Physical Chemistry

Induced decomposition of di(*tert*-butyl)trioxide

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Thermal decomposition of di(*tert*-butyl)trioxide (Bu^tOOOBu^t) in a wide range of concentrations was studied by visible and IR chemiluminescence. Induced decomposition of Bu^tOOOBu^t caused by its reaction with the peroxy radicals formed in the solvent (CH_2Cl_2) was found and investigated.

Key words: trioxides, thermal decomposition, mechanism; di(*tert*-butyl)trioxide, induced decomposition; chemiluminescence.

Di(*tert*-butyl)trioxide Bu^tOOOBu^t has been studied in a number of works.[1–6] Chemiluminescence (CL) in visible and IR regions accompanying the process of thermal decomposition of Bu^tOOOBu^t was found.[4] The formation of free radicals in this reaction was studied[1,3,5] and dependences of the rate of thermolysis of Bu^tOOOBu^t on temperature[1,4] and the nature of the solvent[6] were investigated.

Thermal decomposition of compounds containing a peroxide —O—O— fragment often proceeds *via* a homolytic mechanism. Free radicals formed in this case can react with the initial peroxide, accelerating its decomposition. This phenomenon is called induced decomposition, and it was observed in a large number of compounds. Induced decomposition of peroxides, hydroperoxides, diacylperoxides,[7,8] and peroxy ethers[9] has been well studied. Induced decomposition of cumyl hydrotrioxide in thermolysis has been observed.[10]

In this work, induced decomposition of dialkyltrioxides was first found and investigated by the example of di(*tert*-butyl)trioxide.

Experimental

Di(*tert*-butyl)trioxide (Bu^tOOOBu^t) was obtained according to a known procedure[2,4] by ozonization of potassium and sodium salts of *tert*-butyl hydroperoxide in CH_2Cl_2 and $CFCl_3$, respectively, at −60 °C. Solutions of Bu^tOOOBu^t were stored in darkness in liquid nitrogen. Bu^tOOOBu^t and products of its decomposition were identified by the GC—MS technique and ^1H and ^{13}C NMR spectroscopy. The concentration of Bu^tOOOBu^t was determined using triphenylphosphine[11] and from the ^1H NMR spectra. The kinetics of the decomposition of trioxide were studied using the CL decay in visible and IR regions[12] in the temperature interval −20.5—+17.0 °C. Methylene dichloride (18—20 mL) was placed into a reactor of volume 50 mL, thermostated at a specified temperature, and then 0.25—2.0 mL of cold (−60 °C) solution of Bu^tOOOBu^t (0.01—0.2 mol L^{-1}) was added. The concentration of trioxide in the reactor was varied in the range of $(0.1-20.0)\cdot10^{-3}$ mol L^{-1}. According to volumetric data, Bu^tOH, Me_2CO, Bu^tOOBu^t, and O_2 were found to be the products of the decomposition of Bu^tOOOBu^t. The temperature in the reactor was monitored using a thermocouple. Temperature changes in the course of the decomposition did not exceed 0.3 °C. The

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 924—927, May, 1997.

solvents (CH_2Cl_2 and $CFCl_3$) were purified according to the previously described procedure.[13]

Results and Discussion

The rate of thermolysis of $\mathrm{Bu^tOOOBu^t}$ over the whole range of concentrations is well described by the first-order kinetic equation (the correlation coefficient of semilogarithmic anamorphose of the kinetic curve $r > 0.991$):

$$W = k_{\mathrm{eff}}[\mathrm{Bu^tOOOBu^t}].$$

Typical experimental curves of a decrease in the CL intensity and their anamorphoses are shown in Fig. 1. The k_{eff} values obtained in the regions of both visible and infrared CL coincide within the limits of experimental error.

The rate constant for thermolysis depends on the concentration of trioxide (Fig. 2), which is evidence for the induced decomposition of $\mathrm{Bu^tOOOBu^t}$. The order of the kinetics of the induced decomposition of peroxide is determined by the source of radicals and the type of the chain termination reaction. The experimentally observed first-order kinetics are due to the reaction of the radical of a solvent with the peroxide compound proceeding in the stage of the induced decomposition and to the cross-reaction of the chain termination.[7]

Taken altogether with the published data,[4,5,14–22] the obtained experimental results suggest the mechanism of the induced decomposition of di(*tert*-butyl)trioxide (Scheme 1).

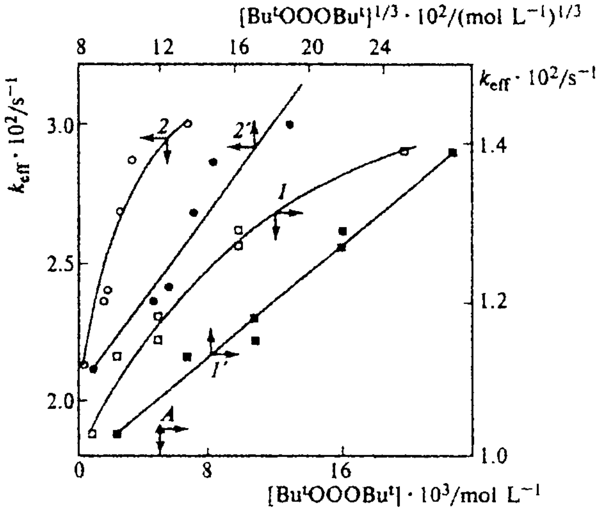


Fig. 2. Dependence of the effective rate constant for decomposition of $\mathrm{Bu^tOOOBu^t}$ in CH_2Cl_2 on its concentration (*1*, *2*) and $[\mathrm{Bu^tOOOBu^t}]^{1/3}$ (*1'*, *2'*): *1*, *1'*, visible CL, 0 °C; *2*, *2'*, IR chemiluminescence, 10 °C. *A* point corresponds to the data obtained in the presence of $\mathrm{Et{-}C_6H_4{-}Pr^i}$.

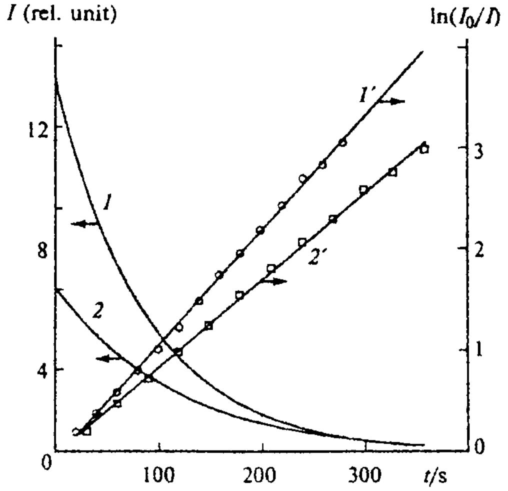


Fig. 1. Kinetic curves of the decrease in the CL intensity (*1*, *2*) in the thermal decomposition of $\mathrm{Bu^tOOOBu^t}$ (0 °C, CH_2Cl_2 as the solvent, $[\mathrm{Bu^tOOOBu^t}]_0 = 3 \cdot 10^{-3}$ mol L^{-1}) and their semilogarithmic anamorphoses (*1'*, *2'*): *1*, visible CL, *2*, IR chemiluminescence.

Scheme 1

$$\mathrm{Bu^tOOOBu^t} \xrightarrow{k_1} \mathrm{Bu^tO^\cdot + {}^\cdot OOBu^t} \qquad (1)$$

$$\mathrm{Bu^tO^\cdot + CH_2Cl_2} \xrightarrow{k_{1a}} \mathrm{Bu^tOH + {}^\cdot CHCl_2} \qquad (1a)$$

$$\mathrm{{}^\cdot CHCl_2 + O_2} \xrightarrow{k_2} \mathrm{Cl_2CHOO^\cdot} \qquad (2)$$

$$\mathrm{Cl_2CHOO^\cdot + Bu^tOOOBu^t} \xrightarrow{k_3} \mathrm{Bu^tOO^\cdot + P_3} \qquad (3)$$

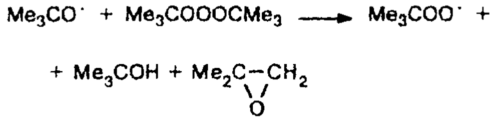
$$\mathrm{Bu^tOO^\cdot + Cl_2CHOO^\cdot} \begin{cases} \xrightarrow{k_{4a}} {}^1\mathrm{O_2}\ (h\nu_{\mathrm{IR}}) + \mathrm{P_{4a}} & (4a) \\ \xrightarrow{k_{4b}} >\mathrm{C{=}O}\ (h\nu_{\mathrm{VIS}}) + \mathrm{P_{4b}} & (4b) \\ \xrightarrow{k_{4c}} \mathrm{P_{4c}} & (4c) \end{cases}$$

$$\mathrm{2\ Bu^tOO^\cdot} \begin{cases} \xrightarrow{k_{5a}} \mathrm{Bu^tOOBu^t + O_2} & (5a) \\ \xrightarrow{k_{5b}} \mathrm{2\ Bu^tO^\cdot + O_2} & (5b) \end{cases}$$

Reaction (1) proceeds *via* a homolytic mechanism, which is confirmed by both thermochemical calculations[4] and experimental observation of the peroxyl and alkoxyl radicals by the ESR spectroscopy technique.[5] In addition to its participation in reaction (1a), the *tert*-butoxyl radical $\mathrm{Me_3CO^\cdot}$ can either undergo β-scission:

$$\mathrm{Me_3CO^\cdot} \xrightarrow{k_{1b}} \mathrm{Me_2C{=}O + {}^\cdot Me} \qquad (1b)$$

or abstract the H atom to form epoxide, *tert*-butyl alcohol, and peroxy radical analogously to the reaction of *tert*-butoxyl radical with di(*tert*-butyl)peroxide[7]:



$$Me_3CO^{\cdot} + Me_3COOOCMe_3 \longrightarrow Me_3COO^{\cdot} + Me_3COH + Me_2\overset{}{C}{-}CH_2 \text{ (with O bridging)} \quad (1c)$$

The rate constants of reactions (1a), (1b), and (1c) at 0 °C were estimated using the published data.[14–16] According to this estimate, stage (1a) is the most probable reaction of consumption of the oxyl radical under our experimental conditions. The corresponding parameters of this stage are: $k_{1a} \approx 10^5$ s^{-1}, $[CH_2Cl_2] = 15.6$ mol L^{-1}, $k_{1b} \approx 10^4$ L mol^{-1} s^{-1}, $k_{1c} \approx 10^5$ L mol^{-1} s^{-1}, and $[Bu^tOOOBu^t] = (0.1-20.0) \cdot 10^{-3}$ mol L^{-1}, whence $W_{1a}/W_{1b} \approx 10^2$ and $W_{1a}/W_{1c} \approx 10^3-10^5$.

It was established using the ^{1}H NMR spectroscopy that the reaction mixture contains no epoxide, while *tert*-butyl alcohol is a predominant product. This is consistent with the assumption of insignificant contributions of reactions (1b) and (1c) to the overall process of consumption of *tert*-butoxyl radicals.

Alkyl radicals rapidly ($k_2 = 4.7 \cdot 10^9$ L mol^{-1} s^{-1})[17] transform into peroxyl radicals in an O_2 atmosphere; therefore, reaction (2) is the only channel of consumption of $^{\cdot}CHCl_2$. The $Cl_2CHOO^{\cdot}$ radical can either induce the decomposition of trioxide (reaction (3)) or terminate the chain through cross-reaction (4). The recombination of $Cl_2CHOO^{\cdot}$ radicals was neglected, since the rate constant of cross-recombination is known to be close to the decay constant of highly-active radicals in the case of the joint decay of peroxyl radicals that differ strongly in their reactivity.[18–20] According to Scheme 1, two peroxy radicals are formed, the rather inactive $Bu^tOO^{\cdot}$ for which $2k_5 = 1.5 \cdot 10^2$ L mol^{-1} s^{-1} (0 °C),[21] and $Cl_2CHOO^{\cdot}$, activated by two Cl atoms. For the recombination reaction of radicals of such type $2k_t = 10^8-10^9$ L mol^{-1} s^{-1} (see Ref. 17). Hence, $k_4 \approx 10^8$ L mol^{-1} s^{-1}. According to our estimates, $[Bu^tOO^{\cdot}]/[Cl_2CHOO^{\cdot}] \geq 10^4$, because of which the recombination of $Cl_2CHOO^{\cdot}$ radicals is negligible.

Cross-recombination of peroxy radicals (see reaction (4)) results in the formation of emitters of luminescence in the visible and IR regions. This is confirmed by the absence of CL in the inert solvents ($CFCl_3$ and CCl_4).

The CL intensity is proportional to the rate of radiative deactivation of the emitter E^*:

$$I = \beta k_d[E^*], \qquad (6)$$

where β is the radiation yield; k_d is the rate constant for deactivation E^*, *i.e.*, the sum of the rate constant for radiative and that for radiationless deactivation. Applying the quasi-steady-state principle to the concentration of the emitter, we can write:

$$d[E^*]/dt = \alpha k_4[SOO^{\cdot}][Bu^tOO^{\cdot}] - k_d[E^*] = 0, \qquad (7)$$

where α is the excitation yield in reaction (4), $SOO^{\cdot} = Cl_2CHOO^{\cdot}$. Combining Eqs. (6) and (7) and taking into account that

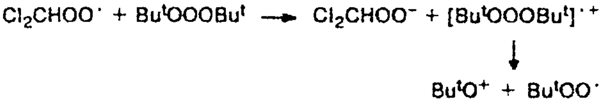
$$k_1[Bu^tOOOBu^t] = k_4[SOO^{\cdot}][Bu^tOO^{\cdot}], \qquad (8)$$

we get $I = \alpha\beta k_1[Bu^tOOOBu^t]$ or in the differential form

$$dI/dt = \alpha\beta k_1 \cdot d[Bu^tOOOBu^t]/dt. \qquad (9)$$

Equation (9) shows that the CL method in the visible and IR regions can be applied to studying the kinetics of reactions with participation of Bu^tOOOBu^t.

It is not completely clear how reaction (3) proceeds. Taking into account that halogen-containing peroxyl radicals are strong one-electron oxidants,[17] we proposed the following mechanism:



$$Cl_2CHOO^{\cdot} + Bu^tOOOBu^t \longrightarrow Cl_2CHOO^- + [Bu^tOOOBu^t]^{\cdot +}$$
$$[Bu^tOOOBu^t]^{\cdot +} \longrightarrow Bu^tO^+ + Bu^tOO^{\cdot}$$

One of the lone electron pairs of the oxygen atoms can serve as an electron donor. A decrease in k_{eff} (see Fig. 2) is observed in the thermolysis of Bu^tOOOBu^t in the presence of *p*-ethylisopropylbenzene. This compound is capable of capturing $Bu^tO^{\cdot}$ radicals (according to the published data,[16] $k \approx 10^6$ L mol^{-1} s^{-1}) and also acting as an electron donor to decrease the contribution of reactions (1) and (3) to the overall process. Thus, participation of the $Cl_2CHOO^{\cdot}$ radicals in the induced decomposition of di(*tert*-butyl)trioxide is confirmed experimentally.

The chain termination proceeds *via* reactions (4) and (5a), the former being predominant. Using the k_4, $2k_5$, and $Bu^tOO^{\cdot}]/[Cl_2CHOO^{\cdot}]$ values and taking into account that $k_5/k_{5a} = 7$ (see Ref. 23), we get $W_4/W_{5a} \approx 10^2$.

It follows from Scheme 1 that

$$-d[Bu^tOOOBu^t]/dt = k_1[Bu^tOOOBu^t] + k_3[SOO^{\cdot}][Bu^tOOOBu^t]. \qquad (10)$$

Applying the quasi-steady-state principle to $[Bu^tOO^{\cdot}]$, we get

$$-d[Bu^tOO^{\cdot}]/dt = k_1[Bu^tOOOBu^t] + k_3[SOO^{\cdot}][Bu^tOOOBu^t] - k_4[SOO^{\cdot}][Bu^tOO^{\cdot}] - 2\,k_{5b}[Bu^tOO^{\cdot}]^2 = 0. \qquad (11)$$

Taking into account relation (8), Eq. (11) can be written as

$$k_3[SOO^{\cdot}][Bu^tOOOBu^t] = 2k_{5b}[Bu^tOO^{\cdot}]^2, \qquad (12)$$

which reflects an obvious equality of the rates of the chain propagation. Combining Eqs. (8) and (12), we get

$$[SOO^{\cdot}] = \{2k_{5b}k_1{}^2/(k_3k_4{}^2) \cdot [Bu^tOOOBu^t]\}^{1/3},$$

from whence, taking into account Eq. (10), the rate of consumption of trioxide is

$$-\mathrm{d}[\mathrm{Bu^tOOOBu^t}]/\mathrm{d}t = k_1[\mathrm{Bu^tOOOBu^t}] + + k'[\mathrm{Bu^tOOOBu^t}]^{4/3}. \qquad (13)$$

Taking into account that $W = k_{\mathrm{eff}}[\mathrm{Bu^tOOOBu^t}]$, we get

$$k_{\mathrm{eff}} = k_1 + k'[\mathrm{Bu^tOOOBu^t}]^{1/3}, \qquad (14)$$

$$k' = (2k_{5b}k_1{}^2k_3{}^2/k_4{}^2)^{1/3}.$$

Equation (14) explains the experimentally observed dependence of k_{eff} on the concentration of di(*tert*-butyl)trioxide (see Fig. 2) and allows one to estimate the constant k_3:

$$k_3 = k_4b^{3/2}/[a\cdot(2k_{5b})^{1/2}]. \qquad (15)$$

Here a and b are the intercept on the ordinate axis and the slope of the dependence of k_{eff} on $[\mathrm{Bu^tOOOBu^t}]^{1/3}$, respectively. It was found from Fig. 2 that $a = (8.2\pm0.6)\cdot10^{-3}$ s^{-1} (at 0 °C) and $(1.3\pm0.7)\cdot10^{-2}$ s^{-1} (at 10 °C); $b = (2.1\pm0.4)\cdot10^{-2}$ (L mol^{-1})$^{1/3}$ s^{-1} (at 0 °C) and $(1.0\pm0.4)\cdot10^{-1}$ (L mol^{-1})$^{1/3}\cdot$s^{-1} (at 10 °C). The $2k_{5b}$ value was calculated using the published data:[21,23] $2k_{5b} = 1.3\cdot10^2$ L mol^{-1} s^{-1} (at 0 °C) and $3.7\cdot10^2$ L mol^{-1} s^{-1} (at 10 °C). The rate constant k_4 seems to be slightly dependent on the temperature. Assuming that $k_4 = 10^8$ L mol^{-1} s^{-1}, we obtained $k_3 = 3.3\cdot10^6$ L mol^{-1} s^{-1} (at 0 °C) and $1.3\cdot10^7$ L mol^{-1} s^{-1} (at 10 °C). These k_3 values are in agreement with the mechanism of the one-electron oxidation of di(*tert*-butyl)trioxide by dichloromethylperoxyl radical proposed in this work. For this radical the rate constants of one-electron transfer for a series of organic substrates (with H_2O—EtOH as the solvent at room temperature) are in the interval $8\cdot10^6$—$7\cdot10^8$ L mol^{-1} s^{-1}.[17]

The contribution of the reaction of the induced decomposition of $\mathrm{Bu^tOOOBu^t}$ to the total rate of the overall decomposition is relatively small, and the observed order with respect to the concentration of di(*tert*-butyl)trioxide is nearly equal to unity. The temperature dependence of k_{eff}/s^{-1} was studied at $[\mathrm{Bu^tOOOBu^t}]_0 = 2.5\cdot10^{-3}$ mol L^{-1} (in the visible region), when the induced decomposition of the latter can be neglected.

T/°C	−20.5	−15.2	−10.5	−5.3	−0.9	4.3	10.3	17.2
$k_{\mathrm{eff}}\cdot10^3$	0.55	1.26	2.25	5.32	9.95	21.0	51.7	96.0

We obtained $\log k_{\mathrm{eff}} = (14.5\pm0.7) - 20.4\pm0.9)/\theta$, where $\theta = 2.3RT$ (kcal mol^{-1}), $r = 0.999$. It was found previously[4] using the IR chemiluminescence method that $\log(A/\mathrm{s}^{-1}) = 14.5\pm2.2$; $E_a = 20.8\pm0.6$ kcal mol^{-1}, $[\mathrm{Bu^tOOOBu^t}]_0 = 2.0\cdot10^{-3}$ mol L^{-1}. Thus, at low concentrations of trioxide the rate constants of decomposition of $\mathrm{Bu^tOOOBu^t}$ determined by the CL method in the visible and IR regions correspond to reaction (1), while the activation energy of the thermal decomposition corresponds to the O—O bond strength in di(*tert*-butyl)trioxide.

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Received March 13, 1996;
in revised form November 21, 1996