RATE CONSTANTS FOR ISOMERIZATION OF POLYCHLOROALKYL RADICALS WITH 1,2-MIGRATION OF CHLORINE ATOM, AS DETERMINED BY MEANS OF ESR

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The rearrangement of polychloroalkyl radicals with 1,2-migration of Cl atoms in the liquid phase has been studied in many examples by chemical and kinetic methods [1, Chapter XIV] and by ESR spectrometry [2]. In [3-5], by the use of various spin traps, the unrearranged radicals RCH_2CHCCl_2X and CH_2CCl_3 were registered in the form of their spin adducts with 2-methyl-2-nitroso-3-butanol (MNB), and the rearranged radicals $RCH_2CHClCCl_X$ and $ClCH_2CCl_2$ as spin adducts with 2-methyl-2-nitrosopropane (MNP) and nitrosodurene. Even from the results of these studies it can be concluded that the values of the isomerization rate constant will be quite different for radicals of different types. The spin adducts of the radicals RCH_2CHCl_2X (X = Cl, F) with MNB can be observed successfully at 325-330°K [3], but the spin adducts of the radicals CH_2CCl_3 can be registered only below 260°K [5].

The use of MNP in the reaction of phenyl radicals with CCl_3CH_2Cl and $CCl_3CHClCH_2Cl$ [6] has made it possible to register simultaneously, at about 20°C, the initial radicals $CCl_3CHCl (R_1)$ and $CCl_3CClCH_2Cl (R_2)$ and the rearranged radicals $CCl_2CHCl_2 (R_3)$ and $CCl_2CCl_2CH_2Cl (R_4)$, and also to determine the rate constants for isomerization of the radicals R_1 and R_2 to R_3 and R_4 [7].

Here we are reporting on the use of a procedure described in [7] to determine the rate constants for isomerization of tertiary, secondary, and primary polychloroalkyl radicals. In the reaction of the radicals $\dot{C}_{6}H_{5}$ and $\dot{C}Cl_{3}$, generated by procedures given in [3, 4, 8], with $CH_2=C(CH_3)CCl_3$, signals are observed in the ESR spectrum from the spin adducts of the unrearranged radicals (I) ($a_{\rm N}$ = 15.0 Oe) and rearranged radicals (II) ($a_{\rm N}$ = 12; $a_{35}Cl$ = 4.2, $a_{37}Cl$ = 3.8 Oe) with MNP. The formation of these radicals can be described by the scheme

$$\begin{split} \dot{\mathbf{R}} + \mathbf{CH}_2 &= \mathbf{C}(\mathbf{CH}_3)\mathbf{CCl}_3 \rightarrow \mathbf{RCH}_2\dot{\mathbf{C}}(\mathbf{CH}_3)\mathbf{CCl}_3 \text{ (A)} \\ & (\mathbf{A}) \xrightarrow{\mathbf{fer}}_{\mathbf{k_{15}}} \mathbf{RCH}_2\mathbf{CCl}(\mathbf{CH}_3)\mathbf{CCl}_2 \text{ (B)} \\ & (\mathbf{A}) + \mathbf{MNP} \xrightarrow{\mathbf{ter}}_{\mathbf{k_{15}}} \mathbf{RCH}_2\mathbf{C}(\mathbf{CH}_3)(\mathbf{CCl}_3)\mathbf{N}(\dot{\mathbf{O}})\mathbf{C}(\mathbf{CH}_3)_3 \text{ (I)} \\ & (\mathbf{B}) + \mathbf{MNP} \xrightarrow{\mathbf{O}} \mathbf{RCH}_2\mathbf{C}\mathbf{Cl}(\mathbf{CH}_3)\mathbf{CCl}_2\mathbf{N}(\dot{\mathbf{O}})\mathbf{C}(\mathbf{CH}_3)_3 \text{ (II)} \end{split}$$

where $R = C_6H_5$ or CCl_3 .

The addition of the radicals $\dot{C}Cl_2CCl_2H$ and $\dot{C}Cl_2CL_2CL_2CL_2CL$, which are similar in structure to the radicals (B), to MNP at 310°K proceeds with $k_{ad} = 3 \times 10^5$ liters/mole·sec [7], approximately an order of magnitude smaller than the corresponding constants for the radicals $\dot{C}(CH_3)_3$, $\dot{O}C(CH_3)_3$ and $[(CH_3)_3CO]_2CH$ [9-11]. The difference is within the limits of accuracy of the experimental determination, since for identical reactions of this type, the calculated rate constants may differ by a factor of 5 [12]. In view of the electron acceptor character of the CCl_3 group, in the addition of radicals (A) to MNP we should expect a smaller rate constant than for the analogous reaction of tert-butyl radicals, for which $k_{ad} = 3 \times 10^6$ liters/mole·sec [9]. From these considerations, we have taken a value 1×10^5 liters/mole·sec for k_{ad} in addition to MNP.

Applying the method of quasistationary concentrations to this scheme, we obtain

 $k_{is}^{ter} = [II]/[I] \cdot k_{d} [MNP]_0$

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Fig. 1. ESR spectra of nitroxyl radicals formed in reaction of $CH_2=CHCCl_2F$ with radicals \dot{C}_6H_5 , $\dot{C}Cl_3$ and $\dot{B}r$ in the presence of 2-methyl-2-nitrosopropane. Temperature, °K: a) < 210; b) 230-300; c) > 310.

where [I] and [II] are the instantaneous concentrations of radicals (I) and (II); [MNP]₀ is the initial concentration of the trap. The ratio [11]/[I] varies linearly with temperature $(280-310^{\circ}K)$; at $310^{\circ}K$, $[II]/[I] \approx 10$. Substituting this value into Eq. (1) with [MNP]₀ = 1×10^{-2} mole/liter, we find that k^{ter} = 1×10^{4} sec⁻¹. The C-Cl vibration frequencies for the is CCl₃ group in the 530-800 cm⁻¹ region correspond to $pZ \sim 10^{13}$ sec⁻¹ [1, Chapter XV]. On the basis of these data, the activation energy for isomerization of tertiary radicals (A) to form (B) is 12.5 kcal/mole.

The isomerization of secondary radicals was studied in the example of the rearrangement of radicals (C) to (D):

 $\operatorname{RCH}_{2}\dot{\operatorname{CHCCl}}_{2}F$ (C) $\xrightarrow{\operatorname{sec}}$ $\operatorname{RCH}_{2}\operatorname{CHCl}\dot{\operatorname{CCl}}F$ (D)

(C) + MNP \longrightarrow RCH₂CH(CCl₂F)N(O)C(CH₃)₃ (III) (D) + MNP \longrightarrow RCH₂CHClCClFN(O)C(CH₃)₃ (IV)

where $R = C_6H_5$ (a), CCl₃ (b), or Br (c).

In Fig. 1 we show part of the ESR spectrum for the spin adducts formed by addition to CH_2 = CHCCl₂F of the radicals $\dot{C}_{6}H_5$, $\dot{C}Cl_3$ and $\dot{B}r$ in the presence of MNP at various temperatures. At temperatures below 210°K, only the signals of the spin adducts (IIIb) and (IIIc) are observed, and at temperatures above 310°K, only (IVa) and (IVb) (Fig. 1c). In the 230-300°K interval we observe signals of both the radicals (III) and (IV) (Fig. 1b). At 230, 250, 260, and 290°K, the respective ratios (IV)/(III) are 0.87, 2.66, 4.08, and 18.46, these values increasing linearly with increasing reaction temperature. Extrapolating this ratio to 310°K, we obtain (IV)/(III) = 50.5. Whence we find* that with $k_{sec}^{sec} = 1 \times 10^5$ liters/mole·sec and $[MNP]_0 = 2 \times 10^{-2}$ mole/liter, $k_{sec}^{sec} = 1 \times 10^5$ sec⁻¹. Assuming⁺ that $pZ \sim 10^{13}$ sec⁻¹, we obtain *For addition of [(CH₃)₃CO]₂CH radicals to MNP at 310°K, $k_{ad} = 9 \times 10^5$ liters/mole·sec [10], and for CCl₃CClH, $k_{ad} = 3 \times 10^5$ liters/mole·sec [7]. *Replacement of Cl in the CCl₃ group by F may lead to an increase in the lower limit of the C--Cl frequency region, but the frequencies remain within the limits of 600-900 cm⁻¹ [13].



Fig. 2. Logarithm of ratio of areas of signals from spin adducts of RCH₂CHClCClF and RCH₂CHCCl₂F radicals with 2-methyl-2-nitrosopropane, as a function of inverse temperature.

$$k_{is}^{sec} = 10^{13} e^{-\frac{10}{RT}}$$

The temperature dependence of the logarithm of the ratio of areas for signals of the spin adducts of the radicals (D) and (C) is linear (Fig. 2). From the slope of the line (-1.7×10^3) , using Eqs. (1) and (2), we find the activation energy for the stage of radical (C) addition to MNP, equal to 2.5 kcal/mole and coinciding in magnitude with the activation energy for the addition of other radicals to MNP [11].

On the basis of (2), at 330°K, $k_{is}^{sec} = 1 \times 10^{6} \text{ sec}^{-1}$.

According to data reported in [3], when MNB is used, the unrearranged radicals RCH_2 -CHCCl₂X (X = Cl, F) can be registered successfully at 325-330°K:

$$\operatorname{RCH}_{2}\operatorname{CHCCl}_{2}X + \operatorname{MNB} \xrightarrow{h_{2}d} \operatorname{RCH}_{2}\operatorname{CH}(\operatorname{CCl}_{2}X)N(\dot{O})(\operatorname{CH}_{3})_{2}C(\operatorname{COCH}_{3})$$

Substituting the value of [MNB]_o into Eq. (1), we determine that $k_{ad} = 1 \times 10^6$ liters/mole-sec at 330°K. This value of k_{ad} is close to k_{ad} for the addition of various radicals to MNP [12].

The activation energies for the isomerization of tertiary radicals ($E_{is}^{ter} = 12.5 \text{ kcal/}$ mole) and secondary radicals ($E_{is}^{sec} = 10.5 \text{ kcal/mole}$) differ by 2 kcal/mole. This same difference in isomerization activation energies can be expected between the secondary and primary radicals. For the rearranged radicals (E) and (F),

$$\operatorname{CCl}_3\dot{\operatorname{CH}}_2(\mathsf{E}) \xrightarrow{k_{1\mathfrak{S}}} \dot{\operatorname{CCl}}_2\operatorname{CH}_2\operatorname{Cl}(\mathsf{F})$$

we will take $E_{is}^{pri} = 8 \text{ kcal/mole}$, and then $k_{is}^{pri} = 10^{13} \text{ e}^{\frac{8000}{RT}}$. At 310°K , $k_{is}^{pri} = 1 \times 10^{7} \text{ sec}^{-1}$. The values obtained for k_{is}^{pri} provide an explanation for the fact that the unrearranged radicals cannot be registered successfully by means of ESR without the use of spin traps. The application of Eq. (3) [14] to the isomerization of radicals (E) and (F) that was studied in [2] indicates that in order to register the unrearranged radicals, the stationary concentration of the rearranged radicals must be at least 10^{-6} mole/liter, which apparently is difficult to achieve experimentally^{*}:

$$k_{is}^{\text{pri}}/2 k_{tot} = [F]/[E] \cdot ([F] - [E])$$
(3)

(2)

^{*}From the ESR spectrum given in [2], it follows that even at 130°K, the concentration of rearranged radicals is at most 10^{-8} mole/liter (s/n = 2:1).

Thus, on the basis of the data that we have obtained, we can write



These resuls are in accord with data from preparation experiments [1], and they open up the possibility of predicting the direction of an entire group of monotypical reactions of addition, telomerization, and polymerization in which rearrangement of intermediate radicals is possible with 1,2-migration of the Cl atom. In particular, a study of the polymerization of CH₂=CHCCl₂X (X = Cl, F) [15] has shown that the polymer that is formed consists mainly of rearranged $-(CH_2CHClCClX)_n$ — units. Since the rate of isomerization of secondary radicals is at least an order of magnitude greater than the rate of their addition, the RCH₂CHCCl₂X radicals that are formed will isomerize more rapidly than they will add to a new molecule of monomer.

The values obtained for the activation energy of isomerization, particularly for the secondary and primary polychloroalkyl radicals, match up better with an intramolecular character of their rearrangement [5, 6] than with an elimination-addition mechanism.

EXPERIMENTAL

The experimental procedures are described in [7]. The phenyl radicals were generated in accordance with a procedure given in [8], in which the solutions were mixed at a given temperature in a thermostat, after which ampuls containing these solutions were placed in the resonator of the ESR spectrometer, where they were held at this same temperature. The CCl_s radicals were obtained by a procedure given in [4], and the Br radicals were obtained by UV irradiation of Br_2 . In the experiments on the addition of CCl_s and Br radicals to unsaturated compounds, the spin trap was added to the particular reaction mixture under investigation.

SUMMARY

1. By means of ESR using 2-methyl-2-nitrosopropane as a spin trap, rate constants and activation energies have been determined for the isomerization of the radicals $RCH_2\dot{C}(CH_3)CCl_3$ to RCH_2CCl_2 , $RCH_2\dot{C}HCCl_2F$ to $RCH_2CHCl\dot{C}ClF$, and $\dot{C}H_2CCl_3$ to $ClCH_2\dot{C}Cl_2$.

2. The values obtained for the activation energy of isomerization of secondary radicals (10 kcal/mole) and primary radicals (8 kcal/mole) point to an intramolecular character of the rearrangement.

LITERATURE CITED

- 1. R. Kh. Freidlina, F. K. Velichko, et al., Methods of Heteroorganic Chemistry; Chlorine; Aliphatic Compounds [in Russian], Nauka (1973), Chapter XIV (a), Chapter XI (b).
- S. Chen, D. Tang, L. K. Montgomery, and J. K. Kochi, J. Am. Chem. Soc., <u>96</u>, 2201 (1974).
 R. G. Gasanov, I. I. Kandror, M. Ya. Khorlina, and R. Kh. Freidlina, Izv. Akad. Nauk
- SSSR, Ser. Khim., 1758 (1976). 4. R. G. Gasanov, I. I. Kandror, and R. Kh. Freidlina, Dokl. Akad. Nauk SSSR, <u>226</u>, 342
- (1976).
 5. R. G. Gasanov, T. T. Vasil'eva, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 817 (1978).
- 6. R. G. Gasanov and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 2242 (1977).
- 7. R. G. Gasanov, L. V. Ivanova, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 2810 (1979).
- 8. G. A. Razuvaev, G. A. Abakumov, and V. K. Cherkasov, Dokl. Akad. Nauk SSSR, <u>212</u>, 374 (1973).
- 9. Takahisa Doba, Tsuneki Ichikawa, and Hiroshi Yoshida, Bull. Chem. Soc. Jpn., <u>50</u>, 3158 (1977).
- 10. M. J. Perkins and B. P. Roberts, J. Chem. Soc. Perkin Trans. 2, 77 (1975).
- 11. M. J. Perkins and B. P. Roberts, J. Chem. Soc. Perkin Trans. 1, 297 (1974).
- 12. P. Schmid and K. U. Ingold, J. Am. Chem. Soc., 99, 6434 (1977).
- 13. R. G. Gasanov, Dissertation, Moscow (1967).
- 14. B. Maillard and K. U. Ingold, J. Am. Chem. Soc., <u>98</u>, 1224 (1976).
- A. P. Suprun, A. S. Shashkov, T. A. Soboleva, G. K. Semin, T. T. Vasil'eva, G. P. Lopatina, T. A. Babushkina, and R. Kh. Freidlina, Dokl. Akad. Nauk SSSR, <u>173</u>, 1356 (1967).