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Vanadium-Catalysed Oxidative Bromination Using Dilute Mineral Acids and Hydrogen Peroxide: An Option for Recycling Waste Acid Streams

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Abstract:

Vanadium pentoxide, V_2O_5, catalyses the two-electron oxidation of Br^- to Br^+, using aqueous hydrogen peroxide under dilute acidic conditions. In this system, kinetic studies show that HBr can be replaced with a combination of an alkali bromide salt (NaBr, KBr) and a dilute mineral acid (e.g., HCl, H_2SO_4, HNO_3, H_3PO_4). The salt/acid/peroxide system may be used for in situ or ex situ oxidative bromination, e.g. of various aromatic compounds. The application of the above concept towards the recycling of industrial acid waste is discussed. The cost effectiveness, *E* factors, and hazard factors for several bromination and oxidative bromination reagent systems are compared.

Introduction

Bromination of organic compounds is one of the reactions performed today on a very large scale, often resulting in stoichiometric pollutant streams. Classical bromination of aromatics, for example, utilizes only 50% of the halogen, with the other half forming HBr waste (eq 1).

$$\mathrm{ArH} + \mathrm{Br_2} \rightarrow \mathrm{ArBr} + \mathrm{HBr} \qquad (1)$$

Theoretically, it is possible to reoxidise the HBr, e.g. with H_2O_2, and achieve high bromine utilization, between 90 and 95% (eq 2).[1]

$$2\mathrm{HBr} + \mathrm{H_2O_2} \rightarrow \mathrm{Br_2} + 2\mathrm{H_2O} \qquad (2)$$

Thus, activated aromatics, such as phenols, anisoles, and anilines, may be oxybrominated without a catalyst,[2] while inactive (benzene, toluene) but not deactivated (e.g., nitrobenzene) ones, have been oxybrominated in the presence of quaternary ammonium salts.[3] In practice, however, HBr recycling is rarely performed in industrial plants, as the additional step and the corrosiveness of HBr necessitate reactor costs that exceed those of purchasing more Br_2.

Transportation and storage of large quantities of molecular bromine and HBr is extremely hazardous. Bromide recycling can reduce these risks. Several recent publications[2a,4] cite toxicity of Br_2 and HBr as the incentive to investigate various complex oxybromination reagents, but, in real life, two situations have to be distinguished: (a) When molecular bromine is available on-site (as in the Dead Sea Works in Israel, for example), it is the cheapest and *most environmentally friendly* bromination reagent. Used in conjunction with H_2O_2, the stoichiometry would then be $H_2O_2 + 2\,ArH + Br_2 \Rightarrow 2\,ArBr + 2\,H_2O$.[1a] (b) When a bromine-containing reagent has to shipped to the site, only four reagents are cheap enough to matter for large-scale manufacturing: Br_2, HBr (48% aqueous), KBr, and NaBr.

Obviously, it is much safer and cheaper to transport and store large quantities of alkali bromide salts (NaBr, KBr) than either Br_2 or HBr. The drawback is that oxidation of bromide to bromine requires acidic conditions (eq 2), so that in the reaction $H_2O_2 + 2\,Br^- \Rightarrow 2\,BrO^- + 2\,OH^-$, only small amounts of hypobromite are produced.

Although it is known that enzymes such as vanadium bromoperoxidase (VBPO) catalyse brominations under seawater conditions,[5] large-scale enzymatic bromination is problematic.[6] A more realistic industrial option *in the near future*, would be to use simple catalysts and in-plant existing technologies, especially considering the tight profit margins associated with large-scale halogenation. For example, glacial acetic acid was used, together with KBr and Mo(VI), to effect oxybromination of various activated aromatics.[4b] An analogous investigation using nitric acid and metal chloride salts, however, required a 10-fold molar excess of acid and salt for the oxidative chlorination of acetanilide.[7,3]

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(1) (a) Johnson, R.; Reeve K. *Spec. Chem.* **1992**, *11*, 292−299. (b) Ho, T.-L.; Gupta, B. G. B.; Olah, G. A. *Synthesis* **1977**, 676−677. (c) For a recent monograph see Jones, C. W. Applications of Hydrogen Peroxide and Derivatives; In *RSC Clean Technology Monographs*; Clark, J. H., Ed.; Royal Society of Chemistry: Cambridge, 1999; pp 59−61.

(2) (a) Barhate, N. B.; Gajare, A. S.; Wakharkar, R. D.; Bedekar, A. V. *Tetrahedron* **1999**, *55*, 11127−11142. (b) Mukhopadhyay, S.; Ananthakrishnan, S.; Chandalia, S. B. *Org. Process Res. Dev.* **1999**, *3*, 451−454. (c) Lübbecke, H.; Boldt, P. *Tetrahedron* **1978**, *34*, 1577−1579.

(3) Dakka, J.; Sasson, Y. J. *Chem. Soc., Chem. Commun.* **1987**, 1421−1422.

(4) (a) Barhate, N. B.; Gajare, A. S.; Wakharkar, R. D.; Bedekar, A. V. *Tetrahedron Lett.* **1998**, *39*, 6349−6350. (b) Choudary, B. M.; Sudha, Y.; Reddy, P. N. *Synlett* **1994**, 450.

(5) For a recent review, see Butler, A.; Walker, J. V. *Chem. Rev.* **1993**, *93*, 1937−1944.

(6) Enzymatic oxybromination processes are popular research subjects, and several novel ideas have been published. See, for example: (a) Sels, B.; De Vos, D.; Butinx, M.; Pierard, F.; Kirsch-De Mesmaeker, A.; Jacobs, P. *Nature* **1999**, *400*, 855−857. (b) Bhattacharjee, M.; Ganguly, S.; Mukherjee, J. *J. Chem. Res. (S)* **1995**, 80−81. (c) Martinez-Perez, J. A.; Pickel, M. A.; Caroff, E.; Woggon, W.-D. *Synlett* **1999**, 1875−1878. However, implementation of enzymatic processes has serious drawbacks, not least because such reactions are carried out in very dilute solutions, and thus require enormous reaction tanks, meaning high capital costs in a market where the current technology is well-established and retains size advantage. Several VBPO mimics have been reported, but it is unlikely that in the near future they would lead to an enzymatic oxybromination process, which would have to compete on a very narrow profit margin.

(7) (a) Jerzy, G.; Slawomir, Z. *Synth. Commun.* **1997**, *27*, 3291−3299. Generally, for oxychlorination a large excess of HCl is required, see: (b) Thirumalai, P.; Bhatt, M. V. *Tetrahedron Lett.* **1979**, *33*, 3099−3100. (c) Mukhopadhyay, S.; Chandalia, S. B. *Org. Process Res. Dev.* **1999**, *3*, 10−16.

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Here, we examine the option of recycling mineral acid waste streams for the oxidative generation of brominating species, using bromide salts and hydrogen peroxide. The relevance of this concept to industrial waste management and sustainable development is discussed.

Results and Discussion

Definitions. As this study deals mainly with application of dilute acids, the term **acid** refers to a dilute acid of ~1 M in water. Where concentrated acid is used, the concentration is specified. Similarly, the **amounts of V_2O_5** used in all reactions, are 1−2 mol % relative to substrate, unless noted otherwise. Reaction or reagent **productivity** is defined as the amount of substance produced per unit reactor volume per unit time.[8]

Vanadium-Catalysed Generation of Br_2 Using KBr and Mineral Acids. It was recently claimed that vanadium pentoxide catalyses the oxidative bromination of various activated aromatics, without the need for stoichiometric amounts of acid.[9] We found, however, that stoichiometric V_2O_5, which dictates the acidic environment (pH 1−2) is required for the reaction to proceed.

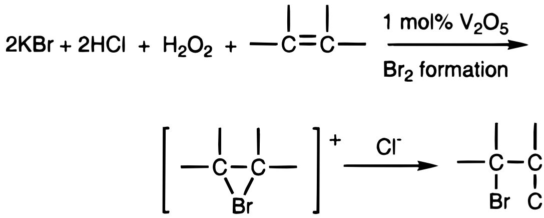
However, vanadium pentoxide may be used to catalyse oxidative bromination in the presence of *dilute* mineral acids, which may solve problems arising from the corrosiveness of 48% HBr, or other combinations of bromide with concentrated acids. This is important, because, although the productivity of processes employing concentrated acids is higher, it is partly due to corrosiveness that recycling of bromides is shunned by the chemical industry. Since HBr is used both as a source of H^+ and Br^- in eq 2, it seems reasonable that any Brönsted acid could be used in conjunction with a metal bromide salt. By far the cheapest and most available alternative to Br_2 and HBr would be the combination of NaBr (or KBr) and sulfuric acid.

When equivalent amounts of KBr and H_2SO_4[10] were dissolved in 10 parts water, and added (in one batch) to hydrogen peroxide (30−35 wt % in water), the solution turned yellow-golden after a few minutes, but appreciable amounts of bromine were not produced (<0.25% conversion of bromide). Upon addition of catalytic amounts (1−2 mol %) of vanadium pentoxide, an exothermic reaction occurred and bromine was produced (eq 3).

$$2KBr + H_2SO_4 + H_2O_2 \xrightarrow[\substack{30\text{ min, }25\text{ °C}\\ 700\text{ rpm stirring}}]{1-2\%\ V_2O_5} Br_2 + 2H_2O + K_2SO_4 \tag{3}$$

Peroxide utilisation improved when the H_2O_2 was added dropwise to the reaction mixture, as H_2O_2 itself undergoes fast decomposition in the presence of bromine (vide infra). The bromine could either be distilled by using a flash distillation apparatus or bubbled directly through the desired organic reaction mixture. It was found that other mineral acids, viz., HNO_3, H_3PO_4, HBr (in which case KBr is unnecessary), and even HCl, may also be as the source of H^+ ions.

Using HCl for bromination is interesting, as it seems possible that companies engaged in chlorination processes may also be interested in bromination, and might have waste HCl streams available on-site. As chlorine is less soluble than bromine in water,[11a] it is reasonable to suppose that the absence of chlorinated products indicates either that no Cl_2 gas is formed when HCl is used as the source of protons (even though, initially, $[Br^-] = [Cl^-]$), or that $k_{\text{chlorination}} \ll k_{\text{bromination}}$.[11b] With the use of this system, ex situ bromination of 1-octene gave >99% selectivity to 1,2-dibromooctane, indicating that for the V_2O_5-catalysed reaction $2HX + H_2O_2 \Rightarrow X_2 + 2H_2O$, $k_{X=Cl} \ll k_{X=Br}$ by at least 2 orders of magnitude. Moreover, an ex situ process is advantageous in this case, because in a one-pot reaction using HCl + KBr, attack of chloride on the cyclic bromonium cation would result in formation of a *vic*-bromo-chloro-product (eq 4). Indeed, Barhate et al. showed that *vic*-bromo-chloro-species were the major products when a combination of concentrated HCl and HBr was used (without a catalyst) in the oxidative halogenation of alkenes.[2a]



(4)

Comparison of HBr with KBr/Acid. The generation of "Br^+" species from H_2O_2/HBr can be compared to that of H_2O_2/KBr/acid by measuring the initial rates of H_2O_2 decomposition, as shown in Figure 1.[12] Repeated experiments evidenced good reproducibility (cf. the two plots for H_3PO_4). Control reactions showed no generation of gas (<0.013 mmol) in the absence of V_2O_5, nor was any gas produced when either the KBr or the acid was absent, proving that H_2O_2 decomposition, catalysed by bromide and acid alone, or by V_2O_5 alone, may be neglected. This is in agreement with the early results of Mohammad and Liebhafsky,[13] who showed that oxygen evolution from H_2O_2 solutions using KBr or KBr/acid is negligible on this time scale.[14]

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(8) For a discussion, see Sheldon, R. A. *Chem. Ind.* **1992**, 903−906; *CHEMTECH* **1994**, 38−47.

(9) Bhattacharjee, M. *Polyhedron* **1992**, *11*, 2817−2818. See also ref 6b, and Bhattacharjee, M.; Chaudhuri, M. K.; Islam, N. S.; Paul, P. C. *Inorg. Chim. Acta* **1990**, *169*, 97−100.

(10) For the purpose of providing an acidic environment for bromide oxidation, H_2SO_4 may be regarded as a dibasic acid, as $pK_a = 1.98$ for the second dissociation. With the weaker acid H_3PO_4, however, only the first dissociation is relevant, as $pK_a = 7.09$ for the second dissociation (*CRC Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, 1995; pp 8/44−8/45).

(11) (a) Compare 0.092 M [Cl_2] with 0.214 M [Br_2] at 25 °C, *The Merck Index*; Merck & Co., Inc.: Rahway, 1989; pp 323; 211. (b) An indication of the difference between the oxidation potentials of chloride and bromide may be obtained by comparing the Standard Electrode Potentials (cf. −1.066 V for $2\ Br^- \Rightarrow Br_2 + 2e^-$ with −1.358 V for $2\ Cl^- \Rightarrow Cl_2 + 2e^-$, *CRC Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, 1995; pp 8/29−8/31).

(12) Direct observation of Br_2 generation kinetics, e.g., using spectroscopic methods, is problematic, due to the fact that several of the possible intermediate species (BrO^-, Br_3^-, and HOBr) evidence spectral changes similar to Br_2.

(13) Mohammad, A.; Liebhafsky, A. H. *J. Am. Chem. Soc.* **1934**, *56*, 1680−1685.

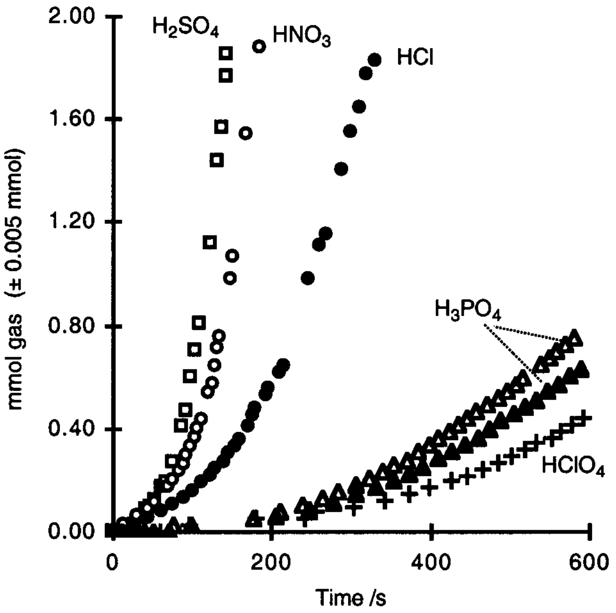

Figure 1. **Vanadium-catalysed H_2O_2 decomposition using dilute acids/KBr. Conditions: 25 °C, 10.0 mmol acid, 10.0 g of water, 10.0 mmol H_2O_2 (35 wt %), 10.0 mmol KBr, 1.5 mol % V_2O_5.**

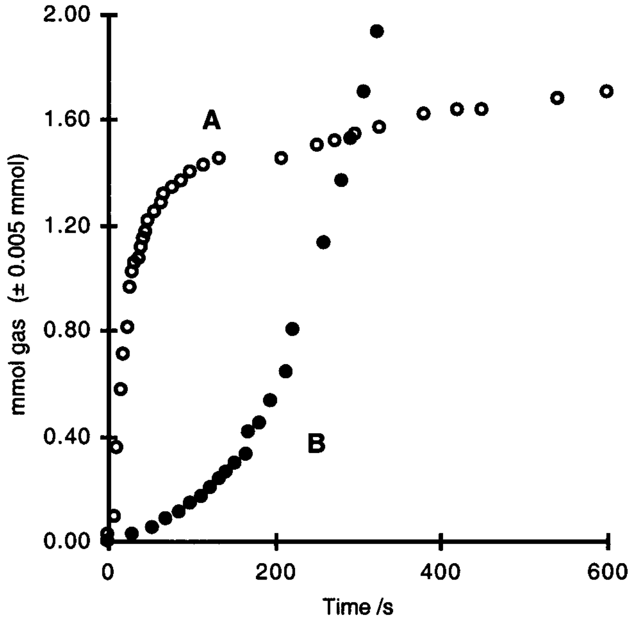

Figure 2. **Decomposition of H_2O_2 at 25 °C. Conditions: 10.0 mmol H_2O_2 (35 wt %), 10.0 g of water; A 5.0 mmol of $Br_{2(l)}$ (no catalyst); B 10.0 mmol HBr (48 wt %), 1.5 mol % V_2O_5.**

Table 1. **Peroxide decomposition rates**[a]

entry	system	k_1 ($\times 10^3$)	k_2 ($\times 10^3$)
1	KBr/H_2SO_4	3.37	24.1
2	KBr/HNO_3	2.95	20.7
3	KBr/HCl	2.03	10.1
4	KBr/$HClO_4$	0.49	2.1
5	KBr/H_3PO_4	0.51	2.3
6	HBr	1.96	9.8
7	Br_2	35.21	0.6

[a] In mmol s^{-1}. Values are the least-squares fit of at least 10 observations, with $r^2 > 0.96$. Conditons are as shown in Figures 1 and 2.

Strong and weak acids evidenced different behaviour in this system.[15] In fact, when acetic acid was used, no reaction was detected on this time-scale even in the presence of V_2O_5. Experimental values of initial decomposition rates are given in Table 1. For each acid, it was possible to distinguish between two regions. Initially, the rate of gas generation (k_1) was low and constant. Then, a much higher rate (k_2) was observed. We suggest that this change is effected when the concentration of bromine increases above a certain level. Experimental evidence supporting this hypothesis was obtained using HBr and $Br_{2(l)}$ as "Br" sources. As shown in Figure 2, decomposition of hydrogen peroxide in the presence of bromine (without a catalyst) was extremely fast initially. Then, almost no gas was released, showing a behaviour typical of acid/KBr systems that contain no V_2O_5. When HBr was used as the bromide source, no reaction occurred in the absence of V_2O_5 (not shown). In the presence of V_2O_5 (Figure 2) the behaviour was similar to other KBr/acid systems. This indicates that it is bromine, rather than HBr, that initiates decomposition of hydrogen peroxide. Although not identical, it can be seen that $k_{1,\text{ bromine}}$ is of the same order of magnitude as $k_{2,\text{ acid/KBr}}$ for H_2SO_4 and HNO_3.[16]

The mechanism of bromide oxidation/H_2O_2 decomposition is complex.[17] In presence of vanadium oxides, mechanistic studies have shown that this system is sensitive to changes in solvent, and that different reaction pathways may dominate, depending on the coordination environment of the catalyst.[18] Different mechanisms have been proposed for V_2O_5-catalysed bromide[19] and iodide[20] oxidations. However, on the basis of our results and the elegant and conclusive mechanistic studies reported by Butler et al.,[19] we suggest that (a) in the presence of V_2O_5, the behaviour of H_2O_2/HBr is nearly identical to that of H_2O_2/KBr/acid; and (b) regardless of the mineral acid used, both Br_2 formation and H_2O_2 decomposition depend on two-electron oxidation and the formation of the common intermediate HOBr.

Oxidative Bromination Using the MBr/H_2SO_4/H_2O_2 System. Oxidative bromination of various aromatics was tested using the above method (eq 5). Results are presented in Table 2. Results were comparable to those obtained using hydrogen peroxide and concentrated HBr. Both NaBr and KBr can be used with equal facility. Only traces (<0.5%)

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(14) However, in all cases (even when using KBr/AcOH in the absence of catalyst), enough bromine was generated to cause coloration of the samples. cf. Maass, O.; Hiebert, P. G. *J. Am. Chem. Soc.* **1924**, *46*, 290−308.

(15) The slow reaction observed with perchloric acid is probably a result of its low solubility in the reaction medium. Significant amounts of solid perchlorates were observed even when the amount of water was doubled.

(16) Theoretically, one would expect that HCl, HNO_3, H_2SO_4, and HBr would all dissociate completely under the aqueous conditions employed. Thus, the differences shown in Figure 1 may reflect possible participation of the inorganic anions in the catalytic decomposition process.

(17) Atkins, P. W. *Physical Chemistry*, 5th ed.; Oxford University Press: Oxford, 1994; p 915.

(18) (a) Butler, A.; Clague, M. J.; Meister G. E. *Chem. Rev.* **1994**, *94*, 625, and references therein; (b) Bortolini, O.; Di Furia, F.; Scrimin, P.; Modena, G. *J. Mol. Catal.* **1980**, *7*, 59.

(19) (a) Clague, M. J.; A. Butler, A. *J. Am. Chem. Soc.* **1995**, *117*, 3475−3484. (b) de la Rosa, R. I.; Clague, M. J.; Butler, A. *J. Am. Chem. Soc.* **1992**, *114*, 760−761.

(20) Secco, F. *Inorg. Chem.* **1980**, *19*, 2722−2725.

Table 2. **Oxidative bromination using MBr/acid/hydrogen peroxide**[a]

entry	substrate	acid (mmol, mol/kg)	H_2O_2/mmol	V_2O_5/mol %	time/min	conv./%	products[b] (% selectivity)
1	anisole	HBr (10, 0.52)	11	None	100	15	4-BA (>99)
2	anisole	HBr (10, 0.52)	11	1.0	100	68	4-BA (>99)
3	anisole[c]	AcOH (84, 5.28)	20	2.5	140	30	4-BA (>99)
4	anisole	H_2SO_4 (5, 0.33)	25	1.5	90	85	4-BA (93); 2,4-DBA (7)
5	anisole[d]	H_2SO_4 (5, 0.33)	25	3.1	35	83	4-BA (94); 2,4-DBA (6)
6	toluene	H_2SO_4 (5, 0.33)	25	2.0	900	60	4-BT (95); 2-BT (3)
7	toluene[d]	H_2SO_4 (5, 0.33)	25	2.5	220	45	4-BT (95); 2-BT (4)
8	ethylbenzene[d]	H_2SO_4 (5, 0.33)	25	2.0	180	35	4-BEB (60); 2-BEB (7)
9	phenol[d]	H_2SO_4 (5, 0.28)	25	3.0	60	90	4-BP (69); 2-BP (31)

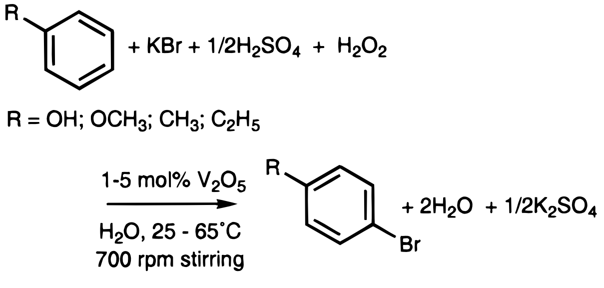
[a] Standard reaction conditions: 10.0 mmol substrate; 10.0 g water; 700 rpm stirring; 25 °C. Yields based on GC area, corrected by the presence of an external standard (*n*-decane). [b] BA = bromaoanisole; DBA = dibromoanisole; BT = bromotoluene; BP = bromophenol; BEB = bromoethylbenzene. [c] Repeating the reaction in presence of 10 mol% TEAB did not affect conversion or selectivity. [d] 10.0 mmol NaBr used instead of KBr.

Table 3. **Raw material costs, *E* factors, and risk factors of industrial bromine alternatives**[a]

entry	Br source	bromine mol %	content wt %	stoichiometric reagents required	total price[b] \$ ton^{-1} ArBr	waste stream	*E* factor[c]	hazard factor
1	$Br_{2(l)}$	100.0	100.0	Br_2	1300	HBr	0.51	high[d]
2	$Br_{2(l)}$	100.0	100.0	$Br_2 + H_2O_2$	840	$2H_2O$	0.11	high[d]
3	$HBr_{(aq)}$	98.7	47.4	$2HBr + H_2O_2$	3920	$4H_2O$	0.23	high[d]
4	$KBr_{(s)}$	67.1	67.1	$2KBr + H_2O_2 + H_2SO_4$	4160	$4H_2O + K_2SO_4$	0.78	low
5	$NaBr_{(s)}$	73.3	73.3	$2NaBr + H_2O_2 + H_2SO_4$	3600	4H2O + Na_2SO_4	2.00	low
6	$MgBr_{2(s)}$	86.7	86.7	$MgBr_2 + H_2O_2 + H_2SO_4$	9990	$4H_2O + MgSO_4$	0.61	low
7	$NaBrO_{3(s)}$[e]	52.9	52.9	$2NaBrO_3 + 2H_2SO_4$	4820	$2NaHSO_4 + 3O_2$	0.56	high[f]

[a] Based on the reaction "Br^{+}" + ArH ⟹ ArBr + H^{+}. For example, for entry 1, the reaction is Br_2 + ArH ⟹ ArBr + HBr. [b] Prices from CMR and industrial sources (\$ ton^{-1}): bromine (liq) 1300; HBr (48 wt % aq) 1500; KBr (powder) 2200; NaBr 1600; $MgBr_2$ 7600; sulfuric acid 100; hydrogen peroxide (35 wt % aq) 600; $NaBrO_3$ (powder) 2500. V_2O_5 approximated at \$10 kg^{-1}, using 1 mol% relative to bromide. Comparison excludes aromatic substrate prices. [c] kg waste/kg product, comparison based on 100% theoretical bromination of benzene (see Supporting Information for details). [d] Transportation/storage risks. [e] For a recent study, see ref 22. [f] Reaction risks (possible explosion/runaway reaction).

of benzyl bromide were obtained in the oxidative bromination of toluene, ruling out an SET free-radical process. Oxybromination of deactivated aromatics using this method, however, was unsuccessful, which points to a drawback of the dilute acid option — it is necessary to find a Lewis acid catalyst, that is stable under acidic aqueous conditions, to promote this reaction. Such catalysts are currently under research in our laboratory.



(5)

Cost Effectiveness of Aromatic Bromination Processes. The raw material costs, *E* factors,[21] and risk factors for various industrial bromination reagents, are presented in Table 3.[22] As a result of the low cost and high productivity of molecular bromine, the MBr/acid/H_2O_2 option will be economically viable only if bromine transportation costs become prohibitive, or if in-plant bromide and acid waste can be utilised. The latter option is increasingly relevant, as the chemical industry moves towards waste minimisation and zero-emission plants.

Conclusions

Vanadium-catalysed oxidative bromination by means of dilute mineral acids, hydrogen peroxide, and alkali bromides is an effective method for the bromination of activated and nonactivated (but not deactivated) aromatic substrates. H_2SO_4, HNO_3, HBr, HCl, and (to a lesser extent) H_3PO_4 may be used, making this an option for recycling industrial acid waste. Furthermore, this method has the advantages of low transportation and storage risks and employs the relatively safe 35% H_2O_2. The drawbacks are high prices and low productivity (compared to using molecular bromine), and the fact that concurrent unwanted decomposition of the peroxide occurs.

Experimental Section

Materials and Instrumentation. Unless stated otherwise, chemicals were purchased from commercial firms (>98% pure) and used without further purification. GC analyses were performed using an HP-5890 gas chromatograph with an HP1 capillary column (25 m/0.25 mm). A standard sample of 1,2-dibromooctane was prepared according to the literature.[23] Products were identified by comparison of their GC retention

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(21) Sheldon, R. A. *Chem. Ind.* **1997**, 12−15; *J. Chem. Technol. Biotechnol.* **1997**, *68*, 3181−388.

(22) Groweiss, A. *Org. Process Res. Dev.* **2000**, *4*, 30−33.

(23) Vogel, A. I., *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: Essex, 1989; pp 509−511.

times with standard reference samples. **CAUTION!** There are hazards associated with using hydrogen peroxide (see ref 1c, pp 21−27).

General Procedure for Measuring Initial H_2O_2 Decomposition Rates. Example: using HCl and KBr, 10.0 mmol (1.19 g) KBr was dissolved in 10.0 g of distilled water, to which was added 10.0 mmol (1.0 g of 35 wt % solution) HCl, and 0.15 mmol (28.0 mg) V_2O_5. After stirring for 1 min at 25 °C, 10.0 mmol H_2O_2 (∼1.0 mL of 35 wt % solution, exact amount determined by iodometric titration) was added in one batch using a syringe. Gas generation was monitored by measuring the volume of water displaced from an upturned biuret connected to the reaction vessel.

General Procedure for in situ Oxybromination. Example: For the oxybromination of anisole, 10.0 mmol (1.19 g) KBr was dissolved in 10.0 g distilled water, to which was added 5.0 mmol (0.49 g of 98 wt % solution) H_2SO_4, 10.0 mmol (1.08 g) anisole, and 0.14 mmol (26.0 mg) V_2O_5. After stirring for 1 min at 25 °C, 100 mmol H_2O_2 (∼10.0 mL of 35 wt % soln) was added dropwise using a pressure-equalizing dropping funnel. The reaction was stirred (700 rpm) at 25−30 °C for 90 min, after which time the organic phase was separated and analysed by GC (*n*-decane external standard).

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Supporting Information Available

Two examples detailing the calculation of *E* factors presented in Table 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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