surface (Ishibashi et al. 2000), is not commonly considered an important oxidant but has been implicated in certain systems (Amalric et al. 1994; Almaric et al. 1995; Pichat et al. 1995; Cermenati et al. 2000). Reactions of As(III) with each of these three oxidants results in a transient As(IV) species, which can then undergo dismutation or react with O_2 or another oxidant to yield As(V) (Table 2.3).

Table 2.3. As oxidation reactions and rate constants derived from solution.

	Reaction	**Rate constant in homogeneous solution**
R1	$As(OH)_3 + {}^{\bullet}OH \rightarrow As^{IV}(OH)_4$	$1.8–8.5 \times 10^9$ M^{-1} s^{-1} [a, b]
R2	$As(OH)_3 + h^+_{VB} \rightarrow As^{IV}(OH)_4$	Unknown
R3	$As(OH)_3 + O_2^{\bullet-} + H_2O + H^+ \rightarrow As^{IV}(OH)_4 + H_2O_2$	3.6×10^6 M^{-1} s^{-1} [c]
R4	$2As^{IV}(OH)_4 \rightarrow As(III) + As(V)$	8.4×10^8 M^{-1} s^{-1} [a, d]
R5	$As^{IV}(OH)_4 + O_2 \rightarrow As(V) + O_2^{\bullet-}$	1.4×10^9 M^{-1} s^{-1} [a, d]

(a) (Klaning et al. 1989)
(b) (Buxton et al. 1988a)
(c) (Xu et al. 2005)
(d) (Daniels 1962)

There is considerable debate regarding the mechanism of As(III) oxidation. Lines of evidence supporting As(III) oxidation by superoxide (Lee and Choi 2002; Ryu and Choi 2004), hydroxyl radicals (Dutta et al. 2005; Xu et al. 2005), and valence band holes (Yoon and Lee 2005) have been reported. These arguments are critically discussed in Chapter 3 and its Addendum.