CONCLUSIONS

1. Aluminum, rare-earth metals (Sm, La), and intermetallic compounds of the composition Al_2M (M = Sc, Y, La, Nd, Sm) efficiently catalyze radical decomposition of benzoyl peroxide and cumene hydroperoxide.

2. The catalytic activity in the Al_2M series increases with an increase in the atomic number of the rare-earth element.

3. The catalytic effect of freshly ground powders of the metals on the decomposition of benzoyl peroxide decreases rapidly due to the formation of an oxide film on their surface.

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EPR DETERMINATION OF RATE CONSTANT OF SPLITTING CHLORINE FROM CCl_4 BY TELOMERIC RADICALS $CCl_3(CH_2CHCl)_n^{\cdot}$ (n = 1, 2) AND THEIR ADDITION TO VINYL CHLORIDE AND NITROSODURENE

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The rate constants have been determined in [1, 2] of splitting Cl from CCl_4 by telomeric radicals $CCl_3(CH_2CH_2)_k^{\cdot}$ ($\dot{R}^k$, k = 1-3) and $CCl_3(CH_2CHMe)_m^{\cdot}$ (R^m, m = 1, 2) according to Eq. (1):

$$k_{tr} = k_{add}\frac{[\mathrm{ND}]_0}{[\mathrm{CCl}_4]_0}\cdot\frac{[\mathrm{B}]}{[\mathrm{A}]} \tag{1}$$

which holds for reactions described by Scheme 1 in an approximation of quasistationary concentrations:

Scheme 1

$$\mathrm{CCl_3(CH_2CHX)}_n^{\cdot} + \left\{ \begin{array}{l} \mathrm{RNO} \xrightarrow{k_{add}} \mathrm{CCl_3(CH_2CHX)}_n\mathrm{N(\dot{O})R} \quad (A) \\ \mathrm{CCl_4} \xrightarrow{k_{tr}} \mathrm{CCl_3(CH_2CHX)}_n\mathrm{Cl}(T_n) + \dot{\mathrm{C}}\mathrm{Cl_3} \end{array} \right.$$

$$\dot{\mathrm{C}}\mathrm{Cl_3} + \mathrm{RNO} \xrightarrow{k^{(1)}_{add}} \mathrm{CCl_3N(\dot{O})R} \quad (B)$$

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TABLE 1. Parameters of EPR Spectra of Nitroxyl Radicals Formed during Photochemical Reaction of $CCl_3(CH_2CHCl)_nI$ (n = 1, 2) with $Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2$ in the Presence or Absence of CCl_4 (spin trap — ND, 40°C, λ 254 nm, *a* — Oe)

Initial compound	Identified radical	a_N	a_H	a_{Cl}	Reaction conditions $[CCl_4]_0$	$[ND]_0 \cdot 10^3$	[B]/[A]†
					mole/liter		
$CCl_3(CH_2CHCl)_nI$	$CCl_3(CH_2CHCl)_n^{\bullet}$‡	15,2	8,1	3,5	–	4,9–0,31	–
$CCl_3CH_2CHClI+$ $+CCl_4$	$CCl_2CH_2\dot{C}HCl$	15,2	8,1	3,5	5,8	1,8	1,03
	$\dot{C}Cl_3$	10,7	–	1,3	7,7	0,93	2,6
$CCl_3(CH_2CHCl)_2I+$ $+CCl_4$	$CCl_3(CH_2CHCl)_2^{\bullet}$	15,2	8,1	3,5	2,1	7,0	0,56
	$\dot{C}Cl_3$	10,7	–	1,3	6,23	3,5	3,18

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*The ND concentration is given, taking into account the monomer—dimer equilibrium, K = 322 liter/mole [3].

†Taking into account ΔH, multiplicity, and line intensity in spectra of radicals A and B. The width of the lines ΔH of the $CCl_3(CH_2CHCl)_nN(\dot{O})R$ (A) (ΔH = 2.0 Oe) and $CCl_3N(\dot{O})R$ (B) radicals (ΔH = 0.56 Oe) (R = 2,3,5,6-Me_4C_6H) was measured from the individual EPR spectra.

‡$CCl_3CH_2\dot{C}HCl$ radicals were generated also by Scheme 3 (see text).

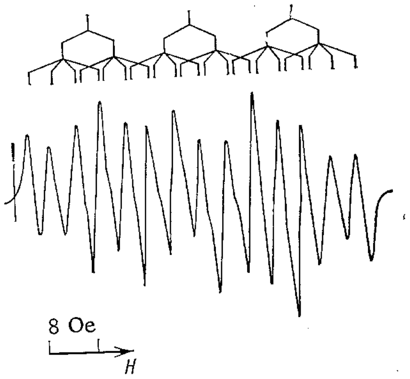

Fig. 1. EPR spectrum of $CCl_3(CH_2(CH_2CHCl)_nN(\dot{O})R$, R = 2,3,5,6-$Me_4C_6H$.

where RNO is nitrosodurene (ND) (here and below, R = 2,3,5,6-Me_4C_6H), X = H or Me.

In the present work, we determined the rate constants of splitting Cl from CCl_4 by telomeric radicals $CCl_3(CH_2CHCl)_n^{\bullet}$ ($\dot{R}^n$, n = 1, 2) and their addition to CH_2=CHCl and RNO at 40°C.

Radicals $\dot{R}^n$ are generated by Scheme 2:

Scheme 2

$$\underset{(T_1,\ n=1;\ T_2,\ n=2)}{CCl_3(CH_2CHCl)_nI} \xrightarrow{\lambda\ 254\ \text{nm}\quad Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2} CCl_3(CH_2CHCl)_n^{\bullet}(\dot{R}^n)$$

Figure 1 shows an EPR spectrum and Table 1 lists the hyperfine interaction (HFI) constants of spin adducts of radicals $\dot{R}^n$ with ND—$CCl_3(CH_2CHCl)_nN(\dot{O})R$ (A).

During irradiation with a λ 254-nm light of a benzene solution of T_1 and T_2 containing $Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2$, ND, and CCl_4, signals of radicals A (Fig. 2, lines *a*) and $CCl_3N(\dot{O})R$ (B) are observed in the EPR spectrum. The formation of radicals A and B identified is described by Scheme 1 (X = Cl) which shows that to determine the rate constants of splitting Cl from CCl_4 by telomeric radicals $\dot{R}^n$, we must know the rate constants of the addition of $\dot{R}^n$ to ND.

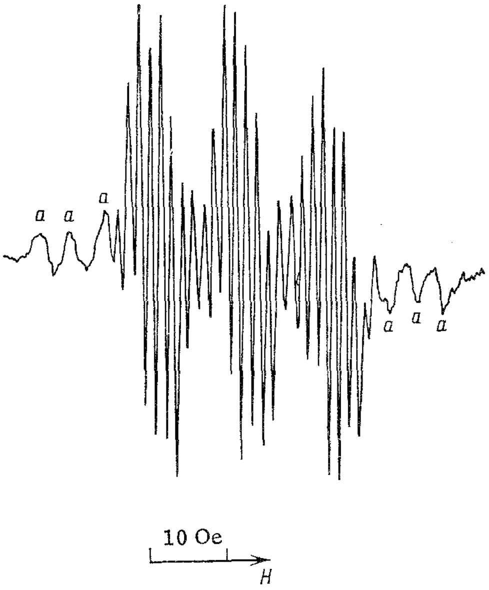

Fig. 2

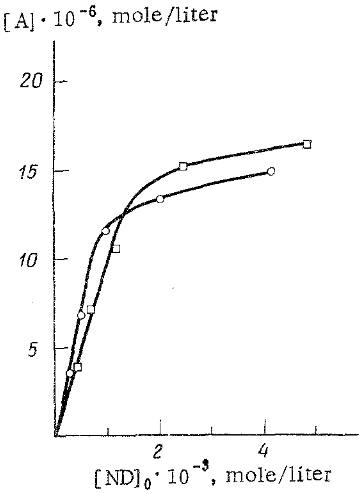

Fig. 3

Fig. 2. EPR spectra of radicals $CCl_3(CH_2CHCl)_nN(\dot{O})R$ (signals *a*) and $CCl_3N(\dot{O})R$, R = 2,3,5,6-Me_4C_6H.

Fig. 3. Dependence of yield of radicals 2,3,5,6-$Me_4C_6HN(\dot{O})$-$CHClCH_2CCl_3$ (A) on ND concentration.

TABLE 2. Rate Constants of Splitting Chlorine (k_{tr}) from CCl_4 by $\dot{R}^n$ Radicals, and Their Addition (k_p) to Vinyl Chloride at 40°C

Radical	$k_{tr} \cdot 10^{-3}$*	$k_p \cdot 10^{-4}$
	mole/liter · sec	
$CCl_3CH\dot{C}HCl$	0,45	16,8
$CCl_3(CH_2CHCl)_2^{\bullet}$	1,76	9,8

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*Relative error ±15%. The same values of (k_{tr}) were obtained in their calculation by a more general equation, which holds for Scheme 1 ($k_{add}^{(1)}$ = 10^7 mole/liter·sec [7]), supplemented by the splitting stages: the interaction of $CCl_3(CH_2CHCl)_n^{\bullet}$ and $\dot{C}Cl_3$ radicals with nitroxyls A and B (k_{spl} = 10^8 mole/liter·sec [8]).

TABLE 3. Parameters of ^{13}C NMR Spectra of T_1 and T_2

Compound	δ ^{13}C, ppm with reference to TMS					$^1J_{C-H}$, Hz			
	C¹	C²	C³	C⁴	C⁵	C²	C³	C⁴	C⁵
$\overset{1}{C}Cl_3\overset{2}{C}H_2\overset{3}{C}HICl(T_1)$	95,7	67,5	17,3			140	176		
$\overset{1}{C}Cl_3\overset{2}{C}H_2\overset{\overset{3}{*}}{C}HCl\overset{4}{C}H_2\overset{\overset{5}{*}}{C}HCl(T_2)$ *	96,0	61,4 61,3	56,4 55,2	54,9 53,5	26,1 21,8	138	157	136	174

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*The signals are doubled in the spectrum of T_2 because of the presence of two asymmetric centers.

The constant k_{add} of the addition of radicals $CCl_3CH_2\dot{C}HCl(\dot{R}^1)$ to ND was determined by using the procedure described in [3]. Radicals $\dot{R}^1$ were generated by Schemes 2 and 3.

Scheme 3

$$CCl_3CH_2CHClBr \xrightarrow{\lambda\,254\ \text{nm},\ Re_2(CO)_{10}} \dot{R}^1 + BrRe(CO)_5$$

$$\dot{R}^1 + RNO \xrightarrow{k_{add}} \dot{A}^1$$

$$2\dot{A}^1 \xrightarrow{2k_{spl}} \text{Nonradical products}$$

$$\dot{A}^1 + \dot{R}^1 \xrightarrow{k_{spl}} \text{Nonradical products}$$

Figure 3 shows the dependence of the stationary concentration of radicals $\dot{A}^1$ on the ND concentration. For reactions described by Scheme 3, k_{add} is calculated from Eq. (2) [3]:

$$k_{add} = k_{spl}\left(\frac{d\dot{A}^1}{d[ND]_0}\right)_{[ND]_0 \to 0} \tag{2}$$

From the data in [3, 4] it can be assumed that $k_{spl} = 10^8$ liter/mole·sec at 40°C. From the experimental results obtained on the change in the stationary concentration of radicals $\dot{A}^1$ as a function of the initial ND concentration (see Fig. 3), according to Eq. (2) we obtain $k_{add} = 1.4 \cdot 10^6$ liter/mole·sec at 40°C.

Table 2 shows the k_{tr} values for splitting Cl from CCl_4 radicals $\dot{R}^n$ at 40°C, obtained by substituting in Eq. (1) the experimental results given in Table 1 and the values of the calculated k_{add} for adding radicals $\dot{R}^n$ to ND. In the same table, the k_p values are also given for the addition radicals $\dot{R}^n$ to $CH_2{=}CHCl$, determined from the values of individual chain transfer constants [5]: $C_n = k_{tr}/k_p$ ($C_1 = 0.00267$, $C_2 = 0.018$) and k_{tr}. The k_{tr} and k_p values obtained for radicals $\dot{R}^n$ show that changes in the values of C_n as a function of n in the telomerization of $CH_2{=}CHCl$ with CCl_4 are due to changes occurring in both the values of k_{tr} and k_p.

EXPERIMENTAL

The EPR spectra were obtained on the RÉ-1306 spectrometer by the method described in [1]. The ^{13}C NMR spectra were run on the "Bruker" WP-200-SY spectrometer. The GLC analysis of the reaction mixtures was carried out on the LKhM-8MD chromatograph in a He current with a katharometer. A 1000 × 3 mm steel column with 5% SE-30 on N-AW Chromatone was used at 180 and 200°C.

The polychloroiodoalkanes T_1 and T_2 were synthesized by radical telomerization of vinyl chloride with CCl_3I (obtained according to [6]). The synthesis was carried out in sealed 4-ml glass ampuls at 90°C. The following were charged into each ampul: 0.05 mmole $(PhCO_2)_2$, 6.5 mmole CCl_3I, and 34.6 mmole C_2H_3Cl ($C_2H_4Cl/CCl_3I = 5.3$). According to the GLC data, the conversion of CCl_3I after 45 min was ∿100%. The reaction mixture contained 46.6% of T_1, 45.4% of T_2 and 8.0% of T_3. The polychloroiodoalkanes were isolated by distillation in vacuo, T_1 was obtained in a pure state. Found: C 11.73; H 1.12; Hal 87.28%. $C_3H_3Cl_4I$. Calculated: C 11.73; H 0.98; Hal 87.31%. According to GLC data, T_2 contained 15% of T_3. Found: C 18.44; H 1.83; Hal 79.88%. Calculated: C 18.49; H 1.89; Hal 79.62%. T_3 was identified by GLC method where a linear dependence of the logarithm of the retention time on the number of monomeric units in the molecule was maintained. The structure of the telomers was confirmed by ^{13}C NMR data (Table 3).

CONCLUSIONS

1. Rate constants of splitting the chlorine atom from CCl_4 by the $CCl_3(CH_2CHCl)_n^{\cdot}$ radicals and addition of these radicals to vinyl chloride and nitrosodurene at 40°C were determined by the EPR method.

2. It was shown that in the telomerization of vinyl chloride with CCl_4, the changes in the individual chain transfer constants are due to changes in the values of both the chain transfer and chain propagation rate constants.

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POLARITY, POLARIZABILITY, AND STERIC STRUCTURE OF CERTAIN THIOESTERS OF TRIVALENT PHOSPHORUS ACIDS

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In continuation of our previous investigations on the thioesters of trivalent phosphorus acids [1], in the present work we studied the polarity and polarizability of the P—S bond, and also conformations of dimethyl methylthiophosphinite (I), diphenyl ethylthiophosphinite (II), and phenyl diethyldithiophosphinite (III).

To determine the dipole moment (DM) of the P—S bond, we chose 2,4-dimethyl-1,3,2-dithiaphosphorinane (IV) as a model compound. In the ^{31}P NMR spectrum of this compound, one signal (δ^{31}P + 10 ppm) is observed, which indicates an axial orientation of the Me group at the P atom. In calculations of polarity and polarizability of (IV), the geometry was taken from [2], and the value m(Alk — S) = 1.31 D used was calculated from the data in [3]. The DM of the S—P bond is equal to 0.8 D. The ellipsoid polarizability axes of this bond, cal-

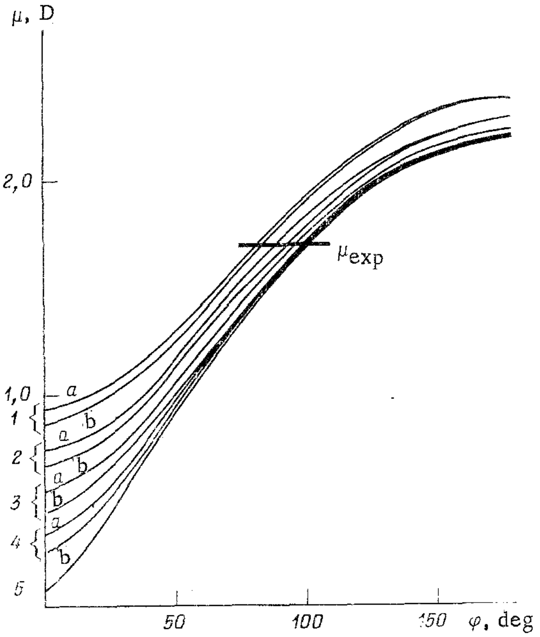

Fig. 1. Influence of change in polarity of P—S bond on conformational dependence DM—φ. Curves 1-5 were calculated for the values of ±m(P—S) = 0.9; 0.7; 0.5; 0.3; 0 D.

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