ESR DETERMINATION OF THE RATE CONSTANT FOR THE ABSTRACTION OF CHLORINE FROM CCl_4 BY TELOMERIC $CCl_3(CH_2CH_2)_n^{\bullet}$ (n = 1-3) RADICALS

R. G. Gasanov, L. V. Ivanova,
and R. Kh. Freidlina

UDC 541.127:543.422.27:
541.515:547.412.133

The telomerization of ethylene with CCl_4 takes place at a sufficiently high concentration of the telogen in accordance with the free-radical chain mechanism [1]

Scheme 1

1. $\text{Initiator} \longrightarrow \dot{R}$
2. $\dot{R} + CCl_4 \rightarrow RCl + \dot{C}Cl_3$
3. $\dot{C}Cl_3 + C_2H_4 \rightarrow CCl_3CH_2\dot{C}H_2$
4. $CCl_3CH_2\dot{C}H_2 + C_2H_4 \xrightarrow{k_p^{I}} CCl_3(CH_2CH_2)_2^{\bullet}$
5. $CCl_3CH_2\dot{C}H_2 + CCl_4 \xrightarrow{k_{tr}^{I}} CCl_3CH_2CH_2Cl(T_1) + \dot{C}Cl_3$
6. $CCl_3(CH_2CH_2)_n^{\bullet} + C_2H_4 \xrightarrow{k_p^{n}} CCl_3(CH_2\dot{C}H_2)_{n+1}$
7. $CCl_3(CH_2CH_2)_n^{\bullet} + CCl_4 \xrightarrow{k_{tr}^{n}} CCl_3(CH_2CH_2)_nCl(T_n) + \dot{C}Cl_3$
8. $2\dot{C}Cl_3 \rightarrow \text{Products.}$

It can be seen from Scheme 1 that the relative yield of the telomeric homolog T_n is solely dependent on the competition between the substitution reaction and the reaction involving the addition of the $CCl_3(CH_2CH_2)_n^{\bullet}$ radicals (steps 4-7). This allows one, by employing the techniques for competitive kinetics, to study the reactivity of short-lived radicals. The determination of the chain-transfer constants $C_n = k_{tr}^{n}/k_p^{n}$ is a widely employed technique for this purpose. A significant difference between $C_I = k_{tr}^{I}/k_p^{I}$ and C_n $(n \geqslant 2)$ is observed in the telomerization of ethylene with CCl_4 [1]. Since C_n is the ratio of the rate constants of two competing elementary processes, indeterminacy in the estimates for these steps always arises during the investigation of the change in the values of C_n.

The aim of the present work was to determine the rate constant for the abstraction of a chlorine atom from CCl_4 by $CCl_3(CH_2CH_2)_n^{\bullet}$ (n = 1-3) radicals (I)-(III) by means of ESR, which would allow one to establish the contribution of each elementary step to the telomerization of

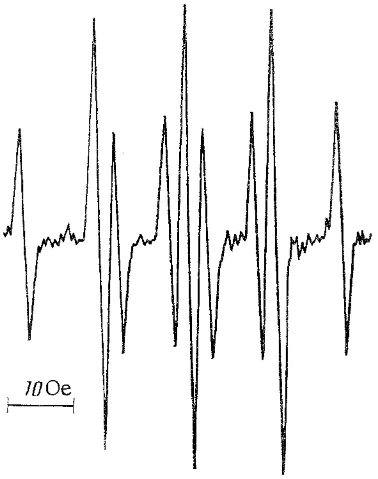

Fig. 1. The ESR spectrum of $2,3,5,6\text{-}Me_4C_6HN(\dot{O})(CH_2CH_2)_2CCl_3$ radicals prepared by the irradiation of $CCl_3(CH_2CH_2)_2I$ with UV light in the presence of nitrosodurene and $Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2$.

A. N. Nesmeyanov Institute of Heteroorganic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1011-1015, May, 1982. Original article submitted June 26, 1981.

0568-5230/82/3105-0895$07.50 © 1982 Plenum Publishing Corporation

TABLE 1. ESR Spectral Parameters of the Nitroxyl Radicals Which Are Formed during the Photochemical Decomposition of $CCl_3(CH_2CH_2)_nI$ (n = 1-3) in Combination with $Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2$ in the Presence or in the Absence of CCl_4 (the trap was nitrosodurene; 40°C; a, Oe)

Experiment No.	Initial compound	Radical identified	$[CCl_4]_0$, M	$[ND]_0 \cdot 10^3$, M*	a_N	a_H	a_{Cl}	[A]/[B]†
1	$CCl_3CH_2CH_2I$	$CCl_3CH_2\dot{C}H_2$ (I) ‡	—	1,15	13,5	11,2	—	—
2	$CCl_3(CH_2CH_2)_2I$	$CCl_3(CH_2CH_2)_2^{\bullet}$ (II)	—	5,94	13,7	10,9	—	—
3	$CCl_3(CH_2CH_2)_3I$	$CCl_3(CH_2CH_2)_3^{\bullet}$ (III)	—	5,94	13,5	10,9	—	—
4	$CCl_3CH_2CH_2I+CCl_4$	$CCl_3CH_2\dot{C}H_2$; $\dot{C}Cl_3$ ‡	5,25	6,0	13,7 10,7	11,2 —	— 1,3	1,94
5	$CCl_3(CH_2CH_2)_2I+CCl_4$	$CCl_3(CH_2CH_2)_2^{\bullet}$; $\dot{C}Cl_3$	5,52	6,0	13,7 10,7	10,9 —	— 1,3	0,56
			6,71	2,34				0,149
			7,04	5,94				0,395
			7,82	1,36				0,073
6	$CCl_3(CH_2CH_2)_3I+CCl_4$	$CCl_3(CH_2CH_2)_3^{\bullet}$; $\dot{C}Cl_3$	7,04	5,94	13,7 10,7	10,9 —	— 1,3	0,245

---

*The concentrations of nitrosodurene are given with allowance for the monomer–dimer equilibrium constant, K = 322 liters/mole [6].

†Taking account of ΔH, the nature of the multiplicity and the intensities of the lines in the spectra of radicals (A) and (B) (see the fragment of the spectrum in Fig. 2).

‡The linewidth ΔH of the $2,3,5,6\text{-}Me_4C_6HN(\dot{O})(CH_2CH_2)_nCCl_3$ (ΔH = 1,34 Oe) and the $2,3,5,6\text{-}Me_4C_6HN(\dot{O})CCl_3$ (ΔH = 0,56 Oe) radicals was measured from their individual ESR spectra.

ethylene by CCl_4.

The radicals (I)-(III) were generated by the photochemical decomposition of $CCl_3(CH_2CH_2)_nI$ in the presence of $Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2^*$ and nitrosodurene(ND) (Fig. 1) at 40°C. It can be seen from Fig. 1 and the data in Table 1 (experiments 1-3) that only signals from the nitroxyls $2,3,5,6\text{-}Me_4C_6HN(\dot{O})(CH_2CH_2)_nCCl_3$ (A) are observed in the ESR spectrum during the decomposition of the trichloroiodoalkanes. When solutions containing $Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2$, ND, and CCl_4 are irradiated, lines from the $2,3,5,6\text{-}Me_4C_6HN(\dot{O})CCl_3$ nitroxyl radicals (B) are observed in the ESR spectrum in addition to the signals from the radicals (A) (Fig. 2, line a). The former were assigned on the basis of an investigation into the dependence of the intensities of the signals due to the nitroxyl radicals (A) and (B) on the concentrations of $[ND]_0$ and $[CCl_4]_0$ (see below) which permits one to calculate, from the ESR spectra which have been obtained, the values of the hyperfine coupling constants for radicals (B) (experiments 4-6) which are in agreement with the corresponding parameters for the same radicals studied in [3]. The formation of the radicals which have been identified can be described by the following scheme:

$$\begin{gathered}
CCl_3(CH_2CH_2)_nI \xrightarrow{\text{initiator},\,h\nu} CCl_3(CH_2CH_2)_n^{\cdot} \\
CCl_3(CH_2CH_2)_n^{\cdot} + \text{ND} \xrightarrow{k_{add}} 2,3,5,6\text{-}Me_4C_6HN(\dot{O})(CH_2CH_2)_nCCl_3(A) \\
CCl_3(CH_2CH_2)_n^{\cdot} + CCl_4 \xrightarrow{k_{tr}^{n}} CCl_3(CH_2CH_2)_nCl(T_n) + \dot{C}Cl_3 \\
\dot{C}Cl_3 + \text{ND} \longrightarrow 2,3,5,6\text{-}Me_4C_6HN(\dot{O})CCl_3\ (B)
\end{gathered} \tag{1}$$

By applying the stationary-state approximation [4] to Scheme 2, we obtain

$$[A]/[B] = k_{add}/k_{tr}^{n}\frac{[ND]_0}{[CCl_4]_0} \tag{2}$$

where [A] and [B] are the current concentrations of the nitroxyl radicals (A) and (B).

The following results agree with the formation of the radicals (A) and (B) in accordance with Scheme 2.

When $CCl_3(CH_2CH2)I$ is irradiated with UV light in the presence of $[Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2] = 1.3\cdot10^{-4}$ M, signals from radical (A) ($[A] \simeq 10^{-6}$ M) are observed in the ESR spectrum. At the same concentration of the initial reagents and under the same experimental conditions but with CCl_4 and without $CCl_3(CH_2CH_2)_nI$, we were unable to observe signals from radical (B) in concentrations sufficient to obtain the hyperfine coupling constant of the spectrum ($[B] \simeq 10^{-8}$ M).* Furthermore, it follows from the data in Table 1 (experiment 5) that there is a linear dependence of the ratio [A]/[B] on $[ND]_0/[CCl_4]_0$ in complete agreement with Eq. (2).

From Eq. (2), when $k_{add} = 4.07\cdot10^7$ liters/mole·sec [6], and the data in Table 1, we obtain: $k_{tr}^{I} = 3.9\cdot10^3$, $k_{tr}^{II} = 9.0\cdot10^4$, and $k_{tr}^{III} = 1.4\cdot10^5$ liters/mole·sec, which correspond to the constants for the abstraction of a chlorine atom from CCl_4 by radicals I, II, and III, respectively.†

Starting out from the values of k_{tr}^{n} and C_n, cited in [2] ($C_1 = 0.087$, $C_2 = 3.0$, $C_3 = 7.5$), the rate constants for the addition of radicals (I)-(III) to ethylene at 40°C are determined as: $k_p^{I} = 4.5\cdot10$, $k_p^{II} = 3.0\cdot10^4$, $k_p^{III} = 1.87\cdot10^4$ liters/mole·sec.

Hence, the changes in the values of C_n in the telomerization of ethylene by CCl_4 are mainly associated with the difference in the rate constants for the abstraction of chlorine from CCl_4 by the telomeric radicals $CCl_3CH_2{}^{\cdot}CH_2$ and $CCl_3(CH_2CH_2)_n^{\cdot}$ ($n \geqslant 2$).

The use of $Fe(CO)_5$ in conjunction with CH_3OH as an initiator for the telomerization of ethylene by CCl_4 leads to a significant increase in the relative yield of $CCl_3CH_2CH_2Cl$ (T_1)

---

*This result agrees with the data in [5] concerning the appreciably faster abstraction of iodine from iodoalkanes by methyl radicals than the abstraction of chlorine from CCl_4.

†On account of the impossibility of integrating the ESR spectral bands and allowing for the accuracy of the values for k_{add} determined in [6], it may be assumed that the error in the absolute values of k_{tr}^{n} will lie within the limits of half an order of magnitude, while the error in the relative values will lie within ±15% (see Table 1, experiment 5).

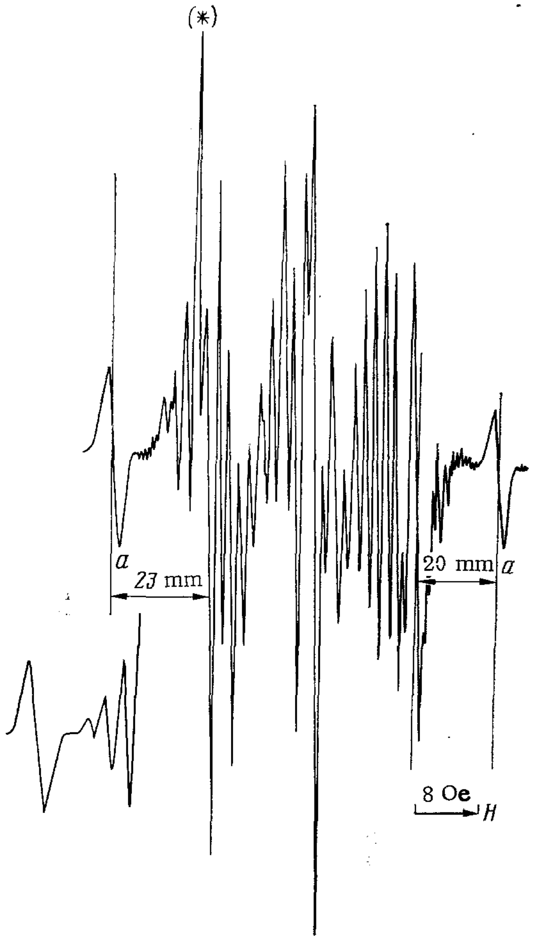

Fig. 2. The ESR spectra of 2,3,5,6-$Me_4C_6HN(\dot{O})(CH_2CH_2)_2CCl_3$ radicals (lines a); only the extreme lines of the triplets are denoted (see Fig. 1) and of 2,3,5,6-$Me_4C_6HN(\dot{O})CCl_3$ radicals (several signals from them which coincide with the signals from radicals (A) have not been noted, see text), obtained by the irradiation of a solution of $CCl_3(CH_2CH_2)_2I$ containing $Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2$. $[ND]_0 = 5.94 \cdot 10^{-3}$ and $[CCl_4]_0 = 7.04$ M, 40°C.

in comparison with peroxide initiators or $Fe(CO)_5$ without an additive. For instance, the yield of T_1 is 3 and 6.3%, respectively, for initiation with peroxide and $Fe(CO)_5$. Under the same experimental conditions and with the same initial monomer–telogen ratios, but with initiation by the $Fe(CO)_5 + CH_3OH$ system, the yield of T_1 increases up to 67%.

The value of k_{tr}^{I} calculated by us enables one to determine the lower limit of the rate constant $k_{tr}^{(Fe-Cl)}$ for the transfer of chlorine from intermediates of the Fe^nCl type which are formed when the telomerization of ethylene by CCl_4 is initiated in the presence of nucleophilic cocatalysts.

The formation of T_1 in the telomerization of ethylene by CCl_4 can be described by step 1 in Scheme 2 and, when $Fe(CO)_5$ is used in conjunction with additives, it may be described by Scheme (3)

$$CCl_3CH_2\dot{C}H_2 + Fe^nCl \xrightarrow{k_{tr}^{(Fe-Cl)}} CCl_3CH_2CH_2Cl + Fe^{n+1} \qquad (3)$$

Starting out from this and taking account of the data presented in [7], we obtain:

$$k^{I}_{tr}/k^{(Fe-Cl)}_{tr}\frac{[CCl_4]_0}{[Fe^nCl]}=\frac{3,0}{66,7}$$

Since $[Fe^nCl] \leqslant [Fe(CO)_5]$, $k_{tr}{}^{(Fe-Cl)} \geqslant 3 \cdot 10^7$ liters/mole•sec. Such a large value for $k_{tr}{}^{(Fe-Cl)}$ is in accord with the fact that the use of catalytic amounts of $Fe(CO)_5$ ($\sim 10^{-3}$ M) in conjunction with various different additives practically completely suppresses the telomerization of ethylene by CCl_4.

Hence, the results which have been obtained demonstrate the decisive role played by the step involving the transfer of chlorine by the intermediate particles of iron carbonyl onto the telomeric radicals which are formed in the telomerization of ethylene by CCl_4 with initiation by $Fe(CO)_5$ in conjunction with CH_3OH.

EXPERIMENTAL

The ESR spectra were recorded on a RÉ-1306 spectrometer. Ampuls containing the solutions were irradiated in the resonant cavity of the spectrometer with the output from a DRSh-500 lamp. $Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2$ and the nitrosodurene was dissolved in $CHCl_3$ and subsequently added to the reaction mixture. The iodotrichloroalkanes were prepared using the method described in [8], taking account of the kinetic data in [9].

CONCLUSIONS

1. The rate constants for the abstraction of chlorine by $CCl_3(CH_2CH_2)_n{}^{\bullet}$ radicals (I-III) (n = 1-3) from CCl_4 at 40° were determined by the ESR method.

2. On the basis of the values obtained for the rate constants for the transfer of chlorine from the intermediate iron complexes, the rate constants for the addition of the telomeric $CCl_3(CH_2CH_2)_n{}^{\bullet}$ radicals to ethylene were calculated. The lower limit of the rate constant for the transfer of chlorine onto the $CCl_3CH_2{}^{\bullet}CH_2$ radical by iron complexes was also determined.

3. The changes in the values of the chain transfer constants in the telomerization of ethylene by CCl_4 during initiation by peroxides and metal carbonyls are associated with the difference in the rate constants for the abstraction of chlorine from CCl_4 by the $CCl_3CH_2{}^{\bullet}CH_2$ and $CCl_3(CH_2CH_2){}^{\bullet}{}_n$ ($n \geqslant 2$) radicals.

LITERATURE CITED

1. R. Kh. Freidlina, F. K. Velichko, E. Ts. Chukovskaya, M. Ya. Khorlina, B. A. Krentsel', D. S. Il'ina, N. V. Kruglova, L. S. Mayants, and R. G. Gasanov, Methods of Heteroorganic Chemistry. Chlorine. Aliphatic Compounds [in Russian], Nauka, Moscow (1973).
2. B. A. Énglin, N. A. Grigor'ev, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1568 (1972).
3. S. Terabe, K. Kuruma, and R. Konaka, J. Chem. Soc., Perkin Trans. 2, 1252 (1973).
4. N. M. Émanuél' and D. G. Knorre, A Course of Chemical Kinetics [in Russian], Vysshaya Shkola, Moscow (1974), p. 400.
5. E. T. Denisov, Rate Constants of Homolytic Liquid-Phase Reactions [in Russian], Nauka, Moscow (1971).
6. Y. Maeda and K. U. Ingold, J. Am. Chem. Soc., 101, 4975 (1979).
7. R. Kh. Freidlina, E. Ts. Chukovskaya, and B. A. Énglin, Dokl. Akad. Nauk SSSR, 159, 1346 (1964).
8. A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, Dokl. Akad. Nauk SSSR, 96, 87 (1954).
9. N. A. Grigor'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 1068 (1977).