Yields of Excited Triplet Products Generated from the Air Oxidation of 3-Methyl-2-butanone and Isopropyl Phenyl Ketone in a Dimethyl Sulfoxide Solution Containing Potassium *t*-Butoxide

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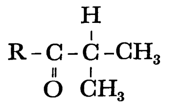
An attempt has been made to evolve the kinetic scheme in order to evaluate the yields (ϕ^*_{react}) of excited triplet products generated from the air oxidation of 3-methyl-2-butanone (**1**) and isopropyl phenyl ketone (**2**). Expressions for the total light emission and quantum yield of the indirect chemiluminescence (CL) can be derived, from which the rates of energy transfer from excited triplet products to singlet 9,10-dibromoanthracene (DBA), k_{TS}, and ϕ^*_{react} were determined on the basis of the CL intensity measured for various DBA concentrations. The values of k_{TS} from **1** and **2** (4×10^8 and 1×10^9 l mol^{-1} s^{-1}) are in fair agreement with the values proposed by several investigators who measured the indirect CL from the thermal cleavage of 1,2-dioxetanes. The markedly small ϕ^*_{react} values (1×10^{-5} and 1×10^{-3}) result from the fact that the CL arises from a minor reaction.

In previous studies,[1)] Kamiya and Sugimoto have found that many simple ketones exhibit indirect chemiluminescence (CL) by air oxidation in alkaline aprotic solvents containing 9,10-diphenylanthracene (DPA) or 9,10-dibromoanthracene (DBA), and that the intensity for solvents containing DBA was markedly higher than for those containing DPA, in spite of the much higher fluorescence efficiency of DPA. The results indicate that excited species, mainly in the triplet state, are produced during the oxidation of the ketones, since DBA is more efficient at converting the energy of the excited triplet species into singlet energy than is DPA due to the heavy-atom effect.[2)] Further, they observed that the CL intensity was dramatically affected by the class of C–H bonds adjacent to the carbonyl group; generally, the intensity increased in the order, primary <secondary< tertiary. The results suggest that the CL efficiency depends upon the tendency to loose a proton from the C–H bond. This argument was supported by evidence that the ordinary carboxylic acids, having a C–H bond adjacent to the carboxyl group, are very weakly acidic and exhibit neither direct nor indirect CL. However, such keto acids as β-benzoylpropionic and β-phenylpyruvic acids exhibit emission.

Summarizing their results, they concluded that excited products, predominantly in the triplet rather than in the singlet state, were surely generated during air oxidation of those compounds having a –CO–CH– group *via* dioxetane intermediates. These intermediates were generated by oxygenation of the anion of the compounds formed *via* the loss of a proton from the α-carbon atom.

The overall reaction in systems of several ketones is very complicated, since the molar ratios of the absorbed oxygen to the reactants were found to be greater than 2 and the spent reaction solutions were dark orange or red owing to other competitive and/or sequential reactions. However, two ketones, 3-methyl-2-butanone (**1**) and isopropyl phenyl ketone (**2**), which possess a tertiary C–H bond adjacent to the carbonyl group and exhibited relatively intense emission, showed rather simple reaction characteristics: an equimolar amount of oxygen was absorbed, and acetone and acetic acid, and acetone and benzoic acid were produced as main products from **1** and **2**, respectively. No color change was observed in the spent reaction solutions under the experimental conditions employed in this study. (See experimental section.)



$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}\overset{H}{\underset{CH_3}{C}}{-}CH_3}$$

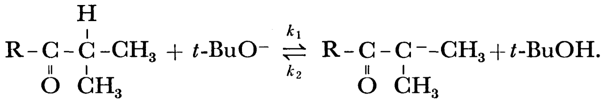
1: $R=CH_3$
2: $R=C_6H_5$

In the present study, an attempt has been made to evolve the kinetic scheme for indirect CL with DBA in order to evaluate the yields of the excited triplet products generated from **1** and **2**.

Results and Discussion

From the results described above, the following kinetic scheme appears plausible for indirect CL.

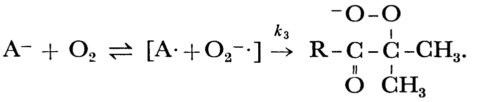
The ketones (AH) transfer their proton to the *t*-butoxide ion (*t*-BuO$^-$) when a potassium *t*-butoxide (*t*-BuOK) solution in *t*-butyl alcohol (*t*-BuOH) is added to solutions of **1** and **2**:



$$\underset{\text{(AH)}}{\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}\overset{H}{\underset{CH_3}{C}}{-}CH_3}} + t\text{-BuO}^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} \underset{\text{(A}^-\text{)}}{\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}\underset{CH_3}{C^-}{-}CH_3}} + t\text{-BuOH}.$$

(AH) (A$^-$)

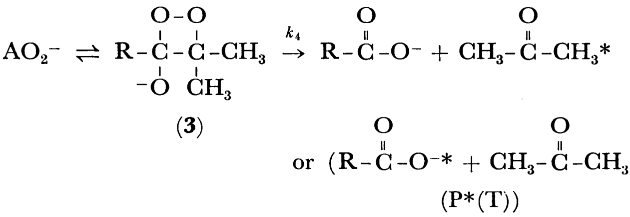
A possible mechanism for the reaction of A$^-$ with oxygen would be oxygenation *via* a *radical pair*:[3)]



$$\mathrm{A^- + O_2 \rightleftarrows [A\cdot + O_2^-\cdot] \xrightarrow{k_3} R{-}\underset{\underset{O}{\|}}{C}{-}\overset{^-O{-}O}{\underset{CH_3}{C}}{-}CH_3}.$$

(AO$_2^-$)

Of the decomposition processes of the hydroperoxy ketone anion (AO$_2^-$), one is cleavage *via* a dioxetane intermediate (**3**) generating two products, one in the excited state (mainly in the triplet state, P*(T)) and the other in the ground state;[4)]



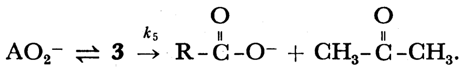
$$\mathrm{AO_2^- \rightleftarrows R{-}\overset{O{-}}{\underset{^-O}{C}}{-}\overset{O}{\underset{CH_3}{C}}{-}CH_3 \xrightarrow{k_4} R{-}\overset{O}{\overset{\|}{C}}{-}O^- + CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3{}^*}$$

(**3**)

$$\text{or } \mathrm{(R{-}\overset{O}{\overset{\|}{C}}{-}O^{-*} + CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3)},$$

(P*(T))

or, both in the ground state,



$$AO_2^- \rightleftharpoons \mathbf{3} \xrightarrow{k_5} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^- + CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3.$$

Other AO_2^- cleavage processes *via* acyclic intermediates[5] will compete with cleavage *via* the dioxetane intermediate. Let us write all the reactions together in the following scheme:

$$AO_2^- \rightleftharpoons AO_2H \rightarrow \text{(acyclic intermediate)} \xrightarrow{k_6} \text{products.}$$

In the presence of DBA, the following steps will occur:
triplet-singlet energy transfer from P*(T) to DBA,

$$P^*(T) + DBA \xrightarrow{k_{TS}} P + DBA^*(S),$$

triplet-triplet energy transfer form P*(T) to DBA,

$$P^*(T) + DBA \xrightarrow{k_{TT}} P + DBA^*(T)$$

(where DBA*(S) and DBA*(T) are the excited singlet and triplet states of DBA, respectively),
radiationless deactivation of P*(T),

$$P^*(T) \xrightarrow{k_7} P,$$

quenching of P*(T) by oxygen,

$$P^*(T) + O_2 \xrightarrow{k_8} P + O_2^*(\Delta),$$

fluorescence emission from DBA*(S),

$$DBA^*(S) \xrightarrow{k_f} DBA + h\nu,$$

radiationless deactivation of DBA*(S),

$$DBA^*(S) \xrightarrow{k_9} DBA,$$

and intersystem crossing from DBA*(S) to DBA*(T),

$$DBA^*(S) \xrightarrow{k_{10}} DBA^*(T).$$

Since the emission intensity with DPA was much lower than that with DBA (DPA and DBA are often used as monitors for excited singlet and triplet products, respectively[6]), the step for generating excited singlet products is ignored. Moreover, triplet-triplet annihilation of DBA*(T), DBA*(T)+DBA*(T)→DBA*(S)+DBA, is not taken into account, because the process has been reported to occur with low probability.[7]

According to the above scheme, the intensity of the indirect CL emission (I_{CL}) is given by:

$$I_{CL} = k_f[DBA^*(S)].$$

Using the steady-state approximation for which $d[P^*(T)]/dt=0$ and $d[DBA^*(S)]/dt=0$, I_{CL} can be written as

$$I_{CL} = \frac{k_4 k_{TS}\phi_f[DBA][AO_2^-]}{\{(k_{TS}+k_{TT})[DBA]+k_7+k_8[O_2]\}}, \qquad (1)$$

where ϕ_f is the fluorescenec efficiency of DBA and is given by

$$\phi_f = k_f/(k_f+k_9+k_{10}).$$

If $[O_2]$ and [DBA] are maintained constant during the air oxidation, the total light emission is given by:

$$\int I_{CL}dt = \frac{k_4 k_{TS}\phi_f[DBA]}{\{(k_{TS}+k_{TT})[DBA]+k_7+k_8[O_2]\}]} \times \int [AO_2^-]dt. \qquad (2)$$

Furthermore, from the scheme we can write

$$-d[AH]/dt = k_1[AH][t\text{-BuO}^-] - k_2[A^-][t\text{-BuOH}], \qquad (3)$$

$$d[A^-]/dt = k_1[AH][t\text{-BuO}^-] - k_2[A^-][t\text{-BuOH}] - k_3[A^-][O_2], \qquad (4)$$

and

$$d[AO_2^-]/dt = k_3[A^-][O_2] - (k_4+k_5+k_6)[AO_2^-], \qquad (5)$$

thence,

$$-\int d[AH] - \int d[A^-] - \int d[AO_2^-] = (k_4+k_5+k_6) \times \int [AO_2^-]dt = [AH]_0, \qquad (6)$$

since

$$\int d[A^-] = \int d[AO_2^-] = 0$$

and

$-\int d[AH] = [AH]_0$, where $[AH]_0$ is the initial ketone concentration.

Upon substituting Eq. 6 for Eq. 2, the total light emission is found to be:

$$\int I_{CL}dt = \frac{k_4 k_{TS}[DBA]\phi_f[AH]_0}{(k_4+k_5+k_6)\{(k_{TS}+k_{TT})[DBA]+k_7+k_8[O_2]\}}, \qquad (7)$$

The curves of the emission intensity *versus* time (*I-t* curves) for the indirect CL upon adding a solution of *t*-BuOK in *t*-BuOH to solutions of **1** and **2** of various concentrations in dimethyl sulfoxide (DMSO) containing DBA, are illustrated in Figs. 1 and 2, respectively. The results indicate that both the intensity and total light emission are proportional to the initial concentration of the ketone ($[AH]_0$) when $[AH]_0$ is comparably low.[8] The *I-t* curves obtained by adding *t*-BuOK solutions of different concentrations to solutions of **1** and **2** are illustrated in Figs. 3 and 4, respectively. The results indicate that the peak of the emission increases and that duration of the emission decreases with increasing *t*-BuOK concentration, while the total light emission remains almost constant provided that $[AH]_0$ is kept constant. Thus, it may be concluded that the

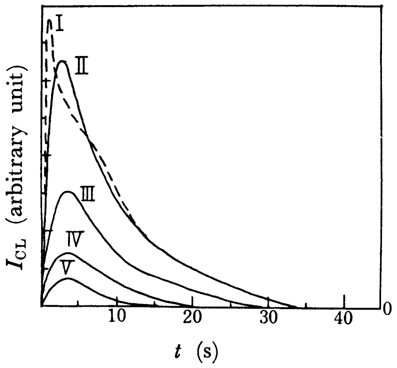


Fig. 1. Effect of the concentration of 3-methyl-2-butanone (**1**) on *I-t* curve of the indirect CL from **1** in a DMSO–*t*-BuOK/*t*-BuOH system containing DBA at 313 K. The initial concentration of **1** in 10^{-3} mol l^{-1}: I, 2.4; II, 1.2; III, 0.60; IV, 0.30; V, 0.15. The initial concentrations of *t*-BuOK and DBA are 3.0×10^{-3} and 5×10^{-4} mol l^{-1}, respectively.

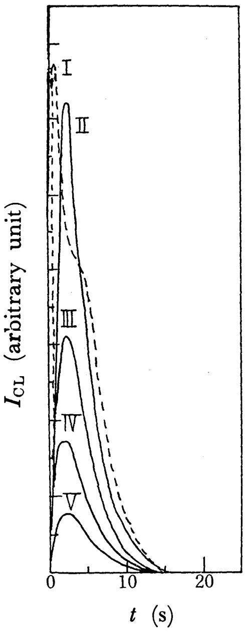


Fig. 2. Effect of the concentration of isopropyl phenyl ketone (**2**) on *I-t* curve of the indirect CL from **2** in a DMSO-*t*-BuOK/*t*-BuOH system containing DBA at 313 K. The initial concentration of **2** in 10^{-4} mol l^{-1}: I, 14; II, 7.0; III, 3.5; IV, 1.8; V, 0.9. The initial concentrations of *t*-BuOK and DBA are 3.0×10^{-3} and 5×10^{-4} mol l^{-1}, respectively.

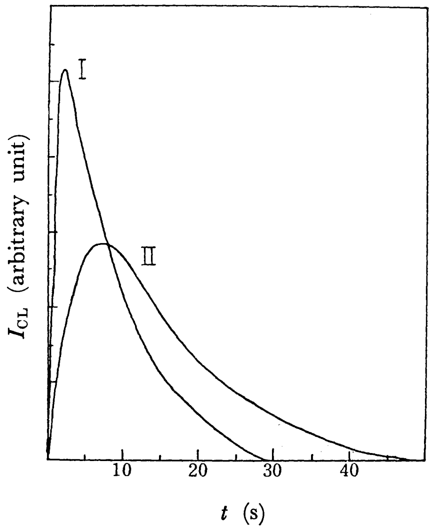


Fig. 3. Effect of the concentration of *t*-BuOK on *I-t* curve of the indirect CL from 3-methyl-2-butanone (**1**) in a DMSO-*t*-BuOK/*t*-BuOH system containing DBA at 313 K. The initial concentration of *t*-BuOK in 10^{-3} mol l^{-1}: I, 3.0; II, 0.75. The initial concentrations of **1** and DBA are 3.0×10^{-4} and 5×10^{-4} mol l^{-1}, respectively.

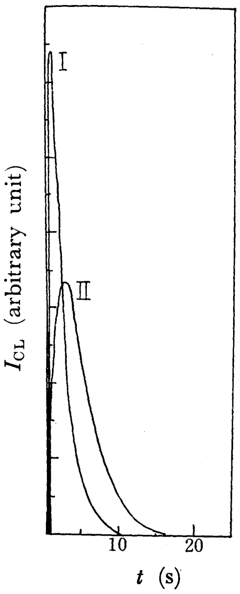


Fig. 4. Effect of the concentration of *t*-BuOK on *I-t* curve of the indirect CL from isopropyl phenyl ketone (**2**) in a DMSO-*t*-BuOK/*t*-BuOH system containing DBA at 313 K. The initial concentration of *t*-BuOK in 10^{-3} mol l^{-1}: I, 3.0; II, 0.75. The initial concentrations of **2** and DBA are 1.8×10^{-4} and 5×10^{-4} mol l^{-1}, respectively.

experimental results support the validity of Eq. 7.

From Eq. 7, the indirect CL quantum yield can be written as

$$\phi_{CL}=\frac{\int I_{CL}\mathrm{d}t}{[\mathrm{AH}]_0}=\frac{k_4k_{TS}[\mathrm{DBA}]\phi_f}{(k_4+k_5+k_6)\{(k_{TS}+k_{TT})[\mathrm{DBA}]+k_7+k_8[\mathrm{O_2}]\}},$$

or

$$\frac{1}{\phi_{CL}}=\frac{1}{\phi^*_{react}\phi_{ET}\phi_f}\left(1+\frac{k_7+k_8[\mathrm{O_2}]}{(k_{TS}+k_{TT})[\mathrm{DBA}]}\right), \tag{8}$$

where

$\phi^*_{react}=k_4/(k_4+k_5+k_6)$ and $\phi_{ET}=k_{TS}/(k_{TS}+k_{TT})$.

The quantum yields for the indirect CL of **1** and **2** were determined from the *I-t* curves measured by varying the DBA concentration. (See experimental section.) Plots of $1/\phi_{CL}$ *versus* $1/[\mathrm{DBA}]$ are shown in Figs. 5 and 6 for **1** and **2**, respectively. These linear plots indicate that Eq. 8 is plausible.

The values of the *abscissa intercept* ($1/\phi_{CL}$ at infinite DBA concentration, $1/\phi^\infty_{CL}$) were found from the figures to be 5.0×10^6 and 3.8×10^4 mol einstein^{-1} for **1** and **2**, respectively. Thus, the values of ϕ^∞_{CL} for **1** and **2** were calculated to be 2.0×10^{-7} and 2.6×10^{-5} eins mol^{-1}, respectively.

From Eq. 8, the value of $(k_7+k_8[\mathrm{O_2}])/(k_{TS}+k_{TT})$ is given by the *line slope/intercept*, which is found from Figs. 5 and 6 to be $2.5\times10^3/5.0\times10^6=5.0\times10^{-4}$ and $7.5/3.8\times10^4=2.0\times10^{-4}$ mol l^{-1} for **1** and **2**, respectively. Considering that the stationary concentration of dissolved oxygen is lower than the initial concentration due to consumption during oxygenation, the decay rate of P*(T), $k_7+k_8[\mathrm{O_2}]$, is assumed to be $\approx10^6$ s^{-1}, although

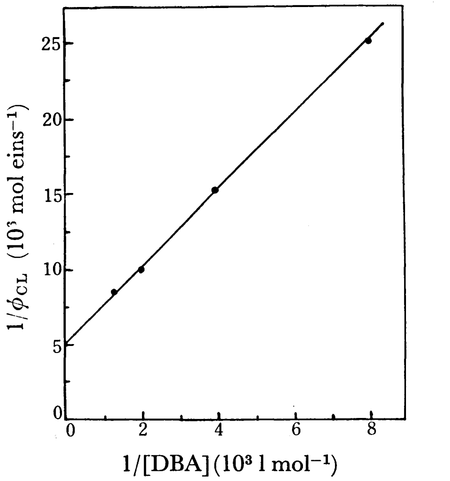


Fig. 5. Effect of the concentration of [DBA] on the quantum yield of the indirect CL from 3-methyl-2-butanone (**1**) in a DMSO-*t*-BuOK/*t*-BuOH system at 313 K. The initial concentrations of **1** and *t*-BuOK are 1.2×10^{-3} and 3.0×10^{-3} mol l^{-1}, respectively.

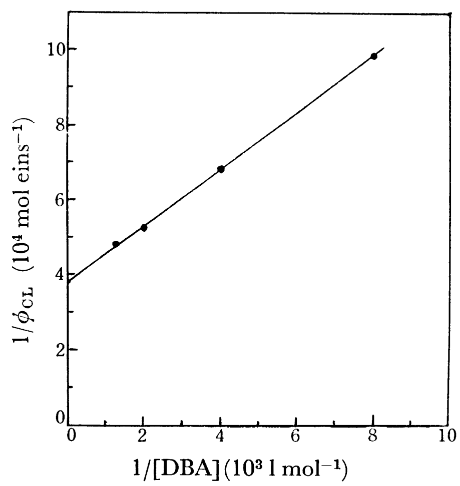


Fig. 6. Effect of the concentration of DBA on the quantum yield of the indirect CL from isopropyl phenyl ketone (**2**) in a DMSO-*t*-BuOK/*t*-BuOH system at 313 K. The initial concentrations of **2** and *t*-BuOK are 7.0×10^{-4} and 3.0×10^{-3} mol l^{-1}, respectively.

this value is an order of magnitude smaller than that proposed by Turro *et al.*[9] Then, using the value $\phi_{ET}=k_{TS}/(k_{TS}+k_{TT})=0.2$ reported by Wilson *et al.*,[6] the k_{TS} values for **1** and **2** were calculated to be 4×10^8 and 1×10^9 l mol^{-1} s^{-1}, respectively. These values are in fairly good agreement with the values reported by Belyakov and Vassilév,[10] Turro *et al.*[9] and Wilson *et al.*[6] for the rate of energy transfer from triplet carbonyl compounds to singlet DBA.

The yield of the excited triplet product (ϕ^*_{react}) can be written as:

$$\phi^*_{react} = \phi^{\infty}_{CL}/\phi_{ET}\phi_f.$$

Since $\phi^{\infty}_{CL}=2.0\times10^{-7}$ and 2.6×10^{-5} eins mol^{-1} (for **1** and **2**, respectively), $\phi_{ET}=0.2$, and $\phi_f=0.1$,[9] the values of ϕ^*_{react} for **1** and **2** were calculated to be 1×10^{-5} and 1×10^{-3}, respectively. These values are markedly lower than the yields of excited triplet products generated in the thermal cleavage of various 1,2-dioxetanes (0.5—0.02[11]). These very small values are presumably due to the fact that CL *via* a dioxetane intermediate arises from a minor reaction.[12]

Experimental

Commercially available 3-methyl-2-butanone, isopropyl phenyl ketone, DBA (all from Tokyo Kasei and of guaranteed reagent grade), and *t*-BuOK (from Merck, for synthesis) were used without further purification. Luminol (from Nakarai Kagaku) was recrystallized from dilute hydrochloric acid prior to use. All solvents, DMSO (from Merck, for spectroscopy) and *t*-BuOH (from Tokyo Kasei, extra pure grade), were used without further purification.

The luminescent reaction was initiated by adding 0.2 ml of a *t*-BuOK solution (in *t*-BuOH) to 2 ml of an aerated solution of **1** or **2** with stirring in a quartz cell ($10\times10\times45$ mm) which was situated in a thermostatically-controlled cell holder.

The CL intensity at 430 nm (the peak of the DBA fluorescence) *versus* time was measured on a Hitachi MPF-2A fluorescence spectrophotometer with no exciting source. The total light emission was determined graphically from the *I-t* curves.

A standard solution of luminol in anhydrous DMSO having an optical density at 359.5 nm (the absorption peak) of 0.010 (1.26×10^{-6} mol l^{-1}) was prepared, and the *I-t* curve of the CL initiated by adding 0.2 ml of a *t*-BuOK solution to 2 ml of the standard solution was measured on the same apparatus at 313 K.

Using the value of 1.28×10^{-2} eins mol^{-1} proposed by Lee *et al.* for the CL exhibited from the luminol solution,[13] the quantum yields for indirect CL from **1** and **2** were determined from the ratios of the total light emitted from the luminol solution to the total measured light emission from the ketone solutions.

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4) For example, N. J. Turro, P. Lechtken, N. E. Schore, G. Schuster, H.-C. Steinmetzer, and A. Yekta, *Acc. Chem. Res.*, **7**, 97 (1974).

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8) The *I-t* curves indicate that the luminescent reaction arises from consecutive reactions. An expression for I_{CL} can be derived from Eqs. 1, 3, 4, and 5 by assuming that $d[A^-]/dt=0$, $k_2[A^-][t\text{-BuOH}]\gg k_3[A^-][O_2]$, and that $k_1[t\text{-BuO}^-]/k_2[t\text{-BuOH}]$ remains constant during the luminescent reaction, thus

$$I_{CL} = \frac{k[AH]_0 k_4 k_{TS}\phi_f[DBA]}{(k-\sum k_i)\{(k_{TS}+k_{TT})[DBA]+k_7+k_8[O_2]\}}\times \{\exp(-\sum k_i t) - \exp(-kt)\},$$

where $k = k_1[t\text{-BuO}^-]/k_2[t\text{-BuOH}]$

and $\sum k_i = k_4+k_5+k_6.$

9) k_T(decay rate of P*(T)) 10^7 s^{-1}: N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H.-C. Steinmetzer, and W. Adam, *J. Am. Chem. Soc.*, **96**, 1627 (1974).

10) $k_{TS}=3\times10^8$ l mol^{-1} s^{-1} (Ref. 2 (a)); 1×10^9 l mol^{-1} s^{-1} (Ref. 9).

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