

"Surface-Mediated Reactions. 8. Oxidation of Sulfides and Sulfoxides with *tert*-Butyl Hydroperoxide and OXONE" Kropp, P. J.; Breton, G. W.; Fields, J. D.; Tung, J. C.; Loomis, B. R. *Journal of the American Chemical Society*, 2000, 122, 4280-4285.

Abstract: Silica gel and alumina have been found to mediate the oxidation of sulfides and sulfoxides with  $(\text{CH}_3)_3\text{COOH}$  and OXONE. With all combinations except  $(\text{CH}_3)_3\text{COOH}$ /alumina, sulfides were oxidized with reasonably good selectivity to sulfoxides. These studies afforded insights into the mechanisms of surface-mediated processes. Absorption studies, combined with the effect of partial silylation of silica gel, indicate that oxidation of sulfides by  $(\text{CH}_3)_3\text{COOH}$ /silica gel occurs at least predominantly via nucleophilic attack by the sulfide on  $(\text{CH}_3)_3\text{COOH}$ , which is activated by being bound to isolated silanol sites on the silica gel surface (Scheme 2), whereas oxidation of sulfoxides involved nucleophilic attack by  $(\text{CH}_3)_3\text{COOH}$  on the sulfoxide, which is activated by being bound to associated silanol sites (Scheme 3). Oxidation of sulfoxides by  $(\text{CH}_3)_3\text{COOH}$ /alumina involves attack of  $(\text{CH}_3)_3\text{COO}^-$  on the sulfoxide bound to free  $\text{Al}^+$  sites on the surface (Scheme 4B). Mediation of oxidation by OXONE involves instead activation by its being dispersed on the surface of the adsorbent, providing contact between  $\text{KOSO}_2\text{OOH}$ , the oxidizing component, and the substrate. With silica gel, binding involves the associated silanol sites (Scheme 5). It is proposed that this is a general model for surface mediation of inorganic salts.