

# Structural and Kinetic Relations Holding in the Halogen Abstraction from Organohalogen Compounds by Alkyl Radicals

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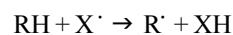
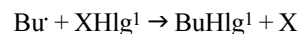
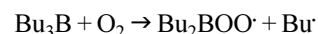
Received April 21, 2004

**Abstract**—The relative rate constants were determined, and the absolute rate constants were estimated, for halogen transfer from *N,N*-dihaloarenesulfonamides, (dichloroiodo)arenes, benzyl bromides, and arenesulfonyl chlorides to cyclohexyl radical and from *N,N*-dihaloarenesulfonamides to benzyl radical. Polar effect of the substituent was found to be the main factor determining the rate of halogen transfer from benzyl bromides and arenesulfonyl chlorides; it increases with rise in the electrophilicity of the organohalogen substrate due mainly to charge distribution in the transition state.

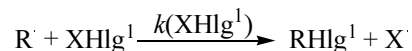
While considering the relations between the structure of organic molecules and the rate of radical transfer of hydrogen, the main factor is the heat effect of the hydrogen transfer stage, and its rate increases in parallel with the exothermic effect. In keeping with the Bell–Evans–Polanyi principle, in most cases the rate of transfer of an atom is linearly related to the heat effect. Exceptions are possible when a radical to which an atom is transferred possesses pronounced electrophilic or nucleophilic properties. In terms of the model based on the Marcus equation, increase in the electrophilicity or nucleophilicity of a radical leads to change of the internal reaction barrier as a result of charge separation in the transition state [1]. For example, the rate of abstraction of a hydrogen atom by chlorine and some other electrophilic radical species depends on polar effects of substituents in the substrate to a greater extent than on the heat effect. On the other hand, general relations holding in halogen transfer to alkyl radicals have been studied poorly. Therefore, we examined the effect of the structure of organic halogen compounds on the rate of halogen transfer therefrom to alkyl radicals.

We determined the relative rate constants for abstraction of chlorine and bromine atoms from halogenating agents and arenesulfonyl chlorides by cyclohexyl and benzyl radical, following the procedure developed previ-

ously [2]. This procedure is based on competing abstraction of halogen from reagents  $X\text{Hlg}^1$  and  $Y\text{Hlg}^2$  by alkyl radicals generated by radical chain halogenation of the corresponding alkane under conditions excluding formation of molecular halogen. Using the absolute rate constant for bromine transfer from *N*-bromosuccinimide (NBS) to benzyl radical,  $k(\text{NBS}) = (5.0 \pm 0.3) \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$  [3], we estimated the absolute rate constants of halogen transfer in the examined reactions. The relative and absolute rate constants are given in Table 1.



In order to determine the rate constants for halogen abstraction from organohalogen substrates having a C–Hlg bond, the competing reaction technique was modified as follows.



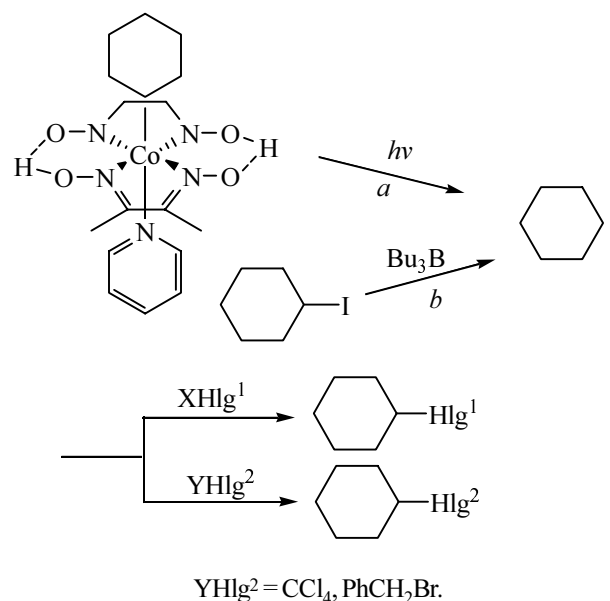
$Y\text{Hlg}^2$  – *N*-bromosuccinimide (NBS).

$$\frac{k(X\text{Hlg}^1)}{k(Y\text{Hlg}^2)} = \frac{[\text{RHlg}^1][Y\text{Hlg}^2]}{[\text{RHlg}^2][X\text{Hlg}^1]} \quad (1)$$

<sup>†</sup> Deceased.

Cyclohexyl radicals were generated by a nonchain process via decomposition of bis(dimethylglyoximate)(pyridine)cyclohexylcobalt(III)  $\text{CyCo}(\text{DmgH})_2\text{Py}$  under UV irradiation or via reaction of iodocyclohexane with tributylborane in the presence of traces of oxygen. Cyclohexyl radicals thus formed react along two pathways, i.e., they abstract halogen atom from the organohalogen compound under study or from  $\text{YHlg}^2$  reagent for which the rate constant of halogen abstraction is known. The relative rate constants were calculated from the concentration ratio of the resulting cyclohexyl halides and initial reactant concentrations according to formula (1).

The relative rate constants of halogen abstraction from the same organohalogen compounds, determined with the use of two methods for generation of cyclohexyl radicals, were very similar. This means that the



**Table 1.** Relative and absolute rate constants for halogen abstraction by cyclohexyl and benzyl radicals at 18°C

Radical $\text{R}^\cdot$	$\text{XHlg}^1$	$\text{YHlg}^2$	$k(\text{XHlg}^1)/k(\text{YHlg}^2)$	$k(\text{XHlg}^1), \text{l}/(\text{mol}\cdot\text{s})$
Cyclohexyl $\text{Cy}^\cdot$	4- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	NBS	$0.0012 \pm 0.0001$	$(1.5 \pm 0.9) \times 10^5$
	$\text{PhSO}_2\text{Cl}$	$\text{YHlg}^2$	$0.0093 \pm 0.0009$	$(1.2 \pm 0.7) \times 10^6$
	4- $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$		$0.12 \pm 0.01$	$(1.6 \pm 0.9) \times 10^7$
	4- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$		$4.8 \pm 0.4$	$(6.2 \pm 3.5) \times 10^8$
	$\text{PhSO}_2\text{NCl}_2$		$1.97 \pm 0.21$	$(2.6 \pm 1.4) \times 10^8$
	4- $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$		$2.95 \pm 0.25$	$(3.8 \pm 2.1) \times 10^8$
	$\text{PhSO}_2\text{N}(\text{Cl})\text{COPh}$		$1.1 \pm 0.1$	$(1.4 \pm 0.8) \times 10^8$
	$\text{CH}_3\text{C}_6\text{H}_4\text{ICl}_2$		$0.64 \pm 0.06$	$(8.3 \pm 1.7) \times 10^7$
	$\text{PhICl}_2$		$0.62 \pm 0.06$	$(8.0 \pm 1.6) \times 10^7$
	3- $\text{NO}_2\text{C}_6\text{H}_4\text{ICl}_2$		$0.58 \pm 0.05$	$(7.6 \pm 1.5) \times 10^7$
	4- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Br}$	$\text{CCl}_4$	$0.13 \pm 0.01$	$(6.5 \pm 0.8) \times 10^2$
	$\text{PhCH}_2\text{Br}$	$\text{YHlg}^2$	$0.9 \pm 0.1$	$(4.5 \pm 0.7) \times 10^3$
	4- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}$		$1.54 \pm 0.10$	$(7.7 \pm 0.9) \times 10^3$
	$\text{PhCHBrCH}_3$		$0.14 \pm 0.01$	$(7.0 \pm 0.5) \times 10^2$
	$\text{BrCH}_2\text{COOCH}_3$		$7.9 \pm 0.8$	$(3.9 \pm 0.6) \times 10^4$
	$\text{PhCH}_2\text{Cl}$	$\text{PhCH}_2\text{Br}$	$0.11 \pm 0.01$	$(4.9 \pm 0.9) \times 10^2$
	$\text{ClCH}_2\text{CN}$	$\text{YHlg}^2$	$0.56 \pm 0.06$	$(2.5 \pm 0.5) \times 10^3$
Benzyl $\text{PhCH}_2^\cdot$	$\text{PhSO}_2\text{NCl}_2$	NBS	$1.91 \pm 0.20$	$(9.6 \pm 1.4) \times 10^5$
	4- $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$	$\text{YHlg}^2$	$30.4 \pm 3.1$	$(1.5 \pm 0.2) \times 10^7$
	4- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$		$7.1 \pm 0.7$	$(3.5 \pm 0.5) \times 10^6$
	$\text{PhSO}_2\text{NCICOPh}$		$5.9 \pm 0.5$	$(3.6 \pm 0.4) \times 10^6$
	4- $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$		$1.04 \pm 0.01$	$(5.0 \pm 0.7) \times 10^2$

**Table 2.** Energies of the C–H and C–Hlg bonds in structurally related molecules

R in R–X	$E(\text{C–X})$ , kJ/mol		
	X = H [6]	X = Cl [7]	X = Br [7]
PhCH <sub>2</sub>	375.7	302.1	241.0
<i>t</i> -Bu	404.3	–	289.6
<i>i</i> -Pr	409.1	337.6	–
CH <sub>3</sub> CH <sub>2</sub>	423.0	347.2	283.7
CH <sub>3</sub>	438.9	354.0	296.6
Ph	473.1	400.4	336.6

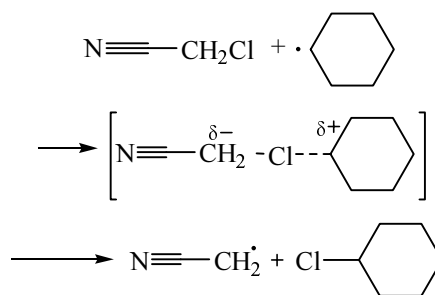
relative rate constants do not depend on the source of cyclohexyl radicals. For example, the relative rate constants of bromine abstraction from benzyl bromide  $k(\text{PhCH}_2\text{Br})/k(\text{CCl}_4)$ , 1-bromo-1-phenylethane  $k(\text{PhCHBrCH}_3)/k(\text{CCl}_4)$ , and methyl bromoacetate  $k(\text{BrCH}_2\text{COOCH}_3)/k(\text{CCl}_4)$  were  $0.9 \pm 0.1$ ,  $0.14 \pm 0.01$ , and  $7.9 \pm 0.8$ , respectively, when cyclohexyl radicals were generated from  $\text{CyCo}(\text{DmgH})_2\text{Py}$ , and  $0.73 \pm 0.10$ ,  $0.22 \pm 0.02$ , and  $11 \pm 1$ , when iodocyclohexane was used as a source of cyclohexyl radicals.

The rate constant for chlorine transfer from carbon tetrachloride to cyclohexyl radical is known:  $k(\text{CCl}_4) = (5.0 \pm 0.3) \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$  [4]. Using this value, we calculated the absolute rate constants of halogen transfer for the substrates under study (Table 1). The calculated absolute rate constant for bromine abstraction from  $\text{BrCH}_2\text{COOCH}_3$  by cyclohexyl radical,  $k(\text{BrCH}_2\text{COOCH}_3) = (3.9 \pm 0.6) \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$  was very consistent with that reported in [5] for bromine transfer from  $\text{BrCH}_2\text{COOCH}_2\text{CH}_3$  to a primary alkyl radical,  $k(\text{BrCH}_2\text{COOCH}_2\text{CH}_3) = 7 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ .

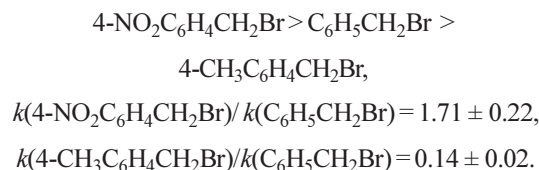
Our results allowed us to reveal some general relations holding in the halogen transfer stage. Decrease in the rate of bromine transfer to cyclohexyl radical in going from  $\text{PhCH}_2\text{Br}$  to  $\text{PhCHBrCH}_3$  (Table 1) indicates that the heat effect is not the only and determining factor affecting the reaction rate. Despite greater heat effect in the abstraction of bromine from  $\text{PhCHBrCH}_3$ , the lower reactivity of the latter as compared to  $\text{PhCH}_2\text{Br}$  is explained by destabilization of the polar transition state  $[\text{PhCHR}^{\delta-} \cdots \text{Br} \cdots \text{Cy}^{\delta+}]^\ddagger$  as a result of introduction of a donor methyl group. By contrast, the rate of bromine transfer from  $\text{BrCH}_2\text{COOCH}_3$  is greater than from  $\text{PhCH}_2\text{Br}$  due to higher electrophilicity of methyl bromoacetate as compared to benzyl bromide.

The data on chlorine transfer from  $\text{PhCH}_2\text{Cl}$  and  $\text{ClCH}_2\text{CN}$  to cyclohexyl radical also indicate that polar

effect is an important factor. Abstraction of chlorine from chloroacetonitrile is characterized by a higher rate than chlorine abstraction from benzyl chloride, though the heat effect of the former reaction is smaller. There are no published data on the energy of dissociation of the C–Cl bond in chloroacetonitrile; nevertheless, this energy may be presumed to exceed the corresponding energy for benzyl chloride on the basis of the following considerations. Analysis of published data on bond energies shows the existence of a rough correlation between  $E(\text{C–H})$  and  $E(\text{C–Cl})$  (Table 2). Depending on the hydrocarbon radical nature, the C–Cl bond is weaker by 13–21 kcal/mol than the respective C–H bond. The energies of the C–H bonds in acetonitrile (389.1 kJ/mol) and toluene (375.7 kJ/mol) [6] suggest that the C–Cl bond in chloroacetonitrile should be stronger than in benzyl chloride; therefore, the higher reactivity of chloroacetonitrile undoubtedly results from the reduced energy of the polar transition state due to effect of the electron-acceptor cyano group.



A more convenient model for estimation of the nucleophilicity of cyclohexyl radical in halogen transfer process is a series of substituted benzyl bromides  $\text{XC}_6\text{H}_4\text{CH}_2\text{Br}$ . The rate of bromine transfer from substituted benzyl bromides to cyclohexyl radical changes as follows:



Presumably, the substituent affects the stability of benzyl radicals, which leads to variation of the heat effect. Available ESR data on the substituent effect on the spin density in benzyl radicals are contradictory; it is generally believed that both donor and acceptor substituents induce spin density redistribution; the spin density on the benzylic carbon atom thus decreases, which should stabilize

the radical [8]. In addition, substituents can change the energy of the initial state due to dipole–dipole interaction with the C–Br bond. However, the recent experimental data on the energy of dissociation of the C–Br bond in benzyl bromides showed that it almost does not depend on the substituent within experimental error (1 kcal/mol) [9]; therefore, the effect of substituent on the stability of benzyl radical via delocalization of the unpaired electron, as well as on the energy of the initial state via dipole–dipole interaction, is negligible.

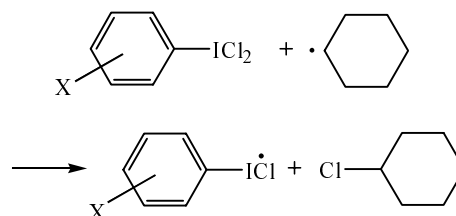
Thus the effect of substituent on the reaction rate cannot be related to the heat effect of bromine transfer. On the other hand, our kinetic data are very consistent with the concepts on charge separation in the transition state, according to which the rate of bromine transfer from substituted benzyl bromides to cyclohexyl increases as the electrophilicity of the substrate rises.

As with substituted benzyl bromides, the rate of chlorine abstraction from  $\text{ArSO}_2\text{Cl}$  by cyclohexyl radical increases in going to the nitro-substituted substrate and decreases when the substituent is a methyl group (Table 1). It is known that the rate of chlorine transfer from arenesulfonyl chlorides to benzyl radical also increases upon introduction of acceptor substituents into the benzene ring of the substrate ( $\rho = +0.31$ ) [10]. We have found no published data on the energy of the S–Cl bond in arenesulfonyl chlorides. Fu *et al.* [11] analyzed the effect of remote substituent Y in the aromatic ring on the energy of dissociation of the X–Z bond in  $\text{YC}_6\text{H}_4\text{–X–Z}$  molecules (RMP2/6-311++G\*\*//UB3LYP/6-31G\*) and found that substituent in the aromatic ring only slightly affects the energy of the C–H and C–F bonds in compounds  $\text{YC}_6\text{H}_4\text{–CH}_2\text{–Z}$  where Z = H, F, which is well consistent with the experimental data [9]. However, the substituent effect on the energy of dissociation of the X–Z bond in  $\text{YC}_6\text{H}_4\text{–S–Z}$  and  $\text{YC}_6\text{H}_4\text{–NH–Z}$  (Z = H, F) turned out to be fairly strong. In going from Y = 4- $\text{NO}_2$  to Y = 4- $\text{CH}_3$ , the energy of the C–H bond in  $\text{YC}_6\text{H}_4\text{CH}_3$  changes by 0.7 kcal/mol, the energy of the S–H bond in  $\text{YC}_6\text{H}_4\text{SH}$  changes by 2.7 kcal/mol, and the energy of the N–H bond in  $\text{YC}_6\text{H}_4\text{NH}_2$  changes by 3.9 kcal/mol. In all cases, acceptor substituents increase the energy of dissociation of the corresponding bond, and the given values agree satisfactorily with the experimental data. Taking into account the above noted relation between the X–H and X–Hlg bond energies, we can expect an appreciable dependence of the energy of dissociation of the S–Cl bond in arenesulfonyl chlorides on the substituent in the aromatic ring. Therefore, the observed acceleration of chlorine

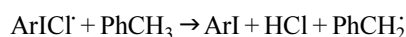
abstraction from arenesulfonyl chlorides by cyclohexyl radical on introduction of electron-acceptor substituents can be interpreted exclusively in terms of the polar effect. Thus the data given in Table 1 indicate a fairly high nucleophilicity of cyclohexyl radical in halogen abstraction processes.

It was shown previously that alkyl radicals act as moderately nucleophilic species in hydrogen transfer processes. For example, hydrogen abstraction from a series of substituted toluenes with undecyl radicals at 80°C is characterized by a positive  $\sigma$  value ( $0.49 \pm 0.04$ ) [12]. Alkyl radicals also exhibit fairly high nucleophilicity in the addition to alkenes [13]. Unlike radical abstraction of hydrogen, where the heat effect is often the main factor determining the reaction rate, the heat effect in halogen transfer is secondary while the main factor is polar effect of substituent on the transition state energy.

Nucleophilic character of alkyl radicals appreciably affects the rate of chlorine abstraction from (dichloroiodo)arenes by cyclohexyl radicals and from *N,N*-dichloroarenesulfonamides by cyclohexyl and benzyl radicals. While studying the selectivity of radical chlorination of hydrocarbons and their derivatives with (dichloroiodo)arenes, electron-donor substituents in the aromatic ring were shown to stabilize arylchloro- $\lambda^3$ -iodanyl radical, and electron-acceptor substituents, to destabilize.



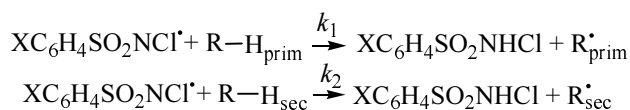
In the abstraction of hydrogen atom from  $\text{PhCH}_3$  by arylchloro-iodanyl radicals, the  $k_{\text{H}}/k_{\text{D}}$  values were found to decrease and the  $|\sigma|$  values were found to increase on introduction of acceptor substituents into  $\text{ArICl}_2$  molecules [14]. The kinetic isotope effect  $k_{\text{H}}/k_{\text{D}}$  is  $2.6 \pm 0.2$  for hydrogen abstraction by  $3\text{-NO}_2\text{C}_6\text{H}_4(\text{Cl})\text{I}^\cdot$  and  $3.7 \pm 0.2$  for hydrogen abstraction by  $\text{Ph}(\text{Cl})\text{I}^\cdot$ , and the corresponding  $\sigma$  values are  $-1.25 \pm 0.09$  and  $-2.75 \pm 0.47$ , respectively [14].



An analogous conclusion follows from analysis of the relation between the structure of  $\text{ArI}$  molecules and the stability of their complexes with chlorine atom. Studies performed with a wide series of organohalogen solvents

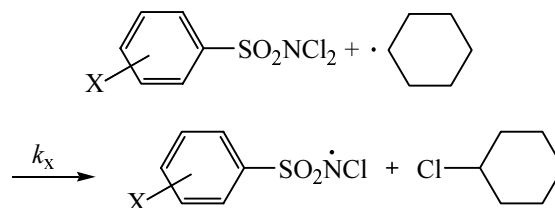
showed that the stability of  $\sigma$ -complexes formed by chlorine atom and organohalogen solvent molecule increases upon introduction of donor substituents into the latter, other conditions being equal [15]. Therefore, the rate of halogen transfer may be expected to increase in going from electron-acceptor substituents to electron-donor. On the other hand, the presence of electron-donor substituents in a (dichloroiodo)arene reduces its electrophilicity, and hence the rate of chlorine transfer should also decrease. These two factors oppositely affect the reaction rate and compensate each other to a considerable extent. As a result, introduction of both acceptor and donor substituents almost does not influence the rate of halogen abstraction: the absolute rate constants for chlorine abstraction from 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>ICl<sub>2</sub>, PhICl<sub>2</sub>, and 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>ICl<sub>2</sub> by cyclohexyl radicals are  $(7.6 \pm 1.5) \times 10^7$ ,  $(8.0 \pm 1.6) \times 10^7$ , and  $(8.3 \pm 1.7) \times 10^7$  l mol<sup>-1</sup> s<sup>-1</sup>, respectively.

Substituents in the aromatic ring of *N,N*-dichloroarenesulfonamides weakly affect the rate of halogen abstraction therefrom by cyclohexyl radicals (Table 1). It should be noted that introduction of both acceptor and donor substituents into the aromatic ring of ArSO<sub>2</sub>NCl<sub>2</sub> accelerates the process. It is known that electron-donor substituents stabilize *N*-chloro(arylsulfonyl)aminy radicals [16], thus increasing the heat effect of the halogen transfer reaction. The less stable is the radical abstracting a hydrogen atom, the more reactive and the less sensitive to the nature of the C–H bond is it, and the lesser is the kinetic isotope effect. We can conclude that *N*-chloro-4-methylphenylsulfonylaminy radical (relative rate constant for abstraction of hydrogen from hexane  $k_2/k_1 = 38.6 \pm 3.3$  and  $k_H/k_D = 11.2 \pm 0.7$ ) is more stable than *N*-chloro(phenylsulfonyl)aminy radical ( $k_2/k_1 = 36.8 \pm 1.5$  and  $k_H/k_D = 8.2 \pm 1.6$ ) and that *N*-chloro-4-nitrophenylsulfonylaminy radical ( $k_2/k_1 = 24.4 \pm 2.7$  and  $k_H/k_D = 8.1 \pm 0.5$ ) is less stable than *N*-chloro(phenylsulfonyl)aminy radical [16].

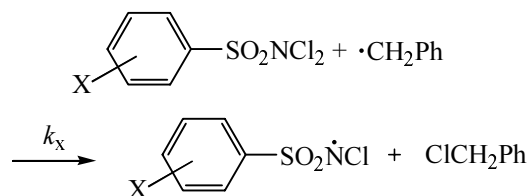


Taking into account the data given in [16], the rate of chlorine transfer from *N,N*-dichloroarenesulfonamides to cyclohexyl (or benzyl) radicals should increase upon introduction of donor substituents into the aromatic ring of the substrate and decrease upon introduction of acceptor substituents.

The results of quantum-chemical calculations also indicate that acceptor substituents increase the bond energy. The energy of dissociation of the N–H bond in anilines increases upon introduction of acceptor substituents and decreases upon introduction of donor substituents into the aromatic ring, and this relation is stronger than that observed for ArSH [11]. Therefore, the rate of halogen transfer should increase upon introduction of donor groups into the benzene ring of PhSO<sub>2</sub>NCl<sub>2</sub>. On the other hand, donor substituents reduce the electrophilicity of the substrate (due to destabilization of transition state with charge separation), which should produce the opposite effect on the rate of chlorine transfer. Thus the substituent exerts opposite effects on the reaction heat and electrophilicity of the reaction center, leading to a complex dependence of the rate of halogen transfer on the substituent nature.



As might be expected taking into account similar nucleophilicities of cyclohexyl and benzyl radicals, chlorine transfer to benzyl radical is less exothermic, and the rate of chlorine abstraction by benzyl radical is lower, as compared to cyclohexyl radical, while the  $k_X/k_H$  value is greater.



Here, the character of the substituent effect on the rate of chlorine transfer does not change (Table 1). Increase in the nucleophilicity of substituted hexenyl radicals in the series  $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2^\bullet < \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CHCH}_3^\bullet < \text{CH}_2=\text{CHCH}_2\text{CH}_2=\text{CH}_2\text{C}(\text{CH}_3)_2^\bullet$  is known to be accompanied by increase in the rate of chlorine transfer from electrophilic carbon tetrachloride [17]. Obviously, this series does not correspond to the order of variation of the heat effect. The rate of chlorine transfer from CCl<sub>4</sub> also increases in going from  $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2^\bullet$  to  $\text{CH}_3\text{CH}_2\text{OC}(\text{CH}_3)_2^\bullet$  [18], which indicates that nucleophilicity of the radical is the main factor determining its reactivity.

Thus the electrophilicity of an organohalogen compound is an important factor affecting the rate of halogen abstraction by alkyl radicals from both weakly reactive substrates, such as  $\text{ArCH}_2\text{Br}$ ,  $\text{PhCHBrCH}_3$ ,  $\text{BrCH}_2\text{COOCH}_3$ ,  $\text{ArSO}_2\text{Cl}$ ,  $\text{PhCH}_2\text{Cl}$ , and  $\text{NCCH}_2\text{Cl}$ , and strong halogenating agents, such as  $\text{ArICl}_2$  and  $\text{ArSO}_2\text{NCl}_2$ . This makes it possible to predict change in the rate of halogen transfer upon variation of the structure of both organohalogen substrate and the radical.

It is known that the rate of polymerization initiation and hence the polydispersity coefficient depend on the system organohalogen compound–transition metal complex [19]. The higher the rate of initiation, the lower the polydispersity coefficient. We showed that the rate of halogen abstraction from organohalogen compounds by nucleophilic cyclohexyl radicals is determined by both the reaction heat and electrophilicity of the substrate. Presumably, the same applies to the rate of halogen transfer from organic halogen compounds to a more nucleophilic (as compared to cyclohexyl radical) transition metal complex. Therefore, the rate of initiation of controlled radical polymerization should increase as the electrophilicity of halogen-containing substrate rises. This assumption is supported by published data on the polydispersity coefficients for controlled radical polymerization: the use of 4-cyanobenzyl bromide, which is more electrophilic than 4-methylbenzyl bromide, in the polymerization of styrene in the presence of  $\text{CuBr}$  and bipyridine leads to reduction in the polydispersity coefficient  $M_w/M_n$  (where  $M_w$  is the weight-average molecular weight, and  $M_n$  is the number-average molecular weight) from 1.17 to 1.10 [19].

## EXPERIMENTAL

Qualitative and quantitative analyses were performed by gas–liquid chromatography on a Tsvet-104 instrument equipped with a flame ionization detector and  $3000 \times 3\text{-mm}$  columns packed with 5% of SE-30 on Inerton N-Super (0.16–0.20 mm) and 10% of XE-60 on Chromosorb W-AW (0.16–0.20 mm); carrier gas argon, flow rate 25 ml/min; injector temperature 150°C; oven temperature 135°C.

Cyclohexane, toluene, methylene chloride, cyclohexyl iodide, substituted benzyl bromides, arenesulfonyl chlorides, benzyl chloride, chloroacetonitrile, methyl bromoacetate, and 1-bromo-1-phenylethane were purified by standard procedures [20]; their physical constants were in agreement with published data. Tributylborane [21], bis(dimethylglyoximate)(pyridine)cyclohexylcobalt(III) [22], *N,N*-dichloroarenesulfonamides [23], and

(dichloriodo)arenes [24] were synthesized by known methods. The purity of the halogenating agents  $\text{XHlg}^1$  was no less than 98% according to the iodometric titration data [25].

The relative rate constants  $k(\text{XHlg}^1)/k(\text{YHlg}^2)$  for halogen abstraction from  $\text{ArSO}_2\text{Cl}$ ,  $\text{ArSO}_2\text{NCl}_2$ , and  $\text{ArICl}_2$  were reported in [2].

**Procedure for determination of the relative rate constants  $k(\text{XHlg}^1)/k(\text{YHlg}^2)$  for halogen abstraction from organohalogen substrates by cyclohexyl radicals.** *a. Using  $\text{CyCo}(\text{DmgH})_2\text{Py}$  as source of cyclohexyl radicals.* A test tube was charged with 18 mg (0.04 mmol) of  $\text{CyCo}(\text{DmgH})_2\text{Py}$ , 2.4 mmol of an organohalogen compound  $\text{XHlg}^1$ , 1.2–4.8 mmol of  $\text{CCl}_4$  or  $\text{PhCH}_2\text{Br}$ , and 10 mg (0.068 mmol) of *o*-dichlorobenzene, and the mixture was adjusted to a volume of 1.2 ml by adding methylene chloride. The mixture was purged with a slight stream of argon (5–7 ml/min) over a period of 5 min and was irradiated with UV light over a period of 5 min at  $18.0 \pm 0.5^\circ\text{C}$  using an OKN-11 lamp at a distance of 0.5 m. The mixture was then passed through a column charged with silica gel using hexane as eluent, and the eluate was analyzed by GLC. Analogous experiments were performed with various amounts of  $\text{YHlg}^2$ . From the obtained data, the cyclohexyl halide concentration ratios  $[\text{CyHlg}^1]/[\text{CyHlg}^2]$  were plotted against the initial reactant concentration ratio  $[\text{XHlg}^1]/[\text{YHlg}^2]$ . The slope of the resulting straight line was equal to the relative rate constant  $k(\text{XHlg}^1)/k(\text{YHlg}^2)$ .

*b. Using cyclohexyl iodide as source of cyclohexyl radicals.* A test tube was charged with 8.4 mg (0.04 mmol) of cyclohexyl iodide, 2.4 mmol of an organohalogen compound  $\text{XHlg}^1$ , 1.2–4.8 mmol of carbon tetrachloride, and 10 mg (0.068 mmol) of *o*-dichlorobenzene, and the mixture was adjusted to a volume of 1.2 ml by adding methylene chloride. The mixture was purged with a slight stream of argon (5–7 ml/min) over a period of 5 min, 2–8 ml of a 0.137 M solution of tributylborane in carbon tetrachloride (0.5–2 mol % with respect to  $\text{XHlg}^1$ ) was added, and the mixture was kept for 15 min at  $18.0 \pm 0.5^\circ\text{C}$  and analyzed by GLC. Analogous experiments were performed with various amounts of  $\text{YHlg}^2$ .

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