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THE PHOTOOXIDATION OF TOLUENE. THE ROLE OF AN EXCITED CHARGE TRANSFER COMPLEX

Kei Sin Wei and Albert H. Adelman
Battelle Memorial Institute
Columbus Laboratories
Columbus, Ohio 43201

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We wish to report some results of a study of the photooxidation of neat liquid toluene which indicate that the course of the reaction is strongly influenced by the presence of a toluene oxygen charge transfer complex. Contrary to prior expectation the photooxidation is not a chain reaction even when it is initiated with light absorbed by toluene rather than the complex. Further, attack by singlet excited oxygen does not contribute materially to the oxidation.

Using the 2537 Å mercury line from a medium pressure lamp, benzaldehyde, benzyl alcohol and benzyl hydroperoxide are found to be the major products of the photolysis of an oxygen saturated neat toluene solution. Contrary to previously reported results,(1) benzoic acid has not been observed in our system nor is there evidence for the formation of a transannular peroxide of toluene. At 25°C the quantum yield has a value of 0.08 ± 0.01 based on the sum of the major products formed during the photolysis. A slightly higher value is obtained if the quantum yield is estimated by the total consumption of oxygen by the toluene solution due to the formation of some unidentified high molecular weight oxidation products. The concentrations of the photolysis products were measured gas chromatographically and the ratios of the concentrations calculated as a function of the photolysis time at 5°C (Fig. I). Their ratios when extrapolated to zero time are 0.1 and 0.3, respectively. The ratio $\Phi\text{-CH}_2\text{OH}/\Phi\text{-CHO}$ is also dependent on the temperature. Benzyl alcohol is present only in small quantity at 5°C as compared with benzaldehyde, but the ratio $\Phi\text{-CH}_2\text{OH}/\Phi\text{-CHO}$ approaches 0.7 at 85°C. On the other hand, the increase of the quantum yield over the same temperature range is fairly small (Fig. II). Chemically generated singlet oxygen produced in a two phase system composed of toluene and

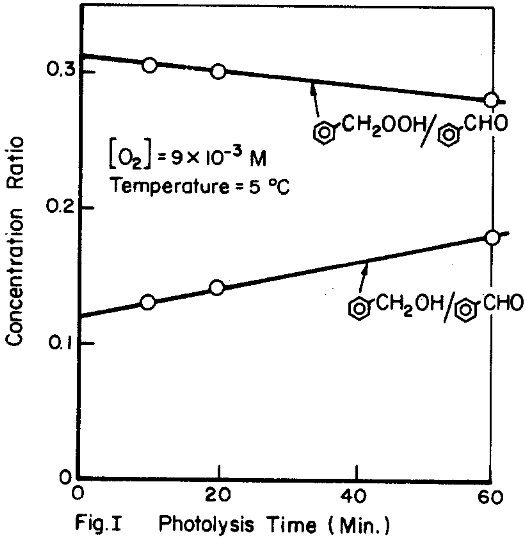

Fig.I

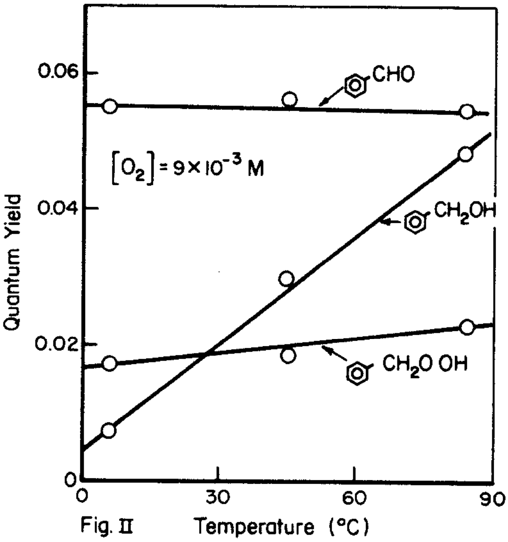

Fig. II

hypochlorite-hydrogen peroxide (2) did not result in the formation of toluene oxidation products. Nor was toluene oxidized when singlet oxygen was produced photochemically using Rose Bengal as a sensitizer (3) in toluene with 8 vol. % of ethanol added to solubilize the dye. We conclude that singlet excited oxygen does not play a significant role in this photooxidation.

The primary photochemical process of toluene is generally regarded as a dissociation with formation of benzyl radical.(4) Since both the photochemical and the catalyzed thermal oxidations of toluene produce similar oxidation products, one would be inclined to believe that the toluene photooxidation also involves the general chain reactions initiated by the photochemically produced $\Phi\text{-}CH_2\cdot$ and $H\cdot$ radicals. The propagation step in this mechanism which generates $\Phi\text{-}CH_2OOH$ and $\Phi\text{-}CH_2\cdot$ radical is known to have an activation energy of 10 Kcal/gmol.(5) Our study, however, shows only very small increase in the yield of $\Phi\text{-}CH_2OOH$ in the range of $5\,^{o}C$ to $85\,^{o}C$. This insensitivity to the temperature change demonstrates that most of the observed $\Phi\text{-}CH_2OOH$ must be produced by some other process. The reaction between the $\Phi\text{-}CH_2\cdot$ and oxygen is usually extremely fast ($k \simeq 10^9\,\ell$/mole sec). In the photolysis of a neat toluene solution the steady-state concentration of $\Phi\text{-}CH_2\cdot$ is very small compared to the oxygen concentration. Consequently, one would expect that the photooxidation rate should be virtually independent of the concentration (i.e., $[O_2] \geq 10^{-3}M$) if the primary processes of toluene only produces benzyl radicals. Our results show that the quantum yield increases significantly from 0.08 to 0.12 as the oxygen concentration is increased from 1.8×10^{-3}M to 9.0×10^{-3}M. Thus, both the temperature and oxygen dependence of the photooxidation are inconsistent with the chain mechanism in the low temperature region.

Neat toluene does not absorb light at wavelengths longer than 2860 Å at room temperature. However, an additional absorption band extending to 3500 Å, due to a contact charge transfer of toluene and oxygen, appears as toluene is saturated with oxygen. Chien (6)has recently reported that upon irradiation this complex undergoes slow photochemical reactions with the consumption of oxygen. In the present investigation, this complex has also been photolyzed with the 3130 Å Hg line which does not excite toluene. The products,as in the case of the direct photolysis,are Φ-CH_2OOH, Φ-CH_2OH, and Φ-CHO;and the ratios among these products are also nearly identical to those obtained with toluene photolyzed with 2537 Å at low temperatures. That is, the direct excitation of toluene at low temperatures and excitation of the complex produce the same results. Hence we contend that the direct photolysis also involves the toluene oxygen complex. Due to the low absorbance of the complex as compared with that of toluene, almost all of the light at 2537 Å is absorbed by toluene. The energy is then transferred to the complex which absorbs at longer wavelengths than toluene. We are led to the conclusion that the photooxidation is a reaction of the excited complex and not of an excited state of toluene or oxygen. That is

$$\Phi\text{-}CH_3 \xrightarrow{h\nu} \Phi\text{-}CH_3^*,\quad \Phi\text{-}CH_3^* + (\Phi\text{-}CH_3\cdot O_2) \longrightarrow \Phi\text{-}CH_3 + (\Phi\text{-}CH_3\cdot O_2)^* \qquad (1,2)$$

$$(\Phi\text{-}CH_3\cdot O_2)^* \begin{array}{l} \nearrow \Phi\text{-}CHO + H_2O \\ \longrightarrow \Phi\text{-}CH_2OOH \\ \searrow \Phi\text{-}CH_2O\cdot + OH\cdot \end{array}$$

Although the Φ-CH_2OOH is thermally stable, it may dissociate photochemically. A dilute solution of authentic Φ-CH_2OOH irradiated with 2537 Å was observed to dissociate with the formation of Φ-CH_2OH and Φ-CHO. This seems to confirm that the benzyl peroxide may, after excitation <u>via</u> energy transfer, produce Φ-CH_2OH and Φ-CHO by a free radical mechanism. At low temperatures Φ-CHO, Φ-CH_2OOH, and possibly Φ-$CH_2O\cdot$ and $OH\cdot$ are being formed initially from the excited complex molecules. The Φ-$CH_2O\cdot$ may then lead to the formation of Φ-CH_2OH. The Φ-CH_2OOH can also dissociate photochemically with the formation of additional Φ-CH_2OH. This is consistent with the experimental observation that the ratio Φ-CH_2OH/Φ-CHO increases steadily with the photolysis time (Fig. I). In the high temperature region the hydrogen-abstracting propagation steps, those reactions with relatively high activation energies, become more important and produce more Φ-CH_2OH. Consequently the ratio Φ-CH_2OH/Φ-CHO increases rapidly with temperature (Fig. II).

The absorbance of the complex decreases with increasing temperature. This might suggest a consequent decrease in the photooxidation rate. However, this reduction can be entirely compensated by the marked increase in rate of the propagation steps. Hence, it is not unexpected that a nearly constant photooxidation rate is observed over the temperature range investigated.

The photooxidation rate is also predicted to increase symbatically with oxygen concentration, again in good agreement with experimental observation.

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