EPR DETERMINATION OF THE RATE CONSTANTS FOR HYDROGEN ABSTRACTION FROM $HCCl_3$ BY $CCl_3(CH_2CHX)_n^{\cdot}$ RADICALS (X = H, Me, n = 1, 2)

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Knowledge of the rate constants for hydrogen abstraction (k_{tr}^H) from RH by $CCl_3(CH_2CHX)_n^{\cdot}$ radicals permits comparison of the activity of these radicals in reactions involving replacement with C–H bond cleavage depending on the position of the CCl_3 group relative to the radical site and nature of X. For this purpose, in the present work, we determined k_{tr}^H values for abstraction from $HCCl_3$ by $CCl_3(CH_2CHX)_n^{\cdot}$ radicals (X = H, Me, n = 1, 2).

Spin-adducts (SA) of $CCl_3(CH_2CHX)_n^{\cdot}$ and $\dot{C}Cl_3$ radicals with nitrosodurene (ND) were detected upon the photochemical decomposition of polychloroiodoalkanes $CCl_3(CH_2CHX)_nI$ in chloroform solution in the presence of $Hg(m\text{-}C_2H_2B_{10}B_9\text{-}9)_2$ and ND using EPR spectroscopy. ND was used as the spin trap (ST). The coupling constants for these radicals calculated from the ESR spectra coincide with the corresponding values given in our previous work [1, 2]. The formation of the radicals identified by EPR spectroscopy is given by the following scheme

$$CCl_3(CH_2CHX)_nI \xrightarrow{Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2,\,h\nu} CCl_3(CH_2CHX)_n^{\cdot}\ (R^{\cdot})$$

$$R^{\cdot} + ND \xrightarrow{k_1} RN(\dot{O})Ar\ (A)$$

$$R^{\cdot} + HCCl_3 \xrightarrow{k_{tr}^{H}} RH + \dot{C}Cl_3$$

$$\dot{C}Cl_3 + ND \rightarrow CCl_3N(\dot{O})Ar$$

$Ar = 2, 3, 5, 6\text{-}Me_4C_6H.$

This scheme indicated that the ratios of the increments in the concentrations of the SA of $R^{\cdot}$ radicals with ND in the absence ($d[A]_{ab}$) and presence ($d[A]_{pr}$) of $HCCl_3$ in the reaction mixture will be given by Eq. (1).

$$B = \frac{d[A]_{ab}}{d[A]_{pr}} = 1 + \frac{k_{tr}^{H}[HCCl_3]_0}{k_1[ND]_0} \qquad (1)$$

Figure 1 shows the changes in intensity over time for the doublet from the SA of $CCl_3CH_2\dot{C}HCH_3$ with ND at different $HCCl_3$ concentrations. Such dependences on the concentrations of $HCCl_3$ and ND were also obtained for other radicals (Table 1). The k_{tr}^H values for $CCl_3(CH_2CHX)_n^{\cdot}$ radicals (Table 2) were determined using Eq. (1) and the data in Table 1 and with $k_1 = 3.2 \cdot 10^7$ liters/mole·sec [3].

Using the values $C_n = k_{tr}^H/k_p$ in the telomerization of ethylene ($C_1 = 0.226$ and $C_2 = 1.62$) and propylene ($C_1 = 0.096$ and $C_2 = 1.43$) with $HCCl_3$ [4], we determined the rate constants for the addition (k_p) of $CCl_3(CH_2CHX)_n^{\cdot}$ radicals to ethylene and propylene. For comparison, the same rate constants from our previous work [1, 2] are given in Table 2 in parentheses. These results indicate good accord of the k_p values of $CCl_3(CH_2CH_2)_n^{\cdot}$ radicals relative to ethylene and of $CCl_3(CH_2CHCH_3)_n^{\cdot}$ radicals relative to propylene calculated using k_{tr}^{Cl} values for the abstraction of Cl from CCl_4 and k_{tr}^H for H abstraction from $HCCl_3$ and the values for $C_n = k_{tr}^{Cl}/k_p$ and $C_n = k_{tr}^H/k_p$ [4].

Thus, using the values of C_n in the telomerization of ethylene, propylene, and vinyl chloride and values of k_p determined in this study and in our previous work [1, 2, 5], it was possible to calculate the k_{tr}^H values for hydrogen abstraction from $HCCl_3$ radicals by

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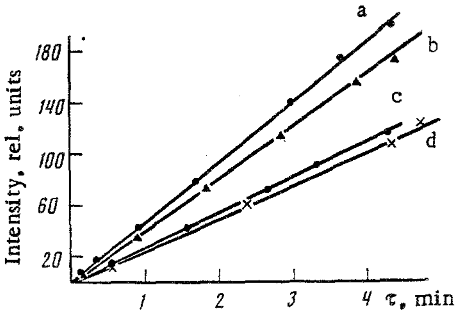

Fig. 1. Kinetics for the change in intensity of the first doublet of the spin-adduct of $CCl_3CH_2\dot{C}HMe$ radicals with nitrosodurene at different $HCCl_3$ concentrations in the reaction mixture. $[HCCl_3]_0$ = 0 (a), 1.45 (b), 2.7 (c), and 3.54 M (d).

TABLE 1. Ratios $d[A]_{ab}/d[A]_{pr} = B$ in the Reaction of $CCl_3(CH_2CHX)_n^{\cdot}$ Radicals (X = H, Me) with $HCCl_3$ in the Presence of Nitrosodurene (ND)

Radical	$[HCCl_3]_0$	$[ND]_0 \cdot 10^3$*	B	Radical	$[HCCl_3]_0$	$[ND]_0 \cdot 10^3$*	B
	M				M		
$CCl_3CH_2\dot{C}H_2$	6.29	2,4	1,288	$CCl_3CH_2\dot{C}HMe$	1,45	0,414	1,112
	8,39	1,06	1,792		2,70	0,414	1,688
	10,27	0,69	3,000		3,54	0,414	1,78
$CCl_3(CH_2CH_2)_2^{\cdot}$	6,29	3,91	2,642	$CCl_3(CH_2CHMe)_2^{\cdot}$	2,5	0,43	1,933
	8,39	3,0	5.137		3,34	0,43	2,636
	10,27	2,1	6,512		4,00	0,43	3,0

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*Monomer form of ND.

$CCl_3(CH_2CHCl)_n^{\cdot}$ radical [6]. = 0.006 and $C_2 = 0.014$) (Table 2, experiments Nos. 6 and 7) and k_{tr}^{Br} values for bromine abstraction from $BrCCl_3$ by $CCl_3(CH_2CHX)_n^{\cdot}$ radicals (X = H, C_1 = 2.00, $C_2 = 7 \cdot 10^3$; X = CH_3, C_1 = 2150, $C_2 = 10^5$; X = Cl, C_1 = 3.4, C_2 = 25) (Table 2).

The k_{tr}^{Br} constants for the $CCl_3(CH_2)_3\dot{C}H_2$ and $CCl_3CH_2CH(CH_3)CH_2\dot{C}H(CH_3)$ radicals are close to the diffusion-controlled values. These constants are three orders of magnitude greater than the corresponding k_{tr}^{Cl} constants for Cl abstraction from CCl_4. The same difference in the rate constants for the abstraction of Cl from CCl_4 and of Br from $BrCCl_3$ was found for the methyl radical [6].

The reactivity of $CCl_3(CH_2CHX)_n^{\cdot}$ radicals ($n \geq 2$) in replacement reactions involving C—H or C—Hal bond cleavage will probably not depend on the position of the CCl_3 group relative to the radical site and their activity will not differ significantly from that of $R(CH_2CHX)_n^{\cdot}$ radicals. Indeed, the k_{tr}^{Cl} constant for the abstraction of chlorine from CCl_4 for telomeric $CCl_3(CH_2CH_2)_n^{\cdot}$ radicals (n = 2, 3) at 313 K are $9 \cdot 10^4$ and $14 \cdot 10^4$ liters/mole·sec. The rate constant for Cl abstraction from CCl_4 by $CH_3(CH_2)_2\dot{C}H_2$ radicals ($8.3 \cdot 10^4$ liters/mole·sec at 313 K [7]) is close to these values.

Thus, the kinetic data for $CCl_3(CH_2CHX)_n^{\cdot}$ radicals ($n \geq 2$) obtained in this work may be used for comparing the reactivity of $R(CH_2CHX)_n^{\cdot}$ radicals (R = alkyl groups, aryl groups, and other functional groups less electronegative than the CCl_3 group) in the abstraction of halogen from polyhalomethanes and of hydrogen from $HCCl_3$.

TABLE 2. Rate Constants for the Abstraction of Hydrogen ($k_{tr}^{H} \cdot 10^{-4}$, liters/mole·sec) from $HCCl_3$, of Chlorine ($k_{tr}^{Cl} \cdot 10^{-4}$, liters/mole·sec) from CCl_4, and of Bromine ($k_{tr}^{Br} \cdot 10^{-4}$, liters/mole·sec) from $BrCCl_3$ by $CCl_3(CH_2CHX)_n^{\cdot}$ Radicals (X = H, Me, Cl, n = 1-3) and Their Addition ($k_p \cdot 10^{-4}$, liters/mole·sec) to $CH_2=CHX$ at 295 K

Experiment no.	Radical	k_{tr}^{H}	k_p	k_{tr}^{Cl} *	k_{tr}^{Br} †
1	$CCl_3CH_2\dot{C}H_2$	0,43±0,024	1,9 (4,5)	0,39	640
2	$CCl_3(CH_2CH_2)_2^{\cdot}$	3,84±0,28	2,4 (3,0)	9,0	18 900
3	$CCl_3(CH_2CH_2)_3^{\cdot}$	–	– (1,9)	14,0	–
4	$CCl_3CH_2\dot{C}HMe$	0,2±0,08	2,6 (0,88)	1,4	3 740
5	$CCl_3(CH_2CHMe)_2^{\cdot}$	0,68±0,039	0,47 (0,42)	20,8	44 500
6	$CCl_3CH_2\dot{C}HCl$	0,097 †	– (16,1)	0,045	54,7
7	$CCl_3(CH_2CHCl)_2^{\cdot}$	0,129 †	– (9,8)	0,175	230

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*At 313 K.

†Calculated using mean values of k_p and the data for C_n from the work of Énglin et al. [4].

EXPERIMENTAL

The EPR spectra were taken on an RÉ-1306 spectrometer at 295 K. The change in the intensity of the signals of the SA of $CCl_3(CH_2CHX)_n^{\cdot}$ radicals with ND over time was approximated by computer using the method of least squares and extended to $\tau = 0$ ($r = 0.97$-0.99). The k_{tr}^{H} values were calculated by the method of least squares using the data in Table 1 assuming that B = 1 in the absence of $HCCl_3$ in the reaction mixture. ND was dissolved in CH_2Cl_2 and then added to the reaction mixtures. The iodotrichloroalkanes were obtained according to our previous procedures [1, 2].

CONCLUSIONS

1. The rate constants were calculated for the abstraction of hydrogen from $HCCl_3$ and of bromine from $BrCCl_3$ by $CCl_3(CH_2CHX)_n^{\cdot}$ radicals.

2. The reactivity of $CCl_3(CH_2CH_2)_n^{\cdot}$ radicals (n = 1, 2) depends on the position of the CCl_3 group and the chain transfer step makes the major contribution to the chain transfer constants in the telomerization of ethylene with $HCCl_3$ and $BrCCl_3$.

3. The reactivity of $CCl_3(CH_2CHX)_n^{\cdot}$ radicals (X = H, Me, Cl) in reactions involving replacement with C–H and C–Hal bond cleavage depends on the nature of X.

LITERATURE CITED

1. R. G. Gasanov, L. V. Ivanova, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1011 (1982).
2. R. G. Gasanov, L. V. Ivanova, N. A. Grigor'ev, et al., Dokl. Akad. Nauk SSSR, 273, 1410 (1983).
3. P. S. Schmid and K. U. Ingold, J. Am. Chem. Soc., 100, 2493 (1978).
4. B. A. Énglin, N. A. Grigor'ev, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1568 (1972).
5. R. G. Gasanov, L. V. Ivanova, and N. A. Grigor'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 1964 (1984).
6. B. T. Denisov, Rate Constants of Homolytic Liquid-Phase Reactions [in Russian], Izd. Nauka, Moscow (1971), p. 64.
7. J. A. Hawari, S. Davis, P. S. Engel, et al., J. Am. Chem. Soc., 107, 4721 (1985).