2,3′,5′,6-Tetra-*t*-butylindophenoxyl, Competitive Scavenging, and Isotope Effects[1]

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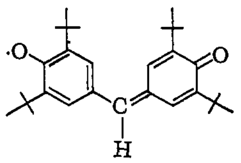
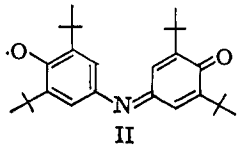
Abstract: The stable free radical II (BIP), mp 155–156°, scavenges short-lived free radicals by direct addition, as does galvinoxyl; the products from *t*-butoxy and cyanoisopropyl radicals have been characterized. BIP agrees with other good scavengers in indicating cage effects of 38–44% for the decomposition of azobisisobutyronitrile (AIBN) in benzene at 34–62°, and of less than 3% for di-*t*-butyl diperoxyoxalate (DBPO) at 25°. Azobisdiphenylmethane is found to have a cage effect of 53–58% at 34°. By competitive scavenging BIP appears to be a scavenger of the same order of efficiency as galvinoxyl (I) toward the cyanoisopropyl and *t*-butoxy radicals, and 4.5 times as efficient toward the cyanoisopropylperoxy radical at 34°. 2,3′,5′,6-Tetra-*t*-butylindophenol (III, BIPH) donates hydrogen atoms efficiently to the *t*-butoxy radical, with the formation of BIP, which then competes with the BIPH for the oxygen radicals. The kinetics of this process (followed by spectrophotometry and by esr) yields rate constant ratios for the competition of these two scavengers at 25°, $k_{\mathrm{BIP}}/k_{\mathrm{BIPH}} = 7.5$. With precautions against back exchange of H for D, the indophenol is found to show an isotope effect $k_{\mathrm{H}}/k_{\mathrm{D}} = 3.6$–$4.4$ toward the tertiary butoxy radical from DBPO at 25°. Toward carbon radicals such as cyanoisopropyl, BIPH is of insufficient reactivity to yield an appreciable steady-state concentration of BIP. The rates and equilibria of certain reactions of hydrogen exchange between stable free radicals have been measured. By direct spectrophotometric measurement the rate constants (l./mole sec) and equilibrium constants at 25° are as follows: BIPH and diphenylpicrylhydrazyl, 13 and 38–46; BIPH and galvinoxyl, >200 and 4–6.

It has been shown previously[2] that the stable free radical, galvinoxyl (I), is a useful scavenger for short-lived free radicals both of carbon and of oxygen;


I

that galvinoxyl is at least ten times as efficient a scavenger as iodine toward the cyanoisopropyl radical from azobisisobutyronitrile; and that it can be used at temperatures up to about 60° for determinations of cage effects in free-radical pairs without complications from its thermal decomposition, which becomes of importance at higher temperatures. In this paper we describe the preparation and characterization of the combination products of the cyanoisopropyl and *t*-butoxy radicals with the "aza" analog of galvinoxyl, 2,3′,5′,6-tetra-*t*-butylindophenoxyl (BIP, II), whose


II

preparation has been described by Coppinger.[3]

Properties of BIP. BIP, after repeated recrystallization from pentane, is a dark green-blue in color. The crystals melt at 155–156°. The infrared spectrum is free of hydroxyl absorption and has a weak peak at 6.18 and a strong one at 6.36 μ. The ultraviolet and visible spectra in isooctane solution (Figure 1) exhibit maxima at 312 mμ (sh) (ε 18,600), 325 (22,300), and 454 (21,900). For kinetic purposes two wavelengths in the visible proved especially useful. The extinction coefficient of a shoulder at 770 mμ (ε 1889 in benzene, 1767 in carbon tetrachloride) was used as a criterion for the purity of different preparations; at 625 mμ ε was 437 in benzene, 370 in carbon tetrachloride. Although BIP absorbed oxygen at a measurable rate at 40°, benzene solutions of the radical after four degassings were stable for more than 5 hr at 61.8°.

Cage Effects. Tables I–III show a comparison of BIP with other scavengers toward the cyanoisopropyl radical from AIBN (Table I) and the *t*-butoxy radical from di-*t*-butyl diperoxyoxalate (Table II), and in the scavenging of the benzhydryl radical from azobisdiphenylmethane (Table III). In each case determinations were run at two wavelengths, small amounts of scavenger being used and the reaction followed to total consumption of scavenger. In Table I, six runs with BIP at 61.83° yielded an average cage effect of 38.4%, while six similar runs with galvinoxyl gave 35.2%. The results within any one set of experiments were quite consistent, no cage effect determined with galvinoxyl being as high as any of the cage effects determined with BIP. The reason for this disagreement is not known, but it is believed that the factors limiting the accuracy in the case of both scavengers are the purity of the scavenger samples and the accuracy of the extinction coefficients. At 33.98° BIP shows a cage effect of 44.2% and galvinoxyl of 41.8%. Incomplete scavenging by either agent is very improbable, since the scavenging curves are straight zero-order lines down to total disappearance of the scavenger.

Earlier measurements with DBPO in this laboratory[2] indicated a cage effect so near zero that we had concluded that the interaction of two *t*-butoxy radicals is not diffusion controlled. Recently Hiatt and Traylor[4]

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[1] Presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 20, 1964.

[2] P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).

[3] G. M. Coppinger, *Tetrahedron*, **18**, 61 (1962).

[4] R. Hiatt and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3766 (1965).

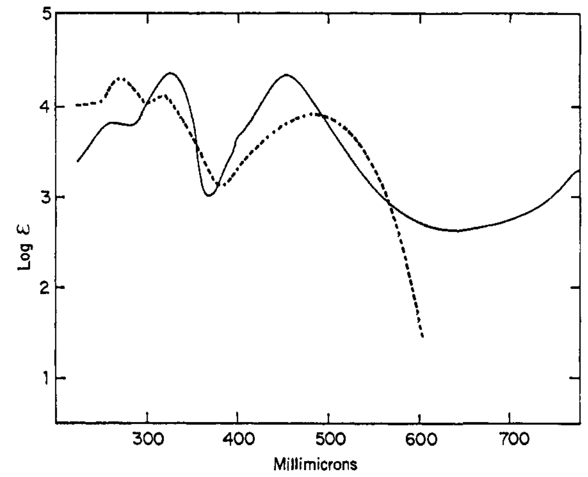

Figure 1. Ultraviolet and visible spectra of tetra-*t*-butylindophenol and tetra-*t*-butylindophenoxyl in isooctane: – – – –, tetra-*t*-butylindophenol (BIPH); ———, tetra-*t*-butylindophenoxyl (BIP).

Table I. Azobisisobutyronitrile Cage Effect Determined with Scavengers in Benzene

Scavenger	Moles/l. $\times 10^4$	[AIBN], moles/l. $\times 10^2$	Temp, °C	λ, mμ	$k \times 10^6$, sec^{-1}	% cage effect[a]
BIP· (II)	9.009	25.86[b]	33.98	770	0.097	43.3
				625	0.094	45.0
G· (I)	9.601	24.76[b]	33.98	770	0.100	40.9
				625	0.098	42.7
BIP·	9.023	2.281[b]	61.83	770	7.92	38.6
				625	7.95	38.4
BIP·	9.118	2.317[b]	61.83	770	7.90	38.8
				625	7.98	38.1
BIP·	9.023	2.354[b]	61.83	770	7.96	38.3
				625	8.00	38.0
G·	16.57	3.638[b]	61.83	770	8.25	36.0
				625	8.32	35.5
G·	16.95	3.754[b]	61.83	770	8.29	35.7
				625	8.29	35.7
G·[c]	11.4	2.182	61.65	765	8.174	34.7
G·[c]	11.6	2.194	61.65	765	8.270	33.9

[a] For corrections and calculations see ref 2. With the rate constant, measured volumetrically at 30.5° by J. P. Van Hook and A. V. Tobolsky, *J. Am. Chem. Soc.*, **80**, 779 (1958), in benzene and their activation energy, the rate constant in the absence of scavenger is 1.71×10^{-7} at 33.98°. [b] The AIBN used gives 99.3 and 98.9% of the theoretical nitrogen after 10 half-lives at 100° in chlorobenzene. Therefore, 99.1% of the AIBN concentration was used in the calculation. [c] P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962); correction not applied.

Table II. Di-*t*-butyl Peroxyoxalate Cage Effect Determined with Scavengers in Benzene

Scavenger	Moles/l. $\times 10^4$	[DBPO], moles/l. $\times 10^2$	Temp., °C	% zero order	λ, mμ	$k \times 10^5$, sec^{-1}	% cage effect[a]
BIP·	5.390	0.918	25.44	96	770	1.41	...
					625	1.42	...
BIP·	5.317	0.946	25.44	97	770	1.41	...
					625	1.40	0.0
G·	8.085	1.717	25.44	94	770	1.43	...
					625	1.43	...
G·	9.419	1.529	25.44	94	770	1.48	...
					625	1.48	...
G·[b]	21.5	3.384	25.48	68	770	1.381	1.4
G·[b]	22.8	3.374	25.48	82	770	1.368	2.3
G·[b]	20.9	3.320	25.48	74	770	1.367	2.4

[a] Based on the $k = 1.40 \times 10^{-5}$ sec^{-1}. [b] P. D. Bartlett and T· Funahash, *J. Am. Chem. Soc.*, **84**, 2596 (1962); correction not applied. The extinction coefficient used for G· in these experiments was 607.

Table III. Azobisdiphenylmethane Cage Effects Obtained with Scavengers

Scavenger	Moles/l. $\times 10^4$	[ADPM], moles/l. $\times 10^2$	Temp, °C	% zero order	λ, mμ	$k \times 10^6$, sec^{-1}	% cage effect[a]
BIP·[c]	9.105	3.011	34.11	71	770	3.87	58.3
BIP·[d]	4.647	1.564	34.11	75	770	4.14	55.4
G·[c]	9.316	3.050	34.11	95	770	3.92	57.8
					625	3.87	58.3
G·[e]	10.84	3.050	34.11	96	770	3.99	57.0
					625	3.94	57.5
BIP·[b,f]	4.979	1.625	33.98	97	770	4.30	52.8
					625	4.12	54.8
G·[f]	9.126	2.928	33.98	25	770	4.22	53.7
					625	4.06	55.4
BIP·[b,g]	4.096	1.980	33.98	96	770	4.29	52.9

[a] With the activation energy, 26.6 kcal, obtained by S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, 77, 2457 (1955), in conjunction with the rate constant, $k_{34.28} = 9.50 \times 10^{-6}$ sec^{-1} (runs 4 and 5), the following rate constants were obtained: $k_{34.11} = 9.28 \times 10^{-6}$ sec^{-1}, $k_{33.98} = 9.11 \times 10^{-6}$ sec^{-1}. [b] Reactions run in the presence of oxygen. [c] 85% pure ADPM. [d] 100% pure ADPM. [e] 86% pure ADPM. [f] 82% pure ADPM. [g] 92% pure ADPM; 5.19×10^{-4} *M* BIPH present.

have shown that the small cage effect is real and can be magnified by the choice of more viscous solvents. Table II shows that with BIP the cage effect in benzene is still indistinguishable from zero. Four new determinations using galvinoxyl at 25° agree in being unable to detect a cage effect but deviate from the BIP runs in the same direction as with AIBN.

Secondary azo compounds present special problems as radical initiators, since they readily isomerize to hydrazones and are quite sensitive to induced decomposition in the present of oxygen.[5] Table III shows that azobisdiphenylmethane yields consistent values of its cage effect with BIP and with galvinoxyl at 34° in benzene in the presence and in the absence of oxygen. Induced oxidation here is evidently held in check by the speed with which the scavenger removes peroxy radicals. To us it was unexpected that pairs of benzhydryl radicals, which possess not only substantial resonance energy but a certain amount of steric hindrance, should show such a large cage effect. (The unstabilized methyl radical pairs[6] from azomethane in benzene show a cage effect of 78.3% in photodecomposition at 25°, corresponding to a ratio of recombination to diffusion rate only three times as great as shown by the benzhydryl radical.) In view of the large expected difference in rate constant, this result must mean that the increase in bulk in going from methyl to benzhydryl causes the diffusion rate to slow down almost in proportion to the rate of radical recombination.

Products of Reaction of BIP with Cyanoisopropyl and *t*-Butoxy Radicals. The cyanoisopropyl coupling product of BIP was isolated as a yellow, crystalline material melting with decomposition at 159–160°. Its infrared spectrum showed a nitrile band at 4.54 and carbonyl peaks at 6.04 and 6.13 μ but no hydroxyl or ketenimine bands.

The *t*-butoxy adduct of BIP was isolated as orange crystals melting with decomposition at 137–139°. This product was less readily separated in crystalline form.

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(5) T. G. Traylor, I. V. Berezin, and R. D. Swigert, unpublished work in this laboratory.

(6) S. Kodama, *Bull. Chem. Soc. Japan*, **35**, 824 (1962).

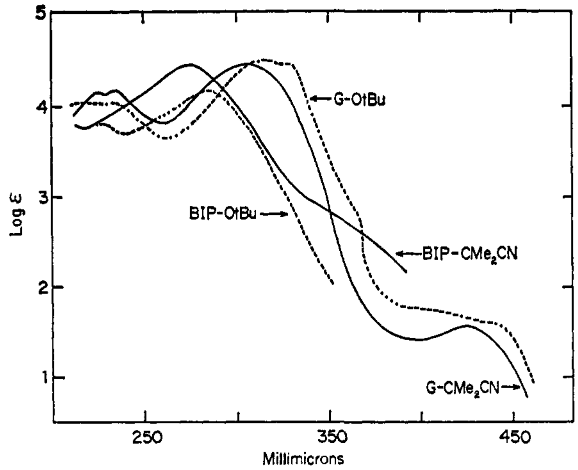


Figure 2. Ultraviolet and visible spectra of galvinoxyl and tetra-*t*-butylindophenoxyl adducts in isooctane: ———, cyanoisopropyl adducts; – – – –, *t*-butoxy adducts.

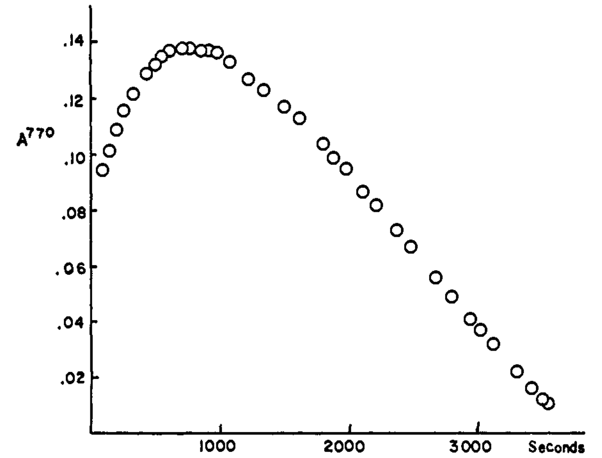
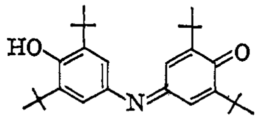


Figure 3. Competitive scavenging of *t*-butoxy radicals by BIPH and BIP. Di-*t*-butyl diperoxyoxalate (DBPO) in substantial excess undergoes thermal decomposition at 25.44° in benzene in the presence of tetra-*t*-butylindophenol (BIPH). Absorbancy at 770 mμ (ordinates) measures the rise and decline of BIP radical concentration (also followed by esr); at the maximum BIP and BIPH are reacting with *t*-butoxy radical at identical rates.

Figure 2 shows the ultraviolet absorption spectra of the cyanoisopropyl and *t*-butoxy adducts of BIP and of galvinoxyl.

Competitive Scavenging. Experiments have been carried out on the characterization of various reactive free radicals by means of their relative rates of reaction with two scavengers whose concentrations are followed by alternate absorbancy measurements at two wavelengths where they absorb differently. This method has been employed by Bartlett and Funahashi.[2] Toward cyanoisopropyl and *t*-butoxy radicals the two scavengers, galvinoxyl and BIP, compete nearly equally; BIP is more reactive toward benzhydrylperoxy and cyanoisopropylperoxy radicals by factors of 2 and 4.5, respectively.

An interesting pair of competitive scavengers are 2,3',5',6-*t*-butylindophenol (III, BIPH) and BIP. If the former is used in the presence of di-*t*-butyl diperoxyoxalate (DBPO) and the absorbancy of the solution at 770 mμ is followed, the concentration of BIP so indicated rises to a maximum and then declines (Figure 3), indicating that the *t*-butoxy radical first removes a hydrogen atom from BIPH and competition ensues between the BIP and the BIPH for the other oxygen radicals. From the absorbancy at the maximum and from the later slope of the curve, independent and agreeing values can be derived of k_2/k_1, the relative scavenging rates of this hydrogen-donating phenol and the radical-accepting phenoxy radical (Table IV). The same result was obtained using esr as the method of following the BIP concentration. The implication that hydrogen atom transfer is the rate-determining step in the reaction of BIPH with the alkoxy radical can be confirmed by repeating this experiment with D_2O-saturated BIPD solutions as starting material. The rate constant ratio k_{BIP}/k_{BIPD} is about four times that for undeuterated phenol (Table V). It was necessary in performing these experiments to displace adventitious water with D_2O to guard against rapid back exchange of H for D.



III

Table IV. Reaction of BIPH and DBPO at Various Temperatures

[BIPH], moles/l. × 10³	[DBPO], moles/l. × 10²	Temp, °C	k_2/k_1 at [BIP·] peak	k_2/k_1 during latter part of reaction
1.098	1.566	25.44	7.16	7.16
1.146	1.745	25.44	7.37	7.30
0.957	1.534	25.44	7.50	7.56
1.336[a]	1.394	25.44	7.65	7.74
1.128[b]	1.575	25.44	7.47	7.51
1.289	1.203	34.11	7.27	7.32
1.317	1.203	34.11	6.81	6.83
1.232	2.014	34.11	7.32	7.27
1.364	1.314	35.67	6.90	6.81
1.364	1.371	35.67	6.84	6.72

[a] Degassed in the presence of 1 ml of H_2O. [b] Using the same procedure as for BIPD.

Table V. Deuterium Isotope Effect for the Reaction of *t*-Butoxy Radicals with Tetra-*t*-butylindophenol

[BIPD], moles/l. × 10³	[DBPO] moles/l. × 10²	k_1/k_2	k_H/k_D
4.719	7.183	26.7	3.6
4.946	7.118	30.4	4.1
4.946	7.551	33.0	4.4

Hydrogen Transfer between Stable Radicals. Even toward rather hindered and stable radicals tetra-*t*-butylindophenol exchanges hydrogen rather rapidly. The exchange equilibrium constant with diphenylpicrylhydrazyl is between 38 and 46, and that with galvinoxyl is about 4–5 (Tables VI and VII). Details are described in the Experimental Section.

Table VI. Equilibrium Constant for $G\cdot + BIPH \overset{K}{\rightleftharpoons} GH + BIP\cdot$

$[G\cdot]_{initial}$, mole/l. × 10^4	$[BIPH]_{initial}$, mole/l. × 10^4	$(A_{625})_{corr}$[a]	$(A_{770})_{corr}$[a]	*K*
8.875[b]	9.096	0.342	1.258	3.1
4.752	4.738	0.187	0.693	4.1
4.589	4.548	0.182	0.664	3.7
5.555	4.643	0.214	0.763	4.0
6.046	4.785[c]	0.235	0.829	4.5

[a] $A_{corr} = A_{soln} - A_{C_6H_6\ vs.\ C_6H_6}$. [b] Degassed four times; if any benzene were lost during this process, *K* would have been decreased. [c] BIPD rather than BIPH used in this run.

Table VII. Alternate Approach to Equilibrium Constant for $G\cdot + BIPH \overset{K}{\rightleftharpoons} GH + BIP\cdot$

$[GH]_{initial}$, mole/l. × 10^4	$[BIP\cdot]_{initial}$, mole/l. × 10^4	$(A_{625})_{corr}$[a]	$(A_{770})_{corr}$[a]	*K*
4.844	4.408	0.178	0.657	5.1
5.081	4.982	0.201	0.753	5.8
4.512	4.386	0.180	0.670	5.9

[a] $A_{corr} = A_{soln} - A_{C_6H_6\ vs.\ C_6H_6}$.

Experimental Section

2,6-Di-*t*-butyl-4-nitrophenol, donated by the Ethyl Corp., was recrystallized from hexane before being used, mp 156–157°. Chlorobenzene from the Fisher Scientific Co. was refluxed and distilled first from phosphorus pentoxide and then from potassium hydroxide, bp 131°.

Eastman White Label azobisisobutyronitrile was recrystallized twice from ethanol at less than 60° before use, mp 103.5–104°. The purity of AIBN was determined by nitrogen evolution. A sample assaying 99.1% pure showed only one peak in the nmr at δ 1.72.

Diphenylpicrylhydrazyl, from the Aldrich Chemical Co., was recrystallized from benzene and dried at 80° under vacuum for 24 hr before being used. It was stored at −20°.

Di-*t*-butyl diperoxyoxalate was prepared by Dr. A. J. Moye by the method of Bartlett, Benzing, and Pincock,[7] mp 51.5–52.3° with rate of heating approximately 2°/min (lit.[7] 51.5°). It was stored at −20°.

Infrared spectra were taken on a Perkin-Elmer Infracord. Nmr spectra were recorded on a Varian A-60 spectrometer. Ultraviolet and visible spectra were obtained on a Cary recording spectrophotometer, Model 14 or Model 11M.

Mass spectra were obtained with the aid of the Consolidated Engineering Corp. mass spectrometer 21-103C.

All boiling points and melting points are uncorrected.

Tetra-*t*-butylindophenol and Tetra-*t*-butylindophenoxyl. To 14 g (0.056 mole) of 2,6-di-*t*-butyl-4-nitrophenol dissolved in 400 ml of ether–hexane (3:1 by volume) and 38 g (0.32 g-atom) of tin was added 75 ml of concentrated hydrochloric acid.[8] Prepurified nitrogen was blown over the system throughout the reduction. The reaction mixture was heated on a steam bath and subsequently cooled to moderate the effervescence. When addition of 1 drop of the organic layer to alkali ceased to produce yellow coloration, the reduction was complete. The reaction mixture was then made alkaline with 60 g of sodium hydroxide in 75 ml of water and extracted three times with ether. The combined ether layers were washed with dilute sodium hydroxide and water and then dried over magnesium sulfate for about 10 min. So far as possible, the extraction was done under nitrogen in order to prevent oxidation of the amine. The ether was replaced by *n*-heptane (or isooctane) and the solution was refluxed under nitrogen until no more ammonia was given off (about 72 hr).[3] The reaction mixture was cooled and O_2 was bubbled through it for 4 hr. The yield of tetra-*t*-butylindophenol ranged from 40 to 60% in different runs; the red crystals melted at 160–161° (lit.[8] mp 132–133°). A carbonyl band at 6.15 and a hydroxyl band at 2.70 μ were observed in the infrared spectrum taken in carbon tetrachloride. In isooctane, the ultraviolet and visible spectra showed the following maxima: 480 mμ (ϵ 8200), 315 (13,400), and 270 (20,700) (Figure 1). The nmr spectrum of BIPH in carbon tetrachloride showed three different *t*-butyl signals τ 8.76 (9 H), 8.67 (9 H), and 8.52 (18 H), hydroxyl at 4.68, and ring protons at 3.20 and 2.96 (2 H each).

Anal. Calcd for $C_{28}H_{41}NO_2$: C, 79.38; H, 9.76; N, 3.31. Found: C, 79.19; H, 9.49; N, 3.39.

In 100 ml of ether 8.5 g (0.2 mole) of tetra-*t*-butylindophenol was stirred with 20 g of lead dioxide for 4.5 hr under N_2. The residue of lead oxides was removed by filtration; the ether was evaporated from the filtrate under a stream of nitrogen leaving 8.1 g of BIP·, a 95% yield of about 90% pure material. The radical was recrystallized from pentane under nitrogen. Pure, crystalline BIP· was very dark green-blue in color, mp 155–156° (lit.[3] mp 135–136°). The infrared spectrum, taken in carbon tetrachloride, showed no bands between 2.5 and 3.3 μ; it showed a weak peak at 6.18 and a strong one at 6.36 μ. The visible and ultraviolet spectra in isooctane exhibited maxima at 312 mμ (shoulder) (ϵ 18,600), 325 (22,300), and 454 (21,900). Through the generosity of Dr. A. Maki, the esr spectrum of a degassed benzene solution of tetra-*t*-butylindophenoxyl was observed; $A_H = 1.10$ and $A_N = 2.10$ gauss (lit.[3] $A_H = 1.13$ and $A_N = 2.25$ gauss).

Anal. Calcd for $C_{28}H_{40}NO_2$: C, 79.57; H, 9.54; N, 3.32. Found: C, 79.65; H, 9.55; N, 3.52.

Oxygen is absorbed by benzene solutions (degassed three times) containing approximately 95% pure tetra-*t*-butylindophenoxyl at 39.92°. The apparatus empolyed for these oxygen absorption runs was similar to that used by Hammond, *et al.*;[9] mercury rather than oil was used to equalize the pressure. In two runs 0.42 and 0.77 mole of oxygen per mole of radical was absorbed. Chromatography of 0.12 g of the product mixture on 6 g of silica gel did not afford separation of the mixture. Chromatography on alumina was not attempted as decomposition of these compounds is known to occur on alumina columns.[2] The infrared spectrum of the crude red reaction mixture showed three carbonyl bands at 5.94, 6.06, and 6.13 μ; it contained no hydroxyl or nitro bands. However, in basic solution, the oxidation product became dark green.

The extinction coefficient (1889 in benzene, 1767 in carbon tetrachloride) observed at 770 mμ, a shoulder, was used as the criterion for the purity of the radical. After repeated recrystallization from pentane, a constant extinction coefficient at 770 and also at 625 mμ (437 in benzene, 370 in carbon tetrachloride) was observed. The solutions were degassed twice before readings were taken. Benzene solutions of tetra-*t*-butylindophenoxyl were stable for more than 20,000 sec at 61.8° after four degassings. Tetra-*t*-butylindophenoxyl was found to adhere to Beer's law at both 770 and 625 mμ.

Hydrogalvinoxyl and Galvinoxyl. Hydrogalvinoxyl was obtained from Dr. T. Funahashi, mp 157–158°. Galvinoxyl, also obtained from Dr. T. Funahashi, was recrystallized from pentane until constant extinction coefficients at 770 and 625 mμ were observed. As with tetra-*t*-butylindophenoxyl, the extinction coefficient was determined at both 25 and 62° on the same sample. After four degassings, benzene solutions of galvinoxyl were found to be stable for more than 20,000 sec.

The absorption of oxygen by galvinoxyl in chlorobenzene at 39.86° was investigated. After three degassings, 0.4091 g of galvinoxyl (7.85 × 10^{-4} mole) in 10 ml of chlorobenzene absorbed 15.96 × 10^{-4} mole of oxygen. The chlorobenzene was removed *in vacuo* and the product was chromatographed on alumina. Identified as one component of the mixture was 2,6-di-*t*-butylquinone, mp 66–68.5° (lit. mp 67°,[10] 66.5–68°,[11] 68°[12]). The infrared spectrum was identical with that of an authentic sample.

The Cyanoisopropyl Adduct of Tetra-*t*-butylindophenoxyl. After three degassings, 0.1394 g of BIP· (3.299 × 10^{-4} mole) and 0.0887 g of AIBN (5.402 × 10^{-4} mole) in 5 ml of benzene under 0.61 atm of N_2 was held at 62.5° for 149 hr (10 half-lives). The solvent was then removed from the reaction mixture *in vacuo* and some tetramethylsuccinonitrile was sublimed from the residue.

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(9) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, 77, 3233 (1955).

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(11) G. R. Yohe, J. E. Dunbar, R. L. Pedrotti, F. M. Scheidt, F. G. H. Lee, and E. C. Smith, *ibid.*, **21**, 1289 (1956).

(12) U. S. Patent 2,657,222 (1953); *Chem. Abstr.*, **48**, 12806c (1954).

The cyanoisopropyl–tetra-*t*-butylindophenoxyl adduct (BIP–CMe_2CN) was separated from residual tetramethylsuccinonitrile by pentane extraction. On cooling the concentrated pentane solution to −25°, yellow crystals formed leaving a red mother liquor. These crystals accounted for about 95% of the colored product. The red residue is believed to be the thermal decomposition product of the adduct. On heating, the yellow solid started to turn red at 130° and became continuously darker until it melted at 159–160°. The infrared spectrum taken in carbon tetrachloride showed a nitrile band at 4.54 and carbonyl bands at 6.04 and 6.13 μ, but no hydroxyl or ketenimine bands. In isooctane the ultraviolet spectrum showed a maximum at 266–267 mμ (ϵ 25,300). From the nmr spectrum in carbon tetrachloride the following τ values were obtained: 8.92, 8.74, 8.70, 8.64 (singlets, *t*-butyl, 36 H); 8.24, 6.40 (multiplets, CH_3, 6 H); 3.47 (singlet, aromatic, 2 H), and 3.28 (quartet, aromatic, 2 H).

Anal. Calcd for $C_{32}H_{46}N_2O_2$: C, 78.32; H, 9.65; N, 5.71. Found: C, 78.52; H, 9.60; N, 5.60.

The cyanoisopropyl–tetra-*t*-butylindophenoxyl adduct decomposed on heating to a red gum which melted at the same temperature as tetra-*t*-butylindophenol. However, the visible and ultraviolet spectra of the decomposition product were qualitatively unlike the spectra of BIPH and methacrylonitrile. In isooctane there was a maximum at 273 and there were shoulders at 425 and 475 mμ.

A mass spectrum taken of the volatile fragments formed on heating the adduct was not identical with the published spectra[13] of methacrylonitrile, isobutylene, or of a mixture of the two.

The *t*-Butoxy Adduct of Tetra-*t*-butylindophenoxyl. A solution of BIP (0.1527 g, 3.613×10^{-4} mole) and DBPO (0.0523 g, 2.124×10^{-4} mole) in 5 ml of benzene was degassed three times; nitrogen was admitted and the reaction was allowed to proceed at 34° for 10 half-lives. The solvent was removed *in vacuo.* A mass spectrum of the vapor was taken in order to determine whether isobutylene was present. The solvent was frozen when the sample was taken, but some benzene was undoutedly present in the sample tube. The mass spectrum obtained was not similar to the published one for isobutylene. The reddish yellow mass was dissolved in pentane and crystallization at −70° attempted. No crystals formed. However, this solution produced orange crystals in a red mother liquor after 24 hr at −20°. The mother liquor and the crystals gave identical infrared spectra. An impurity, 2,6-di-*t*-butylquinonimine, may have been the cause of the red color as well as the small peak at 2.97 μ in the infrared spectrum. The orange crystals melted with decomposition at 137–139°. The melt was pale pink, but darkened rapidly on further heating (or standing at 140°) until it reached a deep wine red. The ultraviolet spectrum in isooctane showed maxima at 285 mμ (ϵ 15,000) and 230 mμ (ϵ 7000).

Anal. Calcd for $C_{32}H_{49}NO_3$: C, 77.53; H, 9.96; N, 2.82. Found: C, 77.03; H, 9.87; N, 3.13.

In a second product study run at 25° for 10 half-lives, no crystals were obtained. The reddish yellow mass in the presence of a small quantity of pentane evolved a gas at room temperature. After no more gas was evolved, 0.127 g of the red mass was dissolved in 15 ml of 95% ethanol and 1 ml of water. Five drops of concentrated sulfuric acid was added and the mixture was allowed to stand overnight. To this solution 0.1274 g of 2,4-dinitrophenylhydrazine in 8 ml of 95% ethanol and 12 drops of concentrated sulfuric acid were then added. After removal of some of the solvent, red crystals of 2,6-di-*t*-butylquinone 2,4-dinitrophenylhydrazone formed, mp 195–197.5° (lit.[14] mp 198–200°). The mixture melting point with an authentic sample of the hydrazone (see below) was 195–197°. Isolation of 0.16 g of the hydrazone was effected; the yield based on two molecules of 2,6-di-*t*-butylquinone expected from one molecule of hydroxytetra-*t*-butylindophenoxyl was 71% of the theoretical. The infrared spectrum of the reaction product and the authentic sample were identical.

Anal. Calcd for $C_{20}H_{24}N_4O_5$: C, 59.99; H, 6.04. Found: C, 60.57; H, 6.31.

The method of preparation of 2,6-di-*t*-butylquinone was adapted from the procedure of Müller, Ley, and Schmidhuber.[15] To 3.7 g of 2,6-di-*t*-butyl-4-methoxyphenol (0.0157 mole) in 100 ml of glacial acetic acid was added dropwise 100 ml of concentrated nitric acid. The mixture was warmed to 50° and allowed to cool. As the reaction was exothermic, the temperature rose spontaneously to 56° before decreasing. When the temperature reached 40°, 700 ml of H_2O was added and a yellow precipitate formed. A crude yield of 2.7 g (0.0123 mole, 78%) was obtained. After recrystallization from methanol, the yellow crystals melted at 65.5–67° (lit. mp 66–68°,[15] 67°,[10] 66.5–68°,[11] 68°[12]). The infrared spectrum exhibited bands at 6.96 and 6.28 μ.

The 2,4-dinitrophenylhydrazone derivative was prepared according to the method of Metro.[14] A red solid crystallized from solution almost immediately in 86% yield (0.30 g, 7.491×10^{-4} mole), mp 195–199° (lit.[14] mp 198–200°). The infrared spectrum showed a carbonyl band at 6.21 μ.

The kinetic runs and determination of cage effect were done as described by Bartlett and Funahashi.[2] In all runs the absorbance was followed at both 770 and 625 mμ.

A correction was made for absorption by the products. In most cases, the product absorption was less than 1% of that of the starting materials; therefore, the correction was negligible. Since the products were formed in a pseudo-zero-order reaction, the absorption correction was linear with time.

Competitive Experiments. Aliquots of both galvinoxyl and tetra-*t*-butylindophenoxyl solutions were added to a known quantity of initiator. The ratio of scavenger to initiator was such that a run took about 40 to 120 min.

The absorbance readings were corrected in the same manner as reported for the cage effect determinations when the product absorption amounted to less than 2% of the initial inhibitor absorption. Since the extinction coefficients at both 770 and 625 mμ had been determined, the concentration of each scavenger could be found at any time with the aid of the following equations. For the runs at 62° in benzene

$$[\mathrm{BIP}\cdot] = 0.000938(A_{770})_{\mathrm{corr}} - 0.001739(A_{625})_{\mathrm{corr}} \quad (1)$$

$$[\mathrm{G}\cdot] = 0.005917(A_{625})_{\mathrm{corr}} - 0.001367(A_{770})_{\mathrm{corr}} \quad (2)$$

and for runs at 15, 25, or 34° in benzene

$$[\mathrm{BIP}\cdot] = 0.000949(A_{770})_{\mathrm{corr}} - 0.001815(A_{625})_{\mathrm{corr}} \quad (3)$$

$$[\mathrm{G}\cdot] = 0.005618(A_{625})_{\mathrm{corr}} - 0.001299(A_{770})_{\mathrm{corr}} \quad (4)$$

Similarly for the competitive runs in carbon tetrachloride at 62°

$$[\mathrm{BIP}\cdot] = 0.000874(A_{770})_{\mathrm{corr}} - 0.001452(A_{625})_{\mathrm{corr}} \quad (5)$$

$$[\mathrm{G}\cdot] = 0.004339(A_{625})_{\mathrm{corr}} - 0.000926(A_{770})_{\mathrm{corr}} \quad (6)$$

and for those at 15, 25, or 34°, followed on a different, separately calibrated Beckman DU spectrophotometer

$$[\mathrm{BIP}\cdot] = 0.001016(A_{770})_{\mathrm{corr}} - 0.002151(A_{625})_{\mathrm{corr}} \quad (7)$$

$$[\mathrm{G}\cdot] = 0.006727(A_{625})_{\mathrm{corr}} - 0.001408(A_{770})_{\mathrm{corr}} \quad (8)$$

Values for the absorbance (A) were read from a graph (40 × 50 cm) of absorbance *vs.* time where the best curves had been drawn through the points at both 770 and 625 mμ. The BIP· and G· concentrations were determined at regular time intervals and a log–log plot made of their concentrations. From the slope of the line $k_{\mathrm{BIP}}/k_{\mathrm{G}}$ was determined.

It was not feasible to do competitive experiments with benzhydryl radical due to decomposition of the benzhydryl–tetra-*t*-butylindophenoxyl adduct.

Tetra-*t*-butylindophenol as a Radical Scavenger. The *t*-Butoxy Radical. Solutions of DBPO and BIPH were made up so that the peroxyoxalate was present in 8- to 15-fold excess. The absorbance at 770 mμ was observed as these solutions decomposed. From its extinction coefficient, the concentration of BIP· was determined at various times. A linear absorbance correction was applied in order to take account of the absorption of product, BIP–O-*t*-Bu, in relation to the absorption of BIPH at 770 mμ.

The concentrations of tetra-*t*-butylindophenol and tetra-*t*-butylindophenoxyl were calculated at various times. Two evaluations of the rate ratio k_2/k_1 were made from each run. The first or "peak" value was determined from the ratio [BIPH]/[BIP·] at the middle of the absorption maximum. The second assessment was calculated from the value of [BIPH]/[BIP·] during the portion of the run where [BIP·] decreased linearly with time. In each run the values obtained by the two methods agreed within experimental error.

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(13) Manufacturing Chemists Association Research Project, Mass Spectral Data, June 30, 1960, No. 104 (methacrylonitrile); American Petroleum Institute Research Projection 44, Mass Spectral Data, Vol. 1, No. 28, Oct 31, 1947 (isobutylene).

(14) S. J. Metro, *J. Am. Chem. Soc.*, 77, 2901 (1955).

(15) E. Müller, K. Ley, and W. Schmidhuber, *Chem. Ber.*, **89**, 1738 (1956).

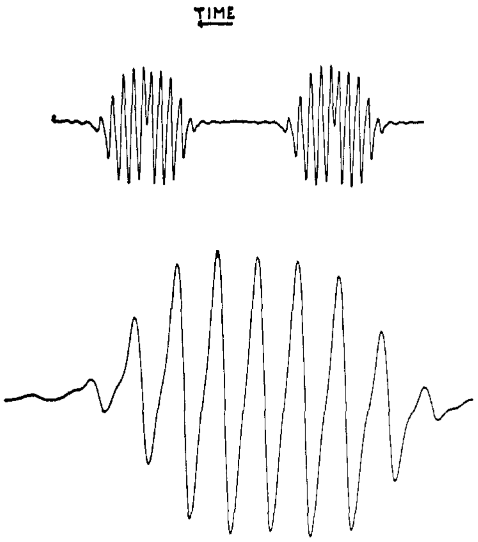

Figure 4. The upper curve represents reaction of tetra-*t*-butylindophenol with di-*t*-butylperoxyoxalate observed by esr. At regular intervals the spectrum was scanned, the scan being reversed at the midpoint. The lower curve represents the esr spectrum of tetra-*t*-butylindophenoxyl.

In order to obtain the difference in activation parameters between abstraction and addition the course of the reaction was followed at 25.4, 34.1, and 35.7°. In order to obtain the rate of DBPO decomposition at each of these temperatures, the rate of disappearance of [BIP] in the presence of a known amount of DBPO was followed on the Beckman DU spectrophotometer. The activation parameters obtained from rates at these temperatures were $\Delta H^* = 25.8 \pm 0.1$ kcal and $\Delta S^* = 4.7 \pm 2.2$ eu; these agree well with those obtained by Bartlett, Benzing, and Pincock[7] ($\Delta H^* = 25.5$ kcal and $\Delta S^* = 5.1$ eu). At 43.7°, the reaction proceeded so fast that thermal equilibrium was not reached. Not surprisingly, the values of k_2/k_1 over this temperature interval changed so little that no $\Delta\Delta H^*$ could be estimated.

Evaluation of the deuterium isotope effect for this system was complicated by the fact that the deuterio-hindered phenols are known to exchange deuterium with hydrogen in any stray moisture present in the solvent.[16] It was found that a benzene solution of BIPH in the presence of D_2O exchanged hydrogen for deuterium in less than 9 min as evidenced by the absence of an OH band (2.80 μ) and the presence of an OD band (3.80 μ) in the infrared spectrum. The spectrum of the deuterium oxide saturated benzene solution was taken in i.r. Trans cells (Connecticut Instrument Corporation, Wilton, Conn.). However, when a benzene solution containing a known amount of BIPH was allowed to exchange, then DBPO was dissolved in an aliquot, and the solution transferred to the apparatus for degassing and kinetics, some exchange with atmospheric moisture took place. This result is evidenced by two facts. First, the isotope effect obtained (about 1.5) varied inversely with the humidity of the day, and second, the tetra-*t*-butylindophenoxyl concentration was not linear with time during the latter part of the reaction.

Various methods were then tried in order to obtain a value of k_H/k_D. The procedure which was adopted gave results independent of humidity and almost linear in [BIP·] with time. The apparatus containing approximately 0.2 g of magnesium sulfate in the cuvette was placed in the oven overnight and was allowed to cool for 10 min before use. The DBPO, which was stored at −20°, was allowed to stand in a closed container at room temperature before weighing at least 10 min to be sure that no water condensed into it. A BIPH solution in 25 ml of benzene which had been exchanged three times with 5-ml portions of deuterium oxide was used as the source of BIPD. A 5-ml aliquot of the BIPD solution was used to dissolve the DBPO which had been weighed out. One milliliter of deuterium oxide was added, the solution was swirled for about 1 min, and the benzene layer was decanted into the degassing part of the apparatus. One additional milliliter of deuterium oxide was added to this solution. The heterogeneous mixture was degassed three times in the usual fashion. Efforts were made to keep the mixture from bumping into the cuvette portion of the apparatus; these were not generally successful. The benzene solution was then decanted into the cuvette, where the emulsion was broken by the magnesium sulfate, and the reaction was followed at 770 mμ. A peak value of k_1/k_2 could not be obtained because the absorbance of the mixture never passed through a maximum. The correction for product absorption was the same as in the BIPH case. A blank run, BIPH and DBPO degassed in the presence of 1 ml of H_2O with about 0.2 g of magnesium sulfate in the cuvette, showed that neither water nor magnesium sulfate interfered with the course of the reaction. It was also shown that DBPO did not partition itself between the benzene and water layers. After shaking a benzene solution of DBPO with water for 1 min, only the benzene layer gave a positive potassium iodide test.

Table V shows the results of the deuterio-tetra-*t*-butylindophenol experiments.

A degassed solution of BIPH and DBPO in a sealed nmr tube was allowed to decompose in the probe of the electron spin resonance spectrometer. The scanning adjustor on the machine had been set so that half of the tetra-*t*-butylindophenoxyl spectrum was recorded, the direction of the scan was reversed, and half of the spectrum was, again recorded. This process was repeated until a signal could no longer be observed. Figure 4 shows a portion of the spectrum observed during the reaction as well as the spectrum of tetra-*t*-butylindophenoxyl.

Hydrogen Transfers between Radicals and Radical-Yielding Molecules. Galvinoxyl and Tetra-*t*-butylindophenol. Since tetra-*t*-butylindophenol reacted so rapidly with galvinoxyl, a rate constant for the reaction could not be obtained. The rate constant was shown to be greater than 200 l. mole^{-1} sec^{-1}. This value is in keeping with the rate constant assigned to the tri-*t*-butylphenol–tri-*t*-butylphenoxy radical exchange.[17]

The reaction mixtures, containing 5-ml aliquots of G· and BIPH solutions, were not degassed due to the rapidity of the reaction. The solutions were mixed in an erlenmeyer flask at zero time; the combined solution was poured into the cuvette portion of the apparatus and absorbance at 770 mμ observed on the Beckman DU. The absorbance was always constant and corresponded to an equilibrium mixture of BIP·, G·, GH, and BIPH.

The concentrations of the four components may be determined from the absorbance of the final solution with the aid of the following equations, since BIPH and GH absorptions were less than 1% of those of their respective radicals.

$$[\mathrm{BIP}\cdot]_{\mathrm{final}} = 0.000949(A_{770})_{\mathrm{corr}} - 0.001815(A_{625})_{\mathrm{corr}} \quad (9)$$

$$[\mathrm{G}\cdot]_{\mathrm{final}} = 0.005618A(_{625})_{\mathrm{corr}} - 0.001299(A_{770})_{\mathrm{corr}} \quad (10)$$

$$[\mathrm{BIPH}]_{\mathrm{final}} = [\mathrm{BIPH}]_{\mathrm{initial}} - [\mathrm{BIP}\cdot]_{\mathrm{final}} \quad (11)$$

$$[\mathrm{GH}]_{\mathrm{final}} = [\mathrm{BIP}\cdot]_{\mathrm{final}} \quad (12)$$

The equation

$$[\mathrm{GH}]_{\mathrm{final}} = [\mathrm{G}\cdot]_{\mathrm{initial}} - [\mathrm{G}\cdot]_{\mathrm{final}} \quad (13)$$

should also hold at equilibrium. However, it was found that the value of [GH] determined with eq 12 differed from that determined with eq 13. This deviation was generally less than 3%. Equation 12 was chosen to calculate [GH] rather than eq 13 because $[\mathrm{BIP}\cdot]_{\mathrm{final}}$ is known with greater accuracy than $[\mathrm{G}\cdot]_{\mathrm{final}}$. The error in the final tetra-*t*-butylindophenoxyl concentration is smaller than in the galvinoxyl concentration since the extinction coefficients of the former are larger. Table VI summarizes the results for the determination of the equilibrium constant.

In order to have a check on the equilibrium constant, the equilibrium was approached from both directions. Five-milliliter aliquots of GH and BIP· solutions were mixed and the absorbance of the resulting mixture observed at 770 and 625 mμ. Equations 9–11 and 14 were used in the calculation of the equilibrium constant.

$$[\mathrm{BIPH}]_{\mathrm{final}} = [\mathrm{G}\cdot]_{\mathrm{final}} \quad (14)$$

The results obtained employing this alternate approach are recorded in Table VII.

A 1% change in the absorbance at 770 mμ results in a 15% change in *K*. As readings on the Beckman DU are reproducible within

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(16) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 40, 1851 (1962).

(17) R. W. Kreilick and S. I. Weissman, *J. Am. Chem. Soc.*, 84, 306 (1962).

1 to 2%, the uncertainty in the resulting K is about 20 to 25%. The results obtained by approaching the equilibrium from both directions are then in reasonable accord.

Diphenylpicrylhydrazyl and Tetra-*t*-butylindophenol. Unlike the reaction of BIPH with G·, the reaction of BIPH with DPPH proceeds at a measurable rate. The extinction coefficients of DPPH were measured at 770 and 625 mμ and found to be 1082 and 5536, respectively. DPPH was found to adhere to Beer's law at the wavelengths used and over the concentration range employed. Solutions of BIP· and DPPH were shown to have additive absorbances and to be stable for over 1200 sec in air at 25.4°. The extinction coefficient of 2,2-diphenylpicrylhydrazine (DPPHH) was found to be 0.59 and 1.27% of that of DPPH at 770 and 625 mμ, respectively. Since the error of the method was greater than this, no correction was made. From the values of the extinction coefficients of DPPH and BIP· at 770 and 625 mμ the equations to determine the concentrations of the two colored species were calculated.

$$[\mathrm{BIP}\cdot] = 0.000554(A_{770})_{\mathrm{corr}} - 0.0001802(A_{625})_{\mathrm{corr}} \quad (15)$$

$$[\mathrm{DPPH}] = 0.000189(A_{625})_{\mathrm{corr}} - 0.0000438(A_{770})_{\mathrm{corr}} \quad (16)$$

Because of the speed of the reaction, the solutions were not degassed. The optical densities at each wavelength were read into the microphone of the tape recorder;[18] zero time was taken as the time of mixing. Rate constants at 25° in three runs were 12.6, 12.7, and 12.4 l./mole sec.

Like the galvinoxyl–tetra-*t*-butylindophenol reaction, the reaction of DPPH and BIPH does not go to completion but to an equilibrium mixture of DPPH, BIP·, DPPHH, and BIPH. In order to obtain the equilibrium constant for the system, the absorbances of equilibrium mixtures were observed. Equations 15 and 16 were used in conjunction with the appropriate difference equations to determine the concentrations of the four components at equilibrium.

Table VIII shows the equilibrium constant obtained for the reaction utilizing approach from both directions. A 1% change in the absorbance at 770 mμ results in a 3–4% change in K.

Table VIII. Equilibrium Constant for BIPH + DPPH $\overset{K}{\rightleftharpoons}$ DPPHH + BIP·

$[\mathrm{R}\cdot]_{\mathrm{initial}}$, mole/l. × 10^4	$[\mathrm{RH}]_{\mathrm{initial}}$, mole/l. × 10^4	$(A_{625})_{\mathrm{corr}}$[a]	$(A_{770})_{\mathrm{corr}}$[a]	K
4.687[b]	29.96	0.894	0.726	41.5
4.386[b]	21.07	0.793	0.730	45.6
4.016[c]	4.643	0.531	0.821	38.4

[a] $A_{\mathrm{corr}} = A_{\mathrm{soln}} - A_{\mathrm{C_6H_6\ vs.\ C_6H_6}}$. [b] [R·] = [BIP·]; [RH] = [DPPHH]. [c] [R·] = [DPPH]; [RH] = [BIPH].

Kinetic Treatment of BIPH–BIP Competition. Because of the high efficiency of production and scavenging of *t*-butoxy radicals, it was assumed that the initial concentration $[\mathrm{BIPH}]_0$ is equal to the total decline in DBPO down to its concentration $[\mathrm{DBPO}]_f$ at the intersection of the [BIP·] line with the time axis. This assumption afforded a direct determination of the first-order rate constant for DBPO decomposition under the conditions of each competition experiment. At each time the BIP· concentration is known by the absorbancy measurements, and the DBPO concentration is calculated from the initial concentration and the rate constant. The concentration [BIPH] is then known from the relationship

$$[\mathrm{BIPH}] = [\mathrm{DBPO}] - [\mathrm{DBPO}]_f - 0.5[\mathrm{BIP}\cdot]$$

Thus there are enough experimental measurements to determine the ratio $x = [\mathrm{BIP}\cdot]/\mathrm{BIPH}]$ for each point on the curve of Figure 3.

The chemical equations

$$\mathrm{DBPO} \xrightarrow{k_0} 2\mathrm{CO_2} + 2t\text{-}\mathrm{BuO}\cdot$$

$$\mathrm{BIPH} + t\text{-}\mathrm{BuO}\cdot \xrightarrow{k_1} t\text{-}\mathrm{BuOH} + \mathrm{BIP}\cdot$$

$$\mathrm{BIP}\cdot + t\text{-}\mathrm{BuO}\cdot \xrightarrow{k_2} t\text{-}\mathrm{BuOBIP}$$

lead to the competition equation

$$\frac{d[\mathrm{BIP}\cdot]}{d[\mathrm{BIPH}]} = \frac{k_2[\mathrm{BIP}\cdot]}{k_1[\mathrm{BIPH}]} - 1 = \frac{k_2}{k_1}x - 1 \quad (17)$$

Replacement of d[BIP·] by its equivalent, d[BIP·] = xd[BIPH] + [BIPH]dx, leads to the integrable equation

$$\frac{d[\mathrm{BIPH}]}{[\mathrm{BIPH}]} = \frac{dx}{((k_2/k_1) - 1)x - 1}$$

The integrated form is

$$\ln \frac{\dfrac{1}{(k_2/k_1) - 1} - x_0}{\dfrac{1}{(k_2/k_1) - 1} - x} = ((k_2/k_1) - 1) \ln \frac{[\mathrm{BIPH}]_0}{[\mathrm{BIPH}]} \quad (18)$$

Two independent determinations of k_2/k_1 can be made, one from the point where [BIP·] reaches a maximum and the other from the final slope of the plot of [BIP·] *vs.* t. From eq 17 it is evident that where d[BIP·]/d[BIPH] changes sign, k_2/k_1 = [BIPH]/[BIP·]. These values appear in column 4 of Table IV.

Now, inspection of eq 18 shows that if $(k_2/k_1) - 1$ is of the order of 6, as it is, the denominator of the left-hand member must approach zero rapidly so that for a considerable time during the latter part of the reaction x is indistinguishable from $1/[(k_2/k_1) - 1]$. In fact x does become constant long before the end of a run, which results in the long linear decline of [BIP·] seen in Figure 3. The final limiting values of x lead to the figures in column 5 of Table IV, by the equation

$$k_2/k_1 = 1 + ([\mathrm{BIPH}]/[\mathrm{BIP}\cdot])_f$$

Acknowledgment. This research was supported by the National Institutes of Health and by the Petroleum Research Fund of the American Chemical Society.

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(18) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).