Monatshefte für Chemie 110, 1113—1121 (1979)

Monatshefte für Chemie

Charge-Transfer Complexes of Cobaltocene and Nickelocene With Tetrachloromethane

Anna Jaworska-Augustyniak and **Jan Wojtczak** *

Photochemistry Laboratory, Institute of Chemistry,
Adam Mickiewicz University, 60-780 Poznań, Poland

(Received 9 November 1977. Accepted 18 May 1978)

The photochemical properties of the systems cobaltocene—tetrachloromethane and nickelocene—tetrachloromethane in ethanol and cyclohexane were investigated; the equilibrium constants and molar extinction coefficients of the donor—acceptor complexes in these systems were determined.

(Keywords: Charge transfer complexes; Cobaltocene; Nickelocene)

Charge-Transfer Komplexe von Kobaltocen und Nickelocen mit Tetrachlorkohlenstoff

Es wurden die photochemischen Eigenschaften der Systeme Kobaltocen—CCl_4 und Nickelocen—CCl_4 in Ethanol und Cyclohexen als Lösungsmittel untersucht. Die Gleichgewichtskonstanten und die molaren Extinctionskoeffizienten der Donor—Acceptor-Komplexe in diesen Systemen wurden bestimmt.

Introduction

Cobaltocene and nickelocene belong, besides ferrocene, to the π-complex metalorganic compounds. Ferrocene has been examined best. Studies on photochemical properties (mostly of qualitative character) mainly concern ferrocene; it was found that ferrocene can sensitize some photoreactions, for instance *cis-trans* isomerization and dimerization of some dienes[1,2,3] and simple olefins[4,5,6]. It was also found that it is an active tripletstate quencher of a number of aromatic compounds[2,7] and is capable of forming intermolecular charge-transfer complexes with halogenated hydrocarbons in case the dissociation energy of the carbon-halogen bond is sufficiently low[8,9]. Some information about nickelocene, its emission and absorption spectra as well as a discussion about its electronic transitions can be found in the paper of *Scott* and *Becker*[10].

0026-9247/79/0110/1113/$ 01.80

This paper presents the results of our investigations on photochemical properties of nickelocene—tetrachloromethane and cobaltocene—tetrachloromethane systems in solvents of different polarity-ethanol and cyclohexane. A considerable analogy was expected here to the ferrocene—tetrachloromethane system examined previously by *Brand* and *Snedden*[8] and *Traverso* and *Scandola*[9]. The studies were aimed to findout whether intermolecular charge-transfer complexes are formed between nickelocene or cobaltocene and tetrachloromethane and how they behave in photochemical reactions.

Experimental

Materials

Nickelocene (Schuchardt), was additionally purified by sublimation under vacuum. Cobaltocene (Schuchardt; 8-9% solution in benzene) was purified similarly after previous slow benzene evaporation. Analar cyclohexane resp. tetrachloromethane, P.O.Ch. products, were distilled (after drying with NaOH) in a *Vigreux* column resp. in a column packed with Raschig rings. Purity was checked chromatographically. Ethanol (96%; Lódzkie Zaklady Przemyslu Spirytusowego) was used without further purification.

Apparatus and Methods

The systems studied were exposed to $\lambda \geq 300$ nm radiation from a Hanau high-pressure mercury lamp with a TQ 81 burner of 70 W using pyrex filter. The reactions substrates were irradiated in a "merry-go-round" system with 4 lamps under thermostat conditions (20 ± 0.2 °C) employing different exposure times from 0.5-8 h. All the investigations were made on solutions of constant metallocene concentration 1×10^{-2} mol/l both deaerated and undeaerated. The solutions were deaerated with an inert gas (helium or nitrogen) previously passed through a rinsing apparatus containing an identic solution. The photoproducts thus obtained were analysed chromatographically using a Pye Unicam type 104 gas chromatograph equipped with a flame ionization detector and 2.2 m columns packed with Triton *X* 305 (15% *X* 305 and 85% Chromosorb *W*, mesh 80/100), temperature programmed in the range from 30-150 °C. As carrier gas, nitrogen of flow rate 3 l/h was used. The spectroanalysis of charge—transfer complexes in the range from 200-800 nm was performed with a self-recording double beam spectrophotometer type Specord UV Vis and a manual spectrophotometer type VSU-2 P (both Zeiss) using 0.996 cm quartz cuvettes. The equilibrium constant of the complex was determined by the method of *Benesi-Hildebrand*[11] with *Ketelaar* modifications for the case of own absorption of the donor molecules in the spectral range studied[12, 13, 14].

Results

Cobaltocene—Tetrachloromethane

In the presence of air: $C_{10}H_{10}Co$ solutions of 1×10^{-2} mol/l concentration in CCl_4—C_2H_5OH (molar ratio 1 : 1) were irradiated. After 2 h exposure the *pH* of the solution changed from neutral to acidic and a number photoproducts were formed. Chromatographically, C_2H_5Cl, HCl, CH_2Cl_2, $CHCl_3$ and 2-chloroethanol (ClC_2H_4OH), and spectrophotometrically, cobaltocenium chloride $C_{10}H_{10}Co\ Cl$ (typical absorption band at $\lambda = 625\,\text{nm}$) were detected. The extension of the exposure time to 8 h brought about quantitative changes in the photoproducts with decreasing HCl in the system. The analysis of the analogous solution of cobaltocene and tetrachloromethane in cyclohexane irradiated for 2 h detected CH_2Cl_2, $CHCl_3$, 1,2-$C_2H_4Cl_2$, cyclo-$C_6H_{11}Cl$ and $C_{10}H_{10}CoCl$ in the form of dark-blue sediment, but no HCl. At extended irradiation the disappearance of 1,2-$C_2H_4Cl_2$ was observed.

Table. 1. *x and y values for cobaltocene—tetrachloromethane systems in ethanol determined at $\lambda = 327\,nm$ and constant CCl_4 concentration* $= 2.5 \times 10^{-5}$ mol/l. Donor molar extinction coefficient $\varepsilon_{C_{10}H_{10}Co} = 742$

$[C_{10}H_{10}Co]$ mol/l	$x = \dfrac{1}{[C_{10}H_{10}Co]}$ $\text{mol}^{-1}\cdot\text{l}$	$y = \dfrac{[CCl_4]l}{d}$ $\text{cm}\cdot\text{mol}\cdot\text{l}^{-1}$
12.5×10^{-4}	8.00×10^2	2.0408×10^{-4}
10.0×10^{-4}	10.00×10^2	5.2083×10^{-4}
7.5×10^{-4}	13.33×10^2	7.4627×10^{-4}
5.0×10^{-4}	20.00×10^2	10.4167×10^{-4}
2.5×10^{-4}	40.00×10^2	17.2414×10^{-4}

Table 2. *x and y values for cobaltocene—tetrachloromethane systems in cyclohexane determined at $\lambda = 327\,nm$ and constant CCl_4 concentration* $= 2.5 \times 10^{-5}$ mol/l. Donor molar extinction coefficient $\varepsilon_{C_{10}H_{10}Co} = 745$

$[C_{10}H_{10}Co]$ mol/l	$x = \dfrac{1}{[C_{10}H_{10}Co]}$ $\text{mol}^{-1}\cdot\text{l}$	$y = \dfrac{[CCl_4]l}{d}$ $\text{cm}\cdot\text{mol}\cdot\text{l}^{-1}$
12.5×10^{-4}	8.00×10^2	21.0437×10^{-5}
10.0×10^{-4}	10.00×10^2	45.4545×10^{-5}
7.5×10^{-4}	13.33×10^2	68.8705×10^{-5}
5.0×10^{-4}	20.00×10^2	142.8571×10^{-5}
2.5×10^{-4}	40.00×10^2	181.1594×10^{-5}

In the absence of air: In order to find the effect of air oxygen upon the course of photoreaction the analogous solutions of cobaltocene and tetrachloromethane in ethanol and cyclohexane were deaerated. On the whole, the presence of the same products was observed but the total number of photoproducts both in ethanol and cyclohexane was greater, which may be indicative of air oxygen participation in free radical reactions. Moreover, it was found that in the deaerated ethanolic solutions the rate of CH_2Cl_2 and $CHCl_3$ formation and that of 2-ClC_2H_4OH disapearance are considerably greater than in the solution containing air oxygen. The latter phenomenon was not observed in cyclohexane.

Nickelocene—Tetrachloromethane

In the presence of air: $C_{10}H_{10}Ni$ solutions of 1×10^{-2} mol/l concentration in CCl_4—C_2H_5OH or CCl_4-cyclohexane (molar ratio 1:1) were subject to a similar procedure. They were irradiated for 0.5 and 2 h. After 0.5 h exposure of the system $C_{10}H_{10}Ni$—CCl_4—C_2H_5OH there was a change in *pH* from neutral to acidic. Spectrophotometrically, the formation of $C_{10}H_{10}Ni$ Cl was found. Chromatographically and by the classical method with $AgNO_3$, the presence of HCl and 2-ClC_2H_4OH was also observed. After extended exposure of this system C_2H_5Cl, CH_2Cl_2 and $CHCl_3$ appeared. Thus, the irradiation resulted in the same photoproducts as it was the case in the system with cobaltocene.

Table 3. *x and y values for nickelocene—tetrachloromethane systems in ethanol determined at* $\lambda = 307$ *nm and constant* CCl_4 *concentration* $= 2.5 \times 10^{-6}$ mol/l. Donor molar extinction coefficient $\varepsilon_{C_{10}H_{10}Ni} = 11{,}500$

$[C_{10}H_{10}Ni]$ mol/l	$x = \frac{1}{[C_{10}H_{10}Ni]}$ $mol^{-1} \cdot l$	$y = \frac{[CCl_4]l}{d}$ $cm \cdot mol \cdot l^{-1}$
10.35×10^{-5}	0.9656×10^4	10.4558×10^{-6}
6.90×10^{-5}	1.4484×10^4	16.0153×10^{-6}
3.45×10^{-5}	2.8968×10^4	26.8817×10^{-6}

Table 4. *x and y values for nickelocene—tetrachloromethane systems in cyclohexane determined at* $\lambda = 307$ *nm and constant* CCl_4 *concentration* $=$ 2.5×10^{-6} mol/l. Donor molar extinction coefficient $\varepsilon_{C_{10}H_{10}Ni} = 11{,}500$

$[C_{10}H_{10}Ni]$ mol/l	$x = \frac{1}{[C_{10}H_{10}Ni]}$ $mol^{-1} \cdot l$	$y = \frac{[CCl_4]l}{d}$ $cm \cdot mol \cdot l^{-1}$
8.25×10^{-5}	1.2121×10^4	38.941×10^{-6}
6.60×10^{-5}	1.5151×10^4	33.069×10^{-6}
4.95×10^{-5}	2.0202×10^4	40.717×10^{-6}
3.30×10^{-5}	3.0303×10^4	74.184×10^{-6}
1.65×10^{-5}	6.0606×10^4	137.363×10^{-6}

The irradiation of nickelocene and tetrachloromethane in cyclohexane resulted in considerably fewer photoproducts than in ethanol. After 0.5 h only two photoproducts were formed, namely, nickelocenium chloride and methylene chloride. The latter disappeared after extended irradiation and a sediment was formed in the solution, which was indicative of the partial decomposition of $C_{10}H_{10}Ni$.

In the absence of air: These systems were deaerated with helium and investigated in the same way. The comparison of the results obtained here with those obtained in the presence of air oxygen leads to the conclusion that in the absence of air the photoproducts were formed more efficiently. It was especially so in the case of $C_{10}H_{10}Ni—CCl_4—C_6H_{12}$ where an exposure of 2 h resulted in $C_{10}H_{10}NiCl$, $CHCl_3$, CH_2Cl_2 and cyclo-$C_6H_{11}Cl$.

Determination of Donor-Acceptor Complex Equilibrium Constants

For determining the equilibrium constants K of donor-acceptor complexes between metallocene and tetrachloromethane both in ethanol and cyclohexane the method of *Benesi-Hildebrand* was employed[11, 12, 13, 14] making use of the formula

$$\frac{[A]l}{d} = \frac{1}{K\varepsilon_c} \times \frac{1}{[D]} + \frac{1}{\varepsilon_c}$$

where: $[A]$—initial acceptor concentration, in this case CCl_4 in mol/l; l—sample path length (1 cm); d—optical density of the complex in the solution, in this case d equals the difference between the absorption of the solution and that of the donor (metallocene); ε_c—molar extinction coefficient of the complex at the wavelength given; $[D]$—initial donor concentration in mol/l.

The formula corresponds to a linear dependence $y = ax + b$. For each system a few series of solutions were prepared of constant acceptor and variable donor concentrations, provided $[D] \gg [A]$ and the absorption E was measured at the wavelength given. In Fig. 1 are shown, by way of example, 2 series of spectra used for further calculations.

The K and ε_c values of the complex for each series of solutions were calculated by the method of least squares[15] and their mean values $\overline{K}$ and $\overline{\varepsilon}_c$ were determined graphically from the diagram $K^{-1} = f(\varepsilon_c)$[14]. In Tab. 1-4 are presented, by way of example, the calculations for one of the series of solutions of each of the systems investigated.

The a and b values in the above equation were determined by the method of least squares; for the above mentioned series of solutions $y = 0.4334 \times 10^{-6}\, x + 0.5575 \times 10^{-4}$ and hence $\varepsilon_c = 17{,}937 \pm 374.88$

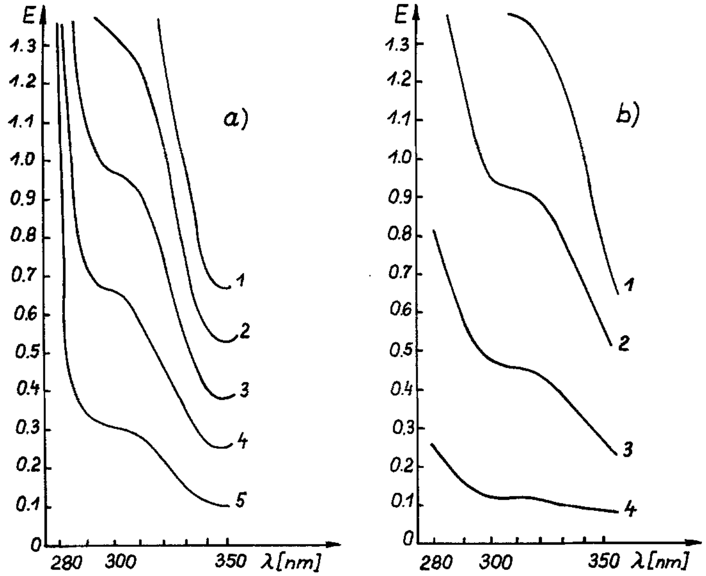

Fig. 1. *a* Cobaltocene absorption spectra in 2.5×10^{-5} mol/l CCl_4 solution in ethanol. Cobaltocene concentration: curve *1* 12.5×10^{-4} mol/l; curve *2* 10×10^{-4} mol/l; curve *3* 7.5×10^{-4} mol/l; curve *4* 5×10^{-4} mol/l, and curve *5* 2.5×10^{-4} mol/l. *b* Nickelocene absorption spectra in 2.5×10^{-6} mol/l CCl_4 solution in ethanol. Nickelocene concentration: curve *1* 10.35×10^{-5} mol/l; curve *2* 6.9×10^{-5} mol/l; curve *3* 3.45×10^{-5} mol/l and curve *4* 0.75×10^{-5} mol/l

Table 5. *Mean values of equilibrium constants* $\bar{K}$ *and molar extinction coefficient* $\bar{\varepsilon}_c$

System	$\bar{K}$ mol$^{-1}\cdot$l	$\bar{\varepsilon}_c$	λ nm
$C_{10}H_{10}Co$—CCl_4—C_2H_5OH	119 ± 11.82	21,000 ± 140	327
$C_{10}H_{10}Co$—CCl_4—C_6H_{12}	110 ± 6.03	19,000 ± 3097	327
$C_{10}H_{10}Ni$—CCl_4—C_2H_5OH	3,795 ± 172.29	318,600 ± 13890.9	307
$C_{10}H_{10}Ni$—CCl_4—C_6H_{12}	3,225 ± 239.94	142,000 ± 2122.9	307

and $K = 128.65 \pm 18$ mol^{-1}l. ε_c and K for the other systems were calculated in the same way:

K and ε_c 89 ± 5.9 mol^{-1}l and $23{,}400 \pm 4{,}028.86$, respectively (Tab. 2); K and ε_c $3{,}793 \pm 148$ mol^{-1}l and $318{,}600 \pm 1{,}820$, resp. (Tab. 3); K and ε_c $3{,}333 \pm 322$ mol^{-1}l and $148{,}500 \pm 2{,}300$, resp. (Tab. 4).

Tab. 5 lists the mean values of the equilibrium constant ($\overline{K}$) and of the molar extinction coefficient ($\bar{\varepsilon}_c$) of the complexes examined from several series.

As can be seen from a comparison of the $\overline{K}$ values in Tab. 5, nickelocene complexes better with CCl_4 than cobaltocene and the $\overline{K}$ constants of the complexes investigated are greater in ethanol (the solvent of high polarity) than in cyclohexane (practically no polarity).

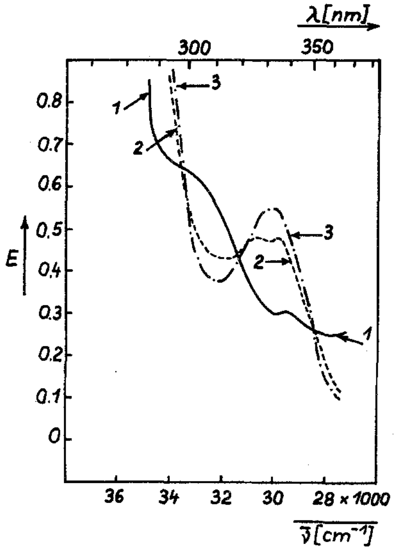

Fig. 2. Absorption spectra of 5×10^{-4} mol/l $C_{10}H_{10}Co$ solutions in *1* ethanol, *2* 1 mol CCl_4 in ethanol, and *3* in CCl_4

Discussion

The results obtained fully confirm the assumption that cobaltocene and nickelocene, like ferrocene, form charge-transfer complexes with CCl_4. For an example Fig. 2 shows absorption spectra of the $C_{10}H_{10}Co—CCl_4—C_2H_5OH$ system indicating that charge-transfer complexes are formed between cobaltocene and CCl_4.

The photoproducts identified are indicative of a free radical mechanism of the reactions, the first stage of which is the formation of an intermolecular complex and its dissociation owing to the radiation absorbed in accord with the equation *Me* stands for cobalt(II) or nickel(II):

$$C_{10}H_{10}Me + CCl_4 \xrightarrow[C_2H_5OH,\ C_6H_{12}]{h\nu} C_{10}H_{10}Me^+ + Cl^- + {}^{\cdot}CCl_3$$

The formation of the photoproducts mentioned above can be accounted for by successive free radical reactions.

In ethanol:

$^{\cdot}CCl_3 + CH_3CH_2OH \rightarrow CHCl_3 + {}^{\cdot}CH_2CH_2OH \rightarrow {}^{\cdot}CHCl_2 + ClCH_2CH_2OH$
$CHCl_3 + {}^{\cdot}CHCl_2 \rightarrow CH_2Cl_2 + {}^{\cdot}CCl_3$
$CCl_4 + {}^{\cdot}CH_2CH_2OH \rightarrow {}^{\cdot}CCl_3 + ClCH_2CH_2OH$
$CCl_4 \xrightarrow[C_{10}H_{10}\mathit{Me}]{h\nu} {}^{\cdot}CCl_3 + {}^{\cdot}Cl$
$^{\cdot}Cl + {}^{\cdot}CH_2CH_2OH \rightarrow ClCH_2CH_2OH$
$CHCl_3 + {}^{\cdot}Cl \rightarrow HCl + {}^{\cdot}CCl_3$
$CH_3CH_2OH + HCl \rightarrow CH_3CH_2Cl + H_2O$

and in cyclohexane:

$^{\cdot}CCl_3 + C_6H_{12} \rightarrow CHCl_3 + {}^{\cdot}C_6H_{11}$
$^{\cdot}CHCl_2 + C_6H_{12} \rightarrow CH_2Cl_2 + {}^{\cdot}C_6H_{11}$
$CCl_4 + {}^{\cdot}C_6H_{11} \rightarrow {}^{\cdot}CCl_3 + C_6H_{11}Cl$
$CH_2Cl_2 + {}^{\cdot}CCl_3 \rightarrow {}^{\cdot}CH_2Cl + CCl_4$
$2\,{}^{\cdot}CH_2Cl \rightarrow C_2H_4Cl_2$

It is to be noticed that the chloroform resulting from an interaction of the $^{\cdot}CCl_3$ radical and a solvent molecule (ethanol or cyclohexane) is also capable of forming an intermolecular charge-transfer complex with metallocene which becomes a source of free radicals $^{\cdot}CHCl_2$ according to the reaction:

$$C_{10}H_{10}\mathit{Me} + CHCl_3 \xrightarrow[C_2H_5OH,\ C_6H_{12}]{h\nu} C_{10}H_{10}\mathit{Me}^{+} + Cl^{-} + {}^{\cdot}CHCl_2$$

Differences in the yields of the photoproducts being formed in the presence of cobalto- and nickelocenes can be accounted for in terms of their stability. Nickelocene is much less stable than cobaltocene (it is readily oxidated) which makes its investigation difficult. A comparison of K and ε_c values obtained for $C_{10}H_{10}Co—CCl_4$ and $C_{10}H_{10}Ni—CCl_4$ with corresponding values for the ferrocene—tetrachloromethane system[8, 9] in ethanol and cyclohexane makes it possible to arrange those compounds according to their increasing complexing power with CCl_4:

$$C_{10}H_{10}Fe < C_{10}H_{10}Co < C_{10}H_{10}Ni$$

In metallocene—CCl_4 complexes the atom of metal is assumed to be the electron donor[16]. The complexing power increasing from ferrocene via cobaltocene to nickelocene can be explained in terms of the tendency to approach the electron configuration of an inert gas. The electron configuration of an inert gas can be reached only in ferrocene (36 electrons in iron atom); it is therefore the most stable of the metallocenes and its oxidizing capacity to the ferricenium ion[17] resembles $Fe^{II} \rightarrow Fe^{III}$. In cobaltocene and nickelocene the number of electrons of the metal atom is greater than that of the inert gas (37 and 38 electrons).Thus, the tendency to reach the inert gas configuration in the cobalt atom accounts for its tendency to form the cobaltocenium cation $C_{10}H_{10}Co^+$, which is isoelectronic with ferrocene. The configuration of an inert gas is never attained in nickelocenium ion $C_{10}H_{10}Ni^+$. The ion $C_{10}H_{10}Ni^{2+}$ isoelectronic with $C_{10}H_{10}Co^+$ and $C_{10}H_{10}Fe$ is not know as yet[17].

The results presented here suggest that metallocenes are very active electron donors and may find application in new methods of synthesis.

The authors thank *Marek Kryger*, M.Sc., for his assistance in some determinations included in this paper.

References

[1] *J. J. Dannenberg* and *J. H. Richards*, J. Amer. Chem. Soc. **87**, 1626 (1965).
[2] *J. H. Richards*, J. Paint Techn. **39**, 569 (1967).
[3] *J. P. Guillory*, *C. F. Cook* and *D. R. Scott*, J. Amer. Chem. Soc. **89**, 6776 (1967).
[4] *A. Jaworska-Augustyniak* and *J. Wojtczak*, PTPN, Wydz. Mat. Przyr., Prace Kom. Mat. Przyr., **T. III**, z. 1,71 (1972).
[5] *J. Wojtczak* and *A. Jaworska-Augustyniak*, ibid., **T. XIII**, z. 2, 33 (1973).
[6] *J. Wojtczak* and *A. Jaworska-Augustyniak*, Chem. Stosowana, **XIX, 3**, 359 (1975).
[7] *M. Kikuchi*, *K. Kikuchi* and *H. Kokubun*, Bull. Chem. Soc. Japan **47**, 1331 (1974).
[8] *J. C. Brand* and *W. Snedden*, Trans. Faraday Soc. **53**, 894 (1967).
[9] *O. Traverso* and *F. Scandola*, Inorg. Chimica Acta **4**, 493 (1970).
[10] *D. R. Scott* and *R. S. Becker*, J. Chem. Phys. **35**, (1961).
[11] *H. A. Benesi* and *J. H. Hildebrand*, J. Amer. Chem. Soc. **71**, 2703 (1949).
[12] *C. N. R. Rao*, Ultraviolet and Visible Spectroscopy, p. 157. London: Butterworths. 1967.
[13] *G. V. Saidov* and *O. V. Sverdlova*, Prakticheskopie rukovodstvo po absorbcionnoi molekularnoi spektroskopii. Leningrad: Izd. Leningrad-Univ. 1973.
[14] *N. J. Rose* and *R. S. Drago*, J. Amer. Chem. Soc. **81**, 6138 (1959).
[15] *K. Leidler*, Kinetika organicheskich reakzii, p. 345. Moskwa: Izd. Mir. 1966.
[16] *R. F. Bozak*, Advances in Photochemistry, Vol. 8, p. 230. New York-London: Wiley Intersc. 1971.
[17] *P. L. Pauson*, Chemia zwiazków metaloorganicznych, p. 152. Warszawa: PWN. 1972.