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Generation of fullerenyl radicals and chemiluminescence in the (C_{60}—R_3Al)—O_2 system

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Fullerenyl radicals (FR) $RC_{60}^{\cdot}$ and chemiluminescence (CL) are generated in the presence of O_2 in C_{60}—R_3Al (R = Et, Bu^i) solutions in toluene (T = 298 K). The FR are formed due to the addition of the $R^{\cdot}$ radical, which is an intermediate of R_3Al autooxidation, to C_{60}. Mass spectroscopy and HPLC were used to identify $Et_nC_{60}H_m$ (n, m = 1—6), Et_pC_{60} (p = 2—6), and dimer $EtC_{60}C_{60}Et$ as stable products of FR transformations. As found by ESR, the $EtC_{60}^{\cdot}$ radical (g = 2.0037) is also generated by photolysis of solutions obtained after interaction in the (C_{60}—R_3Al)—O_2 system. In the presence of dioxygen, the FR is not oxidized but yields complexes with O_2, which appear as broadening of the ESR signals. Chemiluminescence arising in the (C_{60}—R_3Al)—O_2 system is much brighter ($I_{max} = 1.86 \cdot 10^8$ photon s^{-1} mL^{-1}) than the known background CL ($I_{max} = 6.0 \cdot 10^6$ photon s^{-1} mL^{-1}) for the autooxidation of R_3Al and is localized in a longer-wavelength spectral region (λ_{max} = 617 and 664 nm). This CL is generated as a result of energy transfer from the primary emitter $^3CH_3CHO^*$ to the products of FR transformation: $R_nC_{60}H_m$, R_pC_{60}, and $EtC_{60}C_{60}Et$.

Key words: fullerene C_{60}, alkylaluminums, fullerenyl radicals, fullerene ethylhydrides, C_{60} dimer, chemiluminescence.

In investigations of the physicochemical properties of unstable fullerene derivatives, substantial attention is given to the generation and transformations of fullerenyl radicals (FR).[1—4] Usually FR are generated due to the interaction of C_{60} with organic radicals (reaction (1)). Then the FR are transformed *via* two main routes[2]: dimerization (reaction (2)) and/or addition of organic radicals to form the corresponding molecules (reaction (3)).

$$C_{60} + X^{\cdot} \longrightarrow X\dot{C}_{60} \tag{1}$$

$$2\,X\dot{C}_{60} \longrightarrow XC_{60}{-}C_{60}X \tag{2}$$

$$X\dot{C}_{60} + X^{\cdot} \longrightarrow XC_{60}X \tag{3}$$

$X^{\cdot} = R^{\cdot}, RO^{\cdot}, (RO)_2{}^{\cdot}P(O)$ (R is Alk)

It is known[5,6] that only the FR that are monoadducts of C_{60} enter into dimerization. Unlike processes of FR generation studied in detail, the products of transformations of these species are poorly understood. Conclusions about their nature are based,[1,2] as a rule, only on analysis of regularities of the appearance and disappearance of FR signals in the ESR spectra on heating or photoirradiation of the systems under study. Traditional sources of organic radicals are photolysis or thermolysis of the corresponding compounds. At the same time, it is well known that free radicals are generated in many chemical reactions. A striking example is the chain free-radical oxidation of alkylaluminums (R_3Al) with dioxygen[7—9] forming the whole series of radicals: $R^{\cdot}$, $RO^{\cdot}$, and $RO_2^{\cdot}$. In the present work, we studied for the first time a possibility of FR generation in the chemical reaction using as an example the oxidation of toluene solutions of Et_3Al or $Bu^i{}_3Al$ with dioxygen in the presence of fullerene C_{60}. Taking into account the ability of fullerene to enter into chemiluminescence reactions[10—14] and a glow arising upon R_3Al oxidation with dioxygen,[8] we studied the nature of chemiluminescence (CL) arising upon interaction in the (C_{60}—R_3Al)—O_2 system (R = Et, Bu^i).

Experimental

Fullerite C_{60} (obtained from the G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod), whose purity (99.8%) was checked by HPLC and elemental analysis, was used. Reagents Et_3Al and $Bu^i{}_3Al$ were purified by vacuum distillation of 98 and 91% gasoline solutions.[15] Toluene (reagent grade) was treated with 98.3% H_2SO_4, washed with water, distilled, and then refluxed

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and distilled above metallic sodium under argon.[16] The degree of dehydration of toluene was monitored by the absence of the band at 3400 cm^{-1} (OH) in the IR spectrum and ethane evolution upon treatment with Et_3Al. Argon was purified in the PG gas purification device to remove CO_2, O_2, and organic and mechanical admixtures. Oxygen was dried by passing through a system of columns with concentrated H_2SO_4, KOH, and molecular sieves 4 A. Stock solutions of C_{60} ($3.6 \cdot 10^{-3}$ mol L^{-1}) were prepared in the dark by dissolution of a fullerite weighted sample in toluene under argon with magnetic stirring. The reactivity of C_{60} toward Et_3Al ($Bu^i{}_3Al$) was tested by monitoring the intensity of the C_{60} peaks in the HPLC chromatograms of hydrolyzates obtained by the addition of a 5% solution of HCl (3 mL) to a C_{60}—R_3Al mixture in toluene. Solutions of C_{60}—R_3Al and R_3Al in toluene were oxidized with dioxygen in a special cell mounted in the chemiluminescence setup.[12] In standard experiments, aliquots of toluene solutions of C_{60} and R_3Al were syringed under argon into the chemiluminescence cell; then the chemiluminescence compartment was closed and O_2 was purged through a C_{60}—R_3Al solution ($[C_{60}]_0 = 7.4 \cdot 10^{-4}$ mol L^{-1}, $[R_3Al]_0 = 1.4 \cdot 10^{-1}$ mol L^{-1}). In particular runs oxidation was performed by the introduction of an aliquot of C_{60}—Et_3Al solutions in toluene through a septa into the Schlenk flask containing O_2-saturated toluene and connected to the gas burette filled with O_2. Brown homogeneous solutions formed upon oxidation (20 mL) were hydrolyzed with a 5% aqueous solution of HCl (3 mL). This procedure gave an easily separated precipitate and a toluene solution, and the latter was washed with water from HCl to neutral pH and dried above $CaCl_2$. Thus obtained liquid hydrolyzate (LH) was analyzed by HPLC, UV spectroscopy in the visible region, and ESR. Photolysis of the LH after evacuation (10 Torr) was carried out in quartz ampules with the focused non-filtered light of a DRSh-500 mercury lamp. After toluene was removed from the LH (303 K, 10—20 Torr), a dark brown powered product (PP) was analyzed by IR spectroscopy (KBr pellets) and mass spectrometry. An HP 1090 chromatograph with the analytical column (250×4.6 mm), a UV detector (λ = 340 nm), and toluene as the mobile phase (w = 0.8 mL min^{-1}) were used for HPLC. ESR spectra were recorded on a Radiopan EPR Spectrometer SE/X 2542 instrument. The g-factors of samples were measured relative to diphenylpicrylhydrazyl (DPPH) as the standard and calculated by the formula[17]

$$g_x = g_s - (\Delta H/H_s) \cdot g_s, \qquad (4)$$

where g_s is the g-factor of the standard (DPPH); g_x is the g-factor of the desired sample; ΔH is the difference of magnetic fields corresponding to the centers of the spectra; H_s is the magnetic field in the center of the spectrum of the standard. The measurement error of the g-factor (±0.0005) is caused by inaccuracy of determination of the centers of signals when the spectra of DPPH and the sample under study are overlapped.

UV spectra in the visible region and IR spectra were recorded on Specord M 40 and Specord 75 IR spectrophotometers, respectively. Mass spectra of negative ions were obtained on a MI-1201V static mass spectrometer re-equipped for operation in the resonance electron capture mode. The temperature in the ionization chamber (448—473 K) was monitored by a thermocouple calibrated by a reference thermoresistor. The ionization energy was calibrated by the reference signal of SF_0^-/SF_6 (0 eV).

Results and Discussion

Generation of FR in the (C_{60}—R_3Al)—O_2 system. As known, fullerene C_{60} under normal conditions, *i.e.*, at room temperature and without catalysts and photoactivation, reacts readily with such alkylmetals as Bu^tLi [18,19] and AlkMgBr.[18,20,21] Unlike this, we found that under similar conditions C_{60} and R_3Al in toluene do not enter the chemical reaction, which fact was evidenced by unchanged intensity of the C_{60} peak in the HPLC chromatograms of the hydrolyzates of solutions obtained after storage of a C_{60}—Et_3Al (or C_{60}—$Bu^i{}_3Al$) mixture for 3 h at room temperature under argon (Fig. 1). In this case, the characteristic maxima of C_{60} (330, 408, 546, and 600 nm) in the UV absorption spectra in the visible region undergo no changes. The absence of interaction in the C_{60}—R_3Al system under these conditions agree with the known data[22] on the reaction of C_{60} with Et_3Al catalyzed by Cp_2ZrCl_2.

When C_{60}—R_3Al solutions are exposed to O_2, the concentration of C_{60} decreases rapidly and becomes unobservable already ~40 s after O_2 purging (according to the data of HPLC and UV spectra). After the reaction, the solution remains homogeneous and turns brown. Similar solutions are formed for a shorter O_2 purging (incomplete conversion of C_{60}). After hydrolysis of the solutions (at 100% and incomplete conversion of C_{60}), a white pre-

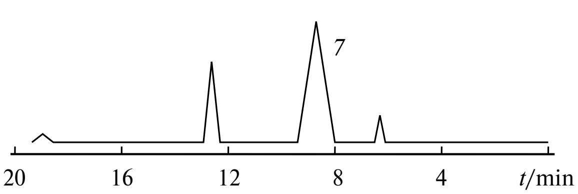


Fig. 1. HPLC chromatograms of the reaction products in the (C_{60}—R_3Al)—O_2 systems: solution of fullerene C_{60} (*1*); hydrolyzates of solutions obtained before and after storage of the C_{60}—Et_3Al mixture for 3 h under argon (*2*); LH of the reaction products in the (C_{60}—Et_3Al)—O_2 system (*3*) and the LH of the products in the same system but after 30 min of UV irradiation (*4*) and 30 min of heating (*5*) at 343 K; solution of the FEH—EF mixture obtained by the method[22] (after chromatographic removal of C_{60}) (*6*); LH of the reaction products in the (C_{60}—$Bu^i{}_3Al$)—O_2 system (*7*). Solvent toluene, 298 K, $[C_{60}]_0 = 7.4 \cdot 10^{-4}$ mol L^{-1}, $[R_3Al]_0 = 1.4 \cdot 10^{-1}$ mol L^{-1}.

cipitate and a brown LH, which contains no Al according to elemental analysis data, are formed. The precipitate contains no C_{60} or its derivatives (no C), being $Al(OH)_3$. Found (%): Al, 34.23; H, 3.78; O, 61.72. Calculated (%): Al, 34.61; H, 3.84; O, 61.53. According to the published data,[15] $Al(OH)_3$ is formed upon hydrolysis of the final products of R_3Al oxidation, *viz.*, alkoxides $(RO)_3Al$. After toluene was removed *in vacuo* at room temperature from the LH obtained by the complete conversion of C_{60}, a solid brown residue remained. The residue is insoluble in organic solvents (toluene, *o*-dichlorobenzene, EtPh, acetone, hexane, alcohols, AcOH, CS_2), water, and HCl. The composition of this, most likely, polymeric product was not determined.

After interaction in the (C_{60}—Et_3Al)—O_2 system (O_2 purging during several seconds), the peak of C_{60} (t_r = 8.72 min) decreases and three new peaks (t_r = 5.76, 11.61, and 17.51 min) (see Fig. 1) with the ratio of surface areas 9.3 : 32.4 : 4 (in %) appear in the HPLC chromatogram of the LH. Similar chromatograms were obtained for the (C_{60}—$Bu^i{}_3Al$)—O_2 system (see Fig. 1). In this case, the t_r values of the corresponding peaks differ insignificantly (by $\leq$1 min) upon changing the nature of R_3Al. The intensities of all HPLC peaks of the LH are retained upon heating for 30 min below 343 K or storing in the dark for ~4 days at 298 K, indicating that the products formed are stable.

It seems reasonable that the new HPLC peaks belong to the products of addition to C_{60} of the $R^•$, $RO^•$, and $RO_2{}^•$ radicals generated[7,8] upon the oxidation of R_3Al with dioxygen. If the $RO_2{}^•$ radical interacts with C_{60}, the effect of fullerene inhibition of R_3Al oxidation with dioxygen would be observed. However, the rates of O_2 absorption from the gas burette during Et_3Al oxidation in the absence and presence of C_{60} are the same (Fig. 2). These results agree well with the earlier[23] observation that fullerene C_{60} is unreactive toward the $RO_2{}^•$ radicals generated by the liquid-phase oxidation of hydrocarbons in the presence of C_{60}. To reveal which of two other radicals, namely, $R^•$ or $RO^•$, attacks C_{60}, we performed mass spectrometric analysis of the PP obtained by O_2 purging through a C_{60}—Et_3Al solution for 30 s. The mass spectrum of negative ions detected at 448—453 K contains the following lines, *m/z* (I_{rel} (%)): 720 [C_{60}] (40), 750 [$C_{60}EtH$]$^-$ (67), 778 [$C_{60}Et_2$]$^-$ (40), 780 [$C_{60}Et_2H_2$]$^-$ (40), 808 [$C_{60}Et_3H$]$^-$ (50), 810 [$C_{60}Et_3H_3$]$^-$ (53), 836 [$C_{60}Et_4$]$^-$ (32), 838 [$C_{60}Et_4H_2$]$^-$ (37), 840 [$C_{60}Et_4H_4$]$^-$ (100), 866 [$C_{60}Et_5H$]$^-$ (82), 868 [$C_{60}Et_5H_3$]$^-$ (78), 870 [$C_{60}Et_5H_5$]$^-$ (46), 894 [$C_{60}Et_6$]$^-$ (32), 896 [$C_{60}Et_6H_2$]$^-$ (18), 898 [$C_{60}Et_6H_4$]$^-$ (12), and 900 [$C_{60}Et_6H_6$]$^-$ (30).

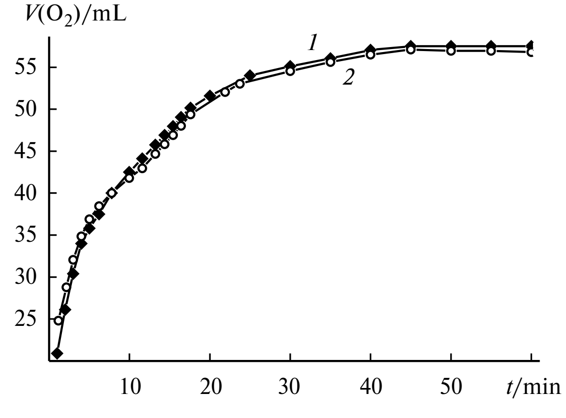


Fig. 2. Kinetics of O_2 absorption from a gas burette by solutions of Et_3Al (*1*) and C_{60}—Et_3Al (*2*). $[C_{60}]_0 = 7 \cdot 10^{-4}$ mol L^{-1}, $[Et_3Al]_0 = 1.4 \cdot 10^{-1}$ mol L^{-1}, measurement accuracy $V(O_2) = \pm 0.8$ mL.

Therefore, fullerene ethylhydrides (FEH) and ethylfullerenes (EF) are formed as the major reaction products in the (C_{60}—Et_3Al)—O_2 system. At this stage of the work, we did not study in detail hydrogen addition to the C_{60} cage in FEH. This is the matter of our further studies. Earlier[22] FEH and EF were found in the hydrolyzate (hereinafter LH-1) of the products of cycloalumination of C_{60} with triethylaluminum catalyzed by Cp_2ZrCl_2. The HPLC chromatograms of the reaction products of the (C_{60}—Et_3Al)—O_2 system and products obtained independently by a described procedure[22] contain the general peaks of C_{60} (t_r = 8.72 min) and the peaks with t_r = 5.76 min. The peaks with t_r = 11.61 and 17.34 min are recorded only for the (C_{60}—Et_3Al)—O_2 system (see Fig. 1). When the LH-1 (from which C_{60} was removed by chromatography) was added to the LH, the intensity of only one peak with t_r = 5.76 min increased by ~3.6 times (see Fig. 1). This means that the peak of the LH with t_r = 5.76 min concerns to a mixture of FEH and EF and the peaks with t_r = 11.61 min and t_r = 17.34 min are of different nature.

It is interesting that FEH with the composition $H_4C_{60}Et_4$ is present in the predominant amount in both the LH and LH-1 obtained by quite different methods. Note that the synthesis of FEH and EF using Cp_2ZrCl_2 as the catalyst by a described procedure[22] takes ~26 h at 303—313 K, whereas in the (C_{60}—R_3Al)—O_2 system these products are obtained only within ~30 min at 298 K without a catalyst.

The results of mass spectrometric analysis of the PP show the formation of a higher number of products than it follows from the HPLC data (see Fig. 1). Probably, this is related to the fact that one HPLC peak contains several products with different numbers of the Et groups and H atoms and with possible decomposition of unstable C_{60} derivatives in the mass spectrometer.

The above mentioned resemblance of the composition of the products formed in the (C_{60}—Et_3Al)—O_2 system in the catalytic reaction studied in Ref. 22 is an additional argument in favor of the fact that these products are alkyl rather than alkoxy derivatives of C_{60}.

Thus, of the series of the $R^{\bullet}$, $RO^{\bullet}$, and $RO_2^{\bullet}$ radicals generated in the reaction of R_3Al with O_2, only the $R^{\bullet}$ radical interacts with C_{60}. This seems surprising because the reactivity of the $RO^{\bullet}$ radical is higher than that of $R^{\bullet}$.[24] We believe that the preferential interaction of C_{60} with the $R^{\bullet}$ radical in the system under study is caused by a substantially higher rate of reaction (5) than that of reaction (6)

$$RO^{\cdot} + {>}AlR \xrightarrow{k_5} {>}AlOR + R^{\cdot}, \quad (5)$$

$$RO^{\cdot} + C_{60} \xrightarrow{k_6} RO\dot{C}_{60}, \quad (6)$$

where the formula >AlR designates (in the general form) the initial R_3Al radical and intermediate products[7,8] of its oxidation, namely, R_2AlOR and $RAl(OR)_2$. This is related to a much higher concentration of R_3Al ($1.4 \cdot 10^{-1}$ mol L^{-1}) compared to the C_{60} concentration ($7.4 \cdot 10^{-4}$ mol L^{-1}).

Published data on the k_5 and k_6 values are lacking for the $EtO^{\bullet}$ radical and other alkoxy radicals, which impedes estimations of the effect of k_5 and k_6 on the rates of these reactions.

Thus, the $RO^{\bullet}$ radical is consumed only in faster steps of R_3Al oxidation and not in addition to C_{60}. Note that the final product of R_3Al oxidation with dioxygen, namely, $Al(OR)_3$, is formed[7,8] just in reaction (5).

It is of interest to elucidate the difference in compositions of the reaction products in the (C_{60}—Et_3Al)—O_2 system and for liquid-phase hydrocarbon oxidation in the presence of C_{60} using a described procedure,[23] because the same radicals, *viz*., $R^{\bullet}$ and $RO_2^{\bullet}$, are generated in both cases. However, no addition products of any of these radicals to C_{60} was observed,[23] which is especially interesting in the case of the $R^{\bullet}$ radicals decaying in the both systems by the reaction with high $k_7 = 5 \cdot 10^7$ L mol^{-1} s^{-1}.[24]

$$R^{\cdot} + O_2 \xrightarrow{k_7} RO_2^{\cdot} \quad (7)$$

This difference can be due to the following fact. According to known data,[25] when hydrocarbons are oxidized by molecular oxygen, its concentration ranges at some constant level, enabling the kinetic regime of the reaction when all $R^{\bullet}$ radicals transform into $RO_2^{\bullet}$ in reaction (7).

As a result, although the k_8 value is high ($4 \cdot 10^7$ L mol^{-1} s^{-1}),[26] no alkyl derivatives of C_{60} are formed in this system. Unlike this, R_3Al is oxidized[7,8] with dioxygen in the diffusion regime due to the very high reaction rate. Finally, the rate of dissolution of purged O_2 is lower than the rate of O_2 consumption in the reaction. This creates a deficiency in O_2 because of which not all $R^{\bullet}$ radicals decay in reaction (7) and some small part of these radicals react with C_{60} in the reaction

$$R^{\cdot} + C_{60} \xrightarrow{k_8} R\dot{C}_{60}. \quad (8)$$

Analogous deficiency in O_2 distinctly appears in the kinetics of background CL (BCL) upon R_3Al oxidation in another regime,[27] *i.e.*, when R_3Al is introduced into toluene saturated with oxygen (O_2 purging continues after saturation is achieved). In this case, the rapidly arising BCL then sharply and almost completely decays due to the instant consumption of dissolved O_2, and only after supply of an additional amount of O_2 to the reaction solution the BCL intensity again increases.

As can be seen from the data in Fig. 1, the HPLC chromatograms of the LH, in addition to the peaks of C_{60}, FEH, and EF, contain two new peaks with $t_r = 11.61$ and 17.34 min. Based on the data of HPLC, mass spectrometry, and experiments on LH photoirradiation (see below), we assigned these peaks to the $EtC_{60}C_{60}Et$ dimer and Et_xC_{180} trimer, respectively. Unlike the FR dimers, the structure of even "classical" C_{180} trimer has not been established so far,[28], and data on the synthesis of the trimers containing functional groups are lacking. Therefore, the formula of the trimer is presented above in the general form. The t_r values for the "classical" C_{120} dimer (14.75 min)[29] and C_{180} trimer (17.34 min)[28] are lower by ~2 and 3 times, respectively, than t_r for C_{60} (7.41 min). As turned out, a similar proportionality is valid in our case: t_r(FEH, EF) : t_r($EtC_{60}C_{60}Et$) : t_r(Et_xC_{180}) = 5.76 : 11.61 : 17.34 = 1 : 2.02 : 3.01. The assignment of the HPLC peak with $t_r = 17.34$ min to the trimer is presumable, unlike the identification of the dimer, whose existence was confirmed by us using ESR.

It is known[1,2] that irradiation of solutions of the $X'C_{60}$—$C_{60}X'$ dimers ($X' = Me_3C$, Me_3CCH_2, 1-$C_{10}H_{15}$, *etc.*) produces the ESR signal of the FR, which rapidly disappears after switching off the light. The ESR effects are the major arguments in favor of formation of the fullerene dimers of different structure due to FR dimerization. Based on these data, we obtained similar evidences for FR formation in the (C_{60}—Et_3Al)—O_2 system. No ESR signal is observed before irradiation of the LH, but a singlet line ($g = 2.0037$) appears upon UV irradiation of the LH and disappears immediately after irradiation was switched off (Fig. 3). These appearance and disappearance of the ESR signal upon switching on and switching off the light can be observed repeatedly. The results of these experiments and known data[1,2] suggest that the ESR signal belongs to the $EtC_{60}^{\bullet}$ FR formed upon photodissociation of the dimer in the reaction

$$EtC_{60}C_{60}Et \xrightarrow{h\nu} 2\ Et\dot{C}_{60}. \quad (9)$$

An additional support for this conclusion could be the coincidence of the *g*-factor measured by us with the literature value. However, known data on FR of the $RC_{60}^{\bullet}$ type are restricted by the data on $MeC_{60}^{\bullet}$ only ($g = 2.00229$ and 2.00231 for different sources of radicals $R^{\bullet}$).[30] At the same time, $g = 2.0024$ for $EtC_{70}^{\bullet}$ was reported.[2] To reveal

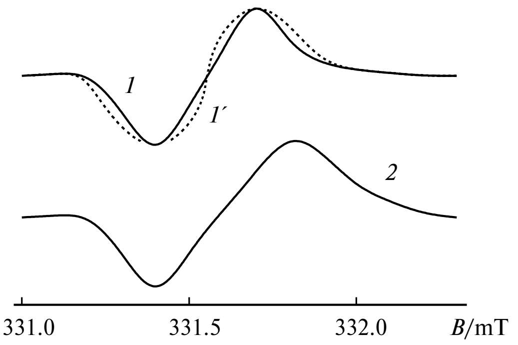


Fig. 3. ESR spectra recorded during photoirradiation of the hydrolyzates (LH and LH-2) of the reaction products in the (C_{60}—Et_3Al)—O_2 (*1, 1′*) and (C_{70}—Et_3Al)—O_2 (*2*) systems after three freezing—evacuation—thawing cycles (*1, 2*) and in air (*1′*).

the nature of the observed ESR signal, we photoirradiated the hydrolyzate (hereinafter LH-2) obtained after interaction in the (C_{70}—Et_3Al)—O_2 model system. In this case, the same ESR effects as for the (C_{60}—Et_3Al)—O_2 system were observed. The *g*-factor of the ESR signal from the irradiated LH-2 is 2.0024, *i.e.*, coincides with published data.[2] These results confirm that our assignment of the ESR signal to $EtC_{60}^{\bullet}$ is correct. In addition to measurements of the *g*-factor of $EtC_{60}^{\bullet}$, we attempted to estimate the strength of the C—C bond in the $EtC_{60}C_{60}Et$ dimer. The bond between two C_{60} cages in the dimers is known[1,2] to be weak. For example, for the dimer of the $(RO)_2{}^{\bullet}P(O)$ radical $\Delta H = 13$ kcal mol^{-1}.[6] No published data on ΔH for the $EtC_{60}C_{60}Et$ dimer are available, but those for dimers of other radicals are known. For instance, for the dimer of the $Me_2CHC_{60}^{\bullet}$ radical, $\Delta H = 35.5$ kcal mol^{-1}.[31] According to published data,[31] the ΔH value is higher for the dimers of simpler radicals. Therefore, the ΔH value for the $EtC_{60}C_{60}Et$ dimer should somewhat exceed 35.5 kcal mol^{-1}. This value is comparable with the average ΔH value of the O—O bond cleavage in organic peroxides[32] decomposing at 343—423 K. Therefore, the absence of peaks of the dimers and trimers in the mass spectrum of the PP is related, most likely, to their thermal decomposition in the ionization chamber, where the temperature is substantially higher (448—473 K).

The IR spectrum of the PP samples contains the following bands/cm^{-1}: 2960 sh, 2925 s, 2864 m, 1620 s, 1453 m, 1426 m (C_{60}), 1380 w, 1260 w, 1220 v.w, 1190 m, 1185 m (C_{60}), 1155 w, 1145 w, 1100 m, 1090 v.w, 1030 v.w, 862 w, 800 v.w, 794 v.w, 770 w, 761 w, 745 v.w, 738 v.w, 731 v.w, 711 v.w, 708 v.w, 660 v.w, 611 w, 580 v.s (C_{60}), 572 m, 562 m, 552 w, 546 v.w, 541 w, 526 v.s (C_{60}), 523 v.w, and 479 w. As can be seen from these data, the spectrum contains no bands at 1736 and 1720 cm^{-1}, *i.e.*, no keto derivatives of fullerene are formed in the system under study. Therefore, oxygen oxidizes R_3Al only rather than fullerene and its derivatives. With an elongation of the interaction in the (C_{60}—R_3Al)—O_2 system, the intensity of the characteristic bands of C_{60} (526, 580, 1185, and 1426 cm^{-1}) decreases and several new bands appear, whose positions coincide with or close (with a difference of 2—9 cm^{-1}) to those of the bands recorded earlier in the IR spectra of the FEH,[18] C_{120} dimer,[29] and $C_{60}H_x$ hydrides (x = 2—36).[33] These bands are not assigned to vibrations of particular bonds,[18,29,33] except for the data[33] where the band at 2853 cm^{-1} in the spectrum of $C_{60}H_{36}$ is attributed to vibrations of the C—H bond. The band with a close position (2866 cm^{-1}) is observed in the IR spectrum of the FEH synthesized in Ref. 18. Therefore, it can be assumed that the band at 2864 cm^{-1} in the IR spectrum of the PP is also caused by vibrations of the C—H bond of the FEH. In addition, we can conclude that the band at 1380 cm^{-1} in the IR spectrum of the PP is due to absorption of just the FEH, because it is absent from the IR spectra of $C_{60}H_x$ (Ref. 33) and the C_{120} dimer.[29] All other strong and weak bands in the IR spectrum of the PP are also observed in the spectra of different C_{60} derivatives: FEH,[18] C_{120},[29] and $C_{60}H_x$.[33]

The UV spectra in the visible region of solutions after interaction in the (C_{60}—Et_3Al)—O_2 system before hydrolysis and the spectra of the LH (Fig. 4) contain maxima (326, 408, 436, 465, and 484 nm), which have earlier been detected (but not assigned) in the spectra of $EtC_{60}H$ [18,20] and $C_{60}H_2$ [33] obtained by other methods. Evidently, the maxima at 326 and 408 nm belong to unreacted C_{60}. The most intense new maximum at 436 nm is characteristic[34] of the 1,2-adducts of C_{60}: the position of this maximum is independent of the radical nature.[35]

Summing up the results of the "dark" study of the (C_{60}—R_3Al)—O_2 system, we can conclude that of the three radicals ($R^{\bullet}$, $RO^{\bullet}$, $RO_2{}^{\bullet}$) generated by R_3Al oxida-

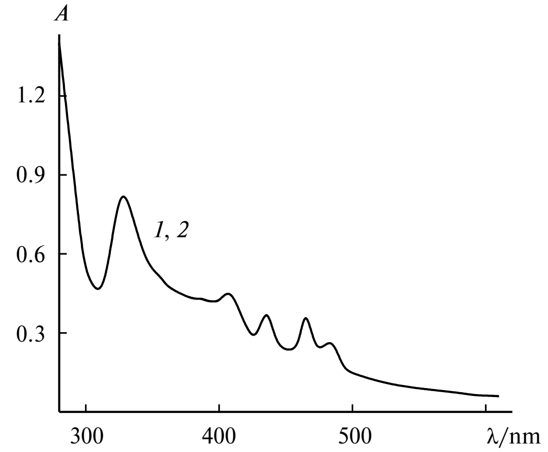


Fig. 4. Absorption spectra of solutions obtained after the interaction in the (C_{60}—Et_3Al)—O_2 system before and after hydrolysis (*1, 2*). Solvent toluene, 298 K, $[C_{60}]_0 = 7 \cdot 10^{-4}$ mol L^{-1}, $[Et_3Al]_0 = 1.4 \cdot 10^{-1}$ mol L^{-1}, $l = 0.1$ cm.

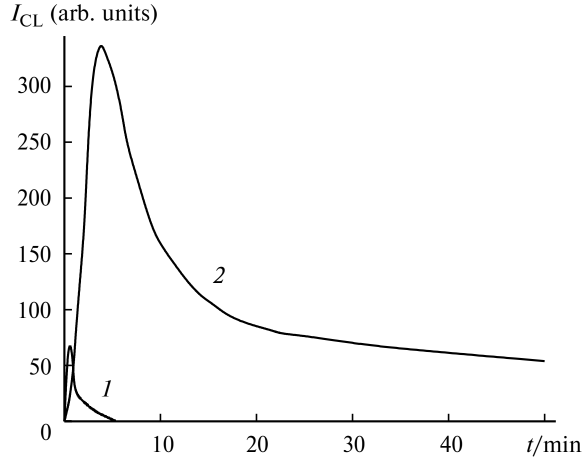


Fig. 5. Background chemiluminescence (*1*) and chemiluminescence (*2*) kinetics. Observation conditions: solvent toluene, 298 K, $[C_{60}]_0 = 7.4 \cdot 10^{-4}$ mol L^{-1}, $[Et_3Al]_0 = 1.4 \cdot 10^{-1}$ mol L^{-1}, O_2 purging through solutions of Et_3Al (*1*) and C_{60}—Et_3Al (*2*).

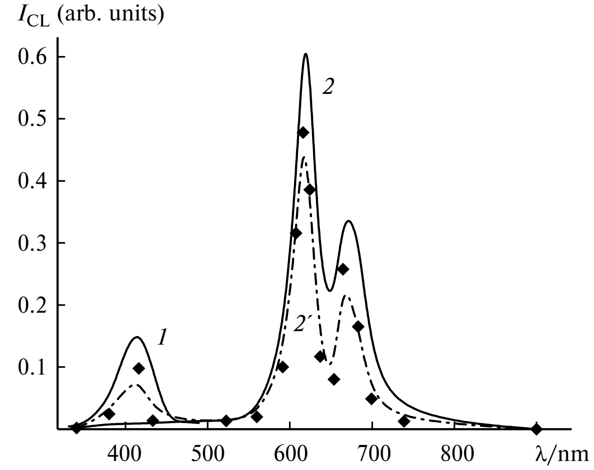


Fig. 6. Background chemiluminescence (*1*) and chemiluminescence (*2*, *2′*) spectra. Observation conditions: solvent toluene, 298 K, $[Et_3Al]_0 = 1.4 \cdot 10^{-1}$ mol L^{-1}, $[C_{60}]_0 = 7.4 \cdot 10^{-4}$ (*2*) and $9.6 \cdot 10^{-6}$ mol L^{-1} (*2′*), O_2 purging through solutions of Et_3Al (*1*) and C_{60}—Et_3Al (*2*, *2′*). The spectra were measured using a set of boundary light filters.

tion only the alkyl radicals add to C_{60} and its derivatives to form FEH, EF, the $EtC_{60}C_{60}Et$ dimer, and, possibly, the Et_xC_{180} trimer as the major products. Varying the nature of the alkyl substituent in R_3Al, different alkyl derivatives of C_{60} can be obtained by a simple method at room temperature and without a catalyst by the interaction in the $(C_{60}$—$R_3Al)$—O_2 system.

CL generation in the $(C_{60}$—$R_3Al)$—O_2 system. We observed earlier undescribed CL upon O_2 action on C_{60}—R_3Al solutions (Fig. 5). Its parameters differ completely from the characteristics of the known[8] BCL arising upon the oxidation of R_3Al with dioxygen. For instance, for the $(C_{60}$—$Et_3Al)$—O_2 system the CL intensity ($I_{max} = 3.2 \cdot 10^7$ photon s^{-1} mL^{-1} at $[C_{60}]_0 = 7.4 \cdot 10^{-4}$ mol L^{-1}) is much higher than that of BCL ($I_{max} = 6.0 \cdot 10^6$ photon s^{-1} mL^{-1}). The ratio of the CL and BCL intensities is 5.3. At $[C_{60}]_0 \geq 7.4 \cdot 10^{-4}$ mol L^{-1} the CL spectrum lies in a longer-wavelength region ($\lambda_{max} = 617$ and 664 nm) compared to the BCL spectrum ($\lambda_{max} = 420$ nm) (Fig. 6).

Two most probable alternative mechanisms can be proposed for the CL observed in the $(C_{60}$—$R_3Al)$—O_2 system. The first mechanism is analogous to that accepted to the liquid-phase CL for hydrocarbon oxidation[36—39] and includes the following key steps: FR oxidation with dioxygen to peroxyl radicals *i.e.*, $RC_{60}O_2^{\bullet}$, and their subsequent disproportionation (photostep).

$$RC_{60}^{\bullet} + O_2 \longrightarrow RC_{60}OO^{\cdot} \qquad (10)$$

$$RC_{60}OO^{\cdot} + RC_{60}OO^{\cdot} \longrightarrow P + CL \qquad (11)$$

P are stable products

The second mechanism assumes energy transfer from triplet-excited aldehyde, *viz.*, BCL emitter ($^3CH_3CHO^*$ for the $(C_{60}$—$Et_3Al)$—O_2) system), to one of the reaction participants.

Several serious arguments contradict the first mechanism. In fact, if the CL is generated in reactions (10) and (11), the oxygen-containing C_{60} derivatives would be formed in the $(C_{60}$—$R_3Al)$—O_2 system, which contradicts the results of IR spectroscopic and mass spectrometric analyses of the products. Unlike the well studied fast reaction of the $R^{\bullet}$ radicals with O_2 with the k value close to k_{diff}, data on quantitative parameters of FR interaction with O_2 are restricted by qualitative estimates only. For instance, it is reported[40] that the $(Bu^tO)_nC_{60}^{\bullet}$ reacts slowly with O_2. Data on the reactions of $Et_nC_{60}^{\bullet}$ and $Bu^i{}_nC_{60}^{\bullet}$ with dioxygen are lacking. Therefore, to estimate the reactivity of the $Et_nC_{60}^{\bullet}$ radicals to O_2, we tested the effect of O_2 on the ESR spectrum of the FR generated by LH photolysis. It turned out that the ESR signal of the $EtC_{60}^{\bullet}$ radical does not decrease in intensity upon LH irradiation in air (see Fig. 3). However, the line in the ESR spectrum is much broader than the signal detected upon irradiation of the LH deaerated by three freezing—evacuation—thawing cycles. Similar "oxygen" broadening of the ESR signal of the $(RO)_2{}^{\bullet}P(O)$ FR has been observed for the first time in Ref. 6. We believe that this reversible ESR effect is caused by the formation of an FR complex with O_2. These experiments show that the FR formed in the $(C_{60}$—$R_3Al)$—O_2 system are not oxidized with dioxygen and, hence, the CL is generated by the mechanism different from that accepted for liquid-phase oxidation of hydrocarbons.

When the C_{60} concentration increases, in the CL spectrum detected for the $(C_{60}$—$Et_3Al)$—O_2 system the intensity of the band with λ_{max} = 420 nm decreases down to the complete disappearance at $[C_{60}]_0$ = $7.4 \cdot 10^{-4}$ mol L^{-1}. The intensity of the bands with λ_{max} = 617 and 664 nm increases simultaneously. This means that the CL is activated and excited due to energy transfer from $^3CH_3CHO^*$ to the initial C_{60} or products, *viz.*, FEH, EF, dimer, and trimer.

It turned out that the increase in the CL intensity with an increase in the C_{60} concentration (Fig. 7) is not due to energy transfer to fullerene. Indeed, the CL spectrum (λ_{max} = 617 and 664 nm) differs substantially from the spectra of fluorescence (λ_{max} = 720—750 nm)**[41]** and phosphorescence (λ_{max} = 796 and 812 nm)**[42]** of C_{60}. In addition, we have earlier**[43]** shown that C_{60} is characteristic of quenching of the electron-excited states of different chemical nature rather than activation. When a fullerene solution ($[C_{60}]_0 \geq 2 \cdot 10^{-3}$ mol L^{-1}) is added at the moment of BCL detection, the glow intensity decreases sharply due to quenching of the primary emitter $^3CH_3CHO^*$ by fullerene (Fig. 8). At the same time, the addition of the LH or LH-1 to the reaction solution during BCL detection (see Fig. 8) enhances the glow. Therefore, the glow activators are stable reaction products in the (C_{60}—R_3Al)—O_2 system, namely, FEH, and the C_{60} dimer and trimer. At this stage of investigation, we could not estimate the relative contribution of each product to the BCL activation, because the effect of additives of individual products on the efficiency of BCL activation should be studied to solve this problem. Two factors favor energy transfer. First, the energy level of the $^3CH_3CHO^*$ donor (λ_{max} = 420 nm, E = 2.95 eV) should be higher than the radiative levels of the energy acceptors estimated by the position of the short-wavelength maximum in the CL spectrum (λ_{max} = 617 nm, E = 2.0 eV). Second, the luminescence spectra of $^3CH_3CHO^*$ (see Fig. 8) well overlap with the absorption spectra of the acceptors, *viz.*, the reaction products (see Fig. 4). If the activation is caused only by the purely physical process of energy transfer from $^3CH_3CHO^*$ to activator molecules, the kinetic curves of BCL and glow after addition of activating additives should be parallel and differ only in intensity. However, after the additives are introduced, the glow decays more slowly than the BCL does (see Fig. 8). This retardation can presumably be caused by the fact that activator introduction induces energy transfer from $^3CH_3CHO^*$ to the activators and also initiates the attack by the $R^\bullet$ radicals (generated in the reaction of R_3Al with O_2) to $Et_nC_{60}H_m$ and Et_pC_{60} with n, $p < 6$ (as shown above, n = 1—6, p = 2—6). As a result of this attack, the contents of $Et_nC_{60}H_m$ and Et_pC_{60} with high n and p increase in the reaction solution. It is most likely that with an increase in n and p the reaction rate of these compounds with the $R^\bullet$ radicals is retarded and the luminescence yield of these activators increases with a decrease in symmetry of the molecules. The longer duration of the CL observed in the (C_{60}—R_3Al)—O_2 system compared to that of BCL can be explained similarly (see Fig. 5).

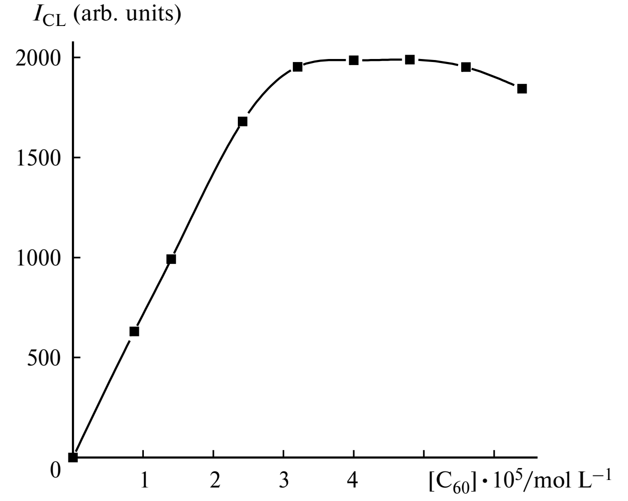


Fig. 7. Plot of the maximum CL intensity (I_{CL}) *vs.* C_{60} concentration in the (C_{60}—Et_3Al)—O_2 system. Solvent toluene, 298 K, $[Et_3Al]_0 = 1.4 \cdot 10^{-1}$ mol L^{-1}.

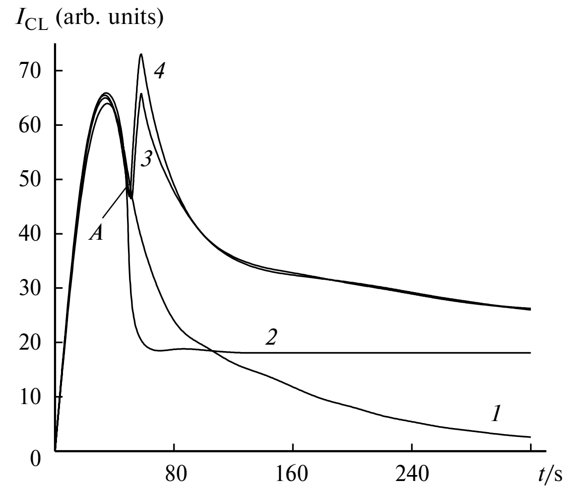


Fig. 8. Effect of the quenching and activating additives on the BCL kinetics: without additives (*1*); with additives of $2 \cdot 10^{-3}$ *M* solution of C_{60} (*2*), LH of the reaction products in the (C_{60}—Et_3Al)—O_2 system (*3*); FEH—EF mixture obtained by the method**[22]** (*4*). *A* is the moment of introduction of an additive. Solvent toluene, 298 K, $[Et_3Al]_0 = 1.4 \cdot 10^{-1}$ mol L^{-1}.

Thus, the increase in the CL intensity with an increase in the C_{60} concentration is caused by the formation of a large amount of activating products. The plots of the CL intensity *vs.* $[C_{60}]_0$ and, correspondingly, the product concentration achieves a plateau. The plateau appears because at some threshold concentration of the products they accept an energy from all primary emitters $^3CH_3CHO$. This is confirmed by the disappearance of the luminescence maximum of $^3CH_3CHO$ at 420 nm in the

CL spectrum. The decrease in the CL intensity after the plateau is caused by absorption of the CL by unreacted C_{60} and the reaction products. The transmission of visually non-transparent LH obtained at $[C_{60}]_0 = 7.4 \cdot 10^{-5}$ mol L^{-1} is 70 (λ_{max} = 617 nm) and 30% (λ_{max} = 664 nm).

Based on the obtained results and according to published data,[8,9,27,44] the mechanism of CL generated in the $(C_{60}—R_3Al)—O_2$ system can be described as follows.

$$>Al—R + O_2 \longrightarrow >AlOO^{\cdot} + R^{\cdot} \qquad (12)$$

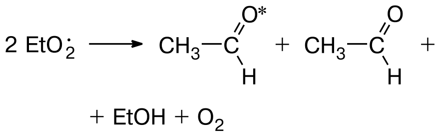
$$>Al—R + O_2 \longrightarrow AlOOR \longrightarrow AlO^{\cdot} + RO^{\cdot} \qquad (13)$$

$$>AlOOR + >Al—R \longrightarrow R^{\cdot} + RO^{\cdot} + P \qquad (14)$$

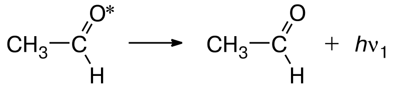
$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot} \qquad (15)$$

$$RO_2^{\cdot} + >Al—R \longrightarrow >AlOOR + R^{\cdot} \qquad (16)$$

$$RO^{\cdot} + >Al—R \longrightarrow >AlOR + R^{\cdot} \qquad (17)$$



$$2\,EtO_2^{\cdot} \longrightarrow CH_3—C(=O^*)H + CH_3—C(=O)H + EtOH + O_2 \qquad (18)$$

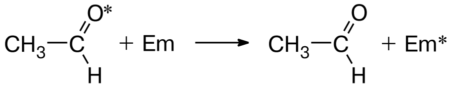


$$CH_3—C(=O^*)H \longrightarrow CH_3—C(=O)H + h\nu_1 \qquad (19)$$

(BCL, λ_{max} = 420 nm)

$$R^{\cdot} + C_{60} \longrightarrow RC_{60}^{\cdot} \qquad (20)$$

$$RC_{60}^{\cdot} \longrightarrow R_nC_{60}H_m + R_pC_{60} + RC_{60}C_{60}R \qquad (21)$$



$$CH_3—C(=O^*)H + Em \longrightarrow CH_3—C(=O)H + Em^* \qquad (22)$$

$$Em^* \longrightarrow Em + h\nu_2 \qquad (23)$$

(CL, λ_{max} = 617 and 664 nm)

Here P are oxygen-containing by-products[27]; Em designates FEH, EF, the dimer and trimer. Reactions (18), (19), and (22) are given for CL in the $(C_{60}—Et_3Al)—O_2$ system.

The $R^{\cdot}$, $RO^{\cdot}$, and $RO_2^{\cdot}$ radicals are formed in reactions (12)—(17).[27,44] Transformations of these primary radicals give the products of R_3Al oxidation: stable $Al(OR)_3$ and unstable >AlOOR in which the Al atom is bonded to the R and RO moieties.[27,44] The BCL emitter ($^3CH_3CHO^*$) appears upon the disproportionation of the $RO_2^{\cdot}$ radicals in reaction (18).[8,9] A small portion of the alkyl radicals, which avoid the attack of O_2 by reaction (15), add to C_{60} to form the FR in reaction (20), and they are further transformed into the stable products P (FEH, EF, dimers, and, possibly, trimers) in reaction (21). The energy of the primary emitter $^3CH_3CHO^*$ is transferred to the products of FR transformations. The latter are transformed in reaction (22) into the electron-excited states, which are deactivated with the CL emission in reaction (23). The presence or absence of luminescence of $^3CH_3CHO^*$ in the CL spectrum depends on $[C_{60}]_0$.

Thus, in the present work we found that the interaction in the $(C_{60}—R_3Al)—O_2$ system generates the FR and CL caused by the emission of the electron-excited states of the products of FR transformations. These results can be used to develop a new approach to fullerene functionalization producing FEH, EF, and FR dimers and trimers.

References

1. V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1211 [*Russ. Chem. Bull.*, 1999, **48**, 1197 (Engl. Transl.)].
2. B. L. Tumanskii, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2396 [*Russ. Chem. Bull.*, 1996, **45**, 2267 (Engl. Transl.)].
3. E. N. Karaulova and E. I. Bagrii, *Usp. Khim.*, 1999, **68**, 979 [*Russ. Chem. Rev.*, 1999, **68** (Engl. Transl.)].
4. M. A. Yurovskaya and I. V. Trushkov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 343 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 367].
5. J. R. Morton, K. F. Preston, P. J. Krusic, S. A. Hill, and E. Wasserman, *J. Am. Chem. Soc.*, 1992, **114**, 5454.
6. B. L. Tumanskii, V. V. Bashilov, N. N. Bubnov, S. P. Solodovnikov, and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1936 [*Russ. Chem. Bull.*, 1992, **41** (Engl. Transl.)].
7. A. G. Davies and B. P. Roberts, *J. Chem. Soc. A*, 1968, 1074.
8. R. G. Bulgakov, V. P. Kazakov, and G. A. Tolstikov, *Khemilyuminestsentsiya metalloorganicheskikh soedinenii* [*Chemiluminescence of Organometallic Compounds*], Nauka, Moscow, 1989, 220 pp. (in Russian).
9. R. G. Bulgakov, V. P. Kazakov, and G. A. Tolstikov, *J. Organomet. Chem.*, 1990, **387**, 11.
10. R. G. Bulgakov, R. G. Akhmadieva, A. S. Musavirova, A. M. Abdrakhmanov, Z. I. Ushakova, and F. M. Sharifullina, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1203 [*Russ. Chem. Bull.*, 1999, **48**, 1190 (Engl. Transl.)].
11. R. G. Bulgakov, R. G. Akhmadieva, A. S. Musavirova, and M. T. Golikova, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 702 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 731].
12. R. G. Bulgakov, A. S. Musavirova, A. M. Abdrakhmanov, E. Yu. Nevyadovskii, S. L. Khursan, and S. D. Razumovskii, *Zh. Prikl. Spektrosk.*, 2002, **69**, 192 [*J. Appl. Spectr.*, 2002, **68** (Engl. Transl.)].
13. R. G. Bulgakov, E. Yu. Nevyadovskii, A. S. Belyaeva, M. T. Golikova, Yu. G. Ponomareva, S. D. Razumovskii, and U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 1700 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 1768].
14. R. G. Bulgakov, E. Yu. Nevyadovskii, Yu. G. Ponomareva, D. Sh. Sabirov, V. P. Budtov, and S. D. Razumovskii, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 2391 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2468].

15. N. N. Korneev, *Khimiya i tekhnologiya alyuminii-organicheskikh soedinenii* [*Chemistry and Technology of Organoaluminum Compounds*], Khimiya, Moscow, 1979, 267 pp. (in Russian).
16. A. Gordon and R. Ford, *Chemist´s Companion*, J. Wiley and Sons, New York—London—Sydney—Toronto, 1972.
17. J. E. Wertz and J. R. Bolton, *Electron Spin Resonance Elementary Theory and Practical Applications*, McGraw-Hill, San Francisco, 1972.
18. A. Hirsch, A. Soi, and H. R. Karfunken, *Angew. Chem.*, 1992, **104**, 808.
19. P. J. Fagan, P. J. Krusic, D. H. Evans, S. A. Lerke, and E. Johnson, *J. Am. Chem. Soc.*, 1992, **114**, 9697.
20. A. Hirsch, T. Grösser, A. Skiebe, and A. Soi, *Chem. Ber.*, 1993, **126**, 1061.
21. M. Sawamura, M. Toganoh, Y. Kuninobu, S. Kato, and E. Nakamura, *Chem. Lett.*, 2000, 270.
22. U. M. Dzhemilev, A. G. Ibragimov, L. O. Khafizova, L. M. Khalilov, Yu. V. Vasil´ev, R. F. Tuktarov, Yu. V. Tomilov, and O. M. Nefedov, *Izv. Akad. Nauk*, *Ser. Khim.*, 1999, 572 [*Russ. Chem. Bull.*, 1999, **48** (Engl. Transl.)].
23. R. G. Bulgakov, Yu. G. Ponomareva, S. I. Maslennikov, E. Yu. Nevyadovskii, and S. V. Antipina, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 1808 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1862].
24. E. T. Denisov, *Kinetika gomogennykh khimicheskikh reaktsii* [*Kinetics of Homogeneous Chemical Reactions*], Vysshaya Shkola, Moscow, 1988, 390 pp. (in Russian).
25. R. F. Vasil´ev, *Dokl. Akad. Nauk SSSR*, 1962, **144**, 143 [*Dokl. Chem.*, 1962 (Engl. Transl.)].
26. R. G. Gasanov, O. G. Kalina, V. V. Bashilov, and B. L. Tumanskii, *Izv. Akad. Nauk*, *Ser. Khim.*, 1999, 2369 [*Russ. Chem. Bull.*, 1999, **48**, 2344 (Engl. Transl.)].
27. R. G. Bulgakov, Doct. Sci. (Chem.) Thesis, Institute of Chemistry, Bashkir Research Center of the USSR Academy of Sciences, Ufa, 1990, 446 pp. (in Russian).
28. K. Komatsu, K. Fujiwara, and Y. Murata, *Chem. Lett.*, 2000, 1016.
29. K. Komatsu, G.-Wu. Wang, Y. Murata, T. Takana, and K. Fujiwara, *J. Org. Chem.*, 1998, **63**, 9358.
30. P. J. Krusic, E. Wasserman, B. A. Parkinson, B. Malone, E. R. Holler, P. N. Keizer, J. R. Morton, and K. F. Preston, *J. Am. Chem. Soc.*, 1991, **113**, 6274.
31. J. R. Morton, K. F. Preston, P. J. Krusic, and E. Wasserman, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1425.
32. V. L. Antonovskii and S. L. Khursan, *Fizicheskaya khimiya organicheskikh peroksidov* [*Physical Chemistry of Organic Peroxides*], Akademkniga, Moscow, 2003, 392 pp. (in Russian).
33. N. F. Gol´dshleger and A. P. Moravskii, *Usp. Khim.*, 1997, **66**, 353 [*Russ. Chem. Rev.*, 1997, **66** (Engl. Transl.)].
34. A. L. Balch and M. M. Olmstead, *Chem. Rev.*, 1998, **98**, 2123.
35. L. N. Sidorov, M. A. Yurovskaya, A. Ya. Barshchevskii, I. V. Trushkov, and I. N. Ioffe, *Fullereny* [*Fullerenes*], Ekzamen, Moscow, 2005, 687 pp. (in Russian).
36. R. F. Vasilie´v, *Nature*, 1962, **194**, 1276.
37. R. F. Vasilie´v, *Nature*, 1962, **196**, 668.
38. R. F. Vasil´ev, *Optika i Spektroskopiya*, 1965, **18**, 236 [*Optics and Spectroscopy*, 1965, **18** (Engl. Transl.)].
39. R. F. Vasilie´v and V. A. Belyakov, *Photochem. Photobiol.*, 1967, **6**, 35.
40. Y.-K. Zhang, E. G. Janzen, and Y. Kotake, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1191.
41. D. Kim and M. Lee, *J. Am. Chem. Soc.*, 1992, **114**, 4429.
42. Y. Zeng, L. Biczok, and H. Linschitz, *J. Phys. Chem.*, 1992, **96**, 5237.
43. R. G. Bulgakov, S. V. Antipina, Yu. G. Ponomareva, E. Yu. Nevyadovsky, S. I. Maslennikov, R. V. Fazulov, and D. I. Galimov, *Abstrs Int. Sci. Conf. "Fullerene and Atomic Clusters" (St. Petersburg, June 27—July 1, 2005)*, St. Petersburg, 2005, 99.
44. V. A. Dodonov, *Elementoorganicheskie peroksidy: nekotorye aspekty sinteza gomoliticheskikh reaktsii i primeneniya dlya nizkotemperaturnoi polimerizatsii vinilovykh monomerov. Metalloorganicheskie soedineniya i radikaly* [*Organoelement Peroxides: Several Aspects of Synthesis of Homolytic Reactions and Application for Low-Temperature Polymerization of Vinyl Monomers. Organometallic Compounds and Radicals*], Ed. M. I. Kabachnik, Nauka, Moscow, 1985, 40 (in Russian).

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