

46. *Some Reactions of the Radical 2,4,6-Tri-t-butylphenoxy.*

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The blue free radical, 2,4,6-tri-t-butylphenoxy, reacts with radicals formed in the breakdown of peroxides and azo-compounds and has been used to measure the relative rates of dissociation of these compounds. Some measurements have also been made of the rates of its reaction with *m*-chloroaniline and t-butyl hydroperoxide.

THE blue free radical, $\alpha\alpha$ -diphenyl- β -picrylhydrazyl, has been used to determine apparent rate constants k for the decompositions of certain compounds which break down to yield free radicals and are used as initiators for vinyl polymerizations.¹ The rate constants are apparent because sometimes not all the molecules of the initiator break down to radicals capable of reacting with the hydrazyl. It has now been found that when an excess of dibenzoyl peroxide or a dialkyl $\alpha\alpha'$ -azoisobutyrate is allowed to decompose in a solution of 2,4,6-tri-t-butylphenoxy in carbon tetrachloride at a constant temperature, the optical

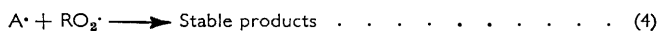
¹ Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216; Bawn and Halford, *ibid.*, 1955, **61**, 780; Hammond, Sen, and Boozer, *J. Amer. Chem. Soc.*, 1955, **77**, 3244.

density falls linearly with time, as it does for solutions of $\alpha\alpha$ -diphenyl- β -picrylhydrazyl. From the rates of disappearance of the colour from solutions of the phenoxyl, relative values for the apparent rates of decompositions of initiators can be calculated. Values for the rates of dissociation, k , of the initiators can be obtained if it is assumed that 2,4,6-tri-*t*-butylphenoxyl reacts with the radicals from dibenzoyl peroxide and the dialkyl $\alpha\alpha'$ -azoisobutyrate with the same efficiency as $\alpha\alpha$ -diphenyl- β -picrylhydrazyl does. 2,4,6-Tri-*t*-butylphenoxyl has some advantages over $\alpha\alpha$ -diphenyl- β -picrylhydrazyl since it normally gives colourless products with other radicals and it contains no nitro-groups, which can themselves react with certain radicals.² 2,4,6-Tri-*t*-butylphenoxyl is prepared³ by the oxidation of 2,4,6-tri-*t*-butylphenol. The radical is destroyed when its solutions are shaken in air, but the reaction with air is sufficiently slow for the radical concentration to be obtained without appreciable error by measurement of the optical density of solutions quickly in open cells in an EEL absorptiometer.

Autoxidations usually proceed⁴ by a chain reaction:



and termination by a hydrogen donor AH is generally attributed to the reactions:



2,4,6-Tri-*t*-butylphenol is an antioxidant,⁵ and 2,4,6-tri-*t*-butylphenoxyl would be the radical A \cdot derived from it. In attempts to find relative values of k for reactions of type (3), a source of radicals such as dibenzoyl peroxide,⁶ $\alpha\alpha'$ -azoisobutyronitrile,^{7,8} or 2,2,3,3-tetra-phenylbutane⁹ has been used to initiate the autoxidation which is carried out in the presence of the inhibitor. According to the above mechanism, the initial rate of uptake of oxygen for a given autoxidation should be proportional to k for reaction (3) and to the initiator concentration, and inversely proportional to the amount of inhibitor. This is what some investigators^{6,8,9} have found. Hammond, Sen, and Boozer,⁷ found, however, that the initial rates of uptake of oxygen were proportional to the square roots of the inhibitor (*N*-methylaniline or phenol) concentrations and suggested that the rate of termination was proportional to [Alkylperoxy-radical]²[Inhibitor]. Harle and Thomas¹⁰ followed the concentration of radicals during the autoxidation of octadecene inhibited by *N*-phenyl- α -naphthylamine by means of electron paramagnetic resonance measurements. Although the results were in approximate agreement with the mechanism suggested by Hammond, Sen, and Boozer,⁷ Harle and Thomas pointed out that their results might be explained if the radicals A \cdot were destroyed rapidly by some oxidation product, for example by peroxide, which rises to a high concentration near the end of the induction period. It is therefore of interest that 2,4,6-tri-*t*-butylphenoxyl has been found to react readily with *t*-butyl hydroperoxide and presumably it reacts with other hydroperoxides as well. The reaction was of the first order with respect to the 2,4,6-tri-*t*-butylphenoxyl and with respect to

² Inamoto and Simamura, *J. Org. Chem.*, 1958, **23**, 408; Jackson, Waters, and Watson, *Chem. and Ind.*, 1959, 59.

³ Cook, *J. Org. Chem.*, 1953, **18**, 261; Cook and Woodworth, *J. Amer. Chem. Soc.*, 1953, **75**, 6242; Muller and Ley, *Chem. Ber.*, 1954, **87**, 922; Muller, Ley, and Kiedaisch, *ibid.*, p. 1605.

⁴ Ziegler and Ewald, *Annalen*, 1933, **504**, 162; Bolland and Gee, *Trans. Faraday Soc.*, 1946, **42**, 236, 244.

⁵ Miller and Quackenbush, *J. Amer. Oil Chemists' Soc.*, 1957, **34**, 249; Penketh, *J. Appl. Chem.*, 1957, **7**, 512.

⁶ Bolland and ten Have, *Discuss. Faraday Soc.*, 1947, **2**, 252.

⁷ Hammond, Sen, and Boozer, *J. Amer. Chem. Soc.*, 1955, **77**, 3239.

⁸ Davies, Goldsmith, Gupta, and Lester, *J.*, 1956, 4926.

⁹ Bickel and Kooyman, *J.*, (a) 1956, 2215; (b) 1957, 2217.

¹⁰ Harle and Thomas, *J. Amer. Chem. Soc.*, 1957, **79**, 2973.

t-butyl hydroperoxide; k was 30 and 90 l. mole⁻¹ min.⁻¹ at 0° and 21° respectively. It was assumed in the attempts to measure relative values of k for reactions of the type (3) that each radical from the initiator starts a chain. This is probably untrue. It is shown here that 2,4,6-tri-*t*-butylphenoxyl is an effective scavenger for the radicals from dibenzoyl peroxide and from a dialkyl $\alpha\alpha'$ -azoisobutyrate which is very similar to $\alpha\alpha'$ -azoisobutyronitrile. It seems likely, therefore, that in some cases a proportion of the radicals from the initiator will combine with A· instead of starting a chain by abstracting a hydrogen atom from RH.

$\alpha\alpha$ -Diphenyl- β -picrylhydrazyl reacts with many compounds which can donate hydrogen. In most of these reactions the second-order law is obeyed, but the reactions of $\alpha\alpha$ -diphenyl- β -picrylhydrazyl with hydroaromatic compounds¹¹ and with aromatic primary amines¹² obeyed the third-order law. In these reactions the hydrogen donor probably forms a complex with one hydrazyl radical, and the reaction is completed when a second hydrazyl radical attacks this complex. Since the nitro-groups in $\alpha\alpha$ -diphenyl- β -picrylhydrazyl may be involved in the formation of the complex, the reactions of 2,4,6-tri-*t*-butylphenoxyl, which has no nitro-groups, were of interest. The reaction between 2,4,6-tri-*t*-butylphenoxyl and *m*-chloroaniline, which was one of the amines used with the hydrazyl, occurred readily and was found to be of the second order ($k = 4.0$ l. mole⁻¹ min.⁻¹ at 23.5° in carbon tetrachloride).

EXPERIMENTAL

2,4,6-Tri-*t*-butylphenoxyl was prepared by the oxidation of 2,4,6-tri-*t*-butylphenol with alkaline ferricyanide.⁵ Potassium ferricyanide (4.9 g.) and potassium hydroxide (0.75 g.) in water (20 ml.) and carbon tetrachloride (100 ml.) were placed in a three-necked flask, fitted with an outlet and tap at the bottom, and stirred for 1 hr. in a slow stream of oxygen-free nitrogen. Then 2,4,6-tri-*t*-butylphenol (1.5 g.) was added and the stirring in nitrogen continued for a further 2 hr. It is important that the oxidation should be complete, since 2,4,6-tri-*t*-butylphenol itself will react with many radicals and with some initiators: Walling and Hodgdon¹³ have, for example, shown that dibenzoyl peroxide when decomposing will oxidise 2,4,6-tri-*t*-butylphenol to 2,4,6-tri-*t*-butylphenoxyl. Some of the concentrated solution of 2,4,6-tri-*t*-butylphenoxyl in carbon tetrachloride was then run into the rest of the carbon tetrachloride which was contained in a three-necked flask and through which carbon dioxide was bubbled. The flask was fitted with a reflux condenser and was placed in a thermostat. When the solution reached the bath-temperature a weighed quantity of the other purified reactant was introduced and the reaction allowed to proceed with carbon dioxide passing. Samples were taken out at intervals and the optical densities measured as quickly as possible in an EEL absorptiometer with filter No. 607. The carbon tetrachloride used in these experiments was of "AnalaR" quality: it was boiled and allowed to cool under carbon dioxide and used without further purification.

The optical densities for solutions of 2,4,6-tri-*t*-butylphenoxyl in carbon tetrachloride containing a large excess of either a dialkyl $\alpha\alpha'$ -azoisobutyrate or dibenzoyl peroxide were measured and showed that the radical disappeared at a constant rate in each case, *i.e.*, the reactions were of zero order with respect to the phenoxyl. Attempts to determine the concentrations of the solutions of 2,4,6-tri-*t*-butylphenoxyl by titration with quinol and with thio-sulphate either alone or after the addition of hydrogen iodide gave unsatisfactory results because the end-points were not sharp. On the assumption that concentrations (mole/l.) of 2,4,6-tri-*t*-butylphenoxyl are given by multiplication of the optical densities for a 1 cm. cell by 2.50×10^{-3} , the following apparent unimolecular rate constants k were calculated from the slopes b of the regression equations $y = a + bt$ of the optical density (y) against time (t , sec.)

¹¹ Braude, Brook, and Linstead, *J.*, 1954, 3574.

¹² McGowan, Powell, and Row *J.*, 1959, 3103.*

¹³ Walling and Hodgdon, *J. Amer. Chem. Soc.*, 1958, 80, 228.

* In reference 12 there are two mistakes:

(a) p. 3106, Table 4, the value of k for 4-chlorophenol is 11, and not 1.1.

(b) p. 3109, Table near bottom of page, the value of k/k_0 for the *p*-chloro-compound should be 2.6, and not 0.26.

With 4.13×10^{-2} mole per l. of dibenzoyl peroxide at 59° in a cell 1 cm. thick, $y = 0.9941 - 4.683 \times 10^{-5}t$, and the standard error on the slope (b) was 8.75×10^{-7} . At 77° , with 4.15×10^{-3} mole per l. of dibenzoyl peroxide in a cell 1 cm. thick, $y = 0.9511 - 5.988 \times 10^{-5}t$, and the standard error on the slope was 1.55×10^{-7} . From these slopes k for dibenzoyl peroxide equals 1.42×10^{-6} sec. $^{-1}$ at 59° , and 1.80×10^{-5} sec. $^{-1}$ at 77° . With 4.82×10^{-2} mole per l. of dialkyl $\alpha\alpha'$ -azoisobutyrate at 60° in a cell 1 cm. thick, $y = 0.9229 - 1.019 \times 10^{-4}t$, and the standard error on the slope was 1.00×10^{-6} ; at 76° with 4.98×10^{-3} mole per l. in a cell 4 cm. thick, $y = 0.9192 - 4.361 \times 10^{-4}t$, and the standard error on the slope was 8.43×10^{-6} . From these slopes k for the dialkyl $\alpha\alpha'$ -azoisobutyrate is 2.64×10^{-6} and 2.74×10^{-5} sec. $^{-1}$ at 60° and 76° respectively. The results are in good agreement with other values¹⁴ for k .

The concentrations of 2,4,6-tri-*t*-butylphenoxyl solutions derived from the optical densities by means of the factor 2.50×10^{-3} showed that 2,4,6-tri-*t*-butylphenol is almost quantitatively oxidised to 2,4,6-tri-*t*-butylphenoxyl by potassium ferricyanide. The concentrations were used in conjunction with measurements with a Unicam spectrophotometer to study the spectrum of solutions of 2,4,6-tri-*t*-butylphenoxyl in carbon tetrachloride. A sharp band with a peak, at $400 \text{ m}\mu$ with ϵ about 3000, and a broad band with a maximum at $615 \text{ m}\mu$ and ϵ equal to 465, were found. Cook and Norcross¹⁵ give for 2,4,6-tri-*t*-butylphenoxyl ϵ 410 at $630 \text{ m}\mu$ in benzene and ϵ 478 at $630 \text{ m}\mu$ in cyclohexane.

The reactions between 2,4,6-tri-*t*-butylphenoxyl and *t*-butyl hydroperoxide were found to be of the first order with respect to both reactants; and, with an excess of the hydroperoxide, straight lines were obtained when values of \log_e (Optical density) were plotted against time. The slopes of the line gives the pseudo-unimolecular rate constants and it is not necessary to convert the optical densities into concentrations. At 21° with 5.55×10^{-3} mole per l. of *t*-butyl hydroperoxide in a cell 1 cm. thick, \log_e (Optical density) = $-0.3775 - 0.5571t$, with the standard error on the slope of 3.66×10^{-3} ; and with 1.163×10^{-3} mole per l. of *t*-butyl hydroperoxide in a cell 4 cm. thick, \log_e (Optical density) = $-0.3923 - 0.0941t$ (standard error on the slope = 9.46×10^{-4}). At 0° , with 1.182×10^{-3} mole per l. of *t*-butyl hydroperoxide in a cell 4 cm. thick, \log_e (Optical density) = $-0.2693 - 0.0354t$ (standard error on the slope = 2.58×10^{-4}). The bimolecular rate constants k , obtained by the division of the pseudo-unimolecular rate constants by the concentration of hydroperoxide, were 90 l. mole $^{-1}$ min. $^{-1}$ at 21° and 30 l. mole $^{-1}$ min. $^{-1}$ at 0° .

The reactions between 2,4,6-tri-*t*-butylphenoxyl and *m*-chloroaniline were studied in a similar way. The products, however, absorbed to some extent in the EEL absorptiometer and corrections were made for the coloured products. The reaction was run practically to completion, and the colour corresponding to complete disappearance of the radical was obtained. It was then assumed that the same coloured products were produced throughout the reaction in proportion to the amount of 2,4,6-tri-*t*-butylphenoxyl which had disappeared. Cells 1 cm. thick were used and at 23.5° , \log_e (Corrected optical density) = $-0.4559 - 0.0877t$ (standard error on the slope = 9.48×10^{-4}) and $-0.0474 - 0.1942t$ (standard error on the slope = 1.149×10^{-3}) for 2.382×10^{-2} and 4.710×10^{-2} mole of *m*-chloroaniline per l. respectively. The average value for the bimolecular constant is 4.0 l. mole $^{-1}$ min. $^{-1}$ at 23.5° .

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¹⁴ McGowan and Powell, *J. Appl. Chem.*, 1959, **9**, 93.

¹⁵ Cook and Norcross, *J. Amer. Chem. Soc.*, 1959, **81**, 1176.