Photoassisted Oxidation of Hydrogen Bromide to Bromine

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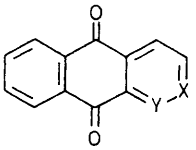
Irradiation of oxygen-swept aqueous HBr solutions in the presence of catalytic amounts of anthraquinone derivatives (*e.g.* 2-sulphonate) produces molecular bromine (up to 3 mmol h^{-1}) with quantum yields of up to 0.07.

Some time ago, Scharf and Weitz[1] succeeded in putting to work an old idea[2] namely the photochemical oxidation of (hydrogen) chloride using electronically excited anthraquinone derivatives as electron-transfer agents but oxygen being the ultimate oxidizer.

We now report that we were able to produce bromine[3—6] by irradiating oxygen-swept aqueous HBr solutions containing catalytic amounts of certain substituted anthraquinone (AQ) derivatives. The irradiations (600 W high-pressure Hg immersion-lamp in Pyrex well) of aqueous HBr solutions (47%) containing anthraquinone-2-sulphonate (AQ-2) (1.3×10^{-3} M) were performed with a continuous oxygen current (*ca.* 400 ml min^{-1}) which was also used to sweep the solution into appropriate traps where bromine was collected at a rate of *ca.* 0.3 mmol h^{-1}, equation (1). Most significantly, the rate of bromine formation did not change over a period of *two weeks* (whence, a yield of *ca.* 7%) and could presumably go on indefinitely.

$$2\,HBr + \tfrac{1}{2}\,O_2 \xrightarrow{h\nu/AQ} Br_2 + H_2O \qquad (1)$$



AQ

A number of factors were found to be crucial in the process, as outlined below. (i) Bromine removal is obligatory and was done by means of the oxygen stream, down to a steady state concentration of $[Br_3^-] \simeq 3 \times 10^{-3}$ in the reactor. To achieve optimal bromine removal however, we resorted to *in situ* α-bromination of 4-t-butylcyclohexanone which gave a 2:8 mixture of 2-bromo- and 2,6-dibromo-4-t-butylcyclohexanone, rapidly enough to speed up bromine production by an order of magnitude, to *ca.* 3 mmol h^{-1} (as deduced from analysis of the isolated products). It appears that one of the contributing factors to the bottle-neck in the process, is the rate of build-up of the Br_3^- absorption at 274 nm (ε 3.6×10^4), the end-absorption of which eventually overlaps with that of

Table 1. Anthraquinone (AQ) photocatalysts for bromide oxidation and the corresponding quantum yields (ϕ) for bromide formation.[a]

	AQ	ϕ
1	1-SO_3H	4×10^{-2}
2	2-SO_3H	5×10^{-2}
3	2-CH_2SO_3H	5×10^{-2}
4	1-Br, 2-CH_2SO_3H	3×10^{-2}
5	1,6-$(SO_3H)_2$	3×10^{-2}
6	X = N	2×10^{-2}
7	Y = N 1,3-Ph_2	$<5 \times 10^{-3}$

[a] At 338 nm and low conversions. The numbers represent minimal values (see text, section iii).

Table 2. Dependence of rate of Br_2 formation on the H^+ and Br^- concentrations.[a]

$[H^+]:[Br^-]$	1:1				2:1			4:1		8:1
$[H^+]$	2.9	1.45	0.72	0.36	2.9	1.45	0.72	2.9	1.45	2.9
$[Br^-]$	2.9	1.45	0.72	0.36	1.45	0.72	0.36	0.72	0.36	0.36
Br_2[b]	5.6	3.4	1.6	0.06	5.2	1.7	0.25	4.3	0.7	1.3

[a] Experimental conditions: 300 ml total volume of HBr and $HClO_4$ (where needed for excess of H^+) aqueous solutions; irradiated by 600 W high-pressure Hg lamp (Hanau); swept continuously by oxygen (0.4 l min^{-1}); 115 mg (0.4 mmol) photocatalyst AQ-2; trap and reactor were monitored every 24 h by titration of aliquots with 0.1 M $Na_2S_2O_3^-$; the numbers in the table refer to the amount of Br_2 in the trap. [b] mmol/24 h.

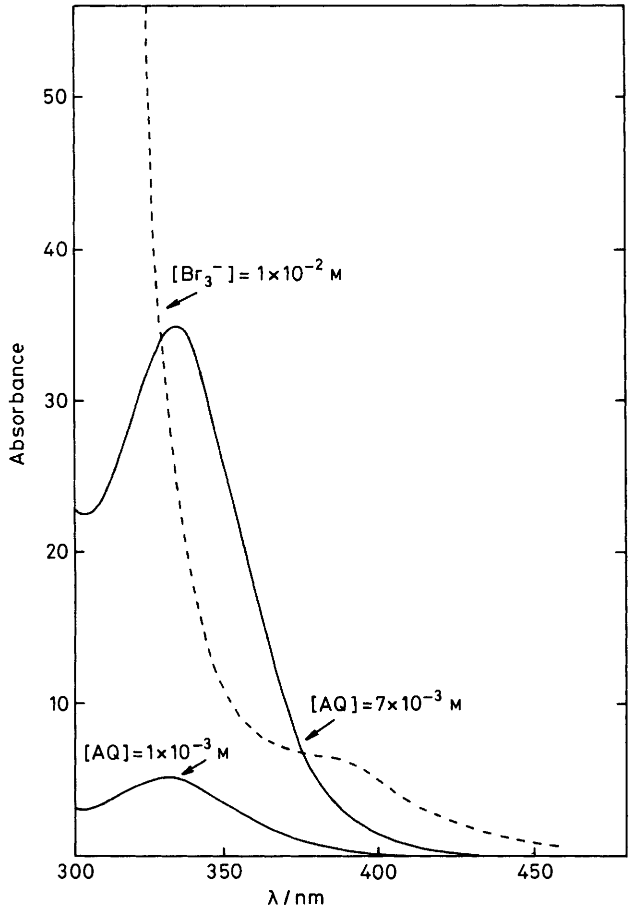


Figure 1. Absorption spectra of aqueous HBr (47%) solutions of bromine (10^{-2} M) and anthraquinone-2-sulphonate (1×10^{-3} and 7×10^{-3} M).

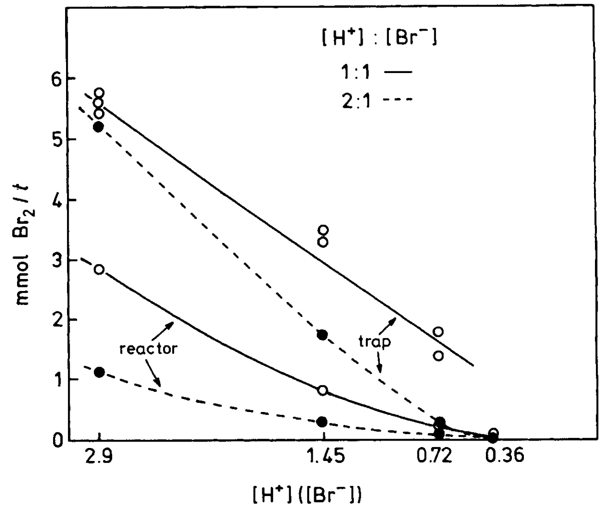


Figure 2. Rate of Br_2 production *vs.* concentrations of Br^- and H^+, as monitored in trap and reactor in typical irradiations of HBr(aq.) 47% solution in Pyrex, 600 W high-pressure Hg lamp (Hanau), O_2-swept at 400 ml min^{-1}, t = 24 h.

the anthraquinone catalyst, *e.g.* AQ-2: $\lambda_{max.}$ 333 nm (ε 4.9 × 10^3) [see (iii) for further elaboration on this and Figure 1].

(ii) Oxygen concentration had to be maintained at a high level, using an oxygen flow rate of up to 400 ml min^{-1} with efficient stirring. While the rates of oxygen flow and of bromine formation showed a roughly linear relationship, a quantitative determination of the reaction rate is still to come.

(iii) Anthraquinone (AQ)[1,7—11] activity, concentration, and photostability are of utmost importance in the process. Of a variety of 23 substituted anthraquinones, seven (AQ 1—7) exhibited catalytic activity and their quantum yields are given in Table 1. The lack of activity of the remaining AQ derivatives was tentatively attributed to (a) poor solubility, (b) intramolecular hydrogen-bonding or -transfer, or (c) intramolecular charge-transfer and no further effort was spent on them. All the detailed and exploratory work was then performed on the 2-sulphonate (AQ-2).

One of the latter's most significant and gratifying properties was its photostability (in contrast to its deterioration by photosubstitution in the photo-oxidation of HCl[1]) in irradiations over long periods (up to 14 days) with practically no change in the rate of bromine formation. Moreover, recovery of the catalyst from the solution led to no significant changes in its spectral (u.v., i.r., n.m.r.) properties, which supports our assertion that the process could be carried on indefinitely.

Nevertheless, the relatively low quantum yield of bromine production was a source of annoyance and called for rationalization and, possibly, remedy. The electronic absorption and emission spectra of anthraquinone derivatives are known[1] and in *aqueous acidic solution* the n,π* absorptions (otherwise well defined around 400 nm with ε ~100) are efficiently covered by the end-absorption of the π,π band peaking at 333 nm (ε ~4000). Since it is by now well documented that anthraquinone (AQ) photoassisted oxidation of alcohols[11,10] and of chloride[1] are due to the lowest triplet excited state ($^3AQ^*$) of n,π* character, its ensconcement by the π,π* band, may contribute to lowering the yield and quantum yield. In Figure 1, it can be seen that the entire AQ absorption region is obscured by the long tail of the Br_3^- absorption band.

To overcome this handicap we shifted the *effective irradiation* to higher wavelength both by proper adjustment of the radiation source and by increasing the catalyst's concentration to [AQ] = 7×10^{-3}, attaining an absorbance of 10—0.4 at 370—420 nm. In this range the ratio $\varepsilon(n,\pi^*)/\varepsilon(\pi,\pi^*)$ is bound to be appreciably higher than at 340 nm and the spurious Br_3^- end-absorption is low.

These changes caused appreciable increase in the rate of bromine production, *viz.* by going from 340 to 420 nm, where *ca.* 0.6 mmol h^{-1} are formed with a quantum yield of 0.07.

(iv) Concentration effects (H^+ and Br^-). There is a definite dependence of bromine formation on the concentration of bromide ions and an even stronger one on that of protons, as shown in Table 2 and Figure 2. Although these, as well as the other above reported data are of a preliminary nature, they are enough to indicate that any of the electron-transfer, protonation, and oxygenation steps may participate in the rate-determining process.

Finally, it is interesting that irradiation of an oxygenated aqueous HBr solution of bromine into its Br_3^- absorption band yields bromine with a quantum yield of 2×10^{-3} (without AQ assistance). It is worth noting in this context, that oxygen and bromide ion have been reported[12] to form charge-transfer complexes (albeit in neutral solutions) and that in the flash photolysis of bromide (aq.), bromine was formed by decay of the transient dihalide ion Br_2^- (albeit with no reference to the role of oxygen, if any, in this process).[4,13]

While the effort continues in both continuous wave and flash photolytic work, we believe that this is a valuable photochemical energy conversion process.

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