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The rate constants for the addition of radicals $CCl_3CH_2{}^{\bullet}CHR$ (R = Ph, CO_2Me, $CONC_4H_8$) to some unsaturated compounds

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The rate constants for the addition of radicals $CCl_3CH_2{}^{\bullet}CHR$ to unsaturated compounds $CH_2{=}CHR$ (R = Ph, CO_2Me, $CONC_4H_8$) and to $CH_2{=}CMeCO_2Me$ were determined at 22 °C by ESR spectroscopy.

Key words: ESR spectroscopy, spin trapping, rate constants for addition, unsaturated compounds, telomer radicals.

The addition of free radicals to the molecules containing unsaturated bonds is one of common reactions of new bond formation and, in some cases, the main step in telomerization processes.[1—3]

It is known[2,3] that there are no fundamental reasons to differentiate reactivities of polymer radicals from their low molecular analogues because a particle size is not essential for its participation in the processes of addition. Thus, it is necessary to know the rate constants for the reactions of telomer radical additions to monomers in order to apply these processes for synthesis.

In this paper the rate constants for addition of $CCl_3CH_2{}^{\bullet}CHR$ (R = Ph ($^{\bullet}\mathbf{R}^1$), CO_2Me ($^{\bullet}\mathbf{R}^2$), $CONC_4H_8$ ($^{\bullet}\mathbf{R}^3$)) telomer radicals to $CH_2{=}CHR$, R = Ph (**1a**), CO_2Me (**1b**), $CONC_4H_8$ (**1c**) and to $CH_2{=}CMeCO_2Me$ (**2**) were determined by ESR spectroscopy.

Experimental

The CCl_3CH_2CHXR (X = I, Br; R = CO_2Me, $CONC_4H_8$, Ph) compounds were obtained by the additions of trichloromethane iodides or trichloromethane bromindes to corresponding unsaturated compounds according to the known techniques.[4,5]

ESR spectra were recorded by a «Varian E-12A» spectrometer. Gas-free reaction solutions in glass ampoules were irradiated by DRSh-1000 lamp inside the resonator of the spectrometer under 22 C. The band of λ ≈ 366 nm was selected by a glass light filter. Required quantity of nitrosodurene (**3**) was dissolved in a small amount of dichlormethane before liquid compounds and benzene.

The TEMPO («Aldrich») ([TEMPO] = $3 \cdot 10^{-3}$ mol L^{-1}) was applied as a reference standard for calculating concentrations of nitroxyl radicals.

Results and Discussion

Radicals $^{\bullet}\mathbf{R}^1$—$^{\bullet}\mathbf{R}^3$ were generated by Br or I atom abstraction from CCl_3CH_2CHXR (X = Br, I) by $Re(CO)_5$ radicals. The latter are formed in the course of photochemical degradation (λ ≈ 366 nm) of $Re_2(CO)_{10}$ [6]:

$$Re_2(CO)_{10} \xrightarrow{h\nu} 2\ {}^{\bullet}Re(CO)_5,$$

$$CCl_3CH_2CHXR + {}^{\bullet}Re(CO)_5 \longrightarrow$$

$$\longrightarrow \underset{{}^{\bullet}\mathbf{R}^1-{}^{\bullet}\mathbf{R}^3}{CCl_3CH_2{}^{\bullet}CHR} + XRe(CO)_5. \qquad (1)$$

In the course of additions of $^{\bullet}\mathbf{R}^2$ or $^{\bullet}\mathbf{R}^3$ radicals to the styrene (**1a**), the secondary radicals $R^2CH_2{}^{\bullet}CHPh$ ($^{\bullet}\mathbf{R}^4$) or $R^3CH_2{}^{\bullet}CHPh$ ($^{\bullet}\mathbf{R}^5$) are formed. In the case of the addition of R^1 to methyl acrylate (**1b**) or to 1-acrylpyrrolidine (**1c**), the $R^1CH_2{}^{\bullet}CHCO_2Me$ ($^{\bullet}\mathbf{R}^6$) or $R^1CH_2{}^{\bullet}CHCONC_4H_8$ ($^{\bullet}\mathbf{R}^7$) radicals are respectively formed. Earlier[7] we showed that the spin-adducts of the secondary radicals $XCH_2{}^{\bullet}CHPh$ with nitrosodurene as a spin trap to hold intermediate free radicals essentially differ in the constant of hyperfine coupling of unpaired electron with proton $a_{\beta\text{-H}}$ from the spin-adducts of the secondary radicals containing other than phenyl substituent nearby a carbon atom at the radical centre

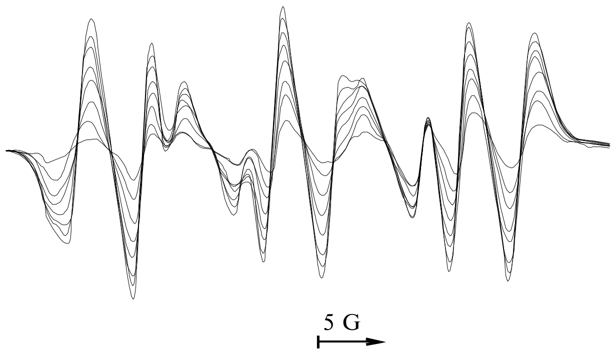

Fig. 1. ESR spectra of the nitroxyl radicals, obtained by light (λ = 366 nm) irradiation of the benzene solutions contained compounds **1b**, **3**, $Re_2(CO)_{10}$, and $CCl_3CH_2CHBrPh$, $[\mathbf{1b}]_0 = 3.92$ mol L^{-1} and $[\mathbf{3}]_0 = 1.1638 \cdot 10^{-3}$ mol L^{-1} at 22 °C.

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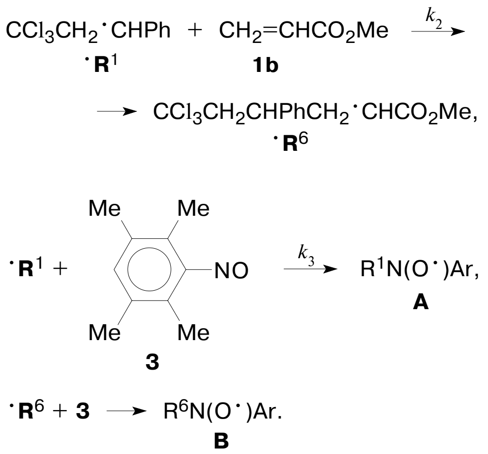
irrespectively of the composition and polarity of the X substituent. Such properties of nitroxyl radicals allow one to identify spin-adducts of $^{\bullet}\mathbf{R}^1$, $^{\bullet}\mathbf{R}^4$, $^{\bullet}\mathbf{R}^5$ and $^{\bullet}\mathbf{R}^2$, $^{\bullet}\mathbf{R}^3$, $^{\bullet}\mathbf{R}^6$, $^{\bullet}\mathbf{R}^7$ radicals by using ESR spectra when the former are all present in the reaction mixture.

Figure 1 shows ESR spectrum of the nitroxyl radicals obtained in the course of irradiation of benzene solutions containing $CCl_3CH_2CHBrPh$, **1b**, **3** and $Re_2(CO)_{10}$. In the spectra signals from two nitroxyl radicals **A** and **B** are observed. The scheme of the formation of the radicals includes step (1):



$$\underset{^{\bullet}\mathbf{R}^1}{CCl_3CH_2{}^{\bullet}CHPh} + \underset{\mathbf{1b}}{CH_2{=}CHCO_2Me} \xrightarrow{k_2} \underset{^{\bullet}\mathbf{R}^6}{CCl_3CH_2CHPhCH_2{}^{\bullet}CHCO_2Me}, \quad (2)$$

$$^{\bullet}\mathbf{R}^1 + \mathbf{3} \xrightarrow{k_3} \underset{\mathbf{A}}{R^1N(O^{\bullet})Ar}, \quad (3)$$

$$^{\bullet}\mathbf{R}^6 + \mathbf{3} \longrightarrow \underset{\mathbf{B}}{R^6N(O^{\bullet})Ar}.$$

Measuring the rates of formation of nitroxyl radicals **A** and **B** in the linear section allows one to determine the value of the rate constant in the reaction of addition of R^1 to methyl acrylate (**1b**)[8] at a given value of the rate constant in the reaction of addition of $^{\bullet}\mathbf{R}^1$ to nitrosodurene (**3**). However, as one can see in Fig. 1, a noticeable linewidth from nitroxyl radicals causes signal aliasing from the both radicals. This essentially hampers measuring the rates of the radical formation during the linear period of changing their concentrations. Therefore, to determine the constant k_2 of addition of $^{\bullet}\mathbf{R}^1$ radicals to **1b** и **1c**, as well as $^{\bullet}\mathbf{R}^2$ or $^{\bullet}\mathbf{R}^3$ radicals to **1a** we used an alternative technique[8] based on the measurement of changing in the rate of spin-adduct formation in the course if $^{\bullet}\mathbf{R}^1$—$^{\bullet}\mathbf{R}^3$ radical interaction with **3** depending on the concentration of unsaturated compound ($CH_2{=}CHR$). For this case:

$$\frac{dA^1}{dA^2} = 1 + \frac{k_2[CH_2{=}CHR]}{k_3[\mathbf{3}]}, \qquad (4)$$

where dA^1 and dA^2 — the rates of nitroxyls **A** formation with or without the monomer in the reaction mixture.

Fig. 2 shows straight lines of the behavior in time of the intensity of signals in the ESR spectra of spin-adducts of $^{\bullet}\mathbf{R}^1$ and $^{\bullet}\mathbf{R}^2$ with **3** without methyl acrylate (**1b**) and styrene (**1a**) (straight lines *1* and *6*) and in the presence of **1b** (straight lines *2—5*) и **1a** (straight lines *7—10*) (correlation coefficient ≥0.97) obtained by the least-squares approximation. The same dependences were obtained for the spin-adducts of radicals R^1 with nitrozodurene (**3**) in the presence of 1-acryloylpyrrolidine (**1c**) as well as for the spin-adducts of radicals $^{\bullet}\mathbf{R}^3$ with **3** in the presence of **1a** (Table 1).

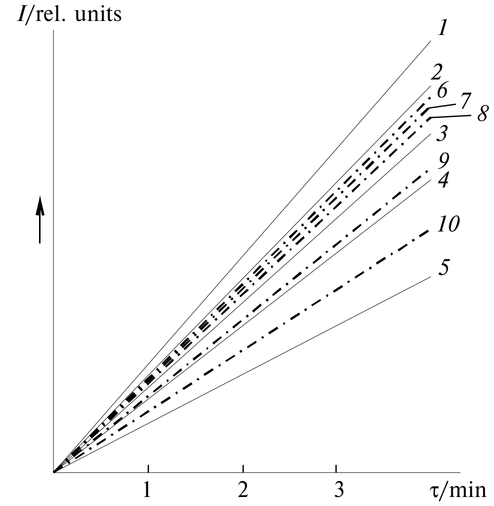


Fig. 2. Dependence of the rate of formation of spin-adducts $^{\bullet}\mathbf{R}^1$ and $^{\bullet}\mathbf{R}^2$ with nitrosodurene upon the concentration of **1b** (*1—5*) and **1a** (*6—10*); $[\mathbf{1b}]_0$/ mol L^{-1}: 0 (*1*), 0.3212 (*2*), 0.7398 (*3*), 1.8502 (*4*), 3.7011 (*5*); $[\mathbf{1a}]_0$/mol L^{-1}: 0 (*6*), 0.0584 (*7*), 0.1162 (*8*), 0.2911 (*9*), 0.5821 (*10*).

The treatment by least-squares adjustment of the data from Table 1 (correlation coefficient >0.98) gives us the following dependences of dA^1/dA^2 on the concentrations of methyl acrylate (**1b**), 1-acryloylpyrrolidine (**1c**) and styrene (**1a**):

for $^{\bullet}\mathbf{R}^2$ radicals:

$$dA^1/dA^2 = 1 + 0.3037\ [\mathbf{1b}], \qquad (5)$$

$$dA^1/dA^2 = 1 + 0.3251\ [\mathbf{1c}], \qquad (6)$$

$$dA^1/dA^2 = 1 + 0.94\ [\mathbf{1a}], \qquad (7)$$

for $^{\bullet}\mathbf{R}^3$ radicals:

$$dA^1/dA^2 = 1 + 1.1041\ [\mathbf{1a}]. \qquad (8)$$

These results prove that the reactions under study are quite adequately described by Eq. (4) and that in order to determine the rate constant for the addition $^{\bullet}\mathbf{R}^1$—$^{\bullet}\mathbf{R}^3$ to **1a—c**, it is necessary to determine the constant k_3.

Table 1. Dependence of dA^1/dA^2 on the concentrations of the monomers $CH_2{=}CHR$ **1a—c** (c/mol L^{-1})

c	dA^1/dA^2		c	dA^1/dA^2	
	1b, R = CO_2Me	**1c**, R = $CONC_4H_8$		**1a**, R = Ph	$^{\bullet}\mathbf{R}^3$
3.7011	2.2228	2.1840	0.5821	1.5666	1.623
1.8502	1.5033	1.4880	0.2911	1.2608	1.385
0.7398	1.3824	1.1952	0.1162	1.0706	1.0923
0.3212	1.1200	1.1240	0.0584	1.002	1.0154

Table 2. Steady-state concentrations of the nitroxyl radicals RN(O$^\bullet$)Ar and the values of the rate constants (k_3/L mol^{-1} s^{-1}) $^\bullet$R addition to nitrosodurene at 22 °C.

$^\bullet$**R**	$[\mathbf{3}]_0 \cdot 10^{4}$*	$[\mathrm{RN(O^\bullet)Ar}] \cdot 10^{5}$	$k_3 \cdot 10^{-7}$
	mol L^{-1}		
$CCl_3CH_2{}^\bullet CHPh$	7.959	3.2458	1.0
	6.598	2.1667	
	4.381	1.1111	
	2.128	0.3886	
$CCl_3CH_2{}^\bullet CHCO_2Me$	11.638	13.33	2.6
	9.246	9.33	
	6.598	6.398	
	2.851	2.566	
$CCl_3CH_2{}^\bullet CHCONC_4H_8$	9.346	19.452	2.7
	5.153	13.372	
	2.147	9.734	
	0.916	8.256	

* Nitrosodurene in the monomer form.

Table 3. The values of the rate constants (k_2) of the $CCl_3CH_2{}^\bullet CHR$ ($^\bullet$**R**^{1}—$^\bullet$**R**^{3}) radicals addition to the $CH_2{=}CHR$ (**1a—c**) and $CH_2{=}CMeCO_2Me$ (**2**) monomers at 22 °C.

CCl_3CH_2R	R	$k_2 \cdot 10^{-3}$/L mol^{-1} s^{-1}			
		1a	**1b**	**1c**	**2**
$^\bullet$**R**^{1}	Ph	0.66*	2.7	3.6	1.2
$^\bullet$**R**^{2}	CO_2Me	30.0	1.8*	—	7.3
$^\bullet$**R**^{3}	$CONC_4H_8$	33.0	—	1.8*	8.1

* Data[11,12] include the activation energy[11].

Table 2 gives values of the constant k_3 for $^\bullet$**R**^{1}—$^\bullet$**R**^{3} radicals obtained from the following equation:

$$k_3 = k_0 \left[\frac{\mathrm{d}[\mathrm{RN(O^\bullet)Ar}]}{\mathrm{d}[\mathbf{3}]}\right]_{[\mathbf{3}] \to 0}, \qquad (9)$$

where k_0 — the rate constant of the interaction of free radicals $^\bullet$**R**^{1}—$^\bullet$**R**^{3} with corresponding radicals:

$$^\bullet\mathbf{R} + \mathrm{RN(O^\bullet)Ar} \xrightarrow{k_0} \text{Stable products}$$

Values of k_3 (see Table 2) determined under the assumption that $k_0 = 2 \cdot 10^8$ L mol^{-1} s^{-1} (see Ref.[8,9]) basically coincide with the corresponding values of the rate constants obtained for other secondary radicals[8,10].

The values of the rate constants of the addition of $^\bullet$**R**^{1}—$^\bullet$**R**^{3} radicals to **1a—c** compounds, determined from Eqs. (5)—(8) considering k_3 values (see Table 2) are given in Table 3. In the Table 3 k_2 values for the reaction of the addition of $^\bullet$**R**^{1}—$^\bullet$**R**^{3} radicals to **2** obtained by changing the rate the formation of spin-adducts of $R_iCH_2{}^\bullet CMeCO_2Me$ (i = 1—3) radicals with **3** as well as the values of growth constants (k_p) for **1a** and acryl monomers are shown[11,12].

From Table 3 one can see that k_2 values depend not only on the polarities of the substituents in unsaturated compounds but also, and in a greater degree, on the nature of telomer radicals added to the monomer. Radical $^\bullet$**R**^{1} shows nucleophilic properties and radicals $^\bullet$**R**^{2} and $^\bullet$**R**^{3} — electrophilic. In a number of cases the results obtained allow one to evaluate the limits of the value of the rate constant for the addition of radicals $^\bullet$**R**^{1}—$^\bullet$**R**^{3} to the substituents using donor-acceptor properties of the latter. Besides, these data combined with the known results of the production of telomer radicals $^\bullet$**R**^{1}—$^\bullet$**R**^{3} by adding, for example, the CCl_3 radicals to monomers[14] allow one to select optimal concentrations of a pair of the monomers for the synthesis of isotactic telomer homologues and copolymers using monomers with chiral and achiral substituents[15].

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