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Jessica L. Cohen

Patrick Hoggard
Santa Clara University, phoggard@scu.edu

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The Photooxidation of Hexabromorhenate(IV) in Ethyl Bromide

JESSICA L. COHEN AND PATRICK E. HOGGARD*

Department of Chemistry, Santa Clara University, Santa Clara, CA 95053, USA

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Irradiation at 254 or 313 nm of solutions of $(Bu_4N)_2[ReBr_6]$ in ethyl bromide exposed to air causes complete conversion of the hexabromorhenate(IV) to perrhenate ion. The rate of the reaction is linearly dependent on the incident light intensity and on a combination of the fraction of light absorbed by the rhenium complex and the fraction absorbed by the ethyl bromide. The experimental results are consistent with a mechanism in which the peroxy radical $CH_3CH(Br)OO$, produced in both the solvent-initiated and metal-initiated pathways, oxidizes $[ReBr_6]^{2-}$ by electron transfer.

Keywords: Rhenium complexes, Hexabromorhenate(IV), Photooxidation, Bromoethane, Perrhenate, Solvent-initiated, Metal-initiated.

INTRODUCTION

A number of metal complexes have been found to undergo photoreactions in chlorinated solvents initiated through absorption of light by the solvent [1]. Such reactions include photoreduction [2], photooxidation [3–6], photosubstitution [7, 8], and protonation [9]. Several photoreactions are known in which light absorption by both the solvent and the metal complex lead to the same product by separate pathways [10–13]. The disparate pathways have in common hydrogen abstraction by the chlorine atoms formed in the primary photochemical process.

$$Cl\cdot + CHCl_3 \rightarrow HCl + \cdot CCl_3 \qquad (1)$$

Solvent-initiated photosubstitution and protonation reactions are generally caused by HCl, photoreduction by $\cdot CCl_3$, and photooxidation by CCl_3OOH, generated by the reaction of the trichloromethyl radicals with oxygen, followed by another hydrogen abstraction.

One might expect that parallel reactions would occur in brominated solvents, but the H–Br bond enthalpy is smaller than most H–C bond enthalpies, and thus hydrogen abstraction is unlikely. We have examined the photochemical behavior of $[ReBr_6]^{2-}$ in C_2H_5Br, with the expectation that a solvent-initiated process might still take place, initiated by photodissociated ethyl radicals.

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*Corresponding author: PHoggard@scu.edu

EXPERIMENTAL

$(Bu_4N)_2[ReBr_6]$ was synthesized by mixing aqueous solutions of $K_2[ReBr_6]$ and Bu_4NBr (both Sigma-Aldrich). The resulting precipitate was collected by filtration, washed with water, and air-dried. Tetrabutylammonium perrhenate was obtained from Sigma-Aldrich.

Photolyses were carried out on solutions in 1-cm quartz cuvettes. Light from a 500-W mercury/xenon lamp (Oriel) was passed through a 25-cm monochromator to irradiate samples, approximately half of the cuvette area being illuminated. Stirring the solution was found to cause no difference in the reaction rate, and most solutions were unstirred. Light intensities were measured with a Thermo Oriel 70260 radiant power meter. Intensities at a single wavelength were varied, when necessary, by adjusting the monochromator slit width. UV-visible spectra were recorded with a Cary 50 spectrophotometer.

Initial concentrations of $(Bu_4N)_2[ReBr_6]$ were determined from the extinction coefficient at the 357 nm peak, $7.36(\pm 0.60) \times 10^3\ M^{-1}cm^{-1}$, from a Beer's Law plot. Exhaustive photolysis led to an absorption at that wavelength corresponding to an extinction coefficient of 2.9×10^3, from which concentrations of $[ReBr_6]^{2-}$ during photolyses could be calculated.

The absorbance of $[ReBr_6]^{2-}$ and by C_2H_5Br at 254 nm, neither of which could be measured directly, are necessary in order to calculate the fraction of light absorbed by each in solutions irradiated at that wavelength. The extinction coefficient of $[ReBr_6]^{2-}$ at 254 nm was taken to be that of $(Bu_4N)_2[ReBr_6]$ in CH_3CN, 5.65×10^3. The absorbance of EtBr in a 1.00-mm cuvette was used to estimate the absorbance in a 1.00-cm cuvette to be 18.4.

RESULTS

Irradiation of ethyl bromide solutions of $(Bu_4N)_2[ReBr_6]$ at 254 nm led to spectral changes as shown in Figure 1. An isosbestic point at 325 nm indicates a conversion to a single set of primary products. Exhaustive photolysis erased all features, leading to a spectrum consisting only of a UV tail. This was tentatively associated with the perrhenate ion, the spectrum of which consists of a manifold of charge transfer transitions beginning at about 250 nm [14]. This part of the spectrum could not be observed due to the strong absorbance by ethyl bromide. The UV tail may also derive in part from the spectrum of the tribromide ion, which has an intense peak around 270 nm [15]. To confirm the product identification, a solution of $(Bu_4N)_2[ReBr_6]$ in ethyl bromide was shaken with a small amount of 30% aqueous hydrogen peroxide, which oxidizes most rhenium species to perrhenate [16, 17]. The spectrum of the ethyl bromide phase matched almost exactly the spectrum

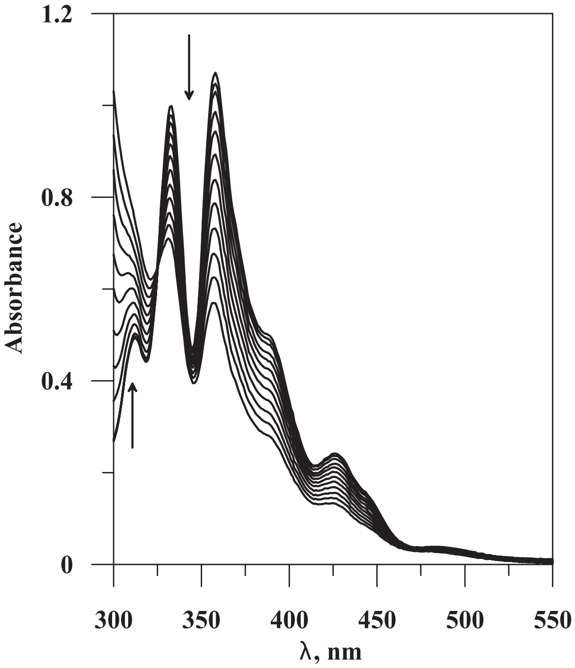

FIGURE 1
Sequential spectra from the 254 nm irradiation of $(Bu_4N)_2[ReBr_6]$ in EtBr. Total irradiation time was 38 min.

produced by exhaustive photolysis of the same solution.

Irradiation of $(Bu_4N)_2[ReBr_6]$ in ethyl bromide at 313 nm proceeded in like manner, with an isosbestic point at 325 nm and yielding ReO_4^- as the final product. Solutions with a concentration around 10^{-4} M reacted approximately four times more slowly under 313 nm irradiation than at 254 nm, despite an intensity about 15 times greater. Under 366 nm irradiation, though that wavelength is strongly absorbed by $[ReBr_6]^{2-}$, the reaction was still slower – about 20-fold slower compared to 313 nm excitation.

We have observed several systems in which a metal complex in chloroform, when irradiated at 254 nm, yields a product formed either partly [10, 11] or entirely [9, 18] by photodissociation of the solvent. Kinetically, the distinction between this pathway and one initiated by the excited state metal complex lies in whether the reaction rate depends on f_R, the fraction of light absorbed by the reacting metal complex, or f_S, the fraction of light absorbed by the solvent, the dependence of f_R and f_S on the concentration, $[R]$, of the metal complex being given by [1]

$$f_R = \{1 - 10^{-(\varepsilon_R[R]+\varepsilon_P[P]+A_S)}\}\frac{\varepsilon_R[R]}{\varepsilon_R[R]+\varepsilon_P[P]+A_S} \tag{2}$$

$$f_S = \{1 - 10^{-(\varepsilon_R[R]+\varepsilon_P[P]+A_S)}\}\frac{A_S}{\varepsilon_R[R]+\varepsilon_P[P]+A_S} \tag{3}$$

In Equations (2) and (3), A_S is the absorbance of the solvent, and ε_R and ε_P are the extinction coefficients of the reactant and product, respectively, at the irradiation wavelength.

To probe the question of whether the photoxidation of $[ReBr_6]^{2-}$ in ethyl bromide results from light absorption by the rhenium complex or by EtBr, initial rates for the disappearance of $[ReBr_6]^{2-}$ under 254 nm irradiation were measured for a range of starting concentrations. There was a negative correlation of the rate with f_S, while a plot of the initial rate as a function of f_R, shown in Figure 2, yielded a good straight line with a positive slope, but a nonzero intercept. The intercept implies that the photochemical reaction rate cannot depend on f_R alone.

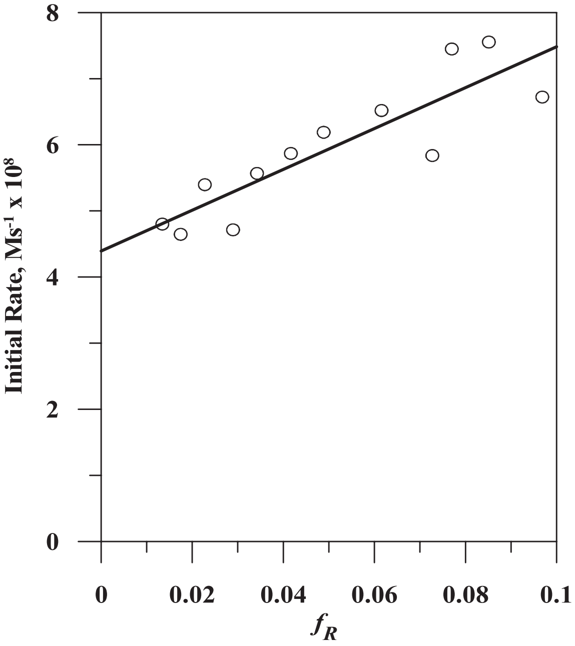

FIGURE 2
Initial rate of disappearance of $[ReBr_6]^{2-}$ in C_2H_5Br under 254 nm irradiation as a function of the fraction of light absorbed by the rhenium complex. $I_0 = 6.3 \times 10^{-10}$ einstein/s; $R^2 = 0.77$.

A plausible supposition, given the data in Figure 2, is that the rate depends predominantly on f_R, but also to some extent on f_S. The solvent-initiated pathway would become more important at very low concentrations of the metal complex. If the rate can be expressed as

$$-\frac{d[ReBr_6^{2-}]}{dt} = af_R + bf_S \tag{4}$$

then a plot of the rate divided by f_R against f_S/f_R should yield a straight line with a slope b and an intercept a. The corresponding graph is shown in Figure 3, yielding $a = 3.7(\pm 0.5) \times 10^{-7}$ Ms^{-1} and $b = 4.3(\pm 0.2) \times 10^{-8}$ Ms^{-1}. This implies that the quantum yield for the metal-initiated pathway is approximately nine times greater than that for the solvent-initiated pathway.

With 254 nm excitation, a plot of the reaction rate of 5.9×10^{-5} M solutions of $(Bu_4N)_2[ReBr_6]$ in EtBr as a function of incident light intensity is consistent with a direct linear relationship, and is illustrated

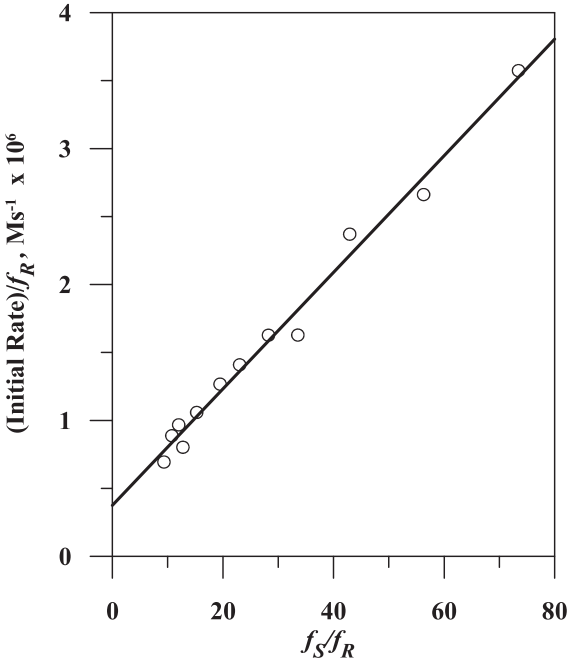

FIGURE 3
Plot of Rate/f_R *vs* f_S/f_R for the 254 nm photolysis of $[ReBr_6]^{2-}$ in EtBr; $R^2 = 0.99$.

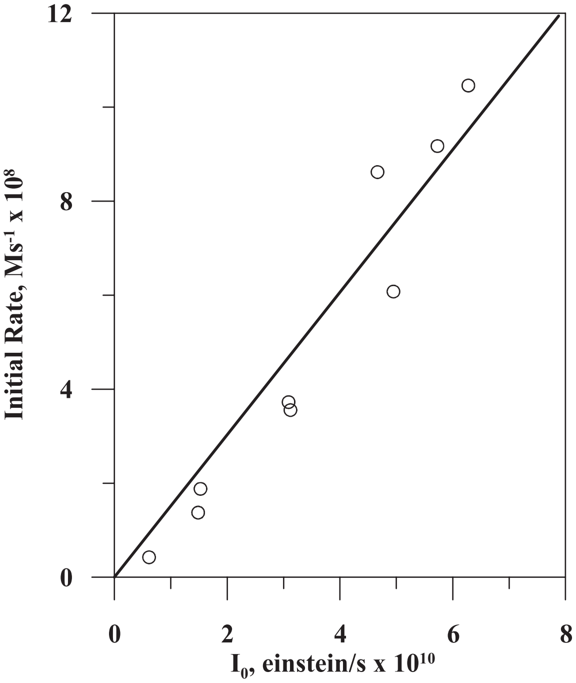

FIGURE 4
Initial rate of disappearance of $[ReBr_6]^{2-}$ in 5.9×10^{-5} M solutions of $(Bu_4N)_2[ReBr_6]$ in EtBr through photolysis at 254 nm at different incident light intensities; $R^2 = 0.97$.

in Figure 4. The slope, 150 M/einstein, corresponds to a quantum yield of 0.45 based on the total light absorbed. The quantum yield for 313 nm excitation was approximately 0.02, relative to the fraction of light absorbed by $[ReBr_6]^{2-}$, assuming the contribution from the solvent-initiated process to be negligible at that wavelength.

No photoreaction occurred when samples were deoxygenated by bubbling argon through them for 10 min.

DISCUSSION

The conversion of $[ReBr_6]^{2-}$ to ReO_4^- must be a very complex process. Mechanistically, the questions we can hope to answer experimentally are: how does oxidation begin and what is the oxidizing agent in the solvent-initiated and metal-initiated pathways?

It is reasonable to expect that a hydroperoxide functions as the oxidizing agent, as it does in many photooxidation reactions in halogenated solvents [3,4, 6,19–23], and in the photodecomposition of haloalkanes exposed to air [24–26]. In chloroform, CCl_3OOH is formed after dissociation of a chlorine atom from either $CHCl_3$ itself or a dissolved chlorine-containing species, abstraction of hydrogen from another $CHCl_3$ molecule, addition of O_2 to form a peroxy radical [27,28], and another hydrogen abstraction to make the hydroperoxide [29].

$$R{-}Cl \rightarrow R + Cl \qquad (5)$$
$$Cl + CHCl_3 \rightarrow HCl + CCl_3 \qquad (6)$$
$$CCl_3 + O_2 \rightarrow CCl_3OO \qquad (7)$$
$$CCl_3OO + CHCl_3 \rightarrow CCl_3OOH + CCl_3 \qquad (8)$$

The hydroperoxide acts as the main oxidizing agent, in preference to CCl_3OO [20], which is also a strong oxidant [30]. The hydroperoxide effects the oxidation by breaking the O–O bond [31–33]. This generally leads to a half-order dependence of the rate on light intensity [1,20].

Photolyses done in ethyl bromide can be expected to exhibit two significant differences from the behavior in chloroform. First, although photodissociation also occurs upon excitation of ethyl bromide [34–36], hydrogen abstraction by bromine is quite slow [37]. The C–H bond energy for the α-hydrogen, 403 kJ/mol [37], is considerably greater than the Br–H dissociation energy, which is 366 kJ/mol in the gas phase [38]. Even more importantly, hydrogen abstraction to form a hydroperoxide, analogous to Equation (8), is unfavorable, because the O–H bond energy in hydroperoxides is generally between 370 and 380 kJ/mol [39, 40]. This is adequate to abstract hydrogen from $CHCl_3$ at a reasonable rate, even though the C–H bond energy is 393 kJ/mol [41], but abstraction from ethyl bromide can be expected to be enough slower that it is not competitive with other reactions of the bromoethylperoxy radical.

Following the photodissociation of ethyl bromide, the resulting ethyl radicals will abstract hydrogen from C_2H_5Br, due to the stronger C–H bond in ethane [42], and this abstraction step is invoked in all proposed mechanisms for the uncatalyzed photodecomposition of liquid [36] and gaseous [34, 35, 43] EtBr. The addition of O_2 to form the peroxy radical is favorable [41].

$$C_2H_5Br \xrightarrow{h\nu} C_2H_5 + Br \tag{9}$$

$$C_2H_5 + C_2H_5Br \xrightarrow{k_9} C_2H_6 + CH_3CHBr \tag{10}$$

$$CH_3CHBr + O_2 \xrightarrow{k_{10}} CH_3CH(Br)OO \tag{11}$$

The rate of Equation (9) can be expressed as $(I_0 f_S \varphi_S / V)$, where I_0 is the incident light intensity, f_S the fraction of light absorbed by EtBr, φ_S the quantum yield for dissociation, and V the solution volume. Hydrogen abstraction will occur almost exclusively from the α-carbon [37], due to the lower C–H bond energy at that position.

Bromoperoxy radicals are among the most reactive peroxy radicals, oxidizing substrates by electron transfer [44]. The reaction with $[ReBr_6]^{2-}$ would yield a rhenium(V) intermediate.

$$\begin{aligned}&[ReBr_6]^{2-} + CH_3CH(Br)OO\\ &\xrightarrow{k_{11}} [ReBr_6]^{-} + CH_3CH(Br)OO^{-}\end{aligned} \tag{12}$$

In the presence of a proton source such as HBr, the peroxide anion will form the hydroperoxide, which may participate in the pathway to ReO_4^-. For example coordinated oxo ligands can arise from reactions such as

$$\begin{aligned}&[ReBr_6]^{-} + CH_3CH(Br)OOH\\ &\quad\to CH_3CH(Br)O + [ReBr_6(OH)]^{-}\\ &\quad\to [ReBr_5O]^{-} + HBr\end{aligned} \tag{13}$$

We can only speculate at this point to what extent the peroxy radical and the hydroperoxide function to introduce oxygen and promote the rhenium to the +7 state, and to what extent the coordinated bromides dissociate as bromide ions or hydrogen bromide, or are oxidized to Br or Br_2. However, applying just Equations (9) through (12), i.e., assuming that the peroxy radical is consumed primarily through Equation (12) rather than self-termination, yields Equation (14) for the rate law the disappearance of $[ReBr_6]^{2-}$.

$$-\frac{d[ReBr_6^{2-}]}{dt} = \frac{I_0 f_S \varphi_S}{V} \tag{14}$$

This is consistent with the linear dependence of the rate on light intensity and on the fraction of light absorbed.

Several possibilities might be considered for the metal-initiated pathway. Given the ligand-to-metal charge transfer (LMCT) nature of the $[ReBr_6]^{2-}$ UV spectrum [45], one could expect bromine atom dissociation to occur upon excitation; however, even if dissociation occurs, the slow hydrogen abstraction from EtBr by atomic bromine renders this pathway to the peroxy radical uncompetitive, especially given that in the solutions studied the ethyl bromide absorbed considerably more 254 nm light than $[ReBr_6]^{2-}$.

An alternative is the reduction of EtBr by excited state $[ReBr_6]^{2-}$:

$$[ReBr_6]^{2-*} + C_2H_5Br \to [ReBr_6]^{-} + C_2H_5 + Br^{-} \tag{15}$$

Similar oxidative electron transfer has been proposed for a number of photoreactions with haloalkanes [46–49]. It has been suggested that this type of reaction is facilitated by absorption into a charge transfer to solvent (CTTS) band [47, 50–52]; however any such spectral feature at 254 nm is completely obscured by solvent absorption, while spectral features between 300 and 350 nm were also present in spectra taken in acetonitrile, and thus cannot represent CTTS absorption.

Following the photogeneration of the ethyl radical, ReO_4^- can form just as in the solvent-initiated pathway. Making the same assumptions, primarily that the peroxy radical reacts more rapidly by oxidizing rhenium than by self-termination, the rate of disappearance of $[ReBr_6]^{2-}$ by both solvent- and metal-initiated pathways is predicted to be

$$-\frac{d[\mathrm{ReBr}_6^{2-}]}{dt} = \frac{I_0}{V}(f_S\varphi_S + f_R\varphi_R) \qquad (16)$$

which is in accord with experiment.

CONCLUSION

Experimentally, the rate of photooxidation of $[ReBr_6]^{2-}$ to ReO_4^- in ethyl bromide is found to vary directly with the incident light intensity. It also varies directly with a linear combination of the fraction of light absorbed by the solvent and the fraction absorbed by the rhenium complex. This is consistent with a mechanism in which $[ReBr_6]^{2-}$ is oxidized by $CH_3CH(Br)OO$ radicals. The peroxy radicals are formed after the initial generation of ethyl radicals, which abstract hydrogen from EtBr to form $CH_3CH(Br)$ radicals that then add O_2. Ethyl radicals can be formed either by direct photodissociation of the solvent or by oxidative quenching of excited $[ReBr_6]^{2-}$.

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