CONCLUSIONS

1. The Sb and Bi dithiocarbamates inhibit the low-temperature initiated oxidation of ethylbenzene. Similarities with the inhibiting action of the divalent metal dithiocarbamates suggest that the inhibition mechanism is the same in both cases.

2. Oxidation potentials have been measured for the Cr(III), Fe(III), Mn(III), Sb(III), and Bi(III) dithiocarbamates.

3. The inhibiting action of the M(Dtc)$_3$ differs from that of the M(Dtc)$_2$ insofar as that it cannot be correlated with the oxidation potential. This is obviously due to the fact that these complexes have octahedral structure, the tendency of the chelate toward ligand exchange reactions being the principal factor in RO$_2^-$ complexing.

LITERATURE CITED


ACID PROPERTIES OF THE
2,2,6,6-TETRAMETHYL-1-OXOPIPERIDINIUM CATION AND
2,2,6,6-TETRAMETHYL-1-HYDROXYPIPERIDINE 1-OXIDE

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The oxopiperidinium salts (I) react with excess alkali to form metal piperidine dioxides (III) [1].

\[
\begin{align*}
\text{O} & \quad \text{X}^- \\
\text{N} & \quad \text{O} \\
\text{Cl}^- & \quad \text{ClO}_4^- \\
\text{K}^+ & \quad \text{Na}^+
\end{align*}
\]

The N-oxide of hydroxy piperidine (II) appears as an intermediate in these reactions. Proof of the existence of such N-oxides has been obtained through the study of nitroxyl oxidation by OH radicals [2]. It has, however, been reported in recent work [3-5], and confirmed in our own experiments [1], that these N-oxides cannot be separated out, either from alkaline solutions of oxammonium salts, or from acidified solutions of the alkaline
salts of (III). Attempts to form these compounds by oxidizing hydroxylamines with H₂O₂ and superacids have also met with failure [6]. We have attempted to discover the causes of these failures by studying the acid—base properties of 2,2,6,6-tetramethyl-1-oxopiperidinyl salts (I) in aqueous solution.

**EXPERIMENTAL**

The oxopiperidinyl salts (I) were prepared by the procedures of [7, 8]. Iodometric analysis showed the products obtained here to be 99.3% pure. The acidity constants of the oxopiperidinium cation, $\overset{+}{N}=O$, and the N-oxide, $\overset{+}{N}(O)OH$, were determined through measurements on chloride (I), a compound which is readily soluble in water. Solutions of the chloride ($C_0 = 0.1-0.01$ mole/liter) and KOH ($[KOH]_0 = 0.1-1$ mole/liter) containing enough KCl to maintain the ionic strength $\mu$ at 1 eq/liter were mixed at 0-10°C, and the mixture carried rapidly to a thermostated spectrometer cell, 1-5 cm in length. The optical density $D$ of the reaction mixture was measured at 470 nm, the maximum of the first band for $\overset{+}{N}=O$ absorption, using a Specord UV-VIS spectrometer. Extrapolation of $D$ to time zero gave the value of $D_0$; knowing $\varepsilon$ to be $19.5 \pm 0.2$ liter/mole-sec the equilibrium $\overset{+}{N}=O$ concentration was calculated from the expression $D_0/\varepsilon l$. From the $C_0 - [\overset{+}{N}=O]$ vs $[O\overset{+}{H}^-]$ relation, the acidity constants for $\overset{+}{N}=O$ and $\overset{+}{N}(O)OH$ were calculated.

**DISCUSSION OF RESULTS**

In neutral and alkaline aqueous solution, the visible region of the electronic spectra of the salts of (I) shows a single $\overset{+}{N}=O$ cation absorption band with a maximum at 470 nm. The intensity of this band varies with the hydroxyl ion concentration in alkaline solution, falling as $[O\overset{+}{H}^-]$ increases and returning to its original value on addition of acids. Such reversible change in the $\overset{+}{N}=O$ concentration suggests the formation of a colorless $\overset{+}{N}(O)OH$ anion [1] and the N-oxide of hydroxypiperidine $\overset{+}{N}(O)OH$.

$$\overset{+}{N}=O + OH^- \overset{K_1}{\rightarrow} O\overset{+}{N}=O + OH^-$$  

$$\overset{+}{N}(O)OH + OH^- \overset{K_2}{\rightarrow} \overset{+}{N}(O)OH^- + H_2O$$

The salts of (I) and (III) also undergo irreversible breakdown in alkaline solution [1]. Experiments were therefore carried out at temperatures no higher than 10°C where the period of half $\overset{+}{N}=O$ decomposition was greater than 10 min and the $[\overset{+}{N}=O]$ equilibrium could be easily determined by extrapolating the current $\overset{+}{N}=O$ concentration to time zero.

Equations (2) and (3) show that the initial concentration of salt (I) is given by $C_0 = [\overset{+}{N}=O] + [\overset{+}{N}(O)OH] + [\overset{+}{N}(O)OH^-]$, and the equilibrium hydroxyl ion concentration by: $[O\overset{+}{H}^-] = [O\overset{+}{H}^-]_0 - [\overset{+}{N}(O)OH^-] - 2[\overset{+}{N}(O)OH]$. When $[O\overset{+}{H}^-]_0 >> C_0$ or the degree of conversion of $\overset{+}{N}=O$ to $\overset{+}{N}(O)OH$ and $\overset{+}{N}(O)OH^-$ is low, one has $[O\overset{+}{H}^-] \approx [O\overset{+}{H}^-]_0$. By drawing on the expressions for the equilibrium constants: $K_1 = [\overset{+}{N}(O)OH]/[\overset{+}{N}=O][O\overset{+}{H}^-]$ and $K_2 = [\overset{+}{N}(O)OH^-]/[\overset{+}{N}(O)OH][O\overset{+}{H}^-]$, one finds that $(C_0 - [\overset{+}{N}=O])/[\overset{+}{N}=O][O\overset{+}{H}^-] = K_1 + K_1K_2[O\overset{+}{H}^-]$. With $[O\overset{+}{H}^-] >> C_0$ and $\mu = 1$ (KCl), the $(C_0 - [\overset{+}{N}=O])/[\overset{+}{N}=O][O\overset{+}{H}^-]_0$ vs $[O\overset{+}{H}^-]_0$ relation plots up to a straight line which does not pass through the origin (Fig. 1). Values of $K_1$ and $K_2$ obtained from the slopes and intercepts of least-squares plots are given in Table 1.

The enthalpy, $\Delta H = -R\partial \ln K/\partial (1/T)$, and entropy, $\Delta S = \Delta H / T + R \ln K$, changes accompanying reaction were calculated from the temperature variation of $K_1$ and $K_2$. At 5°C and $\mu = 1$ (KCl), $\Delta H_{298} = -15.3$ and $+13.6$ kcal/mole, with $\Delta S_{298} = -54.1$ and $+53.2$ e.u., for reactions (2) and (3), respectively. Thus reaction (2) is exothermic and proceeds with a decrease in entropy, whereas reaction (3) is endothermic and proceeds with an increase in entropy.