reactions 24 to 27. This also accounts for the fact that the quantum yield of CO becomes larger than unity.

It would be of considerable interest to know the quantum yield of the energy transfer. However, no accurate estimate can be made at the present time, mainly because of the difficulty in establishing the quantum yield of process 22 and the number of aldehyde molecules which undergo an internal conversion to the ground state. It can, however, be noted that the quantum yield of ethylene reaches a value of 0.25 at the highest butyraldehyde pressures used in this study. Because the latter value is comparable to the quantum yield of this process in the photolysis of pure butyraldehyde from 2537 (quantum yield = 0.3) to 3130 Å. (quantum yield = 0.165), it may be stated that, at sufficiently high concentrations of *n*-butyraldehyde, the quantum yield of process 21 may reach a value close to unity. This is not surprising in view of the fact that, at 3130 Å., the majority of the acetone molecules excited to the upper singlet state undergo an intersystem crossing to the triplet state.[1]

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[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION, RICHMOND, CALIFORNIA]

Chain Transfer in the Autoxidation of Hydrocarbons Retarded by Phenol

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The proposal that the frequently observed concentration dependence of phenol in inhibited autoxidation of hydrocarbons arises from chain transfer between phenoxy radical and hydrocarbon has been tested. In carefully controlled experiments the reaction order with respect to tetralin is found to be 1.19 to 1.09, not 1.5 as is required by this mechanism. Study of the phenol-retarded oxidation rates of tetralin over about a 10^4-fold range of phenol concentration demonstrates that the hydrocarbon chain-transfer mechanism cannot be of paramount importance. Data are presented reaffirming hydroperoxide chain transfer as the important cause of phenol kinetic order behavior. Rate constant estimates of $\geq 2 \times 10^5$ l. mole^{-1} sec.$^{-1}$ for the phenoxy radical–hydroperoxide reaction and $\geq 10^9$ l. mole^{-1} sec.$^{-1}$ for the reaction between phenoxy radical and alkylperoxy radical are confirmed.

Recently, two groups of investigators[1,2] have proposed that chain transfer between inhibitor radical and hydrocarbon is the proper explanation of the inverse half-order dependence of the inhibited oxidation rate upon inhibitor concentration frequently observed and discussed.[1-4] In both instances, the evidence for this proposal is an observed 1.5 order of the phenol-inhibited rate with respect to hydrocarbon concentration using tetralin as well as other oxidizable substrates. This order of hydrocarbon concentration is that anticipated for special limiting conditions of the hydrocarbon chain-transfer mechanism as outlined approximately by Bickel and Kooyman.[5] The work of the latter authors clearly shows that chain transfer between nonhindered phenoxy radicals and hydrocarbon can take place although the experimental conditions demonstrating the existence of this reaction were very different from those normally used to study chain termination by inhibitors.

This note presents additional data on the phenol-inhibited oxidation of tetralin. The data indicate that the reported[1,2] hydrocarbon concentration order of 1.5 probably resulted from chain transfer between phenoxy radical and alkyl hydroperoxide, rather than with hydrocarbon. Further information about the surprisingly rapid rate of reaction between phenoxy radical and hydroperoxides, the importance of which has already been pointed out,[6] is also presented.

Experimental

Materials.—Azobisisobutyronitrile (AIBN) was Eastman Kodak purified by recrystallization from methanol. Baker reagent grade phenol was recrystallized from hexane. DuPont tetralin was twice percolated through a 1.8-m. column packed with Davison activated silica gel. It was stored in the dark under oxygen-free nitrogen until used. Iodometric titration showed the residual hydroperoxide to be 10^{-4} *M* or less. Eastman Kodak chlorobenzene was treated once in an activated silica gel column.

Oxidation Procedure.—The oxidator consisted of a stirred 1-l. flask immersed in a carefully regulated water bath. 500 to 250 cc. of hydrocarbon solution containing the required amount of phenol was placed in the flask, and a moderate stream of oxygen was swept through the vapor space for 5 min. while the solution was stirred. After the system was thermally equilibrated (requiring about 20 min.), small aliquots of tetralin hydroperoxide and/or AIBN solution were added through a controlled opening. After the reaction was initiated with AIBN, the volume change was measured at 1- to 2-min. intervals by manually operating calibrated gas syringes to maintain constant pressure as indicated by a toluene manometer. Measurements were taken for about 30-min. periods. When curvature of the oxygen absorption *vs.* time plot occurred, the initial oxidation rate was determined from the initial slope utilizing, at most, points corresponding to hydroperoxide production of 4×10^{-4} *M*.

Results and Discussion

Proper design of experiments to study this problem and adequate interpretation of the results require an appreciation of the unusually rapid rate of reaction between phenoxy radical and hydroperoxide. An attempt to determine the order of magnitude of this rate constant[6] indicated a value $\geq 2 \times 10^5$ l. mole^{-1} sec.$^{-1}$. This can be compared with 12 l. mole^{-1} sec.$^{-1}$ for cumylperoxy radical abstracting peroxidic hydrogen from tetralin hydroperoxide,[7] 25.2 l. mole^{-1} sec.$^{-1}$ for tetralyl

(1) L. R. Mahoney and F. C. Ferris, *J. Am. Chem. Soc.*, **85**, 2346 (1963).
(2) W. G. Lloyd and C. E. Lange (Preprints, Division Polymer Chemistry, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963; see also *J. Am. Chem. Soc.*, **86**, 1492 (1964).
(3) G. S. Hammond, C. S. Boozer, C. E. Hamilton, and J. N. Sen, *ibid.*, **77**, 3238 (1955).
(4) J. R. Thomas and C. A. Tolman, *ibid.*, **84**, 2930 (1962).
(5) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2215 (1956).
(6) J. R. Thomas, *J. Am. Chem. Soc.*, **85**, 2166 (1963).
(7) J. R. Thomas and C. A. Tolman, *ibid.*, **84**, 2079 (1962).

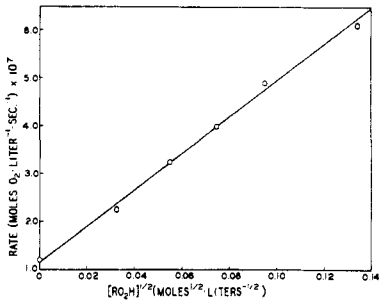

Fig. 1.—Oxidation rate *vs.* [tetralin hydroperoxide]$^{1/2}$. At 57°: tetralin, 1.41 *M*; AIBN, 4×10^{-3} *M*; phenol, 3×10^{-3} *M*.

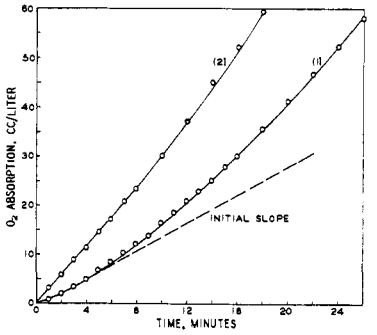

Fig. 2.—Oxygen adsorption *vs.* time. At 57°: tetralin, 5.65 *M*; AIBN, 4×10^{-3} *M*; phenol, 10^{-3} *M*. (1) No added hydroperoxide; (2) 3×10^{-3} *M* tetralin hydroperoxide.

peroxy radical abstracting hydrogen from tetralin,[8] and 0.64 l. mole^{-1} sec.$^{-1}$ for cumyl peroxy radical abstracting hydrogen from cumene,[7] all at 57°.

The profound effect of hydroperoxide upon phenol-inhibited oxidation rates, already demonstrated for cumene,[6] appears again in the tetralin system. In Fig. 1, the inhibited oxidation rates of 1.41 *M* tetralin are plotted as a function of added tetralin hydroperoxide where it is seen that as little as 10^{-4} *M* hydroperoxide increases the rate by about 25%. In this system, as in the previously studied cumene system, hydroperoxide generated by oxidation of substrate tetralin has quantitatively the same effect as added hydroperoxide. The large accelerating effect under these conditions of small concentrations of hydroperoxide necessitates scrupulous care in eliminating, as far as possible, hydroperoxide contaminant in the starting hydrocarbon and the application of as much objective analysis of initial oxidation rate data as possible to minimize the effect of hydroperoxide produced during the process of determining the rate. Figure 2 illustrates the latter problem where it is seen that the inhibited oxidation rate is not constant with time, due to hydroperoxide produced by the reaction. This behavior is more pronounced the larger the kinetic chain length and can tend to give an apparent kinetic order with respect to hydrocarbon concentration greater than the true value.

The kinetic order of inhibited rates with respect to hydrocarbon concentration is of crucial importance to the argument that phenoxy radical–hydrocarbon chain transfer can account for the inverse square root order of the inhibitor concentration (rather than inverse first order). Utilizing very clean tetralin, hydroperoxide contaminant 10^{-4} *M* or less, taking care that minimum oxidation occurred prior to addition of initiator as

(8) C. H. Bamford, and M. J. S. Dewar, *Proc. Roy. Soc.* (London), **A198**, 252 (1949).

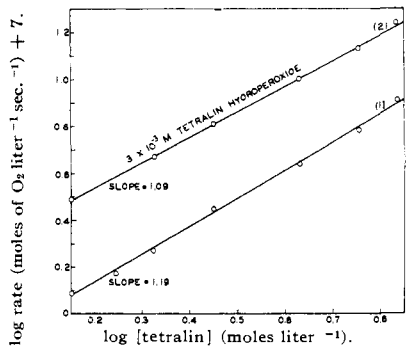

Fig. 3.—Log oxidation rate *vs.* log [tetralin]. (1) 4×10^{-3} *M* AIBN and 3×10^{-3} *M* phenol at 57°; (2) same as (1) plus 3×10^{-3} *M* tetralin hydroperoxide.

described in the experimental section, and making initial oxidation rate determinations under conditions that, at most, 4×10^{-4} *M* hydroperoxide was produced, the data given in Fig. 3, curve 1, were obtained. An illustrative example of the initial rate determination is shown in Fig. 2. The results given in Fig. 3 yield a tetralin concentration kinetic order of 1.19 which can be considered an upper limit since the principal uncertainty tends to make this quantity larger than it should be.[9] Curve 2 in Fig. 3 presents similar data except that 3×10^{-3} *M* tetralin hydroperoxide was present in all cases. Under these conditions, linear oxygen absorption *vs.* time plots are obtained for sufficiently long times that truly objective initial oxidation rates can be easily obtained (see Fig. 2). The reaction order with respect to tetralin by these experiments is 1.09. These experiments fail to confirm the hydrocarbon chain-transfer postulate.

When mechanistic conclusions are based upon kinetic observations, it is quite unjustified to rely upon special limiting solutions of the appropriate kinetic equations without due regard for the quantitative consequences caused by the simplifications made. For the hydrocarbon chain-transfer mechanism, the steady-state-inhibited rate (without further assumptions) is given by

$$\text{rate} = k_p[\text{RH}][\text{RO}_2] + \frac{(k_c/k_2)[\text{RH}][\text{C}_6\text{H}_5\text{OH}][\text{RO}_2]k_1}{(k_c/k_2)[\text{RH}] + [\text{RO}_2]} \quad (1)$$

where k_p is the rate constant of $RO_2 + RH$, k_1 that of $RO_2 + C_6H_5OH$, k_c that of $C_6H_5O + RH$, and k_2 that of $C_6H_5O + RO_2$. The peroxy radical concentration is given

$$[\text{RO}_2] = \frac{R_i}{4k_1[\text{C}_6\text{H}_5\text{OH}]}\left\{1 + \left(1 + (k_c/k_2)\frac{8[\text{RH}][\text{C}_6\text{H}_5\text{OH}]k_1}{R_i}\right)^{1/2}\right\} \quad (2)$$

by (2) where R_i is the initiation rate. Reasonably

(9) Kinetic chain lengths for curve 1 range from 4.0 to 25.8, those for curve 2 from 9.8 to 56.4. The corresponding kinetic chain lengths for the uninhibited reaction range from 55.2 to 213. The oxidation rates reported throughout are uncorrected for nitrogen evolution from AIBN or oxygen absorption by primary AIBN radicals. With an efficiency factor of 0.68 an apparent chain length of 0.36 based only upon volume change would be expected in the absence of oxidizable substrate. In practice, a much lower volume change is recorded rendering even this small correction unnecessary. This behavior has been previously commented upon: C. E. Boozer, G. S. Hammond, C. E. Hamilton, and C. Peterson, *J. Am. Chem. Soc.*, **77**, 3380 (1955).

reliable values of all quantities in (1) and (2) are available except for the ratio k_c/k_2.[10]

In Fig. 4 experimental data for a large range of phenol concentrations are plotted as log rate against log [C_6H_5OH] for two cases. In one, curve 1, oxidation rates are for tetralin free of hydroperoxide; in the other, curve 2, 3×10^{-3} M tetralin hydroperoxide was purposely added. In the hydroperoxide free case, an approximate inverse square root order of rate with phenol concentration is observed at low phenol concentrations. Continuous departure from this behavior is evidenced at higher phenol concentrations, however. Such departure is not entirely unexpected since concentrated solutions of phenol should be far from ideal, *i.e.*, the activity coefficient of phenol should not be constant. That this is not the primary effect, however, is shown by the data of curve 2 (3×10^{-3} M tetralin hydroperoxide present) which shows nearly linear behavior over a far greater range of phenol concentration. Of more interest is the observation that the oxidation rates are *lower* in the presence of hydroperoxide than in its absence at high phenol concentrations. Just the reverse is true at low concentrations. The explanation seems clear. Most of the nonlinear behavior of curve 1 is due to chain transfer between phenoxy radical and tetralin, in agreement with the results of Bickel and Kooyman. In the presence of hydroperoxide, however, the phenoxy radical concentration is markedly lowered by the transfer reaction with hydroperoxide. The evidence indicates again the impressive rate of this reaction. Thus, 3×10^{-3} M hydroperoxide (in the presence of about 1 M phenol) competes favorably with 5.65 M tetralin for the phenoxy radical. The reaction rate constant of phenoxy radical reacting with hydroperoxide must be something greater than 10^3 times that for reaction with tetralin.

The calculated curve in Fig. 4 is due to eq. 1 and 2 utilizing the known rate constants[10] and a value for k_c/k_2 of 1.16×10^{-9}. This value allows approximate fit of the experimental data at low phenol concentrations but fails completely to reproduce the high phenol concentration range. Order of magnitude changes in k_c/k_2 cause little change in the position of the minimum point nor in the general shape of the curve. Smaller values reflect themselves in a rather quick approach to inverse first-order phenol dependence in the low phenol concentration range. Changes to either smaller or larger values cause real departure of the calculated rates from the experimental ones. In order to achieve even a poor approximation to the shape of the experimental curve 1, the value of k_1 must be lowered an order of magnitude while k_c/k_2 must be increased an order of magnitude (in order to retain an approximately inverse square root phenol order). The calculated rates of oxidation increase so much, however, that phenol would not be a noticeable inhibitor of the autoxidation reaction at concentrations much below 10^{-2} M.

It might be argued that in spite of the precautions taken, the data of curve 1 at high phenol concentration are prevented from following their calculated course because of small concentrations of contaminant peroxide. Such an effect might indeed be reflected in the data; although this, in essence, is the point which this

(10) $k_p = 25.2$ l. mole^{-1} sec.$^{-1}$; $k_1 = 3 \times 10^3$ l. mole^{-1} sec.$^{-1}$. See ref. 6 and J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 2800 (1963). With AIBN at 4×10^{-3} M and 57°, $R_i = 3.08 \times 10^{-8}$ mole l.$^{-1}$ sec.$^{-1}$ (ref. 4).

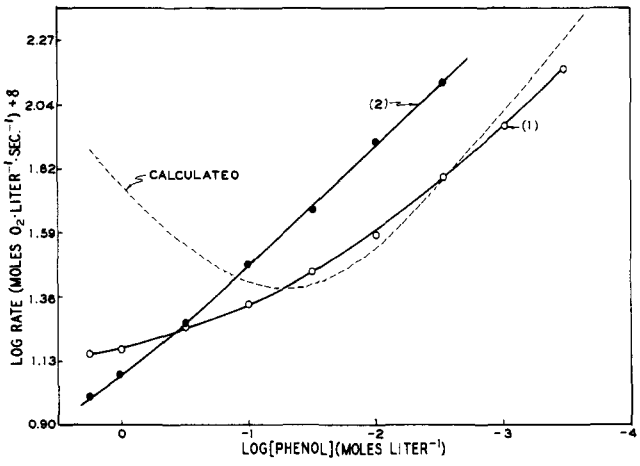

Fig. 4.—Log rate *vs.* log [phenol]. (1) 5.65 M tetralin and 4×10^{-3} M AIBN at 57°; (2) same as (1) plus 3×10^{-3} M tetralin hydroperoxide.

study is attempting to prove. In addition, however, this state of affairs (namely, that the low phenol concentration range behavior is controlled by hydrocarbon transfer while the high phenol range fails to follow its predicted course because of hydroperoxide transfer) would demand a tetralin concentration dependence of order nearly 1.5 at low phenol levels, which is not observed.

The reversal in the effect of hydroperoxide upon inhibited rates can be shown to be in agreement with predicted behavior. Equation 1 can be modified to include the effects of both chain transfer to hydrocarbon and to hydroperoxide by adding the term, $(k_{cp}/k_2)[RO_2H]$, to the denominator of the second term where k_{cp} is the rate constant of the $C_6H_5O + RO_2H$ reaction. Equation 2 is appropriately modified if the term (k_c/k_2) [RH] is replaced by the term (k_c/k_2) [RH] + $(k_{cp}/k_2)[RO_2H]$.

Figure 5 shows log rate *vs.* log [phenol] plots calculated by use of this modified expression which demonstrate the kinetic behavior when chain transfer to both hydrocarbon and hydroperoxide is included. For these calculations values of $k_c/k_2 = 4 \times 10^{-10}$ and $k_{cp}/k_2 = 5.7 \times 10^{-5}$ were assumed. The latter value is that estimated from the cumene system.[6] Agreement between the experimental curves of Fig. 4 and those calculated in Fig. 5 is reasonably good and could probably be improved by more extensive attempts to optimize the choice of constants. However, since activity coefficient variations of the many species involved in the reaction must be ignored, the best fit values would be of little added value. Throughout, the possibility of chain termination by reaction between phenoxy radicals has been ignored. In the presence of hydroperoxide the rapid chain-transfer reaction keeps the phenoxy radical concentration low as indicated by the data already presented, and it appears unnecessary to invoke this reaction. This is further confirmed by the general observation that two alkyl peroxy radicals are destroyed per phenol molecule consumed. In the absence of hydroperoxide, and particularly at high phenol levels, the reaction may be important. Land and Porter[11] report a large rate constant (5.4×10^8 l. mole^{-1} sec.$^{-1}$ in water) which, however, appears somewhat too large to accommodate oxidation kinetic results.

(11) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2016 (1963).

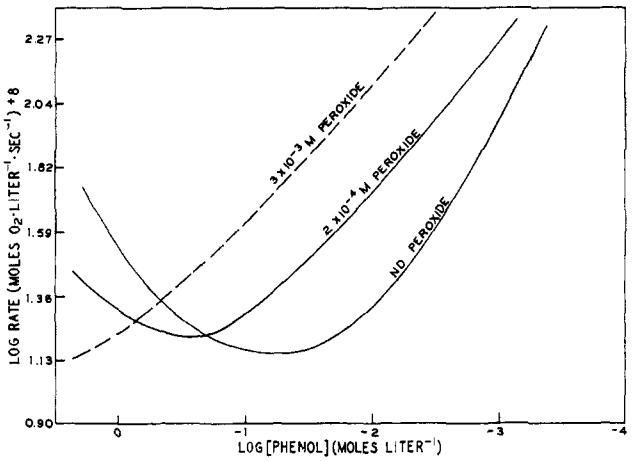

Fig. 5.—Calculated log rate *vs.* log [phenol] plots for chain transfer to both hydrocarbon and hydroperoxide.

The rapid rate of reaction of phenoxy radical with hydroperoxide is unexpected. The previously estimated value, $\geqq 2 \times 10^5$ l. mole^{-1} sec.$^{-1}$, can, however, be confirmed by another line of evidence. McGowan and Powell[12] have determined the rate of reaction of the stable radical, 2,4,6-tri-*t*-butylphenoxyl, with *t*-butyl hydroperoxide. Extrapolation of their data to 57° yields a rate constant of 430 l. mole^{-1} sec.$^{-1}$. It is also known[6] that hydroperoxide at concentrations up to 0.2 *M* does not influence 2,6-*t*-butyl-substituted phenol-inhibited oxidation rates while hydroperoxide concentrations of 2×10^{-4} *M* cause easily detectable effects with phenol itself. From these observations, the rate constant for the phenoxy radical–hydroperoxide reaction must be something greater than 4.3×10^5 l. mole^{-1} sec.$^{-1}$, in agreement with the estimate made previously from more complicated kinetic arguments.[6]

The previous indication of a rate constant the order of 10^9 l. mole^{-1} sec.$^{-1}$ for phenoxy radical reacting with alkyl peroxy radical can also be confirmed. The work of Stone and Waters[13] demonstrates that the phenoxy radical has an easily detectable e.s.r. signal. A repeat of the previous experiment[6] with AIBN-generated RO_2 radicals in a solution of phenol in benzene, using apparatus calibrated with a known concentration of phenoxy radical, confirms the result previously given. This analysis neglects any contribution of the reaction, $C_6H_5O\cdot + C_6H_5O\cdot$, in lowering the steady-state concentration of the phenoxy radical. A similar study with 2,4,6-tributylphenol, which does not undergo a comparable association or disproportionation reaction, leads to a similar conclusion with respect to its rate constant for reaction with peroxy radicals.

It is perhaps worth pointing out explicitly that the rate constant assignment made here implies that the equilibrium constant for

$$RO_2 + C_6H_5OH \rightleftharpoons RO_2H + C_6H_5O$$

is $\leqq 1.5 \times 10^{-2}$. Since the entropy change for this system is small, the data suggest that $D(C_6H_5O - H)$ is $\geqq 2.5$ kcal./mole larger than $D(RO_2 - H)$. This apparently reflects the high degree of stabilization of the alkyl peroxy radical by its three-electron bond which is estimated to be 15–25 kcal./mole.[14]

In summary it can be concluded that the phenoxy radical–hydroperoxide chain-transfer reaction is very much faster than the corresponding transfer reaction with hydrocarbon. Under typical conditions of kinetic investigation of phenol-inhibited autoxidation, the kinetic order of hydrocarbon concentration dependence required by the hydrocarbon transfer mechanism is not observed. Neither can this mechanism reproduce inhibited autoxidation data taken over a wide range of phenol concentration. Most probably the frequently observed inverse square root phenol order upon inhibited oxidation rates arises from chain transfer with hydroperoxide. This effect can quantitatively explain phenol behavior over a wide range of concentration at realistically low contaminant concentration levels of hydroperoxide. Moreover, independent experimental observations confirm that the pertinent rate constants do have the values required. Chain transfer *via* phenoxy radical and hydrocarbon, however, can occur. In a truly hydroperoxide-free system this reaction could yield an approximate inverse square root phenol order upon the rate, although only over a limited range of concentration. It is doubtful that this situation has yet been observed.

Acknowledgment.—The author is indebted to Mr. M. C. Burns for assistance with much of the experimental work and to Dr. L. R. Mahoney for helpful correspondence. Discussion with Dr. K. U. Ingold and Dr. J. A. Howard, who have independently reached many of the same conclusions discussed here, is also appreciated.

(12) J. C. McGowan and T. Powell, *J. Chem. Soc.*, 238 (1960).
(13) T. J. Stone and W. A. Waters, *Proc. Chem. Soc.*, 253 (1962).
(14) The arguments of A. D. Walsh, *J. Chem. Soc.*, 331 (1949), yield the value of 25 kcal./mole if the dissociation energy of the O–O bond in hydrogen peroxide is 48 kcal./mole.