Autoxidation of 1-Octene with *t*-Butyl Hydroperoxide and Chromium(III) Acetylacetonate. II. Solvent Effects and Free-Radical Inhibitors

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The effect of 18 organic solvents has been observed in the autoxidation of 1-octene initiated by *t*-butyl hydroperoxide and chromium(III) acetylacetonate at 30°. *t*-Butyl hydroperoxide decomposition rates were also measured *in vacuo* iodometrically and chromium(III) acetylacetonate disappearance rates were measured spectrophotometrically. *t*-Butyl hydroperoxide and chromium(III) acetylacetonate disappearance rates were relatively insensitive to solvent, but autoxidation rates indicated participation of the solvent in the autoxidation process. The inhibitor effects of phenols, amines, and nitrobenzene has also been observed upon the same reactions. Induction periods for autoxidation, stoichiometric factors for the inhibitors, and oxygen absorption rates during and after inhibition are reported. Initiation rates of autoxidation measured by chromium(III) acetylacetonate disappearance rates are in good agreement with initiation rates obtained from measurements of induction periods.

In the preceding paper[2] the kinetics of 1-octene autoxidation at 0–60° initiated by *t*-butyl hydroperoxide and chromium(III) acetylacetonate was investigated. Both chain autoxidation and chain *t*-butyl hydroperoxide decomposition were observed. In this paper the same type of experimental data are tabulated for runs at 30° in the presence of several organic solvents. The solvents tested showed very little effect upon chromium(III) acetylacetonate disappearance. Most solvents tested showed a small but measurable retarding effect upon *t*-butyl hydroperoxide decomposition *in vacuo* compared to decomposition in 1-chlorooctane. The autoxidation results showed somewhat more complex solvent dependence implying intimate participation of the solvent in the autoxidation process. Some solvents clearly were autoxidized by a chain process. Aromatic solvents not readily autoxidized by a chain process had a retarding effect upon autoxidation rates compared to autoxidations of 1-octene in 1-chlorooctane.

The effects of well-known free-radical inhibitors on these two chain processes is also presented. The inhibitor compounds studied were phenols, amines, and nitrobenzene.[3]

By using measured small quantities of inhibitors and observing induction periods, it is possible to determine stoichiometric factors for inhibitor molecules. The stoichiometric factor, n, is the number of radical chains stopped/molecule of inhibitor and is given by eq 1.[3,4]

$$n = Z/N \tag{1}$$

Z is the number of radicals produced during induction period and is equal to $R_i \times$ induction period; N is the number of molecules of inhibitor originally present and R_i is equal to the rate of production of radicals.

Alternatively it is possible, knowing the stoichiometric factor, to calculate R_i, the rate of the initiation process.

Stoichiometric factors of ~2 obtained for many phenols and anilines[3,4,5] apparently arise from the following termination steps.

$$\mathrm{ROO}\cdot + \mathrm{InH} \xrightarrow{k_{In}} \mathrm{ROOH} + \mathrm{In}\cdot \tag{2}$$

$$\mathrm{ROO}\cdot + \mathrm{In}\cdot \longrightarrow \text{inactive products} \tag{3}$$

Stoichiometric factors greater than 2[3,5,6] would be obtained if the "inactive products" had inhibitor properties or for polyfunctional inhibitors. Stoichiometric factors of less than 2[3,6,7] could be obtained if the species In· were stable (*e.g.*, if the inhibitor molecule were itself a free radical) or if competition between the inhibitor steps and the chain-propagating step[3] (4) is significant.

$$\mathrm{ROO}\cdot + \mathrm{RH} \xrightarrow{k_p} \mathrm{ROOH} + \mathrm{R}\cdot \tag{4}$$

Experimental Section

Chemicals.—Solvents and inhibitors were generally taken from freshly opened bottles and purified by standard procedures.[8]

Butylated hydroxyanisole (a mixture of 2- and 3-*t*-butyl-4-hydroxyanisole, Sigma Chemical Corporation) and DL-α-Tocopherol (Nutritional Biochemical Corporation) were taken from freshly opened bottles and used without purification.

Kinetics.—All kinetics runs were performed as previously described.[2,9] Oxygen absorption runs were permitted to run well past inhibition periods. In all autoxidation runs described, well-defined inhibition periods could be observed, but oxygen absorption rates after the inhibition period did not reach the rate obtained in uninhibited runs, implying that products of the reaction behaved as weak inhibitors or retarders, possibly in the manner of the aromatic solvents herein described.

Results and Discussion

A. Solvent Effects.—Table I sets forth initial chromium(III) acetylacetonate disappearance rates, *t*-butyl hydroperoxide decomposition rates *in vacuo*, and autoxidation rates at 30°.

Chromium(III) Acetylacetonate Disappearance Rates.—The data of Table I show less than a twofold change in chromium(III) acetylacetonate disappearance rates among the solvents listed. Although it has been shown that chromium(III) acetylacetonate disappearance rates are not always a measure of initiation rate,[2] the concentration of reactants chosen generally gave activation parameters[2] and inhibited autoxidation rates (see below) consistent with the chromium(III)

(1) (a) From the Ph.D. Thesis of T. J., City University of New York, 1968; (b) NSF undergraduate research participant.

(2) N. Indictor, T. Jochsberger, and D. Kurnit, *J. Org. Chem.*, 2855 (1969).

(3) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 430 ff.

(4) N. Uri in "Autoxidation and Antioxidants," W. O. Lundberg, Ed., John Wiley & Sons, Inc., New York, N. Y., 1961, p 92.

(5) L. R. Mahoney, *J. Amer. Chem. Soc.*, **88**, 3035 (1966).

(6) C. Boozer, G. Hammond, C. Hamilton, and J. Sen, *ibid.*, **77**, 3233, 3238 (1955).

(7) See ref 3, p 432.

(8) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath & Co., Boston, Mass., 1957.

(9) N. Indictor and T. Jochsberger, *J. Org. Chem.*, **31**, 4271 (1966).

TABLE I

SOLVENT EFFECTS ON THE RATE OF AUTOXIDATION OF 1-OCTENE AND THE RATE OF *t*-BUTYL HYDROPEROXIDE AND CHROMIUM(III) ACETYLACETONATE DISAPPEARANCE[a] (30°)

Solvent	Solvent Concn,[b] *M*	$(-\Delta[O_2]/\Delta t)_0$ × 10^6 *M*/sec	$(-\Delta[t\text{-BuOOH}]/\Delta t)_0$ × 10^4 *M*/sec	$(-\Delta[Cr]/\Delta t)_0$ × 10^9 *M*/sec
1-Octene	5.97	3.12	n[e]	n
1-Chlorooctane[c]	6.75	0.0	1.77	n
1-Chlorooctane	3.06	2.25	0.76	6.46
n-Heptane	2.73	2.40	1.01	8.24
sym-Tetrachloroethane	3.81	2.08	0.68	n
Carbon tetrachloride	4.15	3.08	0.51	n
Benzene[d]	6.31	0.0	n	n
Benzene	4.51	n	0.91	7.22
Benzene	0.68	1.38	n	n
Benzene	1.36	0.95	n	n
Naphthalene	0.57	0.71	n	n
Naphthalene	0.37	n	0.30	n
Phenyl ether	3.28	0.82	n	n
Phenyl ether	2.52	n	0.31	n
Chlorobenzene	3.90	0.36	0.88	n
Cumene	2.88	n	0.32	7.61
Cumene	1.44	2.56	n	n
Tetralin	2.94	n	0.41	n
Tetralin	1.47	1.42	n	n
Pyridine	4.98	0.50	1.15	5.92
t-Butanol	5.56	0.23	n	n
t-Butanol	4.28	0.19	0.83	10.4
Ethanol	6.84	0.24	n	n
Methanol	9.96	0.0	0.56	8.85, 9.92[f]
Acetic acid	5.25	3.30	n	n
Acetic acid	7.00	n	0.27	9.00
Acetic acid	9.10	7.09	n	n
Ethyl acetate	3.07	0.71	n	n
Ethyl acetate	4.08	n	0.35	n
N,N-Dimethylformamide	4.96	n	0.66	8.00
N,N-Dimethylformamide	3.71	2.11	n	n
p-Dioxane	4.71	0.27	0.59	n

[a] *In vacuo.* [b] All runs cited contain 4.00×10^{-4} *M* Cr(acac)$_3$, 0.76 *M* *t*-BuOOH (except where noted), 2.56 *M* 1-octene (except in first two cases), and chlorooctane diluent. [c] No 1-octene present. [d] *t*-BuOOH concentration 0.37 *M*. [e] n = no data. [f] Oxygen not excluded from this run.

acetylacetonate disappearance rates as a measure of chain initiation rate. The insensitiveness of these data to solvents may be interpreted as an indication that the actual chain initiation rates of *t*-butyl hydroperoxide decomposition and 1-octene autoxidation are not sensitive to solvent change.

t-Butyl Hydroperoxide Decomposition Rates.—Table I shows decomposition rates of *t*-butyl hydroperoxide *in vacuo* at 30°. Relative to 1-chlorooctane, all solvents

$$t\text{-BuO}\cdot \text{ or } t\text{-BuOO}\cdot + RX \rightarrow R\cdot \qquad (5)$$

capable of chain-transfer reactions[10] (carbon tetrachloride, cumene, tetralin, methanol, acetic acid, ethyl acetate, dioxane, as well as phenyl ether and naphthalene) show a small but measurable rate retardation of the chromium(III) acetylacetonate catalyzed decomposition of *t*-butyl hydroperoxide.

Presumably the transferred solvent radical is less reactive at 30° toward *t*-butyl hydroperoxide than are *t*-butoxy or *t*-butylperoxy radicals. It has been shown in the preceding paper[2] that 1-octene itself behaves as a chain-transfer agent which retards decomposition at lower temperatures (0–40°) but induces decomposition at elevated temperatures (>50°). Benzene and chlorobenzene appear to have essentially no effect upon *t*-butyl hydroperoxide decomposition rates. The retarding effect of phenyl ether and naphthalene may be a viscosity effect[11] (these solutions were visibly more viscous than others), although this possibility was not demonstrated. The rate-enhancing effect of pyridine was probably from solvent attack producing nonradical product (pyridine N-oxide).[12] It is interesting that pyridine in catalytic quantities behaved as an inhibitor both for *t*-butyl hydroperoxide decomposition and 1-octene autoxidation in the presence of chromium(III) acetylacetonate. (See Table III.)

Many workers have demonstrated solvent–hydroperoxide interactions in describing hydroperoxide decomposition.[13–19] These interactions are probably temperature dependent and of greater significance at elevated temperatures (>60°). In this work, the solvent–hydroperoxide interactions are much less significant (only *ca.* seven-fold change in decomposition rate was noted among different solvents), either because the temperature does not favor them or because solvent–hydroperoxide interactions are insignificant compared

(10) See ref 3, p 150.

(11) A. Factor, C. Russell, and T. Traylor, *J. Amer. Chem. Soc.*, **87**, 3692 (1965).
(12) M. Sheng and J. Zajacek, *J. Org. Chem.*, **33**, 538 (1968).
(13) C. Walling and L. Heaton, *J. Amer. Chem. Soc.*, **87**, 38, 48 (1965).
(14) A. V. Tobolsky and L. R. Matlack, *J. Polym. Sci.*, **55**, 49 (1961).
(15) V. Stannett and R. Mesrobian, *J. Amer. Chem. Soc.*, **72**, 4125 (1950).
(16) N. Indictor and C. Linder, *J. Polym. Sci., Part A-1*, **5**, 1101 (1967).
(17) W. H. Richardson, *J. Amer. Chem. Soc.*, **88**, 975 (1966).
(18) R. Hiatt, *et al.*, *J. Org. Chem.*, **33**, 1416, 1421, 1428, 1430, 1436 (1968).
(19) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **45**, 793 (1967).

with chromium–hydroperoxide interactions. No correlations could be drawn between the effect of solvents on the uncatalyzed decomposition of *t*-butyl hydroperoxide at 73.5°[15] and this work at 30° in the presence of chromium(III) acetylacetonate.

Autoxidation Rates. Aromatic Solvents.—Although the effect of aromatic solvents on chromium(III) acetylacetonate disappearance rates and *t*-butyl hydroperoxide decomposition rates is small, a marked effect is noted on 1-octene autoxidation rates (Table I). Small amounts of benzene in 1-chlorooctane lower the oxygen absorption rate of 2.6 *M* solutions of 1-octene, and in 6 *M* benzene the system showed no oxygen absorption for 72 hr. Similar systems containing diphenyl ether, chlorobenzene, and naphthalene showed decreased rates compared to autoxidations of 1-octene in 1-chlorooctane solvent. Even compounds known to autoxidize readily, such as tetralin and cumene,[20] showed surprisingly low autoxidation rates when compared in separate runs (see Table II) to 1-octene. At

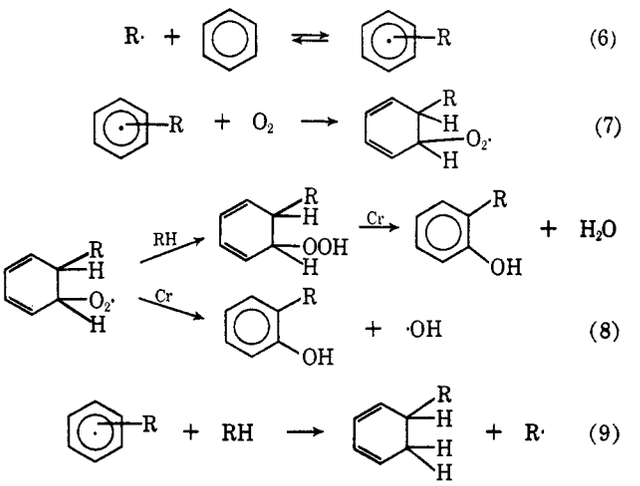
TABLE II
AUTOXIDATIONS WITH CHROMIUM(III) ACETYLACETONATE[a] AND *t*-BUTYL HYDROPEROXIDE[b] AT 30° IN 1-CHLOROOCTANE

Compd	Concn, *M*	$-(d[O_2]/dt)_0 \times 10^6$
1-Octene	1.27	2.09
Cumene	1.44	1.88
Tetralin	1.47	2.03
Acetic acid	12.20	2.08
N,N-Dimethylformamide	8.68	1.27

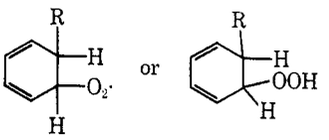
[a] 4.00×10^{-4}. [b] 0.74 *M*.

30° the photochemically induced autoxidations of tetralin, cumene, and 1-octene showed rate ratios of 37:24:1,[19] whereas all three substances autoxidized at about the same rates with chromium(III) acetylacetonate–*t*-butyl hydroperoxide initiator.

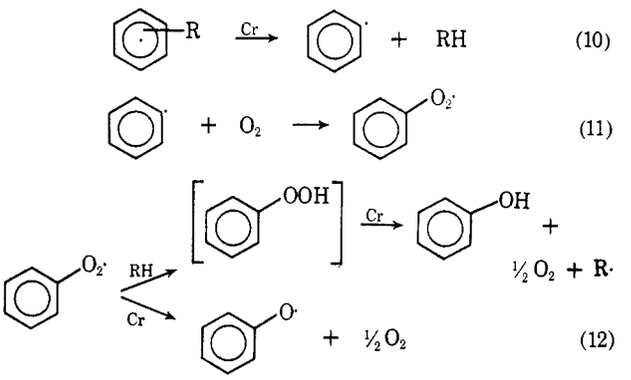
The absence of a large solvent effect in either the chromium(III) acetylacetonate or the *t*-butyl hydroperoxide disappearance rates suggests that the presence of oxygen is important for the retarding effect of aromatic compounds in the autoxidation. Since the presence of aromatic compounds does not apparently affect azo, peroxide, or photochemically initiated autoxidation in a major way,[20] chromium(III) acetylacetone must also be important for the observed retarding effect of aromatic compounds in autoxidation. Richardson[17] has observed a small effect of oxygen on the copper-induced decomposition of *t*-butyl hydroperoxide in chlorobenzene. Several workers[21,22] have demonstrated that aromatic compounds may be converted to phenolic compounds in the presence of peroxides and metals. Hiatt[18] has suggested that phenol may be formed in the AIBN-induced decomposition of *t*-butyl hydroperoxide in benzene in the presence of oxygen. Ingold has observed that some autoxidations are retarded when carried out in aromatic solvents and has suggested phenol formation as the cause.[23] A plausible sequence *via* a radical–aromatic complex[24] followed by attack by oxygen and a chromium species is shown in eq 6–9.



Under most autoxidation conditions[20] (at higher temperature), the dissociated form of the complex (eq 6) would probably be favored. Also at elevated temperatures, the decomposition of the peroxy species



would not necessarily produce radical chain inhibitors. Another path to phenol might involve hydrogen atom abstraction from the aromatic ring (normally a highly exothermic process)[25] facilitated by the presence of chromium (eq 10–12).



Autoxidation Rates. Oxygen-Containing Solvents.—Table I shows that, although the chromium(III) acetylacetonate and *t*-butyl hydroperoxide disappearance rates are only slightly sensitive to changes in solvent, the oxygen absorption rates in aliphatic alcohols, ethyl acetate, and dioxane are discernibly less than and those in acetic acid and N,N-dimethylformamide equal to or greater than oxygen absorption rates of 1-octene in chlorooctane. This effect is most simply interpreted as a coautoxidation of 1-octene and solvent. That these compounds absorb oxygen separately in

(20) See ref 3, Chapter 9.
(21) P. Kovacic and M. Kurz, *J. Amer. Chem. Soc.*, **88**, 2068 (1966); **89**, 4960 (1967).
(22) D. I. Metelitsa and E. T. Denisov, *Neftekhimiya*, **1** (1), 65 (1967); *Chem. Abstr.*, **67**, 21271*n*.
(23) K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).
(24) E. S. Huyser in "Advances in Free Radical Chemistry," G. H. Williams, Ed., Logos Press Ltd., London, 1965, p 77 ff.
(25) T. L. Cotrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths and Co. Ltd, London, 1958.

the presence of chromium(III) acetylacetonate and *t*-butyl hydroperoxide at 30° has been verified in this laboratory[26] (see also Table II). The zero rate reported for methanol undoubtedly arises from gaseous autoxidation products. The 2,4-dinitrophenylhydrazone derivative of formaldehyde was isolated from the gaseous entrapment of a reaction mixture. The retarding effect of *t*-butyl alcohol is interesting in that it is the major product of *t*-butyl hydroperoxide decomposition in the presence of chromium(III) acetylacetonate.[23,27] It must play a role in lowering the autoxidation rate as the reaction proceeds. A falling off from the initial autoxidation rates is invariably observed in chromium(III) acetylacetonate–*t*-butyl hydroperoxide initiated systems. Other workers[11,28] have observed similar rate retardations in the presence of *t*-butyl alcohol.

Product studies of several of the chromium(III) acetylacetonate–*t*-butyl hydroperoxide initiated autoxidations of solvents mentioned in this study are under investigation in this laboratory.

B. Free-Radical Inhibitors.—Table III lists chromium(III) acetylacetonate disappearance rates at 30° in the presence of 2.56 *M* 1-octene, 0.74 *M* *t*-butyl hydroperoxide, and small measured amounts of several known free-radical inhibitors. The rates obtained varied by less than a factor of two compared with the rate measured in the absence of inhibitor. The implication of this result is that the inhibitor species have little or no effect upon the initiation process. A similar result was obtained for the effect of solvents on chromium(III) acetylacetonate disappearance rates (Table I).

Table III also lists *t*-butyl hydroperoxide decomposition rates *in vacuo* under the same reaction conditions used for chromium(III) acetylacetonate disappearance rates. The reduced rates in the presence of inhibitors may be interpreted as a suppression of induced or chain *t*-butyl hydroperoxide decomposition. Apparently the induced decomposition under the conditions described in Table III may account for as much as 90% of the *t*-butyl hydroperoxide decomposition.

Induction periods for the inhibited autoxidation of 1-octene initiated by chromium(III) acetylacetonate–*t*-butyl hydroperoxide at 30° are presented in Table III. Autoxidation rates measured during and after the induction periods are also presented in Table III.

Stoichiometric factors, n, are presented in Table III calculated from eq 1 using R_i values obtained from chromium(III) acetylacetonate disappearance rates. Stoichiometric factors of *ca.* 2 for the phenols and aniline inhibitors present a consistent picture in this system compared with other phenol and aniline inhibited autoxidations,[3-7] and imply an initiation step involving a one-electron change (eq 13).

$$\text{Cr(III)} + t\text{-BuOOH} \longrightarrow \text{Cr(IV)} + t\text{-BuO}\cdot + \text{OH}^- \quad (13)$$

Phenolic Inhibitors.—The usual manner of describing inhibitor efficiency is by evaluation of the inhibitor constant[3,4] k_p/nk_{In} from initial inhibited autoxidation

$$-\mathrm{d[O_2]}/\mathrm{d}t = R_i k_p[\mathrm{RH}]/nk_{In}[\mathrm{InH}] \quad (14)$$

rates; k_p and k_{In} are defined in eq 2 and 4. Values of k_p/nk_{In} are listed in Table III. Assuming a value of k_p *ca.* 1 l./mol sec[19] (from rotating sector experiments at 30°), the values of k_{In} for the attack by peroxy radical obtained from 1-octene on the phenolic inhibitors are *ca.* 10^3 l./mol sec. The hindered phenol, 2,6-dioctadecylphenol, gave k_{In} *ca.* one order of magnitude higher. The data are in reasonable agreement with other studies of inhibitor efficiencies based on tetralin and 9,10-dehydroanthracene[5,29] autoxidation and suggest that allylic peroxy radicals are only slightly less selective than benzylic peroxy radicals toward phenols.

The general equations given by Mahoney,[29] as elegantly demonstrated for phenol-inhibited autoxidations of 9,10-dehydroanthracene initiated by tetraphenylbutane, are the following where RH refers to substrate and AH refers to phenolic inhibitor.

$$\text{initiation} \xrightarrow{k_1}$$

$$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{k_2} \mathrm{ROO}\cdot$$

$$\mathrm{ROO}\cdot + \mathrm{RH} \xrightarrow{k_3} \mathrm{ROOH} + \mathrm{R}\cdot$$

$$2\mathrm{ROO}\cdot \xrightarrow{k_4} \mathrm{O_2} + \text{termination}$$

$$\mathrm{ROO}\cdot + \mathrm{AH} \underset{}{\overset{k_5}{\rightleftharpoons}} \mathrm{ROOH} + \mathrm{A}\cdot$$

$$\mathrm{A}\cdot + \mathrm{ROO}\cdot \xrightarrow{k_6} \text{inert products}$$

$$2\mathrm{A}\cdot \xrightarrow{k_7} \text{inert products}$$

$$<\mathrm{A}\cdot + \mathrm{RH} \xrightarrow{k_8} \mathrm{AH} + \mathrm{R}\cdot$$

When a second weaker inhibitor is present, such as a hindered phenol, the following additional steps were postulated[29] where BH refers to the weaker inhibitor.

$$\mathrm{A}\cdot + \mathrm{BH} \underset{}{\overset{k_9}{\rightleftharpoons}} \mathrm{AH} + \mathrm{B}\cdot$$

$$\mathrm{ROO}\cdot + \mathrm{BH} \xrightarrow{k_5'} \mathrm{ROOH} + \mathrm{B}\cdot$$

$$\mathrm{A}\cdot + \mathrm{B}\cdot \xrightarrow{k_{10}} \text{inert products}$$

$$\mathrm{ROO}\cdot + \mathrm{B}\cdot \xrightarrow{k_{11}} \text{inert products}$$

Mahoney simplified these equations[29] by pointing out two kinetically distinguishable situations based on the relative importance of steps 3 and 5.[30] For $k_5[\mathrm{AH}]/k_3[\mathrm{RH}] < 1$, eq 15 applies where $q = 1$ if termination

$$-\mathrm{d[O_2]}/\mathrm{d}t = R_i k_3[\mathrm{RH}]/\{qk_5[\mathrm{AH}] + qk_5'[\mathrm{BH}]\} \quad (15)$$

is by step 10; q = 2 if termination is by step 11. For $k_5[\mathrm{AH}]/k_3[RH] > 1$, eq 16 applies.

$$-\mathrm{d[O_2]}/\mathrm{d}t = (k_8/k_7^2)[\mathrm{RH}]R_i^{1/2}[1 + \{k_9k_{10}[\mathrm{BH}]/k_7k_{-9}[\mathrm{AH}]\}]^{-1/2} \quad (16)$$

The chromium(III) acetylacetonate–*t*-butyl hydroperoxide initiated autoxidation of 1-octene inhibited by phenol may be regarded as analogous to the doubly inhibited system described by Mahoney in which the weakly inhibiting substance, BH, is the initially present *t*-butyl hydroperoxide. That eq 16 may obtain for phenol is indicated by an increased initial autoxidation rate at higher phenol concentration.

(26) Unpublished data, D. Miller, T. Jochsberger, and N. Indictor.
(27) N. Indictor and W. Brill, *J. Org. Chem.*, **30**, 2074 (1965).
(28) H. Berger and A. Bickel, *Trans. Faraday Soc.*, **57**, 1325 (1961).
(29) L. R. Mahoney, *J. Amer. Chem. Soc.*, **89**, 1895 (1967); **89**, 5619 (1967); **87**, 1089 (1965).
(30) These equations are slightly modified to account for the absence of a step in the initiation process which absorbs oxygen.

TABLE III

THE EFFECT OF FREE-RADICAL INHIBITORS ON THE RATE OF AUTOXIDATION[a] OF 1-OCTENE AND THE RATE OF DISAPPEARANCE[b] OF CHROMIUM(III) ACETYLACETONATE AND *t*-BUTYL HYDROPEROXIDE (30° IN 1-CHLOROOCTANE)

Inhibitor	Inhibitor conen, $M \times 10^4$	Induction period,[c] sec $\times 10^{-3}$	R_{Oi}[d]	R_O[e]	n[f]	$k_p/nk_{In} \times 10^4$	R_{Cr}[g]	R_P[h]
Nitrobenzene	1.63	5.2	0.165	1.08	0.77	4.4	2.43	5.89
Aniline	1.08	8.5	0.500	1.94	2.14	7.8	2.72	4.03
Ethylenediamine	1.83	3.0	0.130	0.851	0.34	4.5	2.06	7.10
Pyridine	2.03	4.0	0.073	2.11	0.28	4.0	1.43	5.21
α-Tocopherol	1.12	6.8	0.500	1.85	1.65	8.0	2.72	2.07
BHA[i]	1.28	8.3	0.408	1.59	2.32	5.7	3.58	4.24
DOP[j]	0.75	5.0	0.113	1.22	2.86	0.8	4.29	8.95
Phenol	0.44	3.5	0.114	1.01	2.99	5.3	3.72	1.59
Phenol	1.74	8.7	0.491	1.52	2.00	8.3	4.00	2.26
None	...	...	9.00[k]	2.44[l]	...	...	2.68	13.7

[a] Oxygen pressure = 1 atm, [1-octene] = 2.56 M, [Cr(acac)$_3$] = 1.6×10^{-3} M, [*t*-BuOOH] = 0.76 M. [b] *In vacuo*, [1-octene] = 2.56 M, [Cr(acac)$_3$] = 1.6×10^{-3} M, [*t*-BuOOH] = 0.76 M. [c] For autoxidation. [d] Rate of oxygen uptake during induction period $\times 10^6$ M/sec. [e] Rate of oxygen uptake after induction period $\times 10^6$ M/sec. [f] Stoichiometric factors. [g] R_{Cr} = rate of Cr(acac)$_3$ disappearance $\times 10^8$ M/sec. [h] R_P = rate of *t*-BuOOH disappearance $\times 10^5$ M/sec. [i] Mixture of 2- and 3-*t*-butyl-4-hydroxyanisole. [j] 2,6-Di-octadecylphenol. [k] Rate for first 1000 sec. [l] Rate after 5000 sec.

Additional reactions which undoubtedly further complicate the kinetics of our system would include

$$t\text{-BuOO}\cdot + \text{RH} \xrightarrow{k_5'} t\text{-BuOOH} + \text{R}\cdot$$

$$t\text{-BuOO}\cdot + \text{ROOH} \xrightarrow{k_{-5}'} t\text{-BuOOH} + \text{RO}_2\cdot$$

It is clear from the data of Table III that inhibitor is involved in the *t*-butyl hydroperoxide decomposition chains, but it is also clear from the stoichiometric factors in Table III that the effectiveness of the phenols in autoxidation inhibition is not reduced by the simultaneous involvement in *t*-butyl hydroperoxide decomposition. The implication of this observation is that propagation steps in peroxide decomposition in this system lead to autoxidation.

Nitrogen-Containing Compounds.—Inhibition of free-radical reactions by amines is well known.[3,4] The mechanism for inhibition by primary and secondary amines almost certainly involves radical abstraction of the N hydrogen.[3,4] The complexing of amines with chromium species is a well-established phenomenon.[31] In the present work it was noted that aniline, ethylenediamine, and pyridine inhibit both autoxidation and *t*-butyl hydroperoxide decomposition chains. Almost no effect is observed on the rate of chromium(III) acetylacetonate disappearance, implying that ligand exchange (if any) at low amine concentrations does not affect the initiation process.

A stoichiometric factor of *ca.* 2 was obtained for aniline, similar to phenols, but pyridine and ethylenediamine gave values less than 0.5, typical of the behavior of weak inhibitors or chain-transfer agents.[3]

Although pyridine inhibits *t*-butyl hydroperoxide decomposition at low concentrations (*ca.* 10^{-4} M) when it is used as a solvent (*ca.* 5 M), it actually enhanced the *t*-butyl hydroperoxide decomposition rate (see Table I). Sheng and Zajacek have recently shown that pyridine reacts slowly with *t*-butyl hydroperoxide in the presence of chromium(III) acetylacetonate (and other metal acetylacetonates) to form pyridine N-oxide. At low pyridine concentrations, this reaction is apparently insignificant.

It has been observed that nitrobenzene acts as an inhibitor toward both the *t*-butyl hydroperoxide decomposition and the autoxidation chains. Nitro compounds have been shown to be effective inhibitors in free-radical polymerizations,[7] but not in cumene or dihydroanthracene[5,29] autoxidations. We should like to suggest that nitro compounds may react with alkoxy radicals but may be inert toward alkyl peroxy radicals and, to the extent that an autoxidizing system contains alkoxy radicals, nitrobenzene will behave as an inhibitor.

Registry No.—Chromium(III) acetylacetonate, 13681-82-8; 1-octene, 111-66-0; *t*-butyl hydroperoxide, 75-91-2.

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(31) J. Kleinberg, Wm. J. Argersinger, Jr., and E. Groswold, "Inorganic Chemistry," D. C. Heath & Co., Boston, Mass., 1960, p 526.