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Studies of the Generation of Excited Singlet Products in the Oxidation of the -CO-CH- Containing Molecules. The Chemiluminescence of Acylcarbazoles

Isao Kamiya* and Takashi Sugimoto
Department of Chemistry, College of General Education, Nagoya University, Chikusa-ku, Nagoya 464

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Direct chemiluminescence emissions have been found from the air oxidation of 3-acyl-9-methyl- (**1**), 3,6-diacyl-9-methyl- (**2**), and 9-acylcarbazoles (**3**) due to the generation of an excited singlet state of monocarboxylate ions (from **1** and **2**) and the carbazole anion (from **3**). The relative intensities *vs.* the reaction time for the luminescent reaction of 3-isobutyryl-9-methylcarbazole could be interpreted by a reaction scheme involving consecutive reactions. Using this reaction scheme, the values of the decomposition rate of intermediates at 30, 40, and 50 °C were determined to be 0.19, 0.42, and 0.98 min^{-1} respectively, which were comparable to the values reported for the decomposition rates of isolated dioxetanes giving excited singlet products.

In the course of our studies, we have established the generation of excited triplet carbonyl products from the air oxidation of various simple ketones with a –CO–CH– group, such as 3-methyl-2-butanone and isopropyl phenyl ketone in alkaline aprotic solvents.[1] We further succeeded in observing the direct chemiluminescence (CL) due to the generation of excited singlet products in the air oxidation of such –CO–CH– containing molecules as 9,10-diisobutyrylanthracene and 9,10-dipropionylanthracene.[2] For the luminescent reaction of the –CO–CH– containing molecules (simple ketones and diacylanthracenes), a reaction pathway involving the cleavage of a dioxetane intermediate was discussed as a possible mechanism.

Two different paths have been reported for the thermolysis of isolated dioxetanes. Simple dioxetanes decompose by homolytic cleavage to afford excited products, mainly in triplet states.[3] On the other hand, complex dioxetanes, which give high yields of excited singlet products, decompose by means of the intermolecular electron-transfer mechanism,[4] which is conceptually similar to the CIEEL mechanism.[5]

Thus, it seems likely that the difference in the state of the excited products is due to the different decomposition paths of the dioxetane intermediates: one (produced from simple ketones) gives an excited triplet product, and the other (from diacylanthracenes), an excited singlet product.

In order to test the validity of, and to broaden the scope of, the luminescent reaction mechanism, we have further examined some acylcarbazoles which contain the –CO–CH– group and a fluorescence moiety for the direct CL by air oxidation under the same experimental conditions. In the present paper, we will report the CL emission features observed from the acylcarbazoles and the kinetic evidence for the reaction path involving a dioxetane intermediate in the luminescent reaction of 3-isobutyryl-9-methylcarbazole.

Results and Discussion

3-Acyl-9-methylcarbazoles. When 0.2 cm^3 of a solution of potassium *t*-butoxide (*t*-BuOK) in *t*-butyl alcohol (2×10^{-2} mol dm^{-3}) was added to 2 cm^3 of an aerated solution of 3-isobutyryl-9-methylcarbazole (**1a**) in *N*,*N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) (1.0×10^{-4} mol dm^{-3}), there appeared a CL emission in the UV region. The CL spectrum measured in a DMF solution had a peak at 370 nm; thus, it was similar to the fluorescence spectrum of the 9-methylcarbazole-3-carboxylate ion (**4**), one of the reaction products, measured in an alkaline DMF solution, as is shown in Fig. 1. Even when the concentration of **1a** was raised to 1.0×10^{-3} mol dm^{-3}, no change in the spectral distribution was observed (*cf*, 3,6-diisobutyryl-9-methylcarbazole below).

9-Methyl-3-propionylcarbazole (**1b**) and 3-acetyl-9-methylcarbazole (**1c**) also exhibited similar CL emissions. However, the carbazole **1b** showed a weaker emission with an intensity one 30th of that from **1a**, and **1c** the weakest (one 1000th). These results indicate that the intensity of the CL emission is much affected by the nature of the C–H bond adjacent to the carbonyl group; it increases in the order of primary<secondary<tertiary. The order of the CL intensity is consistent with those observed in simple ketones and diacylanthracenes. The following reaction scheme, involving the cleavage of a dioxetane intermediate which is produced by the oxygenation of the anion formed by the loss of a proton from the

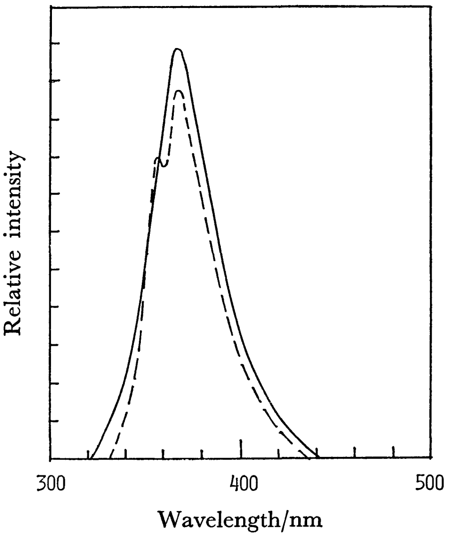
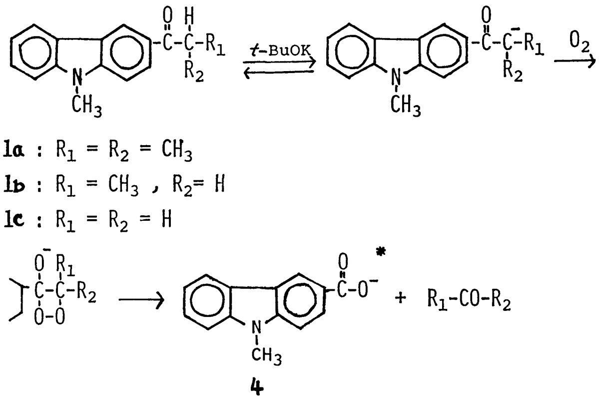


Fig. 1. Chemiluminescence spectrum of **1a** in DMF (solid curve), and fluorescence spectrum of **4** measured in an alkaline DMF solution (broken curve).



α-carbon atom, seems plausible in explaining the emission feature and the emitting product, **4**.

Recently, an intense CL emission arising from the base-induced oxidation of 3-(alkoxycarbonylamino)-benzofuran-2(3*H*)-ones, which contain a –CO–CH– group, has been reported by Lofthouse *et al.*, who also proposed an analogous reaction scheme involving a dioxetane intermediate for the luminescent reaction.[6]

The change in the concentrations of the reactant, **1a**, and the product, **4**, with the reaction time at 30, 40, and 50 °C in the luminescent DMF system [2 cm^3 of a **1a** solution in DMF (1.0×10^{-4} mol dm^{-3})+ 0.2 cm^3 of a *t*-BuOK solution in *t*-butyl alcohol (2×10^{-2} mol dm^{-3})], as measured by high-performance liquid chromatography, are illustrated in Figs. 2a, 2b, and 2c respectively.[7] Each figure shows that the concentration of **1a**, [**1a**], decreases rapidly to a certain value [**1a**]$_\infty$; thereafter, it is kept almost constant because of the extremely slow decrease, probably due to the consumption of *t*-BuOK and dissolved oxygen. In the rapid decay stage, the plots of log([**1a**]$-$[**1a**]$_\infty$) *vs.* the reaction time (t) being almost straight lines, the decomposition of **1a** was found to obey a pseudo-first-order reaction with respect to ([**1a**]$-$[**1a**]$_\infty$), although a slight deviation arose at the final decay stage. From the slopes of the lines, the apparent rate constants (k) at 30, 40, and 50 °C were determined to be 0.22, 0.26, and 0.43 min^{-1} respectively.

The change in the relative intensities of the CL emission (I_R) with the reaction time, measured under the same experimental conditions, are illustrated by a solid curve in each of figures (2a—2c), where the values of I_R are taken to be normal at the maximum intensity. The figure of the emission curve suggests very strongly that the luminescent reaction arises from the following kinetic scheme involving consecutive reactions:

$$\mathrm{AH} \overset{t\text{-BuOK}}{\rightleftharpoons} \mathrm{A}^- - \begin{cases} \xrightarrow{k_1} \mathrm{X} & \text{(I)} \\ \xrightarrow{k_1'} \mathrm{Y} & \text{(II)} \end{cases}$$

$$\mathrm{X} - \begin{cases} \xrightarrow{k_2} \mathrm{P}^* & \text{(III)} \\ \xrightarrow{k_2'} \mathrm{P} & \text{(IV)} \end{cases}$$

$$\mathrm{P}^* \xrightarrow{k_f} \mathrm{P} + h\nu$$

$$\mathrm{P}^* \xrightarrow{k_q} \mathrm{P},$$

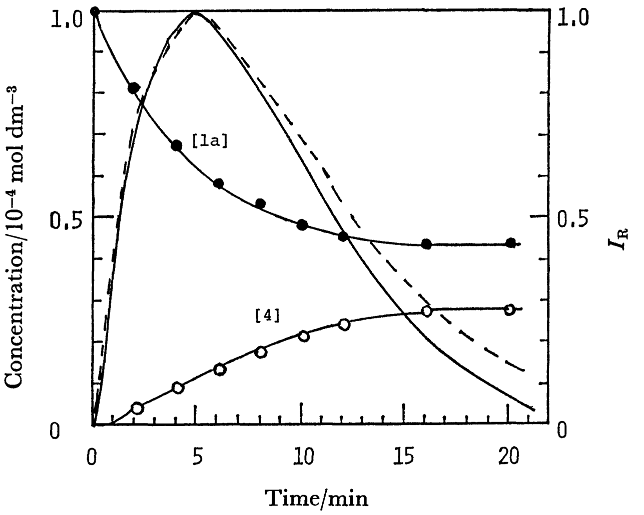


Fig. 2a. Changes in the concentrations of **1a** ([**1a**]) and **4** ([**4**]) with reaction time (t) in DMF at 30 °C, and relative intensities of CL emission (I_R) *vs.* t: observed I_R, solid curve; calculated I_R, broken curve.

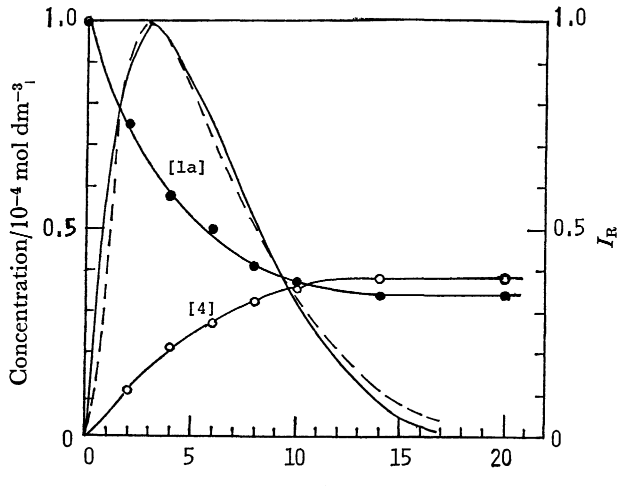


Fig. 2b. Changes in [**1a**] and [**4**], and I_R-t curves in DMF at 40 °C.

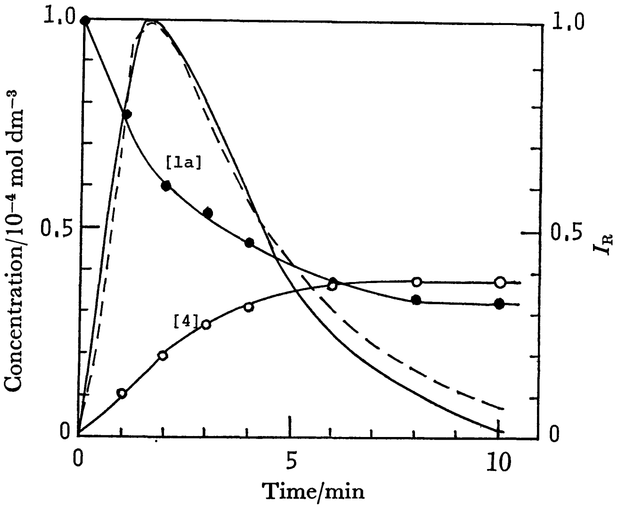


Fig. 2c. Changes in [**1a**] and [**4**], and I_R-t curves in DMF at 50 °C.

where AH=**1a**, X=dioxetane intermediate, Y=other product, and P=**4**.

Assuming that competitive decomposing reactions (III and IV) obey the first-order reaction,8) and recalling the finding that the competitive reactions of I and II also obeyed a pseudo-first-order reaction with respect to ([AH]−[AH]∞), we can write the CL intensity (I) at the initial stage as:

$$\begin{aligned} I &= k_1k_2\Phi_f\{([\mathrm{AH}]_0-[\mathrm{AH}]_\infty)/(k_d-k)\} \\ &\quad \times\{\exp(-kt)-\exp(-k_dt)\} \\ &= \alpha\beta\Phi_f([\mathrm{AH}]_0-[\mathrm{AH}]_\infty)\{kk_d/(k_d-k)\} \\ &\quad \times\{\exp(-kt)-\exp(-k_dt)\}, \qquad (1) \end{aligned}$$

where $[\mathrm{AH}]_0$ is the initial concentration of **1a**, $k_1+k'_1=k$, $k_2+k'_2=k_d$, $\alpha=k_1/k$, $\beta=k_2/k_d$, and $\Phi_f=k_f/(k_f+k_q)$. Putting t_m as the time required to reach the maximum of $I(I_m)$, we can derive the following equations:

$$k_d\exp(-k_dt_m)=k\exp(-kt_m), \qquad (2)$$

and:

$$\begin{aligned} I_m &= \alpha\beta\Phi_f([\mathrm{AH}]_0-[\mathrm{AH}]_\infty)\{kk_d/(k_d-k)\} \\ &\quad \times\{\exp(-kt_m)-\exp(-k_dt_m)\}. \end{aligned}$$

Therefore,

$$\begin{aligned} I_R = I/I_m &= \{\exp(-kt)-\exp(-k_dt)\}/ \\ &\quad \{\exp(-kt_m)-\exp(-k_dt_m)\}. \end{aligned}$$

From the CL emission curves shown in Figs. 2a—2c, t_m being found to be 5.0, 3.0, and 1.5 min at 30, 40, and 50 °C respectively, the values of k_d at these temperatures can be calculated from Eq. 2 to be 0.19, 0.42, and 0.98 min^{-1} using the values of k determined above.

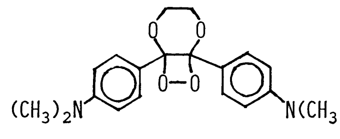
Taking the values of k, k_d, and t_m, we can calculate the values I_R by means of the following numerical equations:

$$\begin{aligned} 30\ ^\circ\mathrm{C};\ I_R &= \{\exp(-0.22t)-\exp(-0.19t)\}/ \\ &\quad \{\exp(-0.22\times5)-\exp(-0.19\times5)\} \\ &= \{\exp(-0.22t)-\exp(-0.19t)\}/(-0.054) \\ 40\ ^\circ\mathrm{C};\ I_R &= \{\exp(-0.26t)-\exp(-0.42t)\}/0.174 \\ 50\ ^\circ\mathrm{C};\ I_R &= \{\exp(-0.43t)-\exp(-0.98t)\}/0.295. \end{aligned}$$

The dotted curves in Figs. 2a—2c illustrate the curves of I_R *vs.* t calculated from the above equations. The curves of I_R thus calculated are in fairly good agreement with those of the observed I_R values (solid curves) at these temperature except at the final stage, where the reactions of I and II obey the first-order reaction no longer.

It should be noted that the values of k_d (for example, 0.42 min^{-1}=7.0×10^{-3} s^{-1} at 40 °C) are comparable to the values reported for the decomposition rates of isolated dioxetanes (6.5×10^{-3} s^{-1} for the **7** dioxetane in DMF at 25 °C,9a) 7.6×10^{-3} s^{-1} for **8** in benzene at 65 °C,9b) 4.6×10^{-3} s^{-1} for **9** in CH_2Cl_2 at 25 °C,9c) and 2.96×10^{-3} s^{-1} for **10** in decane at 79 °C9d)).10)

The activation energy for the decomposition of X (the competitive reactions of II and IV) was estimated to be 68 kJ mol^{-1} from the Arrhenius plot of k_d.



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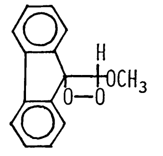

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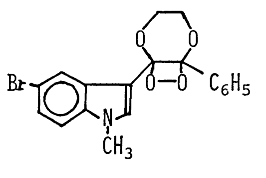

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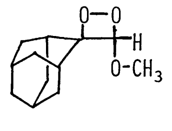

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Analogous values have been obtained for the decomposition of dioxetanes (82.4 kJ mol^{-1} for **7** and 87.9 kJ (21 kcal) mol^{-1} for **8**9a,9b)).

Using the value of 1.28×10^{-2} proposed by Lee *et al.*11) for the efficiency of the CL emission from a standard luminol solution in DMSO (1.26×10^{-6} mol dm^{-3}), the efficiencies of CL from the **1a** solution in DMF [Φ_{CL}=quantity of total light (mol) emitted from 1 dm^3 of the solution/([AH]$_0$−[AH]∞)] at 30, 40, and 50 °C were determined to be 3.5×10^{-4}, 4.2×10^{-4}, and 5.7×10^{-4} respectively from the ratio of the total light emitted from the luminol solution to the total measured light from the **1a** solution.12) From Eq. 1, Φ_{CL} can be written as:

$$\Phi_{CL}=\int I\mathrm{d}t/([\mathrm{AH}]_0-[\mathrm{AH}]_\infty)=\alpha\beta\Phi_f.$$

The value of $\alpha=k_1/(k_1+k'_1)$ is given by [**4**]∞ (the final concentration of **4**)/([AH]$_0$−[AH]∞) and was found to be almost unchanged in the temperature range between 30 °C and 50 °C, since the values of [**4**]∞/([**1a**]$_0$−[**1a**]∞) were obtained to be 0.51, 0.58, and 0.57 at 30, 40, and 50 °C respectively. As Φ_f is not so varied with the temperature, the effect of the temperature on Φ_{CL} may be mainly attributed to the temperature dependence of β $(=k_2/(k_2+k'_2))$, which is itself presumably due to the difference in activation energy between the reaction of III (k_2) and the reaction of IV (k_2'),13) since there has been found a difference in activation energy between a higher-energy path leading to an excited product and a lower-energy path leading to a product in a grand state in the decomposition of dimethyldioxetane.14)

3,6-Diacylcarbazoles. 3,6-Diisobutyryl-9-methylcarbazole (**2a**) also gave rise to CL emission with an intensity comparable to that from **1a**. Figures 3a and 3b illustrate the changes in the spectral distribution with the reaction time observed when 0.2 cm^3 of *t*-BuOK solution in *t*-butyl alcohol (2×10^{-2} mol dm^{-3}) was added to 2 cm^3 of **2a** solution in DMSO in two different concentrations (1.0×10^{-3} mol dm^{-3} and 1.0×10^{-4} mol dm^{-3}). The figures indicate that the spectrum of the CL emission from **2a** varies during the course of the reaction. In a solution with a high **2a** concentration, the apparent emission was, at the initial stage, composed of one intense peak at 440 nm with a spectral distribution similar to that of the fluorescence of **2a**. During the course of the reaction,

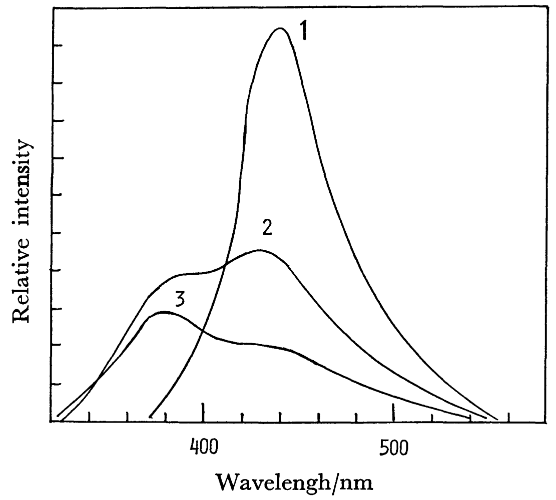


Fig. 3a. Change of CL spectrum of **2a** with reaction time in a DMSO solution of high **2a** concentration (1.0×10^{-3} mol dm^{-3}). 1→2→3.

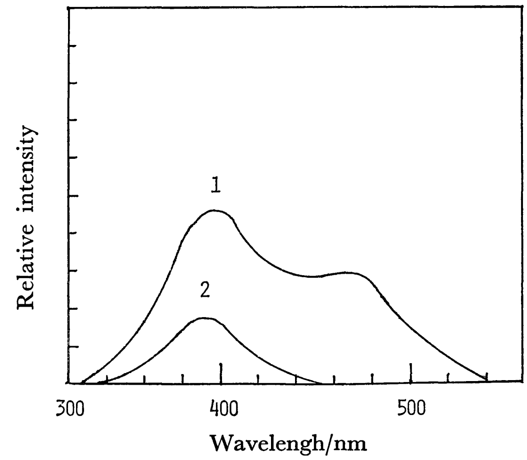


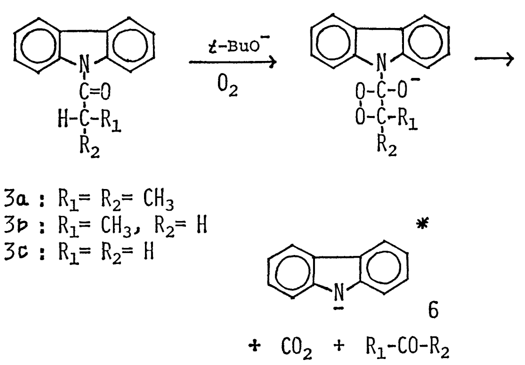
Fig. 3b. Change of CL spectrum of **2a** with reaction time in a DMSO solution of low **2a** concentration (1.0×10^{-4} mol dm^{-3}). 1→2.

the intensity of the peak gradually decreased with a blue shift, and simultaneously a new peak appeared at about 370 nm. In a solution with a low **2a** concentration, the spectrum had two peaks at the initial stage; these peaks also varied with a blue shift until only one peak, at 370 nm, was observed. Thus, it seems likely that a portion of the excited product emits UV light (370 nm), while the other portion of the excited product transfers energy to unoxidized **2a**, thereby exciting **2a** to emit fluorescence (440 nm).

9-Methyl-3,6-dipropionylcarbazole, whose C–H bond adjacent to the carbonyl group is secondary, showed a much weaker emission than **2a**, and 3,6-diacetyl-9-methylcarbazole, which possesses a primary C–H bond, exhibited a very weak emission. From the finding that the emission from the exctied product showed a peak at 370 nm, it seems likely that excited singlet 3-acyl-9-methylcarbazole-6-carboxylate ions (**5**) are generated from the air oxidation by the same mechanism as that proposed for **1a**. In the reaction systems, **5** may be successively oxidized, since the final product was the 9-methylcarbazole-3,6-dicarboxylate ion, which showed a greenish fluorescence with a peak at 450 nm. However, it seems unlikely that the CL emission arises from the oxidation of **5**, since no emission peak at 450 nm was observed in the luminescent reactions.

3,6-Diisobutyrylcarbazole and the lower homologues gave an oxidation product which showed fluorescence with a peak at 470 nm, but an extremely weak emission was observed from its oxidation. This is probably because the luminescent reaction is debased by competitive processes brought about by the hydrogen atom at the 9-position of the carbazole. A similar debasement has been oberved in the oxidation of 9-isobutyrylanthracene.[2]

9-Acylcarbazoles. 9-Isobutyrylcarbazole (**3a**) and 9-propionylcarbazole (**3b**) exhibited CL emission with intensities one 50th of those from **1a** and **2a**. An extremely weak emission was exhibited by 9-acetylcarbazole (**3c**). The spectrum of the fluorescence from the spent reaction solution in DMSO, as measured with exciting at 340 nm, and the roughly estimated spectral distribution of the CL emission from **3a** (because of low intensity) are illustrated in Fig. 4, together with the fluorescence spectrum of



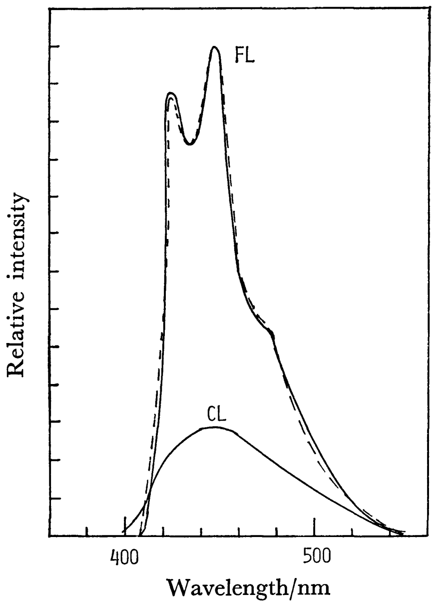


Fig. 4. Spectral distribution of CL emission from **3a** (CL), fluorescence spectrum of the spent reaction solution (FL), and fluorescence spectrum of **6** measured in an alkaline DMSO solution (broken curve).

the carbazole anion (**6**) measured in an alkaline DMSO solution with exciting at 340 nm. The figure shows that the CL spectrum is analogous to the fluorescence of the product, which is very similar to the fluorescence of **6**. Carbazole was isolated, and acetone was also obtained as 2,4-dinitrophenylhydrazone from the oxidation products. These results are interpreted by the reaction scheme shown in the previous page, leading to the generation of an excited-singlet carbazole anion *via* a dioxetane intermediate.

Summarizing the results of the present study, we conclude that excited-singlet products are surely generated in the air oxidation of molecules containing a -CO-CH- group and a fluorescence moiety in alkaline aprotic solvents. The emission features and emitting products generated by oxidation suggest that dioxetanes may be the critical intermediates in giving excited-singlet products. Work is now in progress to search for other -CO-CH- containing molecules which exhibit CL in high yields.

Experimental

The elemental analyses were conducted at the Analytical Section, Meijo University, Nagoya.

*The Preparation of 3-Acyl-9-methylcarbazoles (**1a**—**c**).* Aluminium chloride (11.0 g) was added, in small portions, into a vigorously stirred solution of 9-methylcarbazole[15] (15.0 g) and isobutyryl chloride (11.0 g) in benzene (300 cm^3) at 5—8 °C over a 30-min period. The mixture was stirred at that temperature for an additional 30 min and then at 25—30 °C for 24 h. Thereafter the mixture was poured onto crushed ice (400 g). The benzene layer, after being separated from the aqueous solution, was participated by water, aqueous sodium hydrogencarbonate, and water as usual. The benzene solution was concentrated to about 50 cm^3 and placed in a silica-gel column (Wako Gel C-100, 5×45 cm). The column was eluted first by a 1:1 mixture of benzene and hexane (1.5 dm^3) to remove the unchanged starting material. The column was then eluted by benzene. The subsequent evaporation of the eluate gave an oily residue, which was crystallized from ethanol to give colorless needles (45% yield) of 3-isobutyryl-9-methylcarbazole (**1a**); mp 64.5—66 °C (from ethanol) (Found: C, 81.56; H, 6.69; N, 5.43%. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57%).

Similar treatments of 9-methylcarbazole with propionyl chloride or acetyl chloride gave, respectively, 9-methyl-3-propionylcarbazole (**1b**) [25% yield, mp 83.5—84.5 °C (from ethanol) (Found: C, 80.73; H, 6.17; N, 5.75%. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90%)] and 3-acetyl-9-methylcarbazole (**1c**) [50% yield, mp 99—100 °C (from methanol) (Found: C, 80.86; H, 5.70; N, 6.09%. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27%)].

The Preparation of 3,6-Diacyl-9-methylcarbazoles. 9-Methylcarbazole (20 g) was added, in small portions, to a vigorously stirred mixture of aluminium chloride (60 g) and isobutyryl chloride (40 g) in nitrobenzene (200 cm^3) at 0 °C. The resulting solution was stirred in an ice-bath for 6 h and then at 20—25 °C for 2 d. The solution was subsequently poured onto crushed ice (500 g), and the aqueous layer was discarded. The nitrobenzene solution, after being participated by water, was subjected to steam distillation to remove the solvent. The oily residue was extracted with benzene (2×200 cm^3). The extract was concentrated to about 150 cm^3 and fractionated on a silica-gel column (5×50 cm), eluted by a mixture of ethyl acetate and benzene (1:9). The evaporation of the eluate and subsequent crystallization from acetone gave colorless needles (82% yield) of 3,6-diisobutyryl-9-methylcarbazole (**2a**); mp 128—129.5 °C (from ethanol) (Found: C, 78.60; H, 7.18; N, 4.15%. Calcd for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36%).

The replacement of isobutyryl chloride by propionyl or acetyl chloride in the foregoing reaction gave 9-methyl-3,6-dipropionylcarbazole [66% yield, mp 196—197 °C (from ethanol) (Found: C, 77.92; H, 6.52; N, 4.62%. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77%)] and 3,6-diacetyl-9-methylcarbazole [59% yield, mp 198—199 °C (from ethanol) (Found: C, 75.70; H, 5.61; N, 5.21%. Calcd for $C_{17}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53%)] respectively.

The Preparation of 3,6-Diacylcarbazoles. Carbazole (10 g) was added, in small portions, into a vigorously stirred solution of isobutyric anhydride (10 g) and aluminium chloride (15 g) in nitrobenzene (150 cm^3) at 0—5 °C. The resulting dark green solution was stirred at 4—5 °C for 12 h and then added to ice-cold 0.5 mol dm^{-3} hydrochloric acid (300 cm^3). The nitrobenzene solution was separated from the aqueous layer and submitted to steam distillation to remove the solvent. The residual solid was dissolved in ethyl acetate and fractionated on a silica-gel column (4.5×50 cm), eluted by ethyl acetate–benzene (2:3). The evaporation of the eluate and subsequent crystallization from ethyl acetate gave yellow needles (26% yield) of 3,6-diisobutyrylcarbazole; mp 203.5—204 °C (Found: C, 78.14; H, 6.82; N, 4.96%. Calcd for $C_{20}H_{21}NO_2$: C, 78.14; H, 6.89; N, 4.56%).

3,6-Dipropionylcarbazole [36% yield, mp 238—240 °C (from ethyl acetate) (Found: C, 77.19; H, 5.98; N, 4.76%. Calcd for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01%)] and 3,6-diacetylcarbazole [11% yield, mp 236—237 °C, dec (from ethyl acetate) (Found: C, 76.57; H, 5.04; N, 5.35%. Calcd for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.57%)] were similarly synthesized from carbazole and the appropriate acid anhydride.

*The Preparation of 9-Acylcarbazoles (**3a**—**c**).* A mixture of potassium carbazole (5.0 g), isobutyryl chloride (10 g), and sodium carbonate (5 g) was heated under reflux for 2 h. The mixture was then added to water (50 cm^3), and the product was extracted with ether (2×100 cm^3). The extract, after washing with sodium hydrogencarbonate and water, was evaporated to give an oily residue, which was then fractionated on a silica-gel column (3.4×40 cm), eluated by a 1:1 mixture of hexane and benzene. The eluate was evaporated and subsequently crystallized from methanol to give colorless needles (80% yield) of 9-isobutyrylcarbazole (**3a**); mp 43—44.5 °C (Found: C, 81.01; H, 6.19; N, 6.01%. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 5.90; N, 6.37%).

9-Propionylcarbazole (**3b**) [85% yield, mp 90.5—91 °C (from methanol) (Found: C, 80.69; H, 5.67; N, 6.27%. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27%)] and 9-acetylcarbazole (**3c**) [60% yield, mp 67—68.5 °C (from methanol) (Found: C, 80.14; H, 5.09; N, 6.53%. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69%)] were similarly obtained from potassium carbazole and propionyl or acetyl chloride respectively.

*The Isolation of 9-Methylcarbazole-3-carboxylic Acid and 9-Methylcarbazole-3,6-dicarboxylic Acid from the Oxidation Products of the 3-Isobutyryl or 3,6-Diisobutyryl Precursor (**1a** or **2a**).* 3-Isobutyryl-9-methylcarbazole (500 mg) in DMF was added to *t*-BuOK (4.0 g) in DMF (250 cm^3), after which the mixture was stirred under oxygen at 25 °C for 2 h. Water (100

cm^3) was added to the mixture, and the resulting solution was evaporated to dryness under reduced pressure. The residue was dissolved in water (150 cm^3), and a small amount of an insoluble material was removed by extraction with benzene (2×50 cm^3). The solution was brought to boil, adjusted to pH 2—3 with hydrochloric acid, and then chilled. The colorless needles (385 mg, 86% yield) of 9-methylcarbazole-3-carboxylic acid melted at 258—259 °C (from water) (Found: C, 74.59; H, 4.67; N, 6.09%. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22%).

3,6-Diisobutyryl-9-methylcarbazole, on air oxidation in a way similar to that described above, yielded 9-methylcarbazole-3,6-dicarboxylic acid (95% yield), which did not melt below 300 °C (Found: C, 66.70; H, 4.33; N, 5.23%. Calcd for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20%).

Measurements of the CL Intensity and Fluorescence Spectra. A 2-cm^3 aerated solution of the acylcarbazoles in DMF or DMSO was placed in a quartz cell, which was kept at a constant temperature by means of a thermostatically controlled cell holder. The CL intensity was measured immediately after adding 0.2 cm^3 of a solution of *t*-BuOK in *t*-butyl alcohol (2×10^{-2} mol cm^{-3}) into the solution of the reactant on a Hitachi MPF-2A fluorescence spectrophotometer, with the exciting source turned off. The fluorescence spectra were measured on the same apparatus.

*Measurements of the Changes in the Concentrations of Reactant and Product in CL Reaction of **1a** by High-performance Liquid Chromatography.* We took 0.2-cm^3 aliquots of the reaction solution out at regular intervals and immediately added them to a solution of phosphoric acid in methanol (2×10^{-3} mol dm^{-3}, 0.2 cm^3) to stop the oxidation. A 25-mm^3 aliquot of the solution was subjected to high-performance liquid chromatography using a JASCO Trirotar on a JASCO SS-10-ODS-A reverse-phase column (4.6×250 mm), using methanol as the elution solvent (1.0 cm^3/min). The eluate containing the unchanged reactant (**1a**) and product (9-methylcarbazole-3-carboxylic acid, **4**) was detected on a JASCO UVIDEC-100-II UV spectrometer at 285 nm, and the retention times and the quantities of **1a** and **4** were determined by calculating the areas of the peaks with a Intelligent 5000 E integrator.

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7) Analogous curves showing the increasing concentration of **4** were also obtained by monitoring the increasing fluorescence intensity at 370 nm (the peak of the fluorescence of **4**).

8) It has been reported that the decomposition of various isolated dioxetanes obey the first-order reaction (see Ref. 9).

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10) From the kinetic data, the intermediate X seems relatively stable at a low temperature if it is isolated. However, the oxidation of the carbazole does not proceed appreciably at a low temperature. Thus, it may be difficult to isolate X from the luminescent systems employed here.

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12) When light is detected by the signal of an electrophotometer, the total light intensity per unit volume from a chemiluminescent solution is given by $T = G\int S_t \mathrm{d}t$, where G is the instrumental factor and where S_t is the magnitude of the signal measured over the emission band at time t and is experimentally determined by the graphical integration of the spectral distribution curve, corrected for the wavelength response of the photomultiplier.

Assuming that the ratio of S_t to the magnitude of the signal at the peak of the emission spectrum ($I(\lambda_\mathrm{m})_t$), $\sigma = S_t/I(\lambda_\mathrm{m})_t$, is kept constant during the reaction, we can write: $T = G\sigma\int I(\lambda_\mathrm{m})_t \mathrm{d}t$. $\int I(\lambda_\mathrm{m})_t \mathrm{d}t$ is experimentally determined by the graphical integration of the $I(\lambda_\mathrm{m})_t$ *vs.* t-curve. Thus, $\Phi_\mathrm{CL} = G\sigma\int I(\lambda_\mathrm{m})_t \mathrm{d}t/[\mathrm{M}]$ for a solution ([M] is the concentration decrement of M), and $\Phi'_\mathrm{CL} = G\sigma'\int I'(\lambda'_\mathrm{m})_t \mathrm{d}t/[\mathrm{M}']$ for the other solution, so that:

$$\Phi_\mathrm{CL} = \Phi'_\mathrm{CL}\sigma[\mathrm{M}']\int I(\lambda_\mathrm{m})_t \mathrm{d}t/\sigma'[(\mathrm{M}]\int I'(\lambda'_\mathrm{m})_t \mathrm{d}t.$$

13) Assuming that $k_2 = A\exp(-E_\mathrm{a}/\mathrm{R}T)$, $k'_2 = A'\exp(-E_\mathrm{a}'/\mathrm{R}T)$ and $A \sim A'$, we can write that $1/\beta - 1 = \exp(\Delta E_\mathrm{a}/\mathrm{R}T)$, where $\Delta E_\mathrm{a} = E_\mathrm{a} - E_\mathrm{a}'$ is the difference in activation energy between Reactions III(E_a) and IV(E_a'). If ΔE_a is tentatively taken to be 10 kJ mol^{-1} with reference to the value reported for dimethyldioxetane (13—14 kJ mol^{-1}),[14] the β values are calculated to be 1.8×10^{-2}, 2.1×10^{-2}, and 2.4×10^{-2} at 30, 40, and 50 °C respectively. The ratio of the β values (1.0:1.2:1.3) is roughly agreeable to that the observed Φ_CL values (1.0:1.2:1.6).

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