2356 Russian Chemical Bulletin, International Edition, Vol. 50, No. 12, pp. 2356—2359, December, 2001

Reactivity of esters of 2-cyanoacrylic acid toward some free radicals

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The rate constants for the addition of $^{\cdot}CH(Ph)CH_2CCl_3$, $^{\cdot}CH_2Ph$, $^{\cdot}CH_2Pr^n$, and $^{\cdot}CCl_3$ radicals to the ethyl 2-cyanoacrylate molecule were determined by ESR spectroscopy using the spin trapping technique.

Key words: ESR spectroscopy, spin trapping, rate constants addition, 2-cyanoacrylates.

Elucidation of a relationship between the structures of unsaturated compounds (M) and free radicals and their reactivity in addition reactions is one of the urgent problems of the chemistry of free radicals. With this purpose researchers study the reactions of one radical with several monomers (see Refs. 1—5 and literature cited therein) or those of one monomer with different radicals.[3,6,7]

The rate constants for the addition of some nucleophilic and electrophilic radicals to various acrylic monomers have previously[1—3,6] been determined. It was of interest to study the reactivity of esters of 2-cyanoacrylic acid toward some radicals in addition reactions in order to compare them with other acrylic monomers. The esters of 2-cyanoacrylic acid are widely used as the basis for glues rapidly polymerized at room temperature, starting materials for preparing nanoparticles for medicine and technique, and mono- and multilayer films for microelectronics.[8,9]

In this work, we determined the rate constants for addition of the radicals $Ph^{\cdot}CHCH_2CCl_3$ (R^1), $Ph^{\cdot}CH_2$ (R^2), $Me(CH_2)_3^{\cdot}$ (R^3), and $^{\cdot}CCl_3$ (R^4) to $CH_2=C(CN)CO_2Et$ (M^1) by the ESR method using spin traps (ST). Nitrosodurene (ND) was chosen as ST to capture free radicals in the reactions.

Experimental

Compounds $CH_2=C(CN)CO_2Et$ (M^1) and $CH_2=C(CN)CO_2CH_2CH=CH_2$ (M^2) were prepared by known procedures.[10] To suppress anionic polymerization, we added 0.05% SO_2 and 0.1% *p*-toluenesulfo acid to M^1. ESR spectra were recorded on a Varian E-12A spectrometer. Samples in glass calibrated tubes were degassed by several "freezing—evacuation—defreezing" cycles. The tubes with a reaction mixture were irradiated in the cavity of a spectrometer with a DRSh-1000 lamp at ~20 °C. The band at $\lambda_{max} = 366$ nm was separated with a glass light filter. All kinetic results were processed by the Microsoft Excel program. Radicals R^1—R^4 were generated by the abstraction of the Br atoms from the $PhCHBrCH_2CCl_3$ and $PhCH_2Br$ molecules, the I atoms from the $Me(CH_2)_3I$ molecule, and the Cl atoms from the CCl_4 molecule by the $Re(CO)_5$ radicals, which were produced by the photochemical decomposition of $Re_2(CO)_{10}$.[2]

Results and Discussion

The addition of the R radicals to ST afford stable nitroxyl radicals (A)

$$R + ST \xrightarrow{k_1} A, \quad (1)$$

and the addition to unsaturated compounds M generates radicals R_M:

$$R + M \xrightarrow{k_2} R_M. \quad (2)$$

The latter can also be captured as spin adducts (SA) with ST (B):

$$R_M + ST \longrightarrow B.$$

Measuring the rate of formation of radicals A and B in the linear region of changing intensities of ESR signals under the condition that $dR_M/dt = 0$, from the equation

$$d[A]/d[B] = k_1[ST]_0/k_2[M]_0 \quad (3)$$

with the known rate constant of addition of the R radicals to ST (k_1), we can determine the rate constant for addition of the R radicals to M (k_2). Using the equation

$$d[A_1]/d[A_2] = 1 + k_2[M]_0/k_1[ST]_0, \quad (4)$$

where $d[A_1]/d[A_2]$ is the ratio of the rates of formation of the A radicals in the absence and presence of the M monomer, one can find the rate constant k_2.

Under irradiation of solutions of $CCl_3CH_2CHBrPh$, $Re_2(CO)_{10}$, ND, and M^1 in methylene chloride, the ESR spectra exhibit signals from SA of the R^1 radicals with ND (a triplet of doublets with HFC constants $a_N = 13.75$ G and $a_{\beta\text{-}H} = 4.5$ G) and a triplet with $a_N = 12.5$ G. Since the intensity of the triplet signal

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2248—2251, December, 2001.

increases with an increase in the initial concentration of M^1 in the reaction mixture, we assigned it to SA of the $PhCH(CH_2CCl_3)CH_2{}^{\cdot}C(CN)CO_2Et$ (R^5) radicals with ND. Measuring the rates of formation of the R^1 and R^5 radicals with the trap, using Eq. (3) at $k_1 = 1.2 \cdot 10^7$ L mol^{-1} s^{-1} (see Ref. 11), we found that the rate constant of addition of the R^1 radicals to M^1 (k_2) is $3.1 \cdot 10^5$ L mol^{-1} s^{-1}.

For the photochemical decomposition of $Re_2(CO)_{10}$ in a solution of CH_2Cl_2 containing benzyl bromide and ND, the ESR spectra contain signals from the known[12] SA of the R^2 radicals with ND, which have the following HFC constants: $a_N = 13.7$ G and $a_{\beta\text{-}H} = 8.5$ G (Fig. 1, *a*). When the M^1 monomer is added to these solutions, the ESR spectrum exhibits, in addition to the lines from the SA of the R^2 radicals with ND, a triplet with $a_N = 12.5$ G (see Fig. 1, *b*). Table 1 presents the dependence of the $d[A_1]/d[A_2]$ ratio on the M^1 concentration obtained by measuring the intensity of lines in the ESR spectrum (see Fig. 1, *b*). Processing of these experimental data by the least-squares method gives $d[A_1]/d[A_2] = 1 + 11.048[M^1]_0$ (correlation coefficient 0.95). Accepting for the rate constant for addition of the R^2 radicals to ND $k_1 = 5.6 \cdot 10^6$ L mol^{-1} s^{-1} (see Ref. 13) and using Eq. (4), we obtain $k_2 = 1.4 \cdot 10^5$ L mol^{-1} s^{-1}.

The found rate constant for addition of benzyl radicals to M^1 exceed by more than an order of magnitude the values of the corresponding addition constants to other mono- and α,α-disubstituted compounds, which is explained by the presence of electrophilic substituents at one C atom. Indeed, the rate constant for addition of the R^2 to α-methylacrylonitrile is[4] $6.6 \cdot 10^3$ L mol^{-1} s^{-1}. It follows from a comparison of the reactivity of the nucleophilic radicals $CCl_3(CH_2CHMe)_n{}^{\cdot}$ ($n = 1, 2$) toward propylene and acrylic monomer that the replacement of the methyl group by the CO_2Me group increases the rate constant for the addition by ~20 times.[2,3] Under assumption that the same dependence is also valid for the R^2 radicals and based on the value of the rate constant of their addition to α-methylacrylonitrile, for the rate constant for addition of the R^2 radicals to M^1 we obtain $1.32 \cdot 10^5$ L mol^{-1} s^{-1}, which coincides with k_2 determined in this work.

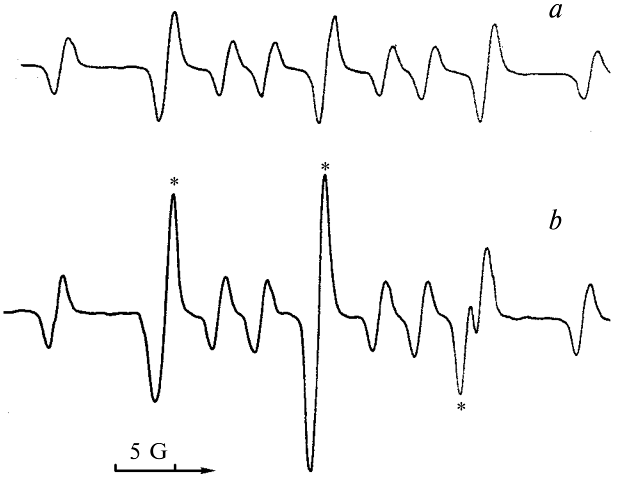

Fig. 1. ESR spectra of nitroxyl radicals under irradiation of solutions of $Re_2(CO)_{10}$ in CH_2Cl_2 containing $PhCH_2Br$ and ND ($2.2997 \cdot 10^{-3}$ mol L^{-1}) (*a*) or $PhCH_2Br$, ND ($2.2997 \cdot 10^{-3}$ mol L^{-1}) and $CH_2{=}C(CN)CO_2Et$ (0.0387 mol L^{-1}) (*b*). Lines of SA of the $PhCH_2{}^{\cdot}C(CN)CO_2Et$ radicals with ND are marked with asterisks.

Table 1. Change in the $d[A_1]/d[A_2]$* values during the addition of radicals R to $CH_2{=}C(CN)CO_2Et$ in the presence of ND

R	$[ND]_0 \cdot 10^3$	$[M^1]_0 \cdot 10^2$	$d[A_1]/d[A_2]$
	mol L^{-1}		
$^{\cdot}CH_2Ph$	2.2997	0.968	1.1274
		2.42	1.2286
		3.872	1.352
		4.84	1.6106
			$1 + 11.048[M^1]$ ($R^2 = 0.8979$)
$Me(CH_2)_3{}^{\cdot}$	7.6681	0.04	1.189
		0.08	1.502
		0.13	2.1
			$1 + 763.44[M^1]$ ($R^2 = 0.8698$)
$^{\cdot}CCl_3$	7.3143	3.52	1.2546
		5.87	1.5
		9.39	1.875
		11.74	2.213
			$1 + 9.6344[M_1]$ ($R^2 = 0.9644$)

* *R* is the correlation coefficient.

Previously[14] we have found the rate constant for styrene polymerization with M^1 equal to $5.4 \cdot 10^4$ L mol^{-1} s^{-1} at 30 °C. This constant is ~5-fold (ignoring the activation energy of the addition stage) lower than the rate constant for addition of the R^1 radicals to M^1. This difference can be resulted from, first, an error of determination of the rate constant for addition using different procedures, second, sizes of the adding R^1 radicals and $—(CH_2{}^{\cdot}CHPh)_n—$ molecules and, third, the presence of the CCl_3 group, which can affect the spin density distribution in the R^1 radical.

The ESR spectrum of the nitroxyl radicals obtained under irradiation of their solutions in CH_2Cl_2 containing $Re_2(CO)_{10}$, $Me(CH_2)_3I$, ND, and $CH_2{=}C(CN)CO_2Et$ (Fig. 2) contains, along with signals from the known[12] SA of the R^3 radicals with ND ($a_N = 13.5$ G, $a_{\beta\text{-}H} = 10.8$ G), a triplet with $a_N = 12.5$ G (the lines are marked with asterisk), which we assigned to the SA of the $Me(CH_2)_3CH_2{}^{\cdot}C(CN)CO_2Et$ radicals (R^6) with ND. The R^6 radicals are obtained due to the addition of the R^3 radicals to M^1. Table 1 contains a dependence of $d[A_1]/d[A_2]$ on the concentration of the M^1 monomer. Accepting $k_1 = 2 \cdot 10^7$ L mol^{-1} s^{-1} for the rate constant

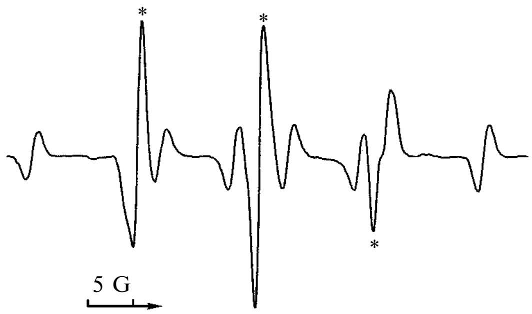

Fig. 2. ESR spectra of nitroxyl radicals under irradiation of dichloromethane solutions of $Re_2(CO)_{10}$, $Me(CH_2)_3I$, ND ($7.6681 \cdot 10^{-3}$ mol L^{-1}), and $CH_2{=}C(CN)CO_2Et$ ($1.321 \cdot 10^{-3}$ mol L^{-1}). Lines of SA of the $Me(CH_2)_3CH_2{}^{\cdot}C(CN)CO_2Et$ radicals with ND are marked with asterisks.

of addition of the primary radicals to ND (see Ref. 15), we determined that in this case $k_2 = 1.5 \cdot 10^8$ L mol^{-1} s^{-1}. The obtained rate constant for the addition exceeds more than by two orders of magnitude the corresponding rate constant for the addition of the primary radicals to monosubstituted unsaturated compounds.[1—3] Such an unusually high reactivity of M^1 with respect to the R^3 radicals can be ascribed to the stability of the R^6 radicals.

When a solution of $Re_2(CO)_{10}$, ND, M^1, and CCl_4 in CH_2Cl_2 is irradiated, its ESR spectrum exhibits signals from the known[12] SA of the ${}^{\cdot}CCl_3$ radicals with ND and a triplet with $a_N = 12.5$ G assigned to the SA of the $CCl_3CH_2{}^{\cdot}C(CN)CO_2Et$ radicals (R^7) with ND. The latter are generated when the ${}^{\cdot}CCl_3$ radicals add to M^1. Using a value of $9.1 \cdot 10^6$ L mol^{-1} s^{-1} for the rate constant of addition of the ${}^{\cdot}CCl_3$ radicals to ND (see Ref. 15) and based on the data in Table 1, we obtain $k_2 = 6.4 \cdot 10^5$ L mol^{-1} s^{-1} for the rate constant for addition of the R^4 radicals to M^1.

The high rate constants for addition of the R^1 and R^2 radicals to M^1 can be explained by the nucleophilicity of these radicals. However, the rate constant for the addition determined for the electrophilic R^4 radical can seem strongly overestimated if we take into account the polarity of M^1 ($e = 2.48$)[13] and the dependence of the rate constant for the addition of the ${}^{\cdot}CCl_3$ radicals on the polarity of the substituents in monosubstituted unsaturated compounds.[1,3] To confirm the validity of our results, we studied the addition of R^4 to $CH_2{=}C(CN)CO_2CH_2CH{=}CH_2$ (M^2) by the ESR method.

The ESR spectrum of the nitroxyl radicals detected under irradiation of a CH_2Cl_2 solution containing $Re_2(CO)_{10}$, CCl_4, ND, and M^2 (Fig. 3) exhibits, along with signals from the SA of the ${}^{\cdot}CCl_3$ radicals with ND, a triplet (*1*) with $a_N = 12.5$ G assigned (taking into account results of this work, to the SA of the $CCl_3CH_2{}^{\cdot}C(CN)CO_2CH_2CH{=}CH_2$ radicals (R^8) with ND. In addition to these signals, the ESR spectrum exhibits signals (*2*), which can be attributed (based on the extension of the spectrum and published data[1]) to the SA of the $CCl_3CH_2{}^{\cdot}CHCH_2CO_2(CN)C{=}CH_2$ (R^9) radicals. The rate constant for addition of the R^4 radicals to $CH_2{=}CHCH_2OMe$ is equal[1] to $6 \cdot 10^4$ L mol^{-1} s^{-1} at 22 °C. If lines *2* in Fig. 3 are referred to the SA of the R^9 radicals with ND, the concentration of these SA turns out to be lower by an order of magnitude than the concentration of the SA of the R^8 radicals with ND. Therefore, the rate constant for addition of the ${}^{\cdot}CCl_3$ radicals to M^2 with the formation of the R^8 radicals has to be of an order of $6 \cdot 10^5$ L mol^{-1} s^{-1}, which agrees with the corresponding rate constant for the addition of the R^4 radicals to M^1.

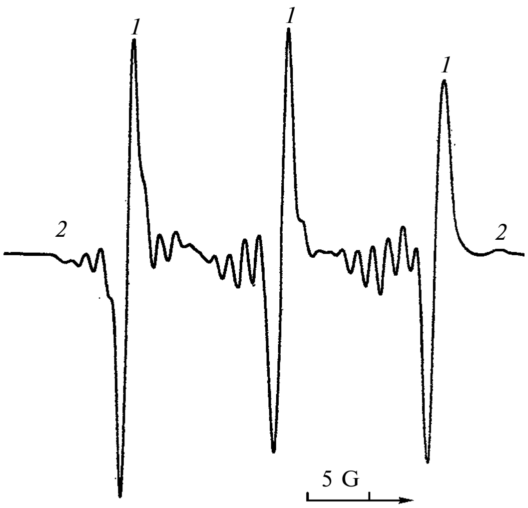

Fig. 3. ESR spectra of nitroxyl radicals under irradiation of dichloromethane solutions of $Re_2(CO)_{10}$, CCl_4, ND ($6.0663 \cdot 10^{-3}$ mol L^{-1}), and $CH_2{=}C(CN)CO_2CH_2CH{=}CH_2$ (0.2903 mol L^{-1}): lines of SA of ND with radicals $CCl_3CH_2{}^{\cdot}C(CN)CO_2CH_2CH{=}CH_2$ (*1*), $CCl_3CH_2{}^{\cdot}CHCH_2CO_2(CN)C{=}CH_2$ (*2*), those of ${}^{\cdot}CCl_3$ are not marked.

In experiments with the addition of the R^1—R^3 radicals to M^2, the ESR spectra contained, along with signals from the SA of the R^1—R^3 radicals with ND, only a triplet with $a_N = 12.5$ G, which was assigned to the SA of the $R^nCH_2{}^{\cdot}C(CN)CO_2CH_2CH{=}CH_2$ radicals ($n = 1$—3) with the trap.

Thus, the results obtained show that the ambiphilic R^3 radical and the electrophilic R^4 radical add predominantly at the same position as the nucleophilic R^1 and R^2 radicals. However, the high reactivity of M^1 with respect to the R^1 and R^2 radicals is determined by the polarity of substituents, whereas the reactivity of M^1 with respect to the R^3 and R^4 radicals is due, most likely, to the stability of the radicals that formed.

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Received February 26, 2001;
in revised form May 11, 2001