Kinetics and Mechanism of the Highly Efficient Generation of Singlet Oxygen in Dimethyldioxirane Decomposition Induced by the Chloride Ion

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Abstract—The decomposition of dimethyldioxirane induced by the chloride anion has been investigated by methods of infrared chemiluminescence and quantum chemistry. The reaction leads to efficient generation of singlet excited molecular oxygen ¹O₂ (the excitation yield in acetone is 61%). A mechanism of peroxide decomposition is proposed in which the key reactions are the addition of the chloride ion to an oxygen atom of dioxirane, resulting in dioxirane ring opening and the formation of the 2-chlorooxy-2-hydroxy propane alcoholate (k_1) , and the interaction of the latter with another dimethyldioxirane molecule. This interaction results either in the formation of an adduct, which further decomposes to evolve ${}^{1}O_{2}$, and catalyst regeneration (k_{2}) or in the formation of the 2-chloroxyisopropyl radical, which leads to the irreversible consumption of the chloride ion catalyst (k_3) . The decay kinetics of the infrared chemiluminescence of ${}^{1}O_2$ has been studied in a wide range of reactant concentrations. The temperature dependence of the rate constant of the reaction of dimethyldioxirane with the chloride ion has been determined by a kinetic analysis of the mechanism proposed: $\log(2k_1) = (11.1 \pm 0.7) - (46 \pm 4)/\Theta$, where $\Theta = 2.3RT$ kJ/mol. Estimation of the ratio of the rates of the reaction of the 2-chlorooxy-2-hydroxy propane alcoholate with dimethyldioxirane via two pathways (k_3/k_2) has demonstrated that the fraction of the process involving electron transfer does not exceed 1.5% under the experimental conditions examined. Nevertheless, the latter reaction, which withdraws the chloride ion from the catalytic cycle of dimethyldioxirane decomposition yielding singlet oxygen, has a marked effect on the overall kinetics of the process.

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Singlet oxygen (${}^{1}O_{2}$) has been attracting researchers' attention for many years due to its essential role in organic synthesis and biological processes [1–11]. The participation of ${}^{1}O_{2}$ in chemiluminescent reactions is also important [11, 12]. A reaction accompanied by the highly efficient generation of ${}^{1}O_{2}$, namely, the decomposition of dioxiranes [13–16] catalyzed by a number of anions (Cl⁻, Br⁻, I⁻, *t*-BuO⁻, O⁻₂, and OH⁻ [17–19], was discovered earlier. The ${}^{1}O_{2}$ yield measured in this peroxide system by infrared chemiluminescence (IRCL) is rather high. For example, the yield of this species from the reaction of dimethyldioxirane (DMD) with the chloride ion in aqueous acetone is almost quantitative [18, 19].

Data concerning this reaction would be useful for gaining a deeper insight into the generation of excited states in reactions of peroxides and into the factors affecting the stability of dioxiranes in solution. In addition, the high yield of ${}^{1}O_{2}$ makes the dioxirane–nucleophilic ion system promising for use in chemical lasers and in organic syntheses. Investigation of the conditions under which the maximum possible yield of ${}^{1}O_{2}$ is attainable requires a detailed study of the reaction mechanism.

An earlier ab initio study [20] suggested a mechanism of ${}^{1}O_{2}$ generation in the reaction of DMD with the chloride ion (Scheme 1). The key role in this mechanism is played by the 2-chlorooxy-2-hydroxy propane alcoholate, and ${}^{1}O_{2}$ results from the exothermic reaction of this intermediate with dioxirane.



Later theoretical studies [21] showed that the regularities revealed by the study of the DMD–Cl[–] system are valid for the process involving methyl(trifluoromethyl)dioxirane (TFD). The present work continues the investigation of the mechanism of the reactions of dioxiranes with anions and is devoted to the kinetics of the reactions that occur in the DMD–Cl⁻ system. The work is aimed at revealing possible side processes affecting the ${}^{1}O_{2}$ yield and at constructing a kinetic scheme consistent with the accumulated array of experimental data.

EXPERIMENTAL

The solvents (CCl₄, CHCl₃, CH₂Cl₂, and acetone) were purified and dried using a standard procedure [23]. 1,4-Dimethylnaphthalene used in endoperoxide synthesis was purified by vacuum distillation. Water was doubly distilled.

The synthesis of DMD was carried out according to a slightly modified standard procedure [24, 25]. Bidistilled water (76 ml), NaHCO₃ (52 g), and acetone (68 ml) were placed in a 1000-ml round-bottom flask connected through an air condenser to a trap cooled with liquid nitrogen. Next, a weak vacuum (0.5- 0.7 kgf/cm^2) was produced with a water jet air pump and an inert gas was passed through the flask. The mixture was vigorously stirred with a mechanical stirrer, and oxone (ternary salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) (35 g) was added. The peroxide started accumulating in the receiver immediately after the beginning of the synthesis. Approximately 20 min after, an additional amount of oxone (35 g) and acetone (15-20 ml) were introduced into the flask. A new portion of oxone (30 g) and acetone (15-20 ml) were added in 20-25 min. The reaction was performed until the complete cessation of the evolution of gas bubbles. The total duration of the procedure was 1-1.5 h. After the end of the synthesis, the trap was warmed and the remaining amount of DMD was let to flow down into the receiver. A yellowish DMD solution (0.09–0.11 mol/l) in acetone was thus obtained. Water was removed from the product by decantation (some amount of H₂O passed from the reaction flask into the DMD solution during the synthesis). A test tube with DMD was placed in an acetone bath cooled to -70° C, and water that was crystallizing on the bottom of the tube was frozen out for 4–6 h. Thereafter, the DMD solution in acetone was decanted in to a clean test tube. The solution of dioxirane in acetone was stored over a molecular sieve at −25°C.

1,4-Dimethylnaphthalene endoperoxide was synthesized according to a known procedure [26, 27].

The reaction of DMD with the chloride ion was studied in wide ranges of DMD concentrations (from 4×10^{-4} to 4×10^{-2} mol/l) and Cl⁻ concentrations (from 5×10^{-5} to 8×10^{-4} mol/l) in the temperature range 278–316 K. The source of chloride ions was the salt *n*-Bu₄NCl, which undergoes almost complete dissociation in acetone [22], which was used in our experiments as the solvent: the degree of dissociation α measured at a tetrabutylammonium chloride concentration of 4×10^{-2} mol/l and T = 293 K is 0.58, which corresponds to $\alpha \ge 0.98$ in the above indicated range of salt concentrations.

Chemiluminescence in the IR spectral range was recorded using an earlier described setup [28] with a liquid nitrogen-cooled FEU-83 photomultiplier, which is sensitive in the IR range. The ${}^{1}O_{2}$ emission wavelength range was cut out using an IKS-7 cutoff light filter ($\lambda = 1000 - 13000$ nm). When studying the kinetics of chemiluminescence decay, a solution of DMD (1 ml) was placed into a temperature-controlled reactor situated above the FEU photocathode. After a specified temperature was reached, a solution of tetrabutylammonium chloride (1 ml) was quickly introduced into the dioxirane solution from a temperature-controlled injector and IRCL was detected. The maximum CL intensity (I_{CL}) was reached in ~1 s, and its decay in time was monitored. The digital signal of $I_{\rm CL}$ as a function of t was processed using nonlinear regression analysis.

A solution of DMD in CCl_4 free of acetone was prepared by a known procedure [29].

Molecular chlorine was identified in a CCl₄ medium. For this purpose, the optical absorption spectrum of the products of the reaction of DMD with the chloride ion in the presence of CF₃COOH was compared to the known absorption spectrum of Cl₂ ($\lambda_{max} = 335$ nm) [30].

The G3MP2B3 composite method [31] was used to calculate the energy characteristics of the process, namely, the heats of particular reaction steps and the electron affinities of the reactants and intermediates. Solvation by acetone was taken into account in the framework of the polarized continuum model [32-34]using the B3LYP hybrid functional [35], which includes the Becke (B3) three-parameter potential [36] and the Lee-Yang-Parr (LYP) correlation potential [37] in combination with the triple splitvalence basis set augmented with d- and p-type polarization functions and the set of diffuse functions [6-311+G(d,p)] [38]. Calculations were performed using the Gaussian 03 Revision-D02 program [39]. The visualization and primary processing of the quantum chemical calculation results were carried out using the ChemCraft program [40].

RESULTS AND DISCUSSION

Dimethyldioxirane is a strong oxidant widely used in organic synthesis [13–16, 41]. The high reactivity of DMD implies its chemical instability; however, under our experimental conditions, DMD in acetone solution is fairly stable. Indeed, the logarithm of the apparent rate constant of the decrease in the peroxide concentration in acetone, $\log k_{app}$, is $(10.2 \pm 0.6) - (90 \pm 4)/\theta$, where $\theta = 2.3RT$ kJ/mol [42], which corresponds to the lifetime $(1/k_{app})$ of DMD from 70 days at 278 K to 16 h at 316 K under the given conditions. Dioxirane disappears rapidly upon the addition of tetrabutylammonium chloride to the DMD solution, and the reac-



Fig. 1. Relative yield of molecular singlet oxygen versus the dimethyldioxirane concentration at $[Cl^-]_0 = (1)$ 2.5 × 10⁻⁴ and (*I'*) 5.0 × 10⁻⁵ mol/l in acetone at 278 K and (2) versus the chloride ion concentration at $[DMD]_0 = 6.0 \times 10^{-3}$ mol/l in acetone at 288 K.



Fig. 2. Typical decay kinetics of IRCL from ${}^{1}O_{2}$ forming in the reaction between DMD and the chloride ion and its semilogarithmic anamorphosis ([DMD]₀ = 6.0×10^{-3} mol/l, [Cl⁻]₀ = 6.5×10^{-4} mol/l, acetone, 283 K).

tion time varies between a few seconds and ~10 min, depending on the initial concentrations of the reactants. The chloride ion induces efficient catalytic decomposition of DMD accompanied by singlet oxygen generation and IR light emission [17–19]. Note that it is the chloride ion that is responsible for the rapid decomposition of DMD, because the replacement of the quaternary ammonium cation n-Bu₄N⁺ with Na⁺ (in the decomposition of dioxirane in aqueous acetone in the presence of sodium chloride) leads to similar results.

The ${}^{1}O_{2}$ yield in the reaction of DMD with Cl⁻ in acetone ([DMD]₀ = 2 × 10⁻³ mol/l, [*n*-Bu₄NCl]₀ = 2 ×

 10^{-4} mol/l, 298 K) determined using the decomposition of 1,4-dimethylnaphthalene endoperoxide as the standard was $61 \pm 10\%$.

Searching for conditions favorable for ¹O₂ generation in the DMD-Cl⁻ system in acetone, we discovered that the ${}^{1}O_{2}$ yield depends on the proportions of the reactants. Indeed, as can be seen from Fig. 1, the ratio of the light sum (S) to the DMD concentration, i.e., the value proportional to the yield of singlet oxygen, remains unchanged at concentration ratios of $[DMD]_0$: $[Cl^-]_0 = 10-30$ and decreases with an increasing peroxide concentration in the reaction solution when the initial DMD concentration exceeds the chloride ion concentration by a factor greater than 50–100. A similar regularity is observed as the chloride ion concentration is varied (Fig. 1): the yield of singlet oxygen remains unchanged at comparatively low $[DMD]_0$: $[Cl^-]_0$ ratios, and a decrease in the catalyst concentration to $1-2 \mod \%$ results in a considerable decrease in the ratio of S to the peroxide concentration in the solution, i.e., in a decrease in the singlet oxygen generation efficiency.

The regularities of chemiluminescence revealed in the DMD–Cl[–] system suggest the existence of a side reaction pathway yielding no ${}^{1}O_{2}$. The larger the excess of dioxirane in the reaction mixture, the stronger the influence of the "dark" reaction on the chlorideinduced decomposition of peroxide.

Kinetics of the Reaction

Evidently, the chemiluminescence intensity is proportional to the rate of DMD decomposition (*w*) induced by the chloride anion. Based on the results of experimental [18, 19] and theoretical [20] studies, we assumed that the reaction proceeds via a catalytic mechanism according to which the variation of the CL intensity during the reaction is described by the reaction

$$I_{\rm CL} = \varphi_{\rm CL} w = \varphi_{\rm CL} k [\rm Cl^-] [\rm DMD], \qquad (1)$$

where φ_{CL} is the quantum yield of CL and k is the rate constant of the catalytic process. Since the concentration of the catalyst is assumed to be constant, the CL intensity should be directly proportional to the current concentration of DMD and Eq. (1) is formally a pseudo-first-order kinetic equation. Therefore, the linearization of the kinetic curves in semilogarithmic coordinates ($\ln I_{CL}-t$) will make it possible to determine the apparent rate constant from the slope ratio of the anamorphosis of a kinetic curve. The apparent rate constant k_{app} is equal to the product of the rate constant of the catalytic process and the initial (current) chloride ion concentration.

Indeed, at a 10- to 30-fold excess of peroxide over the catalyst, the decomposition of DMD in acetone solution induced by chloride anions is a first-order reaction with respect to the DMD concentration throughout the temperature range examined (Fig. 2).



Fig. 3. Typical plots of the apparent rate constant versus The chloride ion concentration at (1) 287.5 and (2) 292 K ($[DMD]_0 = 6.0 \times 10^{-3} \text{ mol/l}$, acetone).



Fig. 4. Decay kinetics of IRCL from ${}^{1}O_{2}$ forming in the reaction between DMD and the chloride ion and its semilogarithmic anamorphosis ([DMD]₀ = 3.0×10^{-2} mol/l, [Cl⁻]₀ = 2.2×10^{-4} mol/l, acetone, 278 K).

In addition, under these conditions, k_{app} depends linearly on the chloride ion concentration (Fig. 3). At the same time, there is experimental evidence that the process examined is more complicated than was initially assumed. Firstly, the straight line representing the dependence of the apparent rate constant on the chloride ion concentration intercepts a short segment on the abscissa axis. This segment is reproduced from one run to another and depends on temperature in a systematic way. The abscissa intercept corresponding to a certain concentration of the chloride ion was interpreted as a measure of the irreversible loss of part of the catalyst in some noncatalytic side process. Secondly, a seemingly paradoxical result was observed for

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the variation of the initial DMD concentration: an increase in the reactant concentration resulted in a noticeable increase in the reaction time (from a few seconds to several minutes), i.e., in a decrease in the apparent rate constant of DMD consumption. However, this experimental observation will not be in conflict with the expected kinetics (Eq. (1)) if the catalyst concentration [Cl⁻] decreases during the process and. Therefore, it can serve as further indirect evidence of the occurrence of a parallel side reaction leading to the irreversible consumption of chloride ions. Moreover, it turned out that, when the reaction is carried out with a >50-fold excess of dioxirane over the chloride ion



Fig. 5. Optical absorption spectrum of the products of the reaction between DMD and the chloride ion (solid line) recorded immediately after mixing the reactants ($[n-Bu_4NCl]_0 = 2.0 \times 10^{-2} \text{ mol/l}$, $[CF_3COOH]_0 = 0.3 \text{ mol/l}$, $[DMD]_0 = 4.5 \times 10^{-2} \text{ mol/l}$, CCl_4 , 295 K) and (for comparison) the spectrum of Cl_2 in CCl_4 [30] (dashed line).

concentration, the IRCL decay does not obey Eq. (2) but follows a different kinetic law (cf. Figs. 2 and 4).

Thus, although ${}^{1}O_{2}$ formation is the dominant process in the reaction of dioxirane with the chloride ion, it is apparently not the only pathway. Note that the kinetic measurements confirm and supplement the results of the studies of the ratio of the IRCL light sum

 Table 1. Ionization potentials of the anions serving as potent catalysts for dioxirane decomposition

	IP, eV		
Compound	experiment [43, 44]	calculation by the G3MP2B3 method	
DMD*	_	1.87	
TFD*	—	2.74	
Cl ⁻	3.62	3.69	
ClO-	2.28	2.32	
Cl_2^-	2.4 ± 0.1**	2.45	
ClO(CH ₃) ₂ CO ⁻	_	2.77	
ClO(CH ₃)(CF ₃)CO ⁻	—	3.60	

Notes: * The values of electron affinity (EA) are given for the dioxiranes.

** Average of 8 measurements.

to the peroxide concentration (Fig. 1), according to which the contribution from the noncatalytic process is pronounced at reactant concentration ratios of $[DMD]_0: [Cl^-]_0 > 50$. The contribution from the non-catalytic process decreases the yield of singlet molecular oxygen and changes the kinetic order of the overall process.

Nature of the "Dark" Reaction Pathway

When analyzing the possibility of a noncatalytic reaction occurring in the system, we based on the fact that, firstly, DMD is a very strong oxidizer and, secondly, the anions involved in the formation of ${}^{1}O_{2}$ (Scheme 1), which oxidized species, are often prone to reduction reactions accompanied by electron transfer. For this reason, we assumed that the side pathway that does not lead to the formation of ${}^{1}O_{2}$ ("dark" reaction) is the oxidation of chlorine-containing anions with dioxirane into catalytically inactive species, such as Cl₂.

Actually, the reactions forming the basis of the known methods of analysis of organic peroxides, namely, iodometry and bromometry, are similar to the hypothesized "dark" reaction of DMD. Chlorine is a stronger oxidizer and is less prone to redox reactions of this type, and this accounts for the minor role of the side pathway of the reaction. Therefore, to prove our assumption, it is necessary to establish conditions favorable for the electron-transfer process and molecular chlorine formation. That is why the reaction of DMD with the chloride ion was carried out in carbon tetrachloride (to prevent possible reactions of radical species with the C–H bonds of the solvent) in the presence of trifluoroacetic acid (to increase the redox potential of dioxirane). We found earlier [18, 19] for

DMD decomposition under the action of the bromine ion that addition of an acid markedly suppresses the catalytic pathway of the reaction. The reaction of DMD with *n*-Bu₄NCl in an acidic medium is indeed accompanied by the appearance of the characteristic odor of chlorine and by the formation of Cl_2 molecules (identified by spectrophotometry) in less than 10 s (Fig. 5).

According to Scheme 1, DMD decomposition is catalyzed by the chloride ion and by its oxidized species, namely, the 2-chlorooxy-2-hydroxy propane alcoholate. To see which of these anionic species is responsible for the electron transfer process, we calculated the electron affinities (EA) of DMD and TFD and the ionization potentials (IP) of the corresponding anions in the gas phase (Table 1).

It can be seen from Table 1 that the method used in the calculation (G3MP2B3) reproduces the experimental values of IP of the anions Cl^{-} , Cl_{2}^{-} , and ClO^{-} with a high accuracy, indicating the reliability of the estimates of the electron affinity of the dioxiranes DMD and TFD and the ionization potentials of the anionic intermediates $ClO(CH_3)(R)CO^-$, where R = CH_3 or CF_3 . It is most likely that, in the process studied, the reducing agent is the oxidized form of the catalyst, namely, the 2-chlorooxy-2-hydroxy propane alcoholate. To take into account the solvating effect of acetone, the solvation energies of the participants of the one-electron transfer were calculated by the polarization continuum method [32–34]. The solvation correction was determined in the B3LYP/6-311+G(d,p)approximation. Indeed, the interaction of 2-chloroxvisopropoxide with DMD is the most favorable process in acetone:

ClO(CH₃)₂CO⁻ + DMD
$$\rightarrow$$
 electron transfer,
 $\Delta G = 62.5 \text{ kJ/mol};$
Cl⁻ + DMD \rightarrow electron transfer,
 $\Delta G = 214 \text{ kJ/mol}.$

Thus, the transfer of one electron from the 2-chlorooxy-2-hydroxy propane alcoholate to the dioxirane requires much less energy than the oxidation of the free Cl⁻ anion. At the same time, electron transfer from 2-chlorooxy-2-hydroxy propane alcoholate to the dioxirane is characterized by a positive Gibbs energy; i.e., the efficiency of the "dark" process should be low as compared to that of the catalytic process. This is in agreement with the experimentally observed regularities of the process examined. We did not study the subsequent fate of the reduced, inactive form of the catalyst (presumably, atomic chlorine). It can be assumed that Cl⁻ abstracts an H atom from the solvent molecule or recombines with a chloride anion. The latter reaction is exothermic (± 125 kJ/mol) and occurs in aqueous solution with a diffusion rate constant of $k_{\rm d} = (7.8 \pm 0.8) \times$ 10^9 L mol⁻¹ s⁻¹ [45]. The resulting radical anion has a comparatively low IP (Table 1) and can transfer the excess electron to the dioxirane molecule, thus completing the redox process and leading to the experimentally observed evolution of molecular chlorine. We cannot exclude the formation, under our experimental conditions, of catalytically inactive compounds with a covalently bonded chlorine atom.

It was assumed previously that the hypochlorite ion can be the oxidized form of the catalyst continuing the catalytic chain of DMD decomposition [18, 19]. However, this is unlikely because of the low ionization potential of ClO⁻ (2.32 eV, see Table 1), since otherwise the one-electron transfer would be efficient at least in the reaction with TFD (2.77 eV, see Table 1). This would be inconsistent with experimental facts: the catalytic decomposition of TFD induced by small amounts of chloride ions occurs at a high rate and with a high yield of singlet oxygen [19]. Thus, the results of the study of the structure carrying the catalytic chain indirectly confirm the validity of the catalytic dioxirane decomposition mechanism in which the $ClO(CH_3)(R)CO^{-}$ anion continues the catalytic chain [20, 21].

Thus, the interaction of the 2-chlorooxy-2hydroxy propane alcoholate with DMD proceeds via two competing pathways (Scheme 2). The first of them (a) generates ${}^{1}O_{2}$, whereas the second one (b) yields an inactive chlorine species (for example, Cl₂) and is a combination of reactions initiated by electron transfer from the catalyst to the dioxirane.



As the DMD concentration is raised, an increasing amount of the chloride anion is oxidized into inactive species. Since the catalytic process is not stoichiometric (i.e., several DMD molecules decompose on one Cl^- anion), even a slight decrease in the chloride ion concentration should decrease the rate of catalytic dioxirane decomposition yielding 1O_2 and, accordingly, the IRCL decay rate.

Kinetic Analysis of the Reaction between DMD and the Chloride Ion

Based on the results of the study of catalytic ${}^{1}O_{2}$ generation [20] and the above-described "dark" chloride ion oxidation leading to catalyst the withdrawal from the system, we proposed the following scheme of the reaction between DMD and the chloride ion:



Reactions (I) and (II) belong to the catalytic pathway of the process, and the electron-transfer reaction (III), which occurs simultaneously with reaction (II), initiates the chain of transformations leading to the irreversible consumption of the Cl⁻ catalyst. The catalytic exothermic reaction (II), which yields ${}^{1}O_{2}$, is dominant [20]. However, endothermic electron transfer (III), which makes a small contribution to the overall reaction (see Table 1), occurs in parallel. One of the products of this interaction (DMD radical anion) is likely consumed in its reaction with the solvent. Another product of redox reaction (III) (2-chloroxyisopropyl radical) converts the catalyst into its inactive form. We did not study this process but formally represented it as steps (IV)–(VI).

The following assumptions were made in the kinetic analysis of the reaction scheme. Firstly, reaction (III) is accepted to be the rate-determining step of the redox process. Secondly, it is assumed that the rad-

ical anion resulting from the reaction of DMD with the oxidized form of the catalyst (reaction (III)) and with the radical anion Cl_2^- (reaction (VI)) is rapidly and irreversibly consumed without ${}^{1}O_2$ formation (for example, via solvent oxidation). Thirdly, the 2-chlorooxy-2-hydroxy propane alcoholate concentration is considered to be approximately quasi-stationary.

For the above reaction scheme, it is easy to set up a system of differential equations describing the joint consumption of the reactants:

$$-\frac{d[DMD]}{dt} = \frac{k_1(2k_2 + 3k_3)[DMD][C1]}{(k_2 + k_3)},$$
 (2)

$$-\frac{d[C1^{-}]}{dt} = \frac{2k_1k_3[DMD][C1^{-}]}{(k_2 + k_3)}.$$
 (3)

The ratio of Eqs. (2) and (3) leads to the following expression relating the current concentrations of the reactants:

$$[Cl^{-}] = [Cl^{-}]_{0} + \gamma([DMD] - [DMD]_{0}), \qquad (4)$$

where $\gamma = \frac{2k_3}{2k_2 + 3k_3} \approx \frac{k_3}{k_2}$ is the quantity characterizing the ratio of the contributions from reactions (II) and (III). The physical meaning of this quantity can also be interpreted as an indicator of catalyst resistance to poisoning in side processes. Evidently, for an ideal catalyst $\gamma = 0$. By substituting Eq. (4) into Eq. (2), one can exclude the chloride ion concentration from this equation. Taking into account that $k_2 \gg k_3$, we obtain

$$-\frac{d[DMD]}{dt}$$

$$= 2k_1([Cl^-]_0 - \gamma[DMD]_0)[DMD] + 2k_1\gamma[DMD]^2.$$
(5)

Thus, for the above scheme of the process with the above assumptions taken into account, the order of the reaction with respect to the DMD concentration can vary from 1 to 2, depending on the reaction conditions. This conclusion is consistent with the kinetics of the process studied by the IRCL method (see above). The analytical solution of Eq. (5) for the DMD concentration takes the form

$$\frac{1}{k_{\rm I}} \ln \frac{[\rm DMD]_0(k_{\rm I} + k_{\rm II}[\rm DMD])}{[\rm DMD](k_{\rm I} + k_{\rm II}[\rm DMD]_0)} = t, \tag{6}$$

where $k_{\rm I}$ and $k_{\rm II}$ are the apparent first- and secondorder rate constants, respectively. The physical meaning of these constants is defined by the equations

$$k_1 = 2k_1([Cl^-]_0 - \gamma[DMD]_0),$$
 (7)

$$k_{\rm II} = 2k_1\gamma. \tag{8}$$

A relationship between the current DMD concentration and $I_{\rm CL}$ should be established for quantitative description of the experimental curves of IRCL intensity decay with time. According to Eq. (1), $I_{\rm CL}$ is proportional to the rate of the catalytic process and, at the initial point in time, is

$$I_0 = \varphi_{\rm CL} 2k_1 [\rm DMD]_0 [\rm Cl^-]_0.$$
(9)

The coefficient 2 reflects the stoichiometry of DMD consumption and singlet oxygen accumulation. Taking into account the change in the concentration $[Cl^-]$ during the process (Eq. (4)), we can state that the IRCL intensity is related to the DMD concentration by the nonlinear equation

$$I_{\rm CL} = \varphi(2k_1([{\rm Cl}^-]_0 - \gamma[{\rm DMD}]_0)[{\rm DMD}] + 2k_1\gamma[{\rm DMD}]^2).$$
(10)

Thus, the normalized IRCL intensity is related to the current DMD concentration in a complicated way:

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Fig. 6. Decay kinetics of IRCL from ${}^{1}O_{2}$ forming in the reaction between DMD and the chloride ion: (*I*) [DMD]₀ = 6.0×10^{-3} mol/1, [Cl⁻]₀ = 4.8×10^{-4} mol/1, concentration ratio of 12.6, acetone, 288 K; (*2*) [DMD]₀ = 6.0×10^{-3} mol/1, [Cl⁻]₀ = 6.8×10^{-5} mol/1, concentration ratio of 88.5, acetone, 303 K. The solid line is the fit to Eq. (12).



Fig. 7. Temperature dependence of the rate constant $2k_1$ and rate constant ratio $k_2/k_3 = 1/\gamma$ in chloride-induced DMD decomposition $([n-Bu_4NCl]_0 = (0.5-8.0) \times 10^{-4} \text{ mol/l}, [DMD]_0 = 6.0 \times 10^{-3} \text{ mol/l}, \text{ acetone}).$

$$\frac{I_{\rm CL}}{I_0} = \frac{[\rm DMD]}{[\rm DMD]_0} - \gamma \frac{[\rm DMD]}{[\rm C1^-]_0} + \gamma \frac{[\rm DMD]^2}{[\rm DMD]_0[\rm C1^-]_0}.$$
 (11)

Solving the quadratic equation (11) for the DMD concentration and substituting the resulting equation into Eq. (7), we finally obtain

 $2k_1 \times 10^{-2}$, L mol⁻¹ s⁻¹ $[(n-Bu)_4NCl]_0 \times 10^4$, mol/l Т, К $\gamma \times 10^2$ 283 1.0 1.37 ± 0.05 1.0 1.02 ± 0.03 1.2 0.89 ± 0.02 1.2 1.16 ± 0.05 2.0 4.01 ± 0.06 _ 3.2 4.50 ± 0.04 4.15 ± 0.05 3.2 4.8 4.34 ± 0.02 6.5 3.77 ± 0.01 _ 8.0 4.11 ± 0.02 _ $\textbf{4.2} \pm \textbf{0.3}$ 1.1 ± 0.2 288 1.0 1.40 ± 0.03 1.12 ± 0.01 1.0 _ 1.2 1.44 ± 0.01 _ 1.65 ± 0.03 2.0 5.96 ± 0.05 2.0 6.12 ± 0.05 _ 3.2 4.55 ± 0.02 _ 4.8 5.31 ± 0.01 _ 4.8 4.83 ± 0.01 6.5 4.94 ± 0.01 _ 6.5 4.62 ± 0.01 _ 5.2 ± 0.6 1.4 ± 0.2 292 1.1 2.03 ± 0.02 1.3 5.06 ± 0.01 _ 1.8 6.58 ± 0.03 1.68 ± 0.02 1.29 ± 0.01 1.8 5.02 ± 0.01 2.0 5.38 ± 0.07 2.5 5.20 ± 0.07 _ 2.5 2.19 ± 0.02 _ 3.4 5.73 ± 0.01 _ 3.4 6.54 ± 0.02 1.47 ± 0.02 4.7 6.27 ± 0.01 _ 4.7 6.04 ± 0.01 _ $\textbf{5.8} \pm \textbf{0.6}$ 1.7 ± 0.4 9.09 ± 0.03 297 1.2 1.13 ± 0.01 1.5 10.5 ± 0.1 1.15 ± 0.01 11.9 ± 0.1 1.5 1.33 ± 0.01 2.2 10.9 ± 0.1 2.43 ± 0.01 2.7 7.74 ± 0.02 _ 2.7 9.57 ± 0.08 _ 8.97 ± 0.05 1.92 ± 0.03 3.3 4.0 9.84 ± 0.07 4.0 8.64 ± 0.02 _ 4.9 10.1 ± 0.1 2.0 ± 0.1 4.9 1.4 ± 0.1 10.3 ± 0.1 6.0 8.92 ± 0.07 _

Table 2. Second-order rate constants of the reaction between DMD and the chloride ion $(2k_1)$ and the rate constant ratio $k_3/k_2(\gamma)$ at various temperatures

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 1.6 ± 0.5

9 ± 2

 Table 2. (Contd.)

Т, К	$[(n-\mathrm{Bu})_4\mathrm{NCl}]_0 \times 10^4, \mathrm{mol/l}$	$2k_1 \times 10^{-2}$, L mol ⁻¹ s ⁻¹	$\gamma imes 10^2$
303	0.7	—	1.10 ± 0.1
	0.9	_	1.07 ± 0.01
	1.2	_	1.39 ± 0.02
	1.6	14.5 ± 0.1	0.93 ± 0.02
	2.1	12.9 ± 0.1	_
	2.1	16.0 ± 0.2	1.11 ± 0.05
	2.9	14.4 ± 0.1	_
	3.8	13.9 ± 0.1	_
	3.8	14.5 ± 0.1	_
	5.1	13.5 ± 0.1	_
	5.1	12.8 ± 0.1	_
		14 ± 1	$\textbf{1.2}\pm\textbf{0.2}$
307	1.3	24.0 ± 0.2	1.93 ± 0.04
	1.3	23.9 ± 0.1	1.31 ± 0.01
	2.0	19.7 ± 0.1	_
	2.0	21.0 ± 0.2	1.18 ± 0.03
	2.0	21.7 ± 0.2	1.70 ± 0.03
	2.0	_	1.27 ± 0.06
	3.3	_	1.90 ± 0.1
	3.3	20.6 ± 0.1	_
		22 ± 2	$\textbf{1.5}\pm\textbf{0.3}$
316	0.9	_	1.26 ± 0.03
	0.9	28.2 ± 0.2	1.26 ± 0.02
	3.8	25.9 ± 0.1	_
		27 ± 2	$\textbf{1.26} \pm \textbf{0.04}$

Note: Reaction conditions: acetone as the solvent; $[DMD]_0 = 6.0 \times 10^{-3} \text{ mol/l}$. Dashes mean that, in this case, the kinetic curve is low-sensitive to variation of the rate constant or the ratio of constants. The correlation factor of nonlinear approximation is at least 0.994 (the typical value is 0.999).

$$\frac{1}{2k_{1}([Cl^{-}]_{0} - \gamma[DMD]_{0})} \ln \frac{4\gamma^{2} \frac{I_{CL}}{I_{0}} [DMD]_{0}^{2}}{\left(\sqrt{([Cl^{-}]_{0} - \gamma[DMD]_{0})^{2} + 4\gamma \frac{I_{CL}}{I_{0}} [Cl^{-}]_{0} [DMD]_{0}} - ([Cl^{-}]_{0} - \gamma[DMD]_{0})\right)^{2}} = t.$$
(12)

Equation (12) accounts for the observed variable reaction order. In the limiting case of the absence of the irreversible consumption of the catalyst in the side process, Eq. (12) reduces to a first-order kinetic equation with the apparent rate constant equal to $2k_1[Cl^-]_0$. Indeed, using the Lopital–Bernoulli rule, it can readily be shown that the limit of the ratio in the logarithmic term tends to I_{CL}/I_0 at $\gamma \rightarrow 0$.

The second-order rate constant $2k_1$ and the rate constant ratio γ were determined by nonlinear regression analysis, approximating the observed dependence of I_{CL} on t (Table 2). The initial intensity I_0 was optimized along with these kinetic constants. This was necessary for adequate description of the kinetic curves, because a certain time (~1 s; see Experimental) is required for the CL intensity to reach its maximum. This time is due to mixing of the reactants and instru-

ne (~1 s; see Experimental) for A_1 of the catalytic d nsity to reach its maximum. chloride ion were de of the reactants and instru- dependence of the rate

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mental factors, and the reactants are partially consumed during this period. The results of regression analysis indicate that the observed maximum CL intensity is underestimated to an extent of 10-20%. Equation (12) describes, with a high correlation factor, the dependence of the IRCL intensity on the reaction time under various experimental conditions (temperature, ratio of the initial concentrations of the reactants), indicating that the generalized scheme proposed for the interaction of DMD with the chloride ion is valid (Scheme 3). The experimental curves and approximations obtained using Eq. (12) are shown in Fig. 6 by way of example.

The activation energy E_{lact} and preexponential factor A_1 of the catalytic decomposition of DMD by the chloride ion were derived from the temperature dependence of the rate constant $2k_1$ (Table 2, Fig. 7):

 $E_{\text{lact}} = 46 \pm 4 \text{ kJ/mol}, \log A_1 = 11.1 \pm 0.7 \text{ [L mol^{-1} s^{-1}]}.$ The value of the preexponential factor is typical of bimolecular reactions in the liquid phase. A comparison between the apparent activation energy and the strength of the peroxide bond in DMD for its homolytic cleavage (95 kJ/mol [46]) demonstrates that the chloride ion acts as a catalyst, i.e., a component of the system lowering the energy barrier for the reaction examined.

Note that the low activation energy of the catalytic process is fairly consistent with the theoretical value obtained by quantum chemical calculations [20], according to which $\Delta H^{\neq} = 17$ kJ/mol. In view of the difficulty of taking into account the solvation of the reactants, especially for anionic intermediates, the agreement between the theory and the experiment is satisfactory.

Correlation between the Catalytic and "Dark" Pathways of the Reaction

The results of the kinetic analysis along with the chemiluminescence and theoretical estimates confirm the conclusion about the minor contribution of the side "dark" pathway (reaction (III)) to the total rate of disappearance of the 2-chloroxyisopropyl anionic intermediate. In the temperature range examined, the rate constant ratio $\gamma = k_3/k_2$ (Table 2, Fig. 7) is almost temperature-independent, being 0.014 ± 0.003; i.e., the proportion of the "dark" pathway does not exceed 1.5%.

In spite of the small value of γ , the instant reduced rate of the process, $w/[DMD] = 2k_1[Cl^-]$, determined by the slope ratio of the plot of $\ln(I_{CL}/I_0)$ versus *t* (Fig. 4) at a considerable excess of the dioxirane over the catalyst, decreases substantially in the experiment. This fact is seemingly in conflict with kinetic conceptions, but it allows a simple explanation in the framework of the above kinetic model. Equation (4) describes the stoichiometry of reactant disappearance, which is determined by the value of γ . From this equation, one can readily derive the dependence of the chloride ion conversion $\xi = ([Cl^-]_0 - [Cl^-])/[Cl^-]_0$ on the DMD conversion. Let us estimate the value of ξ at 90% dioxirane conversion:

$$\xi = \frac{0.9\gamma [DMD]_0}{[C1^-]_0}.$$
 (13)

At a 50-fold excess of DMD over the chloride ions, $\xi = 63\%$; i.e., nearly two thirds of the catalyst is irreversibly consumed in the redox process. Therefore, during the reaction the apparent rate constant of catalytic decomposition, $k_{app} = 2k_1[Cl^-]$, decreases almost by a factor of 3, thus inducing a considerable decrease in the DMD consumption rate. According to Eq. (13), at $[DMD]_0$: $[Cl^-]_0 \le 10$ the chloride ion conversion does not exceed 13%. In this case, the introduced perturbation exerts almost no effect on the reaction order with respect to the DMD concentration, which remains to be unity, but it causes the k_{app} versus $[Cl^-]_0$ straight line to intercept some segment on the concentration axis (Fig. 3). At a 50–100-fold excess of DMD over the catalyst, the Cl⁻ concentration decreases considerably during the process and, as a result, DMD consumption obeys a complicated kinetic law.

Thus, the reaction scheme (I)–(VI) accounts for the basic regularities observed for DMD decomposition in the presence of chloride ions. The reaction proceeds via two pathways, namely, the catalytic decomposition of the peroxide yielding singlet oxygen (major pathway) and the oxidation of the chloride ion resulting in its withdrawal from the catalytic cycle (minor pathway).

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