6-Thiocyanolhexanoic acid, $NCSCH_2(CH_2)_4CO_2H$, bp 152°C (0.08 mm). Methyl ester $NCS\overset{\alpha}{CH_2}\overset{\beta}{CH_2}\overset{\gamma}{CH_2}\overset{\delta}{CH_2}\overset{\varepsilon}{CH_2}COOCH_3$, bp 180°C (15 mm) [3]. PMR spectrum (in CCl_4, δ, ppm): 1.50 m (2H, γ-CH_2), 1.68 m (2H, δ-CH_2), 1.87 m (2H, β-CH_2), 2.36 t (2H, ε-CH_2, J = 7.5 Hz), 2.98 t (2H, α-CH_2, J = 7.25 Hz), 3.68 s (3H, CO_2CH_3). The ^{13}C NMR spectrum was taken with partial proton decoupling in $CDCl_3$ (δ, ppm): 23.7 t (C_γ), 27.1 t (C_δ), 29.3 t (C_β), 33.3 t (C_ε), 33.5 t (C_α), 51.2 q ($O^{13}CH_3$), 111.7 s ($N^{13}CS$), 173.2 s ($^{13}C{=}O$). IR spectrum (ν, cm^{-1}): 1740 ($O{-}C{=}O$), 2161 ($S{-}C{\equiv}N$). Mass spectrum (m/z): 187 M^+, 156 $(M-OCH_3)^+$, 155 $(M-CH_3OH)^+$, 127 $(M-CH_3COO)^+$, 101 $C_3H_7SCN^+$.

7-Chloroheptanoic acid $ClCH_2(CH_2)_5CO_2H$, bp 171 (12 mm). PMR spectrum (in CCl_4, δ, ppm): 1.50 br.s (8H, $(CH_2)_4$), 2.27 t (2H, $\underline{C}H_2CO_2H$, J = 6.2 Hz), 3.38 t (2H, CH_2Cl, J = 6.3 Hz), 10.95 s (1H, CO_2H).

7-Thiocyanoheptanoic acid, $NCSCH_2(CH_2)_5CO_2H$, bp 175°C (0.08 mm). IR spectrum (ν, cm^{-1}): 1740 ($O{-}C{=}O$), 2162 ($S{-}C{\equiv}N$).

CONCLUSIONS

The action of catalytic amounts of copper ions in the presence of MX salts (M = K and Na, X = Cl, Br, I, SCN) leads to the decomposition of the hydroperoxides of C_5-C_7 cycloalkanones with the formation of ω-chloro-, ω-bromo-, ω-iodo-, and ω-thiocyanoalkanoic acids.

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ESR DETERMINATION OF THE RATE CONSTANT FOR THE ADDITION OF $Cp\dot{W}(CO)_3$ TO SPIN TRAPS

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ESR spectroscopy in conjunction with the spin trap ST technique [1-3] is commonly used in the study of the mechanisms of radical reactions initiated by Cr, Mn, and Fe carbonyls [4]. The formation of metal-centered metal carbonyl radicals in addition to organic radicals has been shown in the case of several reactions, in particular, in the reaction of metal carbonyls (MC) with halogen-containing compounds [5-8]. Knowledge of the rate constants for the addition of these metal-centered radicals to ST is required in the ESR study of homolytic reactions using the spin trap technique.

In the present work, rate constants were found for the addition of $Cp\dot{W}(CO)_3$ radicals (I) to 2,4,6-tri-tert-butylnitrosobenzene (BNB) and α-phenyl-N-tert-butylnitrone (PBN).

Signals are observed in the ESR spectrum upon irradiation of a benzene solution of $[CpW(CO)_3]_2$ at 366 nm in the presence of BNB with $a_N = 10.8$ and $a_{m-H} = 1.6$ Oe (g = 2.0040). Knowledge of these coupling constants and the g factor and the use of the data of Terabe and Konaka [9] permit us to assign these signals to spin adducts of radicals (I) with BNB, whose formation may be described by Scheme 1

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Scheme 1

$$[\mathrm{CpW(CO)_3}]_2 \xrightarrow{h\nu} \underset{\text{(I)}}{2\mathrm{Cp\dot{W}(CO)_3}}$$

$$\text{(I)} + \text{BNB} \xrightarrow{k_{\text{ad}}^{\text{BNB}}} \underset{\text{(II)}}{\mathrm{Ar\dot{N}OW(CO)_3Cp}}$$

Here and subsequently, Ar = $2,4,6\text{-}(\mathrm{Me_3C})_3\mathrm{C_6H_2}$.

When using PNB, the ESR spectrum shows a triplet of doublets ($a_N = 14.9$, $a_H = 2.0$ Oe) which characterizes radical (III)

$$\text{(I)} + \text{PNB} \xrightarrow{k_{\text{ad}}^{\text{PNB}}} \underset{\text{(III)}}{\mathrm{PhCH[CpW(CO)_3]N(\dot{O})CMe_3}}$$

In the photochemical decomposition of $[\mathrm{CpW(CO)_3}]_2$ at 366 nm in $\mathrm{PhCH_2Cl}$ solution in the presence of $[\mathrm{BNB}]_0 = 0.013$ M, the ESR spectrum shows lines for the spin adducts of $\mathrm{Ph\dot{C}H_2}$ radicals (IV), which are obtained by Scheme 2, in addition to signals for radicals (II).

Scheme 2

$$\text{(I)} + \mathrm{PhCH_2Cl} \xrightarrow{k_{\text{ab}}} \mathrm{CpW(CO)_3Cl} + \underset{\text{(IV)}}{\mathrm{Ph\dot{C}H_2}}$$

$$\text{(IV)} + \text{BNB} \rightarrow \underset{\text{(V)}}{\mathrm{ArN(\dot{O})CH_2Ph}}$$

The concentration of radicals (V) increases linearly with decreasing BNB concentration. In the quasisteady state for Schemes 1 and 2, we find

$$k_{\text{ad}}^{\text{BNB}} = k_{\text{ab}} \frac{[\mathrm{PhCH_2Cl}]_0}{[\mathrm{BNB}]_0} \cdot \frac{[\text{(II)}]}{[\text{(IV)}]} \tag{1}$$

The simultaneous detection of radicals (II) and (IV) permits determination of the rate of addition of radicals (I) to BNB assuming that $k_{\text{ab}} = 14$ liters/mole·sec at 20°C [10] and using Eq. (1): $k_{\text{ad}}^{\text{BNB}} = 6.7 \cdot 10^5$ liters/mole·sec.

The rate constant $k_{\text{ad}}^{\text{BNB}}$ was also determined in a study of the decomposition of $\mathrm{CpW(CO)_3Me}$.

Upon the irradiation of a benzene solution of $\mathrm{CpW(CO)_3Me}$ in the presence of BNB, ESR signals are observed for radicals (I) and $\mathrm{\dot{C}H_3}$ with $a_N = 13.11$, $a_{m\text{-}H} = 0.8$, and $a_{\beta\text{-}H} = 12.4$ Oe, which are in accord with the parameters of the spin adducts of methyl radicals with BNB [9]. Assuming that the rate constant for the addition of methyl radicals to BNB at 20°C is $5.4 \cdot 10^5$ liters/mole·sec,* we may use the ESR spectrum obtained upon the decomposition of $\mathrm{CpW(CO_3)Me}$ in the presence of BNB: $k_{\text{ad}}^{\text{BNB}} = 7.0 \cdot 10^5$ liters/mole·sec.

Thus, the $k_{\text{ad}}^{\text{BNB}}$ values for radicals (I) obtained by different procedures are identical.

In the photochemical decomposition of a benzene solution of $[\mathrm{CpW(CO)_3}]_2$ with the presence of both $[\mathrm{BNB}]_0 = 1.38 \cdot 10^{-2}$ and $[\mathrm{PNB}]_0 = 7.74 \cdot 10^{-2}$ M, ESR signals are found for radicals (II) and (III). Using the ratio of the experimentally determined ratio of the concentrations of radicals (II) and (III) and taking $k_{\text{ad}}^{\text{BNB}} = 6.7 \cdot 10^5\text{–}7.0 \cdot 10^5$ liters/mole·sec, we obtain $k_{\text{ad}}^{\text{PNB}} = 5.8 \cdot 10^4\text{–}6.1 \cdot 10^4$ liters/mole·sec.

Comparison of the values for $k_{\text{ad}}^{\text{BNB}}$ and $k_{\text{ad}}^{\text{PNB}}$ with the corresponding values for the individual radicals shows that radicals (I) are similar in their reactivity to alkyl radicals [14] in the reaction with the spin traps studied.

These results indicate a new approach for the determination of the corresponding rate constants for many metal carbonyl metal-centered radicals in their addition to a large number of spin traps.

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* The rate constant for the addition of $\mathrm{\dot{C}H_3}$ radicals generated by the chemical decomposition of MeI in the presence of $\mathrm{Hg}(m\text{-}\mathrm{C_2H_2B_{10}H_9\text{-}9})_2$ [11, 12] was determined in the competitive reaction of $\mathrm{\dot{C}H_3}$ with BNB and $\mathrm{PhCH_2Me}$. In this reaction, spin adducts for $\mathrm{\dot{C}H_3}$ and $\mathrm{Ph\dot{C}HCH_3}$ were detected. The formation of $\mathrm{Ph\dot{C}HCH_3}$ was attributed to abstraction of hydrogen atoms by $\mathrm{\dot{C}H_3}$ from $\mathrm{PhCH_2CH_3}$; the rate constant for this process was taken as $1.1 \cdot 10^3$ liters/mole·sec at 20°C [13].

EXPERIMENTAL

The ESR spectra were taken on a RÉ-1306 spectrometer at about 20°C. Degassed solutions were irradiated in cylindrical glass ampules in the spectrometer probe using a DRSh-500 lamp.

Samples of $[CpW(CO)_3]_2$ and $CpW(CO)_3Me$ sublimated prior to use were obtained according to the procedures given by Nesmeyanov et al. [15].

CONCLUSIONS

The reaction of $[CpW(CO)_3]_2$ with $PhCH_2Cl$ and the decomposition of $CpW(CO)_3Me$ were studied by ESR spectroscopy using 2,4,6-tri-tert-butylnitrobenzene (BNB) and α-phenyl-N-tert-butylnitrone (PNB) as spin traps. The rate constants for the addition of $Cp\dot{W}(CO)_3$ radicals to the spin traps at ~ 20°C were determined by identification of the intermediate radicals in these reactions: $k_{ad}^{BNB} = 6.7 \cdot 10^5 – 7.0 \cdot 10^5$ and $k_{ad}^{PNB} = 5.8 \cdot 10^4 – 6.1 \cdot 10^4$ liters/mole·sec.

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