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Free-radical chain decomposition of ozone initiated by di(*tert*-butyl) trioxide

A. F. Khalizov,[a] S. L. Khursan,[b]* and V. V. Shereshovets[a]†

[a]Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066. E-mail: chemox@anrb.ru
[b]Bashkir State University,
32 ul. Frunze, 450074 Ufa, Russian Federation

Di(*tert*-butyl) trioxide in a solution of $CFCl_3$ (Freon-11) at −23 °C exists in equilibrium with the *tert*-butoxyl and *tert*-butylperoxyl radicals virtually without irreversible decomposition. The above radicals decompose ozone to dioxygen with a high effective rate constant, which is proprotional to the square root of the Bu^tOOOBu^t concentration. The kinetic scheme describing the found relationships was proposed.

Key words: dialkyl trioxides, ozone, free radicals, chain decomposition.

The interaction of ozone with organic compounds produces free radicals that actively react with both the starting compound and ozone. The presence of free radicals in the atmosphere is a factor stipulating the formation and consumption of ozone, peroxides, and peroxyl nitrates.[1]

The study of the reactivity of ozone toward free radicals is important for revealing the nature of processes involving ozone. The interaction of O_3 with the radicals has been studied for several gas phase[2—4] and liquid phase systems.[5—9] In the gas phase, the radicals were predominantly generated by physical methods (radiolysis, photolysis), and in solution they were produced chemically (the interaction of O_3 with hydrocarbons and hydroperoxides). Reactions in these systems are usually characterized by a complex mechanism, which impedes interpretation of the results.

In this work, di(*tert*-butyl) trioxide (DBO) was used as the radical source, whose thermal decomposition in an inert medium gives only peroxyl and alkoxyl radicals, and this fact reduces to a minimum the contribution of side reactions. The $Bu^tOOOBu^t + O_3$ system is also of interest for understanding the mechanism of Bu^tOOOBu^t formation because the same reactions occur in the synthesis of alkyl trioxides and their decomposition in the presence of O_3.

Experimental

Di(*tert*-butyl) trioxide was prepared by the ozonization of sodium *tert*-butyl hydroperoxide in $CFCl_3$ at −60 °C.[10,11] The concentration of DBO was determined by the ^1H NMR spectra relatively to the signal of the standard (benzene). The products of DBO decomposition were identified by ^1H NMR and GLC comparing with authentic samples. The decomposition products were analyzed by GLC. Freon-11 was treated with ozone, washed with a solution of Na_2CO_3, dried with anhydrous $MgSO_4$, passed through a column packed with activated Al_2O_3, and distilled. The product was stored above active molecular sieves 4 A.

The kinetics of O_3 consumption was studied using the spectrophotometric method by the absorbance at λ = 310 nm ($\varepsilon = 54\pm3$ L mol^{-1} cm^{-1}). $CFCl_3$ (1.8—1.4 mL) was placed into a cell and cooled to −23 °C (the temperature was monitored by a thermocouple). Then a 0.13 *M* solution (0.2—0.6 mL) of DBO in $CFCl_3$ was added with a cooled pipet. The solution was stirred and saturated with a pre-cooled O_3—O_2 (30 mL min^{-1}) mixture to the concentration $[O_3]_0$ = 0.003—0.01 mol L^{-1}. Then the valves at the inlet and outlet of the cell were closed, and the kinetics of O_3 consumption in the solution was monitored.

NMR spectra were recorded on a Bruker AM 300 high-resolution instrument. GLC analysis was carried out on a Chrom 5 chromatograph (glass column, 200×0.3 cm, XE-60, flame-ionization detector, temperature of the column 50 °C, temperature of the evaporator 150 °C, temperature of the detector 200 °C). Electronic absorption spectra of ozone and the products of Bu^tOOOBu^t decomposition were recorded on a Specord M 40 instrument. Kinetic experiments were carried out in a quartz thermostatted cell placed in the cell compartment of an SF 26 spectrophotometer.

Results and Discussion

Over the whole range of the concentrations of O_3 ($0.5 \cdot 10^{-2}$—$1.0 \cdot 10^{-2}$ mol L^{-1}) and DBO ($3.3 \cdot 10^{-3}$—$2.6 \cdot 10^{-2}$ mol L^{-1}), the kinetic curves of O_3 consumption are well linearized in the coordinates of a first-order reaction to the 85—90% conversion (Fig. 1). The effective rate constant of ozone consumption k_{eff} (−23 °C, solvent $CFCl_3$) depends on the initial DBO concentration:

$[Bu^tOOOBu^t] \cdot 10^3$/mol L^{-1}	3.3	6.5	13.0	13.0	19.5	26.0
$k_{\mathrm{eff}} \cdot 10^4$/s^{-1}	1.08	1.12	1.67	1.76	1.89	2.33

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† Deceased.

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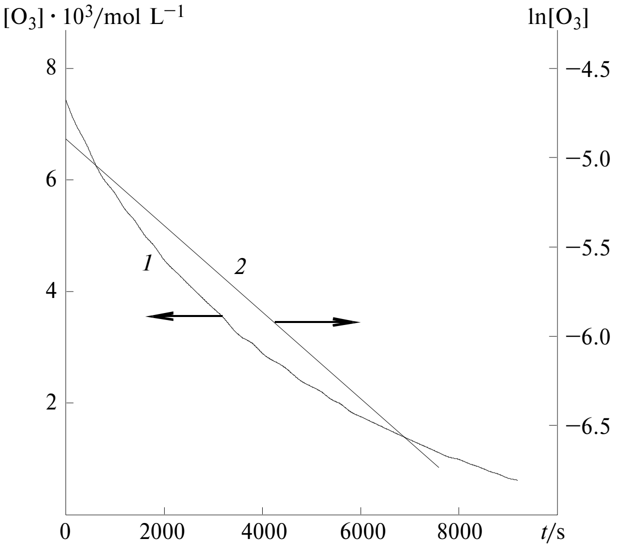

Fig. 1. Kinetic scheme of O_3 consumption (*1*) and its semilogarithmic anamorphosis (*2*) (−23 °C, $[Bu^tOOOBu^t]_0$ = 0.013 mol L^{-1}).

The products of DBO decomposition were analyzed when the reaction was carried out in two regimes. In the first case, a solution of DBO in Freon-11 was saturated with ozone to a concentration of ~10^{-2} mol L^{-1}, stored at −23 °C to the complete decomposition of O_3, and heated to a room temperature. Then the reaction products were analyzed. In the control experiment, DBO was decomposed under similar conditions, but without a preliminary saturation of the solution with ozone. Analysis of the reaction mixture showed a predominant amount of *tert*-butanol, acetone, and di(*tert*-butyl) peroxide. The composition and ratio of the products (Bu^tOH : MeCOMe : Bu^tOOBu^t) in the reaction mixture after DBO decomposition with ozone saturation (100 : 10 : 11) and in the absence of ozone (100 : 13 : 9) virtually do not differ. The identical compositions of the products obtained under different conditions indicate that until O_3 is present in the reaction mixture, the DBO decomposition products are virtually not formed.

Based on the published data[5,12–15] and taking into account the composition of the obtained products and regularities of their formation, we can assume the following sequence of reactions that occur in the Bu^tOOOBu^t—$CFCl_3$—O_3 system:

$$\text{ROOOR} \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \text{RO}^{\cdot} + \text{ROO}^{\cdot}, \qquad (1)$$

$$\text{RO}^{\cdot} + O_3 \longrightarrow \text{ROO}^{\cdot} + O_2, \qquad (2a)$$

$$\text{RO}^{\cdot} \longrightarrow \text{MeCOMe} + \text{Me}, \qquad (2b)$$

$$\text{RO}^{\cdot} + \text{R}'\text{H} \longrightarrow \text{ROH} + \text{R}'^{\cdot}, \qquad (2c)$$

$$\text{ROO}^{\cdot} + O_3 \longrightarrow \text{RO}^{\cdot} + 2\,O_2, \qquad (3)$$

$$2\,\text{ROO}^{\cdot} \xrightarrow{a} 2\,\text{RO}^{\cdot} + O_2 \qquad (4a)$$

$$2\,\text{ROO}^{\cdot} \xrightarrow{b} \text{ROOR} + O_2, \qquad (4b)$$

where R is Bu^t, and R′H are Bu^tOOOBu^t and products of its decomposition.

The direct reaction of ozone with DBO can be neglected. In fact, in the presence of a 0.02 *M* solution of di(*tert*-butyl) peroxide, whose C—H bond strength is close to that in DBO, ozone is not consumed in a solution of $CFCl_3$. The control experiment showed that the reaction products have no noticeable absorbance at λ = 310 nm. Hence, a change in the absorbance during the process corresponds only to a change in the concentration of O_3. Thus, the primary reaction in the Bu^tOOOBu^t—$CFCl_3$—O_3 system is DBO thermal decomposition to form the *tert*-butoxyl and *tert*-butylperoxyl radicals, and ozone is consumed in subsequent radical processes.

The decomposition of DBO in $CFCl_3$ at −23 °C has the rate constant $k_{+1} = 7.4 \cdot 10^{-5}$ s^{-1}.[15] The inverse reaction (−1), the recombination of the *tert*-butyoxyl and *tert*-butylperoxyl radicals, is most likely activationless. The rate constant of the diffusion-controlled process k_{-1} was calculated by the Debye—Stokes—Einstein equation

$$k_{-1} = k_D = (\sigma/f)(8RT/3000\eta),$$

which takes into account the correction to microfriction f during motion of the reactants in the solvent[16] and the probability of formation of a singlet radical pair $\sigma = 1/4$. The f value was calculated by the equation

$$f = 0.56[0.9 + 0.15(T - T_m)/(T_b - T_m)],$$

where $T_m = -111$ °C and $T_b = 23.8$ °C are the temperatures of $CFCl_3$ phase transitions. The viscosity values of Freon-11 are 0.740 (−25 °C), 0.539 (0 °C), and 0.421 cP (25 °C).[17] Based on these data, the activation energy of viscous flow is 1.66 kcal mol^{-1}. Using this value, we calculated η (−23 °C) = 0.720 cP and k_{-1} = $3.4 \cdot 10^9$ L mol^{-1} s^{-1}.

The products of reactions (2b) and (4b), namely, acetone and di(*tert*-butyl) peroxide, respectively, are present in amounts an order of magnitude lower than *tert*-butanol (reaction (2c)); therefore, reactions (2b) and (4b) can be neglected. Now we consider the competing reactions of $Bu^tO^{\cdot}$ with $Bu^tOO^{\cdot}$ (−1) and R′H (2c). In reaction (−1), the cross-recombination of the radicals results in the formation of the DBO molecule. In reaction (2c), alkyl radicals form, which rapidly transform into the primary alkyl peroxyl radicals, whose recombination occurs with diffusion rate constants. The reaction rate of H atom elimination from the DBO molecule (2c) was estimated from the kinetic data obtained for the interaction of the *tert*-butoxyl radical with the nonactivated methyl group at −23 °C[18,19]:

$\log k_{2c} = 10.46 - 7.05/\theta$, where $\theta = 2.3RT$ kcal mol^{-1}, and, correspondingly, $k_{2c} = 2 \cdot 10^4$ L mol^{-1} s^{-1}. The ratio of the reaction rates (−1) and (2c) is expressed by the following equation ($[\mathrm{Bu^tOOOBu^t}] = 10^{-2}$ mol L^{-1}):

$$w_{-1}/w_{2c} = (k_{-1}/k_{2c})([\mathrm{Bu^tOO^{\cdot}}]/[\mathrm{Bu^tOOOBu^t}]) = \\ = 1.7 \cdot 10^7[\mathrm{Bu^tOO^{\cdot}}].$$

To obtain the numerical value of the w_{-1}/w_{2c} ratio, we need the absolute concentration of the *tert*-butylperoxyl radicals in the reaction system. It follows from the kinetic scheme of reactions (1)—(4) that the consumption rate of ozone is determined by the equation

$$w(\mathrm{O_3}) = -\mathrm{d}[\mathrm{O_3}]/\mathrm{d}t = k_{2a}[\mathrm{Bu^tO^{\cdot}}][\mathrm{O_3}] + k_3[\mathrm{Bu^tOO^{\cdot}}][\mathrm{O_3}]. \quad (5)$$

Under steady-state approximation for $[\mathrm{Bu^tO^{\cdot}}]$ and $[\mathrm{Bu^tOO^{\cdot}}]$, we can write

$$\mathrm{d}[\mathrm{Bu^tO^{\cdot}}]/\mathrm{d}t = k_{+1}[\mathrm{Bu^tOOOBu^t}] - k_{2a}[\mathrm{Bu^tO^{\cdot}}][\mathrm{O_3}] + \\ + k_3[\mathrm{Bu^tOO^{\cdot}}][\mathrm{O_3}] - k_{-1}[\mathrm{Bu^tO^{\cdot}}][\mathrm{Bu^tOO^{\cdot}}] + \\ + 2k_{4a}[\mathrm{Bu^tOO^{\cdot}}][\mathrm{Bu^tOO^{\cdot}}] = 0, \quad (6)$$

$$\mathrm{d}[\mathrm{Bu^tOO^{\cdot}}]/\mathrm{d}t = k_{+1}[\mathrm{Bu^tOOOBu^t}] + k_{2a}[\mathrm{Bu^tO^{\cdot}}][\mathrm{O_3}] - \\ - k_3[\mathrm{Bu^tOO^{\cdot}}][\mathrm{O_3}] - k_{-1}[\mathrm{Bu^tO^{\cdot}}][\mathrm{Bu^tOO^{\cdot}}] - \\ - 2k_{4a}[\mathrm{Bu^tOO^{\cdot}}][\mathrm{Bu^tOO^{\cdot}}] - \\ - 2k_{4b}[\mathrm{Bu^tOO^{\cdot}}][\mathrm{Bu^tOO^{\cdot}}] = 0. \quad (7)$$

The summation of Eqs. (6) and (7) gives

$$[\mathrm{Bu^tO^{\cdot}}] = (k_{+1}[\mathrm{Bu^tOOOBu^t}] - \\ - k_{4b}[\mathrm{Bu^tOO^{\cdot}}]^2)(k_{-1}[\mathrm{Bu^tOO^{\cdot}}])^{-1}. \quad (8)$$

Subtracting Eq. (6) from Eq. (7), we obtain

$$k_{2a}[\mathrm{Bu^tO^{\cdot}}][\mathrm{O_3}] - k_3[\mathrm{Bu^tOO^{\cdot}}][\mathrm{O_3}] - \\ - (k_{4b} + k_{4a})[\mathrm{Bu^tOO^{\cdot}}][\mathrm{Bu^tOO^{\cdot}}] = 0. \quad (9)$$

Inserting Eq. (9) into (5), we have

$$\mathrm{d}[\mathrm{O_3}]/\mathrm{d}t = 2k_3[\mathrm{Bu^tOO^{\cdot}}][\mathrm{O_3}] + \\ + (k_{4a} + k_{4b})[\mathrm{Bu^tOO^{\cdot}}][\mathrm{Bu^tOO^{\cdot}}]. \quad (10)$$

The further insertion of Eq. (8) into (9) results in the algebraic third-power equation with respect to $[\mathrm{Bu^tOO^{\cdot}}]$:

$$k_{-1}(k_4 + k_{4a})[\mathrm{Bu^tOO^{\cdot}}]^3 + \\ + (k_3k_{-1} + k_{2a}k_{4b})[\mathrm{O_3}][\mathrm{Bu^tOO^{\cdot}}]^2 - \\ - k_{+1}k_{2a}[\mathrm{O_3}][\mathrm{Bu^tOOOBu^t}] = 0. \quad (11)$$

Using the values of k_{2a}, k_3, k_{4a}, and k_{4b} (at −23 °C), we can numerically solve Eq. (11) at constant concentrations of $\mathrm{O_3}$ and $\mathrm{Bu^tOOOBu^t}$. The rate constant of *tert*-butylperoxyl radicals recombination was calculated from the published data**[20]**: $2k_4 = 1.4 \cdot 10^{10}\exp(-10200/(RT)) = 16$ L mol^{-1} s^{-1}. Using the ratio of the rate constants of chain propagation and termination by the recombination of the *tert*-butylperoxyl radicals k_{4a}/k_{4b} equal to 7,[21] we obtained $k_{4a} = 14$ and $k_{4b} = 2$ L mol^{-1} s^{-1}. The k_3 values were varied from 1 to 10^2 L mol^{-1} s^{-1} (estimation from two temperatures, according to the published data,[5,8] gives k_3 ~1.0 L mol^{-1} s^{-1}). Taking into account that the methoxyl radical reacts with $\mathrm{O_3}$ in the gas phase by at least two orders of magnitude more rapidly than the methylperoxyl radical**[4]** and accepting that this ratio remains unchanged in a solution, we varied k_{2a} from 10^2 to 10^6 L mol^{-1} s^{-1}. Solution of Eq. (11) for −23 °C at unchanged $[\mathrm{O_3}] = 0.01$ mol L^{-1} and $[\mathrm{Bu^tOOOBu^t}] = 0.01$ mol L^{-1} over the whole range of k_3 and k_{2a} gives one positive root. The obtained minimum and maximum concentrations of peroxyl radicals are $[\mathrm{Bu^tOO^{\cdot}}] = 1.5 \cdot 10^{-7}$ and $1.4 \cdot 10^{-5}$ mol L^{-1}, respectively. Then the ratios of reaction rates w_{-1}/w_{2c} are 2.5 and 250, respectively, and the last value seems more probable. In addition, the DBO concentration remains almost unchanged within the duration of kinetic experiment (~10^4 s) (see below). This indicates a negligible contribution of reaction (2c) to the total rate of consumption of the *tert*-butoxyl radical. The ratio of transformation rates for the $\mathrm{Bu^tOO^{\cdot}}$ radicals w_{-1}/w_{4b}, taking into account the known values of $[\mathrm{Bu^tOO^{\cdot}}]$ and $[\mathrm{Bu^tO^{\cdot}}]$ equal to $1.5 \cdot 10^{-9}$ and $1.5 \cdot 10^{-11}$ mol L^{-1} and calculated by Eq. (8), is $1.7 \cdot 10^7$ and $1.8 \cdot 10^3$, respectively. Therefore, reactions (2c), (4a), and (4b) can be neglected, and Eqs. (8) and (9) are transformed into the form

$$k_{+1}[\mathrm{Bu^tOOOBu^t}] = k_{-1}[\mathrm{Bu^tO^{\cdot}}][\mathrm{Bu^tOO^{\cdot}}], \\ k_{2a}[\mathrm{Bu^tO^{\cdot}}] = k_3[\mathrm{Bu^tOO^{\cdot}}].$$

Thus, the termination of kinetic chains occurs only by the recombination of the peroxyl and alkoxyl radicals to form DBO due to which its concentration remains unchanged. The concentration of the $\mathrm{Bu^tOO^{\cdot}}$ radicals is determined by the equation

$$[\mathrm{Bu^tOO^{\cdot}}] = \{k_{+1}k_{2a}(k_{-1}k_3)^{-1}[\mathrm{Bu^tOOOBu^t}]\}^{0.5},$$

and Eq. (10) is simplified

$$-\mathrm{d}[\mathrm{O_3}]/\mathrm{d}t = 2(K_{\mathrm{eq}}k_{2a}k_3[\mathrm{Bu^tOOOBu^t}])^{0.5}[\mathrm{O_3}], \quad (12)$$

where $K_{\mathrm{eq}} = k_{+1}/k_{-1} = 2.2 \cdot 10^{-14}$ mol L^{-1}. At a constant DBO concentration, the consumption of $\mathrm{O_3}$ should occur according to a kinetic law of the first order with the effective rate constant

$$k_{\mathrm{eff}} = 2(K_{\mathrm{eq}}k_{2a}k_3[\mathrm{Bu^tOOOBu^t}])^{0.5}, \quad (13)$$

which is observed experimentally. The k_{eff} value should linearly depend on the square root of the initial concentration of $\mathrm{Bu^tOOOBu^t}$, and this condition is also well fulfilled in experiment (Fig. 2). In an additional experiment we proved that the DBO concentration remained almost unchanged in the time scale of kinetic experiments (10^4 s). A solution of DBO was placed in a cell cooled to −23 °C, saturated with ozone, and left to stay for the time interval $\tau_{1/2} = \ln 2/k_{+1}$ ~10^4 s, during which DBO should be decomposed by half. When the concentration of $\mathrm{O_3}$ halved, the solution was again saturated with ozone, *etc.* (Fig. 3). The regions of kinetic curves where the concentration of $\mathrm{O_3}$ decreases (shown in Fig. 3) are well linearized in the coordinates of the first-order kinetic equation. The effective rate constant of $\mathrm{O_3}$

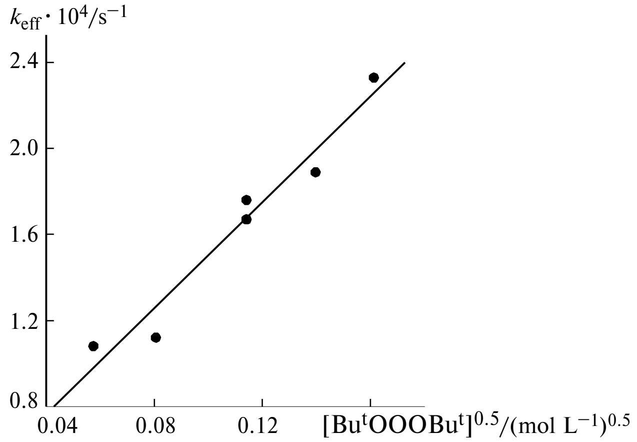

Fig. 2. Effective rate constant of O_3 consumption (k_{eff}) as a function of the square root of initial concentration of DBO (−23 °C).

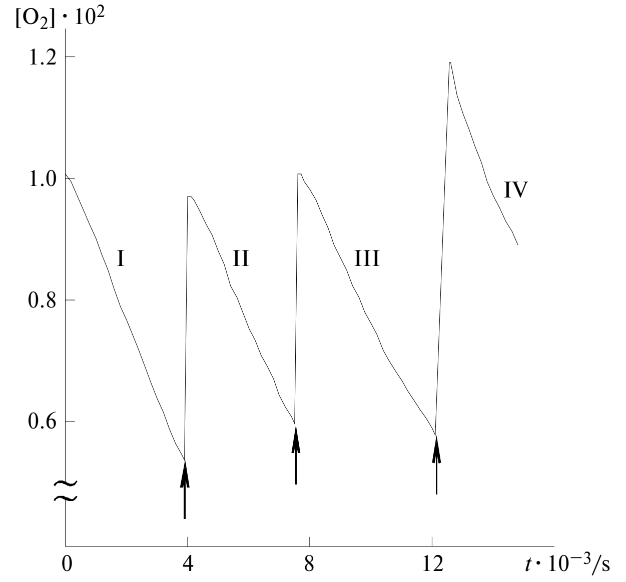

Fig. 3. DBO-initiated consumption of O_3 (−23 °C, $[Bu^tOOOBu^t]_0 = 0.013$ mol L^{-1}). Arrows indicate the instant of periodical saturation of DBO with O_3. I—IV are the numbers of regions in the kinetic curves.

consumption decreases insignificantly in each subsequent region:

Region of curve	I	II	III	IV
$k_{eff} \cdot 10^4$/s^{-1}	1.76±0.06	1.54±0.03	1.31±0.01	1.24±0.05

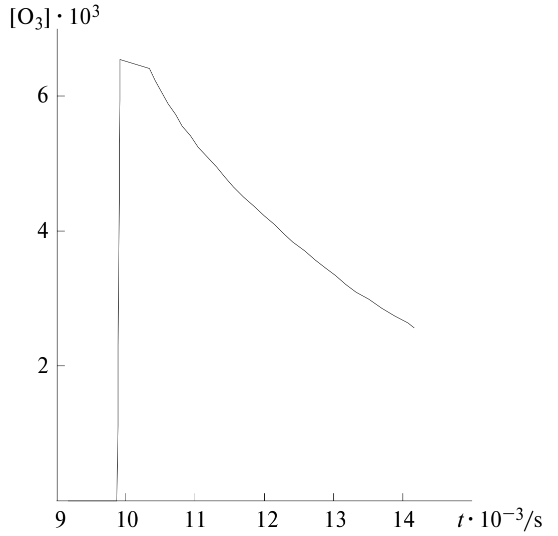

Fig. 4. DBO-initiated O_3 decomposition with preliminary storage of the solution for 10^4 s without additional O_3 supply (−23 °C, $[Bu^tOOOBu^t]_0 = 0.013$ mol L^{-1}).

Moreover, the concentration of Bu^tOOOBu^t in a $CFCl_3$ solution also remains almost unchanged in the absence of O_3. A solution of DBO was placed in a cell cooled to −23 °C and left to stay for ~10^4 s, then the solution was saturated with ozone, and the kinetics of its consumption was recorded (Fig. 4). The k_{eff} value determined by this method was $(1.61 \pm 0.04) \cdot 10^{-4}$ s^{-1}, which is close to that obtained under similar conditions without preliminary storing of the solution $(1.70 \pm 0.01) \cdot 10^{-4}$ s^{-1}. If DBO is consumed, k_{eff} calculated by Eq. (13) would equal to $0.97 \cdot 10^{-4}$ s^{-1} (the product $K_{eq}k_{2a}k_3 = 3.78 \cdot 10^{-7}$ L mol^{-1} s^{-2} necessary for calculation was determined from the slope of the experimental plot of k_{eff} *vs.* $[Bu^tOOOBu^t]^{0.5}$, see Fig. 2).

The observed phenomenon, somewhat unexpected at first glance, is regular and can easily be explained. The published kinetic data for DBO were obtained under the conditions of its irreversible decomposition where the active alkoxyl radicals that formed were removed from the system by reactions with the solvent,[22] radical acceptor,[15] or *tert*-butyl hydroperoxide.[5,12] In the absence of channels of irreversible radical decay, the kinetic chains terminate by reaction (−1). Therefore, the DBO concentration remains unchanged, and the peroxyl radical acts as a "trap" for the alkoxyl radical. When O_3 is added to this system, the peroxyl and alkoxyl radicals react with them by reactions (2a) and (3) to be transformed into each other. In essence, DBO acts as a catalyst for chain decomposition of ozone and is not consumed. Thus, one DBO molecule can lead to the decomposition of a significant amount of O_3.

The obtained kinetic data make it possible to estimate the product of the rate constants for the reactions of alkoxyl (2a) and peroxyl (3) radicals with ozone $k_{2a}k_3$. Since $K_{eq}k_{2a}k_3 = 3.78 \cdot 10^{-7}$ L mol^{-1} s^{-2} (see Fig. 2, Eq. (13)) and $K_{eq} = 2.2 \cdot 10^{-14}$ mol L^{-1}, then $k_{2a}k_3 = 1.7 \cdot 10^7$ L^2 mol^{-2} s^{-2}. Using the found above value $k_3 = 1.0$ L mol^{-1} s^{-1} for the rate constant of the reaction of O_3 with the *tert*-butylperoxyl radical (−23 °C), we obtain $k_{2a} = 1.7 \cdot 10^7$ L mol^{-1} s^{-1}.

Taking into account the found k_{2a} and k_3 values, we calculated the initial rates (mol L^{-1} s^{-1}) of reactions (1)—(4), their ratios, and chain length $\nu = w_{2a}/w_{-1}$, which are in good agreement with the found experimental regularities.

w_{+1}	$7.4 \cdot 10^{-7}$	w_3	$5.6 \cdot 10^{-7}$
w_{-1}	$7.3 \cdot 10^{-7}$	w_{4a}	$4.4 \cdot 10^{-8}$
w_{2a}	$6.6 \cdot 10^{-7}$	w_{4b}	$6.2 \cdot 10^{-9}$
w_{2c}	$7.8 \cdot 10^{-10}$	w_{-1}/w_{4b}	120
w_{2a}/w_{2c}	840	ν	0.9

The closeness of the calculated decomposition rates of di(*tert*-butyl) trioxide to the oxyl and peroxyl radicals and their reversible recombination confirms the experimentally observed low rate of irreversible decomposition of di(*tert*-butyl) trioxide. Side reactions (2c) and (4b) occur with negligible rates, which is illustrated by the ratios w_{2a}/w_{2c} and w_{-1}/w_{4b}. It is of interest that the calculated value of chain length is sufficiently low, although up to twenty O_3 molecules are consumed per molecule of the irreversibly decomposed DBO. This reflects the fact that the recombination of the radicals involved in the chain decomposition of ozone results in the regeneration of the initiator, *viz.*, DBO. Under the conditions of a low efficiency of free radical recombination (for example, in the upper atmospheric layers), we can expect that the radical chain decomposition of O_3 occurs with longer chains.

The significant thermal effect of reactions (2a) and (3) and the fulfillment of the rule of spin conservation can result in the formation of dioxygen molecules in the excited singlet state $^1O_2$. To verify this hypothesis, we attempted to detect IR chemiluminescence in the region of 1000—1300 nm, which is characteristic of the emission from $^1O_2$.[23] The detection was performed along with passing an ozone—oxygen mixture (2 vol.% O_3) through a 0.2 *M* solution of di(*tert*-butyl) trioxide in $CFCl_3$ (−10—0 °C) or adding a 0.1 *M* solution (0.2—0.5 mL) of DBO to 2.5—2.8 mL of a solution of O_3 in $CFCl_3$ (~0.03 mol L^{-1}). However, in both cases, we failed to detect IR chemiluminescence, *i.e.*, singlet dioxygen is not formed in reactions (2a) and (3).

The data obtained give an insight into the mechanism of formation of dialkyl trioxides by the low-temperature ozonization of the potassium or sodium salts of hydroperoxides.

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