Phenols are widely used to stabilize petroleum products, oils, fats, and various polymeric materials [1, 2]. The protective action of the phenols is determined by their ability to react with free radicals, by the reactivity of the intermediate phenoxy radicals, and by the stability of the phenols themselves toward decomposition under the action of external factors such as light. There has been little study of either the direct or sensitized photolysis of phenolic compounds, and this despite the fact that the duration of the phenol protective action depends on the rates of these reactions.

The present work was a study of the kinetics and mechanism of the photosensitized oxidation of phenols, with determination of rate constants (k_r values) for the interaction of various sterically hindered phenols with singlet oxygen. The value of k_r is known only for α-tocopherol in pyridine (2 × 10^6 liters/mole-sec). Values of k_q, the rate constant for singlet oxygen quenching, are also known for α-tocopherol and hydroquinone in pyridine (2.5 × 10^8 and 6.9 × 10^7 liters/mole-sec, respectively) [3]. Various reaction mechanisms based on final product analyses have appeared in the literature [4-8], but these are contradictory and, in part, mutually exclusive. Thus it has been suggested that the first step in the phenol-singlet oxygen reaction is the formation of a phenoxy radical [4, 5], a trans-annelar peroxide [6, 7], or a dioxetano derivative [8]. The dark reactions of any of these compounds would lead to the observed final reaction products.

EXPERIMENTAL

The reactivities of the various phenols with respect to ^1O_2 were determined by measuring the rate of oxidation of naphthalene in the presence of various amounts of the phenol and n-butanol at 20°C, using methylene blue (MB) as a sensitizing agent. The butanol used here had been purified by the method of [9]; the naphthalene, by threefold recrystallization from ethanol solution. The methylene blue was a Apolda company product and was used without further treatment. The sterically hindered phenols studied here had the general formula

\[
\begin{align*}
R^1 = & \text{C(CH_3)_3}, \\
R^2 = & \text{COOHCH_2 (I), OCH_3 (II), Br (III), H (IV), Cl (V), C(CH_3)_3 (VI),} \\
& \text{CH_3 (VII), CH_3 (VIII), OC(CH_3)_3 (IX), OCH_3 (X)}
\end{align*}
\]

They had been recrystallized from ethanol and purified by thin-layer chromatography on silica gel; their physical constants corresponded to the values given in the literature.

Reactions were carried out in four quartz cells. Each cell was filled with a solution containing MB (3 × 10^-6 mole/liter), naphthalene (3 × 10^-3 mole/liter), and phenol, the latter at concentration ranging from 3 × 10^-3 to 13 × 10^-2 mole/liter, clamped in the holder of an SF-4 spectrophotometer, and there irradiated with light from an incandescent lamp which had been passed through a ZhS-13 filter to remove components with wavelength less than 500 nm. The variation of the optical density of the naphthalene in the course of the photocatalytic reaction was followed with an SF-4A spectrophotometer, working at 470 nm. The photosensitizer was transparent, and the solvent and reaction products showed no absorption, in this region of the spectrum. The phenols studied here either showed essentially no absorption in this part of the spectrum, or their absorption...
Fig. 1. Kinetic curves showing the consumption of naphthalene in the presence of phenol (II), at the following concentrations, mole/liter: 1) 0; 2) 5.67 \times 10^{-2}; 3) 9.90 \times 10^{-2}; 4) 12.75 \times 10^{-2}. Naphthalene concentration, 3.1 \times 10^{-5} mole/liter; [MB] = 3 \times 10^{-6} mole/liter. Solvent, air-saturated butanol; temperature, \sim 20^\circ C; wavelength of light, \lambda \geq 500 nm.

Fig. 2. Variation of the rate of naphthalene consumption with the naphthalene concentration, plotted in the coordinates of Eq. (1). The solution was air-saturated; the temperature, \sim 20^\circ C; [MB] = 3 \times 10^{-6} mole/liter; the wavelength of light \lambda \geq 500 nm.

Fig. 3. Variation of the rate of naphthalene consumption with the concentration of phenol (VII), plotted in the coordinates of Eq. (3). Air-saturated solution; temperature, \sim 20^\circ C; [MB] = 3 \times 10^{-6} mole/liter; wavelength of light \lambda \geq 500 nm.

was so slight that it could be allowed for the calculations. The alteration in the concentrations of phenols (X) and (VII) in the course of the photooxidation was determined from the decrease in the optical density at 286 and 265 nm, respectively.