

Review

CHEMILUMINESCENCE OF ORGANOMETALLICS IN SOLUTION

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(Received January 3rd, 1990)

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INTRODUCTION

Among numerous reactions of organometallic compounds (OMC), those with chemical energy transformed into luminous radiation are considered the most unusual and interesting. The first chemical OMC reactions exhibiting luminescence called chemiluminescence (CL) was discovered by Wedekind [1] in 1906, when the chemistry of organometallics was going through its "childhood". This review is the first research account to cover all reported studies into CL of OMC in solution from 1906 to 1988 inclusive. In early publications, the information on CL of OMC was represented by rather isolated examples [2,3]; thus, very few reactions of adducts of alkali metals and Grignard reagents are described in [2], and only two luminous reactions of rhenium and platinum OMC are analyzed in [3]. Our previous review [4] was concerned with reactions proceeding in both liquid and gaseous phases. Since that publication, a fair amount of new CL reactions have been discovered, those exhibiting excited states of metal ions and free radicals.

As we and our coworkers reported in [5,6], the ability of OMC to enter redox reactions with the subsequent formation of luminescent excited states

can be regarded a new common feature inherent to OMC. Therefore, the formation and deactivation processes of electron-excited reaction products should be considered to gain up-to-date insight into chemical transformations.

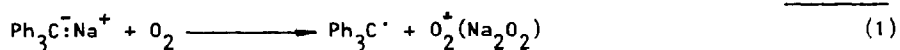
1. CHEMILUMINESCENCE OF ORGANOMETALLICS OF FIRST GROUP METALS OF THE PERIODIC TABLE.

1.1 Reactions of lithium and sodium alkyls, cyclopentadienyls, aryls with oxygen, xenon difluoride, and organic peroxides.

Gilman et al. happened to observe CL with ether solution of PhLi effected by O_2 [7] in their designing of optimal synthetic techniques for lithium alkyls and aryls. Luminescence was also reported with oxidation of solid PhLi, PhNa, and PhK [8]. Both publications just stated the fact that CL occurred. An attempt to detect the CL spectrum (a wide band was obtained in 320-600 nm region) was unsuccessful due to CL absorption by an intensely colored solution even with $[PhLi]=10^{-3}M$ [9]. Recently, CL visible with the naked eye has been observed in reactions of BuLi and CpNa with O_2 [5] as a result of emission by excited aldehydes and ketones formed by oxidating the butyl radical or Cp-ring. Still more recently, CL of a new type was found out with OMC autoxidation; as opposed to CL reported in [6], it is notable that the luminescence emitter is not an organic molecule but the excited intermediate radical $(Ph_3C^*)^*$ formed from reaction of Ph_3CNa with O_2 [10, 11]. In both partially oxidized tetrahydrofuran (THF) and toluene solutions of Ph_3CNa absorption bands (Fig.1) and e.p.r. signals (Fig.2) have been recorded matching those of Ph_3C^* which was synthesized by Gomberg by reaction of Ph_3CCl with zing dust.

Further oxidation by O_2 is followed by disappearance of those absorption bands and e.p.r. signals. The CL emitter was identified by a match with the CL and fluorescence (FL) spectra for Ph_3C^* solution prepared by Gomberg's method as well as by the FL spectrum described in [12,13] (Fig.3). The difference between the FL spectrum of a partially oxidized Ph_3CNa solution and the CL and FL spectra of Ph_3C^* can be rationalized either in terms of radical complexation or of the formation of radical substituted derivatives exhibiting FL at longer wavelength.

On the basis of CL and FL studies [10,11] and of the data reported in [14,15] for the "dark chemistry" of the reaction $Ph_3CNa + O_2$, the following reaction scheme is suggested.



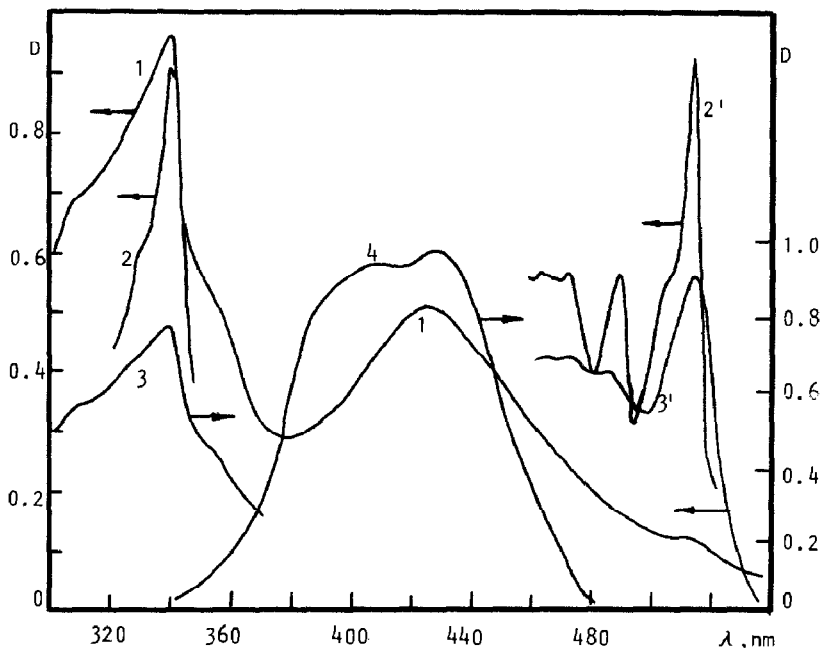
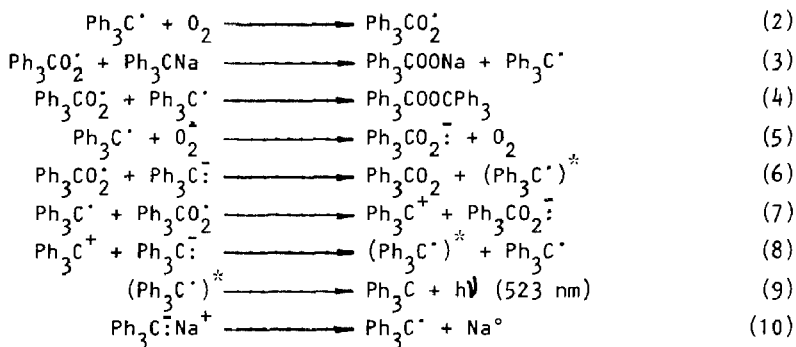


Fig.1 Absorption spectra of triphenylmethyl prepared by different techniques (1-3). (1) by partial O_2 oxidation of 0.03M solution of triphenylmethylsodium in THF [11]; (2,2') by γ -radiation of 10^{-4} and $5 \cdot 10^{-3}$ M solutions, respectively, of triphenylmethylchloride [12]; (3,3') with 0.0002M and 0.002M solutions, respectively, of the radical synthesized by Gomberg's reaction in THF, 300 K [11]; (4) 0.0005M triphenylmethyl cation in 98.3% sulfuric acid, 300 K [11].



Reactions (6) and (8) are inferred as the most obvious source of the excited emitter $(\text{Ph}_3\text{C}^\cdot)^*$.

Weak CL observable only with a photomultiplier (PEM) was investigated in reactions of BuLi with benzoyl, lauryl, and tert-butyl peroxides in organic solvents by FL, PMR, IR, UV spectral methods [16]. The energy released in

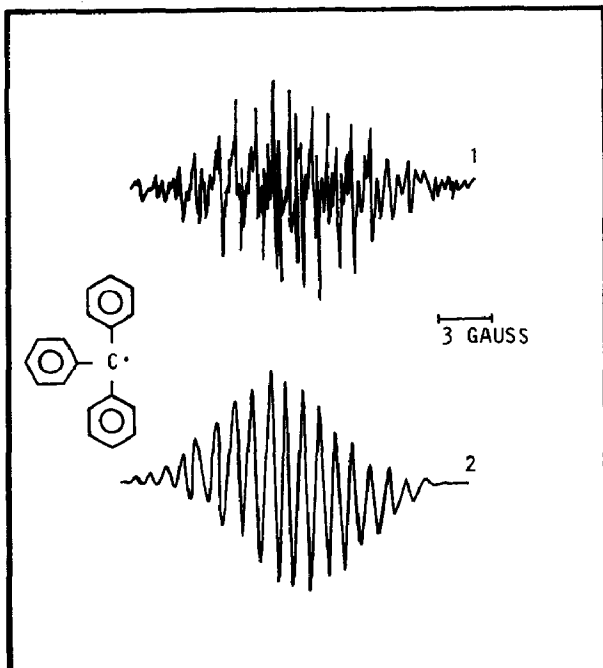


Fig.2 EPR spectra of triphenylmethyl prepared by different techniques in THF. (1) with partially O_2 oxidized triphenylmethylsodium; (2) by Gomberg's reaction.

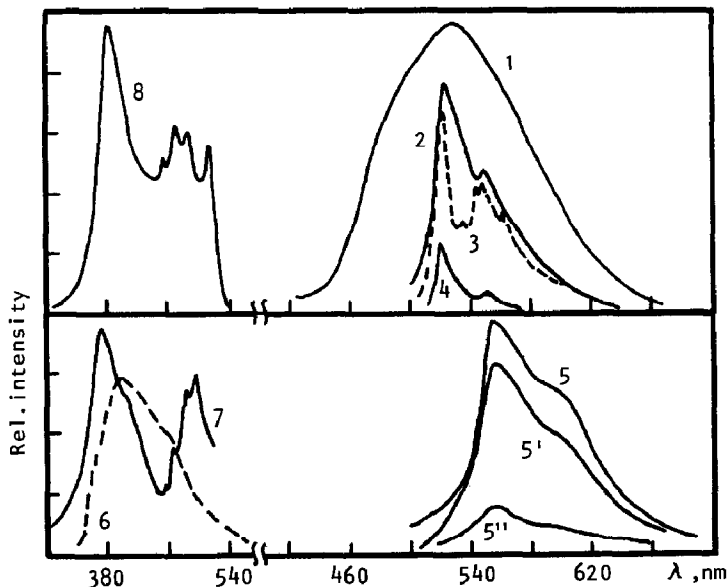


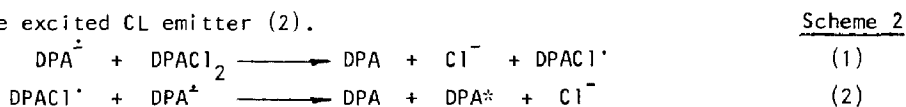
Fig.3 Spectra of CL(1), FL(2-6), and excited FL(7,8) for the triphenylmethyl radical. (1) 0.2M triphenylmethylsodium with O_2 in THF, 300 K [11]; (2) 0.002M species synthesized by Gomberg's method, 300 K [11]; (3) as in (2), 77 K; (4) reported measurements [12]; (5) partially oxidized triphenylmethylsodium, 300 K [11]; (5', 5'') with further oxidized triphenylmethylsodium; (6) 0.0005M solution of triphenylmethyl cation in sulfuric acid [11]; (7) λ (excitation) = 350 nm; (8) reported data [12].

the first reaction step $\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ph} + \text{BuLi} \longrightarrow \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OLi} + \text{Bu}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ph}$ is accepted by butyl vinyl ketone in the second reaction step $\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Bu} + \text{BuLi} \longrightarrow \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Bu} + \text{BuOLi}$, but the primarily excited product

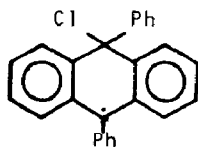
from which energy was transferred was not identified. The final products are formed in the third step $\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Bu} + \text{BuLi} \longrightarrow \text{Ph}-\text{CBu}_2-\text{OLi}$. The complex of butyl phenyl ketone with lithium alcoholate was recognized to be a CL emitter mainly because the CL spectrum (wide bands in 400-600 nm region) did not agree with the FL spectrum for alkyl phenyl ketones but it was close to the FL spectrum for a heptane solution of acetonitrile and BuLi ($\lambda_{\text{max}} = 460 \text{ nm}$). The second emitter (emission at 540 nm) remained unidentified.

1.2. Reactions of polycyclic hydrocarbon adducts of alkali metals and their ketyls with electron acceptors and oxygen.

Chandross et al. originally discovered a new class of bright CL reactions with electron transfer for a number of adducts of alkali metals with polycyclic and aromatic hydrocarbons upon reaction with organic and inorganic electron acceptors [17,18]. The CL and FL spectra were bright enough to allow the identification of the CL emitting species as the organic moieties of the adducts. The first stage of electron transfer from the OMC anion-radical to the electron acceptor was shown to be common to all these reactions. If organic and inorganic compounds containing chlorine act as electron acceptors, the reaction results in unstable intermediate radical DPACl' (DPA stands for diphenyl anthracene) as in (1) (Scheme 2). That intermediate reacts further with another OMC anion-radical and accepts an electron from the latter with the concomitant elimination of a chlorine ion to lead thus to the excited CL emitter (2).



where DPACl' is



The transfer of an electron from $\text{DPA}^{\dot{-}}$ into DPACl' can yield DPACl^{-*} if the electron enters the lowest antibonding level of the radical DPACl'. An analogous CL scheme was assumed for the oxidation of sodium naphthalenide with the same oxidant. CL arises only upon OMC oxidation with an aromatic peroxide.

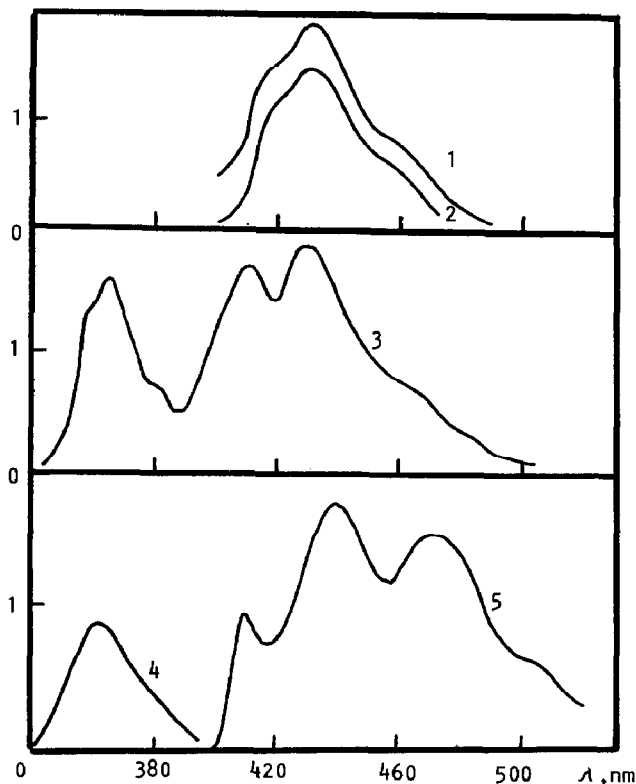
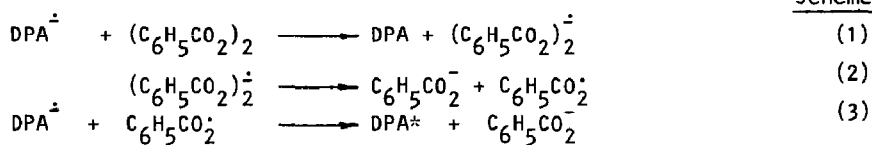


Fig.4 (1) CL spectrum for the potassium adduct of 0.03M DPA and 0.04M benzoyl peroxide (BPO) in dioxane [18]; (2) FL of DPA; (3) CL spectrum of the potassium adduct of 0.05M N-phenylcarbazole and 0.04M BPO in dioxane [18]; (4) FL of 0.01M N-phenylcarbazole in dioxane; (5) phosphorescence of N-phenylcarbazole, 80 K, λ (excitation)=300 nm [18].

The effect of the nature of the peroxide on the absence or presence of luminescence impelled the authors of [17,18] to advance a somewhat different mechanism of CL for the reaction with benzoyl peroxide.



Scheme 3

The above scheme is unusual in that the electron transfer to the peroxide acceptor is followed by decomposition of the latter into benzoate ion and benzoate radical (2). The CL emitter is excited by electron transfer from the higher bonding orbital of another OMC anion-radical to the benzoate radical (3). The absence of CL upon oxidation with aliphatic peroxides as opposed to arylcarboxylate radicals is explained by that the stability of an arylcarboxylate radical is much higher than that of an alkylcarboxylate radical. Thus, alkylcarboxyl radicals might decarboxylate before they could react with $\text{DPA}^{\dot{-}}$ to form excited molecules $\text{DPA}^{\dot{*}}$.

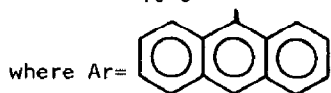
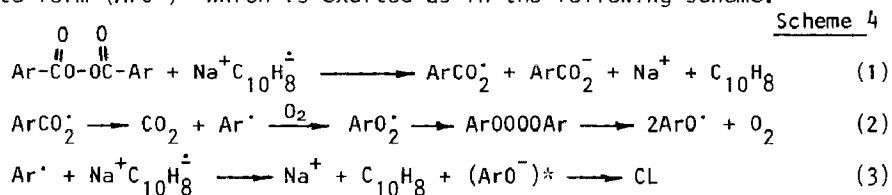
CL spectra of sodium and potassium adducts of N-phenylcarbazole with

the exception of N-phenylcarbazole FL at 365 nm show a long wavelength component at 410 and 430 nm (Fig.4). Eximer and phosphorescence possibilities were considered to account for the long wavelength CL, the latter being preferred [18]. Later on, Chandross rejected that interpretation of the CL emitter; he assumed that CL was caused by the emission of carbazole anion, formed upon the phenylcarbazole decomposition [19].

The excitation of polycyclic hydrocarbons in reactions of their OMC with positively charged ions was demonstrated by Weller et al. [20]. An ethereal solution of the adducts of aromatic anion-radicals was let flow through a powdered mixture of glass and crystalline Wurster's blue cation: $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{C}_{10}\text{H}_8^+(\text{WB}^+\text{C}_{10}\text{H}_8^-)$; the CL spectra were found to be similar to the FL spectra of aromatic hydrocarbons (Ar) such as chrysene, picene, pyrene, 1,2-benzanthracene, anthracene, perylene, tetracene. Besides, phosphorescence bands and eximer emission were recorded for chrysene and pyrene anions, respectively. The thermal effect in the reaction $\text{Ar}^- + \text{WB}^+$ was in all cases insufficient to excite even the lower singlet states of the CL emitters, while being enough to generate triplet molecules. Therefore, the CL emitter is most obviously generated through consecutive steps: $\text{Ar}^- + \text{WB}^+ \longrightarrow {}^3\text{Ar}^* + \text{WB}$ and ${}^3\text{Ar} + {}^3\text{Ar}^* \longrightarrow {}^1\text{Ar} + \text{Ar}$.

A bright blue CL can be seen also in a homogeneous CH_3CN solution of $\text{WB}^+\text{C}_{10}\text{H}_8^-$, that being perceived in not too bright daylight.

No CL was found upon reaction of $\text{NaC}_{10}\text{H}_8$ with di-9-anthranoyl peroxide in an argon atmosphere, while in the presence of O_2 in diglyme solution a bright yellow CL was visually identified [21]. CL and FL spectral assignments are given in Fig.5. The CL arises from emission by anthrone in its anthronolate form $(\text{ArO}^-)^*$ which is excited as in the following scheme.



The radical $\text{ArCO}_2^{\cdot-}$ formed in the first stage (1) is decarboxylated to radicals Ar^{\cdot} which react with oxygen to give peroxy and oxyl radicals of anthracene (2). The CL emitter is then generated by electron transfer from anti-bonding orbital to that of 9-oxyanthracene (3). As reported in [2a], the authors of [22] observed no CL when oxygen reacted with $\text{Na}^+\text{C}_{10}\text{H}_8^{\cdot-}$. This is surprising,

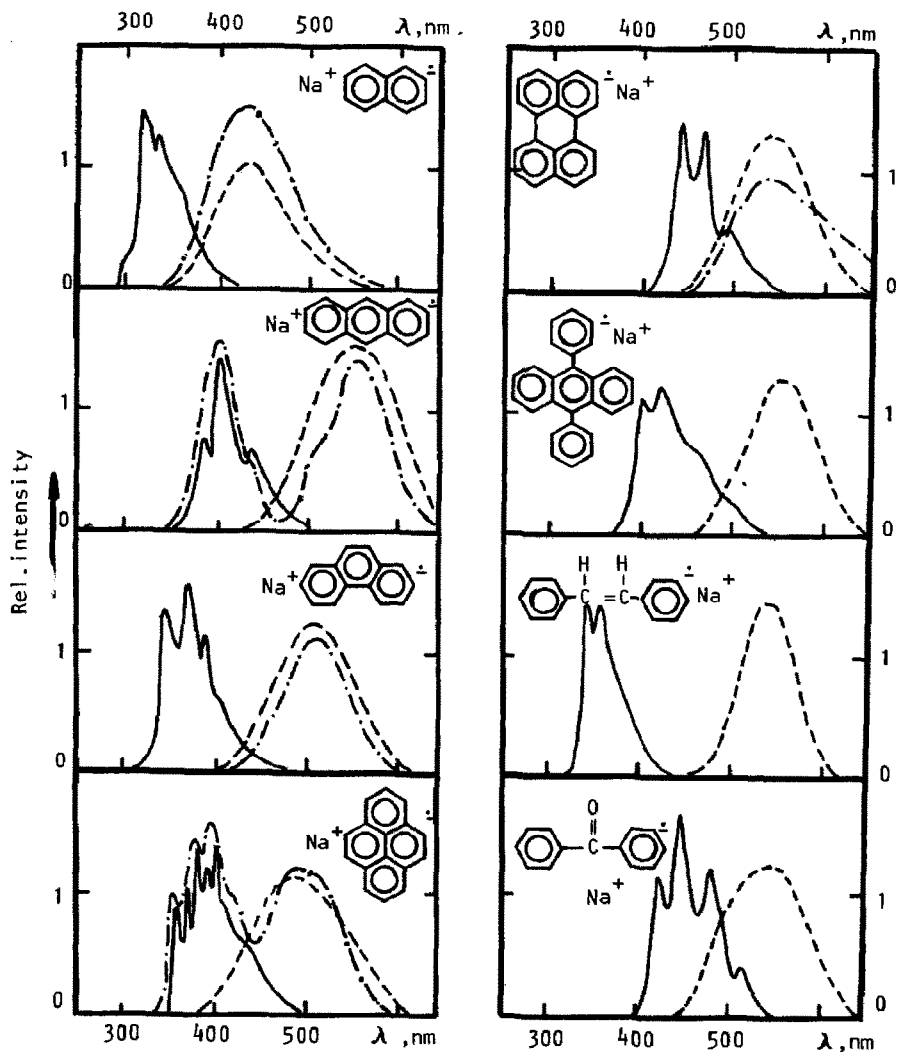


Fig.6 ——— FL spectra of aromatic hydrocarbons in THF, 300 K [23,24];
 ----- CL spectra registered upon autoxidation of sodium adducts of aromatic hydrocarbons in THF, 300 K [23,24];
 FL spectra (77 K) and electrochemiluminescence (ECL) spectra for aromatic hydrocarbon eximers (ECL only for phenanthrene and anthracene, 300 K [24]).

Thus, solid sodium peroxide poured into THF gives rise to CL which is close to the CL observed on autoxidation of sodium OMC, but its intensity is much lower and its spectrum is reproducible only with glass filters. It appears that metallic sodium added to argon-saturated THF (with O_2 traces) also yields a CL which is two orders of magnitude brighter when air is bubbled through the solvent. We have attributed that CL to the ionization of sodium with ether

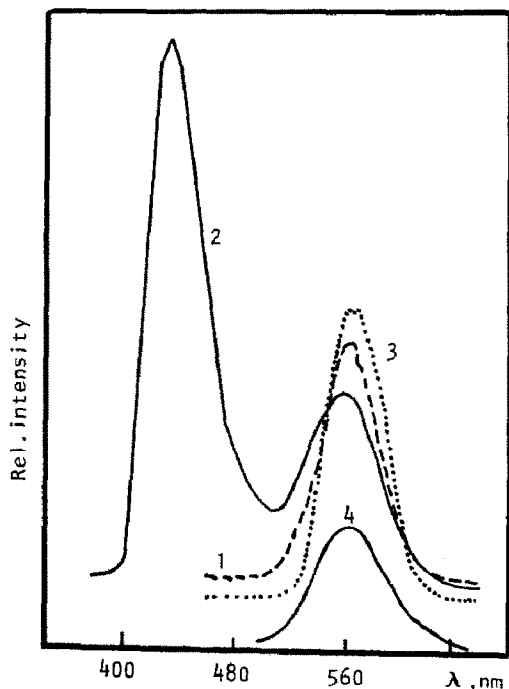
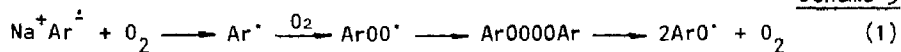


Fig.5 (1) CL spectrum for 0.0004M di-9-anthranoyl peroxide and 0.01M sodium naphthalenide with oxygen in dimethoxyethane (DME) [21]; (2) FL spectrum for the above solution after reaction; (3) FL spectrum for 0.0004M anthrone in KOBu(t) solution in DME [21]; (4) CL spectrum for 0.01M sodium naphthalenide and oxygen in THF [23,24].

since CL was easily identified visually when the sodium adducts of anion-radicals of many aromatic hydrocarbons reacted with O_2 [23,24]. Further, the CL is observed in autoxidation of the blue solution of sodium benzophenone ketyl which is widely used experimentally.

A comparison of CL and FL spectra unambiguously indicates that singlet-excited states of aromatic hydrocarbons are not CL emitters, but maximum bands in the CL spectra agree well with the known emission of those hydrocarbons' eximers generated either electrochemically [24a] or upon photoirradiation (Fig.6). Both CL and eximer emissions reveal their wide band maxima without detailed vibrational structures. This provides a basis for the assumption that CL results from the emission of aromatic eximers $^1(ArAr)^*$ which can be excited by impact and as $^1Ar^* + Ar \rightarrow ^1(ArAr)^*$ or ion-ion annihilation and as $Ar^+ + Ar^- \rightarrow ^1(ArAr)^*$. The alternative suggestion has been made that the CL is a species similar to anthrone in its anthranolate form $(ArO^-)^*$, which is excited as in Scheme 5.

Scheme 5

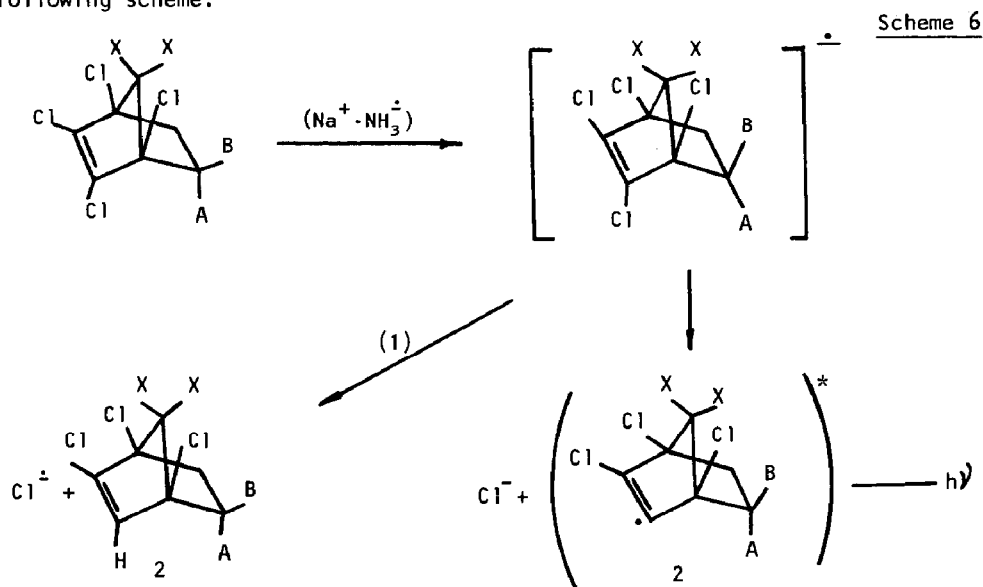


In the autoxidation of sodium anion-radicals of hydrocarbons, light emission can be observed in reaction of different other components of the system.

to form the related adduct which gives CL through its further reaction with oxygen: $\text{Na}^\circ + \text{S} \longrightarrow (\text{Na}^+\text{S}^-) \xrightarrow{\text{O}_2} \text{CL}$. The oxidation of sodium adducts of aromatic hydrocarbons with XeF_2 gives a visible CL which is still much brighter than with O_2 [5].

1.3. Reactions of alkali metal solutions with chloronorborene derivatives in liquid ammonia.

An interesting type of visible green CL was reported for various chloronorborene derivatives (THF solutions) with electron-donating solutions of Li, Na, and K in liquid ammonia [25]. The CL mechanism suggested here the following scheme.



where M - metal; X, A, B - substituents such as Cl, H, OMe, OBU and OAc, OH, CO_2Et .

The first stage here involves electron transfer to the acceptor molecule to give an anion-radical which eliminates a chloride anion. The basic difference between the above scheme and that given by Chandross [19] is that the CL was assigned to the vinyl radical in its $^2\Pi$ -state rather than to an organic molecule. That vinyl radical upon transition to its ground state $^2\Sigma$ releases 2.4 eV energy corresponding to green luminescence (2.2-2.5 eV). The main route for transformation of the $^2\Pi$ vinyl anion radical is nonadiabatic, i.e. radiationless (1). The alternative adiabatic transition $^2\Pi \longrightarrow ^2\Sigma$ (2) is favoured by both geometric (pyramidalization of the olefinic carbon atom) and electronic

(substituent) factors. The latter is displayed by the presence of the required substituent. CL reveals its highest brightness with substituents X-OMe, A-OH, B-H involved in the initial substrate.

In addition to norbornene chloroderivatives, Birch transformations yielded CL with bromoanalogues too [25].

2. CHEMILUMINESCENCE OF ORGANOMETALLICS OF SECOND GROUP METALS OF THE PERIODIC TABLE.

2.1. Reactions of Grignard reagents with haloidpicrines.

The history of OMC chemiluminescence started from the observations made by Wedekind for reactions of PhMgBr with chloropicrine [1,26]. Unfortunately, almost all abstracts from that pioneer report were inadequately cited by the authors of research works concerning CL with Grignard reagents [27-47] as well as by the authors of the recently published book [28]. In honour of the discoverer, that CL was called the "Wedekind reactions". Later on, luminescent reactions were observed with some other Grignard compounds [34-36], iodides exhibiting the brightest CL. On the contrary, CL intensity is higher with chloropicrine and bromopicrine than with iodopicrine. The CL recorded in vacuo using a photoelectron multiplier was different from that caused by oxygen [44]. The mechanism of the "Wedekind reaction" remains unstudied.

2.2. Reactions of Grignard compounds with oxygen. The effect of magnetic field. Electrochemiluminescence (ECL).

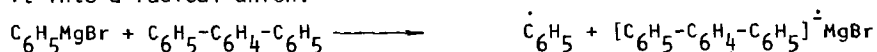
Following Wedekind, Heczko originally observed CL upon contact of Grignard reagents (PhMgBr, PhMgI) with air [28,29]. In his experiment, a Grignard reagent was slowly poured onto a sloping black board. Later, that discovery was wrongly ascribed to Wedekind [47].

Extremely bright CL was first observed by Spatch in the reaction of p-ClC₆H₄MgBr with O₂ [31]. That dark blue CL was brighter than in oxidation of luciferin, and this was confirmed by the pyrometric measurements of brightness in both reactions [36]. In the oxidation of p-BrC₆H₄MgBr, the CL was somewhat fainter [36]. This CL was given the name "Moeller-Evans reaction" [35] and, as observed in a 0.5 l flask, emitted greenish-blue light bright enough for reading a printed paper [35].

It can be concluded from the CL regularities with Grignard reagents reported in early works that the nature of the organic fragment is of paramount importance. Isocyclic radicals favour the emission of more light than acyclic ones do. For both types, the CL is brighter when magnesium is attached to an unsaturated carbon atom. The substitution of one hydrogen

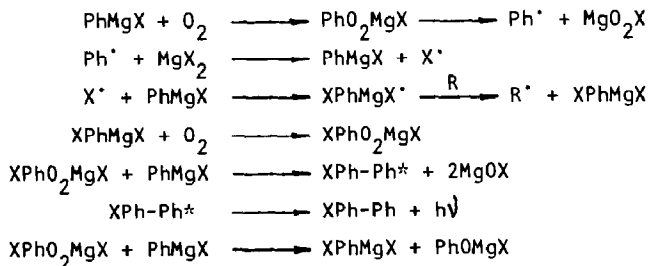
in the benzene ring for any other atom or radical increases the intensity of luminescence. The substitution position also affects the CL, the brightness decreasing in the series p->o->m- [39]. With the same chemical nature and position of the substituent, OMC with higher weight radicals exhibit the brighter luminescence. With change in the substituent (X) in ArMgX, the CL intensity reduces in the series Cl>CH₃>Br>I.

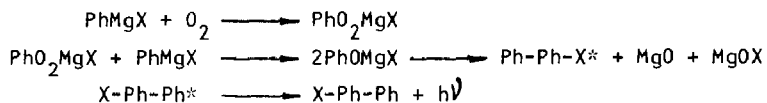
Photographic CL spectra of the reaction of Grignard reagents with O₂ (3-12 hs exposure) [37] gave the first experimental recordings of CL with synthesized species. Previous luminescence photographs were only with natural species such as bacteria. Organomagnesium chlorides showed longer wavelength (green)CL, and organomagnesium iodides showed shorter wavelength (blue) CL [37]. With a substituent position in the benzene ring, the CL wavelength increases in the series m->o->p- [36]. In some early works as well as in those published later, the FL intensity was found to grow during the course of oxidation of Grignard reagents. The initial assignments [36,39,43] of different species to the CL and FL emitters were considered wrong in recent papers [9,46], since the most intense bands are positioned similarly in the CL and FL spectra, e.g. 448 and 518 nm for C₆H₅MgBr and p-ClC₆H₄MgBr, respectively. Bardsley and Hercules suggested the following reaction mechanism [9]: the starting C₆H₅MgBr reacts with p-terphenyl which is produced to transform it into a radical anion.



which is then oxidized by O₂ or peroxide to generate singlet-excited p-terphenyl, which was believed to be the CL emitter. Bolton and Kearns questioned identification and suggested brominated biphenyls to be the emitters [46]. An attempt made to choose between these possibilities by observing the effect of inhibitors upon luminescence brightness appeared to rule out both the molecular and free-radical mechanism for the CL excitation, and two alternative schemes were suggested.

Scheme 7





Both schemes assume reactions of organomagnesium peroxide to be the excitation source, but there is no experimental evidence as to stage at which light is emitted.

The effect of magnetic field upon the oxidation of Grignard reagents by O_2 was originally found by Dufford et al. [40] when a strong field of 1500 gauss was applied to a solution of $\text{C}_6\text{H}_5\text{MgBr}$ being oxidized by O_2 . One effect was visible clearly: there was a distinct tendency for most of the emission to occur in the most intense regions of the field, near the pole pieces. The authors assumed that field interactions with labile paramagnetic species were responsible for the effect.

Electrochemiluminescence (ECL) of Grignard reagents was reported by Dafford [40] upon electrolysis of an ether solution of $\text{C}_6\text{H}_5\text{MgBr}$. The luminescence was so much bright that the contours of the Pt electrodes could be seen at a distance of six metres. The nature of the emission during electrolysis was assumed to be different from that during the reaction of Grignard reagents with oxygen [40], while an opposite opinion was also reported [41]. Those visual observations of ECL were later confirmed by the luminescence registered (PEM) under milder conditions of electrolysis [44,45]. Upon electrolysis conducted in vacuo, the emission disappeared after a period of time, providing support for the assignment of anodic ECL to the reaction of impurities containing oxygen which is released upon electrolysis [44]. This observation casts doubt on whether "pure" ECL can occur with Grignard reagents.

2.3. Reactions of Grignard reagents with organic peroxides, benzene triozonide, and carbon tetrachloride.

A somewhat less bright CL was visually identified in reactions of Grignard reagents with benzoyl, ethyl, and diacetyl peroxides than with oxygen [38].

Bright red CL in the reactions of $\text{C}_6\text{H}_5\text{MgBr}$, $p\text{-ClC}_6\text{H}_4\text{MgBr}$, and $p\text{-CH}_3\text{C}_6\text{H}_4\text{MgBr}$ with benzoyl peroxide and tert-butyl peroxybenzoate in diethyl ether or THF was discovered and studied by Bolton and Kearns [47]. Neither aliphatic Grignard compounds nor diphenylmagnesium exhibited similar CL [47].

A good match between the CL and the FL spectra obtained for the solut-

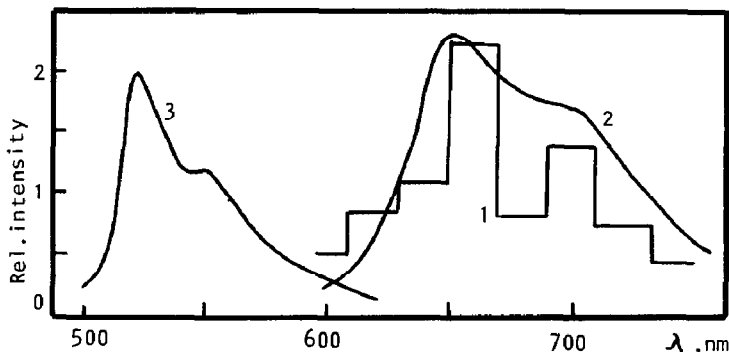


Fig.7 (1) CL spectrum measured with boundary filters for phenylmagnesium - bromide peroxide with BPO in diethyl ether [47]; (2,3) FL spectrum for triphenylmethyl prepared in reaction of triphenylmethylchloride with zinc dust, 300 K, λ (excitation)=447 nm; (2) [47]; (3) [10,11].

ion of Ph_3C^* prepared by Gomberg identified the radical $(\text{Ph}_3\text{C}^*)^*$ as the CL emitter [47] (Fig.7). However, the Ph_3C^* solution prepared in our institute by the same method revealed no FL in the red spectral region (300, 77 K) and showed distinct FL at 523 nm (Fig.7) [10,11] in good agreement with the literature data [49-51]. The red CL exhibited by PhMgBr with benzoyl peroxide is probably of different nature, e.g. it can be excited by the emission of substituted Ph_3C^* derivatives which radiate in the longer wavelength red spectral region [50].

Upon contact of Grignard reagents with different species as H_2O , N_2O , H_2O_2 , SO_2 , CO , NO_2 , CO_2 , Na_2O_2 , no visual CL was observed, while a few reacted violently to liberate much heat [32,33,35]. Grignard reagents mixed with benzene triozonide resulted in CL visible to the eye [36]. Bright red CL was also mentioned for the reaction of PhMgBr with CCl_4 [44]. However, no CL arose in the absence of O_2 which was removed under high vacuum [44].

2.4. Reactions of $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Mg}$ and $(\text{C}_5\text{H}_5)_2\text{Mg}$ with oxygen.

The CL found for the oxidation of $(n\text{-C}_3\text{H}_7)_2\text{Mg}$ and $(\text{C}_5\text{H}_5)_2\text{Mg}$ with O_2 is less bright than that for Grignard reagents [6,52]. The starting $(\text{C}_5\text{H}_5)_2\text{Mg}$ solution displays FL at 440 nm (probably connected with impurities); following oxidation, that is further transformed into the long wavelength FL with its maximum matching the CL maximum at 560 nm. Thus, a stable autoxidation product is proved to be the CL emitter, and this is possibly an excited ketone formed by oxidation of the OMC Cp-ring. An attempt was made to determine the role of free radicals in those processes, but after the introduction of galvinoxyl as an inhibitor, the rate of O_2 absorption by $(\text{C}_5\text{H}_5)_2\text{Mg}$

was not decreased and the CL faded abruptly.

2.5. Reactions of Ca organics with oxygen. Oxidation of $(C_2H_5)_2Zn$ by oxygen and xenon difluoride. Autoxidation of $(C_5H_5)_2Hg$.

PhCaI is one of the first "nonmagnesium" OMC which exhibited CL seen with the naked eye [38]. Upon oxidation by O_2 , PhCaI displays yellow luminescence comparable in intensity to that of PhMgI. CL was not visually observed for EtCaI [38].

No CL was observed in oxidation of Hg- and Zn-organic compounds such as C_6H_5HgBr , $p-CH_3C_6H_4HgBr$ [45], C_6H_5ZnBr , C_6H_5ZnI , $p-BrC_6H_4ZnBr$ [43] by oxygen. However, zinc and mercury OMC are capable of exhibiting CL in solution. Et_2Zn oxidized by O_2 and XeF_2 in toluene reveals rather bright CL ($4.7 \cdot 10^8$ and $1.0 \cdot 10^9$ photon/S·ml, respectively), rapidly fading with time [5,6].

The CL much less bright in autoxidation of $(C_5H_5)_2Hg$ in $5 \cdot 10^{-2} M$ THF solution ($I = 1.4 \cdot 10^6$ photon/S·ml after 0.5 hour air bubbling at $55^\circ C$) [53]. The low brightness of the CL is connected with the slow rate of autoxidation (ca. 1ml of O_2 absorbed per 1h at 298 K). The CL spectrum was measured with a set of boundary glass filters to be in the region of 400-600 nm with its broad maxima at 470, 530, and 580 nm. The starting OMC gives no FL; it appears only after oxidation, and then in the region of the short wavelength CL maxima characteristic of the emission of ketones formed as oxidation products of the Cp-ring.

3. CHEMILUMINESCENCE OF ORGANOMETALLICS OF THIRD GROUP METALS OF THE PERIODIC TABLE.

3.1. Reactions of organoaluminium compounds (OAC) with oxygen.

"Chemical luminescence" is considered a characteristic feature of OAC. Indeed, CL was registered for both cyclic and acyclic OAC [54-63]: trialkyl-aluminium compounds with the number of carbon atoms ranging from two to twenty, their hydride- and halide-substituted derivatives, norbornene, isocamphene, and cyclohexene derivatives, as well as OAC complexes with lithium and coordination compound of ruthenium $Ru(bpy)_3Cl_2$. In $10^{-1-1} M$ solutions, the majority of those compounds display bluish-green CL identified visually in a darkened room. For rapidly oxidized OAC (C_2-C_8), the formation of kinetic CL maxima is conditioned by a combination of three main factors: (i) kinetic - accumulation and consumption of the intermediate OAC peroxides; (ii) diffusion - abruptly falling rate of OAC oxidation at the starting reaction point due to rapid consumption of the solved oxygen, and subsequently

growing oxidation rate due to the increase in the O_2 concentration, caused by the O_2 dissolving from the air flow; (iii) deactivation - removing and establishing the quenching effect of O_2 . That deactivating factor reveals itself in the increase of CL intensity with air bubbling through the reaction solution (open cell) (Fig.8).

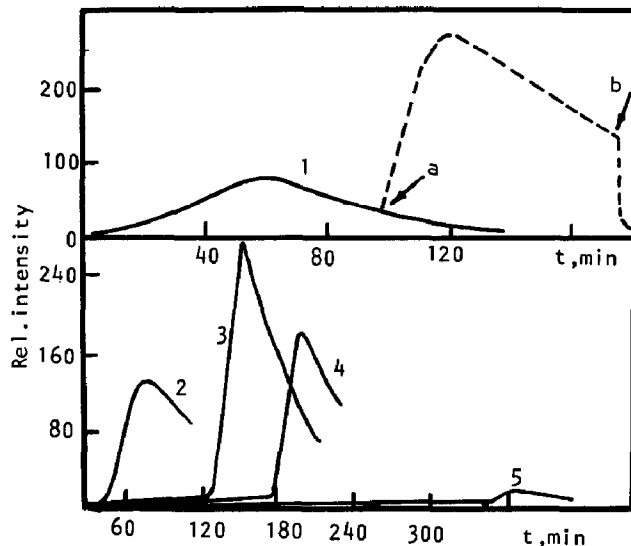


Fig.8 Deactivating effect of oxygen on CL in autoxidation of diethoxyethylaluminum in toluene, 300 K, [56]. (1) $[OAC] = 1M$; (a) with air bubbling off and Ar inlet; (b) with air bubbling on and Ar off (open cell); (2,3) $[OAC] = 0.1, 0.025, 0.02, 0.015M$ with $0.006M$ starting oxygen (closed cell).

The induction period of CL occurs because oxidation in a closed cell (without any gaseous phase) exhibits CL only after the consumption of O_2 has reached its critical value in the solution (O_2 is a quencher of a CL emitter).

In oxidation of OAC of the R_3Al type (R - alkyl), the CL is determined by the total contribution of emission arising at each stage of the successive oxidation of all three Al-C bonds, i.e. initial R_3Al and two intermediates R_2AlOR , $RAI(OR)_2$ [55]. The intensity of CL in this OAC series decreases due to the lowered oxidation rate. Therefore, in the slow oxidation of OAC, the shape of the kinetic curve is determined particularly by the accumulation and consumption of the organoaluminum peroxides. The involvement of those intermediates of OAC autoxidation in CL excitation was shown also by observing CL in the reaction of the stable peroxide $(C_2H_5O)_2AlOOC(CH_3)_3$ with $(i-C_4H_9)_3Al$. Since only the consumption of peroxide occurs in this reaction, the CL kinetics are described by a sloping curve.

Upon OMC autoxidation, the involvement of free radicals in causing emission was first proved by the inhibition of the chemiluminescent reaction $(C_2H_5O)_2AlC_2H_5 + O_2$ [56]. The absorption of oxygen ceases and the CL intensity is abruptly lowered immediately after the galvinoxyl addition. After a short

induction period during which the inhibitor is consumed, both suspended processes are resumed (Fig.9).

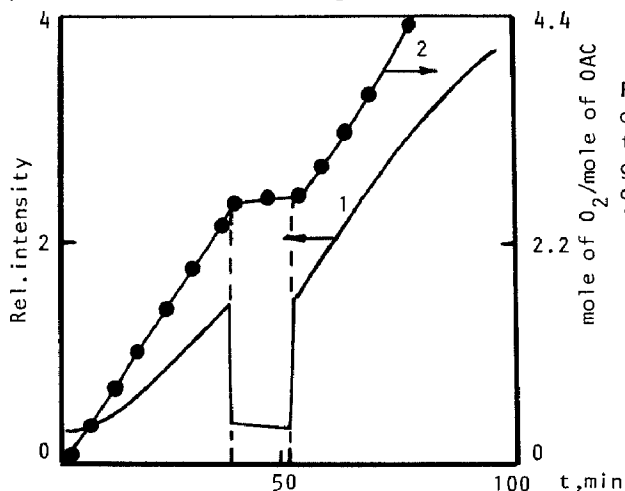
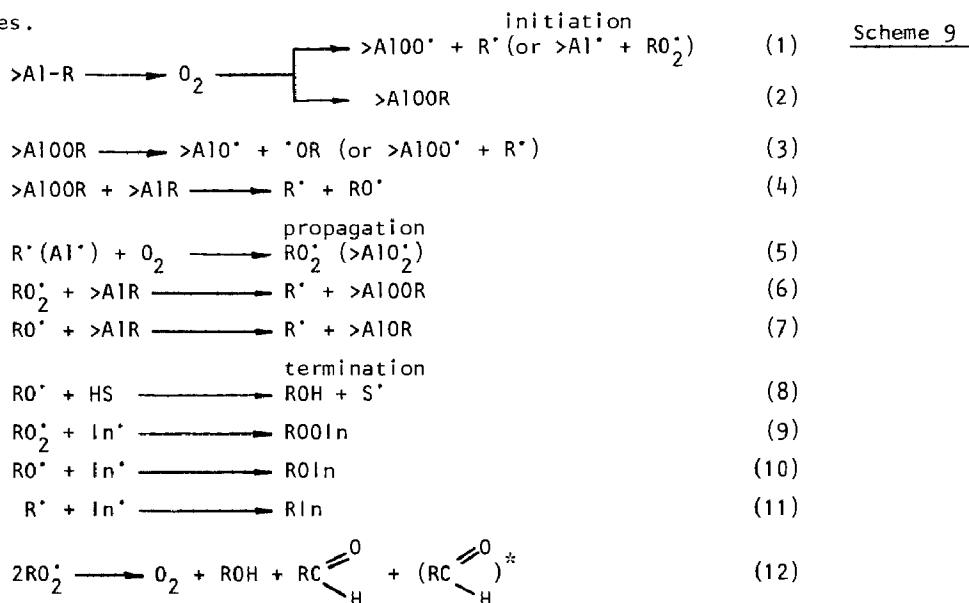
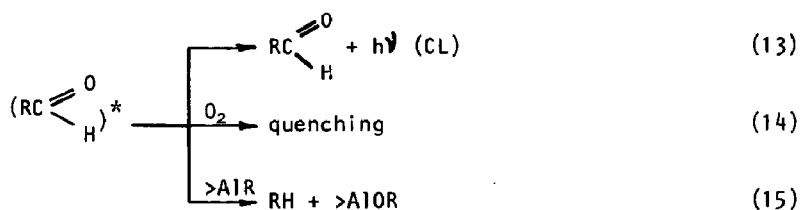


Fig.9 Inhibited CL (1) and oxygen absorption (2) with the addition of 0.00001M galvinoxyl upon autoxidation of 0.1M diethoxyethylaluminium in toluene [56].

The free-radical mechanism of the "dark" autoxidation of $(\text{CH}_3)_3\text{Al}$ and $(\text{C}_6\text{H}_5)_3\text{Al}$ was originally demonstrated by Davies et al. [65] by a decrease in the overall amount of absorbed oxygen. The results of the CL investigation carried out in our institute [54-63] and the reported mechanism of OMC "dark" autoxidation [65-68] lead to the following scheme to account for the formation of the products of the alkyl OAC autoxidation in their ground and electron-excited states.



Scheme 9



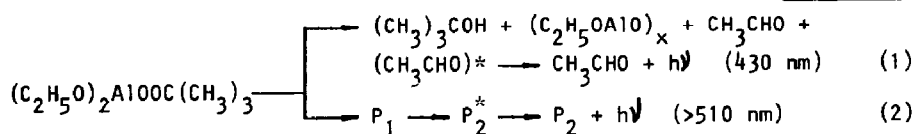
Initiation involves the interaction of OAC with both oxygen (1) and intermediate organoaluminium peroxides (4). The formation of radicals during (4) was established by the method of spin traps [69] as well as by the abrupt decrease in the CL intensity when an inhibitor was introduced into the chemiluminescent diethoxyethylaluminium solution following the removal of O_2 from the solution [56]. With the decomposing organoaluminium peroxide (3), the initiation does not occur with all types of OAC. Thus, for OAC possessing a hydrogen atom at the α -carbon in their alkoxy groups as $(\text{C}_2\text{H}_5\text{O})_2\text{AlC}_2\text{H}_5$, decomposition of the related peroxides occurs by an intramolecular mechanism [59,69] to give no free radicals; processes (1) and (4) are the main initiating reactions for these OAC. Accounting for the data on CL inhibition and oxygen absorption and in view of that CL maximum for R_3Al is in the region assigned for the emission of alkyl compounds each incorporating a carbonyl group, the CL emitters were attributed to excited aldehydes (or ketones) generated through the disproportionation of peroxide radicals (12,13)[6,55]. The latter process is a side reaction to the formation of alkoxides as the main products; the strong CL exhibited by trialkylaluminium compounds results mainly from their high oxidation rate. The CL emitter is quenched by oxygen (14) and by the chemical reaction with OAC (15). Earlier, Vasil'ev and his colleagues reported that ketones were excited owing to the disproportionation of the radicals RO_2^{\cdot} in the oxidation of hydrocarbons [55a].

3.2. Thermolysis and hydrolysis of organoaluminium peroxides.

CL was observed in thermolysis studies with the relatively stable peroxide $(\text{C}_2\text{H}_5\text{O})_2\text{AlOOC}(\text{CH}_3)_3$ [58,59].

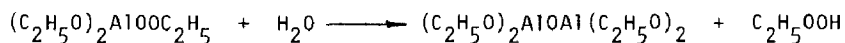
From data on the "dark" thermolysis of that peroxide [69] and on CL and FL spectra [59], the following scheme was suggested for the products formed in their ground and excited states.

Scheme 10



Scheme 10 shows P_1 and P_2 which stand for unidentified products. Intramolecular oxidation of the peroxide alkoxy group gives acetaldehyde as the CL emitter in its excited state together with unexcited aldehyde, alcohol, and aluminoxane compound (1). The excited aldehyde is deactivated to emit light λ (max)=430 nm. The second CL pathway (2) passes through unstable intermediate P_1 and an excited product P_2 which acts as another unidentified CL emitter responsible for luminescence (λ =510 nm).

Upon OMC hydrolysis, CL was for the first time illustrated by stable peroxide $(C_2H_5O)_2AlOOC(CH_3)_3$ [58] and, later on, by less stable $(C_2H_5O)_2AlOOC_2H_5$ [60]. With the latter, that CL can be observed with water added to the solution $(C_2H_5O)_2AlC_2H_5$ reacted with O_2 . The light brutto-stage was identified to be the hydrolysis of that OAC autoxidation intermediate, which resulted in ethyl hydroperoxide.



CL similar to the above described can arise due to the introduction of water at later stages of $(C_2H_5)_3Al$ oxidation with O_2 when the third Al-C bond of triethylaluminium suffers oxidation and a sufficient amount of $(C_2H_5O)_2AlOOC_2H_5$ is accumulated [60]. Of special interest is the high selectivity of CL in reaction of water exactly with an organoaluminium peroxides, while autoxidation in solution involves a few other OAC violently reacting with water.

Upon contact of powdered $Li[AlH_4]$ to water, CL was observed as well to be less bright than with OAC peroxides [48].

3.3. Reactions of OAC with dioxetane, molybdenum peroxy complex, and organic peroxides.

With dioxetans, another new type of CL was originally discovered in the reaction of adamantylideneadamantan-1,2-dioxetane (AAD) with such OAC as $(C_2H_5)_3Al$, $(i-C_4H_9)_3Al$, or $(i-C_4H_9)_2AlH$ in toluene and CH_2Cl_2 [63]. That CL entirely differs from the known CL [70] exhibited upon AAD thermolysis. First of all, adamantanone as the CL emitter during thermolysis is formed neither in its ground state (no FL at 410 nm after the reaction) nor in its excited state (CL is of longer wavelength region than 410 nm). The CL is mainly in the red spectral region and does not result from the emission of singlet-excited oxygen as shown by the absence of emission at 1270 nm. An unidentified intermediate was assumed to be the CL emitter, since the kinetic curves for CL revealed their maxima and no FL corresponding to CL was found in solution after the reaction [63].

Usually, metal complexes react with OAC in the absence of oxygen to

emit no light [71], but the existence of a bound-to-metal peroxy group enables that complex to give CL. Thus, $(C_2H_5)_3Al$ and $(i-C_4H_9)_2AlH$ can be oxidized by a molybdenum peroxy complex in toluene to emit light [6] the intensity of which (ca. 10^8 photon/S·mole) is comparable to the CL displayed by those OAC with dioxetane. CL was registered for $(C_2H_5)_3Al$ and $(i-C_4H_9)_3Al$ in reaction with $(CH_3)_3COOH$ and benzoyl peroxide [6]. In reaction with $(C_2H_5)_3Al$, the CL flash is about three times brighter for benzoyl peroxide, which is evidently the result of higher luminescence yield displayed by the supposed CL emitters [55], i.e. by arylcarbonyl-containing compounds as opposed to their alkyl analogues.

3.4. Reactions of OAC with xenon difluoride.

CL in the reaction of OAC with XeF_2 in CH_2Cl_2 and toluene was originally reported in [72] and was extensively investigated by CL, FL, NMR, and chromatomass-spectrometry methods [5,6,72-80] to elucidate the mechanism of emission and the composition of the species in both their ground and excited states. The principal mode of that reaction involves XeF_2 attacking the OAC active bonds to give fluorine-substituted OAC derivatives as the main products; consequently, these OAC can be efficiently prepared via mild fluorination of the solutions by XeF_2 . To a less degree, XeF_2 reacts with C_2H_5O-Al bonds as confirmed by the presence of ethoxytoluenes in the reaction products [73]. The activity of substituents at an OAC aluminium atom decreases in the series $H>R>OR>Cl$ [73].

CL turned out the most convenient method to derive kinetic parameters of OAC reactions with XeF_2 .

For the reaction of $(C_2H_5O)_2AlC_2H_5$ with XeF_2 , the rate constants derived from the linear curve of CL decay were (2 ± 0.2) , $(6.7 \pm 0.2) \cdot 10^{-1}$ and $(2.9 \pm 0.2) \cdot 10^{-1} M^{-1}s^{-1}$ at 293, 262, and 233 K, respectively, and $E_a = 6.5 \pm 0.2$ kcal/mole [48]. The mechanism of the reaction of the model compound $(C_2H_5O)_2AlC_2H_5$, possessing one active Al-C bond, was investigated in more detail and was shown to be of the free-radical type by the inhibiting effect of galvinoxyl, and the overall composition of products (Table 1) as well as by the chemically induced dynamic nucleus polarization effect (CIDNP); the latter was originally discovered for OMC reactions with XeF_2 [77]. The introduction of galvinoxyl leads to a more abrupt than usually CL decay and to lower gas liberation (Fig.10) [76]. The CIDNP effect was found when solutions of $(C_2H_5O)_2AlC_2H_5$ and XeF_2 were mixed directly in an NMR probe. During 10-15 sec, the PMR spectrum showed multiplet polarization of methylene protons of ethylated toluenes, ethyl fluoride, and butane [77, 78].

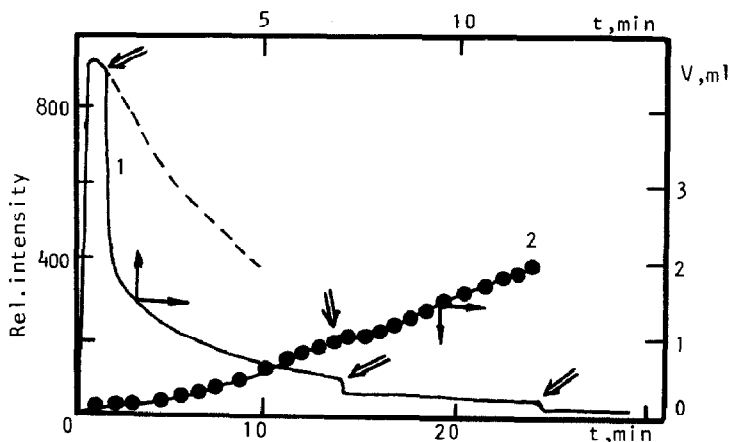


Fig.10 Inhibited CL (1) and gas liberation (2) with the addition of 0.0002M galvinoxyl upon autoxidation of 0.02M diethoxyethylaluminium by 0.01 M xenon difluoride in toluene, 201 K [94]; \Rightarrow points of galvinoxyl additions; V(ml) - total amount of gases.

For $(C_2H_5O)_2AlC_2H_5$ oxidized by XeF_2 , the CL spectrum is in $t. \approx 350-550$ nm region with its maximum at 450 nm and was assigned to the emission of the radical $(XeF^*)^*$ (Fig.11) [79].

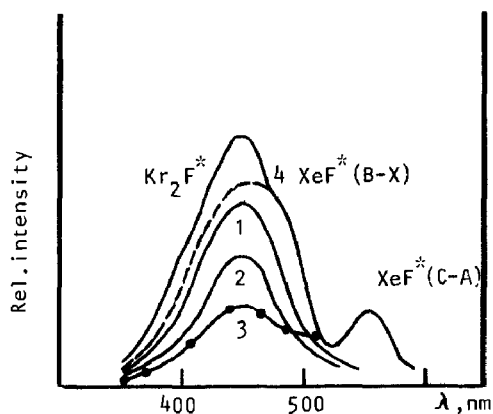


Fig.11 CL spectra recorded in the reaction of diethoxyethylaluminium with xenon difluoride (1-3) [79] and CL spectra for XeF^* emission generated with laser illumination (248 nm) of $Xe+F_2$ mixture in liquid krypton [82,83]. (1) in toluene; (2) in methylene chloride; (3) without solvent; (4) dashed line is for the emission component (B — X) of XeF^* recorded in the background of Kr_2F^* emission.

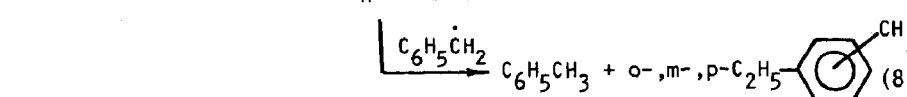
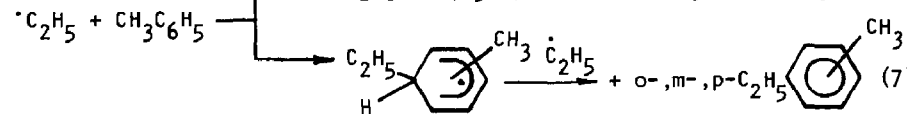
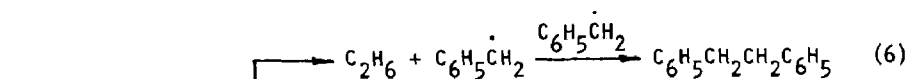
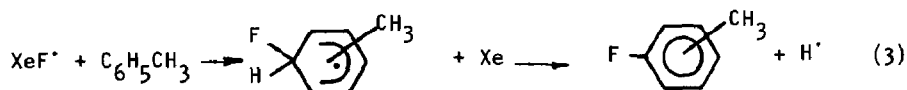
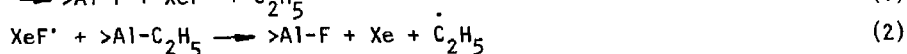
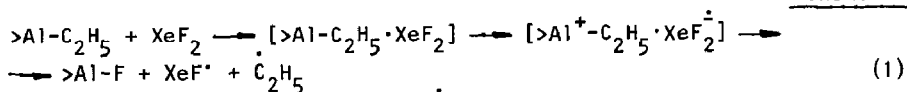
Table 1. Compositions and yields of products formed in the reaction of $1.14 \cdot 10^{-1} \text{M} (\text{C}_2\text{H}_5\text{O})_2\text{AlC}_2\text{H}_5$ with $5.7 \cdot 10^{-2} \text{M} \text{XeF}_2$ in toluene at 300 K.

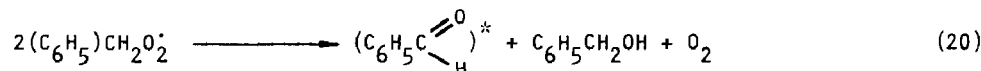
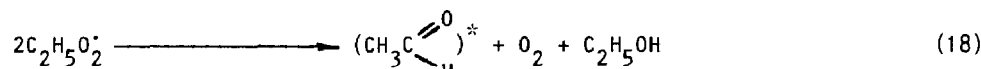
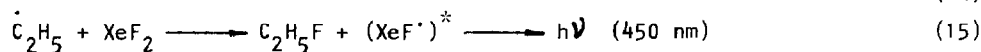
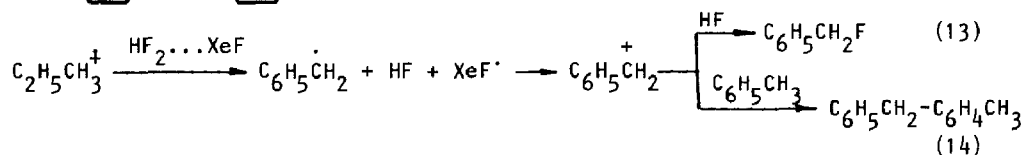
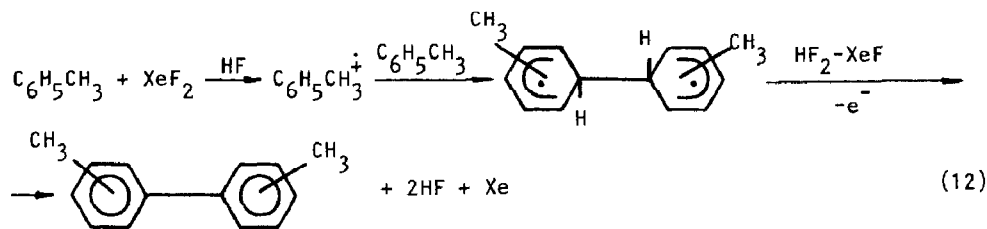
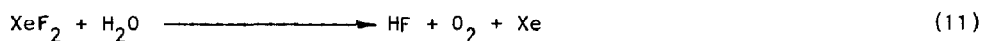
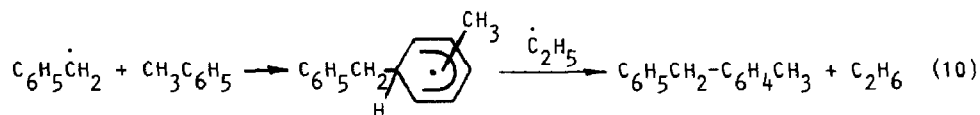
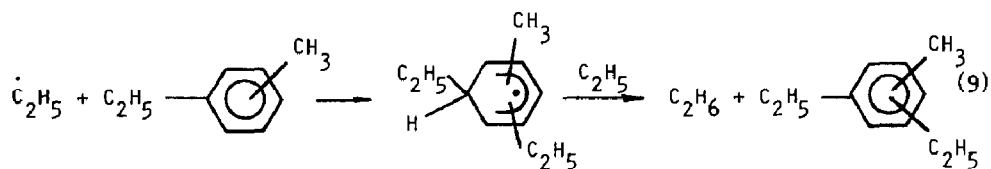
Yield, mole/mole of XeF_2 , %											
$(\text{C}_2\text{H}_5\text{O})_2\text{AlF}$	C_2H_6	C_2H_4	Xe	$n\text{-C}_4\text{H}_{10}$	$\text{C}_2\text{H}_5\text{F}$	Products of reaction with solvent					
						dibenzoyl and di tolyl	o-, m-ethyl toluenes	p-ethyl toluenes	diethyl toluenes	ethoxy toluenes	F-toluenes
1.94	0.90	0.10	0.97	traces	traces	0.15	0.22	0.20	0.025	0.08	tr
97.0	45.0	5.0	97.0			23.5*	65.5*	4.0*	7.0*		

*The total sum of products was taken as 100%. Traces of F-toluenes were detected by chromatomass-spectrometry method, traces of $\text{C}_2\text{H}_5\text{F}$ by CIDNP, traces of $n\text{-C}_4\text{H}_{10}$ by GLC.

The mechanism of that reaction with its products formed in their ground and excited states can be described in the following scheme.

Scheme 11





The reaction starts with electron transfer from OAC to electrophilic XeF_2 to give cation- and anion-radicals (1). A complexed spiroaluminooxane structure [81] in the starting OAC reduces the yield of radicals XeF^+ ; they probably disappear during their interactions with the closest Al-C bond of the OAC (2). The reaction of these radicals with toluene gives only traces of fluorotoluenes (3). Intermediate \dot{C}_2H_5 radicals react (i) with each other to yield traces of ethane, ethylene (4), and butane (5); (ii) with toluene at the

side chain to give dibenzyl (6) and (iii) at the aromatic ring to give ethyl- (7,8) and diethyl-toluenes (9), ethane being also formed in the latter two processes. The radical \dot{C}_2H_5 attacks the aromatic ring to give the σ -complexed ethylmethylcyclohexadienyl radical which, according to the CIDNP data, forms further a radical pair with another ethyl (7) or benzyl (8) radical. The formation of diethyltoluenes (9) and asymmetric ditolyls (10) can be also rationalized in terms of the related intermediate σ -complexes. The radical pairs formed reveal their diffusion nature, since styrene additions suppress completely the CIDNP signals [78].

The excited radical $(XeF^*)^*$ is the CL emitter in reaction (15); the energy (ca.79 cal/mole as calculated by the bond energy balance) released [79] is quite sufficient to excite the B-state of the radical responsible for the luminescence at 450 nm (B \rightarrow X transition) [82,83]. The inhibition of gas liberation and CL suppression by galvinoxyl are due to the occurrence of reaction (16). Oxygen diverts the radicals \dot{C}_2H_5 away from the main process by reactions (17,18), but at $[O_2] < 10^{-4}$, the disproportionation of peroxy radicals can result in a somewhat brighter CL. Emission by excited benzaldehyde may result from a similar reaction of oxygen (19,20).

3.5. Reactions of boralkylhydrides with oxygen.

A visible bluish CL follows autoxidation of boralkylhydrides such as diisopinocampheylborane and 9-borabicyclo[3.3.1]-nonane (9-BBN) [84,85]. CL is exhibited in the oxidation of all active B-H and B-C bonds in those OMC. Triplet-excited ketones such as pinocampnone and cyclooctanone were identified as the CL emitters by matching the spectra of CL and phosphorescence for the individual ketones with those of the solutions after reaction [Fig.12] [85]. An interesting change in the spectra in THF is observed with the oxidation time. Thus, up to the CL kinetic maximum, only a long wavelength component of CL is registered with a monochromator (both components can be seen through glass filters); later, a short wavelength component arises and increases in intensity so that it prevails at the stage of gently sloping CL decay (Fig.12).

Therefore there exists another CL emitter in THF (in addition to ketones), i.e. presumably the radical $>B\dot{O}_2^*$. That statement is well-reasoned. The species of $>B\dot{O}_2^*$ are often met in the classic schemes for OMC autoxidation [67,68]. Earlier, the emission of $\dot{B}O_2^*$ was recorded upon gas-phase oxidation of compounds such as zirconium borohydride, B_2H_6 , and H_3BCO , with B-H bonds; emission bands at 490, 520, 547 nm were found in the long wavelength emission (500-650 nm) [86-88]. Besides, we have established that the long

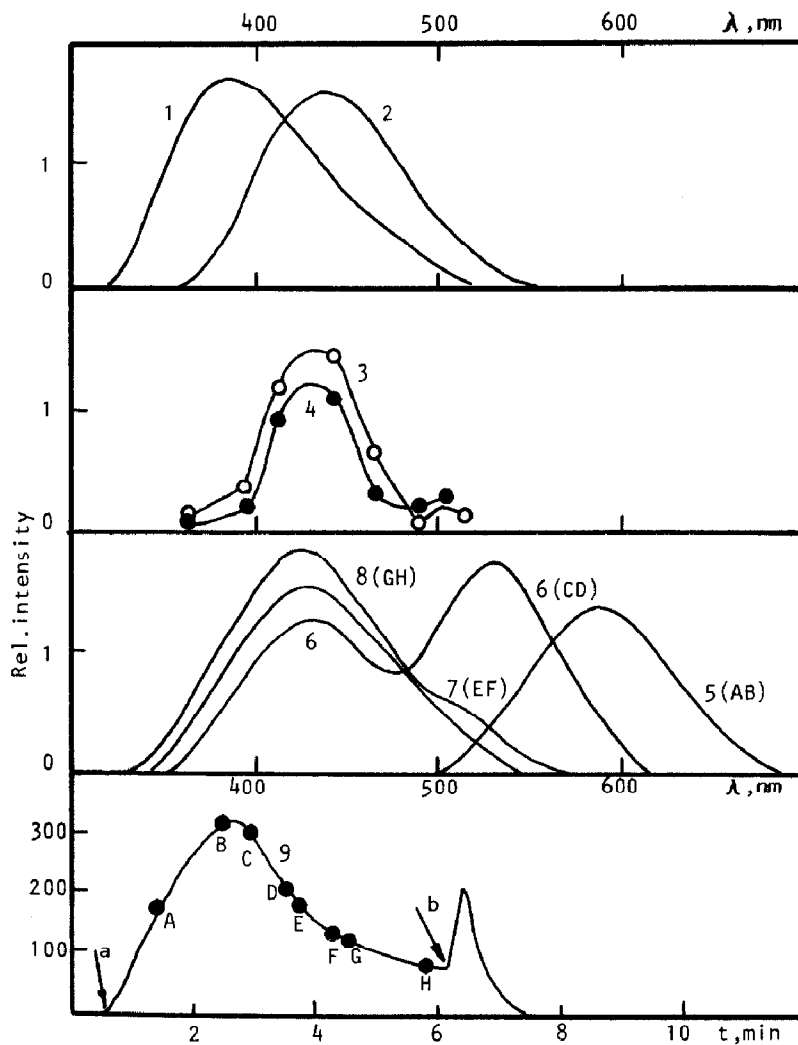


Fig.12 Spectral assignments (1-8) and kinetics (9) of CL upon autoxidation of 9-BBN in THF [85]. (1,2) FL at 298 K and phosphorescence at 77 K of cyclooctanone and the solution after 9-BBN oxidation, λ (excitation)=320 nm; (3,4) CL for 0.1M 9-BBN in benzene and toluene; (5,8, 9) CL for 0.01M 9-BBN in THF; (a) and (b) with air bubbling on and off, respectively; AB, CD, EF, GH-sections of Curve 9 for spectral measurements 5-8.

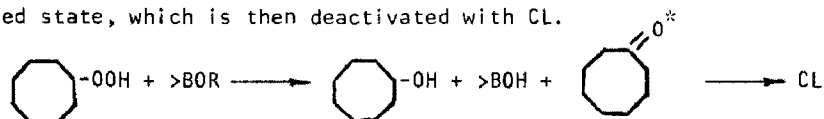
wavelength component of CL is quenched by oxygen more than the short wavelength one. At the same time, the strong quenching effect of oxygen is also inherent in the gas-phase CL exhibited by $\ddot{\text{B}}\text{O}_2$ [86,87]. The mechanism of boralkylhydride autoxidation is described within the following scheme [85].

3.6. Reactions of organoboron peroxides with water.

When water is introduced into THF solutions of 9-BBN oxidized by O_2 , the CL is sharply enhanced and then gently drops [89].

The reaction of intermediate organoboron peroxides with water is considered the most obvious source of excited states with 9-BBN + O_2 under hydrolytic conditions.

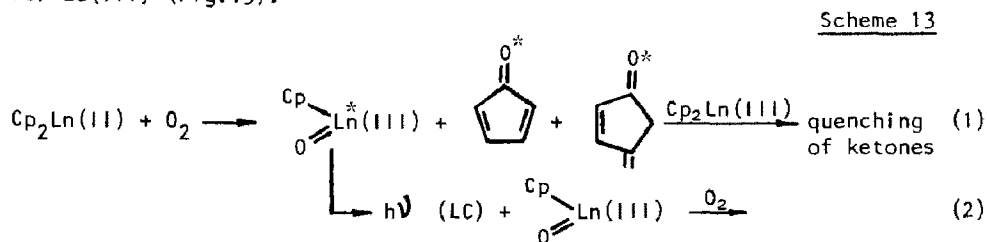
The CL spectrum measured at sloping branch (ca. 3 min) after water addition was in the same spectral region as in "dry" autoxidation. That provides evidence of the similarity of the CL emitters in the both luminescent reactions. We believe the following pathway is followed for CL in the presence of water: an intermediate organoboron peroxide reacts with water to form a hydroperoxide, $\begin{matrix} -\text{BOOR} \\ | \\ \text{OH} \end{matrix} + \text{HOH} \longrightarrow \begin{matrix} -\text{B-OH} \\ | \\ \text{OH} \end{matrix} + \text{ROOH}$ which reacts further with the alkoxy group attached to boron to give a ketone in its excited state, which is then deactivated with CL.

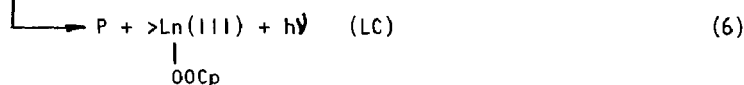
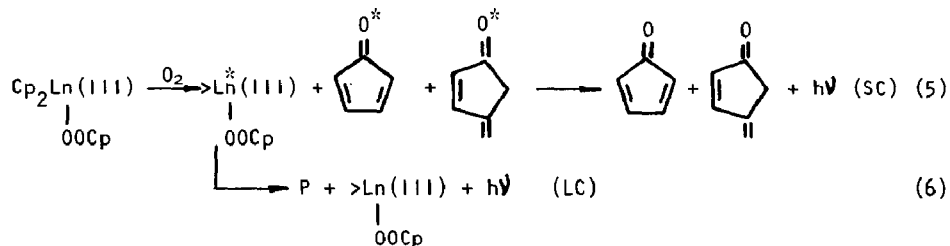
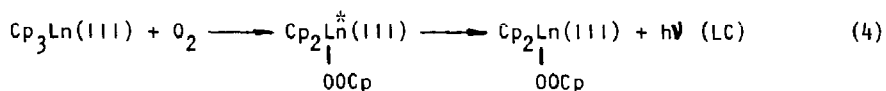
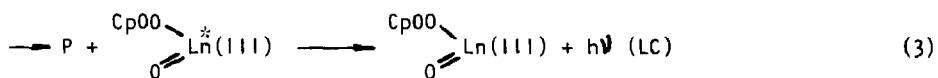


Non-excited ketones are known to result from the reaction of hydroperoxides with OAC containing alkoxy group [91], which provides additional support for the above described CL mechanism. Besides, those processes simulated via the addition of cyclooctane hydroperoxide to a solution of 9-BBN after its oxidation (that containing an alkoxy derivative of boron) yielded CL in the region of cyclooctanone phosphorescence [89]

3.7. Reactions of cyclopentadienyl of Yb, Sm, and Eu with oxygen, water, and xenon difluoride. Hydrolysis of lanthanide organic peroxides.

A new type of OMC CL emitted by the ions of lanthanides Ln^* (III) was discovered upon autoxidation of lanthanide organics (LO) such as $(\text{C}_5\text{Me}_5)_2\text{Yb}$, $(\text{C}_5\text{Me}_5)_2\text{YbCl}$ [92], Cp_2Eu , Cp_2Sm , Cp_3Eu , and Cp_3Sm [5,93,95], where $\text{Me}=\text{CH}_3$ and $\text{Cp}=\text{C}_5\text{H}_5$. After oxidation by O_2 , broad FL maxima of the starting LO at 935 and 440 nm for $(\text{C}_5\text{Me}_5)_2\text{Yb}$ and Cp_2Eu , respectively, are transformed into more narrow FL bands at 980 nm for Yb(III) and at 580, 595, 613, 640 nm for Eu(III) (Fig.13).





(where P stands for a complex mixture of polymers and metal oxides; LC and SC - long and short wavelength components of CL, respectively).

The processes resulting from autoxidation of Eu and Sm LO can be represented in the scheme above [95]. At the first fast stage of Cp_2Ln autoxidation, ketones and $\text{Ln}^*(\text{III})$ as its oxoderivatives are excited (1). The former is effectively quenched by the starting LO (1). Further oxidation yields excited lanthanide organic peroxide, deactivation of which is responsible for the long wavelength "red" component of CL. With Cp_3Ln , except for the case with $\text{Ln}^*(\text{III})$ (4), excited ketones exhibit the emission too. Cyclopentadienone disappears rapidly during the dimerization as well as in its reaction with other reactive participants [95]. A lanthanide organic peroxide was identified as the "red" CL emitter [93,95] by a good match of CL spectra of Eu and Sm LO to FL of the oxidation products each possessing a peroxide group (KI reaction; CL-test with H_2O). The above statement cannot rule out a possible emission by lanthanide oxides either, $\begin{array}{c} \text{Cp} \\ \diagdown \\ \text{O} \\ \diagup \\ \text{Ln}^*(\text{III}) \end{array}$ being the simplest among those to be capable of promoting the "red" CL of divalent lanthanides Cp_2Eu and Cp_2Sm .

The first example of an unusual CL displayed by unoxidized OMC with water was the reported light emission in reaction of Cp_3Sm with water in THF [94,95]. The luminescence of $\text{ca. } 2 \cdot 10^6 \text{ photon/S} \cdot \text{ml}$ ($\sim 5 \text{ min}$) was registered (PEM) with an aliquot of water (0.5 ml) added to the $2 \cdot 10^{-3} \text{ M}$ solution of Cp_2Sm in THF in an argon atmosphere. The CL spectrum consisted of two short (350-450 nm) and one long wavelength components, the bands of the latter matching the CL spectrum of Cp_3Sm autoxidation. Therefore, $\text{Sm}^*(\text{III})$ as its $\text{Sm}(\text{OH})_3$ species is also excited in the hydrolysis of Cp_3Sm to emit CL.

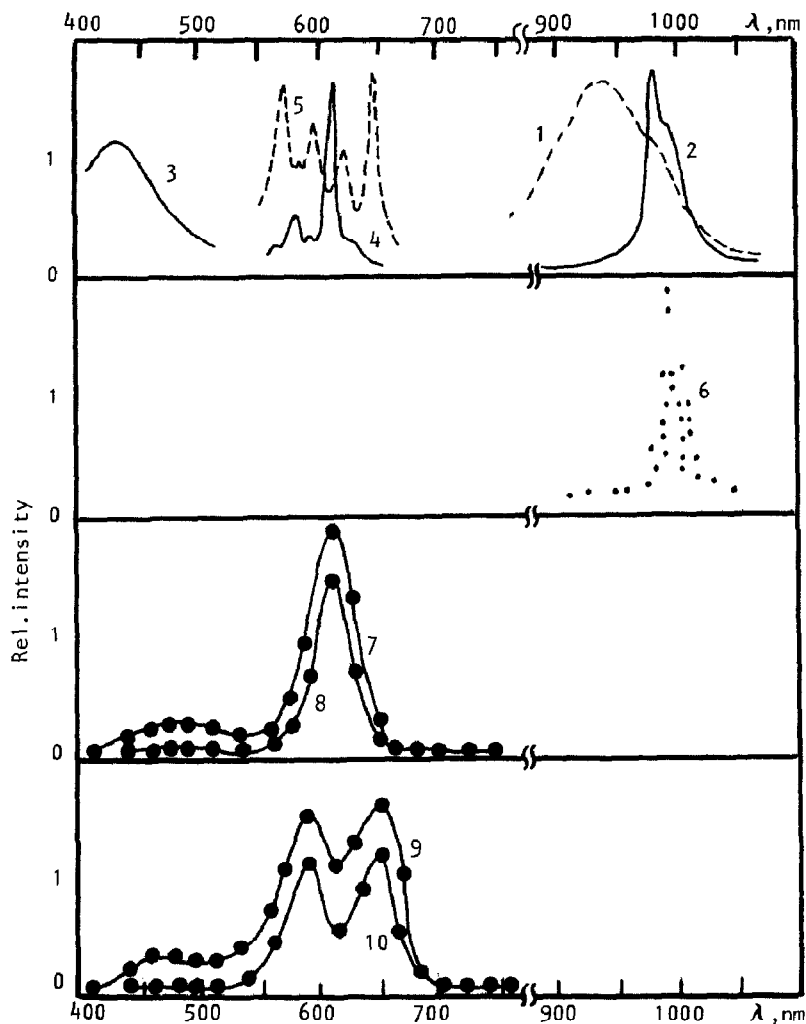


Fig.13 Spectral assignments upon autoxidation of cyclopentadienyls of ytterbium [92], europium and samarium [95]. (1) and (2) - FL registered before and after oxidation of OLYb(II), 295 K; (3) and (4) - FL registered before and after oxidation of OLEu(II), 77 K; (5)- FL for OLSm(III), 77 K; (6)- CL for OLYb(II,III); (7) and (8)- CL for OLEu(III) and Eu(II); (9) and (10)- CL for OLSm(III) and Sm(II); (6-10) - [OL]=0.001M, THF, 295 K.

THF solutions of Cp_2SmCl [5] along with other Eu and Sm LO exhibited CL upon oxidation by a toluene solution of XeF_2 . That CL fades rapidly within three minutes. No spectral measurements were made.

3.8. Reactions of boron hydride complexes of lanthanides with oxygen.

This year, CL and FL were found for the complexes of type $NaLn(BH_4)_4 \cdot nDME$,

where Ln = Eu(III), Sm(III), Pr(III) (n=4), and Tb(III) (n=3) [96]. With Tb compounds, the observed FL is extremely bright, which is caused by the emission of $Tb^{*}(III)$ irrespective of the state of aggregation (either crystalline or dissolved in THF before and after oxidation with O_2) (Fig.14).

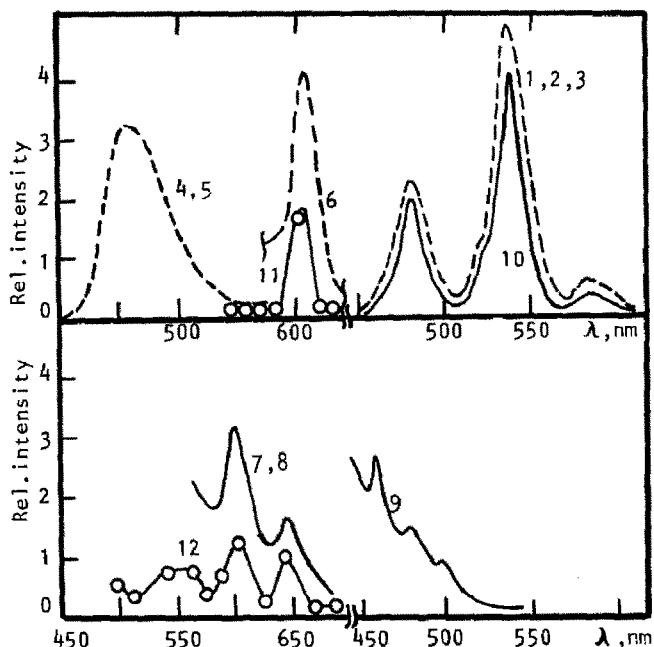


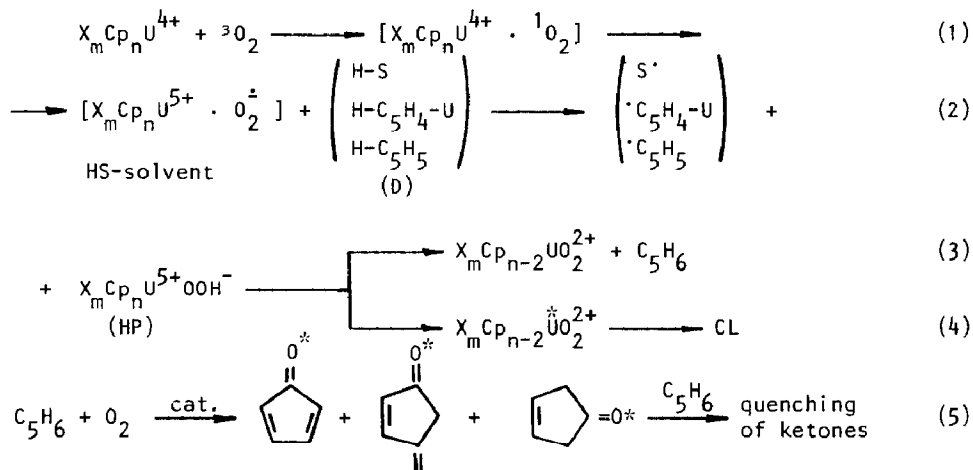
Fig.14 Spectral assignments upon autoxidation of lanthanide boron hydride complexes in THF [96]. (1) and (2) FL for crystals and solution of Tb before and after oxidation (3); (4) and (5) FL for crystals and 0.005M solution of Eu before and after oxidation (6), 77 K; (7) and (8) FL of crystals and solution of Sm after oxidation, 77 K; (9) FL recorded after oxidation of Pr complexes, 77 K; (10,11,12) CL for Tb, Eu, Sm, respectively, 298 K.

Starting solutions of Sm and Pr complexes exhibit no FL at 300 K and 77 K, but on oxidation with O_2 , FL is registered owing to the emission of $Sm^{*}(III)$ and $Pr^{*}(III)$. Of special interest are the results obtained for the Eu complex. Before oxidation with O_2 , its FL is revealed as an intense band in the deep-blue spectral region (max=465, 300 K, 77 K). The red FL is very weak. After oxidation, the blue FL vanishes, transforming into the red FL of $Eu^{*}(III)$. Thus, the blue FL of the Eu complex is very similar to the FL of $Eu(II)$ [97]. THF solutions of those complexes oxidized with O_2 yield CL the intensity of which decreases in the series $Eu > Tb > Sm$ to reach zero for Pr complexes. The CL spectra give unequivocal evidence of lanthanide ions $Ln^{*}(III)$ as the luminescence emitters. It was recently reported [98a] that the CL was emitted by $Ln^{*}(III)$ ions in reactions of lanthanide inorganics.

3.9. Reactions of cyclopentadienyls of uranium (IV) with oxygen and xenon difluoride.

Upon oxidation of uranium organics (UO) by O_2 and XeF_2 , CL was found for Cp_4U and $Cp_3U(n-C_4H_9)$ [48] and for Cp_3UCl [98]. CL is brighter by two orders of magnitude with XeF_2 than with O_2 . The following CL mechanism is suggested for autoxidation of uranocenes Cp_4U , Cp_3UCl , and $CpUCl$, designated as $X_mCp_nU^{4+}$ for short ($X=Cp$ or Cl ; $Cp=C_5H_5$; $m+n=4$).

Scheme 14



According to the data obtained for "dark" autoxidation of UO [99], the triplet state of oxygen in an intermediate complex is transformed into the singlet state with electron transfer with the result that uranium(IV) is oxidized to U(V) and a superoxide ion is formed (1,2). Next, a hydrogen atom is extracted from the donors (D), i.e. from a solvent, uranocene or C_5H_6 formed with the decomposition of hydroperoxide (HP). Simultaneously, decomposition of the HP gives an excited uranyl group which deactivated with CL emission (4). The formation of uranyl-containing products upon autoxidation was demonstrated [98] by the presence of FL characteristic of uranyl at 77 K (Fig.15) in the region of the CL spectral maximum. Uranyl is also excited with further oxidation of Cp-U bonds, which is not shown at the above scheme, since CL is registered until the oxidation of uranocenes is complete. The excited ketones which result from oxidation of C_5H_6 catalyzed by the reaction intermediates (5) [99] are effectively quenched by C_5H_6 molecules, hence the absence of their emission in the CL spectrum. Though radicals appear at stage (2), the "dark" autoxidation and CL do not follow the free-radical mechanism because the addition of galvinoxyl (to $10^{-3}M$) influences neither of those processes [89].

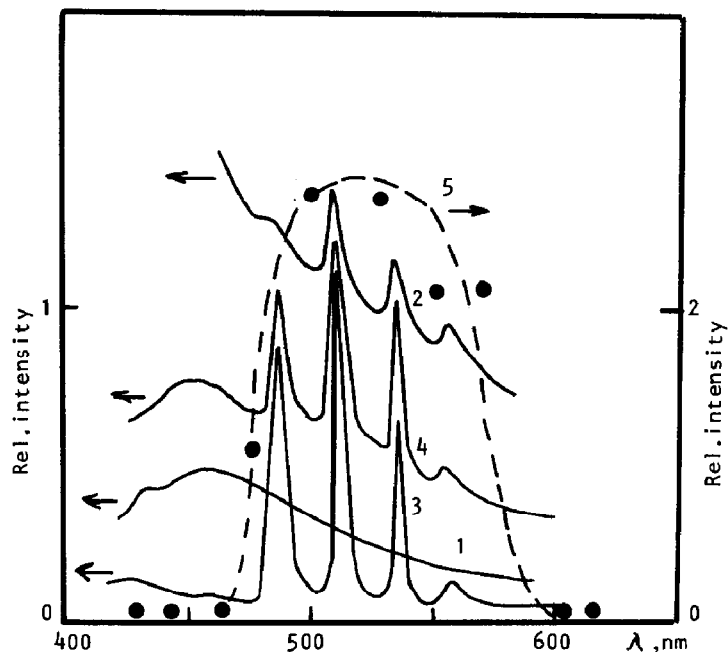


Fig.15 Spectral assignments upon autoxidation of uranium(IV) cyclopentadienyls [98]. (1-4) FL registered after oxidation of Cp_4U (1), Cp_3UCl (2), $CpUCl_3$ (3); (4) FL for hydrolyzed oxidation product Cp_3U in 5M HCl; (5) CL for all uranocenes, saturated solutions in THF, oxygen bubbling.

4. CHEMILUMINESCENCE OF ORGANOMETALLICS OF FOURTH GROUP METALS OF THE PERIODIC TABLE

4.1. Reactions of silicon organics with oxygen and xenon difluoride.

Upon oxidation of $(C_2H_5)_6Si_2$ and $(C_2H_5)_3SiCH_2=CH_2$ by XeF_2 , CL arises immediately after contact of toluene solutions of the reagents to fade rapidly to 20-85% within two minutes. No CL is exhibited with O_2 and $(C_2H_5)_6Si_2$ even at up to $60^\circ C$, because of the inertness of that OMC towards O_2 [5]. Weak CL of $4.3 \cdot 10^6$ photon/s·mole is displayed in the reaction of $(C_2H_5)_3SiCH_2=CH_2$ mainly because of the reactions of intermediate organosilicon peroxides as is shown by a gentle CL decay after the kinetic maximum [5]. The luminescence turns two order of magnitude brighter with XeF_2 . Very weak CL of $3 \cdot 10^6$ photon/s·mole originates when air is bubbled through a toluene solution of $HSiCl_3$. A strong quenching effect of O_2 is one of the reasons for that weakening of the CL. Thus, CL is five-times brighter with bubbling of argon containing only traces of O_2 .

4.2. Reaction of germanium, titanium, and tin organics with oxygen and xenon difluoride.

Upon oxidation by O_2 and XeF_2 , CL was recorded [5,6] for toluene solutions of such OMC as $(C_2H_5O)_3TiC_6H_5 - 8.3 \cdot 10^8 (6.8 \cdot 10^9)$, $(C_2H_5)_6Ge_2 - 1.0 \cdot 10^7 (3.0 \cdot 10^7)$, $(C_2H_5)_2GeH_2 - 2.6 \cdot 10^8 (7.2 \cdot 10^8)$, $(CH_3)_6Sn_2 - 2.5 \cdot 10^6 (2.8 \cdot 10^8)$; the photon/s·mole values are given for the maximum CL intensities with O_2 (XeF_2).

In the course of autoxidation of $(C_2H_5O)_2TiC_6H_5$ in THF, FL is displayed in the region of 400-500 nm with its broad maximum at 450 nm giving a good match with the CL spectrum measured by the flow method. This implies that a stable but unidentified product of autoxidation emits the CL. With germanium and tin organics, CL can be recorded at higher temperatures (60°C) only.

5. CHEMILUMINESCENCE OF ORGANOMETALLICS OF FIFTH GROUP METALS OF THE PERIODIC TABLE.

5.1. Reactions of $(C_2H_5)_3Bi$ and $(C_2H_5)_2BiF$ with oxygen and xenon difluoride.

Reactions of $(C_2H_5)_3Bi$ and $(C_2H_5)_2BiF$ with O_2 in toluene give rapidly fading (ca. 2 min) CL of $1.0 \cdot 10^8$ and $2.5 \cdot 10^7$ photon/s·mole intensities, respectively [5,48].

Brighter CL of $3.4 \cdot 10^8$ photon/s·mole is exhibited in the reaction of $(C_2H_5)_3Bi$ with XeF_2 [48].

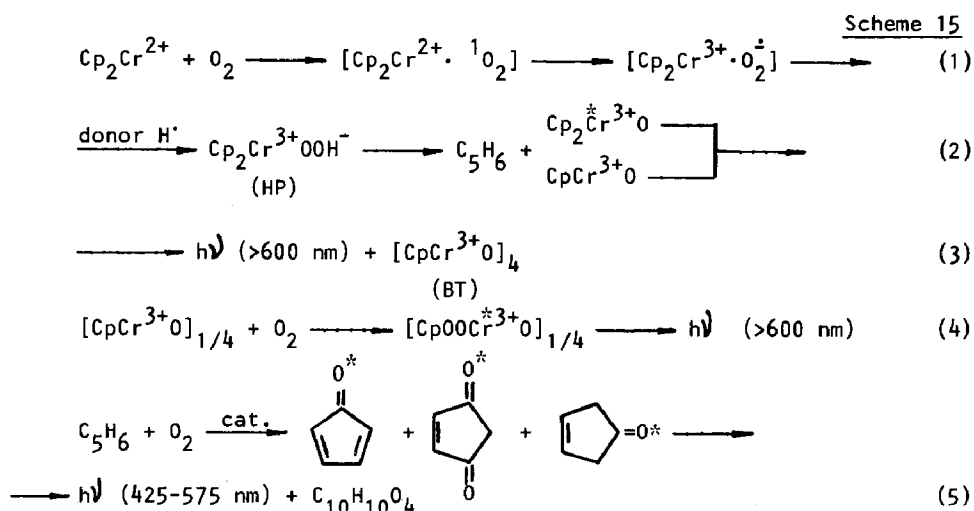
6. CHEMILUMINESCENCE OF ORGANOMETALLICS OF SIXTH GROUP METALS OF THE PERIODIC TABLE.

6.1. Reactions of chromium cyclopentadienyls with oxygen and xenon difluoride.

With air bubbled through $1.5 \cdot 10^{-2} - 1.5 \cdot 10^{-3} M$ THF or toluene solutions of $(C_5H_5)_2Cr$, $[C_5H_5CrO_4]$, or C_5H_5CrF , weak CL was observed to rise ($I_{max} = 6 \cdot 10^6 - 8 \cdot 10^7$ photon/s·mole) and to fade rapidly within a minute [101].

The CL red component (>600 nm) was caused by emitting Cr(III) which is involved as a reaction intermediate. The short wavelength CL (425-575 nm) was assigned to the emission by excited ketones which are products of oxidation of the chromocene Cp-rings, since that CL was displayed in the region of phosphorescence of ketones as they were transformed further into $C_{10}H_{10}O_4$ [102].

In agreement with the results on the mechanism of the "dark" autoxidation of $(C_5H_5)_2Cr$ [102] and those for CL and FL of chromocenes [101], the formation of unexcited and excited products can be accommodated by a scheme similar to that which was given for the CL with uranocenes.



Excited Cr(III) is generated by the decomposing hydroperoxide (HP) (2) as well as by further oxidation of Cp-Cr bonds in the blue tetramer (BT), the latter resulting from the dosed oxidation of Cp_2Cr .

Since the short wavelength CL component is also emitted with the tetramer oxidation, one should assume the formation of excited ketone also by the transformation of peroxide CpOOCrO .

Upon oxidation of $(\text{C}_5\text{H}_5)_2\text{Cr}$ by XeF_2 , the intensity of CL was $I_{\text{max}} = 1.5 \cdot 10^7$ photon/s·mole with $1.6 \cdot 10^{-3}\text{M}$ reagent concentration in THF or toluene; the CL was displayed in the shorter wavelength spectral region ($<600 \text{ nm}$) [101].

6.2. Reactions of $\text{Mo}(\text{CO})_6$ and its derivatives with oxygen and xenon difluoride.

When air is bubbled through a toluene (60°C) of $\text{C}_6\text{H}_5\text{CH}_3\text{Mo}(\text{CO})_3$, weak CL is observed ($9 \cdot 10^6$ photon/s·mole), fading rapidly within a minute. It is believed that O_2 attacks the weak π -bond of molybdenum and a carbon in the toluene ring, since no CL is registered with $\text{Mo}(\text{CO})_6$.

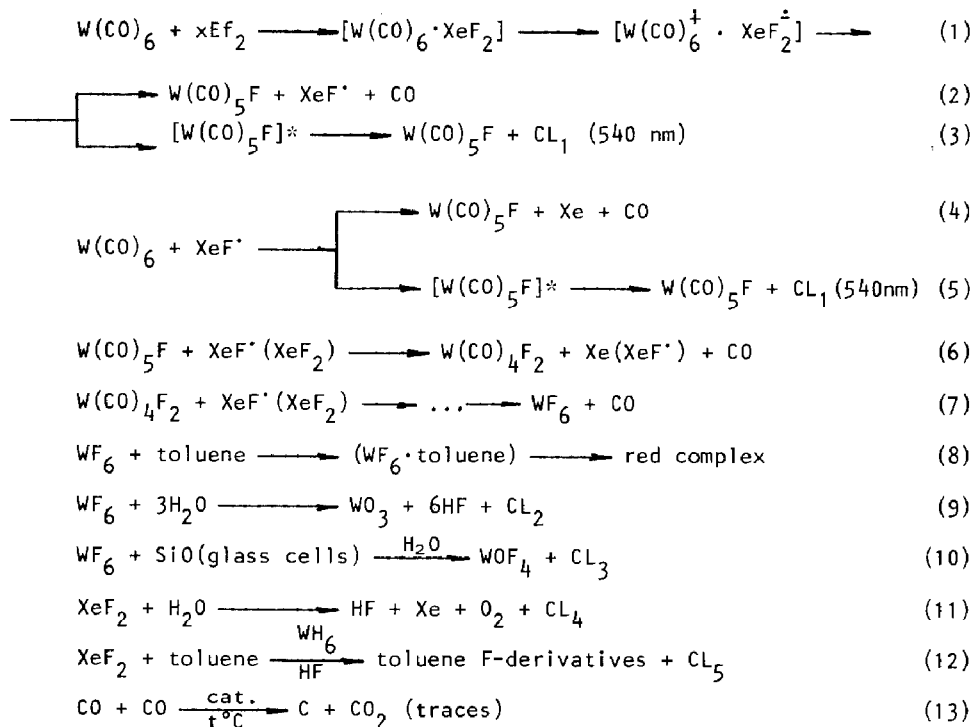
Upon oxidation by XeF_2 , CL is observed at room temperature for $\text{Mo}(\text{CO})_6$ and $\text{C}_6\text{H}_5\text{CH}_3\text{Mo}(\text{CO})_3$ at $1 \cdot 10^9$ and $3.6 \cdot 10^7$ photon/s·mole, respectively. That process is accompanied by intensive gas liberation. The presence of Xe and CO among the gaseous products and the appearance of bands at 727 and 743 cm^{-1} in the solution after reaction (those bands being inherent to the Mo-F bond) give evidence for substitution of carbonyl CO groups by fluorine.

6.3. Reaction of $\text{W}(\text{CO})_6$ with xenon difluoride.

CL reaction of $\text{W}(\text{CO})_6$ with XeF_2 was originally described in [103] to proceed with concomitant gas liberation, precipitation, and multiple colour

changes. The reaction products $W(CO)_4F_2$, Xe, CO, CO_2 , WF_2 are formed in their ground and excited states as shown by the following scheme [103-106].

Scheme 16



(where ... - successive stages of fluorination; cat.- reaction medium).

After electron transfer from tungsten carbonyl to electrophilic XeF_2 (1), the intermediate complex formed in the first stage decomposes to give a certain portion of molecules $W(CO)_5F$ in their excited states (3). CL emitter can be also generated with XeF' attacking the primary carbonyl (5). The emission at 540 nm in the CL spectrum was assigned to deactivation of intermediate $[W(CO)_5F]^*$. The FL exhibited with $W(CO)_5$ and its derivatives was earlier described in [107] to have a maximum at 533 nm. The emitter of long wavelength CL component remained unidentified. By experiments conducted separately, reactions (9-12) were established [105] to give rise to luminescence CL_2 , CL_3 , CL_4 , and CL_5 , though the intensity of the brightest among those - CL_5 (12) was two orders of magnitude lower than CL_1 in the main reaction of $W(CO)_6$ with XeF_2 . The time of the reaction induction period (appearance of CL, start of gas liberation) is reversibly dependent on the reagent concentration and temperature [106]. An induction period exists due to the inhibiting effect of water traces of which are difficult to remove from toluene.

WF_6 , on the other hand, is acting as an initiator.

At higher temperatures (55°C), the kinetic maximum of CL which is usually recorded is followed by a number of reiterated light flashes [104]. This effect is caused by the highly volatile product WF_6 circulating in the solution-gaseous phase of the system; WF_6 which is the reaction catalyst is swept by the argon flow from the reaction medium (Ar makes the atmosphere oxygenless) and is subsequently dissolved in a solvent drop condensed at the end point of the refluxing unit. The CL flashes are thus formed by the falling drops and the effect was called "drop-flashed" CL [104].

7. CHEMILUMINESCENCE OF ORGANOMETALLICS OF SEVENTH GROUP METALS OF THE PERIODIC SYSTEM.

7.1. Reactions of manganese organics with oxygen, xenon difluoride, and benzoyl peroxide.

The existence and brightness of CL with manganese organics were originally described in [5,6] to be appreciably dependent on both the nature of the ligand attached to Mn and the presence of an Mn-Mn bond. In reactions of manganese OMC with O_2 and XeF_2 in toluene and CH_2Cl_2 , the CL brightness (photon/s·mole) decreases in the following series:

(with O_2) C_6H_5MnCl ($6.0 \cdot 10^9$) > $[(C_6H_5)_3Mn]Li$ ($2.0 \cdot 10^9$) > $(C_5H_5)_2Mn$ ($5 \cdot 10^7$) > $Mn_2(CO)_{10}$ (0);

(with XeF_2) $(C_5H_5)_2Mn$ ($4 \cdot 10^8$) > $C_5H_5Mn(CO)_3$ ($2.2 \cdot 10^7$) > $Mn_2(CO)_{10}$ (0).

$Mn_2(CO)_{10}$ does not react with O_2 , whilst a $1.5 \cdot 10^{-2}M$ toluene solution of Cp_2Mn is half oxidized by O_2 in less than a minute. $Mn_2(CO)_{10}$ reacts with XeF_2 at the metal-carbon bond as shown by the liberation of gas (Xe, CO) and the disappearance of Mn-CO absorption bands at 345 nm. In this case, however, CL not only fails to occur but, quite the reverse, when the carbonyl is introduced into the chemiluminescent solution of XeF_2 in toluene or CH_2Cl_2 the background CL is quenched. Such a phenomenon was ascribed to the specific quenching effect of the Mn-Mn bond [103]. Indeed, the addition of $C_5H_5Mn(CO)_3$ does not quench but gives rise to a luminescence flash owing to XeF_2 reacting with the substituted carbonyl C_5H_5 -Mn bond. The absence of CL in reaction of $Mn_2(CO)_{10}$ with XeF_2 was ascribed in [48] to the low reaction rate (60% of the calculated amount of gas CO+Xe was liberated in about seven hours, while that process was seven-times faster with $C_5H_5Mn(CO)_3$).

By analogy with the reaction of C_6H_5MgBr with benzoyl peroxide (BP) [47], we assigned the red CL exhibited in the reaction $C_6H_5MnCl+BP$ to the emission

by $(\text{Ph}_3\text{C}^*)^*$ [6,48]. Now, to account for the results obtained with CL in reaction $\text{Ph}_3\text{CNa} + \text{O}_2$ [10,11], we would rather advocate the alternative of either substituted derivatives of Ph_3C^* , or complex of Ph_3C^* with other reaction intermediates, or triphenylmethide, which is capable of red CL [19].

CL of $I_{\text{max}} = 3.4 \cdot 10^6$ photon/s·ml was also recorded with PhMgCl ($8 \cdot 10^{-2} \text{M}$ in DE+THF) oxidized by O_2 to originate as a rapidly fading light flash (0.5 min) [89].

7.2. Electrochemiluminescence (ECL) of $\text{fac-ClRe}(\text{CO})_3\text{L}$.

ECL originates as separate light flashes upon cyclic AC (alternating current) electrolysis of a CH_3CN solution of $\text{fac-ClRe}(\text{CO})_3\text{L}$ ($\text{L} = 1,10\text{-phenanthroline}$ or $4,7\text{-diphenyl-1,10-phenanthroline}$) containing 0.1M $(n\text{-Bu}_4\text{N})\text{ClO}_4$ for the sake of electroconductivity [108]. The CL emitter was identified by matching the ECL and FL spectra of the initial complex solution with their wide maxima at 580 nm (Fig.16).

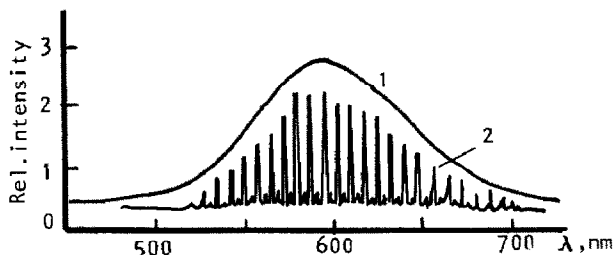
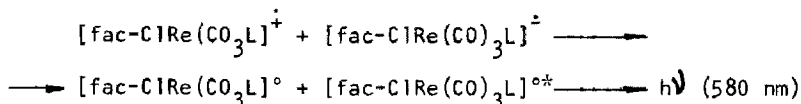


Fig.16 FL(1) and ECL (2) spectra for rhenium carbonyl complex in acetonitrile containing 0.1M tetrabutylammonium perchlorate. (1) λ (excitation) = 420 nm [108].

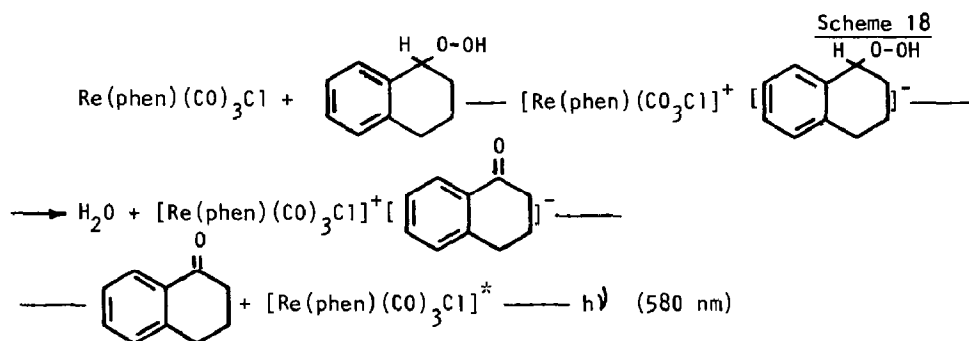
The light reaction of differently charged ion-radicals generated at a Pt-electrode.

Scheme 17

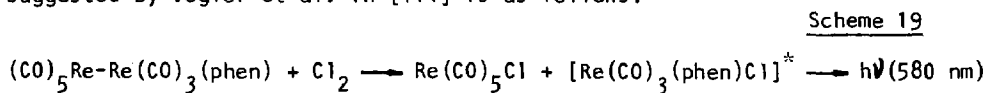


7.3. Reaction of $\text{Re}(\text{phen})(\text{CO})_3\text{Cl}$ with tetralinyl hydroperoxide and reaction of $(\text{CO})_5\text{Re-Re}(\text{CO})_3(\text{phen})$ with chlorine.

Volger et al. found that upon addition of $\text{Re}(\text{phen})(\text{CO})_3\text{Cl}$, the slowly decomposing tetralinyl hydroperoxide in boiling tetralin was rapidly transformed into α -tetralone and water to give bright red CL the spectrum of which matched the FL of the primary rhenium complex [109]. The CL intensity was linearly dependent on the complex concentration indicating that the CL emitter was formed during the bimolecular reaction. The mechanism for CL excitation was described by a scheme [109] similar to that suggested by Schuster et al. [110] for aromatic hydrocarbons, i.e. CIEEL.



Similar CL was reported for $[\text{Ru}(\text{bipy})_3]^{2+}$ catalyzing the decomposition of the same peroxide [109]. The emission of the above rhenium complex was responsible for the bright CL which was observed to originate in the oxidation of $(\text{CO})_5\text{Re}-\text{Re}(\text{CO})_3(\text{phen})$ by chlorine in DMF [111]. The scheme suggested by Vogler et al. in [111] is as follows.

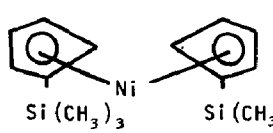


8. CHEMILUMINESCENCE OF ORGANOMETALLICS OF EIGHTH GROUP METALS OF THE PERIODIC TABLE.

8.1. Reactions of Fe, Ni, Rh organics with oxygen and xenon difluoride.

CL is exhibited [5,48] in reactions of some OMC of Fe, Ni, and Rh with O_2 and XeF_2 (Table 2).

Table 2. CL Intensities (I) in Oxidation of Fe, Ni, and Rh OMC by O_2 (330 K) and XeF_2 (300 K) In Toluene [5,48].

no.	OMC	I, photon/s·mole	
		O_2	XeF_2
1	$(\text{C}_5\text{H}_5)_2\text{Fe}$	0.0	0.0
2	$\text{Fe}(\text{CO})_5$	0.0	$1.8 \cdot 10^6$
3	$\text{Fe}_2(\text{CO})_9$	0.0	$1.0 \cdot 10^5$
4	$[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Ni} \rightarrow \text{Si}(\text{CH}_3)_3$	$2.8 \cdot 10^7$	$4.6 \cdot 10^8$
5	 $\text{Ni} \rightarrow \text{Si}(\text{CH}_3)_3$	$9.2 \cdot 10^5$	$2.4 \cdot 10^7$
6	$(\text{acac})\text{Rh}(\text{CO})_2$	$1.7 \cdot 10^6$	$4.8 \cdot 10^7$

Iron carbonyls (entries 2,3) reveal only weak CL with XeF_2 to yield Xe, CO and solid precipitate. Complex OMC with its Ni- and Si-C bonds (entry 4) is oxidized by both reagents to emit CL which is almost an order of magnitude brighter with XeF_2 . Since the $\text{CH}_2\text{-Si}$ bond is passive towards XeF_2 [112], the CL can be assumed to result from the attack of XeF_2 on the Ni-C bond. Less bright CL with XeF_2 (entry 5) compared to that of entry 4 shows the higher activity of the Ni-Ph bond than the Ni-Cp bond.

8.2. Electrochemiluminescence of ortho-metalated platinum (II) complex.

Electrolysis of a solution of a Pt complex with two Pt-C bond yields ECL as the potential of a Pt-electrode changed from -1.5 to +0.85 eV. The spectrum of the ECL is similar to the FL spectrum for the same complex (Fig.17) [113].

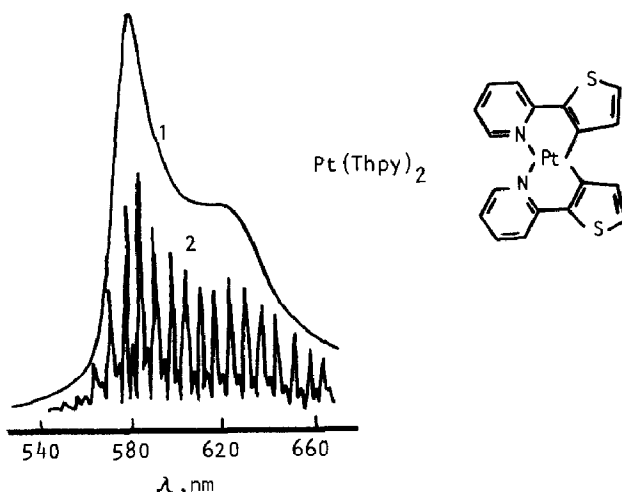
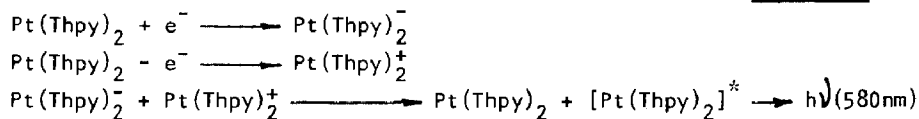


Fig.17 FL (1) and ECL(2) spectra for 0.0001M platinum organometallic complex in DMF, (excitation)=420 nm [113].

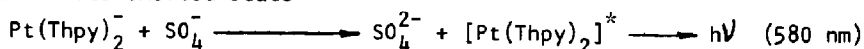
The ECL excitation scheme [113] differs very little from that suggested earlier for the ECL of the rhenium complex.

Scheme 20



In the presence of 10^{-5}M $\text{K}_2\text{S}_2\text{O}_8$, ECL was observed within a different range of the potential changes from -1.8 to 0 eV. This was caused by the interactions of anion Pt(Thpy)_2^- and $\text{S}_2\text{O}_8^{2-}$ -ion with the subsequent formation of

SO_4^- species as strong oxidizers $\text{Pt}(\text{Thpy})_2^- + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{Pt}(\text{Thpy})_2 + \text{SO}_4^{2-} + \text{SO}_4^-$ which take an electron away from another complex anion to generate the latter in its excited state



9. THE EFFECT OF LUMINESCENT ADDITIONS UPON CL OF OMC. LOW-TEMPERATURE CL.

The existing literature data on the activation of CL exhibited by Grignard reagents with O_2 by various luminescent additions are rather discrepant. Indeed, $2.5 \cdot 10^{-4} \text{ M}$ 9,10-diphenylanthracene (DPA) added to the O_2 -saturated butyl ether was reported to bring about the second band in the CL spectrum of PhMgBr , that band matching the FL spectrum of DPA [9], while the same CL spectrum was stated to remain unchanged with the additions of chrysene, anthracene and its 9,10-substituted derivatives [46]. At the same time, both publications reported the absence of any quenching effect upon the CL emitters with those luminescent activators, indicating that the CL emitter was generated in the course of chemical reaction rather than as a result of the energy transfer. The introduction of 10^{-3} M rubrene, penta-cene, or rhodamine does not give rise to any observable energy transfer in the CL of PhMgBr with benzoyl peroxide [47]. We consider the nature of an organic fragment and not that of the metal (otherwise it is the emitter) as a determining factor for the CL activation provided, of course, that all other requirements of the desired CL activator (suitable energy level, etc.) are met. Thus, in oxygen oxidation of $(\text{C}_3\text{H}_7)_2\text{Mg}$, the addition of DBA enhances the luminescence intensity and the CL spectrum shows a new band with its maximum at 420 nm which is the same as in FL of DBA [48].

Upon oxidation of aluminium alkyls [55] and boronalkyl hydrides [85], CL is effectively activated by DBA (Fig.18) and the CL spectrum incorporates the FL of DBA. With the addition of activating agents to the reaction of 9-BBN with O_2 , the coefficient of CL intensity decreases in the series: DBA>rubrene>anthracene>pyrene>DPA [85,89]; vice versa, naphthalin and benzophenone act as quenchers for the CL. The spectrum of activated CL with 9-BBN shows two components: a long wavelength one (unidentified) and a short wavelength component due to the FL of singlet states except for the reactions with DPA. The CL is amplified much less with DPA than it is with pyrene (1.5-fold increase at 10^{-3} M of DPA, and more than 10-fold increase at 10^{-4} M of pyrene); the CL spectrum incorporates no FL of DPA to show only a long wavelength component (max=560 nm). The peculiar effect of DPA suggests that the activator's singlet state is excited not only by direct triplet-triplet energy transfer $\overset{\Delta}{\text{P}}(\text{T}_1) + \text{A}(\text{S}_0) \longrightarrow \text{P}(\text{S}_0) + \overset{\Delta}{\text{A}}(\text{S}_1)$,

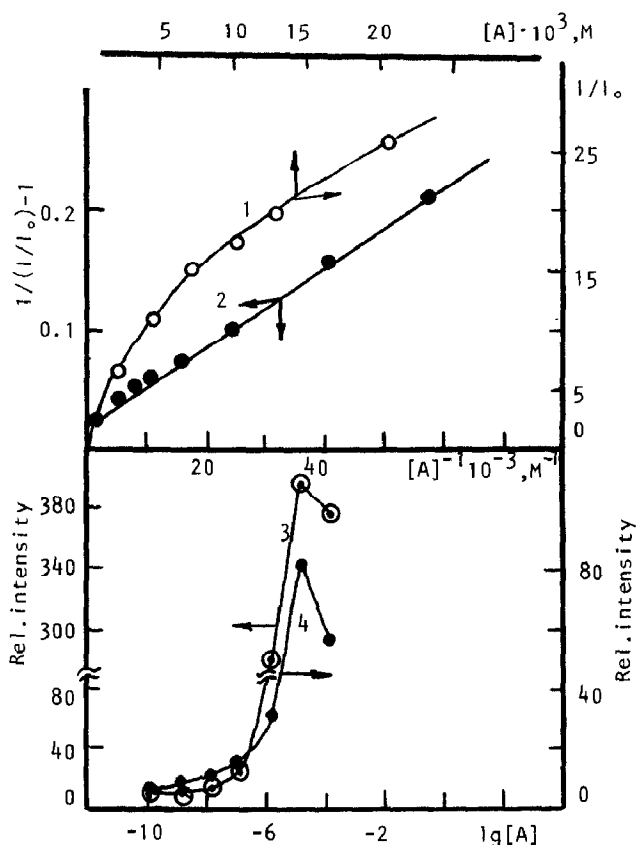
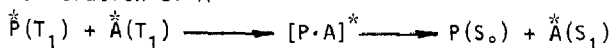


Fig.18. (1) dependence of CL intensity on DBA concentration (A) in autoxidation of 0.0068M 9-BBN in THF [89]; (2) linear representation of (1); (3) and (4) dependence of CL intensity on $\lg[A]$ for DBA and pyrene, respectively, in oxidation of 0.002 diethoxyethylaluminium by 0.001M xenon difluoride in toluene [89].

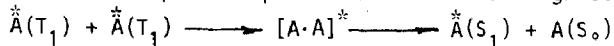
but also via the formation of triplet-excited molecules in the activator - $\ddot{A}(S_1)$



which are further transformed by the reaction with triplet-state ketone at low concentration of A



and due to the triplet-triplet annihilation at high concentration of A



The above scheme for CL activation rationalizes the absence of DPA FL in terms of the low effective formation of its excited states $\ddot{A}(T_1)$ in comparison with different activators.

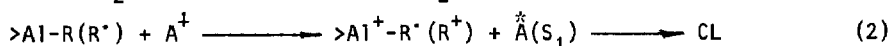
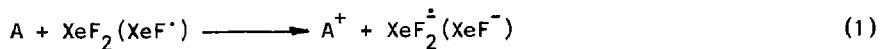
Upon autoxidation of Cp_2Hg [53] and Cp_2Cr [101], the ketones are excited too. However, DBA additions result in only a slightly amplified CL (2.5-fold

increase at $10^{-2}M$ of DBA). The spectrum of activated CL matches that of DBA FL distorted due to the effect of reabsorption of the short wavelength band at high DBA concentration. The low amplification of CL is accounted for by the low effective energy transfer from the excited ketones as the products of Cp-ring transformations. The latter assignment was proved [89] by the low DBA activated CL observed in reaction of C_5H_6 with O_2 in THF, where ketones formed were of the same type as in the autoxidation of Hg and Cr OMC.

Usually, CL activation with anthracene derivatives is appreciably observable at the activator concentration ca. $10^{-5}M$ [114]. We have recently found the addition of even $10^{-9}M$ p-terphenyl, pyrene, anthracene, DBA, and DPA to amplify the CL in the reaction of $(C_2H_5O)_2AlC_2H_5$ with XeF_2 (Fig.18). CL can be identified with the naked eye in $10^{-3}M$ reagent solutions with $[A]=10^{-5}-10^{-3}M$. It is interesting that there was found a new type of concentration dependence which is different from the usual steadily increasing dependence curve of CL intensity with the activator concentration (Fig.18). That curve shape is indicative of the chemical nature of CL activation.

The measurement of an activated CL spectrum is a matter of some difficulty since the emitter of nonactivated CL $(XeF^*)^*$ occupies the same spectral region where the activator FL is displayed. The emission of singlet states of an activator makes a sufficient contribution to the activated CL. With pyrene, it occurs as a sharp maximum at 390 nm. With p-terphenyl, the spectral broadening is observed in the region of its FL (max=345 nm). The singlet states of activators are excited as in the following scheme.

Scheme 21

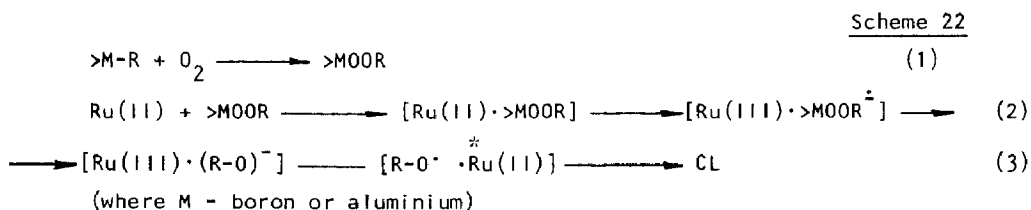


The starting XeF_2 or the reaction intermediate XeF^* oxidizes the activator to its cation A^+ (1). The singlet-excited A^* is generated upon the reduction of A^+ by a molecule of the starting OAC or by another intermediate - alkyl radical R^* (2).

Upon autoxidation of OAC [62] and boralkyl hydrides [115], crystalline $Ru(bipy)_3Cl_2 \cdot 6H_2O$ added to the solution gives rise to an appreciable amplification of CL, the maximum of which is in the red spectral region (600 ± 15 nm); there occurs a redox reaction of the water of crystallization of the solid salt $Ru(bipy)_3Cl_2 \cdot 6H_2O$ (insoluble in toluene and THF) with the OMC involved, with the concomitant liberation of gaseous hydrogen and formation of a soluble complex $[Ru(bipy)_3Cl \cdot (OMC)_n]$, the latter emitting the activated CL. It was established by a match of the activated CL spectrum to FL of the complex.

Two mechanisms were suggested for CL activation in OAC autoxidations - "chemical" and "physical" [62]. Later on in [116], $\text{Ru}(\text{bipy})_3\text{Cl}_2$ was shown to have the lowest intensity as the acceptor of energy from the excited ketones, so it can be considered that the CL activation had a chemical nature. That was confirmed by the differently shaped kinetic dependences for activated and nonactivated CL of OAC [62].

We are rather inclined to advocate the mechanism of chemically initiated electron-exchanged luminescence (CIEEL) according to the below scheme.

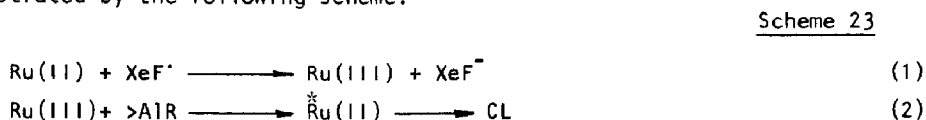


The organometallic peroxide $>\text{MOOR}$ (1) forms an intermediate complex $[\text{Ru}(\text{bipy})_3\text{Cl}_2 \cdot (\text{OMC})_n]$. After electron transfer to the peroxide and oxidation of ruthenium to Ru(III) (2), the complex decomposes to form the ketone radical-anion $\text{R}=\text{O}^{\cdot-}$ from which Ru(III) accepts an electron to be reduced to its divalent excited state (3), the latter being responsible for the emission of activated CL. That mechanism was established by the peculiar feature of CIEEL, i.e. by the existence of a linear dependence of the activated CL intensity on OMC and ruthenium concentrations [48].

The amplified CL was originally observed to follow the CIEEL mechanism with catalytic decomposition of peroxides and excitation of metal complexes in homogeneous media for $\text{Re}^*(\text{phen})(\text{CO})_3$ [109] and in chemical crystalloluminescence of $\text{Ru}^*(\text{bipy})_3\text{Cl}$ [118]. According to the reported data [48], the activation of OMC CL can be assumed to be possible also in crystallization of luminescent metal complexes from OMC reaction solutions.

A homogeneous $<10^{-3}\text{M}$ solution of the complex $[\text{Ru}(\text{bipy})_3\text{Cl}_2(\text{OAC})_n]$ in toluene (or CH_2Cl_2) turned out a good activator for a few other CL reactions of OAC, e.g. with dioxetane [63] and XeF_2 [72]. With the latter, the activation was so effective that a bright red luminescence flashed like a burning flame [48].

The generation of complex $[\text{Ru}^*(\text{bipy})_3\text{Cl}_2(\text{OAC})_n]$ emitting CL at 610 nm is demonstrated by the following scheme.



The presence of the strongly oxidized radical $\text{XeF}^{\cdot-}$ as an intermediate species

in the reaction of OAC with XeF_2 brings about the oxidation of Ru(II) to its trivalent state (1). The emitter of activated CL is excited by the reduction of Ru(III) by OAC (2).

Dark-blue CL exhibited in the presence of complex $[\text{Ru}(\text{bipy})_3\text{Cl}_2 \cdot (\text{OAC})_n]$ at 450 nm is visible due to strong absorption of $\text{Ru}(\text{bipy})_3\text{Cl}_2$ in the 453 nm region ($\epsilon = 14000$).

We have recently observed [89] the addition of 10^{-5}M $\text{Eu}(\text{TTA})_3\text{Phen}$ to amplify the CL of 9-BBN with O_2 by two orders of magnitude. $\text{Eu}(\text{III})$ was the emitter of activated CL (max=613 nm). The CL is activated with a concomitant decrease in the intensity of the FL of $\text{Eu}(\text{III})$ and a new FL arises at 500 nm in the solution. The reaction product of the chelated organic ligand with 9-BBN was established to be one of the possible sources of emission at 500 nm.

Low-temperature CL of OMC illustrated the unique redox reactions of OMC occurring at very low temperatures in frozen solutions [74]. Thus, with a slowly heated mixture of frozen CH_2Cl_2 solutions of $(\text{C}_2\text{H}_5)_3\text{Al}$ and XeF_2 in the presence of the complex $[\text{Ru}(\text{bipy})_3\text{Cl}_2 \cdot (\text{C}_2\text{H}_5)_3\text{Al}]_n$, the luminescence can be registered even at 95 K !

The excited complex of ruthenium with triethylaluminium was reported to be responsible for the low-temperature red CL (max=610 nm) [74]. The curve of the temperature dependence of that CL intensity shows several maxima. The emergence of CL at 95 K was attributed to the starting point of activity of $\text{C}_2\text{H}_5^\cdot$ radicals, which follows from the reported data [117] on the temperature dependence of EPR signals in the region of 100 K (the temperature of recombination of $\text{C}_2\text{H}_5^\cdot$ radicals in an amorphous medium). With increasing temperature, the rate of processes involving $\text{C}_2\text{H}_5^\cdot$ increases, which causes the growing level of CL intensity up to 152 K; at lower temperature the CL decays so the radical concentration is reduced as other chemical transformations occur. Radicals $\text{C}_2\text{H}_5^\cdot$ result from mechanical grinding of the reagent at 77 K (the first technique to observe low-temperature CL) as well as from mixing of liquid reagent solutions (200 K) subsequently frozen to 77 K (the second technique). The CL maximum at 160 K marks the increased reaction rate under exothermal phase transition, i.e. crystallization of CH_2Cl_2 , due to higher chemical activity on the freshly formed surface of crystals. The high temperature maximum at 190 K is of more trivial nature: it is caused by the growing mobility of initial reagents near the melting point of CH_2Cl_2 (176 K).

10. POSSIBLE USES OF APPLICATION OF OMC CHEMILUMINESCENCE IN SOLUTION.

Nowadays, liquid-phase CL with OMC is growing out of its early stages of research development. The overall results obtained so far provide reliable

predictions of some applications for that luminescence.

- A. The quantitative estimation of metal ions becomes possible owing to the ability of some bright fluorescent metal complexes to amplify CL with OMC. Thus, $\text{Ru}(\text{bipy})_3\text{Cl}_2$ added to R_3Al , where R_3Al is either $(\text{C}_2\text{H}_5)_3$ or $(i\text{-C}_4\text{H}_9)_3\text{Al}$ or $(i\text{-C}_4\text{H}_9)_2\text{AlH}$, enables the estimation of ruthenium even in 10^{-8}M solutions by measuring the intensity of the CL exhibited upon direct contact of that solution with O_2 [48].
- B. Small-sized express-CL-testing instruments can be designed for quantitative estimations of metal-carbon (metal-hydride) bonds in solution, which is possible owing to the high intensities of activated and, sometimes, non-activated CL exhibited by OMC with oxygen. The most convenient analysis technique consists in that an aliquot of an OMC solution is syringed into the solvent [48] continuously bubbled with air. The CL intensity is usually proportional to the OMC concentration.
- C. The above approach can be applied to the analytical control of the industrial production of fatty alcohols from OAC (ALFOL process) at the oxidation stage of trialkylaluminium species to their alkoxides by aerobic oxygen [48]. This method has the advantage by a much bigger change in the CL intensity in the course of industrial oxidation of mixtures of OAC (ranging from C_2 to C_{20}) to their alkoxides as opposed to the small change in intensity (below 10%) of IR absorption bands for the starting and final products, which are employed at present to control that important stage of the process. Continuous control can also be implemented with the use of CL.

A few other uses of application of the OMC CL were reported in our book [48].

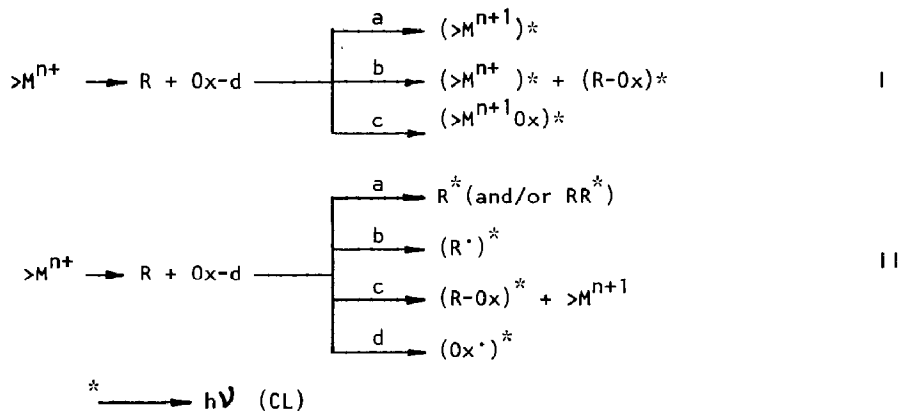
11. CONCLUSIONS. CLASSIFICATION OF LIQUID-PHASE CHEMILUMINESCENT REACTIONS OF OMC.

Light emission can be observed in a great variety of chemical reactions with OMC, which complicates the elucidation of the common regularities for the excitation of OMC transformation products in solution. At the same time, it provides an important basis for the estimation of the potentials of OMC reactions to generate electron-excited states in solution, which is another peculiar feature of OMC. Indeed, as shown in this review, CL arises in reactions of various OMC with species of different chemical nature such as O_2 , XeF_2 , H_2O and with different peroxides including dioxetanes, upon thermal or electrochemical generations of active intermediates. The photo-active stages of CL can be represented by molecular and free-radical processes

involving electron transfer. All CL reactions of OMC are highly exothermic, while that condition is often insufficient to generate excited states.

The mechanisms of the known CL reactions with OMC can be classified by their emitter natures in accordance with the following general schemes for generation of excited species [118].

Scheme 24



(where M - metal; R - OMC organic fragment; Ox-d - oxidant molecule;
* - excited state of CL emitter).

The first pattern of CL includes redox-reactions the emitters of which are represented by electron-excited metal ions. The rate of metal oxidation can vary (I a,c) or remain unchanged (I b). CL is exhibited, for example, in oxidation of metallocenes by O_2 as (I a) Cp_2Eu , Cp_2Sm [93-95], $(C_5Me_5)_2Yb$ [92] and (I b) Cp_3Eu , Cp_3Sm [93-95], $(Cp_5Me_5)_2YbCl$ [92]; with Cp_nUx_m , the oxidized metal attached to an oxidant fragment is the emitter (I c) [98]. The CL pattern is also characterized by the excited products of oxidation of an OMC organic ligand, e.g. Cp-ring based ketones for cyclopentadienyls (I b). The CL displayed in hydrolysis of lanthanide organic peroxides $>LnOOCp$ and Cp_3Ln [94,95] can be attributed to the first pattern as well.

The second CL pattern includes reactions the emitters of which are represented by different types of OMC organic fragments. The emission of molecular R^* (II a) occurs in reactions of adducts of alkali metals and electron acceptors [17,18, 20]. The excitation of an organic fragment as radical $(R^*)^*$ (II b) was registered only in one reaction of Ph_3CNa with O_2 [10,11]. The same is with the emission of oxidant organic fragment $(Ox^*)^*$ (II d), which was found only in reaction of OAC with XeF_2 , radical $(XeF^*)^*$ being the emitter [79]. Reactions following (II c) are much more widespread; their emitters are represented by the oxidized molecular types of OMC organic fragments, those being excited ketones and aldehydes as a rule [6].

We have recently observed CL emitted by singlet-excited molecules of naphthalene, diphenylanthracene, rubrene, and anthracene which are generated in oxidation of sodium adducts of the said hydrocarbons by XeF_2 [119], Ce(IV) , Ru(III) . Besides, with XeF_2 , the emission of hydrocarbon eximers has been recorded.

Despite the existence of only rare instances illustrating each type of CL reactions, one should look forward to future observations of new beautiful light reactions.

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