

Kinetics of radical decomposition of di(*tert*-butyl) trioxide

A. F. Khalizov, S. L. Khursan, and V. V. Shereshovets*

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@academy.bashnet.ru

The kinetics of radical decomposition of di(*tert*-butyl) trioxide was studied by spectrophotometry from the consumption of an acceptor of free radicals, 2,6-di(*tert*-butyl)-4-methylphenol, in CFCl_3 and CH_2Cl_2 (in the latter case, in the presence of 0.1 M Bu^tOOH). The activation parameters of the reaction ($\log(A/s^{-1}) = 14.8 \pm 1.2$ and 14.1 ± 1.6 , $E_a = 21.6 \pm 1.4$ and 20.1 ± 1.9 kcal mol $^{-1}$ in CFCl_3 and CH_2Cl_2 , respectively) and the probability of radical escape to the bulk ($e = 0.9 \pm 0.1$) were determined. The known experimental and calculated values of the O—OO bond strength in trioxides were analyzed.

Key words: trioxides, thermal decomposition, free radicals, acceptors of free radicals.

Dialkyl trioxides (ROOOR) are intermediates of low-temperature radical reactions involving oxygen and ozone. It has been shown previously^{1–3} that the thermal decomposition of ROOOR occurs homolytically with an intermediate formation of free radicals. The overall kinetics of decomposition of dialkyl trioxides has been studied by volumetry¹ and chemiluminescence.⁴ An attempt to study the kinetics of decomposition of dicumyl trioxide by ^1H NMR spectroscopy has been made.⁵ The effect of a solvent nature on the rate of thermolysis of $\text{Bu}^t\text{OOOBu}^t$ has been observed,⁶ and its induced decomposition has been studied.⁷ Despite repeated proofs of formation of free radicals during thermolysis of dialkyl trioxides were found, no direct experimental data on the contribution of the radical route of ROOOR decomposition to the reaction mechanism are available. The activation parameters obtained previously characterize the overall process only.

In this work, we studied the kinetics of radical decomposition of $\text{Bu}^t\text{OOOBu}^t$ from the consumption of an acceptor of free radicals, 2,6-di(*tert*-butyl)-4-methylphenol (ionol, InH) and determined the contribution of the radical channel to the overall process.

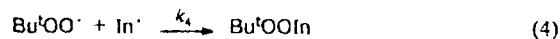
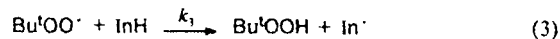
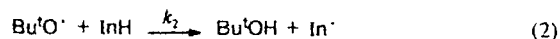
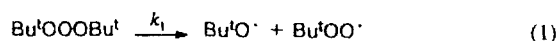
Experimental

Di(*tert*-butyl) trioxide was obtained according to the known procedure^{4,5} by ozonization of sodium salt of *tert*-butyl hydroperoxide in CFCl_3 at -60°C . The concentration of $\text{Bu}^t\text{OOOBu}^t$ was determined from the ^1H NMR spectra on a Bruker AM-300 high-resolution instrument. The kinetics of radical decomposition of $\text{Bu}^t\text{OOOBu}^t$ was studied by spectrophotometry from the consumption of an acceptor of free radicals (InH) in a thermostatted quartz cell (volume 2.5 mL, thickness 1.0 cm, a vacuum jacket to prevent freezing of moisture) placed in the cell chamber of an SF-26 one-beam

spectrophotometer. The temperature was determined by a thermocouple mounted into the cell cap. CFCl_3 or a 0.1 M solution of Bu^tOOH in CH_2Cl_2 was used as the reference solution. The following concentrations of ionol and di(*tert*-butyl) trioxide were used: $[\text{InH}] = (1.1\text{--}3.4) \cdot 10^{-4}$ mol L $^{-1}$, $[\text{Bu}^t\text{OOOBu}^t] = 3.3 \cdot 10^{-5}$ mol L $^{-1}$. A change in the concentration of ionol was recorded in the region of its absorption maximum at 284 nm. Extinction coefficients ($\lambda = 284$ nm) $\epsilon = 3000 \pm 150$ and 2300 ± 170 L mol $^{-1}$ cm $^{-1}$ in CFCl_3 and CH_2Cl_2 , respectively, were determined from the linear dependence of the optical density of a solution of InH on its concentration. It was established preliminarily that under conditions of kinetic experiments, the optical absorption of products of decomposition of $\text{Bu}^t\text{OOOBu}^t$ and products of transformation of InH did not exceed 3% of the absorption of ionol at the beginning of the experiment (A_0^{InH}).

Results and Discussion

It has been shown previously⁵ that 2,6-di(*tert*-butyl)-4-*tert*-butylperoxy-4-methylcyclohexa-2,5-dienone (Bu^tOOIn) is the single product of transformation of ionol added to di(*tert*-butyl) trioxide decomposing in reaction (1).



According to the published data,⁸ the rate constants of hydrogen abstraction from ionol by alkoxyl (reaction (2), k_2) and peroxy (reaction (3), k_3) radicals are equal to 10^8 (22 $^\circ\text{C}$) and 10^4 L mol $^{-1}$ s $^{-1}$ (50 $^\circ\text{C}$), respectively.

Therefore, in an inert solvent, ionol is consumed in reaction (2) only. The rate constants of recombination of phenoxyl radicals with alkoxy and peroxy radicals are virtually independent of the structure of the latter and can be accepted⁸ as $3 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. The steady-state concentration of peroxy radicals in the solution is considerably higher than those of alkoxy radicals. Therefore, if the ionol concentration is sufficiently high to prevent recombination of peroxy radicals, the kinetic chains are terminated by reaction (4).

The rates of consumption of the inhibitor (w_{InH}) and the rates of decomposition of the initiator (w_i) are related by the following correlation:

$$w_{\text{InH}} = (1/f) \cdot e w_i,$$

where f is the stoichiometric coefficient of inhibition (in this case, $f = 2$), and e is the probability of radical escape to the bulk. This equation for trioxide can be rewritten in the form

$$\frac{d[\text{InH}]}{dt} = \frac{2e}{f} \cdot \frac{d[\text{Bu}^t\text{OOOBu}^t]}{dt} = -\frac{2e}{f} k_1 [\text{Bu}^t\text{OOOBu}^t].$$

Taking into account that $[\text{Bu}^t\text{OOOBu}^t] = [\text{Bu}^t\text{OOOBu}^t]_0 \exp(-k_1 t)$, we obtain the equation

$$\frac{d[\text{InH}]}{dt} = -\frac{2e}{f} k_1 [\text{Bu}^t\text{OOOBu}^t]_0 \exp(-k_1 t).$$

Integration of the latter gives

$$[\text{InH}] = [\text{InH}]_0 - (2e/f) \cdot [\text{Bu}^t\text{OOOBu}^t]_0 (1 - \exp(-k_1 t)).$$

Taking into account that at $t \rightarrow \infty$, $[\text{InH}] \rightarrow [\text{InH}]_\infty$ where

$$[\text{InH}]_\infty = [\text{InH}]_0 - (2e/f) \cdot [\text{Bu}^t\text{OOOBu}^t]_0,$$

we obtain equations for the radical escape to the bulk and the rate constant of decomposition of trioxide (Eqs. (5) and (6), respectively).

$$e = \frac{f}{2[\text{Bu}^t\text{OOOBu}^t]} ([\text{InH}]_0 - [\text{InH}]_\infty) \quad (5)$$

$$k_1 t = \ln \frac{[\text{InH}]_0 - [\text{InH}]_\infty}{[\text{InH}] - [\text{InH}]_\infty} \quad (6)$$

The rate constant of decomposition of trioxide k_1 was calculated by two methods. In the first case, it was determined from the slope of the straight line in the coordinates $\ln\{([\text{InH}]_0 - [\text{InH}]_\infty)/([\text{InH}] - [\text{InH}]_\infty)\} - t$. For this purpose, we should know the concentration of ionol $[\text{InH}]_\infty$ for complete decomposition of $\text{Bu}^t\text{OOOBu}^t$; hence, the experiments at low temperatures take a long time. In the second case, the decomposition of trioxide was carried out at a depth of 85–90%, and the $[\text{InH}]_\infty$ and k_1 values were obtained by the nonlinear optimization from Eq. (6).

The kinetic experiments were carried out at the ratio of concentrations $[\text{InH}]_0/[\text{Bu}^t\text{OOOBu}^t]_0 \geq 2$, where the k_1 value is independent of $[\text{InH}]_0$, i.e., all radicals formed during the decomposition of di(*tert*-butyl) trioxide are trapped.

Decomposition of di(*tert*-butyl) trioxide in CFCl_3 . The consumption of ionol during decomposition of $\text{Bu}^t\text{OOOBu}^t$ in CFCl_3 obeys the first-order kinetic law (Fig. 1). Using the temperature dependence of the k_1 constant (a relative error of determination of k_1 does not exceed 10%):

$t/^\circ\text{C}$	-13.5	-7.5	-1.5	3.5	7.0
$k_1 \cdot 10^3/\text{s}^{-1}$	0.5	0.9	2.8	5.6	9.4

we determined the activation parameters of the radical decomposition of di(*tert*-butyl) trioxide in CFCl_3 : $\log(A/\text{s}^{-1}) = 14.8 \pm 1.2$, $E_a = 21.6 \pm 1.4 \text{ kcal mol}^{-1}$.

In the temperature range studied, the e value calculated according to Eq. (5) remains almost unchanged and amounts 0.90 ± 0.05 .

Decomposition of di(*tert*-butyl) trioxide in CH_2Cl_2 . During decomposition of di(*tert*-butyl) trioxide in the presence of InH in CH_2Cl_2 ($\lambda = 284 \text{ nm}$), the relative change in the optical density of the solution $(A_0 - A_\infty)/A_0$ does not exceed 3%. This indicates that no more than 10% radicals formed from trioxide were trapped by the acceptor. The absorption spectrum of the solution obtained by mixing of $\text{Bu}^t\text{OOOBu}^t$ and InH in the 1.0 : 0.8 ratio and exposed at 0°C for four half-decay periods of trioxide does not differ from the spectrum of ionol in CH_2Cl_2 . It can be assumed that the low degree of transformation of InH is due to the competitive reaction of

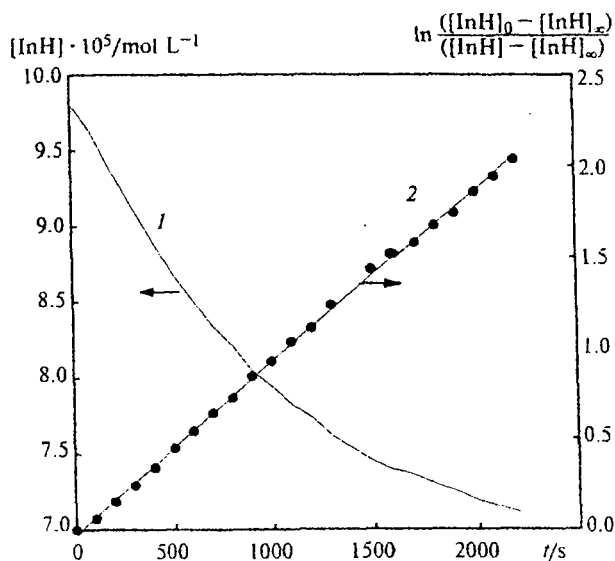
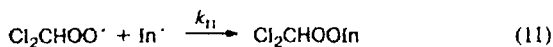
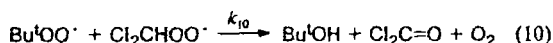
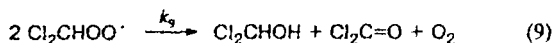
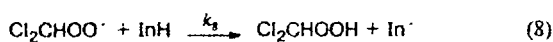
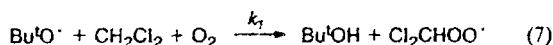


Fig. 1. Kinetic curve of ionol consumption in radical decomposition of $\text{Bu}^t\text{OOOBu}^t$ (1) (change in the optical density of ionol at $\lambda = 284 \text{ nm}$) and its semilogarithmic anamorphosis (2) (-7.5°C , $[\text{Bu}^t\text{OOOBu}^t]_0 = 3.3 \cdot 10^{-5} \text{ mol L}^{-1}$, CFCl_3).

hydrogen abstraction by $\text{Bu}^{\text{t}}\text{O}^{\cdot}$ radicals from the solvent CH_2Cl_2 (reaction (7), k_7). In fact, $k_2 \approx 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$,⁸ $k_7 \approx 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ (22 °C),⁷ $[\text{InH}] = 1 \cdot 10^{-4} \text{ mol L}^{-1}$, and $[\text{CH}_2\text{Cl}_2] = 15.6 \text{ mol L}^{-1}$; then the ratio of the rates $w_7/w_2 \approx 150$. The $\cdot\text{CHCl}_2$ radical formed reacts rapidly ($4.7 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$)⁹ with dissolved oxygen to yield the dichloromethylperoxyl radical. The probability of the reaction of $\cdot\text{CHCl}_2$ with InH is very low, since, according to the published data,⁸ the value of the rate constant of the reaction of alkyl radicals with ionol ranges within $35\text{--}4 \cdot 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ (50 °C). The $\text{Cl}_2\text{CHOO}^{\cdot}$ radicals can abstract the hydrogen atom from ionol (reaction (8), $k_8 \approx 10^4\text{--}10^5 \text{ L mol}^{-1} \text{ s}^{-1}$)⁹ and recombine (reaction (9), $k_9 \approx 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$)⁷ or cross-recombine with *tert*-butylperoxyl (reaction (10), $k_{10} \approx 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$)⁷ and phenoxyl radicals (reaction (11), $k_{11} \approx 10^8\text{--}10^9 \text{ L mol}^{-1} \text{ s}^{-1}$).^{7,9}



For the model including Eqs. (1)–(4) and (7)–(11), using the rate constants and initial concentrations presented above, we obtained the numerical solution from which follows that a considerable number of $\text{Bu}^{\text{t}}\text{OO}^{\cdot}$ and $\text{Cl}_2\text{CHOO}^{\cdot}$ radicals decay in reactions (9) and (10), and the contribution of reactions (3) and (8) becomes noticeable only when the depth of the process increases (Fig. 2). The aforesaid is experimentally confirmed by the fact that when a solution of ionol ($10^{-3} \text{ mol L}^{-1}$) is added to decomposing di(*tert*-butyl) trioxide ($10^{-3} \text{ mol L}^{-1}$) in CH_2Cl_2 , the intensity of IR luminescence (CL) decreases insignificantly. Since emitters of CL are formed in cross-recombination of peroxy radicals from the solvent and trioxide,⁷ it can be concluded that the addition of ionol virtually does not decrease the contribution of reactions (9) and (10).

The kinetic experiment in the presence of additives of *tert*-butyl hydroperoxide, which replaces *tert*-butoxyl radicals by *tert*-butyl peroxy radicals, prevents the participation of the solvent in the reaction. The rate constant of the reaction of $\text{Bu}^{\text{t}}\text{O}^{\cdot}$ with $\text{Bu}^{\text{t}}\text{OOH}$ (reaction (12), k_{12}), according to the published data,¹⁰ is $2.5 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. Thus, at $[\text{Bu}^{\text{t}}\text{OOH}] = 0.1 \text{ mol L}^{-1}$ almost all $\text{Bu}^{\text{t}}\text{O}^{\cdot}$ radicals are trapped by hydroperoxide ($w_{12}/w_7 = 16$), and ionol is consumed in reaction (3) only.

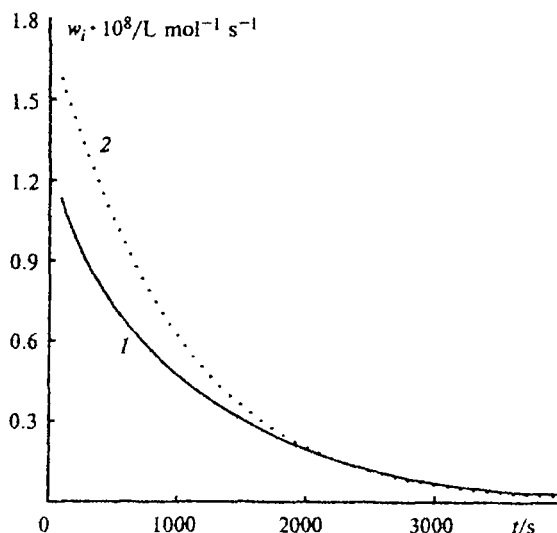
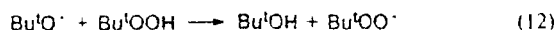


Fig. 2. Time dependences of the reaction rates of peroxy radicals with ionol (1, $w_7 + w_8$) and rates of their cross- and self-recombination (2, $w_9 + w_{10}$).

The extinction coefficient of *tert*-butyl hydroperoxide at $\lambda = 284 \text{ nm}$ is low ($4.0 \text{ L mol}^{-1} \text{ cm}^{-1}$); however, the optical absorption of a 0.1 M solution of $\text{Bu}^{\text{t}}\text{OOH}$ is sufficiently high ($A = 0.4$). Therefore, 0.1 M $\text{Bu}^{\text{t}}\text{OOH}$ in CH_2Cl_2 was used as the reference solution. A change in the concentration of hydroperoxide during experiment can be neglected, since $[\text{Bu}^{\text{t}}\text{OOH}]_0 \gg [\text{Bu}^{\text{t}}\text{OOOBu}^{\text{t}}]_0$.

The spectrum of a solution of CH_2Cl_2 containing $\text{Bu}^{\text{t}}\text{OOH}$ (0.1 mol L^{-1}) and $\text{Bu}^{\text{t}}\text{OOOBu}^{\text{t}}$ and InH in 1.0 : 0.8 ratio (the solution was exposed at 0 °C for four half-periods of trioxide decay) contains no absorption at 284 nm, which indicates complete consumption of ionol.

The kinetics of consumption of ionol during decomposition of di(*tert*-butyl) trioxide in CH_2Cl_2 with a $\text{Bu}^{\text{t}}\text{OOH}$ additive is similar to that observed in CFCl_3 , which confirms the above-mentioned assumption about the competing reactions of the $\text{Bu}^{\text{t}}\text{O}^{\cdot}$ radical with CH_2Cl_2 and InH. The activation parameters of radical decomposition of di(*tert*-butyl) trioxide in CH_2Cl_2 were determined as $\log(A/\text{s}^{-1}) = 14.1 \pm 1.6$, $E_a = 20.1 \pm 1.9 \text{ kcal mol}^{-1}$ from the temperature dependence of the k_1 constant (the relative error of determination of k_1 does not exceed 10%):

$t/^\circ\text{C}$	-21.0	-17.5	-10.5	0.0	0.0	5.5
$k_1 \cdot 10^3/\text{s}^{-1}$	0.3	1.1	3.2	9.2	9.0	20.1

The probability of radical escape to the bulk (e) is virtually temperature-independent and amounts 0.89 ± 0.09 .

Comparison of the rate constants of decomposition of di(*tert*-butyl) trioxide in CFCl_3 and in CH_2Cl_2 at close temperatures shows that they are systematically higher in the latter solvent. This agrees well with the

Table 1. Activation parameters obtained by different methods for decomposition of trioxides

Trioxide ^a	$\log(A/s^{-1})$	$E_a/kcal\ mol^{-1}$	Method (conditions)
Bu ^t OOBu ^t	14.8±1.2	21.6±1.4	Method of free radical acceptors (CFCl ₃)
Bu ^t OOBu ^t	14.1±1.6	20.1±1.9	The same (CH ₂ Cl ₂ , Bu ^t OOH)
Bu ^t OOBu ^t	14.5±2.2	20.8±0.6	IR CL (CH ₂ Cl ₂) ⁴
Bu ^t OOBu ^t	14.5±0.7	20.4±0.9	Visible CL (CH ₂ Cl ₂) ⁴
Bu ^t OOBu ^t	~17	~23	Volumetry (CH ₂ Cl ₂ , Bu ^t OOH) ¹
CumOOOCum	12.6±3.1	18.9±3.7 ^b	¹ H NMR spectroscopy (CFCl ₃) ⁵
CumO—OOH		21.9 ^c	The same (CumH, acetone-d ₆ , InH) ¹⁶
AdO—OOH	12.9±1.4	19.6±1.9	Visible CL (acetone) ¹⁷
Me ₂ C(OH)O—OOH		20.2 ^c	Method of free radical acceptors (Me ₂ CHOH) ¹⁸
Me ₂ C(OH)O—OOH	13.0	20.2 ^d	The same ¹⁸ (gas phase)
ROOOR	16	23	Thermochemical estimation (gas phase) ¹⁹
RO—OOH		20.4±1.0	Quantum-chemical MNDO calculations ¹¹
RO—OOH		20.8±1.0	The same, by the AM1 method ¹¹
MeO—OOH		29.6	<i>Ab initio</i> calculations ¹³
MeO—OOH		28.0	The same ¹³
MeO—OOH		30.1	¹⁴
EtO—OOH		30.2	¹⁴

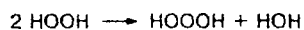
^a Ad is adamantyl, Cum is cumyl.^b Estimated from the kinetic data presented in this work.^c Taking into account the activation energy of viscous flow.¹¹^d Calculated for the gas phase ($A = 10^{13}$) from the linear dependence of E_a on $\log A$.¹¹

effect observed previously for the influence of the medium on the rates of decomposition of trioxide.⁶

The results obtained indicate that the decomposition of dialkyl trioxides is almost completely homolytic. The values of activation energy of the radical decomposition of di(*tert*-butyl) trioxide correspond to the E_a values obtained for this compound by other methods and for other trioxides (Table 1). For example, the activation parameters of thermal decomposition of di(*tert*-butyl) trioxide determined by the method of free radical acceptors and chemiluminescence method agree well. The fact that the dissociation energy of the RO—OO bond in trioxides is independent of the R nature is also confirmed by the results of semiempirical quantum-chemical calculations.^{4,11,12}

At the same time, the recent results of *ab initio* calculations of the bond strength $D(O—O)$ in the series of trioxides (see Table 1) differ strongly from the main data. It can be easily shown that the $D(O—OO)$ values obtained^{13,14} do not correspond to the experimental data. In fact, when the activation energy of decomposition of ROOOR is accepted to be equal to 30 kcal mol⁻¹ and the pre-exponential factor is 10¹⁶ s⁻¹, the calculated lifetime of trioxide is 3.3 years at 273 K. At the same time, the lifetime of trioxides determined experimentally at this temperature is several minutes. However, the strengths of the O—O bond calculated in the same work¹³ agree well with the experimental values. In our opinion, this is explained by the following. The enthal-

pies of formation of polyoxides and bond strengths in these compounds were calculated by the method of isodesmic reactions with group balance.¹³ This implies that the type and number of groups in reagents and products are retained in the isodesmic reactions used. The term "group" implies the central polyvalent atom surrounded by ligands according to Benson's definition.¹⁵ However, the key reactions studied¹³ involving HOOOH and MeOOOH trioxides are not strictly isodesmic. The number and type of chemical bonds are retained in them, but the environments differ. For example, for the reaction



we obtain four O—(H)(O) groups for the reagents, but two O—(H)(O) groups and one O—(O)₂ and one O—(H)₂ group for the products. The fact that the nearest environment is not retained most likely results in an error of *ab initio* calculations of the ΔH° values of reactions involving trioxides due to incomplete account of electron correlation. As applied to peroxides, the approach of the authors of Ref. 13 is rigorous; therefore, the results of the calculation agree well with the known experimental data.

Thus, according to the structure and reactivity, ROOOR dialkyl trioxides can be considered as analogs of ROOR dialkyl peroxides. Homolysis at the O—O bond is the most characteristic reaction of dialkyl trioxides. This reaction is monomolecular and usually the limiting stage of decomposition. The main distinction

between ROOOR and ROOR is the low temperature limit of stability of ROOOR, which is due to the lower strength of the O—OO bond as compared to that of O—O. Therefore, dialkyl trioxides are unique radical initiators, which are efficient at temperatures from -30 to $+10$ °C. Only photochemical and radiation initiation as well as reactions of hydroperoxides with salts of variable valence metals can compete with reactions of dialkyl trioxides in this temperature range. However, these methods are less convenient, because they require complex equipment or contaminate the reaction system.

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