Rate constants for reactions of Cl abstraction from CCl_4 by $CCl_3CH_2{}^{\cdot}CHR$ radicals and Br abstraction from CCl_3CH_2CHBrR ($R = Bu^n$, AcO, $OCNC_4H_8$, CN) by $^{\cdot}Re(CO)_5$ radicals

R. G. Gasanov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The rate constants for reactions of Cl abstraction from CCl_4 by $CCl_3CH_2{}^{\cdot}CHR$ radicals and Br abstraction from CCl_3CH_2CHBrR ($R = Bu^n$, AcO, $OCNC_4H_8$, CN) by $^{\cdot}Re(CO)_5$ radicals were determined by ESR spectroscopy using spin trapping technique. Replacement of H atoms at the C(β) atom by O or N atoms reduces the reactivity of the radicals in the reactions of Cl abstraction from CCl_4 by approximately an order of magnitude. The presence of two polar groups at the C(β) atom results in appreciable decrease in the strength of the C—Br bond in CCl_3CH_2CHBrR adducts.

Key words: ESR spectroscopy, spin trapping technique, rate constants for Br and Cl abstraction reactions, effect of polarity.

Radical adducts formed as a result of addition of free radicals to unsaturated compounds can differ essentially in their reactivity in both substitution and addition reactions depending on the nature of substituents at the C(α) and C(β) atoms.[1] Establishment of dependences of the rate constants for chain propagation and transfer (k_p and k_{tr}, respectively) for acyclic carbon-centered radicals on polar properties of the substituents at the C(α) and C(β) atoms will make it possible to use radical processes for targeted formation of new carbon—carbon and carbon—element bonds by directing the process to telomerization or addition.

Previously,[2,3] we studied the dependence of k_p and k_{tr} on the polar properties of the substituents at the C(α) atom for $(CCl_3CH_2CHX)^{\cdot}_n$ ($n = 1-3$; X = H, Me, Cl) radicals formed as a result of addition of polyhalomethanes to ethylene, propylene, and vinyl chloride.

In this work the rate constants for reactions of Cl abstraction from CCl_4 by $CCl_3CH_2{}^{\cdot}CHR^i$ ($R^i = Bu^n$ (R^1), AcO (R^2), $OCNC_4H_8$ (R^3), CN (R^4)) radical adducts and their dependence on the polar properties of the substituents at the C(β) atom were determined by ESR spectroscopy using the spin trap technique. The choice of these radicals is due to the fact that acrylic systems, in particular, amides of unsaturated carboxylic acids, have been widely used in organic synthesis in the last few years.[4,5]

Results and Discussion

Photochemical decomposition of $Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)$ in CH_2Cl_2 containing $CCl_3CH_2CHHalR$ ($R = Bu^n$ (**1**), AcO (**2**), $OCNC_4H_8$ (**3**), CN (**4**); Hal = I, Br) and a spin trap (nitrosodurene, ND) under the action of light with λ = 366 nm resulted in spin adducts of R^i radicals with ND detected by ESR spectroscopy:

$$CCl_3CH_2CHHalR^i \xrightarrow{Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2} CCl_3CH_2{}^{\cdot}CHR^i, \quad (1)$$

$$R^i + ND \xrightarrow{k_1} \underset{\mathbf{A}}{RN(O^{\cdot})Ar}, \quad (2)$$

$$Ar = 2,3,5,6\text{-}Me_4C_6H_2.$$

The hyperfine interaction (HFI) constants of these radicals calculated from the ESR spectra obtained coincide with the reported data.[6,7] If CCl_4 is added to these solutions, then, depending on its concentration, the signals of nitroxyls **B** are also observed in the ESR spectra in addition to the signals of nitroxyl radicals **A**:

$$R^i + CCl_4 \xrightarrow{k_2} R^iCl + {}^{\cdot}CCl_3, \quad (3)$$

$$^{\cdot}CCl_3 + ND \longrightarrow \underset{\mathbf{B}}{Cl_3CN(O^{\cdot})Ar}. \quad (4)$$

The following equation for the yields of radicals **A** in the absence and in the presence of CCl_4 in the reaction mixture ($[A]_0$ and $[A]_1$, respectively) is valid in linear portions of the curves of changes in the intensities of ESR signals[2]:

$$d[A]_0/d[A]_1 = 1 + k_2/k_1 \cdot [CCl_4]_0/[ND]_0, \quad (5)$$

where $[CCl_4]_0$ and $[ND]_0$ are the initial concentrations of CCl_4 and the spin trap, respectively.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 45—48, January, 2000.

1066-5285/00/4901-0046 $25.00

Changes with time in the signal intensities in the ESR spectra of the spin adducts of R^1 and R^3 radicals with ND at different concentrations of CCl_4 are shown in Fig. 1. Analogous dependences were also obtained for the signals of R^2 and R^4 radicals (Table 1). The k_2/k_1 ratios for R^1—R^4 radicals ($7.820 \cdot 10^{-4}$, $1.052 \cdot 10^{-4}$, $0.619 \cdot 10^{-4}$, and $0.637 \cdot 10^{-4}$, respectively) were calculated by approximating the dependence of the signal intensities for nitroxyl radicals **A** on the CCl_4 concentration (see Table 1) at a constant initial concentration of ND. The rate constants for addition of different secondary radicals to ND are virtually independent of the nature of the substituents at the C(β) atom.[2,8] Assuming that $k_1 = 2 \cdot 10^7$ L mol^{-1} s^{-1} at 22 °C (see Ref. 2), one can determine the rate constants for Cl abstraction from CCl_4 by R^i radicals ($k_2 = k_{tr}$). The results are presented in Table 1.

From the data listed in Table 1 it can be seen that the k_{tr} values for R^1 radicals coincide with the rate constant for Cl abstraction from CCl_4 by $CCl_3CH_2{}^{\cdot}CHMe$ radicals,[3] which means that the replacement of a hydrogen atom at the C(β) atom by an alkyl group has no effect on the reactivity of secondary radicals. However, the substituents containing heteroatoms decrease the activity of secondary radicals by an order of magnitude. The reactivities of R^2—R^4 radicals in the reaction of Cl abstraction from carbon tetrachloride are close to that of $(CCl_3CH_2CHCl)_n{}^{\cdot}$ radicals (see Ref. 3). Hence, oxygen or nitrogen atoms at the C(β) atom have the same effect on the reactivity of secondary radicals in the reaction of Cl abstraction from CCl_4 as the chlorine atom at the C(α) atom[3] (without considering steric factors). This makes it possible to suggest that the rate constants for chain propagation (k_p) for R^2—R^4 radicals are of the same order as for $CCl_3(CH_2CHCl)^{\cdot}_2$ radicals (10^5 L mol^{-1} s^{-1}). Hence, obtaining CCl_3CH_2CHClX adducts by adding CCl_4 to $CH_2{=}CHCX$ (X is electrophilic substituent) in the case of free-radical initiation at close telogen/monomer ratios is impossible. This assumption is in agreement with numerous experimental results,[9] according to which peroxide-initiated addition of CCl_4 to methyl acrylate or acrylonitrile results in telomers only.

The reactivity of radical adducts in reactions of halogen atom abstraction from telogens should be associated with the strength of the carbon—halogen bond that formed, which can be assessed knowing the rate constant for halogen atom abstraction from the adducts of $CCl_3CH_2CHHalCR$ by radicals for which the reactivity scale is known.

We determined the rate constants for Br abstraction from compounds **1**—**3** by $^{\cdot}Re(CO)_5$ radicals formed upon photochemical decomposition of dirhenium decacarbonyl. The reactivity scale of these radicals in halogen abstraction reactions depends on the strength of

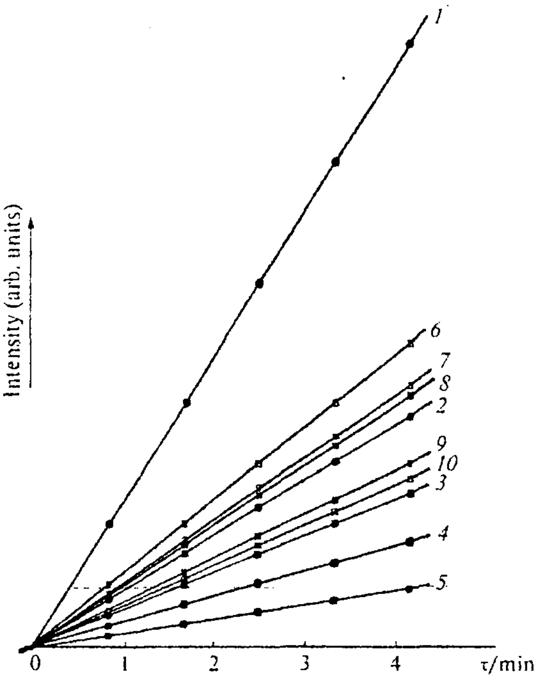


Fig. 1. Kinetics of changes in the intensity of the doublet signal of the spin adducts of $CCl_3CH_2{}^{\cdot}CHR$ (R = Bu^n (*1—5*), $OCNC_4H_8$ (*6—10*)) radicals with nitrosodurene ($[ND]_0$ = $6.9712 \cdot 10^{-4}$ mol L^{-1}) at different concentrations of CCl_4 in the reaction mixture: $[CCl_4]_0$/mol L^{-1} = 0 (*1*, *6*); 1.039 (*2*, *7*); 2.078 (*3*, *8*); 4.156 (*4*, *9*); 8.314 (*5*, *10*).

Table 1. $d[A]_0/d[A]_1$ values for reactions of Cl abstraction from CCl_4 by $CCl_3CH_2{}^{\cdot}CHR$ radicals in the presence of nitrosodurene ($[ND]_0$ = $6.9712 \cdot 10^{-4}$ mol L^{-1})*

R	$[CCl_4]$ /mol L^{-1}	$d[A]_0/d[A]_1$	$k_{tr} \cdot 10^{-3}$ /L mol^{-1} s^{-1}
Bu^n	1.102	2.5808	15.6
	2.345	3.8929	
	4.515	5.5984	
	8.267	10.6729	
AcO	1.052	1.1358	2.1
	2.078	1.3477	
	4.350	1.6552	
	8.178	2.2318	
$OCNC_4H_8$	1.039	1.1471	1.2
	2.078	1.1844	
	4.145	1.6525	
	8.314	1.7840	
CN	2.201	1.1105	1.3
	4.458	1.4476	
	6.915	1.5456	

* Monomeric form of ND.

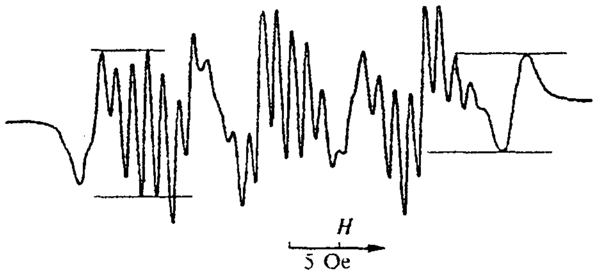
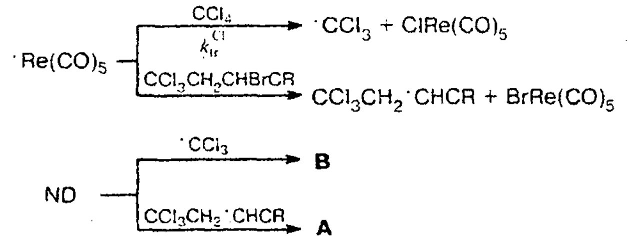


Fig. 2. ESR spectrum of the spin adducts of $CCl_3CH_2{}^{\cdot}CHC_4H_9$ and $^{\cdot}CCl_3$ radicals with ND ($[ND]_0$ = $1.104 \cdot 10^{-5}$ mol L^{-1}, $[CCl_4]$ = $4.13 \cdot 10^{-4}$ mol L^{-1}).

the carbon—halogen bond, as was established for a wide range of substances.[10,11]

Signals of two nitroxyl radicals **A** and **B** are observed in the ESR spectra (Fig. 2) on photochemical decomposition of $Re_2(CO)_{10}$ under the action of light with λ = 300 nm in CH_2Cl_2 containing ND, adducts **1—3**, and CCl_4.



Taking into account the rate constants for reactions of Cl abstraction from CCl_4 and those for reactions of addition of the radicals to ND, we chose the initial concentrations of CCl_4 and the spin trap ($[CCl_4]_0$ = $4.13 \cdot 10^{-4}$ mol L^{-1} and $[ND]_0$ = $1.104 \cdot 10^{-5}$ mol L^{-1}, respectively) in such a way that the rate of reaction (2) is much higher than that of reaction (3). Assuming that the rate constant for Cl abstraction from CCl_4 by $^{\cdot}Re(CO)_5$ radicals is $3 \cdot 10^7$ L mol^{-1} s^{-1} (see Refs. 10 and 11), the rate constants for Br abstraction from compounds **1—3** by $^{\cdot}Re(CO)_5$ radicals ($7 \cdot 10^6$, $8 \cdot 10^7$, and $2 \cdot 10^8$ L mol^{-1} s^{-1}, respectively) were determined from the ratio of the integrated intensities of the signals of nitroxyl radicals **A** and **B**. As can be seen, the strength of the C—Br bond decreases on going from compound **1** to **2** and **3** in parallel to the decrease in the reactivity of R^i radicals in the reactions of Cl abstraction from CCl_4 (see Table 1).

The rate constants for Br abstraction from compounds **2** and **3** by $^{\cdot}Re(CO)_5$ radicals are several times higher than the corresponding rate constant for allyl bromide and are nearly equal to that of benzyl bromide.[10,11] In view of this fact one can suggest that the yields of adducts formed in the addition of bromotrichloromethane to methyl acrylate or to monosubstituted amides of unsaturated carboxylic acids are controlled by thermodynamic factors rather than by kinetic factors. This is favored by the values of the rate constants for Br abstraction from bromotrichloromethane by R^2 and R^3 radical adducts, which are likely 2—3 orders of magnitude higher than that for Cl abstraction from CCl_4 by telomeric radicals[2] and, hence, are of the order of 10^5 L mol^{-1} s^{-1}. The addition stage is accompanied by substantial decrease in entropy and, therefore, must be favored by low temperature. In turn, the cleavage of the C—Br bond is accompanied by an increase in entropy and, hence, becomes predominant at elevated temperatures.[12] This assumption is in agreement with experimental results.[13—15] Thus, the reaction of bromotrichloromethane addition to (2*R*,5*R*)-1-acryloyl-2,5-dimethylpyrrolidine at 0 °C results in the adduct and telomers,[13] whereas no formation of adduct and telomers was observed in the peroxide-initiated addition of the same telogen to methyl methacrylate[14] or to (*R*)-3-acryloyl-4-phenyloxazolidine-2-one[15] at 80 °C.

Experimental

The procedures for recording ESR spectra and processing experimental data were described earlier.[16] Adducts **1—4** were obtained by addition of iodotrichloromethane and bromotrichloromethane to corresponding unsaturated compounds following the known procedures.[17]

References

1. *Substituent Effects in Radical Chemistry*, NATO ASIN, Series C, Reidel, Dordrecht, 1986, **189**, 123.
2. R. G. Gasanov and R. Kh. Freidlina, *Usp. Khim.*, 1987, **56**, 447 [*Russ. Chem. Rev.*, 1987, **56**, 264 (Engl. Transl.)].
3. L. V. Il'inskaya and R. G. Gasanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1402 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 1236 (Engl. Transl.)].
4. N. A. Porter, B. Giese, and D. P. Curran, *Acc. Chem. Res.*, 1991, **24**, 296.
5. W. Smadja, *Synlett*, 1994, **1**, 1.
6. R. G. Gasanov and T. T. Vasil'eva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 800 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 719 (Engl. Transl.)].
7. R. G. Gasanov, T. D. Churkina, L. V. Il'inskaya, K. A. Kochetkov, and D. E. Bodrov, *Dokl. Akad. Nauk SSSR*, 1992, **326**, 126 [*Dokl. Chem.*, 1992 (Engl. Transl.)].
8. R. G. Gasanov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2124 [*Russ. Chem. Bull.*, 1996, **45**, 2019 (Engl. Transl.)].
9. R. Kh. Freidlina, F. K. Velichko, E. Ts. Chukovskaya, M. Ya. Khorlina, B. A. Krentsel', D. E. Il'ina, N. V. Kruglova, L. S. Mayants, and R. G. Gasanov, *Metody elementoorganicheskoi khimii. Khlor. Alifaticheskie soedineniya* [*Methods of the Chemistry of Organoelement Compounds.*

Chlorine. Aliphatic Compounds], Nauka, Moscow, 1978, Ch. 5, 187 (in Russian).

10. R. G. Gasanov, E. G. Sadykhov, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1031 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 936 (Engl. Transl.)].
11. *Organometallic Radical Processes*, in *J. Organomet. Chem. Library 22*, Ed. W. C. Trogler, Amsterdam, 1990, 67.
12. D. C. Nonhebel and J. C. Walton, *Free Radical Chemistry, Structure and Mechanism*, University Press, Cambridge, 1974.
13. N. A. Porter, R. Brayer, E. Swann, J. Nally, J. Pradham, T. Allen, and A. T. McPhail. *J. Am. Chem. Soc.*, 1991, **113**, 7002.
14. F. K. Velichko, L. V. Vinogradova, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 181 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1973, **22** (Engl. Transl.)].
15. V. I. Tararov, T. F. Savel'eva, Yu. T. Struchkov, A. P. Pisarevskii, N. I. Raevskii, and Yu. N. Belokon', *Izv. Akad. Nauk, Ser. Khim.*, 1996, 640 [*Russ. Chem. Bull.*, 1996, **45**, 600 (Engl. Transl.)].
16. R. G. Gasanov, S. O. Videnskaya, V. V. Pinyaskin, and I. V. Stankevich, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 452 [*Russ. Chem. Bull.*, 1995, **44**, 437 (Engl. Transl.)].
17. R. G. Gasanov, S. O. Videnskaya, L. V. Il'inskaya, Yu. N. Belokon', A. P. Pisarevskii, and Yu. T. Struchkov, *Dokl. Akad. Nauk*, 1994, **336**, 485 [*Dokl. Chem.*, 1994 (Engl. Transl.)].

Received March 10, 1999;
in revised form June 28, 1999