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The Chemiluminescence of Organometallic Compounds

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Studies on the liquid-phase and gas-phase reactions of organometallic compounds accompanied by the emission of light are described systematically and discussed. The influence of the magnetic field on the chemiluminescence of Grignard reagents and the study of the electrochemiluminescence of solutions of organometallic compounds are examined. The ways leading to further development of the field of the chemiluminescence of organometallic compounds and certain possible applications of the phenomenon in the monitoring of industrial processes are discussed.
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I. INTRODUCTION

As a phenomenon and as a specific method, capable of yielding much information, for the investigation of the mechanisms of chemical reactions, chemiluminescence (CL) has attracted the attention of investigators in increasing numbers of fields of research. The results of studies of the chemiluminescence excited in the reactions of organic[1-4] and inorganic[5] substances have been fairly fully described in a series of special reviews and have been used to investigate the kinetics of chemical reactions,[6,7] for the analytical determination of submicroamounts of substances in solution,[5,8] and also for the elucidation of the mechanism of the transformation of the energy of chemical reactions into the energy of electronically and vibrationally excited molecules.[9] On the other hand, there have been no reviews giving a systematic account of studies of chemiluminescence involving organometallic compounds (OMC) and only isolated data are available.[10,13]

Despite the fact that the emission of light in chemical reactions involving OMC was observed more than 70 years ago,[11,12] the study of the chemiluminescence of OMC has not been developed as much as it deserves. Nevertheless, the exceptionally extensive applications of OMC involving the large-scale manufacture of various organic products,[13,14] the preparation of specially pure metals,[15] and the creation of the laser technology[16] have made it necessary to resort to physicochemical methods for the investigation of the mechanisms of the reactions of OMC. The employment for this purpose of the chemiluminescence method is especially attractive, because it is possible to record the excited states of the reaction products and intermediates (here and henceforth, unless otherwise stipulated, electronically excited states are considered) without interfering with the system incorporating chemically corrosive OMC. The potential possibility of generating chemiluminescence in the redox reactions of OMC arises from their high rates and exothermic nature. Such reactions frequently constitute the basis of organic catalytic and non-catalytic synthesis. It has been noted[17] that most of the catalytic reactions proceed via the formation of excited states of unstable intermediates. Evidently the search for new chemical reactions involving OMC accompanied by chemiluminescence will make it possible to detect such excited states from their radiative deactivation.

The studies considered in this review have been subdivided in terms of the Groups of the elements in the Periodic System and are concerned with the chemiluminescence in solution and in the gas phase. The ability of many OMC to glow in air is generally known; since the emission of light observed under these conditions includes an equilibrium component, i.e. a glow unrelated to the phenomenon of chemiluminescence, this type of light emission is not considered in this review.

II. THE CHEMILUMINESCENCE OF ORGANOLITHIUM, ORGANOSODIUM, AND ORGANOPOTASSIUM COMPOUNDS

1. The Oxidation of Organolithium, Organosodium, and Organopotassium Compounds by Oxygen

Chemiluminescence in the oxidation of an ethereal solution of C_6H_5Li has been observed by Gilman et al.[18] A glow has also been detected in the analogous reactions of solid specimens of C_6H_5Li, C_6H_5Na, and C_6H_5K.[19] The chemiluminescence spectrum in the interaction of C_6H_5Li with a saturated solution of oxygen in benzene consists of a broad band (from 320 to 600 nm) with maxima at 350 and 530 nm.[20] Even at a low concentration of butyl-lithium (10^{-3} M) the solutions have a deep brown colour, which leads to a marked distortion of the chemiluminescence spectrum as a consequence of the self-absorption by the solution.

2. The Oxidation of Butyl-Lithium by Organic Peroxides

The emission of light in the oxidation of C_4H_9Li by benzoyl peroxide (BP), lauryl peroxide, and t-butyl peroxide in toluene, heptane, and tetrahydrofuran (THF) has been investigated.[21] Two sections, which can be expressed in a linear form in terms of the variables as a second-order kinetic equation, have been differentiated in the kinetic plot of the chemiluminescence intensity in the reaction of C_4H_9Li with BP (Fig.1):

$$I^{-1/2} = (k\eta)^{-1/2}[BP]_0^{-1/2} + (k/\eta)^{1/2}\, t,$$

where k is the reaction rate constant, η the chemiluminescence yield, and $[BP]_0$ the initial BP concentration. The

rate constant k obtained from chemiluminescence measurements[20] and the results of the iodometric titration of BP agreed satisfactorily (0.3 and 0.34 litre mol^{-1} s^{-1} respectively). The chemiluminescence yield η was 10^{-12} photons per single step in the interaction of the reactants. The effective activation energy was obtained from the temperature dependence of I (on the basis of the chemiluminescence kinetics) and is 3.0 ± 0.5 kcal mol^{-1}.

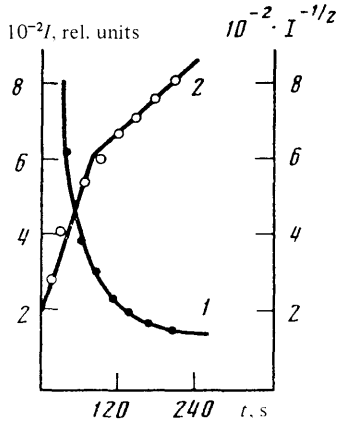
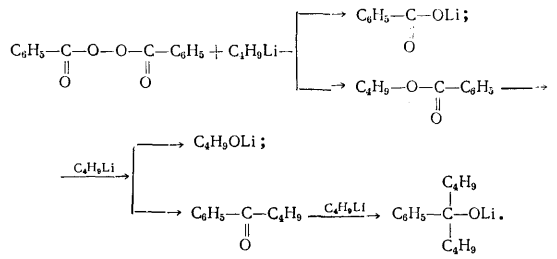


Figure 1. Kinetic curve describing the decrease of the chemiluminescence intensity (curve *1*) and its form in terms of the variables of Eqn.(1) (curve *2*);[21] $[BP]_0 = [C_4H_9Li]_0 = 10^{-2}$ M.

According to the results of the infrared spectroscopic and ^1H NMR analysis of the reaction products and the study of the stoichiometry of the interaction,[21] the mechanism of the complex process involving the oxidation of butyl-lithium by BP can be represented by the following consecutive reactions:



It is assumed that the source of excitation energy is the first, most exothermic stage (90–90 kcal mol^{-1}) [sic] and Panasenko et al.[21] believe that the chemiluminescence emitter is butyl phenyl ketone—the product of the second stage. The difference between the chemiluminescence and photoluminescence spectra of the suggested emitter (Fig.2) is associated with the formation of its complex with another reaction product—lithium butoxide. Indeed, the photoluminescence spectrum of a mixture of chemically non-interacting acetophenone and lithium butoxide agrees with the short-wavelength chemiluminescence maximum (460 nm);[21] the nature of the second, long-wavelength chemiluminescence maximum has remained unelucidated. Thus the excitation of the chemiluminescence emitter occurs as a result of the transfer of the energy of the first stage of the process to butyl phenyl ketone—the product of the second stage. A more clear-cut argument in support of the proposed mechanism of the excitation of the chemiluminescence would have been the detection of an increase in chemiluminescence intensity when butyl phenyl ketone is added to the solution.

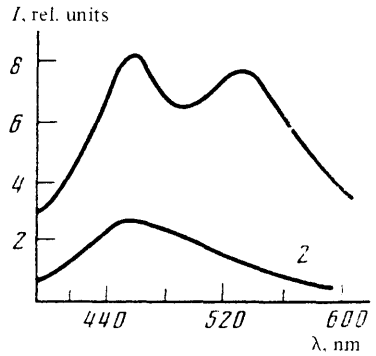


Figure 2. The chemiluminescence spectrum in the reaction of benzoyl peroxide with C_4H_9Li (curve *1*) and the photoluminescence spectrum of a mixture of acetophenone and C_4H_9OLi in heptane (curve *2*); 20 °C; $[BP] = [C_4H_9Li] = 10^{-2}$ M.

III. THE CHEMILUMINESCENCE OF SOLUTIONS OF ORGANOMAGNESIUM AND ORGANOCALCIUM COMPOUNDS

In 1905 Wedekind[22] attempted to obtain nitrotriphenylmethane by the reaction

$$3C_6H_5MgI + Cl_3CNO_2 \rightarrow (C_6H_5)_3CNO_2 + 3MgICl.$$

Although the desired product was not obtained, Wedekind observed a bright chemiluminescence arising when chloropicrin was added to a solution of the Grignard reagent (GR) in ether; the colour of the glow varied from yellow-green to pure green. In a number of his studies of this chemiluminescence, a glow was also detected in the reaction with phenylmagnesium bromide.[11,12,22] He attributed the observed glow to the phenomenon of luminescence (i.e. to a non-equilibrium emission of light), since the temperature of the system did not exceed the boiling point of ether. This first reaction of OMC accompanied by chemiluminescence was called the "Wedekind reaction". We may note that another communication by Wedekind[23] is referred in the literature to the same series of investigations, although it contains no information about chemiluminescence.

Later it was shown that a similar chemiluminescence arises in the interaction of chloropicrin and bromopicrin also with other Grignard reagents;[24] chloropicrin gave rise to a brighter glow. The iodides of Grignard reagents reacted with chloropicrin with emission of a greater amount of light than in the reaction of the chlorides. The mechanism of the chemiluminescence in the Wedekind reaction has still not been investigated. There is only no doubt that the reaction is different from that associated with the glow arising in the oxidation of Grignard reagents by oxygen, because it was observed in diethyl ether also under conditions where oxygen had been thoroughly removed.[25]

1. The Oxidation of Grignard Reagents by Oxygen

On repeating Wedekind's experiments, Heczko[26] observed the emission of light in the oxidation of Grignard reagents by oxygen. (Sometimes[27] the discovery of this chemiluminescence is erroneously attributed to Wedekind.[12]) It was assumed that the appearance of this glow requires moisture but later it was found[24,28] that the presence of moisture inhibits the glow. Subsequent investigations demonstrated that the chemiluminescence associated with the oxidation by oxygen is observed for a whole series of other Grignard reagents having different structures.[29–38] The glow in the oxidation of p-chlorophenylmagnesium bromide[30] is apparently one of the brightest among all the known chemiluminescence reactions in solution. This chemiluminescence, observed independently by Moeller[28] and Evans and Dufford,[32] has been called[24] the Moeller–Evans reaction.

There have been contradictory views concerning the influence of the nature of the Grignard reagent on its capacity for chemiluminescence and oxidation by oxygen. Moeller[28] assumed that this property is characteristic only of aromatic derivatives. According to Lifshitz,[31] the chemiluminescence is associated with the different stabilities of the etherates of aromatic and aliphatic Grignard reagents, because it has been found that all the ether-free Grignard reagents react with oxygen with emission of light; the brightness of the glow in the reactions of aromatic Grignard reagents is only a little lower than that of aromatic compounds. A systematic investigation[32] has shown that the above contradictions were associated with the influence of Grignard reagent concentrations, the optimum value of which (for the observation of the maximum brightness of the chemiluminescence) depends on their nature. Thus the concentration is 2.5 M for phenylmagnesium bromide and 0.33 M for aliphatic linear reagents such as propyl-, butyl-, and ethyl-magnesium bromides; at a concentration of 1 M chemiluminescence is not observed at all for these compounds. Apparently the author[31] dealt with less pure compounds in experiments involving the oxidation of concentrated solutions of aliphatic Grignard reagents.

Despite the lack of spectroscopic techniques available to modern investigators, the chemiluminescence intensities of various Grignard reagents observed in the old investigations (up to 1933) were compared on a quantitative basis using calibrated pyrometers. The spectroscopic characteristics of the glow were obtained either by visual observations or by a photographic procedure. This established many characteristic features of the appearance of the chemiluminescence in the reactions of Grignard reagents.[28,32–35] In the first place it was shown that the chemiluminescence in the oxidation of Grignard reagents by oxygen is a fairly general phenomenon for compounds of this class. Among the 60 Grignard reagents tested by Dufford et al.[24] 40 proved to be capable of chemiluminescence.

A list of these compounds, supplemented by the data of Evans and Diepenhorst[34] with indication of the colour and brightness of the chemiluminescence, is presented in Table 1; data for the chemiluminescence of these compounds in the reactions with chloropicrin and bromopicrin are included for comparison. The type of organic group plays a significant role in the appearance of chemiluminescence in the oxidation of Grignard reagents by oxygen. Compounds with isocyclic organic groups emit more light than those with acyclic groups. A favourable factor for both types of compounds is the presence of a direct bond between magnesium and an unsaturated carbon atom. Among isocyclic derivatives of Grignard reagents, the chemiluminescence is more intense in the reactions of compounds containing an aromatic group. The substitution of one hydrogen atom in the benzene ring by another atom or group leads to an increase of the brightness of the chemiluminescence. The position of the substituent in the benzene ring relative to magnesium is then a decisive factor:[34] The brightness of the chemiluminescence decreases in the sequence *p*- > *o*- > *n*. When the position of the substituent and the chemical nature of the group are the same, the chemiluminescence is more intense for bulkier groups. A change in the chemical nature of the substituent X in RMgX (where R is an aromatic group and X = halogen or CH_3) leads to a decrease of the brightness in the sequence chlorine > ethyl > bromine > iodine.[24,34]

Table 1. Characteristics of the reactions of Grignard reagents in ether accompanied by the brightest chemiluminescence.[24,34]

Compound	Brightness of chemiluminescence in reactions with:		
	O_2	chloropicrin	bromopicrin
p-ClC_6H_4MgBr	v.br.b	w.	nil
p-BrC_6H_4MgBr	v.br.b	v.br	nil
β-$C_{10}H_7MgBr$	v.br.b.	–	–
α-$C_{10}H_7MgBr$	br.g.-b.	nil	nil
p-$ClC_{10}H_6MgBr$	br.g.-b	–	–
C_6H_5MgCl	br.g.	w.	v.w.
C_6H_5MgBr	br.b.	w.	v.w.
o-BrC_6H_4MgBr	br.b	–	–
m-BrC_6H_4MgBr	br.b	–	–
p-ClC_6H_4MgI	br.b.	–	–
p-$ClH_3C_6H_4MgBr$	br.g.-b.	w.	–
p-$CH_3C_6H_4MgI$	br.b.	br.g.	nil
p-$C_2H_5C_6H_4MgBr$	br.b.	m.	m.
p-$C_4H_9C_6H_4MgBr$	br.b.	–	–
p-$C_6H_5C_6H_4MgBr$	br.b.	–	–
p-(*p*'-BrC_6H_4)C_6H_4MgBr	br.g.	–	–
p-, *o*-$(CH_3)_2C_6H_3MgBr$	br.y.-wh.	–	–

Notation: v.br. = very bright; m. = moderate; b. = blue; g. = green; y.-wh. = yellow-whitish [w = weak; v.w. = very weak].

An increase of the number of substituents (more than one) in the benzene ring entails a decrease of the brightness of the flow.[35] Chemiluminescence is observed also for Grignard reagents based on naphthalene and anthracene derivatives in which the MgBr group is in the β-position.

The chemical nature of the solvent (14 different ethers, benzene, and dimethylaniline were tested) does not have a significant influence on the intensity of the glow[34] and the observed differences in brightness are caused by the different solubilities of the Grignard reagents and by the viscosity of the medium. Thus the different stabilities of the etherates of the Grignard reagents do not exert the influence suggested in earlier studies.[31,36]

The nature of the substituent and its position in the benzene ring have an appreciable influence also on the spectroscopic characteristics of the chemiluminescence. It has been found[24] that, in each of the two series of Grignard reagents C_6H_5MgCl, C_6H_5MgBr, C_6H_5MgI and *p*-$CH_3C_6H_4MgCl$, *p*-$CH_3C_6H_4MgBr$, *p*-$CH_3C_6H_4MgI$, the compounds containing chlorine give rise to a longer-wavelength (green light) chemiluminescence, while those containing iodine produce the shortest-wavelength (blue light) chemiluminescence. A similar effect has been observed also for the dihalogeno-derivatives of Grignard reagents: *p*-ClC_6H_4MgCl, *p*-BrC_6H_4MgBr, and *p*-IC_6H_4MgI. When the position of the substituent in the benzene ring relative to magnesium is varied in each of the Grignard reagents investigated, namely $CH_3C_6H_4MgCl$, $CH_3C_6H_4MgBr$,

$CH_3C_6H_4MgI$, ClC_6H_4MgBr, BrC_6H_4MgBr, and ClC_6H_4MgCl, the wavelength of the emission increases in the sequence *m*- < *o*- < *p*- (from violet to green light).[24]

When a solution of the Grignard reagent being oxidised was acted upon by ultraviolet light, a photoluminescence (PL), whose intensity increased with the degree of oxidation, was observed; the initial Grignard reagent did not exhibit a photoluminescence.[30,34,37] Neither phosphorescence nor X-ray luminescence were observed for the products of the oxidation of the Grignard reagents. As a rule, the photoluminescence spectra differed from the chemiluminescence spectra.[30,34,37] The chemiluminescence spectra of Grignard reagents containing chlorine or bromine in the benzene ring (*p*-ClC_6H_4MgBr, *p*-BrC_6H_4MgBr) consisted of a single band extending from 448 to 518 nm.[30] The chemiluminescence and photoluminescence of the Grignard reagents derived from naphthalene each contained one band with markedly different maxima.[34] A bathochromic shift of the bands has been observed in the oxidation of these Grignard reagents and has been attributed to the unusual effect of the emitted chemiluminescence as light exciting the photoluminescence of the oxidation products in a longer-wavelength part of the spectrum. The above differences between the chemiluminescence and photoluminescence spectra led to the conclusion[38] that the nature of the chemiluminescence and photoluminescence emitters is different. The bright photoluminescence occurring in the oxidation of Grignard reagents has been attributed[37] to the emission by ROMgX (where R is an aromatic group and X is a halogen).

In later investigations[20,25,27] the identification of the emitters responsible for the glow, achieved with the aid of a sensitive spectroscopic technique, showed that the chemiluminescence and photoluminescence are caused by the emission of light from the same substances but of a kind different from ROMgX. The spectroscopic characteristics have been obtained in the oxidation by oxygen of solutions of C_6H_5MgBr and *p*-ClC_6H_4MgBr in THF, diethyl ether (Fig. 3),[27] and benzene with an admixture of triethylamine.[26] The nature of this solvent does not influence the form of the spectra. The difference of the chemiluminescence spectra from those obtained previously in studies[34,37] where the emission was detected mainly in the visible region and did not coincide with the photoluminescence spectra of the oxidation products has been attributed[20] to the internal filter effect caused by the high concentrations (1 M) of the solutions of Grignard reagents. It was found that it is essential to apply corrections for this effect at low concentrations of Grignard reagents (10^{-3} M). Although Bardsley and Hercules[20] and Bolton and Kerns[27] obtained identical chemiluminescence spectra, they identified different oxidation products as the emitters. Bolton and Kerns[27] found that excited molecules of brominated biphenyls arise in the oxidation of C_6H_5MgBr and *p*-ClC_6H_4MgBr. The photoluminescence spectra of these substances, obtained by the photolysis of bromobenzene (or 1-bromo-4-chlorobenzene) in ether or by the thermolysis of benzoyl peroxide in bromobenzene, were identical with the photoluminescence spectra of the solutions after the oxidation of C_6H_5MgBr or *p*-ClC_6H_4MgBr respectively and with the chemiluminescence spectra of these Grignard reagents. However, it was not discovered which compounds are responsible for the photoluminescence in the longer-wavelength part of the spectrum, which is excited selectively by the 366 nm line in the light from the mercury lamp (instead of the 313 nm which excites both components of the photoluminescence spectrum). Bardsley and Hercules[20] suggested that the emitter is *p*-terphenyl $C_6H_5C_6H_4C_6H_5$—another product of the oxidation of phenylmagnesium bromide. According to Bolton and Kerns,[27] this identification is erroneous because Bardsley and Hercules[20] compared the chemiluminescence spectrum with an incorrect photoluminescence spectrum of *p*-terphenyl. The actual position of the photoluminescence maximum in the spectrum of *p*-terphenyl (340 nm) according to data in Berlman's book[39] differs markedly from the chemiluminescence peak/365 nm). After the oxidation of *p*-ClC_6H_4MgBr, three fractions exhibiting a blue photoluminescence were isolated[20] by chromatographic separation. The only product identified in these fractions (it is suggested that it is $ClC_6H_5C_6H_4C_6H_5Cl$) has a photoluminescence spectrum (with a maximum at 345 nm) which does not coincide with the chemiluminescence spectrum. Two other products, which were unidentified because of their small amount, exhibit a photoluminescence at 377 and 387 nm, i.e. in the region of the chemiluminescence maxima. Estimations of the quantum efficiency of the chemiluminescence[20] yielded 10^{-6} and 10^{-4} for C_6H_5MgBr and *p*-ClC_6H_4MgBr respectively.

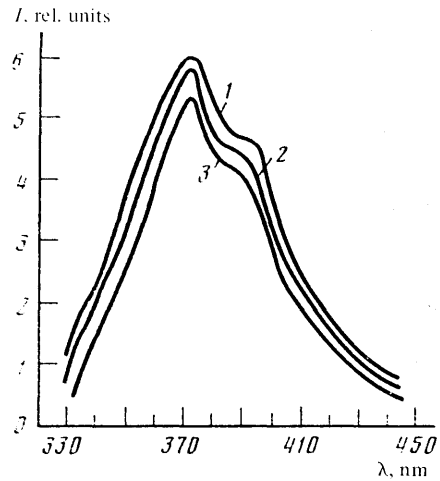


Figure 3. The fluorescence spectrum of the products of the oxidation of phenylmagnesium bromide in diethyl ether[27] with an excitation wavelength λ_e = 313 nm (curve *1*), the fluorescence spectrum of photolysed bromobenzene in ether with λ_e = 313 nm (curve *2*), and the chemiluminescence spectrum in the reaction of a solution of phenylmagnesium bromide in ether with oxygen (curve *3*).

The glow of brominated biphenyls is excited in the elementary reaction step and not as a result of energy transfer,[27] but the introduction of brightly fluorescent additives does not influence the chemiluminescence intensity. It was found that the oxidation of diphenylmagnesium is not accompanied by chemiluminescence.[27] In the same study it was also shown that the unsubstituted biphenyls formed in the oxidation of phenylmagnesium bromide (in yields up to 15%) are not excited in this chemiluminescence system. An EPR signal was detected in the oxidation of phenylmagnesium bromide,[27] which is important, since previously the formation of free radicals in the oxidation of organomagnesium compounds had been demonstrated on the basis of more indirect data: the analysis of the composition of the oxidation products and the study of the stereochemistry of the autoxidation reaction.[40]

Two mechanisms of the oxidation reaction, ensuring sufficient energy for the excitation of the chemiluminescence of brominated biphenyls (90 kcal mol^{-1}), have been proposed.[27] According to the first mechanism, the excitation takes place as a result of the reactions of free radicals:

$$C_6H_5MgX + O_2 \rightarrow C_6H_5O_2MgX \rightarrow C_6H_5^{\cdot} + MgO_2X \xrightarrow{MgX_2} \rightarrow C_6H_5MgX + \dot{X} \rightarrow XC_6H_5MgX \xrightarrow{R} \dot{R} + XC_6H_5MgX \xrightarrow{O_2} XC_6H_5O_2MgX \rightarrow$$

$$\xrightarrow{C_6H_5MgX} \begin{cases} \longrightarrow XC_6H_5MgX + C_6H_5OMgX; \\ \longrightarrow 2MgOX + XC_6H_5C_6H_5^{\cdot} \rightarrow XC_6H_5C_6H_5 + h\nu. \end{cases}$$

It follows from the above mechanism that the emitter is excited on interaction of the organomagnesium peroxide with the initial Grignard reagent. However, no direct evidence for the involvement of the peroxide in the generation of the chemiluminescence has been presented.[27] The low intensity of the EPR signal precluded the identification of the radicals. In order to demonstrate the involvement of the radicals in the chemiluminescence, an attempt was therefore made to investigate the influence of radical trapping agents on the chemiluminescence; the attempt was unsuccessful because of the low solubility of such agents and (or) their interaction with the Grignard reagent. The authors[27] proposed a second, alternative mechanism without the participation of free radicals:

$$C_6H_5MgX + O_2 \rightarrow C_6H_5O_2MgX \xrightarrow{C_6H_5MgX} \rightarrow 2C_6H_5OMgX \rightarrow C_6H_5C_6H_5X^{\cdot} + MgO + MgOX;$$

$$\rightarrow C_6H_5C_6H_5X + h\nu.$$

We may note that these investigators[27] do not give preference to either of the two mechanisms.

2. The Influence of the Magnetic Field

The influence of the magnetic field on chemical reactions is regarded nowadays as a reliably established fact[41-43] although up to 1967 the existence of this effect appeared extremely doubtful.[41] The study,[44] which is apparently the first investigation in which the sensitivity of a chemical reaction to the magnetic field was observed (at any rate, this is absolutely certain in relation to reactions accompanied by chemiluminescence) is of special interest in this connection. The authors[44] thought that in a strong magnetic field there is a possibility of identical orientations of the molecules or molecular orbitals, which may result in the polarisation of the emitted light. They did not observe the polarisation of the chemiluminescence but were able to discover another effect, which consists in an increase of the intensity of the chemiluminescence when the Grignard reagent is oxidised in the magnetic field. The rapid imposition of the field induces a directional flow of a stream of solution and an increase of the brightness of the emission from the sides of the metallic crucible containing the solution. The authors[44] explained the observed phenomenon by the movement of the products of the oxidation of the Grignard reagent, which possess paramagnetic properties, towards the poles of the magnet. This effect has been clearly observed for p-BrC_6H_4MgBr only in strong fields (1500 G).

3. Electrochemiluminescence of Solutions of Grignard Reagents

A glow has usually been observed under severe electrolysis conditions (at potentials ranging from 100 to more than 1000 V),[44,45] with the exception of one study,[46] where, apart from the fact that electrochemiluminescence (ECL) has been detected, no other data concerning the glow of the Grignard reagent were presented. For solutions of C_6H_5MgBr or $C_6H_5CH_2MgBr$ in ether (potential 110–130 V, platinum plate electrode, current 0.02 A), the brightness of the observed ECL was so great that in the case of phenylmagnesium bromide the outline of the anode could be distinguished in a dark room at distances up to 6 m.[45]

A larger series of Grignard reagents has been investigated by Dufford et al.[44] A bright glow has been observed for Grignard reagents based on phenyl bromide (visible at 110 V), p-iodotoluene, and 1,4-bromochloronaphthalene (appears at a potential of 500 V); a weak glow has been found for n-lauryl bromide (visible only at a potential >1000 V) and a very weak glow has been observed for m-bromochlorobenzene (even at 1500 V the ECL is weaker than the chemiluminescence of this compound in its reaction with O_2) and for α-bromonaphthalene; there is no glow in the case of benzyl chloride. The glow is usually excited at the anode and more rarely at the cathode or at both electrodes. A number of compounds, for which chemiluminescence is not excited in their reaction with oxygen, emit light during electrolysis.

A glow during electrolysis has been observed reliably in all cases for compounds with a brighter chemiluminescence; however, the brightness of the emission in electrolysis and in oxidation by oxygen is a maximum for different Grignard reagents. On this basis, it has been concluded[44] that the nature of the glow is different in these processes. In contrast to this, in another study[45] it has been suggested that the mechanisms of the chemiluminescence and the ECL of solutions of Grignard reagents are identical and involve electron transer.

The electrolysis of Grignard reagents is accompanied by the precipitation of metallic magnesium, which exhibits a high catalytic activity.[44,45] One cannot rule out the possibility that this catalytic activity of magnesium influences also the chemiluminescence.

The modern interpretation of the mechanisms of electrode processes involving organomagnesium compounds includes reactions with participation of radicals (organic and organomagnesium radicals):[47]

$$R_2Mg \rightarrow R^{\cdot} + RMg^{\cdot}$$
$$RMg^{\cdot} \rightarrow Mg + R^{\cdot}$$

Consequently, there is a possibility of the excitation of the ECL of solutions of Grignard reagents in radical reactions. Admittedly these reactions reflect processes at the cathode (which is associated with the polarographic method of investigation), whereas, as stated above, the ECL is mainly observed near the anode. It is noteworthy that the glow excited at very high potentials (above 1000 V) is hardly a pure example of the classical ECL and its nature may be similar to that of the emission of light accompanying the so-called non-Faraday electrolysis.[5]

The ECL of phenylmagnesium bromide has been investigated at low potentials (starting with 10 V).[25] The electrolysis was carried out in carefully deoxygenated solutions. After a short time, the glow disappears spontaneously despite the continuous passage of current through the solution without an appreciable consumption of the Grignard reagent. Subsequently this was demonstrated successfully on the basis of the chemiluminescence which arises following the subsequent admission of air into the solution which ceased to emit light during electrolysis. One can therefore conclude that in this case the anodic emission of light is associated with the presence of impurities, containing O_2, the liberation of which takes place as a result of the slow decomposition of the impurities during electrolysis.

Thus, in order to determine the mechanism of the ECL of solutions of Grignard reagents and also to demonstrate the very fact that such a glow takes place, it is necessary to carry out additional experiments with a clear separation of the anodic and cathodic cell compartments and with determination of the compositions of the anolyte and catholyte.

4. Oxidation of Grignard Reagents by Organic Peroxides

The chemiluminescence accompanying the interaction of solutions of Grignard reagents with benzoyl, ethyl, and diacetone peroxides has been observed by Gilman and later confirmed by Dufford et al.[38] The reaction of BP with a number of Grignard reagents (C_6H_5MgBr, p-BrC_6H_4MgBr, p-ClC_6H_4MgBr) is accompanied by the emission of light with a lower intensity than in the oxidation of these Grignard reagents by oxygen.

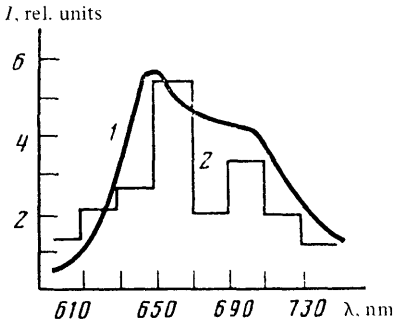


Figure 4. The fluorescence spectrum of a solution of the triphenylmethyl radical in diethyl ether (10^{-4} M) with λ_e = 447 nm (curve *1*) and the chemiluminescence spectrum in the reaction of phenylmagnesium bromide with benzoyl peroxide in ether (line 2).[48]

A detailed investigation of the mechanism of the chemiluminescence arising in the reaction of C_6H_5MgBr, ClC_6H_4. .MgBr, and $CH_3C_6H_4MgBr$ with BP and t-butyl peroxybenzoate in THF and diethyl ether[48] is of special interest. The reactions with diphenylmagnesium and with aliphatic Grignard reagents did not give rise to a glow. The oxidation of phenylmagnesium bromide is accompanied by a very bright (visible to the naked eye) red glow and the colour of the solution then changes from pale-brown to red. The excess peroxide produces a yellow colour owing to the formation of the triphenylmethyl radical, which was characterised by its EPR spectrum and by comparison with the spectrum of the radical synthesised independently. The radical is very stable: on storage in a sealed vessel the EPR signal remains unchanged for a month. The same radical has been identified as the chemiluminescence emitter. (Probably this is a unique case of the chemiluminescence of solutions where the radical is an emitter of the glow associated with a chemical reaction). The emitter has been identified on the basis of the identity of the chemiluminescence spectrum and the photoluminescence spectra of the products of the reaction of BP with phenylmagnesium bromide and a solution of the triphenylmethyl radical (Fig. 4). The time corresponding to a decrease of the chemiluminescence intensity by 50% depends on the nature of the solvent. The chemiluminescence emitter is excited in an elementary reaction step, since in the presence of fluorescent additives (pentacene, rubrene, and rhodamine G) the brightness of the chemiluminescence does not increase.

In order to determine the mechanism of the formation of the triphenylmethyl radical, a study has been made[48] of the reaction of deuteriated phenylmagnesium bromide with peroxide. The EPR signal of the resulting radical is three times wider than in the reaction of the protonated Grignard reagent, which the authors interpreted as evidence for the formation of the triphenylmethyl radical from one of the benzene rings of the Grignard reagent and two peroxide rings. The formation reaction of this radical is a side reaction in relation to the main interaction of the Grignard reagent with the peroxide. This is associated with the low yield of the radical compared with the yield of the stable oxidation products (the interaction of 0.1 M C_6H_5MgBr with an excess of the peroxide produces 10^{-4} M triphenylmethyl radical). However, when the reaction conditions are altered, it is possible[48] to increase the yield of the radical and hence also the chemiluminescence intensity.

5. The Interaction of Grignard Reagents with Other Substances

When a number of substances (H_2O, N_2O, H_2O_2, SO_2, CO, NO_2, H_2, N_2, NO, CO_2, and Na_2O_2) come into contact with solutions of Grignard reagents, a glow does not appear even when highly exothermic reactions take place (with Na_2O_2, H_2O_2, and H_2O).[28,31,32] The appearance of chemiluminescence in the reactions of certain Grignard reagents with benzene triozonide has been mentioned.[24] A bright-red chemiluminescence has been observed[25] in the reaction of phenylmagnesium bromide with carbon tetrachloride in diethyl ether. This extremely vigorous reaction results in the formation of the triphenylmethyl radical. However, in the absence of oxygen chemiluminescence is not observed; the autoxidation of the triphenylmethyl radical is also not accompanied by a glow.

6. The Oxidation of Organocalcium Compounds by Oxygen

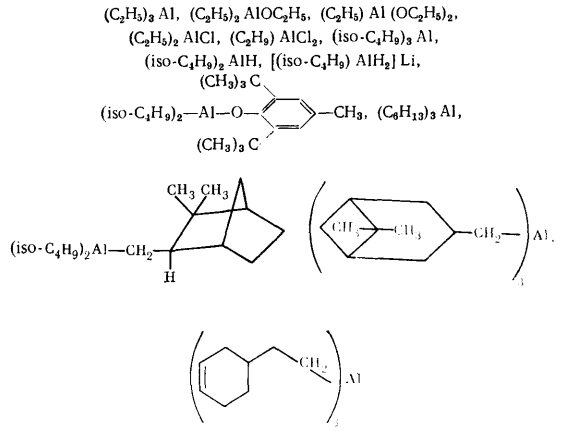
The organocalcium compound C_6H_5CaI was synthesised for the first time by Thomas and Dufford[35] and a yellow chemiluminescence was observed in its oxidation with oxygen. The not unduly high intensity of this chemiluminescence is comparable to that of the chemiluminescence in the analogous reaction of C_6H_5MgI. The alkyl derivative C_2H_5CaI does not chemiluminesce in its reaction with oxygen. A similar negative result has been obtained for organomercury[35] and organozinc[24] compounds: C_6H_5ZnBr, C_6H_5ZnI, and p-BrC_6. .H_4ZnBr.

IV. THE CHEMILUMINESCENCE OF SOLUTIONS OF ORGANOALUMINIUM COMPOUNDS AND THE ELECTROCHEMILUMINESCENCE OF A RHENIUM CARBONYL SOLUTION

1. Oxidation By Oxygen

The chemiluminescence in the oxidation of organoaluminium compounds (OAC) in solution by oxygen has been observed comparatively recently.[49] There is no information about the chemiluminescence of organic compounds of other Group III elements. The ability to enter into a reaction with oxygen

accompanied by chemiluminescence proved to be a characteristic property of solutions of OAC: a glow has been detected for trialkylalanes with different numbers of carbon atoms (C_2–C_6), their hydride and halogeno-derivatives, a complex of the hydride with an alkali metal, derivatives of norbornene, and other OAC:[49–51]



The kinetic plots of the chemiluminescence intensity obtained when air (or oxygen) is bubbled through solutions of the above OAC, have a feature in common: they exhibit one or several luminescence intensity maxima, which indicates the excitation of the chemiluminescence in reactions of intermediates in the oxidation of the OAC. The brightest chemiluminescence has been observed in the oxidation of the complex $[(iso\text{-}C_4H_9)_2AlH_2]Li$;[50] a bright glow has been noted in the oxidation of diisobutyl(2,6-di-t-butyl-4-methylphenoxy)-aluminium.[50]

The quenching of the chemiluminescence by oxygen and the luminescence yield for the primary emitter made it possible to postulate compounds containing the carboxy-group as the likely chemiluminescence emitters.[51] The increase of the brightness of the chemiluminescence following the replacement of the alkyl group in $(iso\text{-}C_4H_9)_3Al$ by the norbornane group is apparently associated with the high yield of ketones in the oxidation of the norbornane derivative. For certain OAC of this kind, the yield of ketones reaches 90%, while in the oxidation of alkyl derivatives ketones are side products.[13]

The brightness of the chemiluminescence in the oxidation of OAC by oxygen (in contrast to the oxidation of Grignard reagents) increases when a fluoroscent additive (9,10-dibromoanthracene) is introduced into the solution. It has been established that the increased chemiluminescence intensity is caused by the sensitising action of this additive, since the rate of oxidation and the form of the kinetic curve do not change under these conditions and the chemiluminescence spectrum coincides with the photoluminescence spectrum of 9,10-dibromoanthracene.[51] The intensification coefficients of the brightness of the chemiluminescence in the presence of identical amounts of the additive depend on the nature of the OAC and diminish in the sequence diisobutyl(isocamphenyl)aluminium (74) > trimyrtanylaluminium (27) > diisobutyl(2,6-di-t-butyl-4-methylphenoxy)aluminium (2).[50] Thus the primary chemiluminescence emitters in the oxidation of these OAC are of different kind and have different luminescence yields.

Three luminescence regions have been differentiated on the kinetic plot of the chemiluminescence intensity in the oxidation of triethylaluminium: two maxima and a long low-slope descent (Fig.5).[51] This kinetic relation indicates the occurrence of several reactions, accompanied by chemiluminescence, of the intermediates formed in consecutive stages. We may note that similar information can be found just as explicitly from the monotonic kinetic variation of the amount of absorbed oxygen, usually obtained in the study of the kinetics of the oxidation of OAC. The complexity of a more detailed interpretation of the kinetic chemiluminescence plot obtained can be understood when a simplified mechanism, reflecting the overall oxidation reaction of trialkylalanes, is considered taking into account the reactions undergone by organoaluminium peroxides:

$$AlR_3 \xrightarrow{O_2} \underset{(I)}{R_2Al(OOR)} \rightarrow R_2Al(OR) \xrightarrow{O_2} \underset{(II)}{RAl(OR)(OOR)};$$

$$RAl(OR)_2 \xrightarrow{O_2} \underset{(III)}{Al(OR)_2(OOR)} \rightarrow Al(OR)_3;$$

$$RAl(OR)(OOR) + AlR_3 \rightarrow RAl(OR)_2 + R_2Al(OR); \quad (1)$$

$$RAl(OR)(OOR) + R_2Al(OR) \rightarrow 2Al(OR)_2; \quad (2)$$

$$RAl(OR)(OOR) + RAl(OR)_2 \rightarrow 2Al(OR)_3; \quad (3)$$

$$R_2Al(OOR) \rightarrow RAl(OR)_2; \quad (4)$$

$$RAl(OR)(OOR) \rightarrow Al(OR)_3. \quad (5)$$

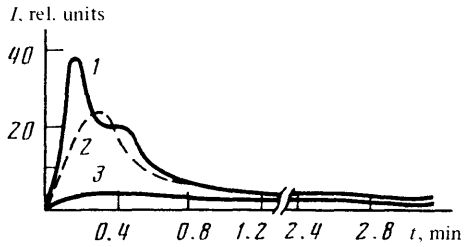


Figure 5. Time variation of the chemiluminescence intensity in the oxidation of solutions of OAC (2.9×10^{-2} M in toluene at 20 °C: *1*) triethylaluminium; *2*) the oxide; *3*) the dioxide.[51]

On the basis of data obtained by Razuvaev and co-workers[52] in a study of the dark oxidation of OAC, Tolstikov et al.[51] concluded that the chemiluminescence develops in a solution containing a complex mixture of OAC with different numbers of alkoxy-groups and organoaluminium peroxides [(I), (II), and (III)]. In order to discover the reactions accompanied by chemiluminescence, the stable oxidation products diethylaluminium ethoxide (oxide), ethylaluminium diethoxide (dioxide), and aluminium triethoxide (trioxide) were synthesised[51] by the reaction of triethylaluminium with ethanol.[51] It was shown that the interaction of these OAC in the absence of oxygen is not accompanied by chemiluminescence even in a highly exothermic reaction such as the formation of the oxide:

$$R_3Al + RAl(OR)_2 \rightarrow 2R_2Al(OR).$$

The interaction with oxygen of each of these OAC (except the trioxide) induces chemiluminescence, on the kinetic plot of which it is possible to differentiate one, two, and three luminescence regions (Fig.5) for the dioxide, oxide, and triethylaluminium respectively. The increase of the chemiluminescence intensity in this sequence is caused by the increased rate of oxidation of the OAC. The set of data

obtained, namely the dependence of the number of chemiluminescence intensity maxima on the number of alkoxy-groups in the OAC, the coincidence of the instant of the emission of the first chemiluminescence intensity peak with the dissociation of the first Al–C bond in triethylaluminium, and correlation of the effective activation energies for each of the three chemiluminescence maxima of triethylaluminium with the activation energies for the dark oxidation of triethylaluminium, the oxide, and the dioxide[52] enabled Tolstikov et al.[51] to conclude that the three regions on the kinetic plot of the luminescence intensity correspond to consecutive changes in the oxidation of the three Al–C bonds of triethylaluminium.

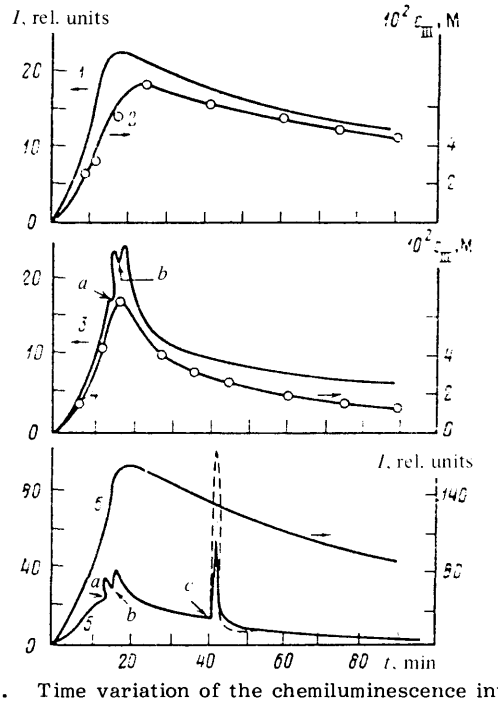


Figure 6. Time variation of the chemiluminescence intensity (curves *1*, *3*, *5*, and *6*) and of the concentration of the peroxide $Al(OR)_2(OOR)$ (III) (curves *2* and *4*) in the oxidation of a solution of the dioxide (0.3 M) in toluene at 20 °C:[51] *1*) and *2*) with constant bubbling of air; *3*) and *5*) the instants when the bubbling with air is stopped (*a*), the bubbling with argon is started (*b*), and the dioxide (continuous line) and the monoxide (dashed line) are added (*c*) are indicated; *6*) the chemiluminescence intensity after the addition of the activator (1×10^{-4} M).

The oxidation of the dioxide yielded parallel kinetic chemiluminescence intensity curves describing the analytical concentration of the organoaluminium peroxide (III) (the intermediate determined by the iodometric titration (Fig.6). The chemiluminescence intensity varies linearly with the concentration of the peroxide (III) (Fig.7). These results and also the absence of significant differences between the mechanisms of the oxidation of triethylaluminium and its alkoxy-derivatives permitted the conclusion that the appearance of chemiluminescence intensity maxima in the oxidation of all three OAC (triethylaluminium, the oxide, and the dioxide) reflects the accumulation and consumption of the corresponding peroxides (I), (II) and (III). We may note that the kinetic plot of the intensity of the chemiluminescence of triethylaluminium is the only experimental "monitor" which makes it possible to follow at the usual temperatures the formation and consumption of the highly reactive peroxides $(C_2H_5)_2AlOOC_2H_5$ and $(C_2H_5)AlOOC_2H_5(OC_2H_5)$, which had been previously [52,54] detected in solution only after extensive cooling of the latter.

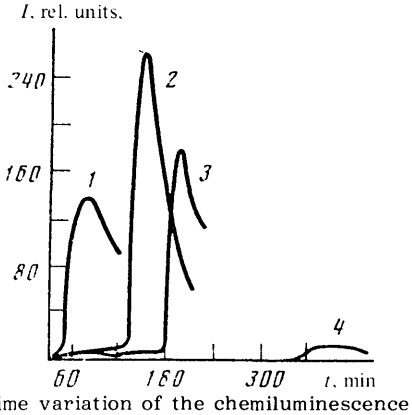


Figure 7. Time variation of the chemiluminescence intensity in the oxidation of solutions of $(C_2H_5O)_2AlC_2H_5$ in toluene in a closed volume (20 ml) under conditions of a constantly decreasing concentration of the dissolved O_2, in the presence of the 9,10-dibromoanthracene concentration [DBA] = 10^{-4} M at 20 °C, and at different initial concentrations of the dioxide (M): *1*) and *5*) 10^{-1}; *2*) 2.5×10^{-2}; *3*) 2.0×10^{-2}; *4*) 1.5×10^{-2}; curves *1–4* represent oxidation by oxygen.

The above reactions of organoaluminium peroxides are the main ones in the mechanism of the consecutive oxidation of the three Al–C bonds of trialkylalanes. In order to determine the contribution of each of these reactions to the excitation of the chemiluminescence, a more detailed study was made of the oxidation of the dioxide,[53] since this OAC has only one unoxidised Al–C bond.[55] Careful purification of this compound showed that only the activated chemiluminescence is observed in its oxidation, which is associated with the low contribution by the luminescence of the primary chemiluminescence emitter. The presence of a glow after the removal of oxygen from solution some time after the start of the oxidation of the dioxide established that the chemiluminescence is not excited in the peroxide formation stage, i.e.

$$(C_2H_5O)_2AlC_2H_5 + O_2 \rightarrow (C_2H_5O)_2AlOOC_2H_5, \qquad (6)$$

but arises in the interaction of the peroxide with the initial OAC:

$$(C_2H_5O)_2AlOOC_2H_5 + (C_2H_5O)_2AlC_2H_5 \rightarrow 2Al(OC_2H_5)_3. \qquad (7)$$

The removal of oxygen (Fig.6) leads merely to the acceleration of the decrease of the luminescence intensity, since the peroxide in consumed in the absence of the source from which it is generated [stage (6)].[51] The straight lines with the same slope $k = (1.9 \pm 0.1) \times 10^{-2}$ min^{-1} correspond to sections reflecting the decrease of the chemiluminescence

intensity and the concentration of the organoaluminium peroxide expressed in terms of semilogarithmic variables.[53] The ratios of the rate constants for the oxidation of the first, second, and third Al–C bonds in triethylaluminium are 100 : 25 : 0.96,[52,54,55] indicating the possibility of the simultaneous presence in solution of the dioxide, the oxide, and a small amount of triethylaluminium and the corresponding peroxides in the initial instant of the triethylaluminium oxidation reaction. Taking this into account as well as the chemiluminescence data for the oxidation of the dioxide and the intensification of the brightness of the chemiluminescence when the oxide and triethylaluminium are added to the solution after the removal of O_2 (Fig.6), one may conclude that the chemiluminescence in the oxidation of triethylaluminium is excited in the overall reactions (1), (2), and (3) and possibly also in the reaction

$$R_2AlOOR + R_3Al \rightarrow 2R_2Al(OR). \qquad (8)$$

The correctness of the identification of the above reactions of organoaluminium peroxides with OAC as the sources of the excitation of the chemiluminescence in the oxidation of the OAC by oxygen has been confirmed by the results of a study[56] in which chemiluminescence was observed in the interaction of triisobutylaluminium with the stable peroxide $(C_2H_5O)_2AlOOC(CH_3)_3$. The kinetic plot of the chemiluminescence intensity has a simpler form in this instance (without maxima), since the consumption of the organoaluminium peroxide is not complicated by the accumulation of the peroxide, as in the oxidation of the OAC by oxygen. It was found that oxygen plays a dual role in the chemiluminescence of OAC. On the one hand, it is essential for the excitation of the chemiluminescence as a source of peroxide and on the other it deactivates the glow.[51,53] The latter property of oxygen is manifested by the decrease of the chemiluminescence intensity when air is replaced by pure oxygen[51] and also by the presence of an induction period preceding the appearance of a brighter chemiluminescence in the oxidation of the dioxide under the conditions of the continuously decreasing concentration of dissolved O_2 (Fig.7).[53]

The addition of radical reaction inhibitors (diphenylamine or diphenylpicrylhydrazine) does not influence the chemiluminescence in the oxidation of OAC,[51] although it is known that these additives suppress the chemiluminescence in the oxidation of hydrocarbons.[3] The use of a more effective free radical trapping agent, namely the galvinoxy-radical (In),[53] induces the appearance of induction periods before the chemiluminescence is generated (when In is added before the start of the supply of O_2 to the solution) or a sharp decrease of the chemiluminescence intensity and the cessation of the absorption of O_2 (when In is added under the conditions of the excitation of the chemiluminescence) (Fig.8). On the grounds that the addition of In does not entail the complete disappearance of the chemiluminescence, the authors concluded[53] that the chemiluminescence in the oxidation of the dioxide by oxygen is excited in two types of reactions: free-radical and molecular reactions. We may note that the formation of free radicals in the interaction of organoaluminium peroxides with OAC has been unambiguously demonstrated only recently in a study[57] of the dark process.

2. Thermolysis of Organoaluminium Peroxides

Apart from the reaction with OAC, there exists another pathway for the consumption of the organoaluminium peroxide (OAP) in solution: thermal decomposition.[58–60] The possibility of the excitation of chemiluminescence in this process has been investigated[56] in relation to the thermolysis of a solution of the stable peroxide $(C_2H_5O)_2AlOOC(CH_3)_3$ in toluene free of O_2. This process is indeed accompanied by chemiluminescence, whose intensity increases with increase of temperature and the OAC concentration. At a constant temperature, the kinetic plot of the chemiluminescence intensity consists of two luminescence regions (Fig.9); in the first region the flash of chemiluminescence resulting from the addition of the OAC to the solvent is followed by a decrease of its intensity and in the second a sharp rise of the chemiluminescence intensity to a maximum followed by a prolonged descent is observed. The kinetic plot of the analytical concentration of the OAC has a simpler form (Fig.6, curve 2) i.e. yields less information.

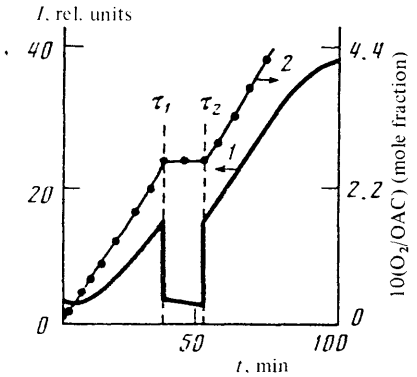


Figure 8. The influence of the addition of the inhibitor in the oxidation of a 10^{-1} M solution of $(C_2H_5O)_2AlC_2H_5$ in toluene on the chemiluminescence intensity (line *1*) and on the rate of absorption of O_2 (line *2*): [DBA] = 10^{-4} M; 20 °C; volume of solution 10 ml; [In] = 2×10^{-5} M; τ_1 = instant of addition of In; τ_2 = instant corresponding to the end of the induction period.

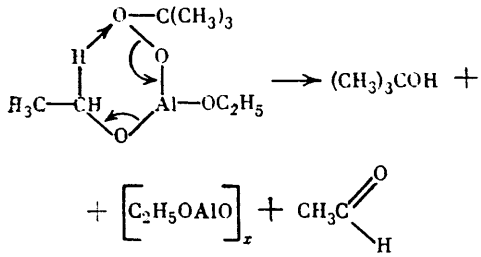
The existence of two thermolysis regions indicates the complexity of the thermolytic process, which has been interpreted in two ways in the literature concerned with the results of dark investigations: as heterolytic[57] or homolytic.[58] The second region in the kinetic plot of the chemiluminescence intensity (Fig.9), where a sharp rise has the form characteristic of the induced decomposition of organic peroxides, has been attributed[56] to the reactions of free radicals produced by the simultaneous dissociation of the O–O and Al–O bonds in the organoaluminium peroxide in conformity with the results of the study of the dark process:[58]

$$(C_2H_5O)_2AlOOC(CH_3)_3 \rightarrow (C_2H_5O)_2AlO^{\cdot} + (CH_3)_3CO^{\cdot};$$

$$(CH_3)_3CO^{\cdot} \rightarrow (CH_3)_2C{=}O + \dot{C}H_3.$$

The rate constant for the thermolysis of the OAP, calculated[56] from the slope of the linear form of the second section of the plot of the time variation of the chemiluminescence intensity (Fig.9*b*) agrees with the values $k = 7.4 \times 10^{-3}$ min^{-1} (T = 353 K) obtained[58] from dark measurements of the rate of decomposition of the same peroxide. The first luminescence region (Fig.9) has been assigned[56] to the consumption of the OAP as a result of the intramolecular oxidation of the ethyl fragment in the cyclic reactive complex, whose mechanism can be represented as follows in conformity with

the data obtained in the dark:[57]



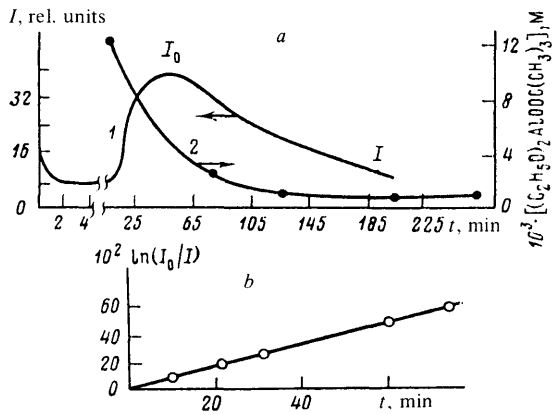


Figure 9. *a*) Time variation of the chemiluminescence intensity (curve *1*) and of the OAP concentration (curve *2*) in the thermal decomposition of the OAP (1.2×10^{-2} M) at 80 °C (the instant of the addition of the OAP to toluene heated to 80 °C was adopted as the starting point for the time readings); *b*) linear form of the I_0-I section in Fig. 9*a*.

The mechanisms presented above for the thermolysis and the homolytic and heterolytic decomposition of the OAP show that aldehydes and ketones, which frequently behave as emitters in the oxidation of hydrocarbons,[2] may be formed. The chemiluminescence spectra in the thermolysis of the OAP contain[56] three luminescence components with maxima at 430, 510, and 550 nm and, whereas the first two can be assigned to emission by excited ketones and aldehydes, the presence of the long-wavelength luminescence components indicates a more complex mechanism of the excitation of the chemiluminescence. In the presence of 9,10-dibromoanthracene the chemiluminescence spectrum corresponds to the emission by an excited activator.

The chemiluminescence data for the thermolysis of OAP show that, in the oxidation of OAC by oxygen, the chemiluminescence may be excited in reactions of two types: in the interaction with the OAC (a precursor of the OAP) or in the thermal decomposition of the OAP.

3. The Interaction of Organoaluminium Peroxides with Water

Yet another variety of the chemiluminescence of OAC has been observed recently, namely that associated with the interaction of OAP with water.[61] The addition of water to a solution of the dioxide being oxidised by oxygen intensifies appreciably the chemiluminescence. It has been shown that, among the series of highly exothermic reactions occurring in the oxidation of the dioxide by moist air in solution, only the reaction of water with the OAP—the intermediate in the oxidation of the dioxide—generates chemiluminescence.

This conclusion has been confirmed by the results of a study[56] where chemiluminescence was observed in the interaction of a stable OAP with H_2O in the absence of O_2 in the solution (Fig. 10). Two most probable mechanisms of the excitation of the chemiluminescence in the reaction of OAC with water have been proposed:[56] the recombination of the hydroperoxy-radicals with formation of an intermediate tetroxide by analogy with the chemiluminescence in the oxidation of hydrocarbons[9] and also the reaction of aluminium-containing radicals. The possibility of the formation of radicals in this system has been confirmed indirectly by the form of the kinetic plot of the chemiluminescence intensity (Fig. 10), which has a very pronounced threshold character.

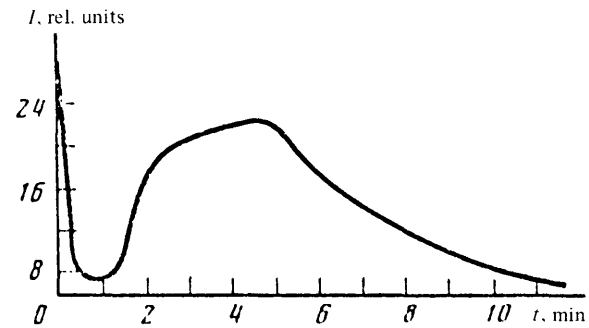


Figure 10. Time variation of the chemiluminescence intensity following the addition of H_2O to a solution of OAP in toluene after heating it for 220 min at 80 °C and then cooling (40 min) to 25 °C; $[OAP]_0 = 10^{-3}$ M; $[H_2O] = 1$ M.

The introduction of water into the system at the beginning of the oxidation of triethylaluminium or the oxide does not entail an increase in the brightness of the chemiluminescence compared with the "dry" oxidation of these OAC in view of the rapid consumption of the OAC owing to hydrolysis, as a consequence of which the OAP, namely $(C_2H_5)_2AlOOC_2H_5$ and $(C_2H_5O)_2AlOOC_2H_5$, do not accumulate in solution. There is no doubt that these highly reactive OAP should emit a brighter light in their reactions with water than in the reactions of $(C_2H_5O)_2AlOOC(CH_3)_3$ or $(C_2H_5O)_2AlOOC_2H_5$. This chemiluminescence can apparently be observed at low temperatures, where the above peroxides accumulate[52,54] in large amounts.

When water is introduced at later stages of the oxidation of triethylaluminium, a chemiluminescence flash is observed,[61] since the relatively stable peroxide $(C_2H_5O)_2AlOOC_2H_5$ has accumulated by that time as a result of the consecutive oxidation of the Al–C bonds in solution (Fig. 11). The brightness of the chemiluminescence in the reaction of this peroxide with water makes it possible to employ it for the quantitative selective determination of the OAP in solution. The generally adopted iodometric titration makes it possible to

determine up to 10^{-3} M peroxides, while 1.2×10^{-5} M peroxide in the presence of [DBA†] = 10^{-3} M can be determined from the linear dependence of the chemiluminescence intensity on the concentration of the OAP. An increase of [DBA] by an order of magnitude makes it possible to detect 10^{-6} M of the peroxide in solution.

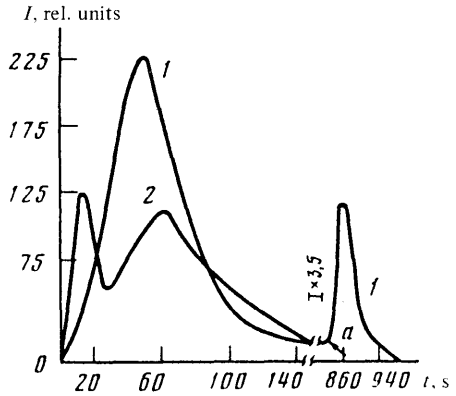


Figure 11. Time variation of the chemiluminescence intensity in the oxidation of a 1.8×10^{-2} M solution of triethylaluminium in toluene in the presence of an activator {[DBA] = 10^{-4} M}: *1*) oxidation with dry air (with addition of 10 ml of H_2O at time *a*); *2*) oxidation with moist air.

4. Oxidation of OAC Complexes with Oxygen

It has been found[62] that the addition of $Ru(bipy)_3Cl_2.6H_2O$ to the solution greatly increases the brightness of the chemiluminescence in the oxidation of OAC by oxygen. It has been established that the interaction of the ruthenium complex of the OAC with triisobutylaluminium, triethylaluminium, diisobutylaluminium hydride leads to the formation of the complex of the OAC with $Ru(bipy)_3Cl_2$ which is soluble in toluene and methylene chloride. The identity of the absorption and fluorescence spectra of the resulting complex demonstrated that ruthenium retains its oxidation state. The complex formation reaction is accompanied by the liberation of gaseous alkanes and the formation of alumino-oxanes—the products of the interaction of the water of crystallisation of the ruthenium compound with the OAC. Depending on the ratio of the amounts of the OAC and the initial ruthenium compound, the complex formed contains the initial OAC or the alumino-oxan as the ligand.

The oxidation of a homogeneous solution of the complex $[Ru(bipy)_3Cl_2(OAC)_n]$ with oxygen is accompanied by a bright-red chemiluminescence, which can be observed with the naked eye.[62] Comparison of the chemiluminescence and fluorescence spectra of the solution oxidised showed that the chemiluminescence emitter is the excited complex $[Ru(bipy)_3.Cl_2(OAC)_n]$. The difference between the forms of the kinetic chemiluminescence curves for the oxidation of the free OAC and their ruthenium complexes is not an adequate argument in support of the excitation of the chemiluminescence emitter in the elementary oxidation step or of an excitation via simple sensitisation, because of the difficulty of determining the exact composition of the ligand in the complex.

5. Electrochemiluminescence of a Rhenium Carbonyl Solution

Analysis of the data on the excitation of chemiluminescence in the redox reactions of OMC in solution permits the conclusion that the luminescence emitters are not the OMC themselves but either organic products of their reactions or the sensitisers introduced as additional species into the reaction zone. Admittedly one cannot rule out the possibility that light is emitted by excited species of the type RC–Al=O or similar formations produced when OAC are oxidised. The chemiluminescence, observed by Luong et al.,[63] in which the rhenium OMC has been reliably identified as the luminescence emitter, is therefore of special interest. The species involved in the chemical reaction and leading to the excitation of the rhenium carbonyl *fac*-$ClRe(CO)_3L$ (where L = 1,10-phenanthroline or 4,7-diphenyl-1,10-phenanthroline) were generated electrochemically. The process was carried out at platinum electrodes via cyclic electrolysis with the potential varied in the range from +1.3 to −1.3 V (in acetonitrile as the solvent). The luminescence emitter was excited by the annihilation interaction of the radical-anion and radical-cation produced by the electrochemical reduction and oxidation of the initial rhenium compound:

$$[fac\text{-}ClRe(CO)_3L]^{+} + [fac\text{-}ClRe(CO)_3L]^{-} \rightarrow 2\ [fac\text{-}ClRe(CO)_3L]^{\cdot}.$$

Comparison of the electrochemiluminescence and fluorescence spectra of the test solution showed that the luminescence emitter is the excited OMC.

V. THE CHEMILUMINESCENCE OF ORGANOMETALLIC COMPOUNDS IN THE GAS PHASE

The reactions of OAC with excited singlet molecular oxygen and with O and N atoms in the gas phase are accompanied by luminescence. Surprisingly, the gas-phase chemiluminescence of OAC has been first observed and investigated[64–66] not under laboratory conditions but in space in the vicinity of the Earth. This luminescence has been used to investigate the geophysical characteristics of the atmosphere (wind, turbulence, and molecular diffusion). For this purpose, liquid trimethylaluminium (1.1 kg)[64] or its mixture with triethylaluminium (20%)[65] was placed in a vessel containing nitrogen under a pressure of 25 atm. The OAC was evaporated in the twilight from a rocket despatched to a height of 85–160 km at a flight velocity of 1 km s^{-1}. This resulted in the formation of a chemiluminescent bluish-green cloud. The atomisation of liquid OAC proved more convenient for geophysical research than a hot mixture containing caesium nitrate and powdered metallic aluminium and magnesium.[64,65]

The luminescence quantum yield varied from 0.3 to 0.6 photons per trimethylaluminium molecule. The form of the glowing cloud resembled a cylinder 20 km long and 1.5 km in diameter. The cloud emitted an overall amount of energy of $10^{10.8}$ erg s^{-1}, which is equivalent to 2 kW; the power of the emission decreased with time in accordance with a kinetic curve having a single diffusion maximum.[64]

Simultaneously with the recording of the chemiluminescence, measurements were made of the kinetic and spectroscopic parameters of the fluorescence of the cloud excited by solar rays directed horizontally. The spectral intensity of this

†9,10-Dibromoanthracene (Translator).

fluorescence makes it possible to determine the temperature of the upper layers of the atmosphere. It was established[65] that the emitter of this chemiluminescence is AlO_2^*, emission being recorded in the form of a diffuse curve (Fig.12). The emitter is excited in the reaction of the intermediate AlO with the oxygen atoms present in the upper layers of the atmosphere: $AlO + O \rightarrow AlO_2^* \rightarrow AlO_2 + h\nu$. The presence of the intermediate (AlO) in this system has been confirmed by recording its blue-green fluorescence (Fig.12) excited by sunlight. The authors[65] put forward two possible pathways leading to the formation of AlO—via the reaction of trimethylaluminium with atomic or molecular oxygen.

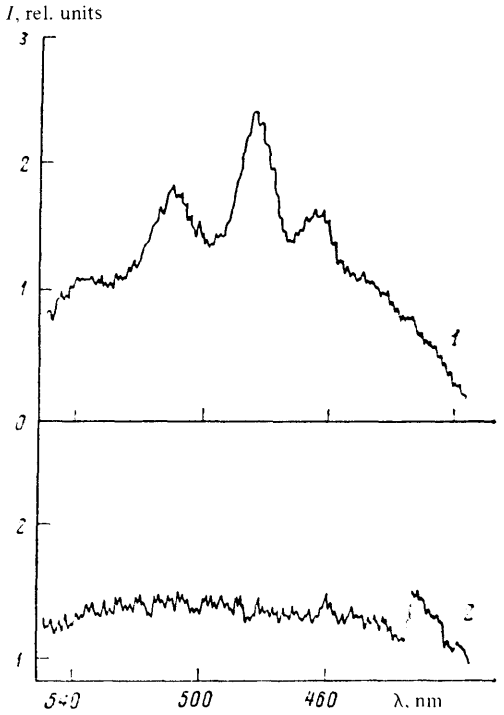


Figure 12. Emission spectra of triethylaluminium observed when the latter is sprayed from a rocket in space in the vicinity of the Earth; *1*) fluorescence spectrum excited by sunlight at a height of 138 km; *2*) chemiluminescence spectrum at a height of 92 km.

The relative contributions of the reactions of oxygen in various states to the gas-phase chemiluminescence were elucidated in laboratory investigations.[67] In these experiments pairs of OAC were introduced into an optically transparent chamber through which molecular oxygen, mixed with a carrier gas (argon) and subjected to a preliminary activation by a microwave discharge, was passed; this gas stream contains $O_2(a^1\Delta)$, $O_2(b^1\Sigma)$, and O atoms. The mixture composition was varied by removing O atoms as a result of the reaction with an HgO mirror deposited in the vicinity of the discharge unit or by introducing water vapour which selectively removes $O_2(b^1\Sigma)$. It was shown[67] that the presence of O atoms is not obligatory for the excitation of the chemiluminescence of trimethylaluminium, i.e. that the chemiluminescence in the upper layers of the atmosphere may be induced both by excited singlet oxygen $O_2(a^1\Delta)$ and O atoms. Without the preliminary activation of oxygen, a glow was not detected. Thus the chemiluminescence of OAC in the gas phase, in contrast to the liquid phase, is not excited in the reaction with molecular oxygen in the ground state.

Subsequent investigations[68,69] dealt solely with the reaction of trimethylaluminium with oxygen atoms. The absence of chemiluminescence in the reaction of trimethylaluminium with non-activated oxygen molecules was confirmed.[68] The authors[68] concluded that the recombination process of the type $AlO + O \rightarrow AlO_2^*$, proposed in earlier studies[64-66] as the excitation stage, is too slow compared with the rate of emission of light from the chemiluminescence cloud to be the source of the generation of the chemiluminescence. They suggested that the chemiluminescence emitter is AlO^* and not AlO_2^*.

A study[69] undertaken to eliminate these contradictions confirmed that the emission rate constant is indeed too high for reactions of the recombination type. However, here too AlO_2^* was identified as the chemiluminescence emitter; this was subsequently demonstrated with the aid of a high-resolution spectroscopic technique (to within 0.05 nm). In order to account for the discrepancies between the rates of emission and generation of chemiluminescence, the authors[69] postulated the existence of a second intermediate, which gives rise to AlO_2^* on reaction with O atoms:

$$RAlO + O \rightarrow AlO_2^* + R;$$

$$AlOR + O \rightarrow AlO_2^* + R.$$

The first process is believed to be energetically more favourable. In the reaction of trimethylaluminium, H_3CAlO has been suggested as an intermediate of this kind. The rate constant for the formation of the emitter via the suggested mechanism is 10^{-13} cm^3 s^{-1}.

A pink-white chemiluminescence has been observed[69] in the reaction of trimethylaluminium with N atoms obtained by activating nitrogen. The chemiluminescence spectrum consisted of well resolved bands, among which components in the red and violet parts of the spectrum predominated. The emissions due to CH and C_2 were grouped at 431.4 and 516.5 nm. Emission from Al at 507.8 and 572.6 nm was also identified. The transitions of Al(I) are manifested at 309, 394.4, and 396.1 nm.

The mechanism of the chemiluminescence, according to which all the methyl groups in the trimethylaluminium molecule are split off from the aluminium atom, was established on the basis of the spectroscopic data indicated; this results in the excitation of the residual aluminium atom. The most probable source of the excitation energy is the recombination of nitrogen atoms ($2N \rightarrow N_2$), in which 9.76 eV is evolved. The dissociation of three Al—C bonds requires an amount of energy of ~9 eV; the excitation energy of the aluminium atom is 4 eV. The following mechanism was proposed for the generation of the chemiluminescence:

$$(CH_3)_3Al + N \rightarrow AlN + 3CH_3;$$

$$AlN + N \rightarrow Al^* + N_2;$$

$$(CH_3)_3Al + 2N \rightarrow Al^* + N_2 + 3CH_3.$$

The existence of the intermediate AlN was demonstrated by means of the emission at 507.8 and 527.6 nm.[69]

Chemiluminescence has also been observed in the reactions of borine carbonyl with O and N atoms. There has been only one investigation of the chemiluminescence of organoboron compounds.[70] A technique analogous to that employed in the investigation of the chemiluminescence of OAC, supplemented by a mass-spectrometric unit for the determination of the composition and the amount of stable reaction products or

intermediates, was employed. The introduction of the complex H_3BCO into a stream of O atoms (in the absence of O_2) induced a dark-blue chemiluminescence in the range 270–390 nm. The chemiluminescence emitter was found to be BO^* (the $A^2\Pi \rightarrow X^2\Sigma$ transition) and the maximum emission was from the $v' = 4$ and $v' = 5$ levels, but emission from the $v' = 11$ and higher levels was also observed. In addition, a very weak glow of the O–H species ($A \rightarrow X$) was also manifested at 306.4 and 307.7 nm. In the presence of O_2, where the O atoms were generated by an electric discharge in an $He-O_2$ mixture, the chemiluminescence had a bright-pink colour. Its diffuse spectrum was mainly caused by the emission from BO_2^*, although here too there was also emission from BO^*.

In order to account for the observed mass spectra, the chemiluminescence, and the reaction stoichiometry, the authors[70] suggested that H_3BCO is decomposed via two possible initiation mechanisms. In the first of these O atoms remove the hydrogen atoms from the H_3B groups; the remaining fragments rapidly react with O atoms, giving rise to the highly excited BO, whose emission is in fact responsible for the chemiluminescence in the visible and near ultraviolet regions:

$$O + H_3BCO \begin{cases} \rightarrow OH + [CH_2BCO]^* \rightarrow OH + BH_2 + CO; \\ \rightarrow H_2O + [HBCO]^* \rightarrow H_2O + BH + CO. \end{cases}$$

The second possible pathway in the initiating stage involves the direct attack by the O atoms on the boron atoms with liberation of CO groups:

$$O + H_3BCO \rightarrow [H_3BO]^* + CO \begin{cases} \rightarrow BO + H_2 + H + CO; \\ \rightarrow HBO + H_2 + CO; \\ \rightarrow HBOH + H + CO; \\ \rightarrow H_2BOH + CO. \end{cases}$$

BO_2 is formed via the reaction

$$BO + O + M \rightarrow BO_2 + M;$$
$$BO + O_2 \rightarrow BO_2 + O.$$

The observed chemiluminescence is due to the last two reactions.

The interaction of H_3BCO with N atoms induces a bluish-green chemiluminescence, which could not be attributed to oxygen admixtures. The authors[70] believe that this chemiluminescence is not caused by the excitation of BN, whose radiative transitions ($^3\Pi \rightarrow X^3\Pi$) at 340–400 nm were recorded after the introduction of BCl_3 into a stream of activated nitrogen. The mechanism of this reaction is more complex than that in the H_3BCO-O system. The possibility of catalysis by one of the intermediates in the recombination reaction of nitrogen atoms has also been suggested.

The chemiluminescence in the reactions of Ni, Fe, Cr, W, Mn, and Co carbonyls with O, H, N, and inert gas (Ar, He, and Ne) atoms in metastable states has been investigated. One of the interesting aspects of the use of metal carbonyls is the gas-phase low-temperature (20–150 °C) generation of metal atoms from them in chemical reactions[71–74] on exposure to electric discharges[75–77] and on photolysis.[78–80] In all these processes some of the metal atoms are formed in an excited state, which leads to the appearance of a visually observable glow. The generation of a laser beam on the basis of Fe and Ni atoms in the ultraviolet and infrared regions of the spectrum has been achieved when the carbonyls of these metals were acted upon by discharges with a double electric pulse[75] and in the flash photolysis of $Fe(CO)_5$.[80] Only studies in which the excited states arose solely as a result of chemical reactions are examined below.

Chemiluminescence has been observed in the interaction of a number of metal carbonyls, namely $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$, $Mn_2(CO)_{10}$, and $Co(NO)(CO)_3$, with N atoms[71,72] and (for the first six carbonyls) also with O atoms.[72] A glow was also observed in the reactions of nickel and iron carbonyls with the inert gas (Ar, He, and Ne) atoms in metastable states. All these reactions were carried out at a reduced pressure (several mmHg) and were accompanied by emission from the excited states of the neutral metal atoms M. Metallic films were then deposited on the walls of the reactors.

The bright-blue chemiluminescence emission spectra in the interaction of metal carbonyls with nitrogen atoms consist exclusively of lines due to emission from neutral atoms.[71] In addition, an intense group of atoms has been noted[72] at 520 nm for the $Mo(CO)_6 + H$ and $Mo(CO)_6 + N$ reactions; they have been assigned to emission from Mo_2^*. On the basis of kinetic and spectroscopic reaction data, the continuous spectrum has been attributed to emission from MCO^*. The mechanism of the excitation of chemiluminescence in the reaction with N atoms includes a series of consecutive stages involving the decomposition of the carbonyls, i.e.

$$M(CO)_n + N \rightarrow M(CO)_{n-1} + NCO.$$

up to the formation of a free metal atom. The metal atoms are excited by collisions with nitrogen molecules in metastable states:

$$M + N_2^*(A^3N) \rightarrow M^* + N_2.$$

The latter are produced in a three-atom recombination reaction and have a short lifetime owing to their destruction on the walls of the reactor.

An analogous mechanism of the stepwise decomposition of the carbonyl has been proposed by Becker and Schurgers,[72] but they explain the excitation of the metal atoms by the retention of the energy, which the metals possess in the carbonyl complex, after the elimination of the CO groups. The chemiluminescence arising in the $M(CO)_n + O$ reaction, was assigned in their study to the emission from MO^*. This glow is observed for all the metals (Cr, W, Fe) investigated except for the molybdenum compound. It is suggested that the MO^* emitter is formed as a result of the direct interaction of oxygen atoms with the metal atoms formed when the CO ligands are removed from the carbonyl. Comparison of the rate constants for the overall reaction $M(CO)_n + O \rightarrow$ products with the rate constants for the reaction leading to chemiluminescence showed that a proportion (several %) of the steps in the overall reaction lead to the formation of substances in an excited state. No differences between the $M(CO)_n + H$ reaction and the $M(CO)_n + N$ (or O) reaction has been reported.[72]

The reactions of iron and nickel carbonyls with the metastable $Ar^*(^3P_2)$, $Ne(^3P_2)$, and $He(2^3S)$ atoms, obtained in a microwave discharge in a hollow cathode, are accompanied by a blue [for $Fe(CO)_5$] or reddish-blue [for $Ni(CO)_4$] chemiluminescence, readily observed with the naked eye.[73,74] The characteristic distinct spectral lines were assigned to the emission by the neutral metal atoms. The N_2 and OH^- emission bands are due to the luminescence by background impurities. The weak bands between 450 and 500 nm in the $Ne^* + Ni(CO)_4$ reaction spectrum are due to the (0,0) and (0,1) transitions of the excited CO^+ formed as a result of ionisation:

$$Ne^*(^3P_2) + CO(x, v=0) \rightarrow Ne + CO^+(A^2\Pi_i; v=0) + e^-.$$

The chemiluminescence intensity in the reactions of both carbonyls is described by linear relations as a function of the concentration of the metastable atoms X and the pressure

of the carbonyl (in the region of low pressures). Kinetic measurements showed that excited states of the metal are produced in the bimolecular process

$$X^* + M(CO)_n \rightarrow X + M^* + nCO.$$

The authors[73,74] found differences between the emission spectra of the metal atoms excited chemically and in an arc discharge.

Table 2. The chemiluminescence and electrochemiluminescence of OMC

Element	Compound	Second reagent	Medium
Li	C_6H_5Li	O_2	S, L
Li	C_4H_9Li	Benzoyl, lauryl, and t-butyl peroxides	L
Na	C_6H_5Na	O_2	S
K	C_6H_5K	O_2	S
Mg	RMgX, XRMgX	O_2	L
Mg	RMgX	Benzoyl, ethyl, and diacetyl peroxides, benzene triozonide, chloroform, carbon tetrachloride, aliphatic nitrocompounds, and picryl chloride	L
Mg	RMgX	Electrolysis	L
Ca	C_6H_5CaI	O_2	L
Al	R'_3Al, R'_2AlCl, $R'AlCl_2$, R'_2AlH, $[R'AlH_2]Li$, $[(R_3Al)_nRu(bipy)_3Cl_2]$, $[(>Al-O-Al<)_nRu(bipy)_3Cl_2]$	O_2	L
Al	R'_3Al, $(R'O)_2AlR'$	$(R'O)_2AlOOR$	L
Al	$(R'O)_2AlOOR'$	H_2O, thermolysis	L
Al	$(CH_3)_3Al$, $(C_2H_5)Al$	$O_2(a^1\Delta)$, O, N, He, Ar, Ne	G
B	H_3BCO	O, N	G
Mo	$Mo(CO)_6$	O, N, H, Ar, He, Ne	G
Cr	$Cr(RO)_6$	O, N, H, Ar, He, Ne	G
W	$W(CO)_6$	O, N, H, Ar, He, Ne	G
Mn	$Mn_2(CO)_{10}$	O, N, H, Ar, He, Ne	G
Fe	$Fe(CO)_5$	O, N, H, Ar, He, Ne	G
Co	$Co(NO)(CO)_3$	O, N, H, Ar, He, Ne	G
Ni	$Ni(CO)_4$	O, N, H, Ar, He, Ne	G
Re	*fac*-$ClRe(CO)_3L$	Electrolysis	L

Notation: S = solid phase, L = solution, G = gas; R = alkyl or aryl; R' = C_2–C_6 alkyls; in the reaction with O_2, R' represents in addition isocamphenyl, myrtanyl, or 3-(3-cyclohexenyl) ethyl [2-(3-cyclohexenyl)ethyl? Editor]; L = 1,10-phenanthroline or 4,7-diphenyl-1,10-phenanthroline.

VI. CONCLUSION

The summarising Table 2 shows that organic compounds of fifteen Group I–III and VI–VIII elements in the Periodic System are capable of chemiluminescence. However, we believe that chemiluminescence is a more general property of OMC, since the compounds of the majority of elements have not yet been tested in this respect and the available negative results in the literature refer to attempts to detect chemiluminescence with the naked eye. We believe that Table 2 reflects only a small proportion of the possible new chemiluminescence reactions of OMC.#

We shall now turn to the energy relations of the reactions. We may conclude that all the known light emitting reactions of OMC are highly exothermic, but by no means all highly exothermic reactions of OMC are accompanied by chemiluminescence. In the reactions with oxygen processes involving organometallic peroxides apparently play an important role in exciting the glow. However, this conclusion requires additional experimental confirmation. Thus the chemiluminescence in the reactions of compounds of Group I elements with oxygen has not been investigated at all. Whereas the involvement of intermediate peroxides in the excitation of the chemiluminescence of OAC in solution has been demonstrated fairly reliably, for Grignard reagents this is so far merely a hypothesis unsupported by experimental data.

The possibilities of the chemiluminescence method in determining the mechanism of the complex process involving the autoxidation of OMC has been demonstrated in a study of the influence of inhibitors on the chemiluminescence kinetics in the oxidation of OAC in solution. As regards the question of the involvement of free radicals in the excitation of the chemiluminescence of Grignard reagents, the available set of results obtained by the direct determination of these species by EPR in the oxidation of phenylmagnesium bromide by oxygen and in the study of the influence of magnetic fields on such luminescence can be interpreted as evidence for a free-radical mechanism. However, it is necessary to study in addition the influence on this chemiluminescence of trapping agents for free galvinoxy-radicals. It has been noted[40] that induction periods then appear in the oxidation of Grignard reagents.

The reactions of these OMC with oxidants other than organic peroxides, accompanied by a bright chemiluminescence, have so far remained almost uninvestigated. Among new types of reactions of OMC accompanied by chemiluminescence, we may note the glow in the thermolysis and hydrolysis of organoaluminium peroxides in solutions, the annihilation electrochemiluminescence of solutions of rhenium carbonyls, and the gas-phase chemiluminescence excited in the reactions of metal carbonyls with nitrogen, hydrogen, oxygen, and inert gas atoms in metastable states. It is of interest to note the difference between the mechanisms of the chemiluminescence in the oxidation of trialkylalanes by oxygen in the gas phase and in solution. In solution the chemiluminescence is excited as a consequence of the reaction of the OAC with molecular oxygen in the ground triplet state. In the gas phase the chemiluminescence is due to the reactions of the excited singlet oxygen.

The chemiluminescence of OMC has found practical applications. The use of the gas-phase chemiluminescence of organoaluminium compounds in the investigation of the geophysical characteristics of the cosmic space in the vicinity of the Earth is of interest. The chemiluminescence in the oxidation of OAC by oxygen in solution and the glow arising when water is introduced into the system attracts interest

#This is confirmed by a study which was published during the preparation of the review for the press: R.G.Bulgakov, G.Ya.Maistrenko, V.N.Yakovlev, S.P.Kuleshov, G.A.Tolstikov, and V.P.Kazakov, Dokl.Akad.Nauk SSSR (in the press). In this investigation chemiluminescence was observed for organic compounds of metals representing all the Groups in Mendeleev's Periodic System.

because of the possibility of their use to monitor the industrial synthesis of liquid alcohols at the stage involving the preparation of alkoxides by the oxidation of trialkylalanes. Measurement of the kinetics of the variation of the chemiluminescence intensity makes it possible to follow all the main reactions in the oxidation of triethylaluminium. The introduction of water into the system incorporating the OAC undergoing oxidation makes it possible to detect reliably the onset and end of the reaction involving the oxidation of the third Al–C bond in the trialkylalane.

Summarising the data presented, it is possible to differentiate several main aspects of the further development of the research into the chemiluminescence of OMC. Firstly, we have the study of the mechanism of the non-trivial pathway involving redox reactions of the OMC with formation of excited states. This will entail the solution of the problem of the mechanism of the overall photochemical processes, the identification of the chemiluminescence emitter, the elementary step in the excitation of chemiluminescence, the chemiluminescence yield, the influence of quenching agents, etc. Secondly, it will be necessary to investigate the possibility of using chemiluminescence in the study of the mechanism of the dark process, the determination of its nature (radical or molecular), the determination of the kinetic characteristics, and the determination of the influence of inhibiting or catalytic additives on the process mechanism and kinetics. In addition, the application of chemiluminescence in the analysis of both the OMC themselves as well as other substances interacting with the OMC or present in the reaction zone may prove to be promising. Finally, a comprehensive investigation of the possibility of devising methods for the chemiluminescence monitoring of industrial processes involving OMC is essential.

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