Brief Communications

Effect of medium on the rate constant of decomposition of di(*tert*-butyl)trioxide

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It was found that the medium affects the rate constant of the thermal decomposition of di(*tert*-butyl)trioxide. In all solvents studied, the decomposition occurred according to the first-order law. The effect of the solvent on the rate constant was analyzed within the framework of the Koppel—Palm equation.

Key words: trioxide, chemiluminescence, decomposition mechanism.

Earlier,[1—3] the rate constants of the decomposition of di(*tert*-butyl)trioxide (ROOOR) in CH_2Cl_2 at $-33\div15$ °C were measured. The purpose of this work was to study the effect of the medium on the rate constant of decomposition of ROOOR.

Experimental

Di(*tert*-butyl)trioxide was obtained by low-temperature (−80 °C) ozonization of a suspension of Bu^tOOK in CH_2Cl_2.[3] The decomposition was studied within the range of trioxide concentrations 0.002—0.02 mol L^{-1}. The concentration of ROOOR was determined by using triphenylphosphine[4] and by ^1H NMR. The kinetics of the decomposition of trioxide was studied using the decay of chemiluminescence (CL) in the IR region of the spectrum.[5] The solvent under study (20 mL) was placed into a thermostatically controlled reactor, and a solution of RCOOOR (1 mL) in CH_2Cl_2 was added with vigorous stirring. The time-dependence of the IR-CL intensity was recorded.

Results and Discussion

In all of the solvents studied, the decomposition of ROOOR occurs according to the first-order law. Table 1 presents the rate constants of the decomposition of ROOOR (k_0) in different solvents. As can be seen from the Table, the nature of the solvent significantly affects the value of k_0.

The effect of the solvents on the rate constant of the decomposition of ROOOR was analyzed using the correlative four-parameter Koppel—Palm equation

$$\log k_0 = \log k_0{}^0 + yY + pP + eE + bB,$$

$$\text{where } Y = (\varepsilon-1)/(2\varepsilon+1),\ P = (n^2-1)/(n^2+2),$$

which takes into account both nonspecific and specific solvation. Parameters E and B were taken from a previously published work,[6] and ε and n values were calculated for 0 °C by the known procedures.[7,8] The values of

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Table 1. Rate constants of the decomposition of di(*tert*-butyl)trioxide (k_0) in different solvents at 0 °C (the mean error was 7 %)

Solvent	$k_0 \cdot 10^3/\mathrm{s}^{-1}$	Solvent	$k_0 \cdot 10^3/\mathrm{s}^{-1}$
CCl_4	0.6	MeCN	5.2
PhMe	0.7	$CHCl_3$	6.5
CCl_2FCF_2Cl	1.7	CH_2Cl_2	7.5
Et_2O	1.9	$MeNO_2$	9.7
MeOH	2.9	C_5H_5N	16.0
PhCl	3.0	CF_3COOH	95.3

E were also recalculated for 0 °C. Processing of the kinetic data for the solvents listed in Table 1 according to the Koppel—Palm equation gave the following coefficients:

$$\log k_0{}^0 = -3.4\pm1.1;\ y = 4.7\pm0.8;\ p = -2.5\pm3.1;$$

$$e = (-3.0\pm1.7)\cdot10^{-2};\ b = (-2.0\pm0.1)\cdot10^{-3};$$

the correlation coefficient was 0.951.

The positive regression coefficient at the Y parameter indicates stabilization of the activated state due to electrostatic interaction and the absence of such stabilization in the starting molecule. The stronger the electrostatic interaction of the solvent with the molecule of trioxide at the transition state, the easier decomposition occurs. Other types of solvation retard decomposition, and their effect is much less pronounced.

The high values of the rate constants of the decomposition of ROOOR in CF_3COOH and C_5H_5N are probably due to the chemical interaction of these solvents with trioxide or to the change in the mechanism of the decomposition of trioxide as a consequence of catalysis.

It is interesting to note that the rate of decomposition also increases for di(*tert*-butyl)peroxide (ROOR) with increasing polarity of the medium. However, this effect is less pronounced than that in the case of di(*tert*-butyl)trioxide. For example, the rates of the decomposition of ROOR in cumene (ε = 2.37) and acetonitrile (ε = 37.5) at 125 °C are $16.0\cdot10^{-6}$ and $34.7\cdot10^{-6}$ s^{-1}, respectively.[9]

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