PULSE PHOTOLYSIS OF DITERTBUTYL PEROXIDE IN BENZENE

S.L. Khursan, R.L. Safiullin,a V.S. Martemianov, A.V. Nikolayev a and I.A. Urozhai

Bashkirian State University, Ufa, 450074, USSR
 Institute of Chemistry, Ural Dept. of the USSR Academy of Sciences, Ufa 450054, USSR

Received August 8, 1988
Accepted December 7, 1988

The method of pulse photolysis has been used to determine termination rate constants of primary peroxy radicals in benzene at 295 K. Radicals \( \text{CH}_3\text{O}^\cdot \) have been found to decay with the rate constant \( 2k_6 = 3.7 \times 10^8 \) \( \text{M}^{-1} \text{s}^{-1} \) and radicals \( \text{(CH}_3\text{)}_3\text{COOC(CH}_3\text{)}\text{CH}_2\text{O}^\cdot \) with \( 2k_8 = 1.2 \times 10^8 \) \( \text{M}^{-1} \text{s}^{-1} \), the rate constant of cross-recombination for both radicals being \( 2.4 \times 10^8 \) \( \text{M}^{-1} \text{s}^{-1} \).

The paper reports the rate constants determined for recombination of primary peroxy radicals formed in the pulse photolysis (PP) of di-tert-butyl peroxide.

Di-tert-butyl peroxide (rOOr) was purified by distillation at low pressure, "UV-spectroscopy-grade" benzene was taken as solvent. The experimental set-up involved a PP apparatus and a rapid spectrophotometric device with its operational param-
eters as described in [1]. All experiments were carried out at 
\( T = 295 \pm 2 \, \text{K} \). The kinetic curves of peroxy radical consumption 
were treated on a 15 IPG 32-003 computer. The current peroxy 
radical concentration was determined by equation 
\( [\text{RO}_2] = \frac{A}{\varepsilon \ell} \), 
where \( A \) is the peroxy radical's optical density, \( \ell \) is the op-
tical path and \( \varepsilon \) is the extinction coefficient. The \( \varepsilon \) value was 
found from the equation \( \varepsilon = \frac{\varepsilon_1}{A_1} \), where \( A \) is the optical den-
sity of primary peroxy radicals formed under PP of \( (1.1 \pm 2.2) \times 10^{-2} \, \text{M rOO}
in benzene; \( A_1 \) is the optical density of dodecyl-
peroxy radicals formed under PP of 0.5 \, \text{M dodecane solution in} 
benzene containing \( (1.1 \pm 2.2) \times 10^{-2} \, \text{M rOO}
, and \( \varepsilon_1 \) is the ex-
tinction coefficient of \( \text{C}_{12}\text{H}_{25}\text{O}_2^+ \) radicals in benzene. The op-
tical spectrum for \( \text{C}_{12}\text{H}_{25}\text{O}_2^+ \) in dodecane (Fig. 1) agrees well 
with that reported in [2]. To calculate \( \varepsilon_1 \), optical spectra of 
peroxy radicals were assumed to be identical with various sol-
vents, whereas the spectrum of \( \text{C}_{12}\text{H}_{25}\text{O}_2^+ \) in benzene 
was distorted due to the overlap of dodecylperoxy radicals and 
solvent spectra. The extinction coefficient \( \varepsilon_1 \) so calculated 
was 415 \, \text{M}^{-1} \, \text{cm}^{-1} \) at 285 nm (Fig. 1). The value \( (200 \pm 30) \, \text{M}^{-1} \, \text{cm}^{-1} \) 
was obtained for three determined values of \( \varepsilon \) at 290 nm (Fig.1).

The following reactions occur with rOO in benzene under PP of 
270 \pm 380 \, \text{nm light (light filter UFS-2):}

\[
\begin{align*}
\text{rOO} & \overset{\text{hv}}{\longrightarrow} 2\text{rO}' \quad (1) \\
\text{rO}' & \rightarrow \text{CH}_3' + \text{CH}_3\text{COCH}_3 \quad (2) \\
\text{rO}' + \text{rOO} & \rightarrow \text{rOH} + \text{rOOC(CH}_3)_2\text{CH}_2'(\text{P}') \quad (3) \\
\text{P}' & \rightarrow \text{rO}' + (\text{CH}_3)_2\text{C} - \text{CH}_2 \quad (4) \\
\text{CH}_3'(\text{P}') + \text{O}_2 & \rightarrow \text{CH}_3\text{O}_2'(\text{PO}_2) \quad (5) \\
\text{CH}_3\text{O}_2' + \text{CH}_3\text{O}_2' & \rightarrow \text{products} \quad (6) \\
\text{CH}_3\text{O}_2' + \text{PO}_2' & \rightarrow \text{products} \quad (7) \\
\text{PO}_2' + \text{PO}_2' & \rightarrow \text{products} \quad (8)
\end{align*}
\]

Decay of peroxy radicals occurs via reactions 6-8. The 
initial content of \( (\text{CH}_3)_3\text{COOC(CH}_3)_2\text{CH}_2\text{O}_2' (\text{PO}_2') \) radicals in the 
total amount of peroxy radicals \( n \) was calculated from the for-