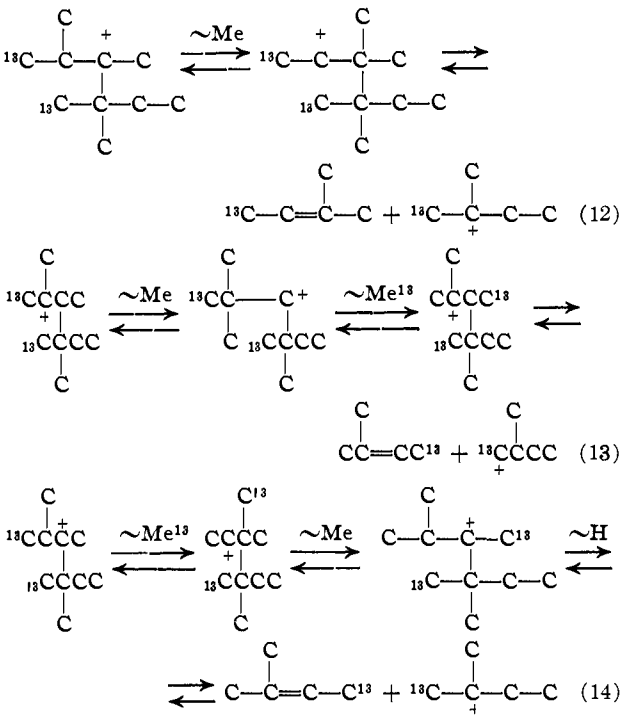
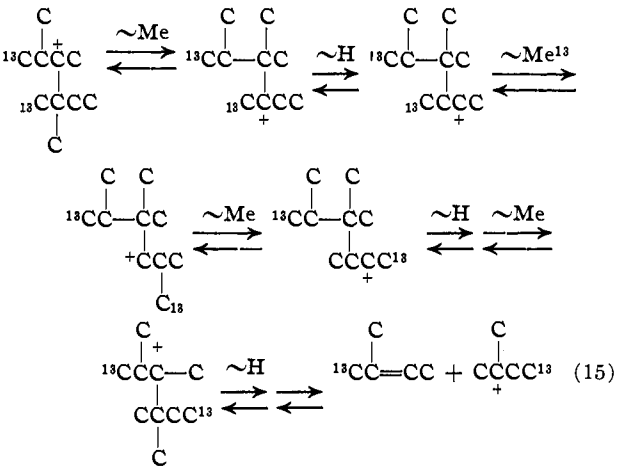


Experimental

Synthesis of C^{13}-Labeled *t*-Amyl Alcohols.—2-Methyl-2-butanol-2-C^{13} was prepared by the usual Grignard reaction involving magnesium (0.456 mole), methyl iodide (0.456 mole) and methyl propionate-carbonyl-C^{13} (0.114 mole). The yield, based on the methyl propionate, was 80%. 2-Methyl-2-butanol-1-C^{13} was synthesized from the Grignard reaction of magnesium (0.150 mole), methyl iodide-C^{13} (0.134 mole) and butanone (0.144 mole). The yield, based on the methyl iodide, was 66%. Both alcohols were purified by use of a Beckman Megachrom.



Synthesis of C^{13}-Labeled *t*-Amyl Chlorides.—The chlorides were prepared by the same method as used by Roberts and his coworkers.[3] The following is a typical experiment. 2-Methyl-2-butanol-2-C^{13} (0.071 mole) and concentrated hydrochloric acid (0.222 mole) were heated together and the fraction boiling at 65–82° was collected and purified. The yield of 2-chloro-2-methylbutane (0.069 mole) was 97%. Both chlorides were purified by use of a Beckman Megachrom.

Reactions of the Labeled *t*-Amyl Chlorides with Aluminum Chloride.—The labeled *t*-amyl chlorides were treated with aluminum chloride as described previously.[2] Both the *t*-amyl chlorides and the hexyl chlorides were separated from the reaction mixture with the aid of a Beckman Megachrom.

Isotopic analysis of the alkyl chlorides and alcohols was done with a Consolidated model 21-103C mass spectrometer. The n.m.r. spectra were taken with a model V4300-2 Varian Associates high resolution n.m.r. spectrometer at 60 Mc.

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Effects of Metallic Compounds in Oxidation Systems. I. Ferric Chloride as an Inhibitor

BY GEORGE S. HAMMOND, LEE R. MAHONEY AND U. S. NANDI

RECEIVED OCTOBER 19, 1962

Ferric chloride is a good inhibitor of the ABN-initiated oxidation of cumene and tetralin in chlorobenzene solution but does not inhibit the oxidation of cyclohexene. A mechanism is proposed to account for the results. Phenols are believed to be produced by rearrangement of cumyl and tetralyl hydroperoxides in the presence of ferric chloride, and chains are broken by reaction of peroxy radicals with ferric phenoxides.

Liquid-phase oxidation of hydrocarbons is well known to be affected by salts of heavy metals.[1-6] At least one of the effects of such additives is acceleration of initiation by hydroperoxides that are commonly formed by the oxidative process.[1,5,6,7] Direct evidence for radical-producing oxidation–reduction reactions between hydroperoxides and metal ions is provided by studies of hydroperoxide decomposition rates[8,9] and by the use of metal ion–hydroperoxide recipes as initiators for vinyl polymerization reactions.

On the other hand, inhibition of oxidation by salts of metals capable of undergoing one-electron oxidation–reduction transformations has been reported. Denisov and Emanuel[5,10] have shown that solutions originally containing cobaltous or manganous stearates show residual inhibitory action after they have ceased to function as initiators. They indicate that inhibition is associated with the existence of the metal ions mainly in their lower oxidation states in the absence of substantial amounts of hydroperoxide. Inhibition of hydrocarbon oxidation by copper stearate has also been reported[11] and induction periods, which can be eliminated by addition of hydroperoxide, in oxidations catalyzed by manganous and cobaltous salts have been reported.[12] Furthermore, Bamford, *et al.*,[13] have shown

(1) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 427.

(2) A. Robertson and W. A. Waters, *Trans. Faraday Soc.*, **42**, 201 (1946).

(3) P. George, E. R. Rideal and A. Robertson, *Proc. Roy. Soc.* (London), **A181**, 119 (1943); **A188**, 10 (1946).

(4) C. E. H. Bawn and J. B. Williamson, *ibid.*, **47**, 735 (1951).

(5) E. Denisov and N. M. Emanuel, *Uspekhi Khimi* (Engl. trans.), 645 (1960).

(6) C. K. Ingold, *Chem. Rev.*, **61**, 563 (1961).

(7) A. V. Tobolsky, D. J. Metz and R. B. Mesrobian, *J. Am. Chem. Soc.*, **72**, 1942 (1950).

(8) W. S. Wise and G. H. Twigg, *J. Chem. Soc.*, 2168 (1953).

(9) A. E. Woodward and R. B. Mesrobian, *J. Am. Chem. Soc.*, **75**, 6189 (1953).

(10) E. T. Denisov and N. M. Emanuel, *Zhur. Fiz. Khim.*, **30**, 2499 (1956).

(11) P. George, E. Rideal and A. Robertson, *Proc. Roy. Soc.* (London), **A185**, 283 (1946).

(12) A. J. Chalk and J. F. Smith, *Trans. Faraday Soc.*, **53**, 1214, 1235 (1957).

(13) C. H. Bamford, A. D. Jenkins and R. Johnston, *Proc. Roy. Soc.* (London), **A239**, 214 (1957).

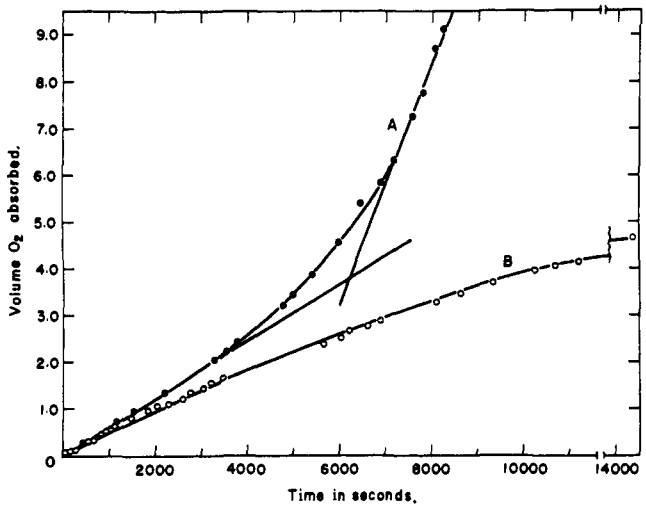


Fig. 1.—Oxidation of tetralin in the presence of ferric chloride: $[FeCl_3]_0 = 0.628 \times 10^{-3}$ *M*, $[ABN]_0 = 4.87 \times 10^{-2}$ *M*, [tetralin] = 2.45 *M*, solvent was chlorobenzene. Curve B for solution originally containing 1.35×10^{-4} *M* cumyl hydroperoxide; *T* = 70°; oxygen volume measured in ml.

that ferric chloride is an efficient inhibitor of vinyl polymerization. Some of the ways in which radicals can interact with metallic compounds are indicated by the recent reports of Kochi.[14] In the light of such experiences by other workers we anticipated that the behavior of ferric chloride in initiated oxidation might be both interesting and complex. Such has proved to be the case.

Results

We have studied the oxidation of tetralin, cumene and cyclohexene in chlorobenzene solution with azobisisobutyronitrile (ABN) as an initiator.[15] Such experiments can be designed so as to give convenient rates of oxidation in the temperature interval 60–80° where autocatalytic effects due to thermal decomposition of hydroperoxides are negligible. The rate of radical production from ABN is well documented.[16]

Addition of small amounts of ferric chloride to standard reaction mixtures containing cumene or tetralin resulted in the development of pronounced, and surprisingly long, inhibition periods. Data from an extensive series of experiments with tetralin as the substrate are summarized in Table I and Fig. 1 shows plots of typical runs. As is illustrated by curve B in Fig. 1, inclusion of small amounts of the hydroperoxide derived from the substrate resulted in further extension of the inhibition periods. In fact, no runs in which hydroperoxide was added were followed long enough to observe the end of the inhibition period. Addition of *t*-butyl hydroperoxide did not increase the inhibition periods.

A careful study was made of the factors which influence the rate of oxygen uptake during the inhibition periods. Lines, such as those shown in Fig. 1, were drawn tangent to the experimental oxidation curves and were taken as a measure of the oxidation rates, R_0, at zero time. Since the rate of radical production (R_i) from ABN is known, one can calculate the apparent kinetic chain lengths, R_0/R_i. In the absence of inhibitors the chain lengths are not long, *e.g.*, 5.3 for 2.45 *M* tetralin and 4.87 × 10^{-2} *M* ABN. Consequently, it is not surprising that the chains in the presence of inhibitor are very short. To even call the reactions in the presence of higher concentrations of ferric chloride chain processes is stretching the terminology.

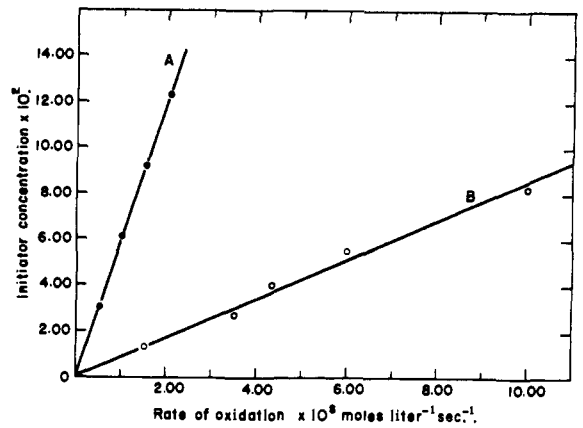


Fig. 2.—Dependence of rate of tetralin oxidation on concentration of ABN: curve A, cumene, $[FeCl_3]_0 = 0.476 \times 10^{-3}$ *M*, initiator = 1,1′-azocyanocyclohexane, *T* = 80°; curve B, tetralin, $[FeCl_3] = 0.214 \times 10^{-3}$ *M*, initiator = ABN, *T* = 70°.

TABLE I

OXIDATION OF TETRALIN IN CHLOROBENZENE IN THE PRESENCE OF FERRIC CHLORIDE[a] AT 70°

Run[a]	$[FeCl_3]_0 \times 10^5$	$[ABN]_0 \times 10^2$	$R_i \times 10^6$, moles l.$^{-1}$ sec.$^{-1}$	$R_0 \times 10^6$, moles l.$^{-1}$ sec.$^{-1}$	R_0/R_i	n[b]
22[c]	207	3.28	1.83	3.11	1.70	10
23	207	3.28	1.83	3.10	1.73	
56	132	4.86	2.68	3.90	1.45	19
9	90	2.04	1.14	1.78	1.56	
59	66	7.22	4.06	7.00	1.63	19
96	62.8	4.87	2.72	4.23	1.55	23
71	54.3	7.22	4.06	5.61	1.40	
69[d]	54.3	4.87	2.72	5.80	2.13	
113	39.2	12.24	6.84	9.82	1.44	
15	31.7	3.14	1.76	3.08	1.75	
16[d]	31.7	3.14	1.76	3.08	1.75	
97	31.4	4.87	2.72	4.33	1.59	
38	25.5	2.74	1.53	2.90	1.90	
48	21.4	8.24	4.60	10.0	2.17	37
52	21.4	5.49	3.07	5.96	1.94	
51	21.4	4.02	2.24	4.32	1.93	
49	21.4	2.75	1.54	3.51	2.27	
53	21.4	1.38	0.768	1.52	1.98	
42	15.3	2.75	1.53	3.38	2.21	48
93	12.6	4.87	2.72	5.52	2.03	55
39	8.50	2.75	1.53	4.35	2.84	58
87	6.28	2.43	1.36	4.26	3.14	74
43	5.67	2.75	1.53	6.36	4.15	47
80	5.34	2.31	1.29	6.75	5.21	37
84	5.34	0.462	0.258	1.22	4.75	
45	5.09	0.549	0.306	1.65	5.40	24.5

[a] Tetralin concentration = 2.44 *M*; p_{O_2} = 740–745 mm. unless otherwise noted. [b] Number of chains stopped during inhibition period; some runs were not followed to the end of the inhibition period. [c] p_{O_2} = 361 mm. [d] 1.205 *M* mesitylene added. [e] p_{O_2} = 320 mm.

As is shown in Fig. 2, the inhibited oxidation rates are directly proportional to the initiator concentration with both substrates. The rates were also independent of the oxygen pressure.

Data obtained with varying concentrations of ferric chloride and constant tetralin concentration are summarized in Table I. In the concentration range 4 × 10^{-4} to 2.2 × 10^{-3} *M* the chain length is essentially

(14) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 774, 1572 (1962); J. K. Kochi and F. F. Rust, *ibid.*, **84**, 2017 (1962); H. E. De La Mare, J. K. Kochi and F. Rust, *ibid.*, **84**, 2013 (1962).

(15) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3233 (1955).

(16) G. S. Hammond, J. N. Sen and C. E. Boozer, *ibid.*, **77**, 3244 (1955); G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin and R. T. Keys, *ibid.*, **82**, 5394 (1960).

constant at 1.5. At lower concentrations of inhibitor the initial chain length rises rapidly to the uninhibited value, and no inhibition period is observed in solution containing less than 5×10^{-5} M ferric chloride. The stoichiometric factors also vary in an interesting manner. The values increase with decreasing concentration of ferric chloride and appear to reach a maximum at 7×10^{-5} M and then fall. However, data for the runs with very low concentrations of ferric chloride do not show well defined induction periods and it is certain that some normal chain termination must have occurred from the outset in such runs. A limited number of runs with cumene showed that the stoichiometric factors were lower, by about 50%, than those observed in comparable runs with tetralin.

Variation of the concentrations of the substrates, with the concentrations of ABN and ferric chloride fixed, gave results summarized in Table II. While insufficient data are available to allow a formal analysis, it is apparent that the rates are much more sensitive to the concentrations of hydrocarbons at low concentrations than at concentrations above one molar. That the effects of variation in substrate concentration may be rather complex is indicated by run 69 in which mesitylene was added. The value of R_0/R_i was increased significantly despite the fact that mesitylene has no effect on the rate of uninhibited oxidation.

TABLE II

DEPENDENCE OF KINETIC CHAIN LENGTH ON HYDROCARBON CONCENTRATION

A. $[FeCl_3]_0 = 0.66 \times 10^{-3}$ M, $[ABN]_0 = 7.22 \times 10^{-2}$ M

Run	Tetralin	$R_0 \times 10^6$	R_0/R_i
59	2.448	7.00	1.63
57	1.224	5.94	1.38
58	0.490	5.41	1.26
60	0.098	4.12	0.958
61	0.0245	3.52	0.819

B. $[FeCl_3]_0 = 0.0628 \times 10^{-3}$ M, $[ABN]_0 = 2.434 \times 10^{-2}$ M

Run	Tetralin	$R_0 \times 10^6$	R_0/R_i
87	2 448	4.26	3.14
88	4.896	5.21	3.83
89	0.098	2.10	1.54
90	1.224	3.82	2.75
91	3.672	4.85	3.49
92	0.490	3.22	2.32

C. $[FeCl_3]_0 = 0.534 \times 10^{-3}$ M, $[ABN]_0 = 7.22 \times 10^{-2}$ M

Run	Tetralin	Mesitylene	R_0/R_i
71	2.448	...	1.40
69	2.448	1.205	2.15

D. $[FeCl_3]_0 = 0.534 \times 10^{-3}$ M, $[ABN]_0 = 7.22 \times 10^{-2}$ M

Run	Cumene	$R_0 \times 10^6$	R_0/R_i
70	2.390	7.04	1.65
72	1.195	5.01	1.17
73	0.598	4.28	1.00

Probably the most informative piece of evidence for the nature of the inhibition of tetralin and cumene oxidation was the observation that *the oxidation of cyclohexene is not inhibited by ferric chloride*. In fact there is a barely perceptible, but probably significant, increase in the rate.

The results imply that oxidation products from tetralin and cumene, probably the hydroperoxides, are involved in the inhibitory action. Kharasch, *et al.*,[17] have reported that ferric chloride catalyzes the disproportionation of cumyl hydroperoxide to acetone and phenol. We have confirmed this observation and have, furthermore, found that the reaction is very fast in chlorobenzene solution. The peroxide titer fell to zero in less than a minute after mixing equal volumes of solutions containing 10^{-5} M ferric chloride and 10^{-2} M cumyl hydroperoxide at room temperature. Attempts to isolate products related to phenol from mixtures obtained in the oxidation of cumene in the presence of ferric chloride were unsuccessful. However, vapor chromatographic analysis showed that acetone

(17) M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

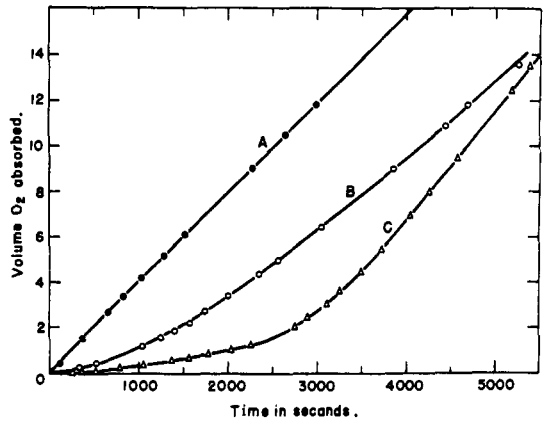


Fig. 3.—Oxidation of cyclohexene: curve A, no inhibitor added; curve B, $[phenol]_0 = 1.80 \times 10^{-3}$ M; curve C, $[phenol]_0 = 1.80 \times 10^{-3}$ M, $[FeCl_3]_0 = 6 \times 10^{-5}$ M; $[ABN] = 3.74 \times 10^{-2}$ M and [cyclohexene] = 1.65 M in all experiments; $T = 70°$.

was formed. Furthermore, production of acetone occurs only during the inhibition period. These experiments were carried out at 80° using 1,1'-azocyanocyclohexane[18] as the initiator since it is known that oxidation of 2-cyano-2-propyl radicals produces some acetone.[19]

Disproportionation of either cumyl hydroperoxide or tetralin hydroperoxide would produce phenols which are known to be moderately active antioxidants. It seemed evident, however, that some other, much more potent, antioxidant must be involved. Since ferric phenoxides seemed to be attractive candidates for such action, the inhibitory action of phenols in the oxidation of cyclohexene both with and without added ferric chloride was studied. The data are summarized in Table III. Figure 3 shows typical runs with phenol.

TABLE III

EFFECT OF PHENOLS AND FERRIC CHLORIDE ON CYCLOHEXENE OXIDATION

Phenol

Run	$[ArOH]_0 \times 10^3$	$[FeCl_3]_0 \times 10^3$	n
122	1.80	None	2.0
123	1.80	Satd.	3.07
130	1.80	1.13	2.10
131	0.90	1.69	2.55
132	.90	1.99	3.01
135	.90[a]	Satd.	5.0

Tetralin hydroperoxide

Run	$[RO_2H]_0 \times 10^3$	$[FeCl_3]_0 \times 10^3$	n
146	0.832	1.15	2.4

p-Cresol

Run	$[ArOH]_0 \times 10^3$	$[FeCl_3]_0 \times 10^3$	n
118	5.96	None	2.2
119	5.96	Satd.	1.5
120	2.98	Satd.	1.5
133	2.98	1.67	1.5
134	2.98	None	2.2

o-Cresol

Run	$[ArOH]_0 \times 10^3$	$[FeCl_3]_0 \times 10^3$	n
126	4.62	None	2.2
127	4.62	1.50	2.2

[a] Benzoquinone, 0.82×10^{-3} M, added

Ferric chloride not only increases the inhibitory potency of phenol, as judged by the rate of oxidation during the inhibition period, but also extends the period of inhibition; *i.e.*, higher values of n are calculated. However, because of the sharpness of the change over after the inhibition period, the rate rises more rapidly toward the uninhibited rate in the presence of ferric chloride; in other words, ferric chloride makes phenol assume the behavior characteristic of a strong inhibitor. Since we judged that such behavior might involve reoxidation of iron(II) species to iron(III), an oxidant, benzoquinone, was added to the mixture in one run.

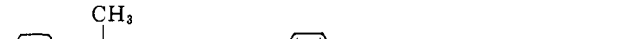
(18) C.-H. S. Wu, G. S. Hammond and J. M. Wright, *J. Am. Chem. Soc.*, **82**, 5386 (1960).

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

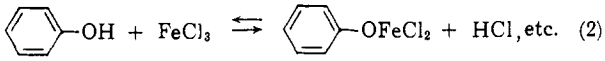
An additional extension of the inhibition period was observed, despite the fact that benzoquinone shows no inhibitory action either by itself or in the presence of ferric chloride if no phenol is added. In contrast to the behavior of phenol, the addition of ferric chloride decreases the length of the induction period produced by *p*-cresol. *p*-Cresol is a sufficiently powerful inhibitor of cyclohexene oxidation to render comparison of the rates during the inhibition periods unmeaningful. The behavior of *o*-cresol is intermediate in that addition of ferric chloride gives no significant change in the length of the induction period. As would be anticipated, the combination tetralin hydroperoxide–ferric chloride inhibits the oxidation of cyclohexene strongly with an apparent stoichiometric factor of 2.4.

Discussion

The reaction system is far too complex to permit thorough testing of any mechanism with the data available. However, semi-intuitive interpretation of the data available suggests mechanisms which seem reasonable. There is a strong implication that cumyl and tetralyl hydroperoxides are involved along with ferric chloride in the inhibitory process. That something more than an oxidative function is involved is implied by the inertness of *t*-butyl hydroperoxide. The fact that ferric chloride alone does not inhibit oxidation of cyclohexene is attributed to the fact that phenols can not be produced by acid-catalyzed rearrangement of cyclohexenyl hydroperoxide or other oxidation products. The following partial mechanism is suggested to account for the observed effects. Cumyl hydroperoxide is used as an example, although analogous changes can be formulated starting with tetralyl hydroperoxide. In the equations X stands for an unspecified ligand, either chloride or phenoxide.



(1)



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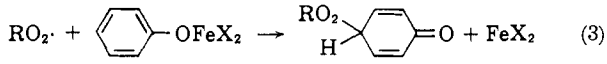
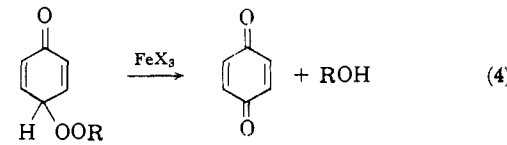
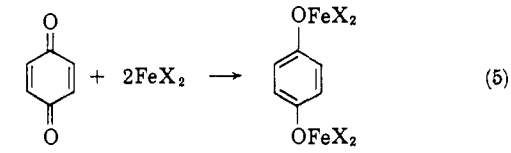


(3)

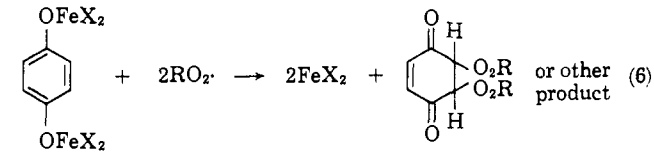
Since the rates of oxygen uptake during the inhibition periods in the runs with tetralin and cumene as substrates were independent of oxygen pressure, it is clear that the actual chain-breaking process involves peroxy radicals rather than R·. The great length of the inhibition periods indicates that reaction 3 must be followed by some step in which iron(II) is reoxidized to iron(III). It is not possible to specify the oxidant which plays this role since oxygen, peroxy radicals, hydroperoxides and products of chain-breaking reactions are all potentially capable of doing the job. Study of the cooperative action of phenols and ferric chloride in the inhibition of cyclohexene oxidation suggests more specific possibilities. If only reaction 3 were involved, a mixture of phenol and ferric chloride should give a stoichiometric factor of 1.0. The observed value of three indicates that each iron(II) species formed in reaction 3 is reoxidized to iron(III) with the concurrent formation of a bifunctional inhibitor. Since benzoquinone was found to extend the inhibition periods, it is tempting to speculate that 4-peroxycyclohexadienones, formed by reaction 3, undergo Lewis acid-catalyzed disproportionation to give benzoquinone. Reduction of the quinone by iron(II) would produce iron(III) derivatives of hydroquinone which might stop two more chains.



(4)

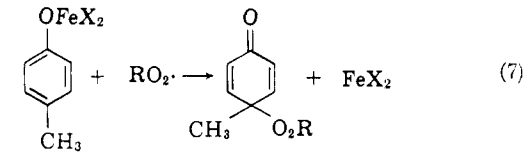


(5)



(6)

The fact that ferric chloride *decreases* the induction period due to *p*-cresol indicates that 4-alkyl-4-peroxydienones do not decompose to give oxidants which can re-enter the oxidation cycle.



(7)

Since the inhibition period owing to *o*-cresol is the same in the absence or the presence of ferric chloride, the ferric derivatives of that compound must react with peroxy radicals to give active and inert products in a ratio which is intermediate between those observed with phenol and those which obtain with *p*-cresol.

The apparent limiting chain length for the oxidation of tetralin in the presence of relatively high concentrations of ferric chloride is about 1.5. Estimation of this value depends upon the assumption that oxygen absorption by initiator fragments is almost exactly balanced by nitrogen evolved from the initiator as is the case if the initiator is decomposed under oxygen in chlorobenzene containing no oxidizable substrate. Consumption of one mole of oxygen by oxidation of the substrate for every mole of radicals produced from the inhibitor is necessary to maintain a steady state in hydroperoxide, the critical co-inhibitor. The over-all stoichiometry of a half cycle would be that given by eq. 8. More peroxy radicals would be diverted from

$$rO_2\cdot + RH + O_2 + FeX_3 \longrightarrow \text{peroxydienone} + CH_3COCH_3 + FeX_2 + HX \quad (8)$$

$rO_2\cdot$ = oxidized initiator radical
RH = substrate

conversion to hydroperoxide (and subsequently to phenols) by reaction with species such as iron(II) hydroquinone. All one can really say is that the observed stoichiometry is not inconsistent with the proposed mechanism.

Experimental

Ferric chloride (Fisher anhydrous, sublimed) was resublimed by the method of Tarr[20] sealed under chlorine in small ampoules. **Tetralin, cumene and chlorobenzene** were purified as described previously. **Azobisisobutyronitrile** (Westville Laboratories) was recrystallized twice from methanol and dried *in vacuo* over phosphorus pentoxide; m.p. 101–102°. **Cumyl hydroperoxide** (Matheson, Coleman, and Bell) was purified by the method of Kharasch, *et al.*[17] The peroxide titer showed 97% purity. *t*-Butyl hydroperoxide (Lucidol) was distilled at reduced pressure, b.p. 38.5–39° at 20 mm.; the peroxide titer showed 95% purity. **Tetralin hydroperoxide** was prepared by the method of Knight and Swern[21]; m.p. 55–56°.

(20) B. R. Tarr, *Inorganic Syntheses*, **3**, 191 (1952).
(21) H. B. Knight and D. Swern, *Org. Syntheses*, **34**, 90 (1954).

Preparation of Solutions.—Reproducible kinetic data were obtained only when moisture was very carefully excluded. All solutions were prepared in a dry-box in the presence of phosphorus pentoxide. Solutions of ferric chloride prepared in this way and stored in flasks wrapped in aluminum foil to exclude light showed no change in activity after 10 to 14 days. Glassware was dried in an oven at 110° and then transferred to the dry-box where it was allowed to cool. The reaction cells used for kinetic runs were filled in the dry-box and immediately transferred to the apparatus previously described.[15]

Determination of Acetone.—The reaction vessel was fitted with a serum stopper and samples were withdrawn periodically by means of a syringe. The samples were transferred to cooled glass vials which were also sealed with serum stoppers. Samples were examined by vapor chromatography on a Carbowax column at 55°. Amounts were estimated by comparison of the areas of the elution peaks in comparison with the peak areas given by standard solutions of acetone in chlorobenzene–cumene. After 3,000 seconds, shortly before the end of the inhibition period, the acetone concentration had risen to 6.7×10^{-3} M. During this time 14.2×10^{-3} mole/liter of oxygen had been absorbed and 9.4×10^{-3} mole/liter of radicals had been produced. Analyses after 17,000 and 25,000 seconds indicated acetone concentrations of 5.8×10^{-3} and 6.3×10^{-3} M, respectively.

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The Basic Strengths of Some Aromatic Aldehydes and Ketones

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The pK_{BH^+} values of ten aromatic carbonyl compounds have been determined. The variations of basic strengths within the series of aromatic aldehydes agree with theoretical predictions based on molecular orbital theory. The discrepancies noted for other aromatic carbonyls are discussed.

Although aromatic aldehydes and ketones are usually regarded as very weak bases, various stable salts of several members of this class of compounds have nonetheless been known for a long time. For example, the perchlorate salts of benzalacetophenone, dibenzalacetone and benzophenone were reported early this century.[1]

It is significant that only salts of the more highly conjugated members appear to be stable enough to allow isolation. There do not appear to be any reports of the isolation of salts of benzaldehyde or acetophenone, for example. The explanation of this apparent significant difference in basic strength appeared then to present an interesting problem and prompted the present investigation. Very little quantitative data on the basic strengths of aromatic aldehydes and ketones were available from the literature and this paper reports these data for some ten such compounds and describes attempts to correlate the observed basic strengths with molecular structure.

Results and Discussion

The basic strengths of the compounds listed in Table I were determined spectrophotometrically in aqueous sulfuric acid solutions using the method reported by Hammett and co-workers[2] for determination of basic strengths of weak bases.

TABLE I

THE pK_{BH^+} VALUES FOR VARIOUS AROMATIC CARBONYL COMPOUNDS

Number	Compound	pK_{BH^+}	σ_{or}[2]
1	Benzaldehyde	−6.99	0.571
2	2-Naphthaldehyde	−6.68	.529
3	9-Phenanthraldehyde	−6.39	.446
4	1-Naphthaldehyde	−6.34	.450
5	1-Anthraldehyde	−5.71	.381
6	9-Anthraldehyde	−4.81	.286
7	Acetophenone	−6.04[a]	.571
8	2-Acetylnaphthalene	−6.04	.529
9	1-Acetylnaphthalene	−5.86	.450
10	1-Acetylanthracene	−5.65	.381
11	Perinaphthenone	−1.40	.167

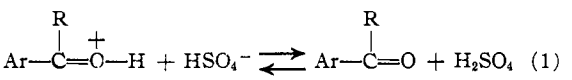
[a] Previously reported by Hammett and co-workers.[2]

(1) (a) K. A. Hofmann, *Ber.*, **42**, 4857 (1909); **43**, 178 (1910); (b) P. Pfeiffer, *Ann.*, **412**, 253 (1916).

(2) L. A. Flexser, L. P. Hammett and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).

With the notable exception of perinaphthenone, the compounds listed vary in basic strengths by a little more than two pK units. 9-Anthraldehyde is the most basic aldehyde of the series; we find it readily forms a red perchlorate salt when treated with perchloric acid.

In any explanation of the variations of pK_{BH^+} shown in Table I it seems safe to assume that salt formation with each base involves protonation of the carbonyl oxygen and that the equilibrium reaction involved is as shown in eq. 1.



$$\mathrm{Ar{-}\overset{R}{\overset{|}{C}}{=}\overset{+}{O}{-}H + HSO_4^- \rightleftharpoons Ar{-}\overset{R}{\overset{|}{C}}{=}O + H_2SO_4} \quad (1)$$

Consider first the aromatic aldehydes. The base and the conjugate acid for each carbonyl compound both possess the same number of π-electrons; hence, unlike variations in basic strengths of arylamines or aromatic hydrocarbons, the variations of pK_{BH^+} values cannot be attributed to changes in π-electron localization energies. Furthermore, of the various factors contributing to the total free energy changes involved in eq. 1, changes in O–H bond energy and changes in solvation energies are not expected to vary significantly from one carbonyl system to another. The one factor which is not expected to remain constant, and which is therefore considered mainly responsible for the variations in the basic strengths, is the change in total π-electron energy when the effective electronegativity of oxygen is changed following protonation. If this change in total π-electron energy of the system is denoted by ΔE_π then it follows that a linear relationship such as eq. 2 should exist between the ΔE_π and the pK_{BH^+} values for the various aldehydes.

$$\Delta E_\pi = a + b \times pK_{BH^+} \quad (2)$$

Attempts to correlate the data in Table I then require determination of ΔE_π. One obvious way this could be done would be to calculate separately, for each molecule, the total π-energy of the protonated and unprotonated species using the Hückel molecular orbital method. However, this approach would require some guess made as to the electronegativity parameters appropriate for oxygen and protonated oxygen. Also the method would involve considerable computation. Instead we have made use of a perturbation method