2. Polymerization, with double-bond rupture in the sodium oleate molecule, results in firm bonding of the oleate film to the metal surface.

3. Thermal treatment of the polymerized adsorbed film leads to molecular reorientation.

4. The adsorption of water vapor on the sodium oleate-modified aluminum surface is almost completely reversible, differing from adsorption on the original hydroxylated aluminum surface insofar as it leads to a reduction in the work function.

LITERATURE CITED


MECHANISM OF THE INHIBITION OF OXIDATION REACTIONS BY METAL COMPLEXES.

7.* CHAIN RUPTURE BY COMPLEXES OF COPPER WITH ALKYL AND PEROXYL RADICALS

G. A. Kevtun and I. I. Moiseev

Transition-metal complexes (ML_m) are capable of rupturing the chains established in the oxidation of organic compounds through their reactions with peroxyl radicals [2, 3]. Our earlier studies on the kinetics of the inhibition of oxidation in the pentaerythritol esters of monocarboxylic acids by copper complexes (I)-(III) have shown that chain rupture in these systems can result from reaction with alkyl, as well as peroxyl, radicals.

\[
\begin{align*}
(I) & : \quad O-Cu=O \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \\
(II) & : \quad O-Cu=O \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \\
(III) & : \quad O-Cu=O \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \\
\end{align*}
\]

R = C(CH_3)_3.

*For Communication 6, see [1].
Fig. 1. Variation of the rate of RH oxidation with [(I)]0 (1) and with PO2 (2) at 140°C, [(I)]0 = 3.5 \times 10^{-4} \text{ mole/liter}; W_i = 8.0 \times 10^{-9} \text{ mole/(liter·sec)}.

Fig. 2. Variation of the rate of inhibited RH oxidation with W_i at 140°C ([III]) = 4.6 \times 10^{-4} \text{ mole/liter}) (1), and plots of W vs PO2 data for complexes (II) and (III) in the coordinates of Eq. (6) (2, 3).

EXPERIMENTAL

The complexes (I) and (III) were separated out from alcoholic solution by Schiff bases and Cu(CH3COO)2·2H2O, following the procedure outlined in [4]. Elemental analysis showed each of the products to have the desired composition. Complex (II), copper (II) bis[2-(N,N-diethylaminomethyl)-4-tert-butylphenolate], was synthesized here for the first time.* Five ml of a 2 N NaOH solution were added to a solution containing 4.7 g (0.02 M) of 2-(N,N-diethylaminomethyl)-4-tert-butylphenolate dissolved in 50 ml of alcohol. The resulting mixture was slowly run into 25 ml of an aqueous solution containing 2.48 g (0.01 mole) of Cu(NO3)2·3H2O under constant stirring. The resulting complex (II) came down as a precipitate which was filtered off, washed on the filter, with 20 ml of ethanol, and then dried for 6 h at 110-115°C. This procedure gave 3.8 g (72%) of the complex. Found: C 67.9; H 8.9; N 5.1; Cu 12.6%. C30H32O2N2Cu. Calculated: C 67.8; H 9.0; N 5.26; Cu 12.0%.

Molecular weight 540 ± 10 (chloroform); calculated: 532.

The inhibiting action of the complexes was studied through the initiated oxidation of solutions containing the C5-C9 fractions of the pentaerythritol monocarboxylate esters (RH) at 115-140°C. After purification by the methods of [5], the characteristics of the RH were as follows: d = 0.995 g/ml; mol. wt. 660 ± 10; degree of hydroxyl group esterification 92 ± 2%. As determined at 140°C, the value of \( k_2/k_b^1/2 \) = \( W_i/[\text{RH}]W_i \), (7.5 ± 0.3) \times 10^{-3} (liters/mole·sec)\(^{1/2}\), was close to that reported in [5]. Here \( k_2 \) and \( k_b \) are the respective rate constants for chain extension and second-power chain rupture; PO2 (= 0.2-1.0 atm) is the pressure of oxygen uptake; and W_i is the rate of initiation by cumene peroxide. Values of \( k_1 \), the initiation rate constant (sec\(^{-1}\)), were calculated from the equation [5]

\[
\log k_1 = 14.5 - 33800/4.57T
\]

The inhibiting action of the complexes was also studied in the pentaerythritol esters of caproic acid (R'H)†. As determined at 140°C, \( k_2/k_b^1/2 \) = \( (6.7 ± 0.4) \times 10^{-3} \) (liters/mole·sec)\(^{1/2}\). The fact that the \( k_2/k_b^1/2 \) ratios of the RH and R'H compounds were nearly identical is consistent with earlier work [5] which showed that it is the alcoholic CH₂ bonds, rather than acid fragments of the ester molecule, which preferentially oxidized in these systems.

Catalase was used for detecting \( \text{H}_2\text{O}_2 \) in the RH oxidates [6].

*We would like to express our thanks to V. V. Peshkov who assisted in the synthesis of complex (II).
†GLC data showed the RH and R'H compounds used here contained neither acids nor free pentaerythritols.