Chemiluminescence in O_2 oxidation of organosodium compounds of polycyclic aromatic hydrocarbons and benzophenone

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Chemiluminescence (CL) in oxidation of organosodium compounds by O_2 in THF was studied. Emitters of CL are excited complexes of polycyclic aromatic hydrocarbons, excimers $^1(R \cdot R)^*$. The mechanism of their formation was proposed. The $Na^+,R^{\cdot-} + O_2$ CL system is a unique source for the selective generation of excimers of aromatic hydrocarbons.

Key words: chemiluminescence, organosodium compounds; O_2 oxidation; excimers.

Mononuclear aromatic or alkene-aromatic hydrocarbons are active components and emitters of electrochemiluminescent (ECL) systems,[1-3] whose emission is excited in chemical reactions of oppositely charged radical ions of hydrocarbons ($R^{\cdot-}$ and $R^{\cdot+}$) generated on electrodes.

Similar radical anions exist in the "ready" form in organosodium compounds (OSC) $Na^+,R^{\cdot-}$ (R = naphthalene (**1**), anthracene (**2**), phenanthrene (**3**), pyrene (**4**), perylene (**5**), diphenylanthracene (**6**), stilbene (**7**), and benzophenone (**8**)), which are peculiar "conserving agents of CL," whose emission can be obtained by the addition of a necessary oxidant. We have previously reported on such CL systems for the oxidation of OSC by xenon difluoride,[4] Ce^{IV} complex,[5] and O_2.[6] Since the mechanism and emitters of CL were determined for the first two oxidants,[4,5] and no data are available for the autooxidation of OSC,[6] the present report is devoted to the study of the CL mechanism in autooxidation of OSC.

Experimental

Naphthalene, anthracene, and stilbene ("scintillation" and "special" purities grade), pyrene, perylene, diphenylanthracene, and phenanthrene ("chemical" purity grade) were used. Benzophenone ("reagent" grade) was preliminarily recrystallized from toluene and sublimed *in vacuo*. $Na_2O_2 \cdot 8H_2O$ ("analytical" purity grade) was purified by a known procedure[7] by recrystallization from ice-cooled bidistilled water, filtered, washed with THF, and dried *in vacuo* at room temperature. NaO_2 was obtained in solution by the oxidation of a solution of sodium ketyl benzophenone by O_2 in THF (see Ref. 7). The concentration of NaO_2 in the solution was determined gasometrically by a standard procedure[7] measuring the volume of O_2 evolved when the $FeSO_4$ + HCl mixture was added to the solution. Compounds **1**—**8** were obtained by a known procedure[8] by intense stirring of solutions of aromatic hydrocarbons in THF with excess metallic sodium as a thin wire in an atmosphere of argon. OSC were analyzed by the decomposition with water followed by titration of the NaOH formed with an aqueous solution of HCl. Procedures of measuring CL and photoluminescence (PL) have been described previously.[9] Organic products of the oxidation of OSC by O_2 were identified by PL spectra after the acid hydrolysis of a solution of an oxidate. The presence of NaO_2 and Na_2O_2 in the sodium oxidate was established (see Refs. 7 and 10) by the determination of the total active oxygen decomposing the sodium oxidate by an aqueous solution of $CuSO_4$, and then the content of the peroxide oxygen was determined by titration with $KMnO_4$. The content of the superoxide oxygen was determined from the difference between these two values.

Results and Discussions

The authors of Ref. 1 have reported an unsuccessful attempt to detect CL in the autooxidation of sodium adducts of aromatic radical anions, which is related to the energy deficiency of this reaction. The previously published work (Ref. 11) also contains no data on the existence of CL in the di-9-anthranyl peroxide+sodium naphthalenide+O_2 system.

Both these facts are of interest, because CL observed visually was determined[6] for a series of OSC including compound **1**. In addition, we detected CL for the autooxidation of a blue solution of sodium ketyl benzophenone **8**,[6] which is widely used in organic synthesis. In this connection, the assertion[12] that CL of the OSC indicated appears only when the electron acceptor and the products of its oxidation are not quenchers of PL is not necessary, especially if it is taken into account that oxygen is a known efficient quencher of excited states.[2]

Solutions of OSC compounds in THF emit light (auto-CL) even in an argon atmosphere (Fig. 1), which is due to the oxidation by the O_2 traces (the content of O_2 does not exceed 10^{-6} vol.%). The subsequent con-

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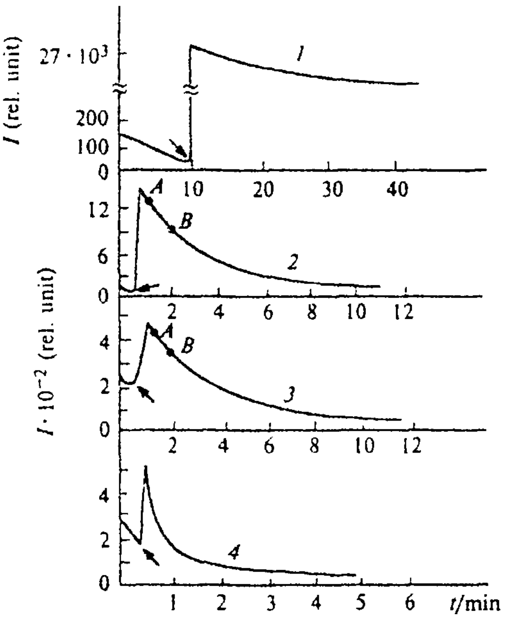


Fig. 1. Dependence of the intensity of PL (*I*) on time in the oxidation of solutions of OSC (mol L^{-1}) in THF by air: *1*, **1** (10^{-3}); *2*, **2** (10^{-4}); *3*, **4** ($2 \cdot 10^{-4}$); *4*, **6** ($3 \cdot 10^{-4}$). Arrows indicate switching on bubbling of air. *A—B*, regions of the curves in which PL spectra were recorded by an MZD-2 monochromator.

tact with air results in an instant (600-fold) increase in the intensity of CL (I_{max} changes from $3 \cdot 10^7$ for **8** to $7 \cdot 10^{10}$ photon s^{-1} mol^{-1} for **1**).

The comparison of the CL spectra of the autooxidation of OSC with the PL spectra of individual hydrocarbons (Fig. 2) suggests that the singlet-excited states ($^1R^*$) are not emitters of CL. In fact, CL is concentrated in a longer-wave region than PL of hydrocarbons from $^1R^*$ states (Table 1). It is established in special experiments on the detection of CL for low-concentrations of OSC solutions ($2 \cdot 10^{-5}$ mol L^{-1}) that the shift of the maxima of the CL spectra relative to PL is not related to the effect of the internal filter caused by the intense color of OSC. In addition, the emission of $^1R^*$ is characterized by the existence of a fine vibrational structure, and the CL spectra are diffuse bands with broad maxima (see Fig. 2). It is known[2] that the phosphorescence (PS) of hydrocarbons is localized in a longer-wave region than fluorescence (FL). However, the position of the maxima in the PS spectra is shifted relative to CL to the long-wave region. For example, the maxima of PS of anthracene and pyrene are observed at 672 and 594.5 nm,[13] and the corresponding maxima of the CL spectra are observed at 542 and 477 nm (see Table 1). Therefore, CL is not caused by the emission of triplet-excited hydrocarbons $^3R^*$.

Analysis of the spectral parameters of CL and ECL of the reactions involving radical anions[1,8,11,14,15] and a comparison with the CL spectra of the autooxidation of OSC make it possible to conclude that excimers of hydrocarbons (products of autooxidation of OSC) are emitters of CL.

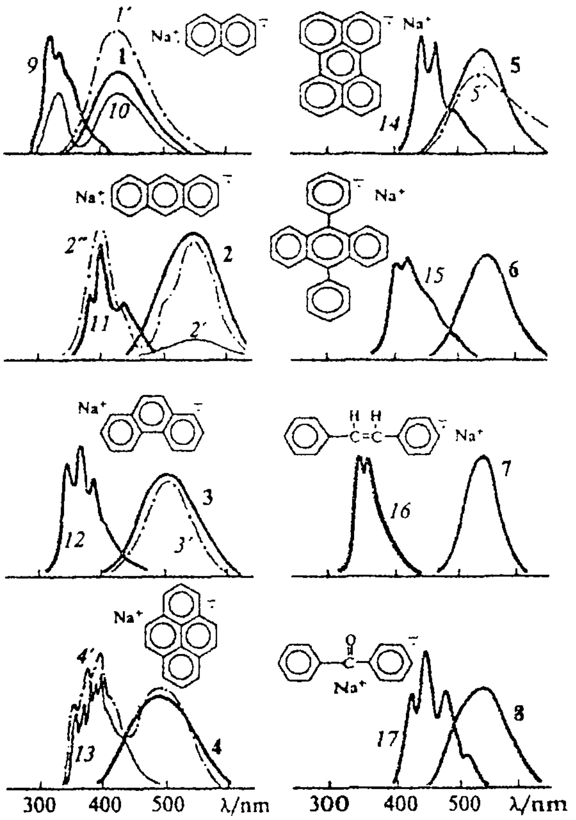


Fig. 2. Spectral parameters of OSC: *1—8*, FL spectra in oxidation by air (300 K, THF) at different [OSC]/mol L^{-1}: **1**, 10^{-3}; **2**, 10^{-4}; **3**, 10^{-3}; **4**, $2 \cdot 10^{-4}$; **5**, 10^{-3}; **6**, $3 \cdot 10^{-4}$; **7** and **8**, $2 \cdot 10^{-3}$. Spectra *1'—5'* and *2''*, published data on the emission of excimers $^1(R \cdot R)^*$: *1'*, FL of naphthalene (77 K, methylcyclohexane);[12] *2'*, FL of anthracene (305 K, THF);[21] *2''*, ECL of anthracene (300 K, DMF);[22] *3'*, ECL of phenanthrene (300 K, DMF);[22] *4'*, FL of pyrene (EtOH); *5'*, ECL of perylene (300 K, DMF).[22] Spectra *9—17*, PL of hydrocarbons (*9—16* at 300 K, *17* at 77 K): *9*, naphthalene (in cyclohexane, λ_{exc} = 265 nm and the same solution after oxidation of **1** (λ_{exc} = 212 nm); *11*, anthracene (in cyclohexane, λ_{exc} = 253 nm); *12*, phenanthrene (in EtOH, λ_{exc} = 212 nm); *13*, pyrene (in cyclohexane, λ_{exc} = 305 nm); *14*, perylene (in DMF, λ_{exc} = 305 nm); *15*, DPA (in cyclohexane, λ_{exc} = 265 nm); *16*, stilbene (in THF, λ_{exc} = 313 nm); *17*, PS of benzophenone (λ_{exc} = 250 nm).

We identified and Na_2O_2 and NaO_2, which are fairly strong oxidants, and aromatic hydrocarbons as the main reaction products.[7,18] Therefore, it was important to determine the possible contribution of their reactions with the other participants of the autooxidation of OSC, *i.e.*, the initial reagents, intermediate or final products, to CL. For this purpose, powder-like Na_2O_2 or a solution of NaO_2 was added to the reaction solution of **1** (10^{-1} mol L^{-1}) + air. In the first case, no effect on CL

Table 1. Energy and spectral parameters of PL of Na-containing derivatives of radical anions of aromatic hydrocarbons in O_2 oxidation in THF

Aromatic hydrocarbon	$-E(R^{\cdot-}/R)$ /eV[a]	$-\Delta H(Na^+,R^{\cdot-}+O_2)$ /eV[b]	E/eV ($^1R^*$/nm)[a]	E/eV ($(R\cdot R)^*$/nm)[b]	λ_{max} PL /nm[b]
Naphthalene	2.79	3.36	3.94 (314)	2.90 (427)	427
Anthracene	1.96	2.52	3.28 (378)	2.30 (540)	542
Pyrene	2.09	2.65	3.34 (371)	2.58 (480)	477
Perylene	1.77	2.33	2.79 (444)	2.29 (540)	540
Stilbene	2.22	2.98	3.79 (327)	—	520
Phenanthrene	2.47	3.03	3.54 (354)	2.40 (516)	520
Diphenylanthracene	1.89	2.45	3.00 (413)	—	560
Benzophenone	2.09	2.65	3.30 (379)[c]	—	525

Note. $-\Delta H(Na^+,R^{\cdot-}+O_2) = E(O_2^{\cdot-}/O_2) - E(R^{\cdot-}/R) - T\Delta S$ (where $E(O_2^{\cdot-}/O_2) = 0.564$ eV,[7] $T\Delta S = 0.2$ eV [2]).

[a] The values were taken from Refs. 2, 3, and 11.

[b] The parameters were obtained in the present work.

[c] The maximum of PL, *i.e.*, the triplet state $^3R^*$, was taken from Ref. 14.

was observed. In the second case, an enhancement of CL was detected. The reactions of a stronger oxidant NaO_2 seem to make a contribution to CL in the autooxidation of OSC. The appearance of CL can be due to both the reaction of NaO_2 with the initial $Na^+,R^{\cdot-}$ and the annihilation of $R^{\cdot+} + R^{\cdot-}$. In the latter case, the radical cation can form in the reaction:

$$R + Na^+O_2^{\cdot-} \longrightarrow R^+ + Na_2^+O_2^{2-}. \tag{1}$$

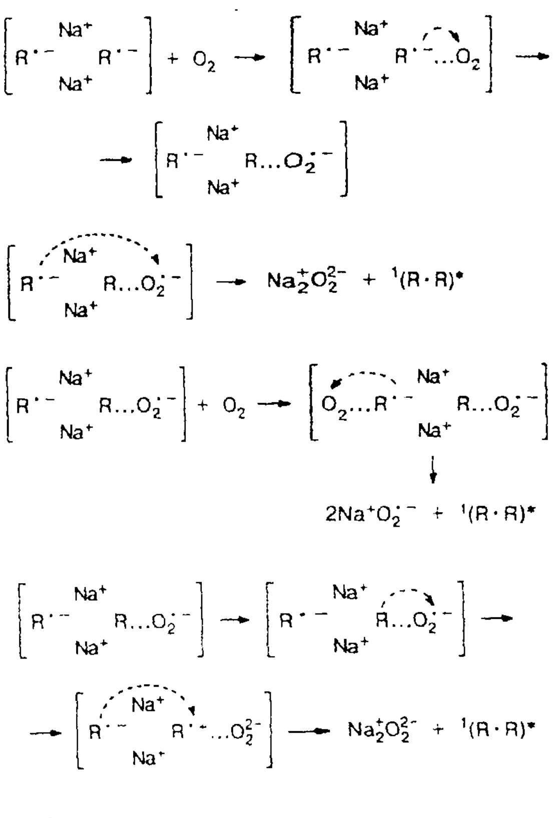
The formation of excimers in chemical and electrochemical reactions is explained by the interaction of the unlikely charged radicals:[2]

$$R^{\cdot+} + R^{\cdot-} \longrightarrow {}^1(R\cdot R)^* \tag{2}$$

or two molecules in the singlet-excited and ground states:

$$^1R^* + R \longrightarrow {}^1(R\cdot R)^*. \tag{3}$$

In both cases, two particles should collide. Therefore, the ability of the contact ion pairs $Na^+,R^{\cdot-}$ to enter various reactions as dimers[16,17] (with different extents of stability) is a more favorable factor for the formation of excimers, because the initial structures of OSC already contain a precursor of the future excimer in the form of two aromatic hydrocarbon fragments (R) that are closely arranged in the dimer. In fact, the interaction of monomeric forms of OSC with O_2 also cannot be excluded, but the probability of the formation of excimers is considerably lower, because the collision of excited and nonexcited hydrocarbon molecules in reaction (3) requires their diffusion through the reaction solution, which increases the probability of the deactivation of $^1R^*$ in other processes. The autooxidation of OSC resulting in the formation of the excimers can be assumed to be the result of subsequent transfer of electrons from the radical anions ($R^{\cdot-}$) that are contained in the dimer (reactions (4)—(9)). When two electrons are subsequently transferred to the same oxygen molecule, sodium peroxide Na_2O_2 forms (see reactions (4) and (5)). When electrons are transferred to different oxygen molecules, superoxide NaO_2 forms (reactions (4) and (6)). Since both compounds were determined as the products of autooxidation, the reaction actually occurs *via* two channels to generate the excimers. The estimation of the heat effects shows that both indicated channels can result in the formation of the excimers. Decomposition of the excimers is accompanied by light emission (reaction (9)). In particular cases, as, *e.g.*, for



$$\left[\begin{matrix} & Na^+ & \\ R^{\cdot-} & & R^{\cdot-} \\ & Na^+ & \end{matrix}\right] + O_2 \longrightarrow \left[\begin{matrix} & Na^+ & \\ R^{\cdot-} & & R^{\cdot-}\ldots O_2 \\ & Na^+ & \end{matrix}\right] \longrightarrow \left[\begin{matrix} & Na^+ & \\ R^{\cdot-} & & R\ldots O_2^{\cdot-} \\ & Na^+ & \end{matrix}\right] \tag{4}$$

$$\left[\begin{matrix} & Na^+ & \\ R^{\cdot-} & & R\ldots O_2^{\cdot-} \\ & Na^+ & \end{matrix}\right] \longrightarrow Na_2^+O_2^{2-} + {}^1(R\cdot R)^* \tag{5}$$

$$\left[\begin{matrix} & Na^+ & \\ R^{\cdot-} & & R\ldots O_2^{\cdot-} \\ & Na^+ & \end{matrix}\right] + O_2 \longrightarrow \left[\begin{matrix} & Na^+ & \\ O_2\ldots R^{\cdot-} & & R\ldots O_2^{\cdot-} \\ & Na^+ & \end{matrix}\right] \longrightarrow 2Na^+O_2^{\cdot-} + {}^1(R\cdot R)^* \tag{6}$$

$$\left[\begin{matrix} & Na^+ & \\ R^{\cdot-} & & R\ldots O_2^{\cdot-} \\ & Na^+ & \end{matrix}\right] \longrightarrow \left[\begin{matrix} & Na^+ & \\ R^{\cdot-} & & R\ldots O_2^{\cdot-} \\ & Na^+ & \end{matrix}\right] \longrightarrow \left[\begin{matrix} & Na^+ & \\ R^{\cdot-} & & R^{\cdot-}\ldots O_2^{2-} \\ & Na^+ & \end{matrix}\right] \longrightarrow Na_2^+O_2^{2-} + {}^1(R\cdot R)^* \tag{7}$$

$$^1(R\cdot R)^* \longrightarrow R + R + h\nu_1 \tag{8}$$

benzophenone, which forms stable dimers, pinacones R—R,[17] the dimer is retained after the light emission. In terms of the mechanism suggested, the annihilation route of the generation of the excimers is also possible due to the oxidation of the R molecule formed at the first stage (reaction (4)) to the $R^{\cdot +}$ radical cation *via* the transfer of an electron to the oxidant, superoxide oxygen ion (reaction (7)). Then $R^{\cdot +}$ reacts with the radical anion to form the excimer (reactions (7) and (8)). This annihilation (stages (7) and (8)) has an unambiguous advantage over the known reaction (2) due to a closer arrangement of oppositely charged radicals. This fact is especially important for hydrocarbons whose radical cations are unstable. For example, it is known that the negative result of the attempt to detect the excited anthracene excimer in annihilation reaction (2) in the ECL system is associated[19,20] precisely with the low stability of the $R^{\cdot +}$ species, which decomposes already before collision with the corresponding $R^{\cdot -}$ radical anion. The ability of the superoxide ion $O_2^{\cdot -}$ to oxidize hydrocarbon molecules to radical cations was estimated from the value of the heat effect calculated from the balance of redox potentials (see Table 1).

It is impossible as yet to decide which of the suggested routes of the formation of the excimers is preferred, the annihilation route ((reactions (7) and (8)) or reactions (5) and (6). It is noteworthy that, unlike ECL of aromatic hydrocarbons (where $^1R^*$ emit),[2] the processes, whose heat effects are sufficient for the formation of excimers of all hydrocarbons studied, occur in the CL system $OSC+O_2$.

The energy released due to the annihilation (reaction (2))[2,3] is often insufficient for the generation of $^1R^*$. Therefore, these chemiluminescence reactions are commonly called "energy-deficient." [2] Our estimations (see Table 1) show that when OSC react with O_2, the heat effect is further lowered. Probably, it is the energy deficiency which is the reason for the absence of the emission of singlet states of hydrocarbons in CL in the autooxidation of OSC. At the same time, the autooxidation of OSC is a quite sufficient energy source for the formation of excimers (see Table 1). The validity of these conclusions is unambiguously confirmed by the detection of the emission from $^1R^*$ in CL when OSC are oxidized by oxidants more stable than oxygen (XeF_2 and Ce^{IV}).[4,5]

It is of interest that, unlike the CL spectrum, the FL spectrum of the reaction solution for several OSC consists of two components. For example, the FL spectrum of **1** consists of a long-wave component, which coincides with the CL spectrum, and a short-wave component caused by the emission of singlet-excited naphthalene (see Fig. 2). The intensity of the latter component increases as the conversion of the reaction increases, and the intensity of the long-wave component decreases down to the complete disappearance after the end of the absorption of O_2. Thus, monitoring PL in the reaction solution makes it possible to follow the accumulation of the reaction product (hydrocarbon) by a change in the intensity of FL of its $^1R^*$ state (it is noteworthy that the initial solutions of OSC do not exhibit PL). The enhancement of the long-wave (excimer) component of PL can be assigned to an increase in the probability of the process (reaction (10)), *i.e.*, the formation of the excimers due to the interaction of the photogenerated $^1R^*$ state with the nonexcited hydrocarbon molecule.

$$R + h\nu \longrightarrow {}^1R^* \xrightarrow{+R} {}^1(R\cdot R)^* \longrightarrow R + R + h\nu \qquad (9)$$

Thus, the reaction of OSC with oxygen is a unique source of the selective generation of hydrocarbon excimers, which have not been detected previously for some hydrocarbons in ECL systems.

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