Rate Constants and Mechanism of Reaction of $SO_4{\cdot}^-$ with Aromatic Compounds[1a]

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Abstract: Absolute rate constants for reaction of $SO_4{\cdot}^-$ with substituted benzenes and benzoates have been determined by pulse radiolysis. The values are found to range from about 5×10^9 M^{-1} s^{-1} for anisole to $<10^6$ M^{-1} s^{-1} for nitrobenzene. A correlation of the rate constants with the Hammett substituent constant σ gave $\rho = -2.4$ for both series of compounds. It is concluded that the reaction takes place by an electron transfer from the ring to $SO_4{\cdot}^-$.

The reaction of the sulfate radical anion, $SO_4{\cdot}^-$, with several aromatic compounds has been shown by ESR to result in the production of hydroxycyclohexadienyl radicals.[2] In the case of methoxy derivatives radical cations have been observed[3] and in the case of several carboxy derivatives decarboxylation has been found to take place, resulting in the production of phenyl radicals.[4,5] These observations can be explained by various mechanisms. The hydroxycyclohexadienyl radicals can be produced by addition to the ring followed by hydrolysis as suggested by Norman et al.,[2] or by electron transfer from the ring to the $SO_4{\cdot}^-$, as suggested by several authors,[6-8] followed by hydroxylation with water or OH^-. The radical cations from anisoles can also be produced by direct electron transfer[3] or via addition followed by elimination. Decarboxylation can occur through direct oxidation of the carboxyl group, as is the case with aliphatic carboxylic acids,[2,8] or again following oxidation of the ring.[5] It appeared that examination of the effect of substituents on the rate constant for reaction of $SO_4{\cdot}^-$ with aromatic compounds might shed some light on the mechanism.

Absolute rate constants for reactions of $SO_4{\cdot}^-$ radical can be determined by kinetic spectrophotometric pulse radiolysis as described previously.[9,10] The pseudo-first-order decay rate of the $SO_4{\cdot}^-$ absorption is measured in the presence of increasing concentrations of the aromatic compound and the second-order rate constant calculated from a linear plot of the rate vs. the concentration. The rate constants were found to vary from 5×10^9 M^{-1} s^{-1} for anisole down to $<10^6$ M^{-1} s^{-1} for nitrobenzene. A Hammett type plot of log k vs. the substituent constant σ gives a value of $\rho = -2.4$, much larger than that observed for reactions of OH radicals.

Experimental Section

Sulfate radical anions were produced in irradiated aqueous solutions by reaction of e_{aq}^- with peroxydisulfate anion.

$$e_{aq}^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4{\cdot}^-$$

This reaction is very rapid ($k = 1.1 \times 10^{10}$ M^{-1} s^{-1})[9] and at the concentrations of peroxydisulfate used (0.01–0.05 M) was virtually complete at the end of the radiation pulse. The decay of $SO_4{\cdot}^-$ in the absence and presence of various solutes was followed at 450 nm. In several cases, where the aromatic product radicals absorb in this region, the decay could be observed more clearly at slightly higher wavelengths. The pulse radiolysis setup for these observations was that described previously,[11] with slight modifications.[12] Pulses of 2.8 MeV electrons from the Van de Graaff accelerator were approximately of 1-μs duration and supplied energy for production of $2\text{–}3 \times 10^{-6}$ M total radical concentration. The change of optical absorption with time was processed by the computer and usually data from 30–50 pulses were averaged for each kinetic calculation. Each solute was examined at least at four different concentrations and at each concentration at least three such kinetic curves were processed. In most cases the rate constants determined are accurate to ±10%.

Sodium persulfate was obtained from Sigma Chemical Co. Potassium phosphates used as buffers were Baker Analyzed reagents as were the potassium hydroxide, perchloric acid, and *tert*-butyl alcohol. The latter was used in certain cases as OH scavenger and to help dissolve the other organic solutes. The aromatic compounds were of the purest grade commercially available from Aldrich, Eastman, and Baker Chemical Companies. Water was purified by distillation and passing the vapor with oxygen through a silica oven at ~600 °C. Solutions were buffered at pH 7 and were deoxygenated by bubbling with prepurified nitrogen.

Results and Discussion

The measured values of second-order rate constants for reaction of $SO_4{\cdot}^-$ radicals with aromatic compounds are summarized in Table I. Also included is a value of 4.9×10^9 M^{-1} s^{-1} for anisole from ref 3. This value is the highest and approaches the diffusion-controlled limit. Several polymethoxybenzenes[3] were found to react with rate constants of $5\text{–}8 \times 10^9$ M^{-1} s^{-1}. Electron-withdrawing substituents are seen to cause a significant decrease in the rate constant, benzonitrile reacts with a rate constant of 1.2×10^8 M^{-1} s^{-1}, and nitrobenzene was found to react very slowly if at all. Substituted benzoic acids also show high rate constants for methoxy and hydroxy derivatives, low for cyano, and very low for nitro. The behavior results from the expected electrophilicity of $SO_4{\cdot}^-$ radicals.

The effect of substituents can be quantitatively represented in a Hammett type plot of the logarithm of rate constant vs. the substituent constant σ. Figure 1 shows such plots for substituted benzenes and benzoate ions. Despite the wide scatter of data, it is clear that for both series straight lines can be drawn, which demonstrate the electrophilic nature of $SO_4{\cdot}^-$. The slopes represent a value of $\rho = -2.4$. The absolute rate constants for the benzoate series are generally lower than those for the benzene series by about a factor of 2. This difference probably results from electrostatic repulsion between the negatively charged $SO_4{\cdot}^-$ and $XC_6H_4CO_2^-$. In the case of the doubly charged terephthalate the rate constant appears to be lowered by an order of magnitude.

The value of $\rho = -2.4$ can be compared with the ρ values determined in a similar fashion for reactions of OH radicals[13] and H atoms[14] with aromatic compounds. The latter species are known to add to the aromatic ring with rate constants of the order of 10^9 M^{-1} s^{-1}. Substituent effects on these rate constants show values of ρ near -0.5 for both OH and H. The present study shows that $SO_4{\cdot}^-$ radicals react very rapidly with aromatic compounds as do OH and H, but with higher selectivity, i.e., the value of ρ is five times greater. These findings indicate that $SO_4{\cdot}^-$ radicals do not react by addition to the aromatic ring, but most likely by an electron-transfer mechanism to produce initially the radical cation. When no other reaction paths are available, as with benzene, the cation will

Table I. Rate Constants for Reaction of $SO_4\cdot^-$ with Aromatic Compounds at pH 7

Aromatic compd	Rate constant, $M^{-1}\,s^{-1}$
Anisole	4.9×10^9 (from ref 3)
Acetanilide	3.6×10^9
Benzene	3×10^9
Benzoic acid	1.2×10^9
Acetophenone	3.1×10^8
Benzamide	1.9×10^8
Trimethylanilinium ion	1.5×10^8
Benzonitrile	1.2×10^8
Nitrobenzene	$\leq 10^6$
p-Methoxybenzoic acid	3.5×10^9
p-Hydroxybenzoic acid	2.5×10^9
m-Toluic acid	2.0×10^9
p-Toluic acid	1.8×10^9
o-Toluic acid	1.4×10^9
Benzoic acid	1.2×10^9
p-Bromobenzoic acid	1.0×10^9
o-Bromobenzoic acid	8.7×10^8
p-Chlorobenzoic acid	3.6×10^8
p-Acetylbenzoic acid	2.0×10^8
Terephthalic acid	1.7×10^8
p-Cyanobenzoic acid	3.3×10^7
p-Nitrobenzoic acid	$\leq 10^6$

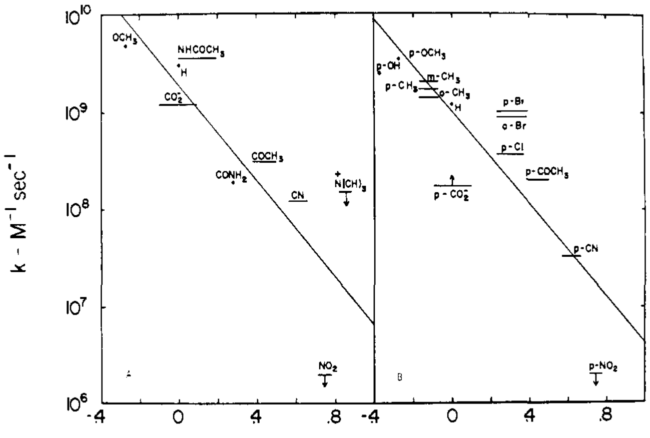

Figure 1. A correlation of rate constants for reaction of $SO_4\cdot^-$ with aromatic compounds with the substituent constants σ: A, substituted benzenes; B, substituted benzoate ions. The values of σ were taken from C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 (1964). In most cases, except for OH and OCH_3, both σ_{meta} and σ_{para} were used as indicated by the horizontal lines. The arrow for $^+N(CH_3)_3$ indicates that the rate constant should be decreased by the contribution from the reaction of $SO_4\cdot^-$ with the methyl groups. The arrow for p-CO_2^- indicates that the rate constant is lowered by the extra negative charge.

then react with water to form the hydroxycyclohexadienyl radical. This radical was experimentally found to be produced within ≤ 0.1 μs following reaction of $SO_4\cdot^-$ with benzene.[16]

The magnitude of ρ for $SO_4\cdot^-$ somewhat resembles that observed for the reaction of e_{aq}^- with monosubstituted benzenes ($\rho = 4.8$).[15] Although the latter reaction is obviously nucleophilic, it is an electron-transfer reaction. The resemblance in the values of ρ may suggest a similarity in mechanism and support the idea of an electron transfer from the ring to $SO_4\cdot^-$. It should be noted, however, that while $SO_4\cdot^-$ yields similar ρ values for substituted benzenes and substituted benzoates, e_{aq}^- reactions show a large difference, i.e., ρ for substituted benzoates is only 0.7. This difference results from the fact that the benzoate anion reacts with e_{aq}^- over two orders of magnitude more rapidly than benzene and, therefore, substituent effects on this rate constant become much smaller. This large difference between the benzene and the benzoate series does not exist in the case of $SO_4\cdot^-$ reactions. One may conclude, therefore, that $SO_4\cdot^-$ oxidizes the aromatic ring with benzoates as well. When decarboxylation is observed the initial step must be electron abstraction from the ring and not directly from the carboxylate group. This conclusion also follows from the high degree of specificity in the site of decarboxylation of benzene polycarboxylic acids.[5] This mechanism is reasonable in view of the fact that aliphatic carboxylate anions are oxidized by $SO_4\cdot^-$ at much lower rates.[10]

The fact that the p-nitrobenzoate anion is not oxidized by $SO_4\cdot^-$ at a measurable rate ($k \leq 10^6$ $M^{-1}\,s^{-1}$), while OH^- is oxidized with $k = 8 \times 10^7$ $M^{-1}\,s^{-1}$ [8,10] suggests that the reduction potential of p-$O_2NC_6H_4C\dot{O}_2$ is higher than that of the OH radical. This conclusion explains the previous finding[17] that the radical $[p$-$O_2NC_6H_4COOOH]\cdot^-$ produced by reduction of p-nitroperoxybenzoic acid breaks down into p-$O_2NC_6H_4CO_2^- + \dot{O}H$ and does not produce p-$O_2NC_6H_4C\dot{O}_2 + OH^-$. Most other substituted peroxybenzoic acids are expected to produce the benzoyloxy radicals upon reduction. Our results suggest that the cyano derivative may be a borderline case where the reduction of the peroxy acid may result in the formation of both OH radicals and cyanophenylcarboxy radicals.

References and Notes

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(16) Experiments with an unbuffered solution of 2.5 mM $Na_2S_2O_8$, 10 mM benzene, and 1 M *tert*-butyl alcohol showed that the formation of the hydroxycyclohexadienyl radical absorption at 310 nm was as rapid as that of the $(SCN)_2^-$ absorption in a 10-mM SCN^- solution. A delay of 0.1 μs would have been detectable. The absorption at 310 nm is attributed to the OH rather than the $SO_4\cdot^-$ adduct, since at 10 μs the full conductivity change associated with formation of the OH adduct is observed.[8] No change in absorption was detected between 1 and 10 μs.
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