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Rate Constants of Halogen Abstraction from Halogenating Agents by Alkyl Radicals

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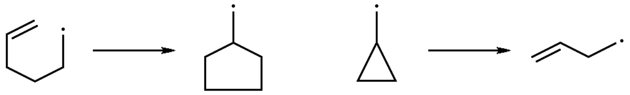
Abstract—A procedure has been developed for determination of the relative rate constants for halogen transfer from a number of halogenating agents to alkyl radicals by the competing reactions technique. In combination with the known data, the developed procedure allows estimation of absolute rate constants of the halogen transfer stage.

Halogen transfer to alkyl radicals is a key stage in the radical chain halogenation of hydrocarbons, as well as in the radical addition of a number of reagents at multiple carbon–carbon bonds. In the latter case, it is especially important to know the rate constant of the halogen transfer stage, for it is responsible for stereoselectivity of the process. Interest in halogen transfer reactions increased considerably in the recent years due to wide application of controlled/"living" radical polymerization of alkenes in the polymer chemistry, which leads to formation of polymers with a required molecular weight and a low polydispersity coefficient [1]. Insofar as controlled/"living" radical polymerization is often initiated by the system organic halogen compound–transition metal complex, data on the rates of halogen transfer are necessary to describe polymerization processes on a quantitative level.

As a rule, the absolute rate constants of halogen transfer are measured by the flash radiolysis technique, but this procedure involves considerable experimental difficulties [2]. Most data were obtained by the method of competing reactions, determination of relative rate constants, and calculation of the absolute rate constants using the known rate constant for a reference reaction. In the recent years, radical rearrangements are widely used as such reference reactions; their absolute rate constants are measured by the ESR method (radical clocks) [3]. Examples are the cyclohexenyl–cyclopentyl and cyclopropylmethyl–homoallyl rearrangements whose rate constants at 25°C are 2.2×10^5 [4] and 9.4×10^7 s^{-1} [5], respectively (Scheme 1). However, the applicability of these procedures is strongly limited, especially in the case of reactive halogen derivatives which can readily be involved in radical substitution and addition processes. As a result, both initial compounds and products give rise to a number of side reactions which considerably reduce the accuracy of kinetic measurements. For example, the rate constant of chlorine atom transfer from *tert*-butyl hypochlorite to primary alkyl radicals was estimated at 3.8×10^5 [6] and 2.6×10^9 l × mol^{-1} s^{-1} [7].

Scheme 1.



Taking into account that information on the rate constants of halogen atom transfer to carbon-centered radicals from highly reactive halogenating agents is necessary for both complete kinetic desription of radical halogenation reactions and prediction of regio- and stereoselectivity of radical addition processes, in the present work we tried to develop a procedure for determination of relative rate constants and estimation of absolute rate constants for halogen atom transfer from a wide series of halogenating agents, which would be free from the above disadvantages. For this purpose, we used a modified method of competing reactions. Cyclohexyl radicals generated in the radical chain halogenation of cyclohexane abstract

Scheme 2.

$$RH + X^{\bullet} \longrightarrow R^{\bullet} + HX$$

$$R^{\bullet} + XHlg^1 \longrightarrow RHlg^1 + X^{\bullet}$$

$$R^{\bullet} + XHlg^2 \longrightarrow RHlg^2 + X^{\bullet}$$

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either the halogen atom from the halogenating agent or iodine atom from molecular iodine or methyl iodide (Scheme 2).

In some cases methanesulfonyl chloride was taken as reference ($YHlg^2$). The relative rate constants were calculated from the ratio of the resulting monohalogen derivatives. Insofar as the rate constants for iodine atom transfer from molecular iodine and for chlorine atom transfer from methanesulfonyl chloride to cyclohexyl radical are known, we can calculate the corresponding absolute rate constants. All experiments were carried out at 18.0±0.5°C.

The application of this procedure is valid only when the halogenating agent does not react with the reference substrate. Moreover, in order to increase the accuracy, such reference substrate must be taken that the rates of halogen transfer would not be strongly different. For the reactions in the presence of molecular iodine ($YHlg^2 = I_2$), the above requirement is met for the following reagents $XHlg^1$: *N*-bromosuccinimide (NBS), *tert*-butyl hypobromite, *N*-bromophthalimide (NBP), *N*,*N*-dibromobenzenesulfonamide $PhSO_2NBr_2$, and *N*-bromosaccharin (NBSa). The lack of halogen exchange was proved by measuring the relative rate constants for abstraction of bromine and iodine atoms at various ratios of the brominating agent and molecular iodine. Analysis of the kinetic scheme shows that the relative rate constant should change if the following equilibrium exists:

$$XBr + I_2 \rightleftharpoons XI + IBr$$

According to the data given in Table 1, the ratio $k(Br)/k(I)$ remains almost unchanged on variation of the $[NBS]_0/[I_2]_0$ ratio by a factor of 5. In addition, the relative rate constants obtained with different reference substrates were similar (see below). In the other cases methyl iodide was taken as reference ($YHlg^2$), and the $XHlg^1$ reagents were NBS, *N*-chlorosuccinimide (NCS), *tert*-butyl hypochlorite, *tert*-butyl hypobromite, and *N*,*N*-dichlorobenzenesulfonamide.

Table 1. Relative rate constants of halogen atom transfer in the system NBS/I_2; $[NBS]_0$ = 0.056 M

$[I_2]_0$, M	$[NBS]_0/[I_2]_0$	$k(Br)/k(I)$
0.0075	7.49	0.0132
0.0067	8.39	0.0169
0.0035	16.23	0.0147
0.0017	32.64	0.0159
0.0015	36.40	0.0160

Table 2. Relative rate constants for halogen abstraction by cyclohexyl and benzyl radicals

Radical $R^\bullet$	Reagent $XHlg^1$	Reagent $YHlg^2$	$k(XHlg^1)/k(YHlg^2)$
cyclo-$C_6H_{11}^\bullet$	NBS	I_2	0.015±0.002
	t-BuOBr		0.165±0.015
	NBP		0.95±0.09
	$PhSO_2NBr_2$		1.36±0.10
	NBSa		1.76±0.25
	NBS	$MeSO_2Cl$	290±30
	NBSa		15400±500
	$PhSO_2NBr_2$		19300±2300
	NCS	MeI	270±40
	NBS		1520±80
	$PhSO_2NCl_2$		2880±250
	t-BuOCl		8200±1000
	t-BuOBr		23000±2000
$PhCH_2^\bullet$	NBS	I_2	0.081±0.005
	NBSa		3.2±0.2

We previously showed that radical chain halogenation processes with overwhelming majority of halogenating agents follow two competing pathways [8, 9] (Scheme 3). Pathway *b* involves formation of molecular halogen in the system, which should affect the rate of halogen atom transfer. In addition, halogen radicals are capable of reacting with methyl iodide with liberation of molecular iodine, which may also distort the results of measurements. Therefore, experiments were carried out under dark initiation with tributylborane up to a low conversion of the halogenating agent. According to our previous data [8], under these conditions the process follows only

Scheme 3.

Pathway *a*

$$RH + X^\bullet \longrightarrow R^\bullet + HX$$

$$R^\bullet + XHlg \longrightarrow RHlg + X^\bullet$$

Pathway *b*

$$RH + Hlg^\bullet \longrightarrow R^\bullet + HHlg$$

$$R^\bullet + Hlg_2 \longrightarrow RHlg + Hlg^\bullet$$

$$HHlg + XHlg \rightleftharpoons XH + Hlg_2$$

pathway *a*, and no molecular halogen is formed. An analogous series of experiments was carried out in order to verify that iodine is not abstracted from alkyl iodides by the above reagents (Table 2). The results showed that the relative rate constant almost does not depend on the concentration ratio of the halogenating agent and reference substrate. No reaction with alkyl iodides was observed in the absence of initiator. For example, keeping of a mixture of hexyl iodide and NBS for 2 h did not result in formation of hexyl bromide.

The fact that the relative rate constants do not depend on the mode of generation of the $R^{\cdot}$ radical can be regarded as an additional proof for validity of the proposed procedure. We have determined the ratios $k(\mathrm{NBS})/k(\mathrm{I_2})$ and $k(\mathrm{NBSa})/k(\mathrm{I_2})$ for halogen atom transfer to benzyl radical generated in two ways: by radical chain halogenation of toluene and by decomposition of $PhCH_2SO_2Cl$ under UV irradiation:

$$\mathrm{PhCH_2SO_2Cl} \longrightarrow \mathrm{PhCH_2^{\cdot}} + \mathrm{SO_2} + \mathrm{Cl^{\cdot}}$$

The relative rate constants of bromine abstraction from NBS and NBSa, $k(\mathrm{NBS})/k(\mathrm{I_2})$ and $k(\mathrm{NBSa})/k(\mathrm{I_2})$, were 0.081 ± 0.005 and 3.2 ± 0.2, respectively, when toluene was used as a source of benzyl radicals and 0.074 ± 0.005 and 3.0 ± 0.2 when the radical species were generated from $PhCH_2SO_2Cl$. These data show that the relative rate constants do not depend on the mode of generation of alkyl radical.

Methanesulfonyl chloride was used as reference substrate for NBS, NBSa, and $PhSO_2NBr_2$. The halogenation of cyclohexane was performed in methylene chloride in the presence of 0.5–2 mol % of tributylborane as initiator. The relative rate constants were calculated from the concentration ratio of cyclohexyl bromide (or cyclohexyl chloride, depending on the halogenating agent) and cyclohexyl iodide, which was determined by GLC. In experiments with methanesulfonyl chloride as reference substrate, the ratio of cyclohexyl bromide and cyclohexyl chloride was determined. The results were treated by several methods.

Table 3. Relative rate constants of halogen atom transfer for the pair NCS/MeI, depending on the reactant ratio

$[\mathrm{NCS}]_0$, M	$[\mathrm{MeI}]_0$, M	$[\mathrm{NCS}]_0/[\mathrm{MeI}]_0$	$k(\mathrm{Cl})/k(\mathrm{I})$
0.0397	13.38	0.0030	264
0.0470	10.70	0.0044	258
0.0361	8.03	0.0045	287
0.0277	5.35	0.0052	244
0.0211	2.68	0.0079	262

(1) When the reference substrate was molecular iodine, the relative rate constant for abstraction of halogen atom $k(\mathrm{XHlg})/k(\mathrm{I_2})$ was calculated by the formula

$$k(\mathrm{XHlg})/k(\mathrm{I_2}) = \frac{\log(1 - [cyclo\text{-}\mathrm{C_6H_{11}Hlg}]/[\mathrm{XHlg}]_0)}{\log(1 - [cyclo\text{-}\mathrm{C_6H_{11}I}]/[\mathrm{I_2}]_0)}.$$

(2) The plot of the concentration ratio of cyclohexyl bromide (cyclohexyl chloride) and cyclohexyl iodide versus conversion

$$[cyclo\text{-}\mathrm{C_6H_{11}Hlg}]_0/[cyclo\text{-}\mathrm{C_6H_{11}I}]_0 = (17.48 \pm 0.62) - (0.17 \pm 0.02)([cyclo\text{-}\mathrm{C_6H_{11}Hlg}]_0 + [cyclo\text{-}\mathrm{C_6H_{11}I}]_0)/[\mathrm{XHlg}],\ R^2 = 0.9574,$$

was extrapolated to the zero conversion. The value of $[cyclo\text{-}\mathrm{C_6H_{11}Hlg}]_0/[\mathrm{cyclo\text{-}C_6H_{11}I}]_0$ was then used to calculate the relative rate constants by the formula

$$k(\mathrm{XHlg})/k(\mathrm{YI}) = [cyclo\text{-}\mathrm{C_6H_{11}Hlg}]_0[\mathrm{YI}]/[cyclo\text{-}\mathrm{C_6H_{11}I}]_0 \times [\mathrm{XHlg}]\ (\mathrm{YI} = \mathrm{MeI},\ \mathrm{I_2}).$$

(3) The plot of $[cyclo\text{-}\mathrm{C_6H_{11}Hlg}]_0/[cyclo\text{-}\mathrm{C_6H_{11}I}]_0$ versus $[\mathrm{XHlg}]_0/[\mathrm{YI}]_0$ was treated by the least-squares procedure. The slope of the resulting straight line corresponds to the relative rate constant $k(\mathrm{XHlg})/k(\mathrm{YI})$: $[cyclo\text{-}\mathrm{C_6H_{11}Hlg}]_0/[cyclo\text{-}\mathrm{C_6H_{11}I}]_0 = (0.34 \pm 3.12) + (23\,000 \pm 2000)[\mathrm{XHlg}]/[\mathrm{YI}]$, $R^2 = 0.9882$. The free term in this equation can be neglected (within the experimental error).

The relative rate constants calculated by the three methods are well consistent with each other. For example, they are $(2.2 \pm 0.2) \times 10^4$, $(2.2 \pm 0.2) \times 10^4$, and $(2.3 \pm 0.2) \times 10^4$, respectively, for the pair *tert*-butyl hypobromite/methyl iodide. Table 3 gives the relative rate constants for all reagents, calculated by method (3).

The absolute rate constants of halogen atom transfer from methanesulfonyl chloride and molecular iodine to cyclohexyl radical are known and are equal to $(2.9 \pm 0.8) \times 10^5$ [10] and $(1.2 \pm 0.5) \times 10^{10}$ $\mathrm{l\,mol^{-1} \times s^{-1}}$ [11], respectively. The absolute rate constant of iodine atom transfer from methyl iodide, $(8.7 \pm 3.4) \times 10^4$ $\mathrm{l\,mol^{-1}\,s^{-1}}$, was calculated using the relative rate constants $k(t\text{-BuOBr})/k(\mathrm{I_2})$ and $k(t\text{-BuOBr})/k(\mathrm{CH_3I})$ and the known value of $k(\mathrm{I_2})$. Table 4 contains the absolute rate constants thus obtained.

Comparison of the absolute rate constants obtained with the use of different reference substrates shows that the developed procedure is sufficiently correct. As a rule, the resulting values coincide within an order of magnitude (Table 4). Also, a good agreement was observed between our data and those reported in the literature. For example, bromine atom transfer from *N*-bromophthalimide is a diffusion-controlled process, and the calculated rate constant is 1.2×10^{10} $\mathrm{l\,mol^{-1}\,s^{-1}}$ [12] which agrees well with our value $(1.1 \pm 0.5) \times 10^{10}$ $\mathrm{l\,mol^{-1}\,s^{-1}}$. In keeping with our data, bromine atom transfer processes from *N*-bromosaccharin and *N*,*N*-dibromobenzenesulfonamide are also controlled by diffusion, which is very consistent with a fairly high reactivity of these halogenating agents and sufficiently long radical chains in their reactions [13]. While considering the selectivity of radical halogenation with regard to the nature of N-centered radical, we have concluded that the selectivity increases in parallel with thermodynamic stability of the corresponding radical. Such increase in stability should lead to acceleration of the halogen transfer stage, in keeping with the data in Table 4. Our results also confirm the validity of the procedure for determination of rate constants of chlorine atom transfer to alkyl radicals, which was reported in [7]. Then, the data given in [6] should be regarded as strongly underestimated.

The developed procedure was also tested through estimation of the rate of bromine atom transfer from bromotrichloromethane to cyclohexyl radical. For this purpose, the following relative rate constants were measured: $k(\mathrm{CBrCl_3})/k(\mathrm{PhSO_2NClCOPh}) = 1.20 \pm 0.15$ and $k(\mathrm{PhSO_2NClCOPh})/k(\mathrm{NBS}) = 1.1 \pm 0.1$. Using the k(NBS) value, $(1.3 \pm 0.9) \times 10^8$ $\mathrm{l\,mol^{-1}\,s^{-1}}$ (average value from Table 4), we have calculated $k(\mathrm{CBrCl_3}) = (1.7 \pm 1.2) \times 10^8$ $\mathrm{l\,mol^{-1}\,s^{-1}}$, which is in a good agreement with available experimental data obtained by the "radical clock" technique. The following values were given for the rate constant of bromine atom abstraction from bromotrichloromethane: 2.6×10^8 (*n*-butyl radical, 80°C) and 6.5×10^8 $\mathrm{l\,mol^{-1}\,s^{-1}}$ (cyclopropylmethyl radical, 25°C) [14]. We can conclude that our procedure is sufficiently general and that it can be applied to estimation of absolute rate constants for halogen atom transfer from a wide series of reagents.

Table 4. Absolute rate constants of halogen atom transfer from halogenating agents

Reagent $\mathrm{XHlg^1}$	Reference substrate	$k(\mathrm{XHlg^1})$, $\mathrm{l\,mol^{-1}\,s^{-1}}$
NCS	MeI	$(2.3 \pm 0.9) \times 10^7$
NBS	MeI	$(1.3 \pm 0.5) \times 10^8$
$\mathrm{PhSO_2NCl_2}$	MeI	$(2.5 \pm 1.0) \times 10^8$
t-BuOCl	MeI	$(7.2 \pm 2.8) \times 10^8$
t-BuOBr	MeI	$(2.0 \pm 0.8) \times 10^9$
NBS	$\mathrm{I_2}$	$(1.7 \pm 0.7) \times 10^8$
NBSa	$\mathrm{I_2}$	$(2.1 \pm 0.8) \times 10^{10}$
t-BuOBr	$\mathrm{I_2}$	$(2.0 \pm 0.8) \times 10^9$
NBP	$\mathrm{I_2}$	$(1.1 \pm 0.5) \times 10^{10}$
$\mathrm{PhSO_2NBr_2}$	$\mathrm{I_2}$	$(1.6 \pm 0.7) \times 10^{10}$
NBS	$\mathrm{MeSO_2Cl}$	$(8.3 \pm 2.4) \times 10^7$
NBSa	$\mathrm{MeSO_2Cl}$	$(4.5 \pm 1.3) \times 10^9$
$\mathrm{PhSO_2NBr_2}$	$\mathrm{MeSO_2Cl}$	$(5.6 \pm 1.6) \times 10^9$

EXPERIMENTAL

Qualitative and quantitative analysis of the reaction mixtures was performed by GLC on a Tsvet-104 chromatograph equipped with a flame ionization detctor; carrier gas argon, flow rate 25 ml/min; 3000 × 3-mm columns packed with 5% of SE-30 on Inerton N-Super (0.16–0.20 mm) or 10% of XE-60 on Chromosorb W-AW (0.16–0.20 mm); injector temperature 150°C; oven temperature 135°C.

Cyclohexane, toluene, methanesulfonyl chloride, methyl iodide, *N*-bromosuccinimide, and methylene chloride were purified by standard procedures [15]. The physical constants of all compounds and solvents were consistent with published data. *N*,*N*-Dichlorobenzenesulfonamide [16], *N*-chlorosuccinimide [17], *t*-butyl hypochlorite, *t*-butyl hypobromite [18], *N*,*N*-dibromobenzenesulfonamide, and *N*-bromosaccharin [19] were synthesized by known methods. According to the iodometric data [18], the halogenating agents $\mathrm{XHlg^1}$ contained no less than 98% of the main substance.

***N*-Benzoyl-*N*-chlorobenzenesulfonamide.** *N*-Benzoylbenzenesulfonamide, 1.5 g (0.0057 mol), was dissolved in 10 ml of *tert*-butyl hypochlorite, and the mixture was kept for 4 days at 5°C. The precipitate was filtered off, washed with a small amount of ice water, dried in a vacuum desiccator over anhydrous $\mathrm{CaCl_2}$, and recrystallized from chloroform. Yield 1.25 g (74%), mp 124–126°C; purity 97.9% (according to the iodometric data). Found, %: C 53.37; H 3.98; N 4.62. $\mathrm{C_{13}H_{10}ClNO_3S}$. Calculated, %: C 52.80; H 3.41; N 4.74.

Reaction of halogenating agents $\mathrm{XHlg^1}$ with alkyl halides. An ampule was charged with 4.2 g (19.81 mmol) of 1-hexyl iodide, 0.09639 g (0.5415 mmol) of NBS, and 0.006 mmol of *o*-dichlorobenzene (as chromatographic standard), and the mixture was kept for 2 h at 18.0 ± 0.5°C. It was then treated with 10 ml of an acidified 20% aqueous solution of KI. According to the GLC data, the amount of 1-bromohexane in the reaction mixture did not exceed 0.0004 mmol.

Analogous experiments were carried out with the other halogenating agents ($PhSO_2NBr_2$, *t*-BuOBr, and NCS); in all cases, no more than 0.001 mmol of 1-bromohexane or 1-chlorohexane was formed.

Determination of the relative rate constants $k(XHlg^1)/k(I_2)$ of halogen atom abstraction by benzyl radicals generated from $PhCH_2SO_2Cl$. A tubular quartz reactor (internal diameter ~0.5 cm) was charged with 11.43 mg (0.06 mmol) of phenylmethanesulfonyl chloride, 0.06 mmol of halogenating agent $XHlg^1$, 0.006 mmol of *o*-dichlorobenzene (as chromatographic standard), and a required amount of I_2 (0.002–0.02 mmol). The volume of the mixture was adjusted to 0.6 ml by adding methylene chloride, and the mixture was purged with a weak stream of argon (5–7 ml/min). The mixture was irradiated by UV light using an OKN-11 lamp which was placed at a distance of 0.5 m from the reactor, maintaining the temperature at 18.0 ± 0.5°C. As in the preceding experiment, the mixture was treated with an acidified 20% aqueous solution of KI, and the organic phase was analyzed by GLC.

General procedure for determination of the relative rate constants $k(XHlg^1)/k(YHlg^2)$ for halogen atom abstraction. To 0.1 ml (0.93 mmol) of cyclohexane (or 0.94 mmol of toluene) we added 0.06 mmol of halogenating agent $XHlg^1$, 0.006 mmol of *o*-dichlorobenzene (as chromatographic standard), and 0.002–2 mmol of $YHlg^2$. The volume of the mixture was adjusted to 0.6 ml by adding methylene chloride, the ampule was purged with a weak stream of argon (5–7 ml/min), and tributylborane was added as initiator (2–8 μl of a 0.137 M solution in CCl_4; 0.5–2 mol % with respect to $XHlg^1$). Every 5 min, a 0.1-ml sample was withdrawn and transferred into 0.5 ml of an acidified 20% aqueous solution of KI to decompose unreacted $XHlg^1$. The organic phase was analyzed by GLC.

A. Determination of the relative rate constants $k(XHlg^1)/k(I^2)$ for halogen atom abstraction by cyclohexyl radicals. A dark glass 1-ml test tube was charged with 0.1 ml (0.93 mmol) of cyclohexane containing *o*-dichlorobenzene as chromatographic standard, 0.06 mmol of halogenating agent $XHlg^1$, and 0.0005–0.0051 g (0.002–0.02 mmol) of I_2. The volume was adjusted to 0.6 ml by adding methylene chloride, and 2 μl (0.5 mol %) of a 0.137 M solution of tributylborane in CCl_4 was added. Every 5 min, a 0.1-ml sample was withdrawn, treated as described above, and analyzed by GLC. Similar experiments were carried out with different amounts of I_2. The results are given in Tables 1 and 3.

The relative rate constants $k(XHlg^1)/k(I_2)$ for halogen atom abstraction by benzyl radicals (Table 3) were determined by a similar procedure using toluene as a source of benzyl radicals.

B. Determination of the relative rate constants $k(XHlg^1)/k(CH_3I)$ for halogen atom abstraction by cyclohexyl radicals. A test tube was charged with 0.1 ml (0.93 mmol) of cyclohexane containing *o*-dichlorobenzene as chromatographic standard, 0.06 mmol of halogenating agent $XHlg^1$, and 0.2–1 g (1.37–6.87 mmol) of methyl iodide. The volume was adjusted to 0.6 ml by adding methylene chloride, and 2–8 μl (0.5–2 mol %) of a 0.137 M solution of tributylborane in CCl_4 was added. Samples were withdrawn and were treated by the procedure described above and analyzed by GLC. Similar experiments were carried out with different amounts of methyl iodide. The results are given in Tables 2 and 3.

C. Determination of the relative rate constants $k(XHlg^1)/k(CH_3SO_2Cl)$ for halogen atom abstraction by cyclohexyl radicals. To 0.1 ml (0.93 mmol) of cyclohexane containing *o*-dichlorobenzene (chromatographic standard) we added 0.06 mmol of halogenating agent $XHlg^1$ and 1.1–3.8 g (10–33 mmol) of methanesulfonyl chloride. The volume was adjusted to 5 ml by adding methylene chloride, and 0.5–2 mol % of tributylborane (2–8 μl of a 0.137 M solution in CCl_4) was added. Samples were withdrawn and were treated as described above and analyzed by GLC. Similar experiments were carried out with different amounts of CH_3SO_2Cl. The results are given in Table 3.

D. Determination of the relative rate constant $k(PhSO_2NClCOPh)/k(NBS)$ for chlorine atom abstraction by cyclohexyl radicals. A test tube was charged with 0.1 ml (0.93 mmol) of cyclohexane containing *o*-dichlorobenzene as chromatographic standard), 0.018 g (0.06 mmol) of $PhSO_2NClCOPh$, 0.03–0.1 g (0.17–0.6 mmol) of NBS, and 0.5 ml of methylene chloride. Tributylborane, 0.5 mol % (with respect to $PhSO_2NClCOPh$; 2 μl of a 0.137 M solution in CCl_4) was then added. Every 5 min, 0.1-ml samples were withdrawn, treated as described above, and analyzed by GLC. Experiments were repeated with different amounts of NBS.

E. Determination of the relative rate constant $k(CBrCl_3)/k(PhSO_2NClCOPh)$ for bromine atom abstraction by cyclohexyl radicals. A test tube was charged with 0.1 ml (0.93 mmol) of cyclohexane containing *o*-dichlorobenzene as chromatographic standard, 0.012 g (0.06 mmol) of $CBrCl_3$, 0.03–0.29 g (0.01–0.1 mmol) of $PhSO_2NClCOPh$, and 0.5 ml of methylene chloride. Tributylborane, 0.5 mol % (with respect to $PhSO_2NClCOPh$; 2 μl of a 0.137 M solution in CCl_4) was then added. Every 5 min, 0.1-ml samples were withdrawn, treated as described above, and analyzed by GLC. Similar experiments were carried out with different amounts of *N*-benzoyl-*N*-chlorobenzenesulfonamide.

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