REACTIVITY OF POLYATOMIC COMPLEX ESTERS IN THE REACTION WITH TRICHLOROMETHYL RADICALS

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The study of the reaction of peroxide radicals with complex polyatomic esters has shown that the presence of several functional groups in the molecule affects the reactivity of each fragment of the molecule [1-5]. This effect was attributed to the collective dipole-dipole interaction between a polar peroxide radical and the complex ester groups [6]. If the dipole-dipole interaction of the reagents is really the cause of this phenomenon, the effect of the nonadditivity of the partial rate constants should disappear in reactions of polyfunctional molecules with a nonpolar species. For this reason, we studied the reactivity of polyatomic esters in the reaction with the CCl_3 radical, which has a planar structure and no dipole moment. CCl_3 is suitable for comparison with the peroxide radical since both of these radicals are electrophilic species, one with and the other without a dipole moment. The chain process involving CCl_3 radicals was studied in the RH- CCl_4 -benzoyl peroxide (initiator) system in which a chain chlorination reaction takes place with formation of RCl and $CHCl_3$. There is little information on the reactivity of trichloromethyl radicals in chain breaking reactions, and the existing data primarily concern the rate constants. The reaction of CCl_3 with polyatomic complex esters has not been studied previously.

EXPERIMENTAL

The esters of pentaerythritol and monocarboxylic acids, CR_4 , were investigated: pentaerythritol tetrapropionate (R = $CH_2OCOCH_2CH_3$) (I), pentaerythritol tetracaproate (R = $CH_2OCO(CH_2)_8CH_3$) (II), and neopentylglycol dipropionate (CH_3)₂ CR_2 (III) and 1,1,1-trimethylolpropane tripropionate $CH_3CH_2CR_3$ (IV) (R = $CH_2OCOCH_2CH_3$); n-heptadecane (V) was used for comparison.

The esters were synthesized according to [7] and purified as described in [3]; (I) and (II) were also repeatedly recrystallized from n-pentane and isopropanol. Branched and olefin hydrocarbon impurities were removed from (V) as in [8]. CCl_4 was purified by ozonization, dried, and distilled over P_2O_5 . Benzoyl peroxide (BP) was recrystallized twice from a $CHCl_3$ -MeOH mixture. Hexachloroethane was synthesized according to [9] and purified twice by recrystallization from ether and ethanol. The kinetic experiments were conducted at 373°K in sealed glass ampuls with a 3-ml volume mixture (solution of ether in CCl_4) in an atmosphere of Ar. The degree of decomposition of the BP was 99%, which was equal to 6.6 of its half-life ($\tau_{1/2}$). The products of transformation of the trichloromethyl radicals were analyzed chromatographically: Chrom-4 chromatograph, column packed with 15% 1,2,3-tris(β -cyanethoxy)propane on Chromosorb W, He carrier gas, 30-160°C temperature of analysis, flame-ionization detector, and n-propanol internal standard.

DISCUSSION OF RESULTS

Decomposition of Benzoyl Peroxide. The decomposition of BP in a medium of ester (III) (1.5 mole/liter) and CCl_4 was studied in a separate series of experiments using the method of iodometric titration for analysis of the BP; when $[BP] \le 2.5 \cdot 10^{-2}$ mole/liter, it decomposed monomolecularly with a rate constant k_d equal to $(3.3 \pm 0.3) \cdot 10^{-4} \sec^{-1} (373^{\circ}\text{K})$. In the range of concentrations of BP = $(2.5 - 7.4) \cdot 10^{-2}$ mole/liter, k_d increased from $3.3 \cdot 10^{-4}$ to $4.0 \cdot 10^4$; this could have been related to the induced decomposition of BP. To exclude this factor, $[BP] \le 2.4 \cdot 10^{-2}$ mole/liter was used in the experiments.

The average yield of radicals in volume e was measured as a function of the consumption of 2,2,6,6tetramethyl-4-benzoylhydroxypiperidine-1-oxyl (VI) in time $5\tau_{1/2}$ of the decomposition of BP. The experiment was performed in Ar in a solution of (III) (1.5 mole/liter) in CCl_4 with $[BP]_0 = 0.5 \cdot 10^{-3}$ mole/liter and $[>NO^{\circ}] =$ $0.8 \cdot 10^{-3}$ mole/liter, with EPR recording of $>NO^{\circ}$. Under these conditions, decomposition of BP catalyzed by (VI) was not observed (cf. [10]): k_d in the presence of (VI) did not exceed the value of k_d obtained in experiments

Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka Branch. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2029-2035, September, 1983. Original article submitted September 27, 1982.

[RH]	[BP] ₀ • 10 ³	Δ [CHCl ₃] · 10 ²		Δ[CHCl ₃]/[RH]·				
mole/liter		$\Delta[CB]/[BP]_0$	$(BP)_0^{1/2}$, (liter/mole) ^{1/2}	$\overline{v} = \frac{\Delta[CHCl_{3}]}{2e [BP]_{0}}$				
Ester (I), $k_p/(2k_t)^{1/2} = (2.8\pm0.1) \cdot 10^{-3} (\text{liter/mole} \cdot \text{sec})^{1/2}; k_p = 1.6 \cdot 10^2 \text{ liter/mole} \cdot \text{sec}$								
1,2 2,0 2,0 2,0	2,43 4,05 9,04 14,70	1,8 3,8 5,3 6,8	0,39 0,27 0,25 0,30	0,31 0,30 0,28 0,28 0,28 Avg. 0,29±0,01	8,4 10,7 6,7 5.3			
Ester (II), $k_p/(2k_i)^{1/2} = (22,3\pm3,5) \cdot 10^{-3} (\text{liter/mole} \cdot \text{sec})^{1/2}$; $k_p = 12.5 \cdot 10^2 \text{ liter/mole} \cdot \text{sec}$								
$\begin{array}{c} 0.96\\ 0.66\\ 0.31\\ 0.25\\ 0.48\\ 0.66\\ 0.66\\ 0.66\\ 0.66\\ 0.66\end{array}$	5,20 5,95 6,11 5,86 6,03 9,52 5,95 1,55 0,83	$\left(\begin{array}{c} 18,8\\ 10,3\\ 6,2\\ 5,0\\ 12,5\\ 14,3\\ 10,3\\ 5,1\\ 2,9\\ \end{array}\right)$	$\begin{array}{c} 0,33\\ 0,22\\ 0,41\\ 0,43\\ 0,40\\ 0,25\\ 0,22\\ 0,22\\ -\end{array}$	$ \begin{array}{c} 2.72 \\ 2.03 \\ 2.55 \\ 2.60 \\ 3.33 \\ \text{Avg.} 2.65 \pm 0.30 \\ 2.23 \\ 2.(3) \\ 1.95 \\ 1.52 \\ \text{Avg.} 1.93 \pm 0.21 \\ \text{A verage of } 1, 2 \\ 2.29 \pm 0.36 \end{array} $	4,1 19,7 11,5 9,7 23,5 17,4 19,7 37.2 39,7			
Ester (III), $k_p/(2k_t)^{1/2} = (1.8 \pm 0.1) \cdot 10^{-3}$ (liter/mole sec) ^{1/2} ; $k_p = 1.0 \cdot 10^2$ liter/mole sec								
1,5 1,5 1,5	5,08 9,62 20,10	1,8 2,8 4,1	$0,43 \\ 0,41 \\ 0,50$	0,17 0,19 0,19 Avg-0,18±0,01	4,0 3,3 2,3			
Ester (IV), $k_p/(2k_t)^{\frac{1}{2}} = (3,1\pm0,5)\cdot10^{-3}$ (liter/mole sec) ^{1/2} ; kp = $1.7\cdot10^2$ liter/mole sec								
2,6 2,6	21,2 45,2	10,4 20,6	0,22 0,22	0,27 0,37 Avg. 0,32±0,05	5,6 5,2			
(V), $k_p/(2k_l)^{\prime h} = (19.6 \pm 2.9) \cdot 10^{-3} (liter/mole \cdot sec)^{1/2}$; $k_p = 11.0 \cdot 10^2 liter/mole \cdot sec$								
0,86 2,15 2,15	1,55 3,88 9,09	$\begin{array}{c} 6,0\\31,0\\40,0\end{array}$		1,79 2,32 1,96 Avg. 2,02±0,30	44.1 90,9 50,0			

TABLE 1. Experimental Conditions and Kinetic Characteristics of the Reactivity of Compounds in the Reaction with Trichloromethyl Radicals, 373°K

without (VI). The value of e, equal to 0.44 ± 0.04 (373°K), satisfactorily coincided with the value of $e = 0.50 \pm 0.06$ (373°K) calculated from the balance equation which correlates the number of free radicals formed on total decomposition of BP with the amount of the product of recombination of CCl₃ radicals (see below) based on the results of the gas chromatographic analysis of C_2Cl_6 .

The value of the initiation rate constant k_i of BP in CCl₄ measured as a function of the rate of consumption of 2,4,6-tri-tert-butylphenoxyl with $[PB]_0 = 4.1 \cdot 10^{-2}$ mole/liter was equal to $3.3 \cdot 10^{-4} \text{ sec}^{-1}$ (373°K) [11, 12]. It is possible to estimate $e = k_i/2k_d = 0.5$ from a comparison of this value of k_i with our value of k_d . The value of e in decomposition of BP in benzene (353°K) was also equal to 0.5 [10], which is in agreement with the data on the volume yield of radicals obtained by the method of inhibitors (343°K) in decomposition of BP in benzene and chlorobenzene [13]; the value of e is thus in good agreement with the data in the literature. In calculating the relative rate constants of the reaction, e = 0.44 and $k_d = 3.3 \cdot 10^{-4} \text{ sec}^{-1}$ were used.

Chain Initiation. Like other acyl peroxides, BP decomposes into radicals according to a general scheme; benzoyl, hydroxy, and phenyl radicals are formed in a solution of CCl_4 [14]. Formation of benzoylhydroxy radicals was confirmed by experiments on decomposition of BP in the presence of an H atom donor: 1,3,5-trimethyl-2,4,6-tris(3',5'-di-tert-butyl-4'-hydroxybenzyl)benzene (VII). The following products (mole/liter) were found on total decomposition of $2 \cdot 10^{-2}$ mole/liter of BP in CCl_4 in the presence of 1.5 mole/liter of (III) and $3 \cdot 10^{-2}$ mole/liter of (VII): $0.2 \cdot 10^{-3}$ diphenyl, $0.8 \cdot 10^{-3}$ phenylbenzoate, $3 \cdot 10^{-3}$ benzoic acid, and $1 \cdot 10^{-2}$ chlorobenzene (CB) in the absence of benzene ($[C_6H_6] < 0.2 \cdot 10^{-3}$ mole/liter). In the BP-CCl₄-RH system without (VII), CB was also formed in the concentration of $1 \cdot 10^{-2}$ mole/liter ($\Delta[CB]/[BP]_0 = 0.5$) in the same experimental conditions, but there was no benzene or benzoic acid ($[C_6H_5COOH] < 7 \cdot 10^{-4}$ mole/liter). Varying the concentration of RH [ester (II)] in the 0.25 - 0.96 mole/liter range also did not alter the yield of CB, and

TABLE 2. Yield of Hexachloroethane as a Function of the Concentration of Ester (II), 373°K

[RH]	[BP] ₀ .10 ³	Δ [C ₂ Cl ₆] · 10 ³	
mo	$\Delta[C_2Cl_5]/[BP]_0$		
0,25 0,31 0,48 0,66 0,96	5,86 6,11 6,03 5,95 5,20	3,5 2,9 3,4 2,8 2,2	0,60 0,47 0,56 0,47 0,42



Fig. 1. Ratio $\Delta [CHCl_3]/[BP]_0^{1/2}$ as a function of the concentration of (II) (1) and \triangle [CHCl₃] as a function of [BP]₀^{1/2} (2) in CCl₄ at 373°K.

the ratio of Δ [CB]/[BP]₀ remained constant and equal to 0.39 ± 0.03 (Table 1). The same yield of CB (within the limits of experimental error) and the absence of analyzable quantities of benzene in the $BP-CCl_4-RH(III)-(VII)$, $BP-CCl_4-RH(III)$, and $BP-CCl_4$ systems when the concentration of RH(II) was varied, as well as the absence of benzoic acid in the $BP-CCl_4-RH(III)$ system thus indicate that CCl_3 radicals are formed according to the reaction

$$C_6H_5 + CCl_4 \rightarrow C_6H_5Cl + CCl_3$$

and C_6H_5 and C_6O_5COO radicals do not attack the CH bond in the esters in these conditions, that is, the reactions:

$$C_6H_5 + RH \rightarrow C_6H_6 + R^*$$

$$C_6H_5COO^* + RH \rightarrow C_6H_5COOH + R^*$$

do not take place to a marked degree. However, the yield of chlorobenzene formed at the end of the experiments was less than the number of radicals formed during total decomposition of BP: $[C_6H_5Cl] < 2e[BP]_0$ (see Table 1). Not only phenyl, but also benzoylhydroxy radicals apparently participate in chain initiation; the products of the reactions were not identified.

Chain Propagation and Breaking. The CCl₃ radicals formed react with the RH substrate with formation of CHCl₃. The amount of chloroform is greater than the number of radicals formed from BP and entering the volume during total decomposition of BP (see Table 1). As a consequence, a chain process with chain propagation according to the following reactions develops in these conditions:

$$\begin{array}{l} \operatorname{CCl}_{\mathfrak{s}}^{\bullet} + \operatorname{RH} \xrightarrow{k_{p}} \operatorname{CHCl}_{\mathfrak{s}} + \operatorname{R}^{\bullet} \\ \operatorname{R}^{\bullet} + \operatorname{CCl}_{\mathfrak{s}} \to \operatorname{RCl} + \operatorname{CCl}_{\mathfrak{s}} \end{array}$$
(1) (2)

$$+ \operatorname{CCl}_4 \rightarrow \operatorname{RCl} + \operatorname{CCl}_3$$

The parameter $\bar{\nu} = \Delta [CHCl_3]/2e[BP]_0$, which characterizes the average chain length, varied from 2 to 40 components in the reaction of CCl₃ with the esters and attained 90 components in the reaction of CCl₃ with n-heptadecane (see Table 1).

TABLE 3. Partial Rate Constants k_{pj} of the Reactions of CCl₃ (373°K) and R'O₂ '(404°K) Radicals with the CH₂OCOCH₂CH₃ (R) Fragment as a Function of the Number of R

Number of	k _{pj} R·10 ² (CCL [*])	$k_{pj}\mathbf{R}(\mathbf{R}'\mathbf{O}_2')$	∧c≠ ki/mole
R groups	liter/m	(R'O ₂ *)	
4 3 2	0,40 0,57 0,50	3,4 2,1 1,5	-4,1 -2,5 -1,4

Stage 1 is limiting in chain propagation, and chain breaking primarily takes place at the CCl_3 radicals according to the reaction:

$$\operatorname{CCl}_3$$
 + CCl_3 $\xrightarrow{2\kappa_t}$ $\operatorname{C}_2\operatorname{Cl}_6$

since the yield of the product of recombination of CCl_3° radicals, hexachloroethane, remains almost constant (within the limits of experimental error) with a variable concentration of RH [ester (II)]: $\Delta [C_2Cl_6]/[BP]_0 = 0.50 \pm 0.06$ (Table 2); as a consequence, the contribution of the reactions:

$$\begin{array}{c} \operatorname{CCl}_3^{\bullet} + \operatorname{R} \to \operatorname{RCCl}_3\\ \operatorname{CCl}_3^{\bullet} + \operatorname{R}^{\bullet} \to \operatorname{R}(-\operatorname{H}) + \operatorname{CHCl}_3\\ \operatorname{R}^{\bullet} + \operatorname{R}^{\bullet} \to \operatorname{disproportionation} + \operatorname{recombination} \end{array}$$

in the steady state is insignificant in chain breaking. This result is in agreement with the findings of studies on radiochemical transformation of CCl_4 -hydrocarbon systems [15, 16], where hexachloroethane was found as the only product of chain breaking. In addition, the yield of hexachloroethane corresponds to the number of radicals formed from BP during total decomposition of the initiator, i.e., $e[BP]_0 = \Delta [C_2Cl_6]$ when RH (II) is varied. The value of e (0.50 ± 0.06) found from the equalities reported above based on the results of chromatographic analysis of C_2Cl_6 in a series of experiments (see Table 2) thus coincided with the similar value obtained from the rate of consumption of radicals (VI) during total decomposition of BP 0.44 ± 0.04. The following ratios are valid for the scheme of reactions given above:

$$\frac{d [\text{CHCl}_3]}{dt} = \frac{k_p [\text{RH}]}{(2k_t^{1/s})} (2ek_d [\text{BP}])^{4/s}$$
$$[\text{BP}] = [\text{BP}]_0 e^{-k_d t}$$

and $[CHCl_3]_{\infty} = 2k_p [RH](2e [BP]_0)^{1/2}/(2k_t k_d)^{1/2}$ is valid for the time of total decomposition of BP. The rules derived from the last equation, the first order of the reaction with respect to [RH], and the order of 1/2 with respect to [BP]_0 (Fig. 1), were followed for n-heptadecane and all of the esters studied (except for ester (IV), see below). The values $k_d = 3.3 \cdot 10^{-4} \sec^{-1}$ and e = 0.44 were used for calculation of $k_p/(2k_t)^{1/2}$ from the experimental data, and the value $2k_t = 3.1 \cdot 10^9$ liter/mole·sec, selected on the basis of the data in the literature [15], was used for calculation of k_p .

The concentration of RH in the experiments remained almost constant: several percent of the ester were consumed during total decomposition of BP, and up to 20% were only consumed in the experiments with (II). The difference with respect to the average value of $k_p/(2k_t)^{1/2}$ was 4-15%, and the error of the chromatographic analysis was $\leq 15\%$.

Only parameter $k_p/(2k_t)^{1/2}$ was estimated for ester (IV) using the results of two experiments with higher concentrations of BP, since the contribution of linear chain breaking at the CCl₃ radicals, observed in the experiments with ester (IV), was very small in this variant.

The partial rate constants k_{pj} of the reaction of CCl_3^* radicals with R fragments (R = $CH_2OCOCH_2CH_3$) in propionic acid esters were calculated with the values of k_p (see Table 1).

$$k_{pj}(\mathbf{R}) = \frac{k_p(\mathbf{I})}{4} = \frac{1.6 \cdot 10^2}{4} = 40 \, \text{liter/mole} \cdot \text{sec (CR}_4)$$
$$k_{pj}(\mathbf{R}) = \frac{k_p(\mathbf{III})}{2} = \frac{1.0 \cdot 10^2}{2} = 50 \, \text{liter/mole} \cdot \text{sec ((CH_3)_2CR}_2)$$

$$k_{pj}(\mathbf{R}) + \frac{1}{3}k_{pj}(\mathbf{CH}_2) = \frac{k_p(\mathbf{IV})}{3} = \frac{1.7 \cdot 10^2}{3} = 57$$
 liter/mole sec,

hence, $k_{Di}(R) < 57$ liter/mole sec (CH₃CH₂CR₃) (the reaction of CCl₃ with CH₃ groups was disregarded [17]). In the case of ester (IV), the trichloromethyl radicals also attacked the CH₂ group as well as the complex ester groups; the reactivity of this group can be estimated by assuming $k_{pj} = 50$ liter/mole.sec (as in the R fragment as a whole); then $1/3 k_{pi}(CH_2)$ will be no more than 16 liter/mole.sec, and $k_{pj}(R)$ will therefore be no less than 40 liter/mole.sec. A comparison of all three values of kpj(R) shows that they are similar, and the average value is $k_{pj}(R) = 49 \pm 6$ liter/mole sec. A different picture was observed in the reaction of these compounds with the cumylperoxide radical [3], where the values of k_{Di}(R) increase with an increase in the number of R groups in the ester molecule (Table 3). If we assume that this effect is related to the inductive effect of the functional groups in the ester molecule, a symbatic relationship would be observed in the reactions of the RO2 and CCl3 radicals in this case, since both are electrophilic. However, the rule of additivity in the group of reactions studied holds for CCl₃ and does not apply to RO₂. The effect of the nonadditivity of the partial rate constants in the reactions of the RO₂ radical cannot be correlated with the electrophilic nature of the attacking species. The hypothesis of the steric factor as a cause of the change in k_{Dj} with an increase in the number of complex ester R groups in the molecule becomes superfluous, since the value of k_{pi}(R) should decrease, but it increases instead (see Table 3); in this case, a symbatic relationship would also be observed in the change in $k_{pj}(R)$ for CCl₃ and RO₂ radicals. As a consequence, the presence of a dipole moment in the peroxide radical and the absence of a dipole moment in CCl₃ is the main cause of the difference in the change in k_{pj} for RO_2° and CCl_3° radicals in reactions with the esters described above. The rate constant k_{pj} of the reaction of CCl_3° radicals with the CH_2 group in n-heptadecane is $1.1 \cdot 10^3/15 = 70$ liter/mole.sec.

The partial rate constant of the reaction of CCl_3° radicals with the β , γ , δ and other CH_2 groups in the acid residue was calculated by assuming that the reactivity of the CH_2 group is the same:

$$k_{pj}$$
 (CH₂) = $\frac{k_p (II) - k_p (I)}{7 \cdot 4} = \frac{(12.5 - 1.6) \cdot 10^2}{28} = 39$ liter/mole·sec

The value of k_{pj} of the CH_2OCOCH_2 fragment is equal to 49 liter/mole sec (see Table 3); it thus follows that the α -CH₂ group of the acid residue of an ester is probably slightly deactivated in comparison to the other methylene groups and the CH₂ group in the n hydrocarbon, which is in agreement with the data on attack of pentaerythritol esters by peroxide radicals [3, 18]. However, in the case of the nonpolar CCl₃^{*} radical, it is also possible that the reaction of CCl₃^{*} with the CH₂O group is hindered due to the proximity of the quaternary C atom, and in this case, the α -CH₂ group will have reactivity similar to the other groups of the acid residue and the CH₂ group in the n-paraffin molecule.

The rule of additivity is thus followed for the reaction of the nonpolar CCl_3° radical with the CH_2OCOCH_2 - CH_3 fragment in a polyatomic complex ester: the rate constant of the reaction is directly proportional to the number of the fragments in the ester molecule. As a consequence, the deviation from additivity observed in reactions of peroxide radicals with polyatomic complex esters [3] is the result of the dipole-dipole interaction of the polar RO_2° radical with the polar groups in the ester molecule.

CONCLUSIONS

1. The kinetics of chlorination of pentaerythritol tetrapropionate and tetracaprate, neopentylglycol dipropionate, and 1,1,1-trimethylolpropane tripropionate in a solution of CCl_4 at 373°K according to the scheme RH + $CCl_4 \rightarrow RCl + CHCl_3$ were studied.

2. Initiation of the reaction by benzoyl peroxide takes place according to a chain mechanism with the participation of CCl_3 radicals in chain propagation; the rate constants of the reaction of CCl_3 with these esters were determined.

3. The partial rate constant of the reaction of CCl_3° with the $CH_2OCOCH_2CH_3$ fragment is 49 ± 6 liter/mole·sec at 373°K and is not dependent on the number of such fragments in the molecule.

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KINETIC MECHANISMS OF POLYMERIZATION OF BUTYL ACRYLATE IN THE PRESENCE OF PORPHYRIN COBALT DURING INDUCTION

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In radical polymerization (PM) of methacrylates [1, 2] and styrene [3], porphyrin cobalts (CoP) effectively catalyze chain transfer to the monomer. Acrylic esters occupy the position next to methacrylate in the order of radical reactivity [4], which indicates the similarity of the reactivity of both the monomers and the corresponding radicals. Nevertheless, in PM of butyl acrylate (BA), CoP does not exhibit the properties of a chain transfer catalyst, but the properties of a "strong" inhibitor of the classic type [5]. The reactivity of acrylic and methacrylic monomers thus differ significantly with respect to CoP.

In contrast to classic inhibitors, the effect of CoP is not depleted during induction but is also manifested in slowing of the process after induction has ended and in a long aftereffect. It has been suggested that inhibition of PM of BA by CoP is "reversible" [6].

The kinetic mechanisms of the starting stage of PM of BA in the presence of CoP based on the concept of the reversibility of inhibition of PM of BA by CoP were studied in detail in the present study.

EXPERIMENTAL

The monomer was successively washed with a 3% solution of NaOH, distilled water, a saturated solution of NaHSO₃, a solution of NaCl, and distilled water until a neutral reaction was obtained to remove impurities which could contaminate the catalyst; it was then dried for 2 h over annealed Na₂SO₄, passed through a column containing Al_2O_3 , and distilled at pressure of 30 mm in an Ar current. Approximately 0.5% of Co(II)-tetraphenylporphyrin was added to the distilled monomer, the solution was measured out into glass ampuls, evacuated at 5·10⁻³ mm, and stored in the refrigerator. Immediately before the experiment, the ampuls were heated

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2036-2042, September, 1983. Original article submitted December 7, 1982.