

TABLE VI
 OVERLAP INTEGRALS

Overlap Integral	Expression	Value
$S(\chi_1, \chi_4^a)$	$(\sqrt{3}/4)S(\text{pxa,pxb}) + (\sqrt{3}/4)S(\text{pya,pyb})$	0.225
$S(\chi_1, \phi_3\text{-sp}^2)$	$(\sqrt{3}/4)S(\text{sa,pxb}) + (3\sqrt{3}/8)S(\text{pxa,pxb}) - (\sqrt{3}/8)S(\text{pya,pyb})$.330
$S(\chi_1, \phi_2\text{-sp}^2)$	$(1/2)S(\text{sa,pxb}) + (\sqrt{3}/2\sqrt{2})S(\text{pxa,pxb}) - (1/2\sqrt{6})S(\text{pya,pyb})$.344
$S(\chi_1, \chi_2)$.191
$S(\text{sp}^2\text{-}\sigma, \text{sp}^3\text{-}\sigma; 1.54 \text{ \AA.})$.646
$S(\text{sp}^2\text{-}\sigma, \text{sp}^2\text{-}\sigma; 1.52 \text{ \AA.})$.673

^a χ_4 here refers only to cases B, D, E.

Species XXIIID.—Similar use of pseudosymmetry was made. Eigenvalues for MO's antisymmetric with respect to the plane employed were $X = -1, -1, 1, 1$. Those for symmetric MO's were obtained from the IBM 650 solution of the 11 by 11 determinant remaining: $X = -2.491, -2.138, -1.906, -1.316, -0.9581, 0.289, 0.924, 1.475, 1.599, 2.053$ and 2.471 .

Species XXIIIE.—Eigenvalues of orbitals symmetric with respect to the species' plane of symmetry were at $X = -2.727, -2.143, -1.880, -1.346, -1.000, -0.936, +0.2549, +0.897, +1.000, +1.511, +1.644, +2.086, +2.639$. Energies of antisymmetric orbitals were found

as follows: one at -2.000 , three at -1.000 , three at $+1.000$ and one at $+2.000$.

The Non-bridged Species.—The MO's used here were merely the zero level atomic p-orbital at carbon 2, the molecular orbitals of the unconjugated phenyl groups, as present and the bonding orbital of the σ -bond bearing the group about to migrate.

Acknowledgment.—Financial support of these investigations by the Research Corporation is gratefully acknowledged.

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Benzoyl Peroxide as an Initiator for Hydrocarbon Oxidation

BY GEORGE S. HAMMOND AND UMA SANKAR NANDI

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The efficiency of benzoyl peroxide as an initiator for tetralin oxidation is anomalously low and the peroxide is essentially no initiator for cumene oxidation. This erratic behavior is somewhat solvent-dependent. The evidence suggests strongly that one of the radicals derived from the peroxide (benzoyloxy, phenyl or an adduct of phenyl to an aromatic nucleus) is incapable of reaction with oxygen and sufficiently long-lived to dominate in the chain-termination step.

For some time we have been using hydrocarbon oxidation as a means of measuring the efficiency of free radical production during the decomposition of azonitriles and ketenimines.¹⁻⁵ We considered it worthwhile to investigate benzoyl peroxide by the same technique with the hope that the study might shed new light on the idiosyncracies in the decomposition of the peroxide⁶ and on the chemistry of the fragments produced in the decomposition. The results, which show that the behavior of the peroxide as an initiator depends strongly on the nature of the substrate and solvent, are reported in this paper.

Results and Discussion

When tetralin was used as a substrate no alarming results were disclosed. Efficiency measurements were made by measuring the induction periods produced by known amounts of 2,6-di-*t*-butyl-*p*-cresol (DBC), an antioxidant which is known¹ to stop two oxidation chains per molecule.

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

(2) G. S. Hammond, J. N. Sen and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

(3) G. S. Hammond, O. D. Trapp, R. T. Keys and D. L. Neff, *ibid.*, **81**, 4878 (1959).

(4) C.-H. S. Wu, G. S. Hammond and J. M. Wright, *ibid.*, **82**, 5386 (1960).

(5) G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin and R. T. Keys, *ibid.*, **82**, 5394 (1960).

(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 474.

Clearly defined breaks marked the end of the inhibition periods. The rates of decomposition of benzoyl peroxide were measured in the presence of nitrogen and the antioxidant, using iodometric assay for residual peroxide. A plot of the data for typical oxidation runs with added inhibitor is shown in Fig. 1, and the data are summarized in Tables I and II. Since the peroxide decomposition rates are independent of concentration, it appears that the scavenger is effective in eliminating induced decomposition.⁷⁻⁹

TABLE I

Solvent	RATE OF DECOMPOSITION OF BENZOYL PEROXIDE IN THE PRESENCE OF 2,6-DI- <i>t</i> -BUTYL- <i>p</i> -CRESOL AT 70° UNDER NITROGEN	
	Init. concn. of Bz_2O_2 , moles l. ⁻¹	$k_d \times 10^4$, sec. ⁻¹
Benzene	0.25	1.18
Benzene	.50	1.17
Acetonitrile	.25	1.76
Chlorobenzene	.25	1.35
Dioxane	.25	1.30

Table II includes the apparent efficiency factors α calculated using the measured peroxide decomposition rates and the data for induction periods.

(7) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

(8) G. S. Hammond, *ibid.*, **72**, 3737 (1950).

(9) C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

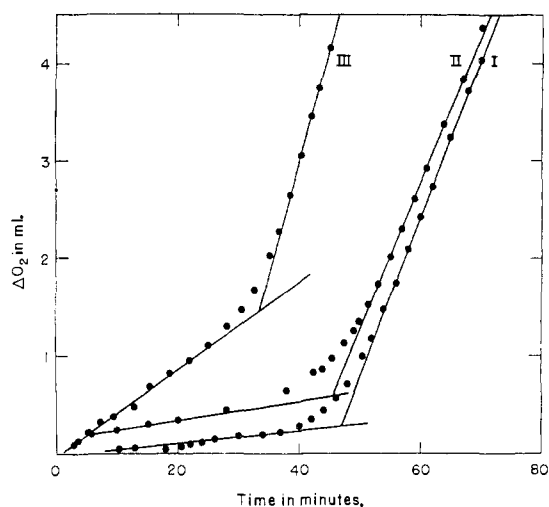


Fig. 1.—Benzoyl peroxide initiated oxidation of tetralin in different solvents in the presence of 2,6-di-*t*-butyl-*p*-cresol (DBC) at 70°: I, benzene; II, chlorobenzene; III nitrobenzene (Bz_2O_2 , 8.33×10^{-3} molar; DBC = 1.66×10^{-3} molar).

Most of the values are surprisingly low. Since it was possible to scavenge 90% or more of the benzoyloxy radicals from benzoyl peroxide with iodine in benzene⁸ or carbon tetrachloride,¹⁰ we expected efficiency factors close to unity.

TABLE II
TETRALIN OXIDATION RATES AND INHIBITION PERIODS PRODUCED BY 2,6-DI-*t*-BUTYL-*p*-CRESOL AT 70°

Solvent ^a	Initiator ^b	$R_0 \times 10^6$, moles l^{-1} sec. ^{-1c}	Inhi- bition period, min. ^d	Effi- ciency factor, a
Benzene	Bz_2O_2	2.09	47.5	0.60
Chlorobenzene	Bz_2O_2	2.39	45.0	0.55
Chlorobenzene	ABN ^e	4.62
Chlorobenzene	ABN + Bz_2O_2 ^f	5.15
Nitrobenzene	Bz_2O_2	3.10	33.8	0.87
Dioxane	Bz_2O_2	2.46	35.0	.74
Acetonitrile	Bz_2O_2	4.93	32.0	.63

^a Tetralin concentration, 2.448 moles l^{-1} . ^b Initiator concentration, 8.33×10^{-2} mole l^{-1} except in experiment with two initiators. ^c Rate of uninhibited oxidation. ^d Inhibitor concentration, 1.67×10^{-3} mole l^{-1} except in experiments with ABN. ^e Azoisobutyronitrile. ^f Both initiators, 8.33×10^{-2} mole l^{-1} .

Study of the rate of uninhibited oxidation provides an alternative approach to estimation of efficiency factors.¹¹ Equation 1 gives the rate law governing the consumption of oxygen in an initiated oxidation.¹²

$$-\frac{dO_2}{dt} = R_0 = 2ak_d[In] + \frac{k_3[RH](2ak_d[In])^{1/2}}{k_t^{1/2}} \quad (1)$$

where

k_d = rate constant for decomposition of the initiator, In
 k_3 = rate constant for the reaction $RO_2 \cdot + RH \rightarrow RO_2H + R \cdot$
 k_t = rate constant for normal chain termination by reaction of two $RO_2 \cdot$

(10) G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950).

(11) G. A. Russell, *ibid.*, **78**, 1044 (1956).

(12) C. E. Boozer, G. S. Hammond, C. E. Hamilton and C. Peterson, *ibid.*, **77**, 3380 (1955).

The first term represents oxidation of initiator fragments and is negligible in comparison with the second term; therefore, the observed oxidation rates may be treated by the approximation of eq 2.

$$\frac{R_0}{[RH](2k_d[In])^{1/2}} = \frac{k_3a^{1/2}}{k_t^{1/2}} \quad (2)$$

Table III lists the values calculated for $a^{1/2}k_3/k_t^{1/2}$ in various solvents using benzoyl peroxide as the initiator. Also included are the values of $k_3/k_t^{1/2}$ calculated from measurement of oxidation rates using azoisobutyronitrile (ABN) as an initiator. We believe that the decomposition of ABN is now well enough understood⁵ to allow assignment of a factors for that initiator with confidence. The values of $k_3a^{1/2}/k_t^{1/2}$, calculated from the data obtained with benzoyl peroxide as the initiator, are smaller than the values of $k_3/k_t^{1/2}$. The last column of the table shows the values of a for benzoyl peroxide calculated from the data for rate of oxidation. Because of the square root relationship between R_0 and a , this is a less accurate method for measurement of a than that based upon measurement of induction periods in the presence of inhibitors. However, the values of efficiency factors obtained by the two methods agree reasonably well.

TABLE III
CORRELATION OF RATES OF TETRALIN OXIDATION IN VARIOUS SOLVENTS AT 70°

Solvent	$R_0 \times 10^6$, moles l^{-1} sec. ⁻¹	$2k_d[Bz_2O_2]$ $\times 10^7$, moles l^{-1} sec. ⁻¹	$\frac{R_0/(2k_d[Bz_2O_2])^{1/2}}{[RH]} \times 10^3$, moles ^{-1/2} sec. ^{-1/2}	$\frac{k_3/k_t^{1/2}}{\times 10^3}$, moles ^{-1/2} sec. ^{-1/2}	a
Benzene	2.10	19.66	6.28	7.53	0.68
Chlorobenzene	2.39	22.50	6.52	8.63	.57
Nitrobenzene	3.10	19.66	9.28	9.82	.89
Acetonitrile	4.94	29.33	7.60	9.77	.61
Dioxane	2.46	21.50	6.85	7.93	.75

We also have investigated the behavior of the system when two initiators, ABN and benzoyl peroxide, are present at the same time. The relationship between the rate with a mixture of initiators and the rates of reactions initiated by the two initiators individually is given by eq. 3

$$R_0^{2(1,2)} = \frac{k_3^2[RH]^2}{k_t} (a_1k_{d(1)}[In_1] + a_2k_{d(2)}[In_2]) = R_0^{2(1)} + R_0^{2(2)} \quad (3)$$

The oxidation rate in the presence of 8.33×10^{-2} mole l^{-1} benzoyl peroxide in chlorobenzene is 2.39×10^{-6} mole l^{-1} sec.⁻¹ ($R_0^{2(1)} = 5.71 \times 10^{-10}$ mole² l^{-2} sec.⁻²); the rate in the presence of the same concentration of ABN was 4.62×10^{-6} mole l^{-1} sec.⁻¹ ($R_0^{2(2)} = 21.34 \times 10^{-10}$ mole² l^{-2} sec.⁻²); and the rate with both initiators present at 8.33×10^{-2} molar was 5.15×10^{-6} mole l^{-1} sec.⁻¹ ($R_0^{2(1,2)} = 26.52 \times 10^{-10}$ mole² l^{-2} sec.⁻²). The sum, $R_0^{2(1)} + R_0^{2(2)}$ is 27.05×10^{-10} mole² l^{-2} sec.⁻². The good agreement between observed and predicted rates in the experiment with two initiators shows that the low efficiency of benzoyl peroxide is not associated with an inhibitory reaction of the peroxide itself.

Our suspicion that benzoyl peroxide is in some way peculiar in its behavior as an initiator was

shown surely to be correct when cumene was used as a substrate. The general character of the results is consistent with the report by Russell¹¹ that the rate of oxidation of cumene with no added solvent is unusually slow when benzoyl peroxide is used as an initiator. We have found that in benzene, chlorobenzene and nitrobenzene solutions the oxidation rates are almost negligible. Rates were appreciably higher, but still smaller than tetralin oxidation rates, in acetonitrile solution or in pure cumene. Since tetralin and cumene oxidation rates differ by only a factor of 2.5 when ABN is used as the initiator,¹³ this observation shows the source of the anomalies must be found specifically in the chemistry of the initiation process. Table IV shows data for apparent rates of cumene oxidation. Because the oxidation rates are very low, it is not feasible to attempt to estimate the efficiency of benzoyl peroxide as an initiator for cumene oxidation by the inhibitor method.

TABLE IV
RATES OF CUMENE OXIDATION INITIATED BY BENZOYL PEROXIDE AT 70°

Solvent ^a	Initiator ^b	$R_0 \times 10^3$, moles l. ⁻¹ sec. ⁻¹
Benzene	Bz ₂ O ₂	0.57
Chlorobenzene	Bz ₂ O ₂	1.19
Chlorobenzene	ABN	18.47
Chlorobenzene	ABN + Bz ₂ O ₂ ^c	16.19
Nitrobenzene	Bz ₂ O ₂	0.93
Acetonitrile	Bz ₂ O ₂	3.32
None	Bz ₂ O ₂	3.37

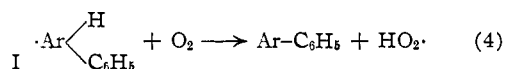
^a Concentration of cumene = 2.39 moles l.⁻¹ except in run in pure cumene. ^b Initiator concentration = 8.33×10^{-2} mole l.⁻¹ except as noted. ^c Both initiators present at concentration of 8.33×10^{-2} mole l.⁻¹.

In contrast to the behavior with tetralin, benzoyl peroxide reduces the rate of ABN-initiated cumene oxidation. One could attribute this behavior to some conventional inhibitory interaction between RO₂ and benzoyl peroxide, but such a hypothesis is unattractive for two reasons: First, it would be hard to account for the fact that peroxy radicals derived from cumene could undergo such a reaction while those from tetralin do not; second, it would be surprising if electron-seeking radicals such as RO₂ proved to be reactive toward an electron-poor substrate such as the peroxide. An alternate possibility, reaction of R· with peroxide, seems most unlikely since even very reactive scavengers for carbon radicals, such as chloranil and trinitrobenzene, show no ability to compete with oxygen for cumyl or tetralyl radicals.¹ Furthermore, the inhibitory reaction would have to be different from that assumed in induced decomposition of peroxide⁷ and in the cleavage of the peroxide by triphenylmethyl radicals.¹⁴

If we tentatively discard hypotheses that radicals react with benzoyl peroxide, we are left with only two alternatives for explaining the unexpected values of the factor $a^{1/2}k_3/k_t^{1/2}$. Since k_3 has nothing to do with the initiator, it cannot be invoked to account for the difference between ABN and

benzoyl peroxide as initiators. One can assume that the values of a are very much lower in a solvent that is one-third cumene than in a similar solvent that is one-third tetralin. Such a curious solvent dependence of the magnitude of the cage effect is not expected and has no precedent in the work on cage effects in the decomposition of azonitriles and ketenimines.⁵ The only remaining possibility for a solution to the problem is wide variation in the values of k_t . Such variation can occur only if the mechanism of chain termination is changed. This requires that RO₂ be destroyed by some radical, or other product, resulting by decomposition of the initiator. This, in turn, means that some radical probably is produced which cannot react rapidly with either oxygen or the oxidation substrate. The three possible candidates are benzoyloxy radicals, phenyl radicals and radicals produced by addition of phenyl to aromatic nuclei. It is unlikely that benzoyloxy will meet the requirements since it is known to decarboxylate rapidly if it is not scavenged promptly. Furthermore, benzoyloxy should have a high aptitude for abstraction of the labile hydrogen atoms of cumene or tetralin.

It seems ridiculous to suppose that phenyl radicals do not react with oxygen to form C₆H₅O₂·; however, the fact remains that no such reaction has ever been observed. In fact, Kochi reported¹⁵ that phenyl radicals produced in the presence of oxygen from N-nitrosoacetanilide or by oxidation of benzenediazonium ion added to acrylonitrile or cinnamic acid to give adducts which were in turn oxidized.¹⁶ At the present time we are unable to decide whether the blame should be laid on the low reactivity of phenyl toward oxygen or on high reactivity of phenyl in addition to the aromatic nuclei. If the latter is the case, we must conclude that radicals such as I do not react with oxygen. We would be surprised if this were the case since reaction 4 looks like a very attractive path.



A possible clue to resolution of the problem is found in the fact that cumene does actually oxidize at a significant rate in aliphatic solvents. This implies that initiator radicals may be wasted by reaction with aromatic solvents. Some wastage would still occur in aliphatic solvents or in pure substrate since attack on the aromatic nuclei of the substrates could still occur in competition with abstraction of hydrogen from the side chains. An indication against this view is the fact that the efficiency of benzoyl peroxide as an initiator for tetralin is higher in nitrobenzene than in benzene or chlorobenzene despite the fact that competitive experiments show that nitrobenzene is the most reactive of the three compounds in the aromatic phenylation reaction.¹⁷

(15) J. K. Kochi, *ibid.*, **78**, 4815 (1956); **79**, 2942 (1957).

(16) Prof. Glenn A. Russell has noted, in private communication, that the inability of phenyl radicals to react rapidly with oxygen may be attributable to the fact that they are not good electron donors. Unpublished evidence from his laboratory indicates that even alkyl radicals may be coupled in the presence of oxygen if they bear suitable electron-attracting substituents.

(17) D. H. Hey and G. H. Williams, *Disc. Faraday Soc.*, **14**, 216 (1953).

(13) Unpublished results in this Laboratory.

(14) G. S. Hammond, J. T. Rudesill and F. J. Modic, *J. Am. Chem. Soc.*, **73**, 3929 (1951).

Whatever the new termination process may be, it is not surprising that the anomaly is more important with cumene than with tetralin. Russell¹⁸ showed that the similarity in oxidation rates of tetralin and cumene is due to the fortuitous cancellation of two effects. The rate of hydrogen abstraction from tetralin is much faster than from cumene, but the rate of termination by interaction of pairs of cumyl peroxy radicals is unusually slow. One consequence of these relationships was the fact that small amounts of tetralin retard the oxidation of cumene because the crossed termination reaction between cumyl peroxy and tetralyl peroxy radicals is much faster than the symmetrical termination step involving only cumyl peroxy. It is the tenor of our suggestions that some radical, derived from benzoyl peroxide, is capable of participating in such a fast, crossed termination with cumyl peroxy radicals. Actually, even $C_6H_5O_2\cdot$ would fulfill the kinetic requirements, but we do not regard this possibility very seriously.

We have also studied the absorption of oxygen and the evolution of carbon dioxide in chlorobenzene solutions containing no easily oxidizable hydrocarbon. Samples consisting of 10^{-3} mole of peroxide in 4 ml. of chlorobenzene were heated in the gas apparatus at 70°. Expansion of the gas volume over the solution was linear with time after the first few minutes for the periods of time over which the reaction was monitored (never more than 10% decomposition). For purposes of comparison the changes in gas volume during reaction times of one hour are recorded in Table V. Decomposition under nitro-

TABLE V
GAS EVOLUTION DURING DECOMPOSITION OF BENZOYL PEROXIDE IN CHLOROBENZENE SOLUTION^a

Atmosphere over reaction cell	[DBC] $\times 10^3$, moles l. ⁻¹	Expansion of gas vol., ml.
Oxygen	None	0.18
Nitrogen	None	1.32
Nitrogen	None	1.35
Nitrogen	1.25	0.83
Nitrogen	2.50	.61
Nitrogen	5.50	.43
Nitrogen	19.8	.21
Nitrogen	41.0	.16

^a Each sample contained 10^{-3} mole benzoyl peroxide in 4 ml. of chlorobenzene, and the heating period was 1 hour in each case.

gen yielded 1.32 ml. of gas, presumed to be carbon dioxide. Using the rate constant measured in the presence of an antioxidant, we calculate that 4.7×10^{-5} mole of peroxide should have decomposed by the spontaneous mechanism.¹⁹ The gas evolved is equivalent to 5.9×10^{-5} mole. Some carbon dioxide must also have remained dissolved to bring the concentration in solution to the saturation level. When a similar experiment was carried out under an atmosphere of oxygen, the increase in gas volume was only 0.18 ml. The difference between the two figures, 1.14 ml., should be approximately²⁰

(18) G. A. Russell, *J. Am. Chem. Soc.*, **77**, 4583 (1955).

(19) Some additional decomposition by the induced process will also have occurred.

(20) This procedure will overestimate by some unknown amount the oxygen absorbed since induced decomposition, which produces some carbon dioxide, is inhibited by oxygen.⁷

equal to the amount of oxygen absorbed by radicals. On this basis we calculate that 5.1×10^{-5} mole of oxygen was absorbed, indicating that one mole of oxygen is taken up for every molecule of peroxide decomposed.

It is reasonable to assume that under these conditions radicals are ultimately destroyed by interaction of pairs of peroxy radicals of some kind. Such interactions usually seem to result in the production of oxygen with the net effect that a pair of carbon radicals permanently consumes one mole of oxygen.²¹⁻²³ This, in turn, indicates that the yield of radicals must be about one per mole as was previously inferred from experiments with iodine as a scavenger.⁸ It indicates, furthermore, that the unreactive radicals that are responsible for chain termination in the oxidation experiments will eventually react with oxygen if they are not given something better to do, such as reacting with RO_2 .

A brief study also was made of the effect of di-*t*-butyl-*p*-cresol on the yield of carbon dioxide from the peroxide. Solutions of the peroxide and varying amounts of the antioxidant were heated under nitrogen. The volume of carbon dioxide evolved decreased as the concentration of DBC was increased. When the inhibitor concentration was 1.64×10^{-3} mole per liter, the gas evolved in one hour had decreased to 0.16 ml. as compared with 1.35 ml. in the control run with no added antioxidant. The effect must be due to scavenging of benzoyloxy radicals by the antioxidant, very possibly by a mechanism similar to that previously proposed for the scavenging of peroxy radicals by the same compound.²⁴ Reduction of the carbon dioxide yield to a low level again indicates that most of the benzoyloxy radicals must have a sufficiently long lifetime to permit them to be scavenged; *i.e.*, no large fraction of the radicals produced in the primary process perishes in diffusion controlled (cage) reactions.

Experimental

Materials.—Benzoyl peroxide (Lucidol, reagent grade) was purified further by repeated precipitation from chloroform solution by ligroin; m.p. 104–104.5°. α, α' -Azobisisobutyronitrile (ABN) (Westville Laboratories, recrystallized grade) was recrystallized twice from methanol; m.p. 101–102°. Tetralin (Eastman Kodak Co., practical grade) was washed with concentrated sulfuric acid until the acid layer showed no more coloration and then was washed with distilled water, dried over anhydrous sodium sulfate, and distilled under reduced pressure; b.p. 65–66° at 5 mm. pressure. Cumene (Matheson Coleman, reagent grade) was purified in the same way as tetralin; b.p. 152–153°. Benzene (Baker and Adamson, reagent grade) was given a treatment similar to that of tetralin, dried over calcium chloride, and distilled; b.p. 80°. Chlorobenzene (Matheson Coleman and Bell, white label, reagent grade) was dried over Drierite and distilled; b.p. 130–131°. Acetonitrile (Matheson Coleman and Bell, reagent grade) was dried over Drierite and distilled; b.p. 81–82°. Dioxane (Eastman Kodak Co., practical grade) was purified after the method of Hess and Frahm,²⁵ distilled over sodium in nitrogen atmosphere, and stored out of contact with air; b.p. 101–101.5°. Nitrobenzene (Matheson Coleman, rea-

(21) C. E. Boozer, B. W. Ponder, J. C. Trisler and C. E. Wrightman, *J. Am. Chem. Soc.*, **78**, 1596 (1956).

(22) G. A. Russell, *ibid.*, **79**, 3871 (1957).

(23) H. S. Blanchard, *ibid.*, **81**, 4548 (1959).

(24) G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3244 (1955).

(25) K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).

gent grade) was used without further purification. 2,6-Di-*t*-butyl-*p*-cresol was purified by repeated recrystallization from ethanol; m.p. 69–70°.

Estimation of Benzoyl Peroxide.—Benzoyl peroxide was assayed by the usual iodometric method.

Inhibition Period and Oxidation Rates.—Absorption of

oxygen was followed using the apparatus described earlier.¹ Gas volumes were measured at 70° and 744 mm.

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[CONTRIBUTION NO. 2601 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

The Effect of Cumyl Hydroperoxide on the Behavior of Oxidation Inhibitors

BY GEORGE S. HAMMOND AND UMA SHANKAR NANDI

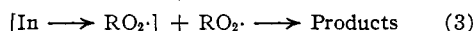
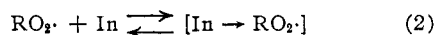
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The nature of the reversible interaction of peroxy radicals with antioxidants has been further investigated. If RO₂ were to equilibrate with inhibitor in a hydrogen abstraction reaction, one would anticipate that the inhibitory efficiency should be decreased by addition of a hydroperoxide. Since no such effect is observed we infer that reversible formation of a molecular complex gives a better account of the facts.

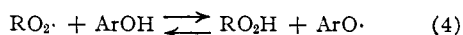
In an earlier paper¹ we reported that the rate of oxidation of tetralin in the presence of weak antioxidants such as phenol or *N*-methylaniline follows the kinetic law of eq. 1.

$$\frac{-dO_2}{dt} = \frac{c[RH][\text{Initiator}]^{1/2}}{[\text{Inhibitor}]^{1/2}} \quad (1)$$

The rate law implies that some reversible interaction occurs between RO₂ and the inhibitors. On the basis of this and other evidence, it was suggested that the antioxidants functioned by virtue of their ability to form charge-transfer complexes with peroxy radicals.



Shortly afterward, Bickel and Kooyman² reported a magnificent study of the rates of oxidation of 9,10-dihydroanthracene in the presence of various phenolic antioxidants. They showed that a wide variety of kinetic laws was observed including the one in eq. 1. They also showed that satisfactory fits to all cases could be based upon the supposition that peroxy radicals abstract hydrogen atoms from the phenols in a step that may or may not be reversible, depending on the structure of the phenol and other variables relating to reaction conditions.



Using this mechanism, which is really that of Bolland and tén Have,³ to explain the rate law of eq. 1 requires that equilibrium be established in reaction 4 with a small equilibrium constant. A test of this hypothesis is readily available since the formulation requires that addition of hydroperoxide should repress the conversion to ArO·, thereby decreasing the potency of the inhibitor.

Results and Discussion

Figure 1 shows the consequences of adding 3.34 × 10⁻² mole per liter of cumyl hydroperoxide to a standard oxidation mixture containing cumene, chlorobenzene, azoisobutyronitrile and phenol at

70°. The fact that the rate of oxygen consumption is slightly lowered by the hydroperoxide is sufficient grounds for elimination of reaction 4 as a reversible step in the mechanism.

Phenol is the most appropriate inhibitor to use in this type of study since the half-order law has been shown to describe the inhibitory action of the compound and because the antioxidant action is weak enough to permit an easily measurable oxidation rate during the induction period. However, experiments have also been done in which cumyl hydroperoxide was added in systems inhibited by *N,N'*-diphenyl-*p*-phenylenediamine and *p*-methoxyphenol, compounds which are more potent antioxidants as judged by the sharpness of inhibition periods. The results are represented in Table I.

TABLE I
EFFECT OF CUMYL HYDROPEROXIDE ON THE INHIBITORY ACTION OF ANTIOXIDANTS IN CUMENE^{a,b,c} OXIDATION AT 70°

Antioxidant	Concn. of cumyl hydroperoxide × 10 ² , mole l. ⁻¹	R ₀ × 10 ⁶ (during induction period), mole l. ⁻¹ sec. ⁻¹	Induction period, minutes
Phenol	Nil	2.97	30.2
	3.34	2.53	29.8
4-Methoxyphenol	Nil	1.10	29.6
	42.0	0.55	32.2
<i>N,N'</i> -Diphenyl- <i>p</i> -phenylenediamine	Nil	4.40	27.0
	1.67	1.98	26.4
	Nil	4.18	27.1
	3.34	1.98	26.0
	42.0	2.11	30.4

^a Cumene, 2.39 mole l.⁻¹; total volume of reaction mixture 6 ml. ^b Oxygen pressure, 744 mm. ^c Azoisobutyronitrile, 8.33 × 10⁻² mole l.⁻¹.

In each case the rate of oxygen absorption was decreased in the presence of the hydroperoxide. As is shown in Fig. 2, addition of hydroperoxide actually increases, by a small amount, the induction period shown by *p*-methoxyphenol.

The small synergistic effect of the hydroperoxide on the antioxidant action is interesting. There are apparently two kinds of effect. In the presence of phenol there is a very small depression of the rate of oxygen uptake during the induction period. In the presence of *p*-methoxyphenol and *N,N'*-diphenyl-

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