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Kinetics and Mechanism of Reactions between Methyl Aromatic Compounds and the Dibromide Radical

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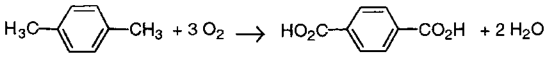
The dibromide radical (believed to be $HBr_2^•$ in acetic acid) reacts with methylarenes, aldehydes, and carboxylic acids in acetic acid. The kinetics of these reactions were studied with the use of laser flash photolysis to generate the dibromide radical. The loss of the radical was monitored as a function of time at 360 nm. The data analysis requires an allowance for the concurrent bimolecular disproportionation reaction, $2HBr_2^• \rightarrow Br_2 + 2HBr$, with $k_d = (2.2 \pm 0.5) \times 10^9$ L mol^{-1} s^{-1} at 23 °C. The reactions between $HBr_2^•$ and substrate were first-order with respect to each concentration, with k between 4×10^3 (methyl-3-methylbenzoate) and 2×10^6 (hexamethylbenzene) L mol^{-1} s^{-1} at 23 °C. The variation of rate constant can be correlated with the reported rates for the overall catalytic conversions. Several compounds with deuterium labels in the methyl side chains were investigated. The presence of a significant kinetic isotope effect suggests that the reactions proceed by abstraction of a hydrogen atom from the α-carbon of the R-group on the aromatic residue. Ring substituents such as CHO and CO_2H have a strong deactivating effect.

Introduction

One of the most successful commercial applications of homogeneous catalysis is the autoxidation of methyl aromatic compounds to carboxylic acids. A particular example is the conversion of *p*-xylene to terephthalic acid:



(1)

As practiced, this reaction, known as the MC process, is conducted in acetic acid with a combined catalyst composed of $Co(OAc)_2$, $Mn(OAc)_2$, and HBr or NaBr. The multistep reaction mechanism has been the subject of many studies.[1−4] As a result of these studies, it is clear that a form of "zerovalent bromine" intermediate carries out one of the most difficult steps. Our goal in this study is to learn more about the reactivity of this intermediate.

Results and Interpretation

In our previous studies in this area, we presented data on the kinetics of oxidation of cobalt(II) and manganese(II), M^{II}, by the same or a different trivalent metal, N^{III}.[5] Put another way, the divalent metal is a catalyst for the oxidation of free bromide by N^{III}, to the point that the catalytic pathway is nearly dominant. The rates of these reactions are dependent on the HBr concentration. Given the formation constants of the individual $M^{II}Br_n$ complexes,[5,6] the data could be resolved into the contributions of each reaction of N^{III} with a given $M^{II}Br_n$ complex. In each case examined, $Co^{III}/Co^{II}Br_2$, $Co^{III}/MnBr_2$, $Mn^{III}/MnBr_2$, and $Mn^{III}/CoBr_2$, it could be shown that the dibromometal(II) reagent was the principal and often exclusive reactant. Consequently, we proposed that the major reaction is

$$N^{III} + M^{II}Br_2 \rightarrow N^{II} + M^{III}Br_2 \quad (M, N = Co, Mn) \quad (2)$$

The bromide studies have established that this is the first step in the favored pathway leading to the zerovalent bromine intermediate. Because $M^{II}Br_2$ is selectively involved, it must offer a particular reactivity advantage over, say, $M^{II}Br$. We inferred that reductive elimination of the dibromide radical from the transient $M^{III}Br_2$ species occurs next, according to this equation

$$M^{III}Br_2 \rightarrow M^{II} + Br_2^{•-} \quad (3a)$$

$$M^{III}(OAc)Br_2 + HOAc \rightarrow M^{II}(OAc)_2 + HBr_2^• \quad (3b)$$

In the alternative cited, a reaction between N^{III} and $M^{II}Br$, the "internal redox" reaction of the monobromo complex so formed, $M^{III}Br_1$, would yield $Br^•$, which at least in aqueous solution is at a considerably higher Gibbs energy than $Br_2^{•-}$. Compare $E° = 1.62$ V for $Br_2^{•-}/Br^-$ in water[7,8] with a value of 1.97 V for $Br^•/Br^-$ in 90% acetic acid.[9] Because dibromide is suggested to be the reactive intermediate from our interpretation of the kinetics and is also the more stable one thermodynamically, this is not an illogical assignment. To provide further support, we have undertaken a direct study of the reactivity of independently generated dibromide radical.

To do so, laser flash photolysis has been used to form the dibromide radical. We recognized that acetic acid is not an ionizing medium: hydrobromic acid is a weak acid with $pK_a = 6.7$.[10,11] Consequently, we assumed that dibromide in this medium exists predominantly as $HBr_2^•$ and will write it as such. The question nonetheless remains: will $HBr_2^•$ react with methyl aromatic compounds, according to the equation

$$HBr_2^• + ArCH_3 \rightarrow 2HBr + ArCH_2^• \quad (k_4) \quad (4)$$

It is not known whether the dibromide radical in acetic acid can undergo this reaction. Extensive tabulations of rate constants, mostly for reactions in aqueous solution, present no data for this class of reaction. Indeed, H-atom abstraction by dibromide from C−H bonds appears unknown at this time.[12] Most of the

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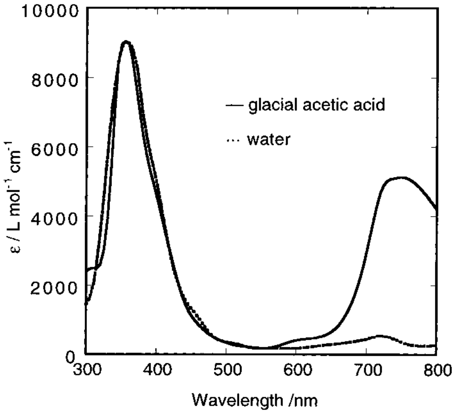

Figure 1. UV−visible absorption spectra for $HBr_2^•$ in glacial acetic acid and for $Br_2^{•-}$ in aq solution from ref 13. Spectra were recorded at 25 °C; [NaBr] = 20 mM, and $[Br_2]$ = 1 mM. Data at each wavelength were obtained individually at 20 nm intervals by setting the monochromator to the desired wavelength and collecting at least three kinetic runs. The maximum absorbance at $t = 0$ was taken as the absorbance of $HBr_2^•$ at that wavelength. The spectrum thereby obtained was normalized to that in water.

existing data pertain to aqueous solutions, where the dibromide radical ion was generated by pulse radiolysis. The dibromide radical anion has been well characterized in aqueous solution;[12,13] $Br_2^{•-}$ has an absorption maximum at 360 nm ($\epsilon = 9 \times 10^3$ L mol^{-1} cm^{-1}). The rate constant for its disproportionation reaction is $k_5 = 2 \times 10^9$ L mol^{-1} s^{-1}. The UV−vis spectra of $Br_2^{•-}$ in water and of $HBr_2^•$ in glacial acetic acid are shown in Figure 1. We have no method for determining the absolute concentration of this transient species in our experiments, and thus, in Figure 1, it was assumed that ϵ at 360 nm was equal to that in aqueous solution. One cannot help but notice an unusual feature, the strong absorption at 750 nm in HOAc, in contrast to a weak band in water. In HOAc, $\epsilon_{360} \sim 2\epsilon_{750}$. We have not explored the origin of the unusual band and have used the traditional 360 nm band to determine the reaction kinetics.

To test the hypothesis that $HBr_2^•$ may be the reactive intermediate, we have generated it by laser dissociation of HBr_3/Br_2. The radical itself was characterized by its visible spectrum and disproportionation rate constant, compared with the analogous values in aqueous solution. The loss of dibromide was followed at its absorption maximum, 360 nm, and reflects the result of the bimolecular disproportionation reaction:

$$2HBr_2^• \rightarrow 2HBr + Br_2 \quad (k_5) \tag{5}$$

The rate constant for the disproportionation of $HBr_2^•$ in glacial acetic acid in the absence of substrate was determined by fitting the data to second-order kinetics in this form

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + \frac{\mathrm{Abs}_0 - \mathrm{Abs}_\infty}{1 + [HBr_2^•]_0 2k_5 t} = \mathrm{Abs}_\infty + \frac{\mathrm{Abs}_0 - \mathrm{Abs}_\infty}{1 + \mathrm{Abs}_0\left(\frac{2k_5}{\epsilon}\right)t} \tag{6}$$

in which l is the cross-sectional diameter of the circular laser beam. The data conform well to second-order kinetics. Because the molar absorptivity of $HBr_2^•$ in acetic acid is not known, only the composite parameter $k_5/\epsilon_{360}l$ could be calculated. We use the roughly estimated value $l \sim 0.5$ cm, giving the average value of k_5/ϵ_{360} as $(2.5 \pm 0.5) \times 10^5$ cm s^{-1}, compared with $k_5/\epsilon_{360} = 2.2 \times 10^5$ cm s^{-1} in aqueous solution. If we *assume* $\epsilon_{360} = 9 \times 10^3$ L mol^{-1} cm^{-1} in acetic acid as well, then $k_5 = (2.3 \pm 0.5) \times 10^9$ L mol^{-1} s^{-1}. It should be recognized that circular logic has been used in assigning separate values to k_5 and ϵ_{360}. In those reactions of major interest here, between the dibromide radical and methylarenes, only the ratio k/ϵ enters, and (because the methylarene term in the rate equation follows first-order kinetics) so the optical path length is not an issue.

We then proceeded to examine whether $HBr_2^•$ reacts with methylarenes and a few related compounds. A considerable number of these substrates were investigated to explore the effects of selected ring substituents. These include methyl aromatics with more than one CH_3 group, those with carboxylic acid, aldehyde, and ester groups, and those with alkyl groups beyond methyl. Varying concentrations of each methylaromatic compound were used to resolve the rate constant for that reaction from that for dibromide disproportionation. In the presence of a reagent that is oxidized by $HBr_2^•$, for $ArCH_3$ in general (when that reagent is used in large excess over dibromide), the rate law and its specific solution for $[HBr_2^•]$ are

$$-\frac{d[HBr_2^•]}{dt} = k_4[ArCH_3][HBr_2^•] + k_5[HBr_2^•]^2 \tag{7}$$

$$[HBr_2^•]_t = \frac{k_\psi[HBr_2^•]_0 \exp(-k_\psi t)}{k_\psi + 2k_5[HBr_2^•]_0\{1 - \exp(-k_\psi t)\}} \tag{8}$$

The pseudo-first-order rate constant k_ψ was evaluated by nonlinear least-squares fit of the data to eq 8 with k_5 fixed at the known value. In each case, k_ψ proved to be a linear function of the concentration of $ArCH_3$, confirming that reaction 4 had been formulated correctly. The values of k_4 for all the substrates are shown in Table 1. It should be noted that none of the values of k_4 is particularly large. That limits the precision of the kinetic data, particularly as k_4 becomes less than about 2×10^4 L mol^{-1} s^{-1} and the k_5 term makes the larger contribution.

The kinetic isotope effect (KIE) was explored for each of the substrates where the deuterated compound was available. An example is given by the data for *p*-xylene, shown for both H and D compounds in Figure 2. KIEs were similarly determined for toluene-d_8, *o*-xylene-d_{10}, and 1,3,5-trimethylbenzene-d_{12} (Table 2). The values are large ($k_H/k_D > 5$), save for toluene where the low value of k_D renders it less reliable. The substantial KIEs can be taken as supporting evidence for reaction 4 proceeding as a H-atom abstraction reaction.

Introduction of an aldehyde or acid group reduced the rate constant considerably. The same is true for the barriers observed for these groups in the commercial autoxidation and with the calculated reactivities of these substrates.[1] Many of the aldehydes had UV absorptions that tailed into the 360 nm region, rendering them impossible to study by this method.

The selectivity of $HBr_2^•$ among these substrates is of interest, because the MC process invariably forms the aromatic carboxylic acid regardless of the length of the aliphatic group (e.g., cumene yields benzoic acid).[1] Two possibilities come to mind: $HBr_2^•$ may abstract a hydrogen atom either from the α-carbon of the R-group or from the other carbons with subsequent reorganizations. To assess this, four substrates can be compared: toluene, ethylbenzene, cumene, and *tert*-butylbenzene. The rate constant (Table 1) for PhEt is ~15-fold larger than that for PhMe, reflecting the additional stabilization of the transition state that leads to the formation of the secondary radical. Table 3 shows that, on a per-hydrogen basis, the reaction of $PhCHMe_2$ is still faster than that of PhEt, continuing that trend. For *tert*-butylbenzene, there is of course no α-H; it comes

TABLE 1: Rate Constants for the Reaction of $HBr_2^•$ with Methyl Aromatic Compounds

compound	$k/(\times 10^4$ L mol^{-1} s$^{-1})$
A. Methyl Arenes	
benzene	<0.5
toluene	1.0 ± 0.2
toluene-d_8	$0.5_7 \pm 0.1$
o-xylene	9.5 ± 0.3
o-xylene-d_{10}	1.12 ± 0.05
m-xylene	4.7 ± 0.1
p-xylene	16 ± 2
p-xylene-d_{10}	3 ± 1
1,2,3-trimethylbenzene	19.9 ± 0.6
1,2,4-trimethylbenzene	19.9 ± 0.3
1,3,5-trimethylbenzene	13.8 ± 0.3
1,3,5-trimethylbenzene-d_{12}	2.2 ± 0.1
1,2,3,5-tetramethylbenzene	39.7 ± 0.4
1,2,4,5-tetramethylbenzene	50.8 ± 0.6
pentamethylbenzene	111 ± 4
hexamethylbenzene	203 ± 15
B. Alkyl Benzenes	
ethylbenzene	14.6 ± 0.3
cumene	11.3 ± 0.4
tert-butylbenzene	0.5 ± 0.1
C. Naphthalenes	
2-methylnaphthalene	12 ± 2
2,6-dimethylnaphthalene	15 ± 1
D. Aldehydes	
p-tolualdehyde	5.0 ± 0.4
E. Carboxylic Acids	
o-toluic acid	0.5 ± 0.1
m-toluic acid	0.57 ± 0.06
p-toluic acid	<0.5
2,4-dimethylbenzoic acid	1.34 ± 0.05
2,5-dimethylbenzoic acid	1.00 ± 0.03
3,5-dimethylbenzoic acid	1.5 ± 0.1
2,4,6-trimethylbenzoic acid	1.51 ± 0.04
F. Others	
1,4-dimethylcyclohexane	0.95 ± 0.03
methyl-3-methyl-benzoate	0.4 ± 0.1

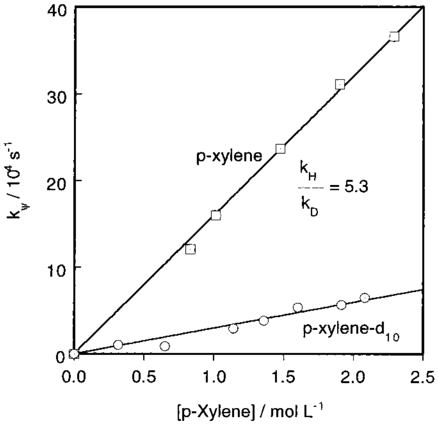

Figure 2. The value of k_ψ from the nonlinear least-squares fitting of the kinetic data to eq 8 varies linearly with [*p*-xylene], as expected from eq 4. The ratio of the slopes for the h_{10} and d_{10} compounds provides the kinetic isotope effect.

as no surprise, therefore, that it has the lowest reaction rate of any of the alkylbenzenes.

Figure 3 shows a plot of the kinetic data for the methylarenes according to Hammett's method; the *x*-axis displays composite σ^+ values.[14] The value of σ^+ for each inequivalent methyl group was obtained by taking the sum of the σ^+ values for the other substituents on the ring, using a contribution of -0.31 for ortho and para and -0.10 for meta groups. When *n* equivalent methyl groups were present (e.g., in *p*-xylene and mesitylene), the value of *k* was divided by *n*. This treatment gives the overall reaction constant as $\rho = -1.4$, consistent with stabilization of the incipient benzyl radicals by the electron donating CH_3 groups. Also, this value of ρ lies in the range of reaction constants obtained for other oxidations of methylarenes which lie between -0.7 and -1.35.[1,15,16]

TABLE 2: H/D Kinetic Isotope Effects for the Reactions of the Dibromide Radical with Selected Methylarenes

compound	k_H/k_D
toluene	(1.8)[a]
o-xylene	8.5
p-xylene	5.3
1,3,5-trimethylbenzene	6.3

[a] The rate constant for toluene-d_8 is so small that it may be unreliable.

TABLE 3: Rate Constants for $HBr_2^•$ Per Reactive Hydrogen Atom for Selected Substrates

compound	k per H/$(\times 10^4$ L mol^{-1} s$^{-1})$
toluene	0.3
ethylbenzene	7.3
cumene	11.3
tert-butylbenzene	0.5

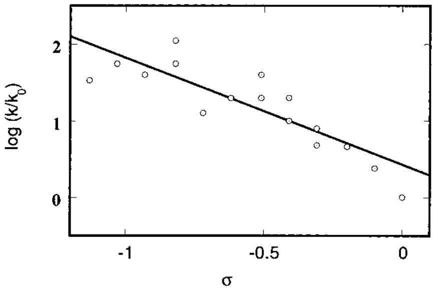

Figure 3. Hammett correlation of log k_4 against the Hammett parameter σ^+. In this case, each methylarene will have as many points plotted as there are inequivalent methyl groups; each value on the ordinate represents log(k/n), where *n* is the number of equivalent methyl groups of a given type ($1 \leq n \leq 6$).

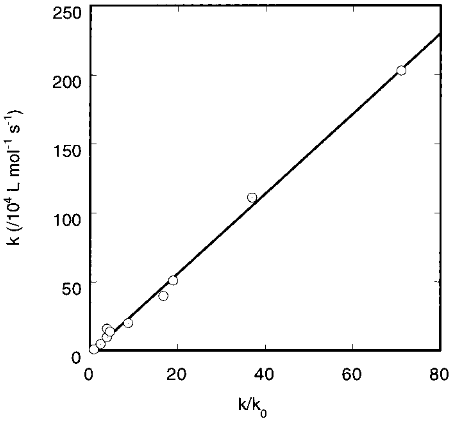

Figure 4. The values of k_4 correlate with the reactivity data for the overall autoxidation of the methyl arenes.

The rate constants in Table 1 also correlate well with the reactivities for the overall oxidation of methylarenes,[1] using $\rho = -0.95$ and composite σ^+ values as explained in the preceding paragraph. Figure 4 presents a reasonable correlation between the rate constants k_4 and the overall rate of the MC process. If this is not coincidental, then it seems that H-atom abstraction is a key limitation to the rate of oxidation.

A final question was raised by a reviewer: does the reaction proceed with atomic bromine rather than with dibromide? The two are related by this reaction:

$$\mathrm{Br}^\bullet + \mathrm{Br}^- \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} \mathrm{Br_2}^{\bullet-} \qquad (9)$$

The rate constants for eq 9 in water at 298 K are $k_9 = 1.2 \times 10^{10}$ L mol^{-1} s^{-1} and $k_{-9} = 2 \times 10^4$ s^{-1}.[17] We shall assume in this analysis that similar values hold in acetic acid. The *equilibrium* proportions of the two radicals at an HBr concentration of 20 mM amount to a ratio of $\mathrm{HBr_2}^\bullet/\mathrm{Br}^\bullet = 1.2 \times 10^4$. The strictest test comes with the most reactive compound, hexamethylbenzene; on the basis that $\mathrm{HBr_2}^\bullet$ is the reagent, its rate constant is 2.0×10^6 L mol^{-1} s^{-1}. Were that reactivity to be attributed to $\mathrm{Br}^\bullet$, its rate constant would be 2.4×10^{10} L mol^{-1} s^{-1}, and the values for all the other compounds would be below that limit. In terms of the diffusion-control limits, these values are high, but within bounds.

The mechanism is nonetheless impermissible. The $\mathrm{Br}^\bullet$ formed in the laser flash would partition between the reaction with the methylarene and the dibromide formation in eq 9, well before the detectable signal was recorded at ∼5 ns. To the extent that the former occurred, the reaction would give rise to no optical signal, which requires dibromide; in any event the amount of dibromide detectable at the first recorded datum would fall with methylarene concentration, well beyond the known effect of internal filtering already noted. Given the value of k_9, however, $\mathrm{HBr_2}^\bullet$ must form to a considerable extent in every experiment, the more so with the less reactive compounds; this is as detected. The reverse reaction, represented by k_{-9}, is ∼10 times smaller than the experimental rate constants, k_ψ. Neither the values of the rate constants nor the kinetic equations (the experimental rates are *not* given by $v = k_{-9}[\mathrm{HBr_2}^\bullet]$) could be consistent with the interpretation that the reverse of reaction 9 provides an important contribution. From this, the contribution of $\mathrm{Br}^\bullet$ to the observed kinetics appears at best to be small.

Experimental Section

The following reagents were provided by BP Chemicals: *p*-tolualdehyde, *p*-toluic acid, terephthalaldehyde, 4-carboxybenzehaldyde, *m*-tolualdehyde, *m*-toluic acid, isophthalaldehyde, methyl-3-methylbenzoate, 2,4-dimethylbenzoic acid, and 2,5-dimethylbenzoic acid. Unless specified otherwise, the other methyl aromatics and other reagents were obtained commercially and used without further purification.

The laser flash photolysis experiments were carried out using a Spectron Laser Systems Nd:YAG SL 800 laser with a wavelength of 355 nm. The reaction progress was monitored at 360 nm by an Applied Photophysics Xe lamp and spectrometer system. In a typical experiment, $\mathrm{HBr_3}$ was formed from sodium bromide (20 mM) and $\mathrm{Br_2}$ (1 mM) in glacial acetic acid. A portion of the methyl aromatic substrate was added, the precise amount being determined by the difference in mass. The laser flash photolysis experiment was then carried out. The absorbance−time data were analyzed by nonlinear least-squares regression as in eq 6.

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Supporting Information Available: Plots of the kinetic data for selected laser flash photolysis experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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