of $RSO_4H \cdot H_2O$; one would suppose that in the presence of acids the contribution of this reaction would not be large.

Assuming that the concentrations $[SO_2 \cdot H_2O]$, $[HOSO_2^-]$, and $[RSO_4H \cdot H_2O]$ are determined only by equilibria (1)-(3) respectively, i.e., $k_1 \cdot [SO_2] \cdot [H_2O] >> k_{-2} \cdot [HOSO_2^-] \cdot [H_3O^+]$, $k_{-1} >> k_2 \cdot [H_2O]$, $k_{-2} \cdot [H_3O^+] >> k_4 \cdot [RSO_4H \cdot H_2O]$, and $k_{-3} >> k_4 \cdot [HOSO_2^-]$, from the process scheme, for the rate of consumption of SO₂ we have

$$-d[SO_{2}]/dt = K_{1} \cdot K_{2} \cdot K_{3} \cdot k_{4} \cdot [RSO_{4}H] \cdot [SO_{2}] \cdot [H_{2}O]^{3}/[H_{3}O^{+}], \qquad (II)$$

where K_1-K_3 are the equilibrium constants of (1)-(3). Since the experiments were carried out with $[RSO_4H]_0 >> [SO_2]_0$, then $[RSO_4H]_0 \approx$ const and hence (II) describes the experimental results.

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REACTIVITY OF RADICALS $CCl_3(CH_2CHR)_n$ (R = H, CH₃, Cl; n = 1, 2) IN ADDITION REACTIONS WITH UNSATURATED COMPOUNDS

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Using EPR spectroscopy, the rate constants for the addition of radicals $CCl_3(CH_2 \cdot CH_2)_n^*$ (R¹ for n = 1 and R² for n = 2), $CCl_3CH_2\dot{C}HCH_3$ (R³), and $CCl_3CH_2\dot{C}HCl$ (R⁴) to unsaturated compounds $CH_2=CHX$ (X = C_6H_5 , $COOCH_3$, CN) and $CH_2=C(CH_3)Y$ (Y = C_6H_5 , $COOCH_3$) at 22°C have been determined. The radicals R¹ and R² exhibit ambiphilic, and R⁴ electrophilic character towards the selected unsaturated compounds. It has been shown that the presence of the CCl_3 group in the γ -position of the radical center has little effect on the reactivity of the radical. Replacement of a hydrogen on the α -carbon in radical R¹ by a CH₃ group or chlorine atom leads to a considerable reduction in the rate of addition of the radicals to the unsaturated compounds examined.

In studies of telomerization, cotelomerization, and polymerization [1] it is necessary to have data on the reactivity of the carbon-centered radicals $CCl_3(CH_2CHR)_n^{\cdot}$ (R = H, CH₃, Cl; n = 1, 2) in addition reactions to unsaturated compounds in relation to the substituents located in different positions relative to the radical center.

In the present work EPR spectroscopy has been used to determine the rate constants for the addition of radicals $CCl_3CH_2\dot{C}H_2$ (R¹), $CCl_3(CH_2CH_2)_2$ (R²), $CCl_3CH_2\dot{C}HCH_3$ (R³), and CCl_3 · $CH_2\dot{C}HCl$ (R⁴) to unsaturated compounds CH_2 =CHX (X = C₆H₅ (I), COOCH₃ (II), CN (III)) and

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TABLE 1. Hyperfine Interaction Constants of Spin Adducts of Radicals R^i with Nitrosodurene Formed by Removal of Iodine from IR^i , a (Oe)

R ⁱ	°N	^а в-н	
$CCl_{3}CH_{2}CH_{2}(R^{1})$ $CCl_{3}(CH_{2}CH_{2})_{2}^{*}(R^{2})$ $CCl_{3}CH_{2}\dot{C}(CH_{3})H(R^{3})$ $CCl_{3}CH_{2}\dot{C}HCl(R^{4}) *$	13.4 13.7 13.7 14.9	11,5 10,6 8,0 8.0	

*Radicals R⁴ also generated by removal of bromine from $CC1_3CH_2CHBrC1$ by $Re(CO)_5$ radicals; $a(^{35}C1) = 3.5$ Oe.

TABLE 2. Hyperfine Interaction Constants of Spin Adducts of Radicals $R^{i}CH_{2}\dot{C}HX$ and $R^{i}CH_{2}\dot{C}(CH_{3})Y$ with Nitrosodurene Obtained by Addition of Radicals R^{i} to $CH_{2}=CHX$ and $CH_{2}=C(CH_{3})Y*$

		x	Y		
a, Oe	C6H5	COOCH3	CN	C ₆ H ₅	СООСН3
a _N a _{β-II}	13,8 3,8	13.5 8,6	13,2 6,9	13,6	13,2

*In the EPR spectra, in addition to signals from the spin adducts of radicals $R^{i}CH_{2}\dot{C}HX$ and $R^{i}CH_{2}\dot{C}(CH_{3})Y$ with nitrosodurene, signals were also observed from radicals $R^{i}N(\dot{O})Ar$ (Ar = 2,3,5,6-C₆HMe₄, i = 1-4, see Table 1).

 $CH_2=C(CH_3)Y$ (Y = C₆H₅ (IV), COOCH₃ (V)) with the object of studying the effect of the type of substitutent at the vinyl group and at the radical center on the reactivity of these radicals and olefins in an addition reaction.

Radicals R_1-R_4 were generated by photochemical decomposition of the corresponding polychloroiodoalkanes $CCl_3(CH_2CH_2)_nI$ (n = 1, 2), $CCl_3CH_2CH(CH_3)I$, and CCl_3CH_2CHCII irradiated with light of $\lambda \sim 366$ nm in the presence of $Re_2(CO)_{10}$ or $Hg(m-C_2H_2B_{10}H_9-9)_2$.

Under the influence of light, these latter compounds yield radicals $Re(CO)_5$ or $Hg(m-C_2H_2B_{10}H_9-9)$ and $m-C_2H_2B_{10}H_9-9$ [2]. Radicals R⁴ were also generated by photochemical removal of bromine from $CCl_3CH_2CHClBrRe(CO)_5$ [2]. Nitrosodurene (ND) was selected as a spin trap for identification of the intermediate radicals.

Table 1 shows the hyperfine interaction constants of the spin adducts of radicals R^{i} (i = 1-4) and Table 2 those of radicals $R^{i}CH_{2}\dot{C}HX$ and $R^{i}CH_{2}\dot{C}(CH_{3})Y$ with ND.

The formation of nitroxyl radicals, identified by EPR spectroscopy, can be described by the scheme

$$\operatorname{CCl}_{3}(\operatorname{CH}_{2}\operatorname{CHR})_{n}\operatorname{I} \xrightarrow{\operatorname{Re}_{2}(\operatorname{CO})_{10}, \lambda 366 \text{ nm}}_{\operatorname{Hg}(m-\operatorname{C}_{2}\operatorname{H}_{2}\operatorname{B}_{10}\operatorname{H}_{9}-9)_{2}, \lambda 366 \text{ nm}} \rightarrow \operatorname{CCl}_{3}(\operatorname{CH}_{2}\operatorname{CHR})_{n} \stackrel{\circ}{\cdot} (\operatorname{R}^{i})$$
(1)

$$R^{i} + ND \xrightarrow{k_{1}} R^{i}N(O)Ar(A),$$

$$R^{i} + CH_{2} = CHX (CH_{2} = C(CH_{3})Y) \xrightarrow{k_{2}} R^{i}CH_{2}CHX(R^{i}CH_{2}C(CH_{3})Y), \qquad (2)$$

$$R^{i}CH_{2}CHX(R^{i}CH_{2}C(CH_{3})Y) + ND \rightarrow R^{i}CH_{2}CHXN(O)Ar(R^{i}CH_{2}C(CH_{3})YN(O)Ar)$$
(3)

(Here and elsewhere in the text $Ar = 2,3,5,6-C_6HMe_4$, i = 1-4).



Fig. 1. Curves of concentrations of spin adducts of radicals R^3 (C₁, curve 1) and radicals $R^3CH_2\dot{C}(CH_3)COOCH_3$ (C₂, curve 2) with ND against time. Dotted lines) experimental data, solid lines) calculated by method of least squares.

Fig. 2. EPR spectra obtained on irradiation of a solution containing $CCl_3CH_2CH(CH_3)I$, $CH_2=C(CH_3)C_6H_5$, $Hg(m-C_2H_2B_{10}H_9-9)_2$, and ND in benzene. Extreme signals (lines a) assigned to spin adducts of $CH_2=C(C_6H_5)\dot{C}H_2$ with ND (lines b correspond to $R^3N(\dot{O})Ar$, line c to $R^3CH_2C(CH_3)C_6H_5N(\dot{O})Ar$)

According to this scheme, measurement of the rate of formation of nitroxyl radicals A and B can be used to determine in each individual case the rate constant k_2 for addition of the radical R^i to the unsaturated compound according to Eq. (4) [3], with a known rate constant k_1 for the addition of R^i to ND.

$$d[A]/d[B] = k_1/k_2 \frac{[ND]_0}{[M]_0},$$
 (4)

where d[A] and d[B] are the increments of concentration of radicals A and B with time (Fig. 1), $[M]_0$ and $[ND]_0$ are the initial concentrations of the unsaturated compound and ND respectively.

Figure 1 shows the experimental results, and the line calculated by the method of least squares, for the variation with time of the concentration of spin adducts of radicals R^3 (amplitude of the first line of the doublet of triplets with intensity 1) and spin adducts of radicals $R^3CH_2\dot{C}(CH_3)COOCH_3$ (amplitude of the first line of the triplet) with the spin trap.

The rate constants for the addition of primary and secondary alkyl radicals and radicals R^3 to ND were determined in [4-6] at 40°C and are of equal magnitude. It was noted in [3] that a CCl₃ group located at the γ -position from the radical center had practically no effect on the reactivity on the radicals on addition to olefins, and the temperature dependence of k_1 is described by the equation log $k_1 = 8.6 \cdot 1.5/2.303 \times RT$ kcal/mole. From these data, we took the rate constant for the addition of radicals R^1 , R^2 , and R^3 to ND as $3.0 \cdot 10^7$ liters/ (mole·sec) at 22°C. The constant k_1 for radicals R^4 was determined in [2] and was equal to $1.4 \cdot 10^6$ liters/(mole·sec) at 20°C.

The ratios of the increments of concentration d[A]/d[B] are shown in Table 3; these have a linear dependence on the ratio $[ND]_0/[M]_0$ in accordance with expression (4) for all the cases examined of addition of radicals R^1-R^4 to unsaturated compounds. On the basis of the value taken for k_1 and the experimentally determined ratios d[A]/d[B] the rate constants k_2 were calculated (Table 3).

er/(mole·sec)) for the Addition of Radicals R^1 - R^4 to CH_2 =CXY at 22°C	ħ2,10-3	R4	12±2	10±2 e	7±2	1,5±0,5 "	0,9±0,2 [€]
		R	29±2	I	160±40		
		R'	135±5	175±35		160±30	190±50
		ц	290±60	270±50	600±15	250±20	145±25
			0,304 d 0,702 0,751 0,751	-	0,536 0,471 0,68 1,714		
	d[A]/d[B]		0,832 c 2,061 4,227 7,13		0,409 0,49 1.548 4,046		
			0,655b 1,544 3,917	0,581 1,575 3,107		0,703 1,473 3,618 5,066	0,529 0,731 2,379 6,61
			0,359 1.4 1,567	0,319 0,661 2,856	0,435 2,009 1,491	0,445 0,963 2,048	0,897 1,793 3,322 5,0
			3,907 d 4,703 7,643 6,679		2,7 2,856 5,398 6,611		
	$\frac{[ND]_{s}}{[CH_{s}=CX Y]_{s}} \cdot 10^{36}$		0,754 c 1,903 3,894 7,443		1,613 3,22 7,085 25,82		
k ₂ , lit			3,056 b 6,949 16,97	3,411 7,463 20,54		3,198 5,835 15,48 32.62	$\begin{array}{c} 4,153\\ 6,195\\ 11,94\\ 30,69\end{array}$
tants (Å		3,244 $\overline{7},610$ 22,10	3.393 7.077 21.34	6.557 32,88 37,82	3,506 8,127 18,38	3,712 7,305 13,24 28,70
Rate Cons			C ₆ H ₅	Cells	COOCH ₃	COOCH _a	CN
3.		×	CH3	Н	CH ₃	Ħ	н
TABLI	Exnt.	No.	-	5	ç	4	Ω

^aMonomeric form of ND which was varied in the range $(2.8-3.8) \cdot 10^{-3}$ M. bIn reaction with $CCl_3(CH_2CH_2)_2I$. CIn reaction with $CCl_3CH_2CH_2(CH_3)I$. dIn reaction with $CCl_3CH_2CH_2(CH_3)I$. eDetermined according to (9) (see Experimental section).

The rate constants for the addition of radicals R^4 to compounds (I)-(III) were determined by selecting as competitive with this reaction the addition of radicals R^4 to (V). In the reaction of R^4 simultaneously with two unsaturated compounds, for example (I) and (V), the formation of intermediate radicals is described by the following scheme:

$$\mathbf{R}^{4} + \mathbf{C}\mathbf{H}_{2} = \mathbf{C}\mathbf{H}\mathbf{C}_{6}\mathbf{H}_{5}\left(\mathbf{I}\right) \xrightarrow{\mathbf{k}_{2}^{1}} \mathbf{R}^{4}\mathbf{C}\mathbf{H}_{2}\dot{\mathbf{C}}\mathbf{H}\mathbf{C}_{6}\mathbf{H}_{5}\left(\mathbf{R}^{5}\right),\tag{5}$$

$$\mathbf{R}^{4} + \mathbf{CH}_{2} = \mathbf{C}(\mathbf{CH}_{3})\mathbf{COOCH}_{3} \xrightarrow{\mathbb{R}_{2}^{V}} \mathbf{R}^{4}\mathbf{CH}_{2}\dot{\mathbf{C}}(\mathbf{CH}_{3})\mathbf{COOCH}_{3}(\mathbf{R}^{6}), \tag{6}$$

$$R^{5} + M \rightarrow R^{4}CH_{2}CH(C_{6}H_{5})N(\dot{O})Ar(C), \qquad (7)$$

$$R^{6} + M^{D} \rightarrow R^{4}CH_{2}C(CH_{3})COOCH_{3}N(\dot{O})Ar(D).$$
(8)

According to this scheme, as the current concentrations of nitroxyl radicals which are being formed changes, Eq. (9) will hold, from which, knowing k_2^V , one can determine the rate constant for the addition of radicals R⁴ to (1) (k_2^{I})

$$d[D]/d[C] = k_2^{V}[V]_0/k_2^{I}[I]_0,$$
(9)

 k_2^{I} and k_2^{V} being the rate constants for the addition of radicals R^4 to (I) and (V) respectively.

An analogous route was used to determine the rate constants for the addition of radicals R^4 to (II) and (III) (Table 3, experiments 2, 4, 5).

It follows from the results in Table 3 that the nature of the substituent on the vinyl group in the series of compounds (I)-(V) has almost no effect on their reactivity with radicals R¹ and R² which is evidence of their ambiphilic character. The activity of the unsaturated compounds in reaction with radical R⁴ falls along the series (IV) > (I) > (V) > (II) \approx (III) which corresponds to the activity series for the radical Cl(CH₂)₂CCl₂(R⁷) [7, 8]. A linear relationship is observed between the logarithm of the rate constant for the addition of radicals R⁴ and R⁷ to unsaturated compounds and the parameter e which characterizes the donor-acceptor properties of the substituent on the vinyl group in (I)-(V) [8]. It follows from these results that the activity of the compounds listed relative to radicals R⁴ is determined by the polar effects of the substituents. The tangents of the angles of slope of the straight line plots of log k₂ against e in the case of the addition of radicals R⁴ and R⁷ to (I)-(V) are of similar magnitude (log k₂ (for R⁴) = 3.62-0.44e; correlation coefficient = 0.988 and log k₂ (for R⁷) = 4.16-0.73e; correlation coefficient = 0.972, see [7]), which shows the electrophilic nature of radical R⁴.

It was shown in [2, 8, 9] that the reactivity of radicals R^1 and R^2 , R^3 and $CCl_3(CH_2 \cdot CHCH_3)_2$; R^4 and $CCl_3(CH_2CHCI)_2$ in addition reactions with ethylene, propylene, and vinyl chloride are insensitive to the influence of the CCl_3 group in the γ - or ω -position relative to the radical center. Consequently, the reactivity of radicals R^1 , R^2 and R^3 , $CCl_3(CH_2CH \cdot CH_3)_2$ must not differ markedly from the reactivity of primary and secondary alkyl radicals in addition reactions. In fact, the rate constants for the addition of radicals R^1 and R^2 to (I)-(III) and (V) (Table 3, experiments 2-5) are close to the analagous constants for the radicals $n-\dot{C}_7H_{15}$ (9.3·10⁴, 2.2·10⁵, 5.5·10⁵, and 7.3·10⁵ liters/(mole·sec) respectively at 25°C [10, 11]. Making use of the data of [10, 11], one can postulate that the rate constants for the addition of radicals R^1 and R^2 to $CCl_2=CCl_2$ and $CH_2=CHCH=CH_2$ at 22°C will be 500 and 10⁵ liters/(mole·sec).

The results in Table 3 show that radicals R^1 are more active by an order of magnitude than radicals R^4 in addition reactions with (I) and (IV), and by two orders of magnitude in additions to (II), (III), and (V). At the same time, radicals R^1 are an order of magnitude more active than R^3 in additions to (I) and three times more active in additions to (V). Consequently, replacing the hydrogen on the carbon atom on which the radical center in radicals R^1 is located by a CH₃ group or a chlorine atom results in a considerable reduction in the reactivity of such radicals (i.e., R^3 and R^4) in addition reactions with unsaturated compounds and this could be associated with an increase in steric hindrance in the radicals R^3 and R^4 . On the other hand, replacing a hydrogen by chlorine on the α -carbon in radicals R^1 not only considerably reduces the reactivity but also leads to the change of polarity of radicals R^4 . From a comparison of the reactivity of radicals R^4 and R^7 [7] it is seen thar R^7 is slightly more active in additions to (I) and (IV) $(5.0 \cdot 10^4 \text{ and } 1.4 \cdot 10^5 \text{ liters/(mole \cdot sec)}$ in spite of being more sterically hindered than R⁴. However, one can assume that the reactivity of radicals R⁴ and R⁷ will not differ greatly on addition to certain unsaturated compounds studied in [7, 8]. Hence it is probable that the rate constants for the addition of radicals R⁴ to CH₂=CHC(0)CH₃ and CH₂=CHOC₂H₅ at 22°C will be ~10⁴ and ~10³ liters/(mole \cdot sec) respectively.

Since the dimensions of the particles has little effect on the addition process [1], the results obtained for the reactivity of the low-molecular-weight radicals (R^1-R^4) can be realistically used to model the reactivity of their polymeric analogs. However, in contrast to addition reactions using radicals $CCl_3(CH_2CHR)_n^{\circ}$ as low-molecular-weight analogs of polymeric radicals, in substitution reactions, which take place in stages, where reaction products are formed with rupture of C-H and C-Hal bonds, one must make allowance for the effect of the CCl, group on the reactivity of the radicals. It was shown in [3, 12] that the rate constants for removal of halogen from CCl₄ and BrCCl₃, and also hydrogen from HCCl₃, depends considerably on the location of the CCl_3 group relative to the radical center. At the same time, the reactivity of the radicals $CCl_3(CH_2CHR)_n$ (R = H, CH_3) with $n \ge 2$ in these reactions does not depend on the distance of the CCl₃ group from the radical center, and the activity of such radicals will not be significantly different from the activity of the corresponding alkyl radicals Alk(CH₂CHR) \dot{n} In fact, the rate constant for removal of chlorine from CCl₄ by radicals R_2 has the value 9.10⁴ liters/(mole.sec) [9], and by radicals $CH_3(CH_2)_2CH_2$, 8.3. 10⁴ liters/(more·sec) at 40°C [13]. Hence only radicals R², CCl₃(CH₂CHCH₃)² and CCl₃(CH₂· CHCl); can be considered as low-molecular-weight analogs of the corresponding polymeric radicals when modeling their reactivities in copolymerization and polymerization.

In the reaction of radicals $R^{1}-R^{4}$ with (IV) and radicals R^{3} and R^{4} with (V) in the presence of ND, the EPR spectrum shows, in addition to signals from the spin adducts of radicals $R^{1}CH_{2}\dot{C}(CH_{3})C_{6}H_{5}$ (i = 1-4) and $R^{1}CH_{2}\dot{C}(CH_{3})COOCH_{3}$ (i = 3, 4), signals from the spin adducts of radicals $CH_2 = C(C_6H_5)CH_2$ (R⁸) (a_N = 13.4, a_{R-H} = 9.3 Oe), and $CH_2 = C(COOCH_3)CH_2$ (R⁹) (a_N = 13.5 and $a_{B-H} = 10.3$ Oe) with ND. Formation of these radicals is explained by the removal of hydrogen from the methyl group in (IV) and (V) by the radicals An EPR spectrum obtained during the addition of radicals R^3 to (IV) is R1. shown in Fig. 2. The extreme signals in the spectrum (lines a) are assigned to spin adducts of radicals R⁸ with ND arising from the length of the spectrum. To confirm the correctness of this assignment these radicals were generated by removal of hydrogen from (IV) or (V) by radicals $(CH_3)_3CO$, which are formed in the photochemical decomposition of $[(CH_3)_3CO]_2$ in benzene solution in the presence of (IV) or (V) and ND. Spin adducts of radicals R⁸ and R⁹ with 2-methyl-2-nitroisopropane(MNP) were identified in the addition reaction of radicals (CH₃)₃CO[•] to (IV) and (V) using MNP as a spin trap for the intermediate radicals [14, 15]. Simultaneous identification by EPR spectroscopy of spin adducts of radicals R³ and R⁸ with ND makes it possible to determine the rate constant for removal of hydrogen from (IV) by radicals R³, equal to (1.2 ± 0.08)·10⁴ liter/(mole·sec). Stages (10) and (11) were used for this purpose in addition to stages (1)-(3):

 $R^{3} + CH_{2} = C(C_{8}H_{5})CH_{3} \xrightarrow{k_{3}} CCl_{3}CH_{2}CH_{2}CH_{3} + R^{8},$ (10)

$$\mathbf{R}^{\mathbf{g}} + \mathbf{N} \mathbf{D} \rightarrow \mathbf{C} \mathbf{H}_{2} = \mathbf{C}(\mathbf{C}_{\mathbf{g}} \mathbf{H}_{5}) \mathbf{C} \mathbf{H}_{2} \mathbf{N}(\mathbf{O}) \mathbf{A} \mathbf{r} \quad (\mathbf{D}).$$
(11)

Taking into consideration stages (1)-(3) and (10)-(11), we obtain the expression $d[B]/d[D] = k_2/k_3$ from which k_3 is determined. A similar method was used to determine the rate constant for the removal of hydrogen from (IV) by radicals R⁴, equal to $(5.4 \pm 0.3) \cdot 10^3$ liters/(mole·sec) at 22°C. The difference observed in k_3 for radicals R³ and R⁴ in removing hydrogen from (IV) corresponds to the difference in the rate constants for the removal of hydrogen by these radicals from HCCl₃ [12].

EXPERIMENTAL

EPR spectra were run on an SE/X-2547 spectrometer. Reaction mixtures were degassed by several "freeze-evacuate-defreeze" cycles and were then irradiated with light of λ -366 nm in the resonator of the spectrometer at 22°C. Benzene was used a solvent in all the experiments. Before addition of the reaction mixtures to ND, it was first dissolved in CH₂Cl₂. The concentrations of the monomeric form of ND and the unsaturated compound were chosen with regard to the rate of homopolymerization in order to exclude the formation of telomeric radicals.

The initial concentration of $Hg(m-C_2H_2B_{10}H_9-9)_2$ and of $Re_2(CO)_{10}$ did not exceed 6·10⁻³ and 4·10⁻³ mole/liter respectively. Initial concentrations of polyhaloalkanes (mole/liter): $[CCl_3(CH_2CH_2)_nI] = 0.25-0.36$ (n = 1, 2), $[CCl_3CH_2CH(CH_3)I] = 0.3-0.34$, $[CCl_3CH_2CHCII] = 0.6-1.5$, and $[CCl_3CH_2CHCIBr] = 0.3-0.32$, In the determination of k_2 for radicals R⁴ in experiments 2, 4, 5 (Table 3) the ratio of the initial concentrations of the unsaturated compounds were selected as follows: [V]/[I] = 0.477 ($[V]_0 = 0.996$ M); [V]/[II] = 0.482, 0.217, 0.124 ($[V]_0 = 0.421$ M); [V]/[III] = 0.204 ($[V]_0 = 0.842$ M) and the ratios of the nitroxyl radicals formed were respectively 3.545; 0.567, 0.490, 1.363; 0.639. In the determination of k_3 for radicals R³ and R⁴ d[B]/d[D] = 2.381 and 1.309 respectively. For all d[A]/d[B] and d[B]/d[D] average values are quoted from the results of three independent experiments.

The polyhaloalkane starting materials were prepared by the methods of [2, 6, 9] and purified by vacuum distillation immediately before the commencement of the experiment.

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