

6-Thiocyanolhexanoic acid,  $\text{NCSCH}_2(\text{CH}_2)_4\text{CO}_2\text{H}$ , bp  $152^\circ\text{C}$  (0.08 mm). Methyl ester  $\text{NCS}^\alpha\text{CH}_2^\beta\text{CH}_2^\gamma\text{CH}_2^\delta\text{CH}_2^\epsilon\text{COOCH}_3$ , bp  $180^\circ\text{C}$  (15 mm) [3]. PMR spectrum (in  $\text{CCl}_4$ ,  $\delta$ , ppm): 1.50 m (2H,  $\gamma\text{-CH}_2$ ), 1.68 m (2H,  $\delta\text{-CH}_2$ ), 1.87 m (2H,  $\beta\text{-CH}_2$ ), 2.36 t (2H,  $\epsilon\text{-CH}_2$ ,  $J = 7.5$  Hz), 2.98 t (2H,  $\alpha\text{-CH}_2$ ,  $J = 7.25$  Hz), 3.68 s (3H,  $\text{CO}_2\text{CH}_3$ ). The  $^{13}\text{C}$  NMR spectrum was taken with partial proton decoupling in  $\text{CDCl}_3$  ( $\delta$ , ppm): 23.7 t ( $\text{C}_\gamma$ ), 27.1 t ( $\text{C}_\delta$ ), 29.3 t ( $\text{C}_\beta$ ), 33.3 t ( $\text{C}_\epsilon$ ), 33.5 t ( $\text{C}_\alpha$ ), 51.2 q ( $\text{O}^{13}\text{CH}_3$ ), 111.7 s ( $\text{N}^{13}\text{CS}$ ), 173.2 s ( $^{13}\text{C}=\text{O}$ ). IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 1740 ( $\text{O}-\text{C}=\text{O}$ ), 2161 ( $\text{S}-\text{C}\equiv\text{N}$ ). Mass spectrum ( $m/z$ ): 187  $\text{M}^+$ , 156 ( $\text{M}-\text{OCH}_3$ ) $^+$ , 155 ( $\text{M}-\text{CH}_3\text{OH}$ ) $^+$ , 127 ( $\text{M}-\text{CH}_3\text{COO}$ ) $^+$ , 101  $\text{C}_3\text{H}_7\text{SCN}^+$ .

7-Chloroheptanoic acid  $\text{ClCH}_2(\text{CH}_2)_5\text{CO}_2\text{H}$ , bp  $171$  (12 mm). PMR spectrum (in  $\text{CCl}_4$ ,  $\delta$ , ppm): 1.50 br.s (8H,  $(\text{CH}_2)_4$ ), 2.27 t (2H,  $\text{CH}_2\text{CO}_2\text{H}$ ,  $J = 6.2$  Hz), 3.38 t (2H,  $\text{CH}_2\text{Cl}$ ,  $J = 6.3$  Hz), 10.95 s (1H,  $\text{CO}_2\text{H}$ ).

7-Thiocyanoheptanoic acid,  $\text{NCSCH}_2(\text{CH}_2)_5\text{CO}_2\text{H}$ , bp  $175^\circ\text{C}$  (0.08 mm). IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 1740 ( $\text{O}-\text{C}=\text{O}$ ), 2162 ( $\text{S}-\text{C}\equiv\text{N}$ ).

## CONCLUSIONS

The action of catalytic amounts of copper ions in the presence of MX salts ( $\text{M} = \text{K}$  and  $\text{Na}$ ,  $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{SCN}$ ) leads to the decomposition of the hydroperoxides of  $\text{C}_5\text{-C}_7$  cycloalkanones with the formation of  $\omega$ -chloro-,  $\omega$ -bromo-,  $\omega$ -iodo-, and  $\omega$ -thiocyanoalkanoic acids.

## LITERATURE CITED

1. E. G. E. Hawkins, *J. Chem. Soc.*, 3463 (1955).
2. F. Minisci, *Gazz. Chim. Ital.*, **89**, 1910 (1959).
3. F. Minisci, *Gazz. Chim. Ital.*, **89**, 2428 (1959).
4. H. E. De La Mare, J. K. Kochi, and F. F. Rust, *J. Am. Chem. Soc.*, **85**, 1437 (1963).
5. N. A. Milas, S. A. Harries, and P. S. Panagiotocos, *J. Am. Chem. Soc.*, 2430 (1939).
6. Yu. V. Il'in, V. A. Plakhotnik, V. G. Glukhovtsev, and G. I. Nikishin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2243 (1982).
7. K. J. McCullough, A. R. Morgan, D. C. Nonhebel, P. L. Pauson, and G. J. White, *J. Chem. Res. (S)*, 34 (1980).
8. Weygand-Hilgetag, *Experimental Methods in Organic Chemistry* [Russian translation], Khimiya, Moscow (1968), p. 548.

## ESR DETERMINATION OF THE RATE CONSTANT FOR THE ADDITION OF $\text{CpW}(\text{CO})_3$ TO SPIN TRAPS

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UDC 543.422.27:541.127:542.955:541.515

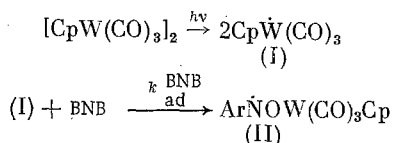
ESR spectroscopy in conjunction with the spin trap ST technique [1-3] is commonly used in the study of the mechanisms of radical reactions initiated by Cr, Mn, and Fe carbonyls [4]. The formation of metal-centered metal carbonyl radicals in addition to organic radicals has been shown in the case of several 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  $\text{CpW}(\text{CO})_3$  radicals (I) to 2,4,6-tri-tert-butyl nitrosobenzene (BNB) and  $\alpha$ -phenyl-N-tert-butyl nitron (PBN).

Signals are observed in the ESR spectrum upon irradiation of a benzene solution of  $[\text{CpW}(\text{CO})_3]_2$  at 366 nm in the presence of BNB with  $a_N = 10.8$  and  $a_{\text{m-H}} = 1.6$  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

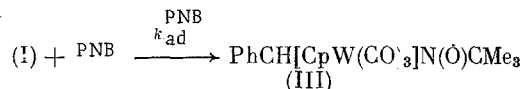
A. N. Nesmeyanov Institute of Heteroorganic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 11, pp. 2631-2633, November, 1984. Original article submitted February 29, 1984.

## Scheme 1



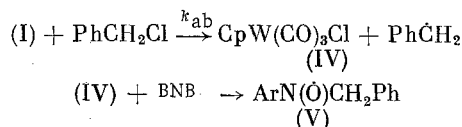
Here and subsequently, Ar = 2,4,6-(Me<sub>3</sub>C)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>.

When using PNB, the ESR spectrum shows a triplet of doublets ( $a_{\text{N}} = 14.9$ ,  $a_{\text{H}} = 2.0$  Oe) which characterizes radical (III)



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

## Scheme 2



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

$$k_{\text{ad}}^{\text{BNB}} = k_{\text{ab}} \frac{[\text{PhCH}_2\text{Cl}]_0}{[\text{BNB}]_0} \cdot \frac{[(\text{II})]}{[(\text{IV})]} \quad (1)$$

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  $\text{CpW}(\text{CO})_3\text{Me}$ .

Upon the irradiation of a benzene solution of  $\text{CpW}(\text{CO})_3\text{Me}$  in the presence of BNB, ESR signals are observed for radicals (I) and  $\dot{\text{C}}\text{H}_3$  with  $a_{\text{N}} = 13.11$ ,  $a_{\text{m-H}} = 0.8$ , 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  $\text{CpW}(\text{CO})_3\text{Me}$  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  $[\text{CpW}(\text{CO})_3]_2$  with the presence of both  $[\text{BNB}]_0 = 1.38 \cdot 10^{-2}$  and  $[\text{PNB}]_0 = 7.74 \cdot 10^{-2}$  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  $k_{\text{ad}}^{\text{BNB}} = 6.7 \cdot 10^5 - 7.0 \cdot 10^5$  liters/mole·sec, we obtain  $k_{\text{ad}}^{\text{PNB}} = 5.8 \cdot 10^4 - 6.1 \cdot 10^4$  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.

\* The rate constant for the addition of  $\dot{\text{C}}\text{H}_3$  radicals generated by the chemical decomposition of MeI in the presence of  $\text{Hg}(\text{m-C}_2\text{H}_4\text{B}_{10}\text{H}_9-9)_2$  [11, 12] was determined in the competitive reaction of  $\dot{\text{C}}\text{H}_3$  with BNB and PhCH<sub>2</sub>Me. In this reaction, spin adducts for  $\dot{\text{C}}\text{H}_3$  and Ph $\dot{\text{C}}\text{HCH}_3$  were detected. The formation of Ph $\dot{\text{C}}\text{HCH}_3$  was attributed to abstraction of hydrogen atoms by  $\dot{\text{C}}\text{H}_3$  from PhCH<sub>2</sub>CH<sub>3</sub>; 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 RE-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  $[\text{CpW}(\text{CO})_3]_2$  and  $\text{CpW}(\text{CO})_3\text{Me}$  sublimated prior to use were obtained according to the procedures given by Nesmeyanov et al. [15].

## CONCLUSIONS

The reaction of  $[\text{CpW}(\text{CO})_3]_2$  with  $\text{PhCH}_2\text{Cl}$  and the decomposition of  $\text{CpW}(\text{CO})_3\text{Me}$  were studied by ESR spectroscopy using 2,4,6-tri-tert-butylnitrobenzene (BNB) and  $\alpha$ -phenyl-N-tert-butyl-nitrone (PNB) as spin traps. The rate constants for the addition of  $\text{CpW}(\text{CO})_3$  radicals to the spin traps at  $\sim 20^\circ\text{C}$  were determined by identification of the intermediate radicals in these reactions:  $k_{\text{ad}}^{\text{BNB}} = 6.7 \cdot 10^5 - 7.0 \cdot 10^5$  and  $k_{\text{ad}}^{\text{PNB}} = 5.8 \cdot 10^4 - 6.1 \cdot 10^4$  liters/mole·sec.

## LITERATURE CITED

1. R. Kh. Freidlina, I. I. Kandrор, and R. G. Gasanov, *Usp. Khim.*, **47**, 508 (1978).
2. V. E. Zubarev, V. N. Belevskii, and L. T. Bugaenko, *Usp. Khim.*, **48**, 1361 (1979).
3. M. J. Perkins, in: *Advances in Physical Organic Chemistry*, Vol. 17, Academic Press (1980), p. 1.
4. E. Ts. Chukovskaya, R. G. Gasanov, I. I. Kandrор, and R. Kh. Freidlina, *Zh. Vses. Khim. Obshch. im. D. I. Mandeleeva*, **24**, 161 (1979).
5. R. G. Gasanov and R. Kh. Freidlina, *Dokl. Akad. Nauk SSSR*, **235**, 1309 (1977).
6. R. G. Gasanov and R. Kh. Freidlina, *Dokl. Akad. Nauk SSSR*, **254**, 113 (1980).
7. R. G. Gasanov and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1244 (1981).
8. R. G. Gasanov, L. V. Ivanova, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1045 (1983).
9. S. Terabe and R. Konaka, *J. Chem. Soc., Perkin Trans. 2*, 369 (1973).
10. R. M. Laine and P. C. Ford, *Inorg. Chem.*, **16**, 388 (1977).
11. B. L. Tumanskii, A. N. Degtyarev, N. N. Bubnov, S. P. Solodovnikov, V. I. Bregadze, N. N. Godovikov, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2627 (1980).
12. R. G. Gasanov, L. V. Ivanova, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1011 (1982).
13. E. T. Denisov, *Rate Constants of Homolytic Liquid-Phase Reactions* [in Russian], Izd. Nauka, Moscow (1971), p. 262.
14. Y. Maeda and K. U. Ingold, *J. Am. Chem. Soc.*, **101**, 4975 (1979).
15. A. N. Nesmeyanov, T. V. Nikitina, and O. V. Nogina, *Methods in Heteroorganic Chemistry, Copper, Scandium, Titanium, Vanadium, Chromium, Manganese Subgroup. Lanthanides and Actinides* [in Russian], Book 2, Nauka, Moscow (1974).