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Features of Thermal Decomposition of Acrylates and Methacrylates Based on *tert*-Butylperoxy-α-chloroalkoxyethanes

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Abstract—The kinetics of thermal decomposition of acrylic and methacrylic peroxides of general formula $(CH_3)_3COOCH_2CH_2OCH(R^1)OC(O)R^2$, where R^1 = H, Me, Et and R^2 = CH=CH$_2$, (CH$_3$)C=CH$_2$, Et, in the absence of solvent was studied.

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Synthesis of peroxide acetal acylals, where acrylate and methacrylate groups are remote from the peroxy moiety [1], through a nucleophilic substitution of chlorine in α-chloroethers of 2-*tert*-butylperoxyethanol is known [2]. To evaluate the thermal stability of the peroxy monomers we studied the kinetics of thermal decomposition of 1-*tert*-butylperoxy-2-(acryloyloxymethoxy)ethane (**I**), 1-*tert*-butylperoxy-2-[1'-(acryloyloxy)ethoxy]ethane (**II**), 1-*tert*-butylperoxy-2-[1'-(acryloyloxy)propoxy]ethane (**III**), 1-*tert*-butylperoxy-2-(methacryloyloxymethoxy)ethane (**IV**) and 1-*tert*-butylperoxy-2-(propanoyloxy)methoxyethane (**V**) as a saturated analog for comparison under the same conditions. A convenient express-method of direct determination of the thermal decomposition reaction rates, differential scanning calorimetry, was used [3].

Kinetics of the thermal decomposition was studied under solvent-free condition using a kinetic calorimetric set [4] operating at quasi-isothermal and scanning modes with sensitivity of 3×10^{-5} cal s^{-1} mm^{-1} in the temperature range of 25–200°C.

The samples of peroxides **I**–**V** were subjected to preliminary warming for 4 h at 80°C for the self-initiated homopolymerization. The rate of decay of peroxy groups at this temperature is low, so they are practically retained up to the polymerization completion. The thermal decomposition of the peroxide at the O–O bond occurs in a polymeric medium. This is of interest, since the use of peroxy-containing copolymers based on these monomers assumes further thermal decomposition of the peroxide bond in the highly viscous polymer solutions.

All the studied peroxides are highly thermally stable compounds. Kinetic parameters of the thermal decomposition process (see the table) indicate the homolytic nature of decomposition.

High values of entropy indicate that the thermal decomposition of peroxides occurs through a transition state, which differs from the starting compound by the structure. The functional group at δ-position of the peroxide moiety has practically no influence on it: the rate of thermal decomposition and activation parameters for peroxide monomers and their saturated analog are close. For peroxide polymers derived from monomers **II** and **III** the rate constants are by 3–4 times higher than those for the saturated analog, as seen for polymeric peroxides [5].

The thermal decomposition of peroxide monomer **III** was studied in the quasi-isothermal mode at 126, 130, 135°C. The obtained kinetic parameters are similar to parameters for this peroxide obtained in the scanning mode K_{135} 15.1×10^{-4} s^{-1}, E 174.3 kJ mol^{-1}, log A 21.2.

Thermal decomposition of peroxide monomers **II** and **IV** was carried out without preliminary warming up when the homolytic decomposition of the peroxide proceeds, as well as free radical initiation, polymerization, and cross-linking. The small difference in the values of the rate constants of the thermal

Kinetic parameters of the thermal decomposition of peroxides $(CH_3)_3COOCH_2CH_2OCH(R^1)OC(O)R^2$ in the solvent-free conditions

`	R^1	R^2	T, °C	$K\times10^4$, s^{-1}	log A, (A, s^{-1})	E, kJ mol^{-1}	ΔS, , entr. units
I	H	$CH_2{=}CH$	129	4.80	14.3	155.9	14.2
			139	12.8			
			149	32.4			
			158	71.0			
II	CH_3	$CH_2{=}CH$	128	4.73	17.4	159.4	18.4
			138	15.4			
			148	44.9			
			158	133			
II[a]	CH_3	$CH_2{=}CH$	119	2.78	13.8	130.5	2.04
			128	6.22			
			139	18.70			
			148	28.7			
III	C_2H_5	$CH_2{=}CH$	130	4.89	18.7	169.0	24.3
			139	18.4			
			147	51.5			
			158	146			
IV[a]	H	$CH_2{=}C(CH_3)$	118	1.51	14.5	137.2	5.24
			129	4.86			
			138	12.7			
			147	28.3			
V	H	$CH_3–CH_2$	129	1.53	17.8	166.9	20.3
			138	4.31			
			148	13.9			
			158	42.7			

[a] Without preheating.

decomposition of monomeric peroxide and polymer based on it is due to the different contribution to the mechanism of their decomposition of homolysis of the O–O bond and polymerization.

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