STUDY OF CHEMICAL AGENT DECONTAMINATION SYSTEMS FOR MULTIPURPOSE USE
FIFTH BIMONTHLY PROGRESS REPORT

Covering the Period
17 February 1964 to 20 April 1964

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ABSTRACT

Competitive hydrogen transfer studies were conducted for methyl benzoate, diisopropyl methyl phosphonate (DIMP), GB, GF and HD vs. carbon tetrachloride in each case employing phenylazotriphenylmethane (PAT) as a source of phenyl radicals.

The cooxidation of GB with benzaldehyde, and of GF with 2, 2-azobis (isobutyronitrile) (AIBN), indene, and with cyclooctene was investigated at 25°C.

The kinetics of the autoxidation of GF in the presence of Co(II) catalyst at 75-135°C were investigated. In addition, the autoxidation reaction was investigated in the absence of catalyst and in the presence of varying quantities of catalyst. The effect of 2,6-di-tert-butylphenol (DTBP) as an inhibitor was investigated.

The autoxidation of HD in the absence and in the presence of Co(II) catalyst at 105°C was examined.

The use of ferrous phthalocyanine as a heterogeneous catalyst for the autoxidation of GF at 25°C was examined.

The results obtained here are compared with those reported for the autoxidation of carboxylic esters.
SUMMARY

Competitive hydrogen transfer studies were initiated during this period to assess the relative reactivity of C-H bonds in various CW agents. The co-oxidation of GB and GF with various co-oxidants at 25°C was studied to determine the ease of initiation and degree of propagation. These results confirm the feasibility of initiation of autoxidation of GB and GF at 25°C and indicate the possibility of some chain propagation.

Studies on the autoxidation of GF at elevated temperatures, 75-135°C, were continued during this period. The results suggest the presence of a free radical chain mechanism. Cobaltous naphthenate markedly catalyzes the rate of autoxidation. Its exact role is however still not clear.

Comparison of the results obtained on the elevated temperature autoxidation of GF with those reported in the literature for certain dibasic carboxylic esters suggests that chain branching may be an important factor.
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1. INTRODUCTION AND STATEMENT OF TASK

This is the Fifth Bimonthly Progress report, submitted in response to the schedule for contract number DA 18-108-ANC-203(A). The task is to investigate the feasibility of developing a catalyst system for multi-purpose decontamination of persistent CW agents.

2. OVERALL OBJECTIVE

To develop a catalyst system for effecting the decontamination of various CW agents under ambient conditions.

3. OBJECTIVES FOR THE REPORT PERIOD

a. Establish the feasibility of oxidation by air of the phosphonoxy alkyl radicals derived from agents under ambient conditions (cooxidation studies).

b. Investigate the relative ease of radical abstraction of hydrogen from various CW agents by phenyl radicals.

c. Investigate the kinetics and mechanism of the autoxidation of GF in the presence and absence of cobaltous naphthenate at various temperatures.

d. Investigate the autoxidation of HD at various temperatures as time permits.

e. Continue screening different "catalysts" (as cobalt naphthenate) and co-catalysts for the autoxidation of GF.

4. RESULTS AND DISCUSSION

4.1 Hydrogen Transfer Studies

Hydrogen transfer studies were extended during this period to the use of phenyl radicals. Phenyl radicals are neutral reactive species and are considered not to be strongly influenced by polar effects. Relative
reactivity data of the CW agents towards the action of this radical can provide information on the relative ease of radical initiation of autoxidation.

Professor G. A. Russell, our consultant, has obtained extensive data on the competitive reactivity of several classes of compounds towards phenyl radicals. Carbon tetrachloride serves as the common substrate to which the reactivity of each of over 100 compounds was compared.

We have followed his procedure so that our results may be compared with his results. The phenyl radicals were generated by the thermal decomposition of phenylazotriphenylmethane (PAT).

4.1.1 Reaction of PAT With G-agents and With Dimethyl Methylphosphonate

The results we obtained are given in table 1.

A duplicate run on methyl benzoate was included to check out our procedure. The results obtained in this case agreed very well with those reported by Russell.

However, unpublished data presented by Professor Russell, at the meeting on March 25, 1964, with members of the USACRDL and Melpar personnel, contained a lower value for dimethyl methylphosphonate in reactivity toward PAT (by a factor of ten) than the Melpar data. Experiments with dimethyl methylphosphonate are now being repeated at two concentrations.

The reactivity of the G-agents toward hydrogen abstraction by phenyl radicals is in excess of that of dimethyl methylphosphonate (by a factor of ten to a hundred). This may reflect the difference in reactivity of 3° hydrogen over 1° hydrogen and/or the presence of the fluorine atom which...
<table>
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<tr>
<th>SUBSTRATE</th>
<th>(\frac{\omega H_s}{\text{RH}})</th>
<th>(C_6H_6)</th>
<th>(C_6H_5Cl)</th>
<th>(\frac{k}{k_c})</th>
<th>Av.</th>
<th>(\frac{k_{C-H}}{k_c} \times 10^2)</th>
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</thead>
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<td>Methyl Benzoate</td>
<td>0.259</td>
<td>0.077</td>
<td>0.256</td>
<td>0.017</td>
<td>0.017</td>
<td>0.5</td>
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<td>Dimethyl Methylphosphonate</td>
<td>0.259</td>
<td>0.22</td>
<td>0.304</td>
<td>0.14</td>
<td></td>
<td>2.3</td>
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<td>GF</td>
<td>0.259</td>
<td>0.471</td>
<td>0.218</td>
<td>0.50</td>
<td></td>
<td>50</td>
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<td>GB (Redistilled Sample)</td>
<td>0.259</td>
<td>0.301</td>
<td>0.573</td>
<td>0.11</td>
<td></td>
<td>11</td>
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<tr>
<td>(Not Distilled)</td>
<td>0.259</td>
<td>0.215</td>
<td>0.278</td>
<td>0.15</td>
<td></td>
<td>(15)</td>
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may weaken the alkoxy carbon hydrogen bond. If such bond weakening by the fluorne does occur a similar weakening may occur at the methyl C-H bond. A comparison of diisopropyl methylphosphonate vs. OD would answer this question.

4.1.2 Reaction of PAT with HD

Table 2 presents the data for HD. The value for $k_e - H/k_e x 10^2$ for HD shows a twofold increase in reactivity over that of a $2^o$ hydrogen of a normal alkane. The value in Professor Russell's data for $k_e - H/k_e x 10^2$ for a $2^o$ hydrogen is 9.1. Extrapolation of data presented in Prof. Russell's paper, where the mercapto substituent presumably contributes to radical stabilization by resonance of the type,

\[
\begin{align*}
\text{S} & \quad \text{CH} \quad \text{CH} \quad \text{Cl} \\
\text{S} & \quad \text{CH} \quad \text{CH} \quad \text{Cl}
\end{align*}
\]

suggests that the increase in reactivity could be up to tenfold for a structure $Z - CH_3$, where $Z$ is the activating group (mercapto in this case) and the hydrogens are primary. In the case, such as we are dealing with, where $Z$ activates a $2^o$ hydrogen, the enhancement of reactivity appears to be smaller ($\approx 5$ fold in the case of $Z = \text{phenyl}$).

No data appear available for sulfides in which the $\alpha$-hydrogens are $2^o$ hydrogens.

The recent data of W. A. Pryor and H. Guard on the hydrogen abstraction by phenyl radicals from disulfides, which show that the $\alpha$ hydrogens are comparable in activity to benzylic hydrogens, provide a further comparison with our results for HD. Their results for diethyl disulfide are shown in table 2. It should be noted that if a correction
<table>
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<th>Substrate</th>
<th>CCl₄</th>
<th>C₆H₆</th>
<th>C₆H₅Cl</th>
<th>kₜ/kₒ</th>
<th>kₜ/C x 10²</th>
</tr>
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<tr>
<td>ClCH₂CH₂S CH₂CH₂Cl</td>
<td>1.79</td>
<td>.26</td>
<td>.457</td>
<td>0.83</td>
<td>21</td>
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<tr>
<td>CH₃CH₂S SCH₂CH₃</td>
<td></td>
<td></td>
<td></td>
<td>1.3</td>
<td>32.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.75</td>
<td>29</td>
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a. Data of Pryor and Guard, J. Am. Chem. Soc., 86, 1150 (1964)

b. Per mole Cal kₜ/kₒ [CCl₄] [C₆H₆ - 0.05] / [RH] [C₆H₅Cl]

c. This figure is that of Pryor. It is based on the yield of benzene, CA% attack on hydrogen, and does not appear to correct for the benzene formed in the cage process.

d. This figure is calculated on the basis of a 3% formation of benzene by the cage process.
factor (3%), due to the production of benzene is applied, the $k_{\text{OCN}}/k_0$ agree closely. (Prof. Russell's data and our data employ a correction factor of 5%, the initial concentration of PAT being 0.1M.) Since Pryor's data is based on averages in which several lower concentrations of PAT from 0.1M to 0.001M are used, a smaller correction factor should be applied. However, the exact correction required is uncertain.
4.1.3 Reaction of Acetyl Peroxide with Hexachlorobutadiene

Hexachlorobutadiene was chosen as the next diluent standard for the acetyl peroxide - HD reaction described in our Fourth Bimonthly Progress Report. The choice was based on the report that the analogous tetrachloroethylene is unreactive to methyl radicals. The low attack (20%) observed by us on HD suggested that the hexachlorobutadiene might not be as inert as previously considered. A control run in which hexachlorobutadiene was allowed to react with acetylperoxide showed that the hexachlorobutadiene did react.

The extent of reaction of HD with acetylperoxide is therefore greater than previously reported.

4.2 Co-oxidation Studies

Studies were continued on the co-oxidation of GF to provide fundamental information on (a) the feasibility and mode of its atmospheric oxidation, (b) the fate of agent O₂ radical, and on (c) the relative reactivity of various SO₂ radicals with GF.

4.2.1 Co-oxidation of GF with Azobisisobutyronitrile (AIBN) and Oxygen

As reported in the Fourth Bimonthly Progress Report, no change in GF concentration was observed when AIBN was decomposed in the presence of oxygen at 85°C. In a similar experiment, but at 65°C, it was again observed that no decrease in GF concentration occurred. The higher expected yield of isobutyronitrileperoxy radicals, favored by the greater solubility of oxygen and slower rate of decomposition of AIBN at the lower temperature apparently did not occur as evidenced by the high yield (N 50%) of tetramethylsuccinonitrile.
As described in the previous report, the formation of some peroxy radicals would be expected. The absence of any attack on GF by such a radical may be due to one or more reasons such as follows: (a) the isobutyronitriloperoxy radical may not be powerful enough to effect a hydrogen transfer from GF, (b) the nitrile group on the peroxy radical may cause this radical to become electronegative and thereby be repelled by the electronegative fluorine atom of GF, and (c) the steric requirements may be excessive. Thus, the $^3\sigma$ hydrogen of GF will be predominantly in the axial position with the bulkier phosphonoxy group preferring the equitorial position.

![Chemical structure](image)

The axial hydrogens on the 3- and 5- carbon atoms of the cyclohexyl group therefore hinder attack at the $^3\sigma$ hydrogen (which is assumed to be the primary position of attack).

An experiment in which the oxygen is pressurized into the system with good agitation in order to favor the conversion of isobutyronitrilo radicals to isobutyronitriloperoxy radicals would be of interest. The reactivity of the isobutyronitriloperoxy radicals would then be more rigidly established.
4.2.2 Benzaldehyde Co-oxidation of GB

As reported in the Fourth Bimonthly Report a fairly large attack (40% in 3 hours) was achieved when the simulant DIMP was co-oxidized with benzaldehyde at ambient temperature. However, when this system was tested with GF no attack whatsoever occurred. In order to ascertain whether this startling difference might be due to steric factors, i.e., isopropyl (DIMP) vs. cyclohexyl (GF) undergoing attack by perbenzoyl radicals, an experiment was carried out with GB, which contains the isopropyl group as well as fluorine. The following results were obtained using the same reaction conditions as had been used with DIMP and GF. Initially, GB co-oxidized at a substantial rate, 10 percent attack in 4 hours. After a 4 hour reaction time, however, the benzaldehyde had been completely consumed and further reaction up to 71 hours gave only an additional 2-3 percent reduction in GB concentration. Thus, steric factors appear to play a part in the originally observed difference between the DIMP and GF co-oxidations by benzaldehyde. Other factors however, are also important here since the rate of attack on DIMP was still substantially higher than on GB. The possible electronic factors involved herein will be discussed under the mechanistic considerations section of this report.

4.2.3 Co-oxidation of GF with Dibenzyl Ether

Since it is known that dibenzyl ether autoxidizes at room temperature, an attempt was made to co-oxidize GF with dibenzyl ether. No reaction of GF was observed even after 167 hours contact with oxygen at ambient temperature. Surprisingly, the dibenzyl ether did not oxidize in this reaction either. This was unexpected and most probably involved inhibition of dibenzyl ether autoxidation by the stabilizer or other impurity present in the GF. In
contrast to this finding, it had been observed that benzaldehyde autoxidation in the presence of GF proceeded at a fairly rapid rate, under these reaction conditions. This result also reflects the relative ease of abstraction of the aldehydic hydrogen in benzaldehyde compared to the 2\textsuperscript{o} carbon-hydrogen in dibenzyl ether.

4.2.4 Co-oxidation of GF with Indene and with Cyclooctene

Oxygen was passed through a solution containing GF, the internal standard, and the co-oxidant. The results are summarized in table 3 and in figures 1 and 2.

It was found that in each case, i.e., employing indene or cyclooctene as the co-oxidant, GF underwent appreciable oxidative attack at 25\textdegree C.

It appears reasonable to assume that oxygen initiates a reaction with indene forming indene peroxyl and hydroperoxyl radicals as follows:

\[
\text{Indene} + 2 \text{O}_2 \rightarrow \text{Indene}^\ddagger + \cdot \text{O}_2 \cdot \text{H} \quad (i)
\]

The radicals can then attack the GF as follows:

\[
\text{Indene}^\ddagger + \cdot \text{O}_2 \cdot \text{H} \quad \text{or} \quad \cdot \text{H}_2 \text{O}_2 \quad (z)
\]
### TABLE 3

OXIDATION OF GF IN THE PRESENCE OF CO-OXIDANTS

<table>
<thead>
<tr>
<th>Agent (moles)</th>
<th>TCB* (moles)</th>
<th>Co-oxidant (moles)</th>
<th>Temp. °C</th>
<th>Time Hours</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF, 0.032</td>
<td>0.0173</td>
<td>Indene, 0.02</td>
<td>25°</td>
<td>264</td>
<td>58% decrease in GF accompanied by a decrease in indene of 20%. Cyclohexanol produced (10%).</td>
</tr>
<tr>
<td>GF, 0.032</td>
<td>0.0173</td>
<td>Indene, 0.031</td>
<td>50°</td>
<td>200</td>
<td>90% decrease in GF 80-90% decrease in indene</td>
</tr>
<tr>
<td>GF, 0.032</td>
<td>0.0173</td>
<td>Cyclooctene, 0.023</td>
<td>25°</td>
<td>250</td>
<td>28% decrease in GF All cyclooctene disappeared. (new volatile product appeared)</td>
</tr>
</tbody>
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* 1,2,4-Trichlorobenzene
Figure 1. Co-Oxidation of GF with Air and Indene at 25°C
Figure 2. Co-Oxidation of GF with Air and Indene at 50°C
The radical, II, can then react with oxygen yielding the new peroxy radical III. The latter can then react with additional GF, thereby initiating a new chain.

\[ \text{II} + \text{O}_2 \rightarrow \text{III} \]

It should be noted that at 25°C 4 molecules of GF were destroyed per 1 molecule of indene. Concurrently, with the above mechanism for the decomposition of GF, some hydrolysis may occur since water is a product of the autooxidative process.

\[ 2\text{ROOH} \rightarrow \text{RO}_2^+ + \text{RO}^+ + \text{H}_2\text{O} \]

In either case, this constitutes the first report of an apparent oxidative chain of a CW agent at 25°C, though the chain length was low.

4.3 The Autoxidation of GF at Various Temperatures in the Presence of Cobaltous Naphthenate

4.3.1 Temperature Profile Study

In continuing the study of the "elevated" temperature autoxidation of GF as described in the last Bimonthly Report we have investigated the autoxidation of GF in the presence of about 2 percent weight of Co(II)
(II) catalyst at $75^\circ$, $90^\circ$, $105^\circ$, $120^\circ$ and $135^\circ$C. In each case the disappearance of OF was measured as a function of time via VFC analyses. These results are shown graphically in figure 3. First order plots were then made as shown in figure 4. As seen from figure 4, the reactions appear to follow reasonably good first order kinetics with respect to the disappearance of OF. The rate constants calculated from these straight lines together with the observed and calculated half-lives are given in table 4. Attempts were made to obtain second order fits to the data at the various temperatures, but they were not as good as the first order fits (even as low as 25% reaction, see figure 5).

An Arrhenius plot of the apparent first order rate constants was then made. As seen from figure 6, a good straight line fit was obtained for the lower four points. From the slope of this line an "activation energy of oxidative degradation" of OF was calculated and found to be on the order of 14 kcal/mole. The fifth point, corresponding to the reaction at $135^\circ$C does not fall on this line. This is not surprising in that at this temperature the rate of reaction of OF is so rapid that the curve drawn (see figure 1) is only an approximation of the actual decrease of OF with time. The only apparent conclusions that may be drawn at this time are as follows.

a. The kinetics appear to be simply first order or pseudo first order in the disappearance of OF at $75-135^\circ$C.

b. The reaction behaves as if there is no gradual or detectable change in mechanism over the temperature range of $75-120^\circ$C.
Figure 3. The Autoxidation of GF - Temperature Profile Studies
Figure 4. The Autoxidation of GF - Temperature Profile Studies Log Concentration vs. Time
Figure 5. Second Order Plot of the Autoxidation of GF at 75°C
Figure 6. The Autoxidation of GF - Temperature Profile Studies - Log Rate Constant vs. Reciprocal of Absolute Temperature

SLOPE = -3270
\[ \Delta H = (3270)(1.98)(2.303) \]
= 14,190 CAL/ MOLE
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Rate Constant (Sec⁻¹)</th>
<th>Half-Life</th>
<th>(Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>CA 190 x 10⁻⁶</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>30.8 x 10⁻⁶</td>
<td>5</td>
<td>6.3</td>
</tr>
<tr>
<td>105</td>
<td>13.5 x 10⁻⁶</td>
<td>15</td>
<td>15.7</td>
</tr>
<tr>
<td>90</td>
<td>4.76 x 10⁻⁶</td>
<td>24</td>
<td>40.5</td>
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<tr>
<td>75</td>
<td>1.55 x 10⁻⁶</td>
<td>--</td>
<td>124</td>
</tr>
</tbody>
</table>
4.3.2 Catalyst Quantity Requirements

In carrying out the temperature profile studies already discussed, the amount of catalyst utilized was standardized at the approximately two percent level. In order to determine the amount of catalyst for maximum efficiency in degrading GF, several experiments were carried out in which the amount of catalyst was varied from run to run. This data is presented graphically in figures 7 and 8. As can be seen therein, the amount of catalyst has a pronounced effect on the rate of oxidative degradation of GF. Further experimentation will be required to fully elucidate this phenomenon. One is left with the impression, however, that larger amounts of catalyst may be operable at still lower temperatures, perhaps even down to ambient temperature.

4.3.3 The Nature of the Elevated Temperature Autoxidation of GF

In order to determine whether the autoxidation of GF at elevated temperatures involves a free radical process the following reactions and observations were carried out.

a. Look for the presence of an induction period in the absence of catalyst.

b. Add an inhibitor such as 2,6-di-tert-butylphenol and determine whether the observed degradation of GF is retarded.

As can be seen from figure 9 when GF was autoxidized at 105°C, in the absence of Co(II) catalyst, an induction period of approximately 35 hours was observed. Further reaction led to a decrease in GF concentration with time. When 2,6-di-tert-butylphenol was added to a reaction mixture in the presence
Figure 7. The Autoxidation of GF - Co(II) Catalyst Concentration Effect at 75°C
Figure 8. The Autoxidation of GF - Co(II) Catalyst Concentration Effect at 90°C
Figure 9. The Autoxidation of GF - Inhibition Studies
of CO(II) catalyst at 90°C, and induction period of about 25 hours was observed which was followed by a gradual decrease in GF concentration with time. In a similar reaction at 105°C, no induction period was observed. However, the rate of decrease of GF with time was reduced by a factor of about 4 when compared to a run without the added phenolic inhibitor. These data are shown graphically in figure 10. In summary, the half-lives for the autoxidations of GF in the absence and presence of cobaltous naphthenate and 2,6-di-tert-butylphenol at 105°C were as follows:

N0 Cobalt, t1/2 = 37 hrs. after induction period
2% Cobalt, t1/2 = 15 hrs. with no induction period
2% Cobalt + inhibitor, t1/2 = 70 hrs. with no induction period (at 105°C).

Since the presence of an induction period and the retardation of reaction by phenolic inhibitors are traditional diagnostic tests for a free radical reaction their presence here is indicative of a free radical autoxidation reaction mechanism for our systems wherein GF is oxidatively degraded at elevated temperatures. The mechanistic significance of these results will be discussed further in section 5.

1.4 Preliminary Investigation of the HD/CO(II)/O2 System

In order to extend the elevated temperature studies to other CW agents an experiment was carried out using HD together with CO(II) catalyst at 105°C. In addition an experiment without catalyst was also carried out. As can be seen in figure 11 the presence of CO(II) catalyst has a pronounced effect on the oxidative degradation of HD at 105°C. The cause of the leveling off at about 60% HD at about 40 hours reaction time is unknown at this time. However, one is tempted to speculate that perhaps an intermediate
Figure 10. The Autoxidation of GF - Inhibition Studies
Figure 11. The Autooxidation of HD at 105°C

<table>
<thead>
<tr>
<th>Weight Percent HD (on Solvent and Impurity Free Basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>80</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>40</td>
</tr>
</tbody>
</table>

![Graph showing weight percent HD over time](image)

2738-67
2 ML HD (11-18-63)
2 ML TCB
2 ML COBALT NAPHTHENATE (6%) ≡ CA 2% CO (II)
105°C, 30-40 ML O₂ FLOW

NO CATALYST ADDED

2738-68
DITTO, EXCEPT:
NO CATALYST ADDED

CA 2% Co(II)
sulfoxide or sulfone might have reached a high enough concentration after 40 hours to inhibit further reaction of the HD with oxygen.

4.5 Catalyst Screening Studies

During this period ferrous phthalocyanine was tested as a catalyst for the oxidative degradation of GF at 25°C and at 60°C. Since this catalyst functions as an oxygen carrier through some sort of surface phenomenon, at least in the case of simple hydrocarbons, such as cumene, enough catalyst was added to exceed the solubility in GF and thus insure the presence of some "solid catalyst" in the reactions mixture. After 150 hours at ambient temperature no reaction of GF was observed nor was reaction observed in another experiment at 60°C after 21 hours. Thus this catalyst is not effective in promoting the oxidative degradation of GF at these temperatures.
5. MECHANISTIC CONSIDERATIONS

As of the last Bimonthly Report, it had been demonstrated that initiation via hydrogen abstraction is feasible with methyl and perbenzoyl radicals at 25°C in the case of DIMP and with methyl radicals at 90°C or oxygen and cobaltous naphthenate at 105°C in the case of GF. In addition, it had been found that GF undergoes moderately rapid autoxidation in the presence of cobaltous naphthenate at 105°C.

It has now been found that GF can be induced to undergo oxidation at 25°C via the use of indene as a co-oxidant. Since indene is known to autoxidize fairly easily to indene peroxyl radicals it seems reasonable to assume that initiation occurred via hydrogen abstraction from GF by the indene peroxyl radicals. Moreover, the consumption of 4 moles of GF per mole of indene is suggestive of some propagation even at 25°C.

From the competitive hydrogen transfer studies employing phenyl radicals it appears that the reactivity of the 3°C hydrogen in GF approximates that of the benzylic hydrogens in ethylbenzene. A similar situation appears to be true for HD. Further definition of the relative reactivity of the hydrogens in GF, HD, and other CW agents is however necessary before such a comparison can be made with certainty.

As in the case of GF with indene it has now also been demonstrated that GB may be induced to undergo oxidation at 25°C by the use of benzaldehyde at 25°C as a co-oxidant. The latter result contrasts with the unreactivity of GF in the presence of benzaldehyde and points up an apparently greater reactivity of GF compared to GF toward hydrogen abstraction by the perbenzoyl
radical (note apparent difference in reactivity toward phenyl radicals, table 1). Examination of the corresponding co-oxidation of GB with indene would be of interest to determine the relative reactivity of GB to GF toward indeneperoxy radicals.

On the basis of these results, one can now say with reasonable certainty that initiation by hydrogen abstraction at 25°C is possible in the case of GF and GB, provided appropriate radical initiators are employed. The specific radicals which are evidently effective, viz., perbenzoyl in the case of GB and indeneperoxy in the case of GF, are also practical radicals to employ since they can be spontaneously generated at 25°C from convenient starting materials, viz., benzaldehyde and indene, respectively.

The extent of propagation possible at 25°C, on the other hand, still remains subject to question. At elevated temperatures, i.e., 75°C and up, there does not appear to be any question now that we are dealing with a chain process, although it may be an "energy chain". The results obtained for GF in the absence of cobaltous naphthenate appear to be particularly significant. In the absence of cobaltous naphthenate the presence of a long induction period, even at 105°C, points up the urgency of effective initiation at 25°C. The fact that GF undergoes autoxidation at 105°C once the induction period is overcome indicates that autoxidation by a chain process occurs. Moreover, by analogy with the work done on the autoxidation of esters, it appears reasonable to assume that the predominant chain process occurs via a free radical mechanism rather than through an energy chain mechanism. The first few tenths of a percent reaction may however occur via the energy chain scheme.
The hydroperoxide is thereby generated leading to some free radicals. The latter then initiate the rate controlling radical chain process. The energy chain-radical chain initiating scheme may be pictured as follows

\[
\begin{align*}
&\text{GH} \xrightarrow{\Delta} \text{GH}^* \quad (5) \\
&\text{GH}^* + \text{O}_2 \quad \rightarrow \quad [\text{GH-O}_2]^* \quad (6) \\
&[\text{GH-O}_2]^* + \text{GH} \quad \rightarrow \quad \text{GO}_2\text{H} + \text{GH}^* \quad (7) \\
&2\text{GO}_2\text{H} \quad \rightarrow \quad \text{GO}^* + \text{GO}_2^* + \text{H}_2\text{O} \quad (8) \\
&\text{GO}_2^* + \text{GH} \quad \rightarrow \quad \text{GO}_2\text{H} + \text{G}^* \quad (9) \\
&\text{G}^* + \text{O}_2 \quad \rightarrow \quad \text{GO}_2^* \quad (10)
\end{align*}
\]

In this scheme GH is the agent, equations (5), (6), and (7) are the energy chain reactions, and equations (8), (9) and (10) are the radical chain reactions.

It is of course possible, if not imperative in the case of the CW agents, that the chain process is a result of chain branching at these temperatures which in turn results in propagation. If this is true, it would be desirable to find means for inducing such chain branching at 25°C. The possibility exists that ketones can be produced from the G-agents which may initiate further chains, as follows:

\[
\begin{align*}
&\text{CH}_3 - \text{P} - \text{O} - \text{C}^\text{R} + \text{R'}\text{O}_2 \quad \rightarrow \quad \text{CH}_3 - \text{P} - \text{O} - \text{C}^\text{R} + \text{R'O}_2 \quad (11) \\
&\text{CH}_3 - \text{P} - \text{O} - \text{C}^\text{R} + \text{O}_2 \quad \rightarrow \quad \text{CH}_3 - \text{P} - \text{O} - \text{C}^\text{R} \quad (12) \\
&\text{CH}_3 - \text{P} - \text{O} - \text{C} - \text{OO} \quad \rightarrow \quad \text{CH}_3 - \text{P} - \text{OOH} \quad (13)
\end{align*}
\]
Alternative modes of breakdown of the phosphonoxyperoxyl radical can of course be envisioned instead of that indicated by equation (13).

Although the appreciably greater rate of autoxidation of GF in the presence of cobaltous naphthenate suggests that the reaction may be occurring by a mechanism different from that prevailing in the absence of cobaltous naphthenate, the results can be simply interpreted on the basis that the cobaltous naphthenate catalyzes hydroperoxide breakdown as follows:

$$\text{RO}_2\text{H} + \text{Co}^{(II)} \rightarrow \text{RO}^+ \cdot \text{OH}^- + \text{Co}^{(III)} \quad (16)$$

$$\text{RO}_2\text{H} + \text{Co}^{(III)} \rightarrow \text{RO}^+ \cdot + \text{H}^+ + \text{Co}^{(II)} \quad (17)$$

$$\text{GH} + \text{RO}^+ \text{or} \text{RO}^\ddagger \rightarrow \text{G}^+ \cdot \text{ROH} \text{or} \text{RO}_2\text{H} \quad (18)$$

$$\text{G}^+ \cdot + \text{O}_2 \rightarrow \text{GO}_2^\ddagger \quad (19)$$

$$-\frac{d[GH]}{dt} \alpha \left[\text{GH}\right]^P \left[\text{O}_2\right]^Q \left[\text{Co}^{(II)}\right]^R \quad (20)$$

Alternatively, the cobalt catalyst may indeed function by another mechanism involving direct or indirect attack on the $3^\circ \text{C-H}$ bond as follows

$$\text{GH} + \text{Co}^{(III)} \rightarrow \text{G}^+ \cdot + \text{Co}^{(II)} + \text{H}^+ \quad (21)$$

$$\text{or} \quad \text{GH} + \text{Co}^{(II)} \rightarrow \text{G} + \text{Co}^{(II)} \quad (22)$$

In this case, the occurrence of a chain process necessitates that the cobalt catalyst behave as a regenerative initiator. If this is true in the case of the elevated temperature autoxidation of GF and HD, search for more powerful regenerative initiators for use at 25°C would be indicated.
To date, we have not attempted to formulate a kinetic expression for any mechanism for the autoxidation of a CW agent. In view of the positive results now obtained with Co(II) catalyst at higher temperatures it appears desirable to formulate kinetic expressions for various possible autoxidative mechanisms. A comprehensive treatment of this problem will therefore be carried out during the next work period.
6. EXPERIMENTAL

6.1 Reagents

Methylbenzoate was prepared by standard procedures and a redistilled fraction was used in the experiments.

Phenyldiazotriphenylmethane (PAT) was prepared as described in the Second Bimonthly report.

Cyclooctene was a gift of Columbian Carbon Company, Princeton, N. J. and was distilled from inhibitor before use.

Indene was obtained from Neville Chemical Company, Springfield, Pa. and distilled from inhibitor before use.

1,3-bis-(Trifluoromethyl)benzene was a gift of Hooker Chemical Company.

Azobisisobutyronitrile (AIBN) was a commercial product from Eastman Kodak.

Dimethyl Methylphosphonate was obtained from Hooker Chemical Company.

Carbon Tetrachloride. Baker's reagent grade was used directly.

6.2 Gas Chromatographic Analysis

An Aerograph, model A-90-P, fitted with a thermal ionization detector was used throughout this work except for the determination of methane and ethane. The methane and ethane were determined as described in our previous report with the aid of a tritium detector. The columns which we have employed are listed in table 5. The conditions employed during V.P.C. analysis have been described for each experiment. Each of the columns was packed in 1/4 inch O.D. copper tubing.

Relative peak heights or peak areas were used depending upon the case in question. In the co-oxidation experiments with indene and with cyclooctene the reproducibility was within 1%.
<table>
<thead>
<tr>
<th>Liquid Phase</th>
<th>Solid Support (Mesh)</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Igepal 4%</td>
<td>ANAKROM (ABS), 90/100</td>
<td>4 feet</td>
</tr>
<tr>
<td>XE-60-General Electric nitrile silicone 12%</td>
<td>ANAKROM (ABS), 90/100</td>
<td>4 feet</td>
</tr>
<tr>
<td>XE-60-General Electric nitrile silicone 12%</td>
<td>ANAKROM (ABS), 90/100</td>
<td>10 feet</td>
</tr>
<tr>
<td>Diethylene Glycol Succinate 20%</td>
<td>DIATOPORT P 80/100</td>
<td>3 feet</td>
</tr>
<tr>
<td>Diethylene Glycol Succinate 20% + 5% H₃PO₄</td>
<td>CHROMOSORB W</td>
<td>12 feet</td>
</tr>
</tbody>
</table>

*The details of preparation of the various chromatic columns will be reported in the next report.*
6.3 Reaction of Acetyl Peroxide with Hexachlorobutadiene

To hexachlorobutadiene (6.98g., 0.0267 moles) maintained at 90°, joined to an ascarite tube and a gas burette, was added a 4.2 ml. solution of bis-(trifluoromethyl) benzene and acetyl peroxide (prepared from 1.8g., 0.015 moles of acetyl peroxide and 2.5 ml. (3.46g.) of 1,3-bis-(trifluoro-methyl) benzene). The addition was accomplished by means of a syringe over a period of four hours. Five gas samples were taken periodically. The ascarite tube absorbed 0.44g. (0.0091 moles) of carbon dioxide and 234 ml. of gas (0.01 mole). Analysis of the gas samples for the methane-ethane ratio showed that the successive samples varied in the methane-ethane ratio from 9:1 to 3:1. The methane-ethane ratio was determined by vapor phase chromatography as described in our Fourth Bimonthly Progress Report.

The density of the final solution, which weighed 9.68g., was 1.52g/cc.

The amount of hexachlorobutadiene which remained in the reaction mixture was determined by comparison with known solutions containing hexachlorobutadiene and of 1,3-bis-(trifluoromethyl) benzene employing a 4 feet XE-60 silicone nitrile on 90/100 mesh Anakrom (ABS) with the column at 120°C. A 35% decrease in the amount of hexachlorobutadiene was observed.

6.4 Competitive Decomposition of Phenylazotriphenylmethane (PAT) in Carbon Tetrachloride-Solvent Substrates

6.4.1 Methyl Benzoate

Into the ampule containing a weighed sample of PAT (0.334g., 0.00096 moles) was added 10.00ml. of a stock solution consisting of methyl benzoate and carbon tetrachloride. The stock solution had a ratio of 0.259 moles of carbon tetrachloride per mole of methyl benzoate.
The ampule was cooled in dry ice and sealed in a vacuum. It was placed in a 60°C oven for 4 hours, and stored in dry ice until time for analysis. Analysis was performed using a 1/4 inch O.D. 3 feet long degs. column followed by a 4 foot XE-60 column (column temperatures 67°C, injection temperature 130°C) and run at 50 psi of He. After the carbon tetrachloride came off, the benzene came off in 5.2 minutes, while chlorobenzene appeared in 11.1 minutes.

6.4.2 Dimethyl Methylphosphonate

The same procedure as described above was used with the solvent system, carbon tetrachloride-dimethyl methylphosphonate, mole ratio of 0.259. The products were analyzed using a 3 foot, 1/4 inch DB3S column followed by a 1 foot, 1/4 inch, XE-60 column all at 50°C, and He at 50 psi. The benzene was retained for 4 minutes while the chlorobenzene came out in 20.4 minutes.

6.4.3 Cyclohexyl Methylphosphonyl Fluoridate (GF)

The mole ratio of the solvent system, carbon tetrachloride-GF, was 0.259. The products were analyzed on a 10 foot, 1/4 inch, XE-60 column maintained at 55°C and 50 psi of He. The benzene came out in 3.5 minutes while the chlorobenzene was retained for 17.45 minutes.

6.4.4 Isopropyl Methylphosphonyl Fluoridate (GB)

The mole ratio of carbon tetrachloride to GB was kept at 0.259. Analysis was performed with a 1/4 inch, 10 foot, XE-60 column maintained at 50°C and 50 psi of He. The benzene was retained for 4 minutes followed by an unknown product (not acetone or isopropyl alcohol) at 6.1 minutes, and chlorobenzene at 21.5 minutes.
6.4.5 Mustard (HD)

The mole ratio of carbon tetrachloride to HD was 1.79. Analysis was performed with a 1/4 inch, 10 foot, XE-60 column, maintained at 50°C and 50 psi of He. The benzene was retained for 4 minutes, while the chlorobenzene came off in 21.5 minutes.

6.5 Autoxidation and Co-oxidation of GF and GB with Oxygen

6.5.1 The Co-oxidation of GF in the Presence of Azobisisobutyronitrile

A stream of oxygen (20 ml./minute) was passed through a solution of 10.0 ml. of GF (94.4% 0.064 moles) and 5.00 ml. of 1,2,4-trichlorobenzene maintained at 65°C. The outlet of the flask was filled with a dry ice condenser to minimize loss of liquid by the flow air stream. To this solution was added, over a period of 10 hours, 6.55g. of solid azobisisobutyronitrile (0.04 mole). The reaction was kept at 65°C two additional hours. A control addition under identical circumstances showed that approximately 1.3g of the azo compound remained along the side of the vessel, resulting in the addition of 5.25g. or 0.032 moles. An initial sample and three additional samples were taken during the addition, while the final sample was taken after twelve hours.

The samples were subjected to V.P.C. V.P.C. analysis was carried out (with the 1,2,4-trichlorobenzene (TCB) serving as the invariant internal standard) using an XE-60 column maintained at 115°C, with a flow rate of 100 ml. of He/min. The TCB appeared in 2 minutes while GF appeared in 6 1/2 minutes. The dimeric product tetramethylsuccinonitrile appeared in 4 1/2 minutes. The ratio of peak heights showed no change in GF concentration. The amount of tetramethylsuccinonitrile produced could be observed as increasing in each successive sample. A yield of 50% dimer was calculated based on a comparison of its peak area with the peak area of a solution of known concentration of dimer and on an estimate of the total volume of solution at the end of the reaction.
Similar results were obtained on a 4 foot Igepal, 1/4 inch, column maintained at 130°C and 100 ml/min. of He. The TCB came off in 3 minutes and GF after 5 minutes. No tetramethylsuccinonitrile was observed on this column.

6.5.2 The Co-oxidation of GB in the Presence of Benzaldehyde

The co-oxidation of GB with benzaldehyde was carried out by placing 2 ml GB (0.0114 moles), 1.14 ml benzaldehyde (0.0114 moles), 2 ml of orthodichlorobenzene and 1 drop of cobalt naphthenate (6% Co) catalyst in a reactor (as already described) and passing through oxygen at ambient temperature. Samples were removed and analyzed periodically for both GB and benzaldehyde via V.P.C. It was found that after 4 hours reaction time the benzaldehyde had been completely consumed and a 10 percent reduction in GB had been achieved. Further reaction up to 71 hours led to only a 2-3 percent further reduction in GB concentration.

6.5.3 The Co-oxidation of GF in the Presence of Dibenzyl Ether

Two ml GF (97.4%) (0.0111 moles) and 2.2 ml of dibenzylether (0.0111 moles) together with 2 ml. 1,2,4-trichlorobenzene and 1 drop of cobalt naphthenate (6%, Co(II)) were placed in a reactor (as already described) and oxygenated for 167 hours, at ambient temperature. Periodic sampling and analysis via VPC showed no decrease in GF nor any decrease in the co-oxidant, dibenzyl-ether.

6.5.4 Co-oxidation of GF in the Presence of Indene

a. At 25°C. A solution containing 5.00 ml of GF (0.032 moles) 2.4 ml of redistilled indene (0.02 moles) and 2.00 ml (0.0173 m) of 1,2,4-trichlorobenzene (TCB) was prepared. After withdrawing an initial sample, a slow stream of dry oxygen was passed through the solution. Samples were taken
periodically from the solution. After two days a yellow color developed in the reaction mixture, which slowly deepened. Toward the end of the reaction white solids appeared in the solution.

The samples were analyzed by V.P.C. using a 4 foot Igepal column maintained at 130°C and a flow rate of 100 ml. He/min. The indene came out in 1 1/2 minutes while the TCB was retained for 3 minutes, and the GF 7 minutes.

b. At 50°C. A similar experiment was carried out at this temperature with 5.00 ml. of GF (0.032 moles), 3.7 ml (0.031 moles) of indene and 2.0 ml of TCB. Analysis was performed with a 4 foot, 1/4 inch XE 60 column maintained at 124°C and 100 ml He/min. flow rate. The indene appeared after 1 1/2 min., TCB after 2 1/2 min, and GF after 6 min.

6.5.5 Co-oxidation of GF in the Presence of Cyclooctene

A solution of 5.00 ml of GF, 2.40 ml of redistilled cyclooctene, and 2.00 ml of TCB was prepared and a stream of oxygen at 20 ml/min. was passed through the solution. Analysis was performed as described above with the 4 ft, XE 60 column, Col. Temp. 124°C, flow rate 100 ml/min. The presence of cyclooctene was shown by comparison with a known sample employing a 1/4 inch, 10 foot, XE 60 column maintained at 60°C. The cyclooctene was retained for 12 minutes.

6.6 Autoxidation of GF at Various Temperatures in the Presence of Cobaltous Naphthenate

6.6.1 Temperature Profile Studies

All the temperature profile studies were carried out by placing 2 ml each of GF (94.7%), 1,2,4-trichlorobenzene and cobalt naphthenate solution (6% Co (II) ) in a cylindrical reactor containing a gas sparger tube extending
essentially to the bottom of the reactor. The reactor was then placed in an oil bath at the required temperature and 30-40 ml/min. of O₂ was passed through the gas sparger tube. Samples were removed periodically through an s.s. needle via a syringe and subsequently analyzed via VPC for the disappearance of GF.

The data thus obtained were used to draw the concentration-time plots in figure 3, for the various temperatures investigated. In drawing the log conc. vs time plots (figure 4), however, values were picked at random from the smooth curves up to about 60 percent degradation of GF for all temperatures except 135°C. Values at relatively low conversions were used since at higher conversions competing side reactions could obscure the initial kinetics of the interest. In the case of the 135°C reaction, however, the slope of the curve was so steep that values considerably above 60 percent reaction had to be used, thus possibly leading to the poor fit in the Arrhenius plot (figure 6).

6.6.2 The Effect of Amount of Co(II) Catalyst on the Elevated Temperature Autoxidation of GF

In studying the effect of the amount of Co(II) catalyst on the oxidative degradation of GF the general procedures as already outlined were followed. As indicated in figures 7 and 8, the amount of cobalt naphthenate catalyst solution was varied to give the appropriate concentrations of Co(II) catalyst. Periodic sampling and analyses were carried out as already described.

6.6.3 The GF/O₂/105°C System

In studying the non-catalyzed reaction, 2 ml each of GF (94.7%) and 1, 2, 4-trichlorobenzene were placed in a reactor as described in 6.6.1 above.
The reactor was then placed in oil bath at 105°C and 30-40 ml/min of O2 passed through the gas sparger tube. Samples were removed periodically and analyzed via VPC for the disappearance of GF. (Figure 9).

6.6.4 The GF/Co(II)/O2/Inhibitor System

In order to determine whether a phenolic inhibitor would retard the oxidative degradation of GF the following two experiments were carried out.

a. Two ml each of GF (94.7%), cobalt naphthenate (6% Co), 1,2,4-trichlorobenzene and 0.5 gms of 2,6-di-tert-buylphenol were placed in a reactor as described above and placed in an oil bath at 105°C. Oxygenation was carried out as already described as were the analyses for the disappearance of GF.

b. The reaction of 90°C was carried out in the same manner except that the oil bath was maintained at 90°C. The results obtained from these experiments, namely the retardation at 105°C and the induction period at 90°C are shown in figure 10.

6.7 The Co(II) Catalyzed Oxidative Degradation of HD

The reactors and procedures used in this preliminary investigation of the Co(II) catalyzed oxidative degradation of HD were the same as have already been described. The two experiments completed to date in this area were as follows:

a. Two ml HD (11-18-63 sample), 2 ml 1,2,4 trichlorobenzene and 2 ml of cobalt naphthenate (6% of Co(II)) were oxygenated for about 120 hours. The results thus obtained are depicted in figure 11.

b. In this non-catalyzed reaction study the amounts of materials were the same as used in (a) above except that the catalyst solution was omitted. Both these reactions were conducted at 105°C.
6.8 Ferrous Phthalocyanine as an Oxidation Catalyst for GF

The reactors utilized were as already described. Two ml each of GF (94.7%) and 1,2,4-trichlorobenzene together with 0.5 gms of ferrous phthalocyanine were placed in a reactor and oxygenated for 150 hours at ambient temperature. Periodic sampling showed no decrease in GF concentration. In another experiment using the same amounts of the components above, but at 60°C, oxygenation was carried out for 21 hours. Periodic sampling showed no decrease in GF concentration. In these experiments solid catalyst was present in the reaction mixture.

7. SUMMARY OF RESULTS

a. Competitive reaction of phenyl radicals generated from PAT with the G-agents demonstrates a reactivity of the hydrogen to be greater than that of hydrocarbons with 2° hydrogens.

b. Competitive reaction of phenyl radicals generated from PAT with HD demonstrate a reactivity of the hydrogen approaching that of benzylic hydrogens.

c. Co-oxidation of GF with AIBN and Oxygen at 65°C gave no attack on GF. The isobutyronitriloperoxy radical is apparently too weak to effect a hydrogen transfer from GF.

d. GB undergoes oxidative attack at 25°C in the presence of benzaldehyde as the co-oxidant. The reaction, however, appears to stop after about 13% attack, the point at which consumption of the benzaldehyde is complete.

e. GF appears to inhibit the autoxidation of dibenzyl ether, employed as a potential co-oxidant, at 25°C.
f. Co-oxidation of GF in the presence of indene or cyclooctene results in an appreciable decrease in GF at ambient temperatures. In one experiment 4 molecules of GF disappeared to one molecule of indene at 25°C.

g. The autoxidation of GF in the presence of cobalt naphthenate employed in catalytic quantities exhibits good apparent first order kinetics with respect to GF over the temperature range of 75 to 135°C and up to no less than 25% reaction of the GF.

h. The apparent first order rate constants over the temperature range of 75 to 125°C fit a good linear Arrhenius plot yielding an apparent activation energy of 14 kcal/mole.

i. The amount of cobalt catalyst employed appears to have a pronounced effect upon the rate up to at least 2 or 3%, depending in part upon the temperature employed. Thus, in going from 1% cobalt naphthenate to 2% cobalt naphthenate at 90°C, the rate of consumption of GF (for 30% consumption) increases by a factor of four.

j. GF undergoes autoxidation at 105°C without requiring a catalyst. However, it has about a 35 hour induction period.

k. 2,6-di-tert-butylphenol markedly inhibits the autoxidation of GF in the presence of cobalt naphthenate catalyst resulting in a 25 hour induction period at 90°C and a slowing of the rate at 105°C.

l. The rates of autoxidation of GF differ in the absence and in the presence of cobalt catalyst as well as in the presence of 2,6-di-tert-butylphenol inhibitor plus cobalt catalyst.

m. HD undergoes autoxidative attack at 105°C in the presence of cobaltous naphthenate with about 40% attack occurring within a period of 40 hours. However, the reaction appears to level off at this % attack.
n. Use of ferrous phthalocyanine as a catalyst even under heterogeneous conditions fails to promote the autoxidation of GF at 25°C.

8. CONCLUSIONS

a. The reaction of the CW agents with methyl radicals and phenyl radicals demonstrates that autooxidative chain initiation is feasible.

b. The results of the competitive reactions with PAT sh--- that the reactivity of the agents is in excess of that of an alkane with 2° hydrogens. Furthermore, the reactivity of HD approaches that of benzyl hydrogens.

c. Chain propagation appears possible at 25°C based on the results obtained with GF in the presence of indene. The chain length may however be low, as was the case here.

d. Extensive chain autoxidation appears to occur at elevated temperatures, e.g., at 75° or higher. It seems probable that the reaction in the absence of the cobalt catalyst at 105°C involves a free radical chain process.

e. Based on our work, taken together with work reported on the autoxidation of esters, it appears reasonable to assume that chain branching is important for the autoxidation of GF at elevated temperatures.

f. The role of the cobalt catalyst can be accounted for most simply in terms of its enhancement of chain branching via its inducing hydroperoxide breakdown.

g. It appears that for effective catalytic multipurpose decontamination of CW agents under ambient conditions it will be necessary to augment chain propagation via (1) More effective GO₂ chain transfer, so as to diminish its termination, (2) Production of branching via transition metal or other catalysts which induce the breakdown of GO₂ to radical products, and/or (3) Development of a regenerative initiator.
9. PLANS FOR THE NEXT WORK PERIOD

The next work period is the last work period under this contract. Accordingly, every effort will be made to achieve as many of the objectives initially set forth as possible. In accord with the USA CRDL Project Officer, it has been agreed that major emphasis will be continued in rigorously establishing the basic prerequisites for catalytic autoxidative decontamination before moving into a developmental effort of what we have found to date. Accordingly, the following work plan is proposed for the next work period.

a. Attempt autoxidation of GF using di-tert-butylperoxalate as the initiator at ambient temperature. The use of this peroxide as an autoxidation initiator at 25°C has been described previously by T. G. Traylor, *J. Am. Chem. Soc.*, 85, 2413 (1963), for the autoxidation of tetralin. These experiments will determine a kinetic chain length and thereby yield information on the extent of propagation.

b. Allowing AIBN to react with GF under oxygen pressures will insure a good yield of the isobutylene• radical. Such an experiment will also yield information on the effect of oxygen on chain propagation and termination steps.

c. Continue to screen various co-oxidants such as aldehydes, olefins, ethers, anthroquinols, to obtain basic information for the design of a most favorable catalyst system.

d. In order to establish the extent of propagation in the elevated temperature autoxidation of GF, kinetic chain length studies using an initiator such as t-butylperoxide will be carried out.
e. Since the main objective of this program is the "ambient temperature" oxidative degradation of GF and other agents, increasing amounts of Co(II) catalyst at lower temperatures will be investigated.

f. Oxygen absorption studies coupled with analysis for the disappearance of GF will be a powerful tool in helping determine the mode of initiation involved in these reactions.

g. Continued transition metal catalyst screening studies particularly with such catalysts as Co(II), Co(III), Fe(II) and Mn(III) acetylacetonates. In addition, the oxygen carrying Co(II) bis-salicylaldehyde-ethylene diamine chelate will be prepared and tested.

10. REFERENCES

APPENDICES

1. Meeting with Dr. G. A. Russell, and USACHDL Personnel.

2. Autoxidation of the Saturated Aliphatic Diesters
APPENDIX 1

1. **Meeting with Dr. G. A. Russell, Melpar Consultant, and USA CRDL Personnel**

   On March 25, 1964, a meeting was held at Melpar with Melpar's consultant, Dr. Glenn A. Russell and with the USA CRDL personnel Dr. David H. Rosenblatt and Mr. John B. Jackson.

   The results obtained by Melpar to date were presented. Dr. S. Preis discussed feasibility experiments identifying free radical chain initiation in the ambient temperature range for G-agents and for HD.

   Mr. Zale Oser discussed "developmental" studies in which the oxidative decomposition of G-agents, HD and DIMP were presented, including a study of the cobalt naphthenate catalyzed autoxidation of GF.

   During the discussion that ensued, the following suggestions and comments were made.

   a. Prof. Russell presented his own data on hydrogen abstraction and while the quantitative data was at variance with that of Melpar's data, the general conclusion remained the same—that is, initiation of autoxidative chains is feasible.

   b. The data presented by Prof. Russell suggest a lower activity of dimethyl methylphosphate than is reported here.

   c. Professor Russell also commented that the value for HD was lower than he might have expected. A comparison of the value for HD may be made with the data of Pryer and Guard, *J. Am. Chem. Soc.*, 86, 1150 (1964), c.f., section 4.1.2).
d. In response to a question on how the kinetic chain length of the autoxidation of GF at elevated temperatures might be assessed, Dr. Russell suggested comparing the rate of decomposition of GF per mole of di-tert-butylperoxide with the rate of generation of tert-butoxy radicals from the latter at a convenient temperature. Comparison of the former result with that obtained in the presence of cobaltous naphthenate may also shed some light on the role of cobalt.

e. Dr. Russell suggested that the cobalt probably functions via Co (III) initiating the oxidation of GF. The cobalt may also complex with the P=O or F within an associated aggregate of species thereby augmenting the catalysis.

f. In reference to a question on the effect of water on free radical reactions, Dr. Russell stated that water is inert to most free radical processes, and should not alter our current conclusions regarding feasibility.

g. Concerning the generation of various types of RO₂ radicals at 25°C, Dr. Russell suggested the photochemical decomposition of t-BuN=N-t-Bu (available from Merck in Canada). In this manner t-BuO₂ radicals would be produced in the presence of air.

h. In response to a question on how termination reactions may be reduced, Dr. Russell suggested the use of reagents which change the radicals to ones capable of yielding longer kinetic chains. These include Cl, NO, and Br. Specific reagents and/or reactions for this purpose are as follows:
\[
\begin{align*}
\text{RO}_2^+ + \text{HBr} & \rightarrow \text{RO}_2\text{H} + \text{Br}^- \\
\text{RO}_2^+ + \text{PCl}_3 & \rightarrow \text{ROPOCl}_2 + \text{Cl}^- \\
\text{RO}_2^+ + \text{R}_2\text{S} & \rightarrow \text{R}_2\text{SO} + \text{RO}^- \\
\text{RO}_2^+ + \text{O}_3 & \rightarrow 2 \text{O}_2 + \text{RO}^- \\
\end{align*}
\]

i. In response to a question on whether the autoxidation breakdown products of \textit{OF} agents like \textit{OF}, such as cyclohexanone, may induce further propagation, Dr. Russell stated that this sounded like a promising approach. He pointed out that certain ketones such as benzophenone and acetone form hydroperoxide adducts quite readily which in turn break down to free radicals. The \textit{Co}(II) catalyst could then break down the hydroperoxide yielding \textit{Co}(III) which serves to promote further oxidation. Dr. Russell also suggested that cyclohexanone might be added to the \textit{OF}-cobalt catalyst-oxygen system to check this point.

j. In reference to hydroperoxide formation of ketones, Dr. Russell cited the following photochemically induced autoxidations (photosensitized by benzophenone).

\[
\begin{align*}
\phi_2\text{C}=\text{D} + \text{O}_2 & \xrightarrow{\text{hv}, \text{H}_2\text{O}} \phi-\text{C}-\text{OOH} \xrightarrow{\Delta} \phi_2\text{C}=\text{O} + \text{H}_2\text{O} \\
\end{align*}
\]

k. In order to test the role of ferrous phthalocyanine as a heterogeneous autoxidation catalyst, Dr. Rosenblatt suggested that \textit{OF} be overloaded with the \textit{Fe}(II) catalyst followed by the gradual addition of cumene in the presence of oxygen.
Autoxidation of the Saturated Aliphatic Diesters

By M. Wesley Rigg and Henry Gisser

Received September 24, 1952

This report describes an investigation of the thermal oxidation of the saturated esters of adipic acid. The preparation and physical properties of esters from alcohols having 5 and 0 carbon atoms are given. The esters were oxidized both by continuous passage of air through the esters and by oxidation in an apparatus which recorded rate of oxygen consumption. It was found that the distance of a tertiary carbon atom from the ester group exerts a considerable effect on oxidation rate, the rate decreasing as the distance is decreased. This effect is attributed to resonance of the ester group which results in an inductive effect along the carbon chain lowering the availability of electrons at the carbon in which oxidation is taking place. In general, esters from the n-alcohols oxidize at a lower rate than esters from the branched-chain alcohols. Activation energies for autoxidation of several esters were determined. The values reflect the effect of alcohol structure with respect to distance of the tertiary carbon from the ester group.

Kinetics of di-(3-methylbutyl) adipate autoxidation was studied in diethyl adipate solutions. In the early stages of oxidation (before appreciable hydroperoxide decomposition takes place) the rate of oxygen consumption, calculated per mole of ester, is proportional to the square of the ester concentration. As oxidation proceeds the rate of oxidation increases and becomes constant. At this stage, the rate of oxygen consumption is proportional to the square root of the ester concentration (when extent of oxidation is still small so that the concentration of ester has changed very little from the original). It is proposed that the oxidation mechanism involves chain branching due to hydroperoxide decomposition and this mechanism is found to explain the observed kinetics. Data are presented to show that the concentration of peroxide is independent of ester concentration.

In the autoxidation of saturated hydrocarbons the preponderance of evidence indicates that oxidation takes place preferentially at a tertiary C-H bond. Secondary C-H bonds are attacked less readily and primary C-H bonds are still more stable.

1 Contribution from the Chemistry Laboratories, Temple University, and the Pitman-Dunn Laboratories, Frankford Arsenal.

2 From the Ph.D. Thesis of H. Gisser.
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RECEIVED SEPTEMBER 24, 1952

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1  From the Ph.D. Thesis of H. Gisser.
to oxidation. George and Robertson\(^3\) showed that the thermal oxidation of tetralin proceeded via an energy chain, while the peroxide-catalyzed autoxidation of tetralin proceeded via a radical chain.\(^4\)

In the former case the autoxidation rate was proportional to the square of the tetralin concentration. Walsh\(^5\) proposed that hydroperoxides may decompose by thermal scission yielding RO- and HO radicals. With tertiary hydroperoxides, the RO-radicals decompose further by breaking the weakest C-C bond with the formation of a ketone and R\(^4\). The latter may then serve to initiate new oxidation changes. These observations and ideas have been applied to the study of the autoxidation of saturated aliphatic diesters, which are currently of interest as lubricants.

**Experimental**

**Materials.**—The alcohols were prepared by fractionation of commercial materials, except for ethyl alcohol where the USP grade was used without further treatment. Adipic acid was obtained from Distillation Products Company (Eastman grade) and used without further treatment. The azelaic acid was a commercial grade obtained from Inamco Industries and was recrystallized once from thiourea-free benzene and twice from distilled water before use. The melting point of the purified material was 106\(^\circ\). The esters were prepared by mixing the alcohol and adipic acid in the ratio of 2.5 moles of alcohol per mole of adipic acid, with 1 g. of \(p\)-toluenesulfonic acid monohydrate per mole of alcohol and refluxing in an apparatus fitted with a continuous water-take-off adapter. For alcohols having more than five carbon atoms, 100 ml. of xylene were added per mole of acid. When no more water collected, the excess alcohol and xylene (if present) were removed under reduced pressure using a water-pump. Three grams of finely powdered anhydrous potassium carbonate per mole of adipic acid were then added and the mixture distilled with an oil-pump (1 to 5 mm.). The distillate was mixed with 1 g. of finely powdered anhydrous potassium carbonate per mole of adipic acid and permitted to remain overnight. The mixture was filtered and the filtrate distilled, the ester being collected over a maximum boiling range of 0.3\(^\circ\) (except for di-n-pentyl adipate which was collected over a 0.5\(^\circ\) range). All of the distillations were conducted in a current of dry nitrogen.

Esters of ethyl alcohol were made in a similar manner except that 30 ml. of thiophene-free benzene were added per mole of adipic acid and a fractionating column was interposed between the reaction flask and the reflux condenser to separate the alcohol from the water-benzene azeotrope. Consist- erable benzene and alcohol remained dissolved in the collected water and to replace these, 30 ml. each of ethyl alcohol


\[^4\] P. George, ibid., 155A, 337 (1946).

**Table I**

<table>
<thead>
<tr>
<th>Ester</th>
<th>Adipic acid</th>
<th>Reflux time</th>
<th>Yield</th>
<th>Sapon. equiv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl adipate</td>
<td>1450</td>
<td>10</td>
<td>30</td>
<td>1652</td>
</tr>
<tr>
<td>Di-n-pentyl adipate</td>
<td>876</td>
<td>6</td>
<td>6</td>
<td>1270</td>
</tr>
<tr>
<td>Di-1-(methylbutyl) adipate</td>
<td>731</td>
<td>5</td>
<td>24</td>
<td>1216</td>
</tr>
<tr>
<td>Di-1-(ethylpropyl) adipate</td>
<td>870</td>
<td>6</td>
<td>24</td>
<td>1444</td>
</tr>
<tr>
<td>Di-2-(methylbutyl) adipate</td>
<td>584</td>
<td>4</td>
<td>6</td>
<td>808</td>
</tr>
<tr>
<td>Di-n-hexyl adipate</td>
<td>584</td>
<td>10</td>
<td>8</td>
<td>1458</td>
</tr>
<tr>
<td>Di-1-(ethy1butyl) adipate</td>
<td>876</td>
<td>6</td>
<td>0</td>
<td>1520</td>
</tr>
<tr>
<td>Di-2-(methylhexyl) adipate</td>
<td>584</td>
<td>4</td>
<td>6</td>
<td>1025</td>
</tr>
<tr>
<td>Di-2-(methylpentyl) adipate</td>
<td>730</td>
<td>5</td>
<td>0</td>
<td>1280</td>
</tr>
<tr>
<td>Diethyl azelate</td>
<td>609*</td>
<td>3.2</td>
<td>30</td>
<td>560</td>
</tr>
</tbody>
</table>

* Azelaic acid.

**Table II**

<table>
<thead>
<tr>
<th>Ester</th>
<th>B.p. (\circ)</th>
<th>M. (%)</th>
<th>F.(\circ)</th>
<th>(\text{mg. KOH/gm. ester})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl adipate</td>
<td>99.1</td>
<td>14.3</td>
<td>1.2770</td>
<td>1.096</td>
</tr>
<tr>
<td>Di-n-butyl adipate</td>
<td>148.3</td>
<td>2.3</td>
<td>1.4320</td>
<td>0.964</td>
</tr>
<tr>
<td>Di-n-pentyl adipate</td>
<td>148.3</td>
<td>1.5</td>
<td>1.4302</td>
<td>0.964</td>
</tr>
<tr>
<td>Di-1-(methylbutyl) adipate</td>
<td>123</td>
<td>1</td>
<td>1.4330</td>
<td>0.964</td>
</tr>
<tr>
<td>Di-1-(ethylpropyl) adipate</td>
<td>135.2</td>
<td>2.8</td>
<td>1.4363</td>
<td>0.964</td>
</tr>
<tr>
<td>Di-2-(methylbutyl) adipate</td>
<td>142</td>
<td>1.1</td>
<td>1.4370</td>
<td>0.964</td>
</tr>
<tr>
<td>Di-2-(methylpentyl) adipate</td>
<td>112</td>
<td>1.3</td>
<td>1.4370</td>
<td>0.964</td>
</tr>
<tr>
<td>Di-n-hexyl adipate</td>
<td>144.5</td>
<td>3</td>
<td>1.4400</td>
<td>0.964</td>
</tr>
<tr>
<td>Di-1-dimethylbutyl) adipate</td>
<td>115</td>
<td>1.3</td>
<td>1.4345</td>
<td>0.964</td>
</tr>
<tr>
<td>Di-2-dimethylbutyl) adipate</td>
<td>106.8</td>
<td>1</td>
<td>1.4345</td>
<td>0.964</td>
</tr>
<tr>
<td>Di-2-(methylpentyl) adipate</td>
<td>121</td>
<td>1</td>
<td>1.4345</td>
<td>0.964</td>
</tr>
<tr>
<td>Diethyl azelate</td>
<td>134.8</td>
<td>1.0</td>
<td>1.4345</td>
<td>0.964</td>
</tr>
</tbody>
</table>

and thiophene-free benzene were added to the reaction mixture for each mole of adipic acid initially used when the reaction was approximately half completed. The freshly distilled esters were colorless and had acid numbers less than 0.01 mg. of KOH per gram of ester. The ethyl esters had faint fruity odors, while the other esters were odorless. These properties were retained for at least six months. Details of the preparations of the esters and physical properties of esters are given in Tables I and II, respectively.

**Oxidation Techniques.**—The esters were autoxidized by two methods, in one of which oxygen consumption rate was recorded and in the other the rate of formation of peroxy acid during passage of a stream of air through the ester was determined. The oxygen absorption apparatus was that described by Von Fuchs and Diamond\(^6\) using the gas pump of Larsen and his co-workers. Most of the oxygen absorption measurements were made at 110\(^\circ\). Tenth-mole quantities of the esters were oxidized and oxidation was continued until 200 ml. of oxygen had been consumed.

Air oxidation was accomplished by passing dry air previously passed through towers of soda lime and cotton wool at a rate of 8.0 ± 0.5 liters per hour through 150 g. of ester in a tube fitted with a reflux condenser. The effluent gases were passed through traps to collect peroxy acid or acid escaping from the system (in different runs). At intervals, samples of the esters were removed and peroxy acid and acid were determined. (Peroxy acid and acid data were corrected for "volatile" material collected in the traps.) The oxidation reactions were run at 100\(^\circ\).

**Results and Discussion**

**Effect of Structure.**—The oxygen absorption data are shown in Figs. 1 and 2. The course of


AUTOXIDATION
or.
SATURATED ALIPHATIC DIASPERS

oxidation is similar to that found in the autoxidation of tetralin. The oxygen consumption curve is linear for a shorter or longer period of time depending on the material under study. After this period the oxidation rate progressively increases and eventually becomes constant. This rate is referred to in the following as the "steady" rate. The steady rate was obtained in most instances when approximately 0.01 mole of oxygen had been consumed per mole of ester. The initial and steady rates (calculated from the slopes of the linear portions of the curves in Figs. 1 and 2) are given in Tables III and IV.

The oxygen absorption data indicate that as the distance of the side chain from the ester group increases, the rate of oxidation also increases. The greater susceptibility to oxidation of the tertiary C-H bond than the secondary C-H bond is also evident from Tables III and IV, when the tertiary C-H bond is sufficiently far removed from the ester group. An increase in the molecular weight of the ester is expected to increase the oxidation rate but it is improper to compare rates of oxidation per gram of ester because no relative values are available for tertiary and secondary C-H bonds. In addition, the secondary C-H bonds are also affected by their distance from the ester group. The oxidation rates of the n-alkyl adipates per CH₂ group are given in Table V assuming that no oxidation takes place in the end methyl group. Evidently the CH₃ groups of ethyl azelate are more susceptible to oxidation than those of the adipate.

### Table III

<table>
<thead>
<tr>
<th>Adipate</th>
<th>Initial rate X 10⁻⁸ (mole O₂/mole ester/sec)</th>
<th>&quot;steady&quot; rate X 10⁻⁸ (mole O₂/mole ester/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Methylbutyl</td>
<td>0.143</td>
<td>1.38</td>
</tr>
<tr>
<td>2-Methylbutyl</td>
<td>0.401</td>
<td>2.07</td>
</tr>
<tr>
<td>3-Methylbutyl</td>
<td>1.15</td>
<td>8.48</td>
</tr>
<tr>
<td>1-Rthylpropyl</td>
<td>0.161</td>
<td>1.25</td>
</tr>
<tr>
<td>2-Rthylpropyl</td>
<td>.502</td>
<td>4.95</td>
</tr>
<tr>
<td>2-Rthylbutyl</td>
<td>.639</td>
<td>3.97</td>
</tr>
<tr>
<td>1,3-Dimethylbutyl</td>
<td>1.05</td>
<td>11.3</td>
</tr>
</tbody>
</table>

### Table IV

<table>
<thead>
<tr>
<th>Ester</th>
<th>Initial rate X 10⁻⁸ (mole O₂/mole ester/sec)</th>
<th>&quot;steady&quot; rate X 10⁻⁸ (mole O₂/mole ester/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl adipate</td>
<td>0.178</td>
<td>1.98</td>
</tr>
<tr>
<td>Di-n-pentyl adipate</td>
<td>.364</td>
<td>2.20</td>
</tr>
<tr>
<td>Di-n-hexyl adipate</td>
<td>.348</td>
<td>2.97</td>
</tr>
<tr>
<td>Diethyl azelate</td>
<td>.708</td>
<td>4.83</td>
</tr>
</tbody>
</table>

In the air oxidations, it was found that the concentration of peroxide built up slowly, reached a maximum and then slowly decreased probably approaching a steady or near steady state. The observed concentration of peroxide is the difference between the amount formed and the amount decomposed and is therefore an indication of both oxidation rate and hydroperoxide stability at the temperature of oxidation. As a result, the concentration of hydroperoxide is useful for rate comparison at best during the initial stages of oxidation when relatively little hydroperoxide decomposition takes place. The concentration of acid built up
slowly at first, and then increased quite rapidly. Except for esters in which the side chain was on the γ-carbon from the ester group, the increase in rate of acid formation began to decrease. With esters whose tertiary carbons were in the γ-position to the ester group, acid formation approximately followed peroxide formation for approximately 200 hr., following which, the rate of peroxide formation began to decrease. The initial rates of peroxide formation and the rates of acid formation confirmed the oxygen absorption data in the effect of structure on rate.

The effect of structure on autoxidation rate may be attributed to the availability of electrons at the carbon atom in question due to the ester group. Resonance of the ester group may be illustrated as

\[
\begin{align*}
\text{H} & \quad \text{:\:O}^{-} \\
\text{C-C:O:C:C-} & \quad \leftrightarrow \quad \text{C-C:O:C:C-} \\
\text{I} & \quad \leftrightarrow \quad \text{II} \\
\text{H} & \quad \text{:\:O}^{-} \\
\text{C-C:O:C:C-} & \quad \leftrightarrow \quad \text{C-C:O:C:C-} \\
\text{III}
\end{align*}
\]

In III, the positively charged oxygen results in an inductive effect along the carbon chain attracting electrons to the ester group, and this effect falls off as the distance from the ester group increases. If oxidation is initiated at the tertiary carbon by formation of a free radical (by reaction with another free radical) or by the formation of an energy-rich molecule having high energy in the vibrational mode of the C–H bond, it would be expected that as electron availability decreases, the ease of oxidation should decrease.

**Oxidation Kinetics.** —The autoxidation of di-(3-methylbutyl) adipate was studied in diethyl adipate solutions. The rates in the initial and steady parts of the oxidation, calculated from the appropriate slopes of oxygen consumption curves, (corrected for oxidation of diethyl adipate assuming no interactions) are plotted in Figs. 3 and 4, respectively. The oxidation process may be considered as taking the following course: Oxidation chains are initiated thermally, with the formation of hydroperoxide. The hydroperoxide decomposes resulting in free radicals which initiate new oxidation chains. In the initial period, the amount of hydroperoxide which is decomposing is small and most of the oxidation is initiated by thermal means and the rate of oxygen consumption is proportional to the square of ester concentration. As hydroperoxide formation and decomposition continue, free radical initiation competes with thermal initiation, the reaction speeds up and, after a period of time, most of the oxidation chains are initiated by previously formed hydroperoxide. At this stage the rate is again constant and is proportional to the square root of ester concentration. It should be noted that the oxidations were run until no more than 5% of the ester had been oxidized and as a result the ester concentration had changed relatively little and its effect on rate during the run was negligible.

The dependence of the initial rate on the square of ester concentration may be explained by the high energy chain proposed by George and Robertson for tetralin. Dependence of the steady rate on the square root of ester concentration may be explained by assuming a chain-branching process in which hydroperoxide decomposes by the mechanism proposed by Walsh. The oxidation mechanism may be formulated as follows taking into account chain branching due to hydroperoxide decomposition.

Initiation:

\[
RH \rightarrow X
\]

**Autoxidation of Saturated Aliphatic Diesters**

Fig. 5.—"Steady" oxidation rates of dialkyl adipates.

**Propagatio**n:

\[ X + O_2 \rightarrow_{k_a} P \]

\[ P + RH \rightarrow_{k_b} ROH + X \]

**Termination**:

\[ P \rightarrow \text{products} \]

**Branching**:

\[ ROH \rightarrow_{k_i} RO + HO \]

\[ RO \rightarrow_{k_s} R + \text{carbonyl compounds} \]

**Propagation**:

\[ R_1 + O_2 \rightarrow_{k_{R1O2}} R_1O_2 \]

\[ R_2O_2 + RH \rightarrow_{k_b} R_2O_2H + R \]

\[ R + O_2 \rightarrow_{k_{RRO2}} RO \]

\[ RO + RH \rightarrow_{k_b} ROH + R \]

**Termination**:

\[ HO \rightarrow_{k_d} ? \]

\[ RO + R \rightarrow_{k_{RO}} RO \]

where RH is the ester, X is a high energy ester molecule, P is a high energy complex of the ester and oxygen, and the k's are rate constants.

As a result of the oxidative degradation, radicals and molecules of lower carbon content than the original ester appear, e.g., R1O2H. It will now be assumed that all radicals and molecules of the same type undergo similar reactions with approximately equal rate constants. Subscripts will therefore be dropped, and the indicated concentration of any compound will be the sum of concentrations of all compounds of that type. Neglecting the energy chains, since their contribution to the oxidation rate is small during the steady reaction, the following steady state equations are obtained

\[ \frac{d(RO)}{dt} = k_a(ROH) - K_a(RO) = 0 \]  

(1)

\[ \frac{d(R^-)}{dt} = k_a(RO^-) - k_a(R^-XO^-) + k_a(RO)(RH) \]

\[ - K_a(R^-XO^-) = 0 \]  

(2)

\[ \frac{d(RO_2^-)}{dt} = k_a(R^-XO^-) - k_a(RO_2^-XRH) \]

\[ - K_a(RO_2^-XRH) = 0 \]  

(3)

Elimination of \((RO^-)\) and \((RO_2^-)\) yields the following equation for \((R^-)\)

\[ (R^-)^{k_a} - \frac{k_a(R^-)(RO)}{2k_a(O^2)} = 0 \]  

(4)

since \((R^-) < 1\) and \(k_a > k_b\), the term in \((R^-)\) may be neglected, and

\[ (R^-)^{k_a} = \left[ \frac{k_a(R^-)(RO)}{2k_a(O^2)} \right]^{1/4} \]  

(5)

since

\[ \frac{dO}{dt} = k_a(R^-XO) \]  

(6)

\[ \frac{dO}{dt} = k(R^-XO)^{1/4} \]  

(7)

where

\[ k = \left[ \frac{k_a^2k_b(RO)(ROH)}{2k_a} \right]^{1/4} \]  

(8)

The steady rate is therefore proportional to the square root of ester concentration provided \((RO_2^-)\) is constant. \((O_2)\) is constant because the oxidations were conducted at constant pressure.

Solutions of di-(3-methylbutyl) adipate and diethyl adipate were oxidized by a stream of dry air at 100° and peroxide was determined at 24 hr. intervals. The results are given in Table VI (where the figures have been corrected for oxidation of diethyl adipate assuming no interactions) from which it appears that the peroxide concentration per mole of di-(3-methylbutyl) adipate is independent of concentration of di-(3-methylbutyl) adipate at mole fractions of 0.267 and higher. The rate of oxygen
consumption referred to above is the rate per mole of di-(3-methylbutyl) adipate. It has already been indicated that the peroxide concentration during oxidation probably approaches a steady state. It therefore follows that concentration of hydroperoxide in the above kinetic treatment may be assumed constant.

**Table VI**

<table>
<thead>
<tr>
<th>Mole fraction di-(3-methylbutyl) adipate</th>
<th>24 hr.</th>
<th>48 hr.</th>
<th>72 hr.</th>
<th>96 hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.179</td>
<td>2.06</td>
<td>3.02</td>
<td>6.86</td>
<td></td>
</tr>
<tr>
<td>0.307</td>
<td>2.59</td>
<td>6.03</td>
<td>12.1</td>
<td>18.2</td>
</tr>
<tr>
<td>0.500</td>
<td>6.22</td>
<td>11.7</td>
<td>18.1</td>
<td></td>
</tr>
<tr>
<td>0.778</td>
<td>6.66</td>
<td>12.8</td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.80</td>
<td>7.00</td>
<td>11.0</td>
<td>23.4</td>
</tr>
</tbody>
</table>

The kinetic analysis above does not account for the fate of HO· nor the formation of acid. While it is probable that HO· is associated with the later stages of oxidation, further work is required to clarify this point.

**Energy of Activation.**—Energies of activation for steady oxidations were determined on di-(3-methylbutyl) adipate, di-(1-ethylpropyl) adipate and di-n-pentyl adipate. The log of oxidation rate (moles oxygen consumed per mole ester per second) are plotted against reciprocal of absolute temperature in Fig. 5 and the calculated activation energies are in Table VII. These data provide further evidence for the effect of structure on oxidation rate.

**Table VII**

<table>
<thead>
<tr>
<th>Ester</th>
<th>Energy of activation (Cal./Mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-(3-methylbutyl) adipate</td>
<td>21,000</td>
</tr>
<tr>
<td>Di-(1-ethylpropyl) adipate</td>
<td>20,300</td>
</tr>
<tr>
<td>Di-n-pentyl adipate</td>
<td>20,100</td>
</tr>
</tbody>
</table>

**Acknowledgment.**—The authors are indebted to the Chemistry Staff of the Pitman-Dunn Laboratories, Frankford Arsenal, where this investigation was conducted in part as an Army Ordnance Project.
Information Report

Data and analytical products related to the potential impact of climate change on the DoD have been developed by researchers and analysts working in various disciplines. These products provide information on the physical and societal impacts of climate change, as well as the potential for adaptation and mitigation strategies.

In addition, the DoD has developed strategies to reduce its carbon footprint and increase energy efficiency. These strategies include the use of renewable energy sources, improvements in building design and operation, and the implementation of energy-saving technologies.

Furthermore, the DoD is working to develop and implement climate change adaptation measures. These measures include the development of contingency plans for military installations in areas that may be affected by climate change, as well as the implementation of infrastructure improvements to enhance resilience.

Overall, the DoD is committed to understanding the potential impacts of climate change and developing strategies to mitigate these impacts and adapt to the changing environment.