within the detection limits of our chromatographic means (GC), except for one unidentified product detected by HPLC.

CONCLUSIONS

Products and reaction intermediates observed in the present study are rationalized by a dual reactivity of the $CO_2^{\cdot-}$ radical anion with substituted benzenes, i.e. one-electron reduction of and radical addition to the aromatic ring. For substrates with electron-withdrawing substituents, i.e., with positive σ values such as X = NO_2, COOH and COH, the observed products can be explained by an electron transfer from $CO_2^{\cdot-}$ to the substrates as the primary reaction channel. Benzene and chlorobenzene react by both electron transfer and radical addition. For toluene, with an electron-donating substituent, products of radical addition are found. The dual reactivity of $CO_2^{\cdot-}$ radical anion has recently been reported for thymine,[47] in agreement with our observations.

H abstraction by the $CO_2^{\cdot-}$ radical is only supported by one of the routes proposed for the formation of benzoic acid in our experiments with benzene. If such a reaction channel were of importance, formation of substituted benzoic acids should have been observed for other substituted benzenes, as the dissociation energy of the C—H bonds in these compounds is expected to be of the same order as in benzene. Moreover, formation of products derived from the benzyl radical was not observed in our experiments with toluene. We therefore conclude that the contribution of H-abstraction channel by $CO_2^{\cdot-}$ radical ions as a potential reaction channel of this intermediate is negligible under our experimental conditions.

The observed tendency in the dual reactivity of $CO_2^{\cdot-}$ radical anion may be rationalized by the reduction potential of the substrate. An electron transfer mechanism is observed for those substituted benzenes which are reduced by the hydrated electron with diffusion-controlled rates.[27] For substrates showing lower reactivity towards the hydrated electron, i.e. which are more difficult to reduce, $CO_2^{\cdot-}$ addition is the preferred reaction channel. These observations are in line with studies reporting the reduction of nitro compounds by α-hydroxyalkyl radicals, where the redox potential of the nitro compound determines the probability of radical addition or electron transfer.[48]

EXPERIMENTAL

Distilled water was passed through a Millipore filter. All the chemicals were of p.a. quality (Merck) and used as received. All experiments were performed with oxygen-free argon-saturated solutions.

VUV irradiation experiments. For the VUV irradiation experiments, an excimer lamp emitting at 172 nm (200 mm long, 35 mm diameter[18,23]) was used. The lamp was immersed in a photochemical reactor of annular geometry and a total volume of 400 ml. The reactor was immersed in a water-bath at constant temperature.

Aqueous solutions of the substrates in the concentration range 0.5–23 mM were used. The pH of the solutions was adjusted to 4 by addition of $HClO_4$. Samples were taken at constant time intervals and the total volume of sample withdrawn was always less than 10% of the volume of the reactor.

Chromatographic analyses. Organic substrates were extracted from the aqueous solutions with a fixed volume of chloroform and the extracts stored at 4 °C in glass vials with PTFE/silicone septum-lined screw-caps and minimized headspace. Analysis of the extracts was performed by GC with an HP 6890 gas chromatograph equipped with an HP5-MS fused-silica capillary column and coupled to an HP 5973 mass-selective detector. The analyses were performed with a temperature program starting at 80 °C and ending at 200 °C at a rate of 10 °C min^{-1}, and the final temperature being held at 200 °C for 5 min. Helium was used as the carrier gas at a flow-rate of 29 cm^3 s^{-1}. Injection volumes were 20 μl.

Substrate depletion and product formation were also followed by HPLC with an HP1090 Series II liquid chromatograph with a diode-array detector. A 10% methanol–water mixture was used as eluent.

Formate analysis was performed by ion chromatography (Dionex DX 500) with suppressed conductivity detection. A 250 × 4 mm i.d. IONPAC AS11 (Dionex) column and a 50 × 4 mm i.d. IONPAC AG11 (Dionex) guard were used. The eluent was 60 mM aqueous NaOH. The flow-rate was 1 ml min^{-1}.

Laser photolysis experiments. Flash photolysis experiments were performed with a Spectron SL400 Nd:YAG system generating 266 nm pulses (~8 ns pulse width). The laser beam was defocused in order to cover the entire pathlength (1 cm) of the analysing beam produced by a 150 W Xe lamp. The experiments were performed with a quartz cell in a 90° geometry. The detection system comprised a PTI monochromator coupled to a Hamamatsu R666 PM tube. The signals were acquired and averaged by a digitising oscilloscope (Hewlett-Packard Model 54504) and transferred to a computer for further treatment.

The concentrations of $S_2O_8^{2-}$ and formate were 22.5 and 400 mM, respectively, and the concentrations of the aromatic substrates were 3 mM for nitrobenzene and 10 mM for benzene. Under these reactions, the reactions of the organic substrates with $SO_4^{\cdot-}$ are negligible.

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