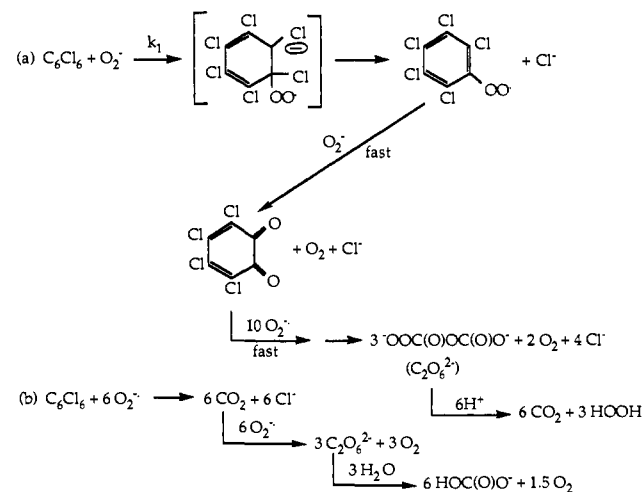


Table I. Reactions of Superoxide Ion with Polychloro Aromatics in Dimethylformamide^a

substrates (S)	E_{pc}^b V vs SCE	$O_2^{\cdot-}/S$	Cl^- released/S	base released/S	$k_1/[S]^c$ M ⁻¹ s ⁻¹
$C_6Cl_6^d$	-1.48, -1.69	12.0 ± 1.0	6.0 ± 0.5	6.0 ± 0.6	1×10^3
C_6HCl_5	-1.70, -1.98	11.0 ± 1.0	5.0 ± 0.5	6.0 ± 0.6	8×10^1
1,2,3,4- $C_6H_2Cl_4$	-1.90, -2.18	10.0 ± 1.0	4.0 ± 0.5	6.0 ± 1.0	2×10^0
1,2,3,5- $C_6H_2Cl_4$	-1.95, -2.19	10.0 ± 1.0	4.0 ± 0.5	6.0 ± 1.0	1×10^0
1,2,4,5- $C_6H_2Cl_4$	-1.95, -2.19	10.0 ± 1.0	4.0 ± 0.5	6.0 ± 1.0	3×10^0
1,2,4- $C_6H_3Cl_3$	-2.16, -2.45				2×10^{-2}
$C_{12}Cl_{10}$	-1.50, -1.78	22.0 ± 4.0	10.0 ± 1.0	12.0 ± 2.0^e	2×10^2
CCl_4^f	-1.2	5.0 ± 0.6	4.0 ± 0.4	1.0 ± 0.1	1×10^3
$PhCCl_3^f$	-1.47	4.0 ± 0.4	3.0 ± 0.4		4×10^1

^a Overall reactions: (1) $C_6Cl_6 + 12O_2^{\cdot-} \rightarrow 3C_2O_6^{2-} + 6Cl^- + 3O_2$; (2) $C_6H_2Cl_4 + 10O_2^{\cdot-} \rightarrow 2C_2O_6^{2-} + 2HOC(O)O^- + 4Cl^- + O_2$; (3) $C_{12}Cl_{10} + 22O_2^{\cdot-} \rightarrow 6C_2O_6^{2-} + 10Cl^- + 4O_2$. ^b First two reduction peaks are listed; a separate peak is observed for each chlorine atom. For C_6Cl_6 the other peak potentials are -1.95, -2.18, -2.44, and -2.70 V (also the reduction potential for PhCl). ^c Apparent pseudo-first-order rate constants, k (normalized to unit substrate concentration [S]), were determined from the ratio ($i_{anodic}/i_{cathodic}$) for the cyclic voltammogram of O_2 in the presence of excess substrate, ref 6. ^d The values of $k_1/[S]$ for C_6Cl_6 in MeCN and Me₂SO solvents are 92 and 47 M⁻¹ s⁻¹, respectively. ^e Titration curve indicates the presence of a weak base, and a white precipitate forms during the last part of the titration; both consistent with the presence of oxalate ion. ^f The ring-disc voltammetric technique for reaction rates gave values for $k_1/[S]$ of 3.8×10^3 M⁻¹ s⁻¹ for CCl_4 and 50 M⁻¹ s⁻¹ for $PhCCl_3$ (ref 3).

Scheme I

of chloride ion will give a benzoperoxy radical, which will be reduced by a second $O_2^{\cdot-}$ to become a peroxy nucleophile that can attack the adjacent carbocloro center with displacement of its chloride and apparent formation of an orthoquinone. The latter undergoes facile reactions with $O_2^{\cdot-}$ to give peroxy dicarbonate ($C_2O_6^{2-}$)^{7,8} and chloride ions. The $C_2O_6^{2-}$ ions are hydrolyzed by water to $HOC(O)O^-$ and O_2 . Thus, Scheme I outlines a possible mechanism, but the fragmentation steps are speculative and not supported by the detection of any intermediate species.

When Arochlor 1268 (a commercial PCB fraction that contains a mixture of Cl_7 , Cl_8 , Cl_9 , and Cl_{10} polychlorobiphenyls) is combined with excess $O_2^{\cdot-}$, the entire mixture is degraded. Samples taken during the course of the reaction confirm that (a) the most heavily chlorinated members react first (the initial nucleophilic addition is the rate determining step) and (b) all components are completely dehalogenated. Tests with other PCB mixtures establish that those components with three or more chlorine atoms per phenyl ring are completely degraded by $O_2^{\cdot-}$ within several hours.

The present results also indicate that in-vivo superoxide ion may react with ingested C_6Cl_6 (a known animal carcinogen),⁹ PCB's (environmental toxins that cause birth defects, organ damage, and tumors in experimental animals),¹⁰ and other polyhalogenated hydrocarbons. The proposed peroxy radical intermediates of

(7) Benzyl (an α -dicarbonyl) undergoes nucleophilic addition and oxidative cleavage by $O_2^{\cdot-}$ to give two benzoate ions; Sawyer, D. T.; Stamp, J. J.; Menton, K. A. *J. Org. Chem.* **1983**, *48*, 3733-3736. *o*-Tetrachloroquinone undergoes rapid and complete degradation by $10 O_2^{\cdot-}$ ions to $3C_2O_6^{2-}$ and $4Cl^-$ ions.

(8) Superoxide ion reacts with CO_2 to give peroxy dicarbonate ($C_2O_6^{2-}$), which hydrolytically decomposes to $HOC(O)O^-$ and O_2 ; Roberts, J. L., Jr.; Sawyer, D. T. *J. Am. Chem. Soc.* **1984**, *106*, 4667-4670.

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Scheme I are likely toxins, and their reactivity with biomembranes and lipids may represent the mechanism for the cytotoxicity of C_6Cl_6 and PCB's.

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Oxidation of *tert*-Butyl Alcohol to Isobutylene Oxide: Rate-Limiting C-H Activation by a Ag(110) Surface

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The oxidation of primary and secondary alcohols on Ag(110)^{1,2} and Cu(110)²⁻⁵ surfaces under ultrahigh vacuum conditions (UHV) is now fairly well understood. Generally, the first step involves the reaction of an adsorbed alcohol molecule with surface oxygen to form a surface bound alkoxide and water. Upon further heating the surface alkoxide reacts and yields an aldehyde (or ketone) and $H_{(a)}$, presumably by reaction of the hydrogen α to oxygen with the surface. Recombination reactions produce the parent alcohol, water, and/or H_2 .

We report here the reaction of *tert*-butyl alcohol on pre-oxygenated Ag(110) surfaces. This is the first study of the reaction of a tertiary alcohol with a metal surface, although the homogeneous chemistry of tertiary metal alkoxides has been studied extensively.⁶ Indeed, this alcohol exhibits much different surface chemistry than do primary and secondary alcohols. *tert*-Butyl alcohol reacts on oxygen-covered silver below 200 K yielding *t*-BuO_(a) and water.⁷ At higher temperatures (420-600 K), *t*-BuO_(a) reacts to yield isobutylene oxide (rel yield 100%), *tert*-butyl alcohol (50%), water (45%), isobutylene (50%), acetone (20%), and CO_2 (8%). No H_2 or CO were produced. *t*-BuO_(a) is stable to temperatures 160-250 K higher than primary and secondary alkoxides on this surface.^{1,2}

The surface of a Ag(110) crystal at 120 K covered with 0.25 mL of $O_{(a)}$ was dosed with 2 L of $(CH_3)_3COD$ and heated to 700

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(7) *tert*-Butyl alcohol does not react with the clean Ag(110) surface.

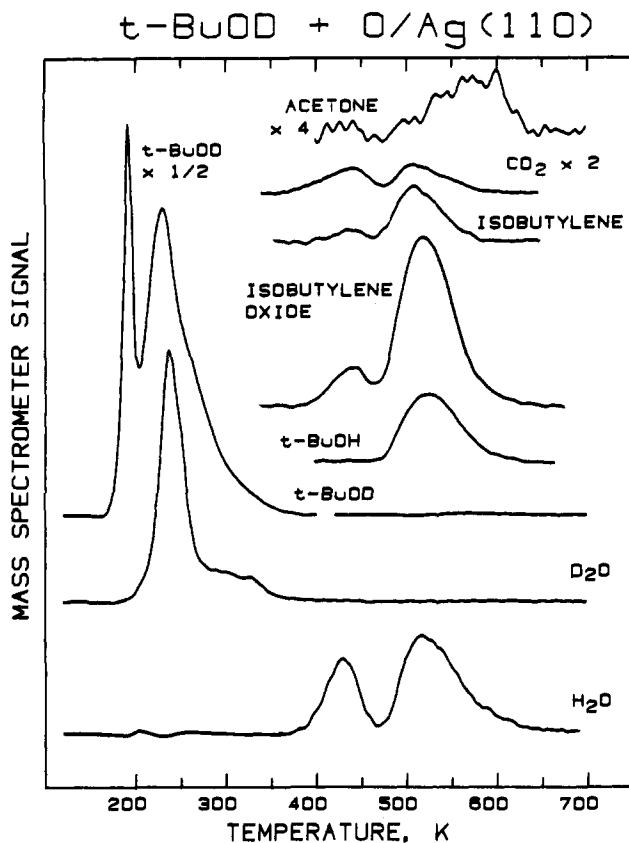
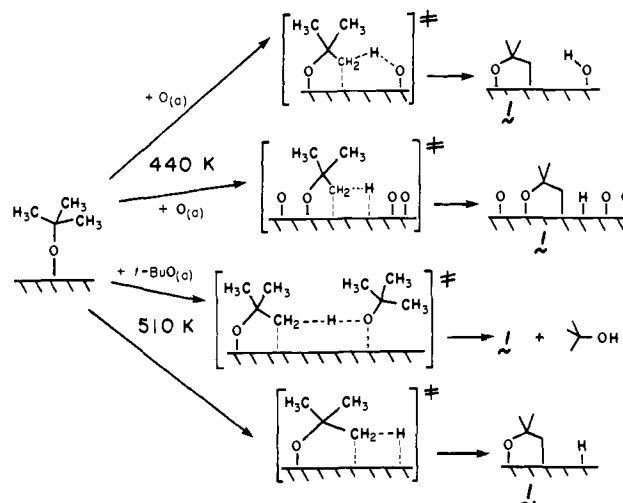


Figure 1. TPRS spectrum of the reaction of *tert*-butyl alcohol- d_1 (3 L) with a Ag(110) surface covered with 0.25 mL $O_{(a)}$. The masses used to follow each product were as follows: *tert*-butyl alcohol (59), *tert*-butyl alcohol- d_1 (60), isobutylene (56), isobutylene oxide (42), acetone (58), H_2O (18), D_2O (20), and CO_2 (44). Heating rate = 10 K/s.

K (Figure 1),⁸ with use of temperature programmed reaction spectroscopy (TPRS) techniques previously described.⁹ *tert*-Butyl alcohol desorbs from a multilayer at 190 K and a molecularly bound state at 230 K. D_2O desorbs at distinct temperatures between 200 and 350 K characteristic of molecular water and OD(H) recombination on O/Ag(110)¹⁰ and thus is a product of a reaction in which the O-D bond of the alcohol is broken below 200 K to form the alkoxide.¹¹ Isobutylene oxide, isobutylene, H_2O , and CO_2 desorb in reaction-limited peaks at 440 and 510 K; *tert*-butyl alcohol is formed only at 510 K. The observation that these products desorb simultaneously, yielding peaks with similar shapes is evidence that each array of products (at 440 and 510 K) results from a single-rate-limiting step. Further, the observation that *tert*-butyl alcohol- d_0 and H_2O desorb instead of *tert*-butyl alcohol- d_1 and D_2O at 440 and 510 K shows that a methyl C-H bond in $t-BuO_{(a)}$ is broken during these two reaction pathways. A small amount of acetone is produced at 590 K.

By using the activation parameters for both *tert*-butyl alcohol- d_0 ,¹² the deuterium kinetic isotope effects were determined to be $k_H/k_D = 3.6 \pm 1$, 1.6 ± 0.4 , and 1.0 ± 0.3 at 500 K for these reactions. These latter results support mechanisms in which C-H(D) bond breaking processes are rate-limiting during the

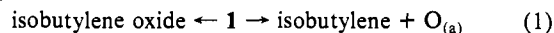
Scheme I. Possible Mechanisms for the Reactions Occurring at 440 and 510 K



reactions producing isobutylene and isobutylene oxide but not during the reaction which produces acetone.

At a fixed oxygen coverage of 0.25 mL, low doses of *tert*-butyl alcohol favor the low-temperature route to isobutylene oxide (440 K), whereas large doses favor the high-temperature route (510 K). In a separate experiment under conditions in which the coverage of $O_{(a)}$ was low (0.03–0.06 mL) and the exposure of *tert*-butyl alcohol was high (25 L), only the high-temperature peak (510 K) was observed. These results indicate that the lower temperature channel proceeds via the same intermediate as the higher temperature path, but the intermediate is destabilized by excess oxygen, as observed for formate¹³ and acetate¹⁴ on the same surface.

Scheme I illustrates the most probable rate-limiting transition states for reactions occurring at 440 and 510 K. Two possible mechanisms are suggested for the oxygen-assisted reaction at 440 K. Both mechanisms involve rate-limiting C-H bond breaking and metallacycle **1**. The first involves active participation of $O_{(a)}$; the second involves C-H bond breaking by surface silver atom(s) which have enhanced reactivity due to the proximity of several oxygen atoms.¹⁵ The direct transfer to $O_{(a)}$ is favored by the absence of H_2 or *tert*-butyl alcohol as products of this low-temperature reaction. The absence of these products in the second mechanism can be rationalized if $H_{(a)}$ reacts with the excess $O_{(a)}$ more rapidly than it does with $t-BuO_{(a)}$ or with itself. Metallacycle **1** can clearly decompose via reductive elimination to form isobutylene oxide and $O_{(a)}$ (eq 1).



Two possible mechanisms are suggested for the reaction occurring at 510 K. Again, both mechanisms involve rate-limiting C-H activation and metallacycle **1**. The first involves rate-limiting C-H bond breaking assisted by a second $t-BuO_{(a)}$ adsorbate yielding *tert*-BuOH and thus is favored by the absence of H_2 as a product. The second involves oxidative addition of surface silver atom(s) to a methyl C-H bond and yields $H_{(a)}$. Although we are unable to completely rule out the possibility that $H_{(a)}$ reacts with $t-BuO_{(a)}$ or $O_{(a)}$ more quickly than it does with itself, the absence of H_2 as a product makes this mechanism less likely. Metallacycle **1** decomposes yielding isobutylene oxide, isobutylene, and $O_{(a)}$ (eq 1). The kinetic isotope effect experiments are consistent with the rate-limiting C-H(D) bond breaking proposed in Scheme I.

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(8) The reaction products were identified by comparing the TPRS mass spectra with mass spectra of the authentic compounds (m/e , rel %): isobutylene oxide (42, 100; 56, 10; 59, 0; 58, 2), isobutylene (42, 19; 56, 100; 59, 0; 58, 0), *tert*-butyl alcohol (42, 67; 56, 12; 59, 100; 58, 4), acetone (42, 67; 56, 0; 59, 0; 58, 100). The raw TPRS data were deconvoluted based on these cracking fractions by using a computer program.

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(11) No H_2O was produced during this low-temperature reaction. Similarly, $(CD_3)_3COH$ reacts with O/Ag(110) at low temperatures forming mainly H_2O with very little HOD or D_2O .

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