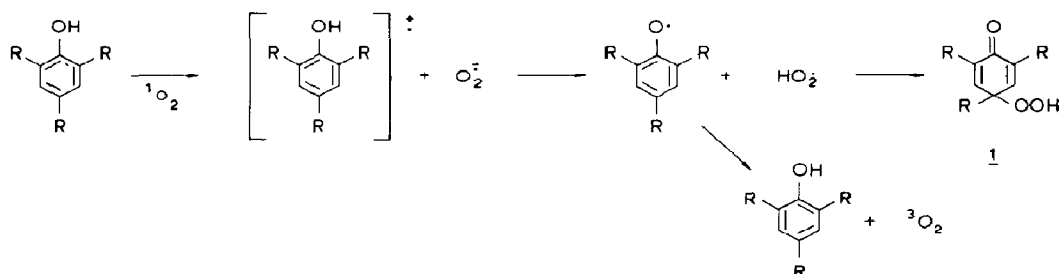## Q5
Photooxidation of Phenols

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The photooxidation of substituted phenols has been studied. Techniques include kinetics, product studies and spectroscopic detection of intermediates. The reaction proceeds via the intermediacy of singlet oxygen, and the evidence indicates that an electron transfer process is involved, since phenol methyl ethers react at the same rate as phenols of the same oxidation potential. The phenoxy radical which is produced by deprotonation of the initial radical cation has been detected spectroscopically. Products are *para*-hydroperoxides (1), or products derived from them; in some cases the reaction appears to reverse completely and the only result is quenching of singlet oxygen.

α-Tocopherol is a special case of phenol photooxidation. In methanol the rate of reaction is 5×10^7 $M^{-1}s^{-1}$ and physical quenching is 6.2×10^8 $M^{-1}s^{-1}$.

R2
Collisional Quenching of Electronically Excited Oxygen Atoms, O(^{1}D): Temperature Dependence of Some Rate Coefficients

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Absolute rate coefficients have been measured for the quenching of electronically excited oxygen atoms, O(^{1}D) by the gases O_3, O_2, N_2, CO_2, N_2O, H_2O, H_2, NH_3 and HCl over the temperature range 156 - 393 K. In addition rate coefficients have been measured for CH_4 and D_2 and an upper limit measured for Ne at 298 K. The oxygen atoms were observed in time-resolved decay of the O(^{1}D) – O(^{3}P) radiation at 630 nm after photolysis of ozone at 265 nm. This work represents the first absolute rate measurement for NH_3 and HCl and the first known study of the temperature dependence of O(^{1}D) deactivation. The rate constants at 298 K in units of $10^{-10}cm^3$/molecule s are O_3, 2.4 ± 0.35; O_2, 0.41 ± 0.06; N_2, 0.30 ± 0.05; CO_2, 1.2 ± 0.18; N_2O, 1.4 ± 0.21; H_2O, 2.1 ± 1; CH_4, $1.3 + 0.4$; H_2, 1.3 ± 0.19; D_2, 1.3 ± 0.19; HCl, 1.4 ± 0.4; NH_3, 3.4 ± 0.51; Ne, <0.0013.

The reaction with O_3 exhibits no temperature dependence and that with HCl does not fit an Arrhenius equation. The temperature dependences of the other reactions, in terms of Arrhenius equations, are O_2, 2.46×10^{-11} exp($313/RT$); N_2, 1.34×10^{-11} exp($522/RT$); CO_2, 5.13×10^{-11} exp($448/RT$); N_2O, 6.74×10^{-10} exp($-846/RT$); NH_3, 7.29×10^{-10} exp($-430/RT$); H_2, 5.07×10^{-10} exp($-805/RT$); H_2O, 7.96×10^{-11} exp($511/RT$).

These results have direct application to the reactions of O(^{1}D) in the stratosphere and to our understanding of the chemical processes in the natural or perturbed stratosphere.