EXPERIMENTAL

The studied arsenic compounds were synthesized by the Grignard reaction in ether. The reaction mixture was decomposed with dilute HCl solution. After drying the ether solution the products were isolated in up to 80% yields. The melting points of triphenylarsine (60°, from alcohol), tri-p-tolylarsine (151°, from alcohol), and tri-p-chlorophenylarsine (107°, from alcohol) agree with the data given in [12-14]. $(p\text{-}ClC_6H_4)_3As$. Found: Cl 25.64%. $C_{18}H_{12}AsCl_3$. Calculated: Cl 26.00%. When preparing trimesitylarsine the reaction was run in an ether—tetrahydrofuran mixture. The product has mp 177° (from n-hexane, cf. [13]).

CONCLUSIONS

Based on measuring the dipole moments of triphenyl-, tri-p-tolyl-, tri-p-chlorophenyl-, and trimesitylarsine, the value of the CAsC valence angle was estimated for the first three compounds (102°). This angle should be substantially greater for trimesitylarsine.

LITERATURE CITED

1. I. P. Romm, E. N. Gur'yanova, and K. A. Kocheskhov, Dokl. Akad. Nauk SSSR, 212, 112 (1973).
2. I. O. Romm, V. I. Lodochnikova, O. P. Syutkina, E. N. Gur'yanova, and E. M. Panov, Zh. Strukt. Khim., 16, 498 (1975).
3. I. P. Romm, N. A. Rozanel'skaya, E. N. Gur'yanova, A. I. Bokanov, and B. I. Stepanov, Zh. Obshch. Khim., 43, 1650 (1973).
4. E. Bergmann and W. Schutz, Z. Physik. Chem., 19, 401 (1932).
5. M. J. Aroney, R. J. W. Le Fevre, and J. D. Saxby, J. Chem. Soc., 1739 (1963).
6. B. D. Chernokal'skii, A. S. Gel'fond, F. Yu. Akhmadulina, and Yu. G. Galyametdinov, Dokl. Akad. Nauk SSSR, 222, 893 (1975).
7. K. I. Kuz'min and Gil'm Kamai, Dokl. Akad. Nauk SSSR, 73, 709 (1950).
8. J. Trotter, Can. J. Chem., 41, 14 (1963).
9. J. Trotter, Acta Crystallogr., 16, 1187 (1963).
10. A. N. Sobolev, L. A. Chetkina, I. P. Romm, and E. N. Gur'yanova, Zh. Strukt. Khim., 17, 103 (1976).
11. J. F. Blount, C. A. Maryanoff, and K. Mislow, Tetrahedron Lett., 913 (1975).
12. G. Kh. Kamai, R. D. Gigauri, B. D. Chernokal'skii, and M. M. Ugulova, Zh. Obshch. Khim., 41, 1506 (1971).
13. W. R. Cullen, B. R. Green, and R. M. Hochstrasser, J. Inorg. Nucl. Chem., 27, 641 (1965).
14. T. B. Brill and G. G. Long, Inorg. Chem., 11, 225 (1972).

CHEMILUMINESCENCE IN REACTIONS OF ORGANIC PEROXIDES WITH BUTYLLITHIUM

A. A. Panasenko, V. S. Sultanova,
V. G. Kozlov, and V. P. Kazakov

UDC 535.379: 542.91:
547.528.3: 547.253.4

Chemiluminescence (CL) was observed in the reactions of Grignard reagents and alkali-metal organometallic compounds with oxygen [1, 2], and also of aromatic Grignard reagents with aromatic peroxides [3].

The results of studying a new luminescent reaction of the organic peroxides: benzoyl, lauryl, and tert-butyl peroxide with butyllithium in either toluene, heptane, or THF solution are reported in the present paper.

Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 470-473, February, 1977. Original article submitted August 5, 1976.

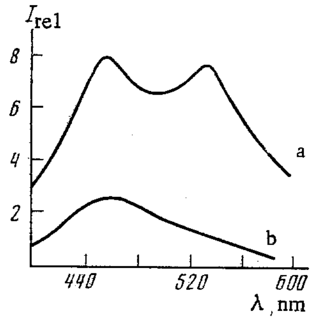


Fig. 1. Chemiluminescence spectra of reaction of BP with BuLi (a) and photoluminescence of heptane solution of mixture of acetophenone and C_4H_9OLi (b) (20°, [BP] = [BuLi] = 0.01 mole/liter).

EXPERIMENTAL

The CL intensity was measured in the lightproof chamber of a PEA-39 photoelectronic amplifier and recorded on an automatic EPPV-60 electronic potentiometer. The apparatus made it possible to record emission with a brightness of $5.5 \cdot 10^3$ photons/sec from the reaction chamber. The absolute CL intensity was estimated by comparing with a standard calibrated radioluminescent source of light. The spectral composition of the emission was measured on a high-transmission SSR-1 monochromator. The fluorescence spectra were recorded on a fluorimeter, which was assembled on the monochromator of an SF-4 spectrophotometer. The solutions were excited with 313-nm light, which was separated out by a DMR-4 monochromator and generated by a high-pressure mercury lamp (DRSh-250-3).

The reaction was run in a dry argon atmosphere, which was freed of traces of oxygen using Ni—Al alloy, in a thermostatted glass vessel in the range −15 to 30°C. The peroxide solutions were placed in the reactor, which was blown with argon for 30 min to remove the O_2, placed ahead of the PEA, and thermostatted to the desired temperature. With good mixing, a solution of a double molar excess of BuLi ($\leq$ 1 ml) was added to the reactor from a syringe without upsetting the lightproofness of the chamber. The end of adding the BuLi (time of the operation 1-2 sec) was considered to be the start of reaction. The reaction of benzoyl peroxide (BP) with BuLi (parallel with the CL study) was studied iodometrically [4] based on the peroxide consumption.

The cp toluene and heptane were refluxed for 6 h over sodium and then distilled in an inert atmosphere. The analytical grade THF was freed of peroxide by standard procedures and then distilled over sodium. The acyl peroxides were reprecipitated from chloroform solution with methanol and then dried in vacuo to constant weight. The BuLi was synthesized from butyl chloride as described in [5].

To identify the products formed when an acyl peroxide is reacted with BuLi, we reacted NP with BuLi as described in [6]. The reaction products were identified via the IR and NMR spectra (Table 1).

DISCUSSION OF RESULTS

We studied the CL in the BP—BuLi system in the greatest detail. Judging by the formed products, the reaction bears a complex character and proceeds through a number of successive steps. The reaction apparently begins with the reaction shown on the following page.

TABLE 1. Reaction Products of BP with BuLi (1:2) and Their IR and NMR Spectra

Reaction products	Infrared spectrum, ν, cm^{-1}	NMR spectrum, δ, ppm
$C_6H_5COOC_4H_9$	1730 (C=O)	4,2 t (CH$_2$O)
$C_6H_5COC_4H_9$	1700 (C=O)	2,8 t (CH$_2$C=O)
$C_6H_5C(OH)(C_4H_9)_2$	3500 (OH)	2,8 s (OH)
C_6H_5COOH	1705 (C=O)	1,72 m (CH$_2$)
C_4H_9OH	3500 (OH)	3,50 t (CH$_2$O)

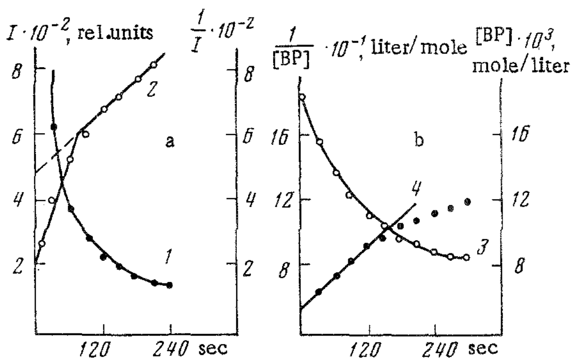
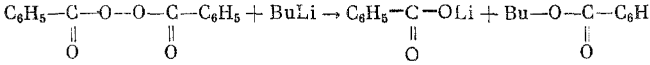
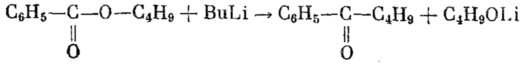


Fig. 2. Kinetic curves: a) drop in CL intensity (1) and its anamorphosis (2) in the coordinates of Eq. (II); b) consumption of BP (3) and its anamorphosis (4) in the coordinates of Eq. (I); [BP] = [BuLi] = 10^{-2} mole/liter.

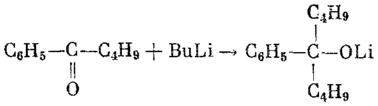


$$\mathrm{C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}O{-}O{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5 + BuLi \rightarrow C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}OLi + Bu{-}O{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5} \tag{1}$$

as is evidenced by the formation of ~ 1 mole of lithium benzoate per mole of reacted BP. The butyl phenyl ketone and lithium alcoholates are formed by the subsequent reaction of BuLi with butyl benzoate and the obtained butyl phenyl ketone via reactions (2) and (3) [5].



$$\mathrm{C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}O{-}C_4H_9 + BuLi \rightarrow C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}C_4H_9 + C_4H_9OLi} \tag{2}$$



$$\mathrm{C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}C_4H_9 + BuLi \rightarrow C_6H_5{-}\overset{\overset{C_4H_9}{|}}{\underset{\underset{C_4H_9}{|}}{C}}{-}OLi} \tag{3}$$

Step (1) is the most exothermic. The heat effect of this reaction, calculated from the energy balance of the bonds, is 90-95 kcal/mole. This energy is entirely sufficient to excite the n—π* level of the ketone, which is formed by reaction (2).

The CL spectra represent either a single structureless band (for the reaction of tert-butyl peroxide) or broad doublet bands (for BP and lauryl peroxide). The position of the CL bands (Fig. 1a) does not coincide with the radiation maximum of alkyl phenyl ketones [7]. However, a heptane solution of an acetophenone—BuLi mixture gives a photoluminescence spectrum whose maximum coincides with the CL maximum at 460 nm (see Fig. 1b). Acetophenone does not react with lithium alcoholates to form new chemical products. In the given case the shift of the photoluminescence spectrum of acetophenone when a lithium alcoholate is added to it is due to the complex formation that occurs between these particles. The formation of a complex is also observed by the change in the UV absorption spectra of the mixture. Consequently, one of the emitters of the CL radiation in the reaction of BuLi with an acyl peroxide is the ketone that is attached to the lithium alcoholate in the complex. The nature of the second maximum is not clear and requires further study. It is entirely possible that the second maximum is formed by the excitation of another secondary product that is present in the solution.

The rate of drop in the CL radiation bears a complex character (Fig. 2). Two sections are observed on the kinetic curve, which are linearized when plotted in the coordinates of the equation of a second-order reaction. At equimolar concentrations of BuLi and BP it is possible to propose equations, analogous to those given in [8], to describe the rate of the chemical reaction and the CL radiation:

$$[\mathrm{BuLi}]^{-1} = [\mathrm{BP}]]^{-1} = [\mathrm{BP}]_0^{-1} + kt \tag{I}$$

$$I = \eta d\,[\mathrm{BuLi}]/dt = \eta d\,[\mathrm{BP}]/dt = \eta k\,[\mathrm{BuLi}]\,[\mathrm{BP}]$$

$$I_0 = \eta k\,]\mathrm{BuLi}]_0\,[\mathrm{BP}]_0$$

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

where k is the reaction rate constant, and η is the CL output. Eqs. (I) and (II) are obeyed well, which can be seen from a processing of the iodometric data and the CL intensity (see Fig. 2). It should be mentioned that the k found from the slope of line 4, satisfactorily coincides with the k obtained for the second section of line 2 (see Fig. 2). They are respectively equal to 0.30 and 0.34 liter/mole · sec. The CL output is $\sim 10^{-12}$ photons per reaction act of BP with BuLi.

From the plot of k vs temperature (k was determined from the CL rate in the range −15 to 30°) it was found that the effective activation energy of the process is equal to 3 ± 0.5 kcal/mole.

CONCLUSIONS

1. A new chemiluminescent reaction of BuLi with organic peroxides was discovered.

2. The chemiluminescence rate when BuLi is reacted with benzoyl peroxide is described by a second-order equation. The rate constant of the reaction at 20° and the activation energy were determined.

3. One of the chemiluminescence emitters is butyl phenyl ketone, which is attached to the lithium alcoholate as a complex.

LITERATURE CITED

1. T. G. Brilkina and V. A. Shushunov, Reactions of Organometallic Compounds with Oxygen and Peroxides [in Russian], Nauka (1966).
2. P. H. Bolton and D. R. Kearns, J. Am. Chem. Soc., 96, 4651 (1974).
3. P. H. Bolton and D. R. Kearns, J. Phys. Chem., 78, 1896 (1974).
4. N. D. Cheronis and T. S. Ma, Micro- and Semimicromethods in Organic Functional Analysis [in Russian], Khimiya (1973).
5. T. V. Talalaeva and K. A. Kocheshkov, Methods in Heteroorganic Chemistry [in Russian], Vol. 1, Nauka (1971).
6. V. I. Savin, I. D. Temyachev, and F. D. Yambushev, Zh. Org. Khim., 12, 275 (1976).
7. S. P. McGlynn, T. Azumi, and M. Kinoshita, Molecular Spectroscopy of the Triplet State [Russian translation], Mir (1972).
8. R. F. Vasil'ev and D. M. Nalbandyan, Kinet. Katal., 13, 1159 (1972).

CHARACTERISTICS OF HYDROLYTIC POLYMERIZATION OF METAL AQUO-IONS IN MIXED AQUEOUS SOLUTIONS OF Fe(III)—Al(III) SALTS

M. A. Fedotov, O. P. Krivoruchko,
A. V. Golovin, and R. A. Buyanov

UDC 541.64: 546.212-128: 546.72-38-145.2: 546.623-38-145.2

The aluminum—iron oxide system is widely used as catalysts, sorbents, and intermediates for the production of ferrites. The most widespread method for their preparation is by the coprecipitation of the hydrogels from mixed solutions of the salts and subsequent ignition or aging of the precipitates. Data are lacking on the reaction between Al(III) and Fe(III) in the step of polymerizing the metal aquo-ions in aqueous solutions as an intermediate step in forming the coprecipitated hydrogels.

In the present paper we studied the formation of the polynuclear hydroxo complexes and their reaction with anions in mixed aqueous solutions of Fe(III)—Al(III) nitrates and chlorides employing the NMR and nuclear magnetic relaxation (NM relaxation) methods, and also the static magnetic method.

Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 473–475, February, 1977. Original article submitted August 10, 1976.