two single peaks, one at $\tau$ 8.0, equivalent to three hydrogens, from the methyl group on the carbonyl, and the other at $\tau$ 8.8, equivalent to six hydrogens, from the dimethyl group $\beta$ to the carbonyl and the double bond.

*Anal.* Calcd. for $C_7H_{12}O$: C, 74.9; H, 10.8. Found: C, 74.9; H, 10.6.

**Methyl dimethylvinylacetate** had b.p. 126.6°, $n^{20}_{D}$ 1.4162. The n.m.r. spectrum shows an ABC pattern for a vinyl group attached to a completely substituted carbon in the $\tau$ 4–5 region. There are two other single peaks, one at $\tau$ 6.4, equivalent to three hydrogens, from the methoxy group, and the other at $\tau$ 8.8, equivalent to six hydrogens, from the dimethyl group $\beta$ to the carbonyl and the double bond.

*Anal.* Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 66.4; H, 9.7.

**3-Amino-1-hexene** had b.p. 114°. The n.m.r. spectrum shows an ABCX pattern in the $\tau$ 4–5 region for the vinyl groups attached to a tertiary carbon. A broad, unresolved resonance at $\tau$ 6.8, equivalent to one hydrogen, is in the region expected for the single hydrogen $\alpha$ to both the double bond and the amino group. A complex methylene resonance, equivalent to four hydrogens, occurs at $\tau$ 8.6. A methyl resonance is present at $\tau$ 9.0. The amino group is identified with a single peak, equivalent to two hydrogens, which occurs at $\tau$ 8.8 in the pure liquid, shifting to 9.0 for a 25% solution in carbon tetrachloride.

**Acknowledgment.**—The authors are indebted to Mrs. Joy Buell and Dr. R. S. Silas for obtaining and interpreting the n.m.r. data.

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# Generation of Free Radicals through Organic Oxidation–Reduction Systems

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The oxidation–reduction reaction between alkyl hydroperoxides, acyl and aroyl peroxides, and organometallic compounds such as manganous acetylacetonate and ferrocene as a means of generation of free radicals in organic solvents at ambient temperatures was studied. The radical nature of these reactions was indicated by the initiation of vinyl polymerization and the chain addition of sodium bisulfite, mercaptans, and ethyl $\alpha$-bromoacetate to olefins.

The interaction between hydrogen peroxide and ferrous ion known as Fenton's[2] reagent affords a unique method to generate hydroxy free radicals in aqueous solution at low temperature. This reaction involves a complicated sequence of transformations and can be simplified as a one-electron transfer process whereby one hydroxy radical is reduced to hydroxide ion and ferrous ion is oxidized to ferric ion.

$$Fe^{2+} + HOOH \longrightarrow Fe^{3+} + HO^- + HO$$

This reaction has been extensively studied[3] and expanded[4] through the years. Different oxidizable metal ions including some organometallic ions have been used with various organic hydroperoxides and acyl peroxides. Enormous development has been achieved in the field of low-temperature emulsion polymerization in the past 20 years.[5] The use of organometallic compounds instead of inorganic metal salts in the oxidation–reduction systems has the advantage that the reaction can be carried out in organic solutions instead of either in aqueous or emulsion systems, thus polymerization in bulk can be carried out at ambient temperature range. Uri[6] indicated that the presence of very low concentrations of ferrous and cuprous phthalocyanine catalyzed the autoxidation of linoleic acid. Lowell[7] reported that ferrocene reacted with benzoyl peroxide to initiate free-radical chain reactions, and Konish and Namba[8] polymerized vinyl chloride with lauroyl peroxide and ferrous caproate as the oxidation–reduction couple.

Systems which involve oxidation–reduction cleavage of chemical bonds other than oxygen–oxygen have been proposed by Evans and Baxendale and their co-workers on the cleavage of oxygen–nitrogen bond in hydroxylamine with titanous ion[9] and on the bromine–bromine bond cleavage with ferrous ion.[10] Both systems have induced vinyl polymerization and the radical nature of such systems was well established. The oxidation–reduction cleavage of the sulfur–sulfur bond in aryl and cyclic alkyl disulfides by organometallic compounds and amines was reported recently.[11] Reduction of phenylmercuric cation whereby phenyl free radical[12] is produced, and of triethyllead cation leading to the formation of ethyl radical[13] constitute examples of oxidation–reduction cleavage of chemical bonds between carbon and metals.

In this paper we wish to report some more additional findings on the oxidation–reduction cleavage of acyl peroxide and alkyl hydroperoxides with organometallic compounds in organic solvents.

## Results and Discussion

We noticed that the electron-transfer process between organic acyl peroxides or hydroperoxides with organometallics is almost a general reaction. In addition to the oxidizable metal phthalocyanines and metallocenes, metal chelates such as acetylacetonates with metal at lower valency state which can be oxidized further by a one-electron transfer mechanism interact with acyl peroxides and alkyl hydroperoxides whereby a free radical is generated in organic solvent at or below room temperatures. The radical nature of this reac-

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TABLE I

POLYMERIZATION OF *n*-BUTYL METHACRYLATE[a]

| Catalyst | | Temp., °C. | Polymer yield |
|---|---|---|---|
| CHP[b] | Metal compd. | | |
| 20 | Ferrocene | −2 | 15% conversion |
| 20 | Cobaltocene | −2 | Trace |
| 20 | $V(C_5H_7O_2)_3$[c] | −2 | 70% conversion |
| 20 | $Mn(C_5H_7O_2)_2$ | −2 | 100% conversion |
| 20 | $Ni(C_5H_7O_2)_2$ | −2 | 0 |
| 20 | $Mg(C_5H_7O_2)_2$ | −2 | 0 |
| 20 | $V(C_5H_7O_2)_3$ | −18 | 5% conversion |
| 20 | $Mn(C_5H_7O_2)_2$ | −18 | Trace |
| None | $V(C_5H_7O_2)_3$ | −2 | 0 |
| None | $Mn(C_5H_7O_2)_2$ | −2 | 0 |
| 20 | 0 | −2 | 0 |

[a] Reaction time was 70 hr.; 10 ml. of monomer and 5 mg. of metal compound were used. [b] CHP = cumene hydroperoxide. [c] $M(C_5H_7O_2)_x$ = metal acetylacetonate.

TABLE II

| Additive (mole) | Olefin (mole) | Catalyst | Reaction time | % yield of addition product |
|---|---|---|---|---|
| Sodium bisulfite (0.28) | 1-Octene (0.2) | $Mn(C_5H_7O_2)_2 + (PhCOO)_2$ | 3 days | 30 |
| Sodium bisulfite (0.28) | Cyclohexene | $Mn(C_5H_7O_2)_2 + (PhCOO)_2$ | 3 days | 56 |
| Sodium bisulfite (0.28) | 1-Hexadecene | $Mn(C_5H_7O_2)_2 + (PhCOO)_2$ | 3 days | 17 |
| Sodium bisulfite (0.28) | 1-Octene | $(PhCOO)_2$ | 3 days | Trace |
| Sodium bisulfite (0.28) | 1-Octene | $Mn(C_5H_7O_2)_2$ | 3 days | 0 |
| Sodium bisulfite (0.28) | Cyclohexene | $(PhCOO)_2$ | 3 days | 0 |
| Sodium bisulfite (0.28) | Cyclohexene | $Mn(C_5H_7O_2)_2$ | 3 days | 0 |
| Thiophenol (0.4) | 1-Hexene (0.2) | $Mn(C_5H_7O_2)_2 + (PhCOO)_2$ | 20 hr. | 30 |
| Thiophenol (0.4) | 1-Hexene (0.2) | $(PhCOO)_2$ | 20 hr. | 0 |
| Thiophenol (0.4) | 1-Hexene (0.2) | $Mn(C_5H_7O_2)_2$ | 20 hr. | 0 |
| Ethyl α-bromoacetate (0.04) | 1-Octene (0.2) | $Mn(C_5H_7O_2)_2 + (PhCOO)_2$ | 3 days | 22 |
| Ethyl α-bromoacetate (0.04) | 1-Octene (0.2) | $Mn(C_5H_7O_2)_2$ | 3 days | Trace |
| Ethyl α-bromoacetate (0.04) | 1-Octene (0.2) | $(PhCOO)_2$ | 3 days | Trace |

tion was indicated by both initiation of vinyl polymerization, and chain addition of sodium bisulfite,[14] mercaptans,[15] and ethyl α-bromoacetate to olefins.[4] The results of initiation of vinyl polymerization by metal acetylacetonates and cumene hydroperoxide are summarized in Table I. There is obviously no parallel correlation between the efficiency of metal chelates as initiators of free-radical chain reactions and the oxidation–reduction potentials of the free metal ions. It is also well known that the oxidation–reduction potentials of a metal ion is affected by the nature of the ligands bonded to it.[16] It was also indicated recently that these chelate compounds do not exist in their monomeric forms[17] and their activity is subjected to steric and electronic factors.[18]

The result of chain addition of some compounds to olefins is summarized in Table II. The oxidation–reduction pair used in this series of experiments was 100 mg. each of manganous acetylacetonate and benzoyl peroxide unless stated otherwise. All experiments were carried out at room temperature with vigorous stirring under nitrogen atmosphere.

It is obvious that the metal compound–peroxide couple is necessary to initiate the radical chain reaction. The trace amount yields of octylsulfonic acid with benzoyl peroxide alone as catalyst could be attributed to the slow thermal decomposition of benzoyl peroxide which then initiated the bisulfite addition to 1-octene This certainly should also explain the small yield of ethyl 4-bromo-1-decanoate with benzoyl peroxide alone as catalyst. However, when managanous acetylacetonate alone is used, a trace of the addition compound was also obtained. It probably resulted from the relatively slow oxidation–reduction reaction between ethyl α-bromoacetate and the organometallic compound. Examples of alkyl halides–metal ion oxidation–reduction couples are well known.[19]

The addition product of thiophenol to 1-hexene was established to be *n*-hexyl phenyl sulfide from both elementary and n.m.r. analysis. Elementary analysis shows that the product should either be *n*-hexyl phenyl sulfide or 2-hexyl phenyl sulfide. N.m.r. data indicate that aliphatic protons α to the sulfur atom appear as a triplet at 2.8 p.p.m. The area of the triplet corresponds to two protons and the triplet structure demands only two β-protons. This conclusion is, of course, in accord with the free-radical mechanism of addition to olefins.

## Experimental Section[20]

**Polymerization.**—*n*-Butyl methacrylate (Matheson) was washed with 10% of sodium hydroxide and then water and dried over anhydrous sodium sulfate. The monomer was then distilled under nitrogen. The fraction boiling at 161–163° was collected and used in these experiments.

*n*-Butyl methacrylate (10 ml.) containing 1 drop of cumene hydroperoxide in a Thunberg tube was frozen in liquid nitrogen and degassed. After the contents were subjected to repeated thawing and freezing operations to remove the dissolved gases, 5 mg. of organometallic compound, placed in the hollow stopper, was introduced by tilting the tube. Later the content was poured into 200 ml. of methanol and the precipitated polymers were filtered, washed with methanol, and dried overnight *in vacuo* at 40°, then allowed to cool to room temperature, and weighed. In those cases where total conversion was observed, no attempt was made to isolate and purify the polymeric material.

In the accompanying control runs for each case, only cumene hydroperoxide or organometallic compound alone was used. The experiments were carried out under identical conditions.

Comparable results were obtained from 2,5-dimethylhexyldihydroperoxide and various metal acetylacetonates.

**Addition of Sodium Bisulfite to 1-Octene.**—A mixture of 30 g. (0.28 mole) of sodium bisulfite and 22.4 g. (0.2 mole) of 1-octene (Eastman, freshly distilled, b.p. 124–126°) in 300 ml. of methanol and 30 ml. of water containing 100 mg. of benzoyl peroxide

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and 100 mg. of manganous acetylacetonate was stirred at room temperature over a period of 3 days. After removal of the solvent at reduced pressure an oily residue was obtained. It dissolved in water with soapy foams upon shaking. Isolation of pure alkylsulfonic acid was tedious and the free acid is extremely hygroscopic. Quantitative isolation was carried out by acidifying the aqueous solution of sodium alkylsulfonate and precipitating the sulfonic acid as its lead salt with lead acetate, 30% yield.

*Anal.* Calcd. for $C_{16}H_{34}O_6PbS_2$: C, 33; H, 5.7; S, 10.8. Found: C, 32.8; H, 6.1; S, 11.

The infrared spectrum showed absorptions at 3.0 (w), 3.4, 3.48, 3.5 (s), 6.3 (w), 6.9 (s), 7.05 (m), 7.1 (s), 8.3 (s), 9.25 (s), and 11.0 (s-b) μ.

**Addition of Thiophenol to 1-Hexene.**—The mixture of 17 g. (0.2 mole) of 1-hexene and 4.4 g. (0.4 mole) of thiophenol with 100 mg. each of benzoyl peroxide and manganous acetylacetonate was stirred overnight. The reaction mixture was treated with 25 ml. of ether and 10 ml. of 10% sodium hydroxide. The aqueous layer was further extracted with ether. The ether extracts furnished 2.2 g. (30%) of *n*-hexyl phenyl thioether, b.p. 265–270°.

*Anal.* Calcd. for $C_{12}H_{18}S$: C, 74.16; H, 9.34; S, 16.49. Found: C, 74.21; H, 9.13; S, 16.78.

**Addition of Ethyl α-Bromoacetate to 1-Octene.**—The mixture of 22.4 g (0.2 mole) of 1-octene and 6.7 g. (0.04 mole) of ethyl α-bromoacetate with 0.1 g. of each of benzoyl peroxide and manganous acetylacetonate was stirred at room temperature over the weekend. The solid material was filtered and the filtrate afforded 2.5 g. (22%) of the desired product, ethyl 4-bromo-1-decanoate, boiling at 125–130° (15 mm.), lit.[21] b.p. 140° (20 mm.).

Attempts to add formamide, acetic acid, and methanol to such olefins failed.

In the blank runs, the experiments were carried out in the same manner except no oxidation–reduction couple was used.

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# The Reaction of 2,3-Dichloronaphthoquinone with Nucleophiles. II. Reaction with Ethyl Acetoacetate

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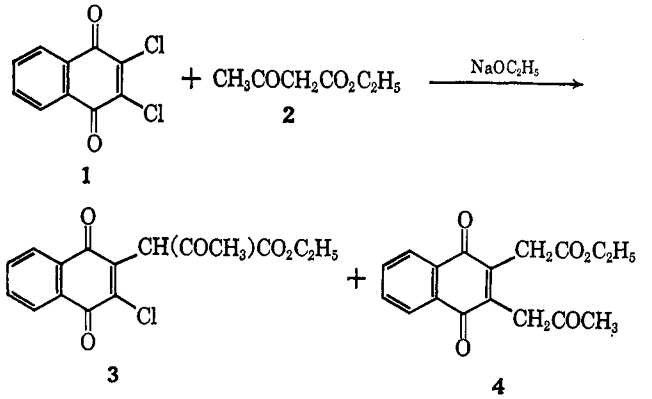
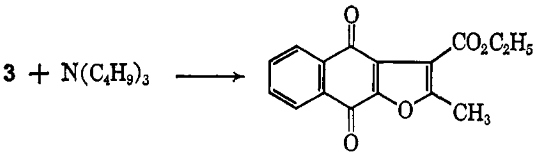
The course of the reaction of 2,3-dichloro-1,4-naphthoquinone and ethyl acetoacetate under basic conditions was investigated, and the structures of the products were demonstrated. A satisfactory synthesis for two of these products, 5 and 15, is described.

In continuation of our investigation of some reactions of 2,3-dichloro-1,4-naphthoquinone (1) with nucleophilic reagents,[1] we examined the reaction of 1 with ethyl acetoacetate (2) in the presence of basic reagents. This reaction was first reported by Michel[2] who found that the addition of the sodium salt of 2 to a suspension of 1 in ethanol gave the yellow ethyl 3-chloro-1,4-naphthoquinone-2-acetoacetate (3) and a red by-product (A) to which he assigned the structure 4 on the basis of elementary analysis and molecular weight (301), determined by the ebullioscopic method using benzene as the solvent. This preparative method has been modified slightly[3] by adding 1 to a boiling alcoholic solution of the active methylene compound and sodium ethoxide. According to Pratt and Rice,[4] the latter procedure proved to be superior for the preparation of 3. They[4] showed that 3 was cyclized to a furan derivative 5 on treatment with bases such as tributylamine. Pratt, *et al.*, reported[5] that A was obtained from reaction of 2 with 2-bromo-1,4-naphthoquinone, 1,4-naphthoquinone, or potassium 1,4-naphthoquinone-2-sulfonate under basic conditions. Pratt found it interesting that, during the formation of A, which he also formulated as structure 4, one of the added ethyl acetoacetate moieties lost an acetyl group while the other lost a carbethoxyl group.



1 2

3 4



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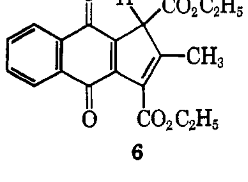
At about the same time of Pratt's[5] work, Suryanarayana and Telak[3] proposed a new structure for A. These authors objected to the assignment of structure 4 mainly on the basis of the red color of the material, reasoning that a compound of this structure should be yellow. They proposed structure 6 for A. Although 6 has a different molecular weight from 4, the elementary compositions of both are similar. An attempt to determine the molecular weight by Rast's camphor method was not successful because of the deep color.



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