

# DECOMPOSITION OF TRIPHENYLBISMUTH DICROTONATE IN LIGHT IN THE PRESENCE OF 2-METHYL-2-NITROSOPROPANE

A.V. Gushchin<sup>1</sup>, gushchin@chem.unn.ru

O.S. Kalistratova<sup>1</sup>, olga.kalistratova@yandex.ru

A.I. Maleeva<sup>1</sup>, AlevtinaMaleeva@mail.ru

V.A. Kuropatov<sup>2</sup>, viach@iomc.ras.ru

<sup>1</sup> Lobachevsky State University of Nizhni Novgorod, Nizhni Novgorod, Russian Federation

<sup>2</sup> G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhni Novgorod, Russian Federation

Triphenylbismuth dicrotonate  $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCH}=\text{CHCH}_3)_2$  in benzene solution in the presence of 2-methyl-2-nitrosopropane decomposes in light. The phenyl radicals formed as the result of  $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCH}=\text{CHCH}_3)_2$  decomposition are confirmed by the spin-trapping method; they can initiate the methylmethacrylate polymerization at room temperature. In the absence of light the decomposition has not been observed.

*Keywords:* electron paramagnetic resonance, triphenylbismuth dicrotonate, 2-methyl-2-nitrosopropane.

## Introduction

Previously, polymethylmethacrylate (PMMA) with addition of various Bi(V) organometallic compounds was obtained with the use of radical polymerization in the presence of initiators [1, 2]. It was established that Bi(V) acrylates accelerated the polymerization reaction. It was suggested that the acceleration was caused by decomposition of organometallic compounds on exposure to diffused light, as the polymerization slowed in the dark. The character of the process was not studied. When various diacyl derivatives of triphenylbismuth were used, no significant change in polymerization rate or molar mass was observed, indicating the predominant role of the  $\text{Ph}_3\text{Bi}(\text{V})$  fragment. Besides, the previous study of the photo-induced cation polymerization of oxiranes and vinyl monomers was carried out with triaryl(1-pyrenyl)bismuth salts as initiators [3, 4]. When such compounds were irradiated by visible light, the homolysis of Bi–C(pyrene) bond occurred with the formation of pyrenyl radical and cation radical of triaryl bismuth, which subsequently initiated polymerization. It is also known that organometallic compounds of bismuth(III) can cause the controlled living radical polymerization [5, 6].

In this connection it seems interesting to study decomposition of Bi(V) compounds by the example of triphenylbismuth dicrotonate (TPBDCr) in diffused light by the spin-trapping method, as well as formation of metal-containing PMMA, with the use of this compound in the role of initiator. The structure of TPBDCr and other acyl derivatives of triphenylbismuth has recently been described in the literature [7, 8].

## Experimental

*Purification of solvents and reagents.* Benzene,  $\text{Et}_2\text{O}$  and THF were dried over anhydrous calcium chloride, then distilled and kept over sodium wire. Chloroform was dried over anhydrous calcium chloride and distilled. Petroleum spirit was used without previous purification. Anhydrous  $\text{BiCl}_3$  was purified by sublimation (350 °C, 0.5 torr).

*Synthesis of  $\text{Ph}_3\text{Bi}$ .* Triphenylbismuth was synthesized according to conventional procedure [9] from  $\text{BiCl}_3$  and  $\text{PhMgBr}$  with the use of the benzene and THF (1:2) mixture as the solvent.

*Synthesis of  $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCH}=\text{CHCH}_3)_2$ .* The synthesis of triphenylbismuth dicrotonate was carried out according to conventional procedure [10] by the oxidative addition reaction at room temperature in  $\text{Et}_2\text{O}$  from triphenylbismuth, crotonic acid and *tert*-butylhydroperoxide (reagent ratio 1:2:1). The product was purified by recrystallization from the medium petroleum spirit – chloroform (4:1). The yield of the purified reaction product equaled 73 %, melting point 153 °C.

## Химия элементоорганических соединений

*Synthesis of 2-methyl-2-nitrosopropane (MNP).* MNP was synthesized by oxidation of *tert*-butylamine by 20 % aqueous solution of hydrogen peroxide in the presence of sodium tungstate as a catalyst [11].

*Polymerization of MMA in the presence of TPBDCr.* Solutions of TPBDCr (1–5 % m/m) were prepared in methylmethacrylate (MMA) without an initiator. The polymerization was carried out in degassed vacuumed ampoules both in diffused light and in the dark at temperature 19–24 °C.

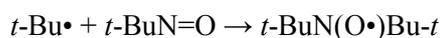
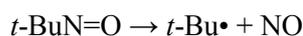
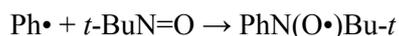
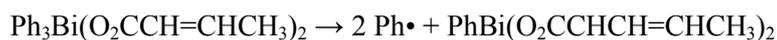
*Photodecomposition of TPBDCr in the presence of MNP.* The solutions for investigation of TPBDCr decomposition in diffused light were prepared as follows: in one elbow of H-ampoule for EPR a sample of MNP (0.2 mol/L) was placed, while the other elbow was filled by the benzene solution of TPBDCr. The ampoule was degassed, sealed, and after mixing the EPR spectrum was registered.

*EPR spectra* were registered on the Bruker ER200D-SRC apparatus with the operating frequency 9.5 GHz in degassed tubes.

### Results and Discussion

We have investigated the decomposition of triphenylbismuth dicrotonate  $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCH}=\text{CHCH}_3)_2$  in benzene in the presence of MNP by EPR method. The choice of the solvent is due to its low activity in radical reactions at the chosen conditions. The concentrations of TPBDCr and MNP are 0.2 mol/L, the reaction has been carried out in light in a sealed and degassed ampoule.

The reaction has resulted in addition compounds of phenyl radicals formed by decomposition of triphenylbismuth dicrotonate, with the spin trap  $\text{PhN}(\text{O}\cdot)\text{Bu-}t$ , as well as in di-*tert*-butylnitroxyl radicals  $t\text{-BuN}(\text{O}\cdot)\text{Bu-}t$  formed by decomposition of the spin trap itself, according to the following scheme:



The EPR spectrum of triphenylbismuth dicrotonate in benzene (with MNP as the spin trap) is shown in Fig. 1.

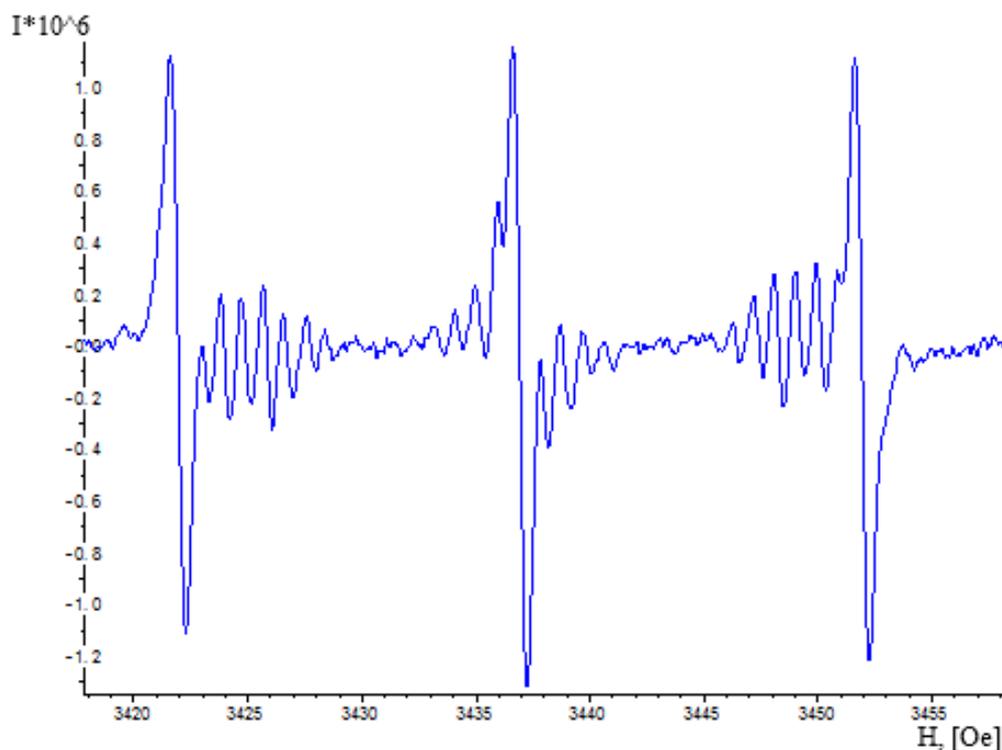


Fig. 1. The EPR spectrum of triphenylbismuth dicrotonate in benzene, the spin trap is MNP

For the addition compound  $\text{PhN}(\text{O}\cdot)\text{Bu}-t$  the values of hyperfine interaction constants have been determined:  $a_{\text{N}} = 12.3$  Oe,  $a_{\text{H1}} = 1.8$  Oe,  $a_{\text{H2}} = 0.85$  Oe,  $g = 2.0056$ , which are in agreement with the literature data for the addition compound generated in benzene by photolysis of  $\text{Ph}_3\text{Bi}$  ( $a_{\text{N}} = 12.0$  Oe,  $a_{\text{H1}} = 1.8$  Oe,  $a_{\text{H2}} = 1.0$  Oe),  $\text{Ph}_3\text{Sb}$  ( $a_{\text{N}} = 11.9$  Oe,  $a_{\text{H1}} = 1.8$  Oe,  $a_{\text{H2}} = 0.9$  Oe),  $\text{Ph}_3\text{As}$  ( $a_{\text{N}} = 11.8$  Oe,  $a_{\text{H1}} = 1.8$  Oe,  $a_{\text{H2}} = 0.9$  Oe) [12], as well as with the data obtained for other sources of phenyl radical in benzene ( $a_{\text{N}} = 12.3$  Oe,  $a_{\text{H1}} = 2.0$  Oe,  $a_{\text{H2}} = 0.9$  Oe) [13]. For the addition compound  $t\text{-BuN}(\text{O}\cdot)\text{Bu}-t$  the values  $a_{\text{N}} = 15.4$  Oe,  $g = 2.0061$ , which are also in agreement with the literature data for the corresponding addition compound generated in benzene by decomposition of  $\alpha$ -isopropylazide ( $a_{\text{N}} = 15.4$  Oe,  $g = 2.0061$ ) [14] and by photolysis of 2-methyl-2-nitrosopropane ( $a_{\text{N}} = 15.4$  Oe,  $g = 2.0057$ ) [15].

Formation of phenyl radicals can also be confirmed by thermodynamic and X-ray diffraction data. It is known that the dissociation energy of the Bi–C(Ph) bond equals 46.2 kcal/mol for triphenylbismuth [16], while the dissociation energy of the Bi–O bond equals 80.6 kcal/mol for bismuth monoxide [17]. The X-ray diffraction analysis points at the bidentate character of acyl ligands binding with a bismuth atom; though the bond length of Bi–O is somewhat greater, the breaking occurs to the Bi–C bonds [5].

The fact of free radical formation was used by us to obtain PMMA. The polymerization of MMA, with various content of dissolved TPBDCr as an initiator, was carried out in diffused light at room temperature. Formation of the solid block was observed in less than 20 h. After storage of the ampoule for 30 days the obtained samples were yellow and opaque, practically insoluble in organic solvents, which indicated additional linking of macromolecules. Low solubility significantly hampered the subsequent analysis of such polymers. It is necessary to emphasize that storage of TPBDCr in methymethacrylate at similar conditions, but in the absence of light, did not lead to polymerization. Solidification of the solution was not observed even in 2 weeks. At present the study is on for production of transparent polymer samples, containing triphenylbismuth diacylates, at similar conditions.

### Conclusions

1. Decomposition of triphenylbismuth dicrotonate in diffused light in benzene solution in the presence of 2-methyl-2-nitrosopropane leads to formation of phenyl radicals that are registered in the form of the addition compound  $\text{PhN}(\text{O}\cdot)\text{Bu}-t$ .

2. Polymerization of methymethacrylate with addition of triphenylbismuth dicrotonate (1–5 % m/m) as a radical initiator is carried out in diffused light at room temperature with formation of yellow-colored opaque polymethymethacrylate blocks that are insoluble in organic solvents. In the absence of light the polymerization does not occur.

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### РАСПАД ДИКРОТОНАТА ТРИФЕНИЛВИСМУТА НА СВЕТУ В ПРИСУТСТВИИ 2-МЕТИЛ-2-НИТРОЗОПРОПАНА

**А.В. Гуцин<sup>1</sup>, О.С. Калистратова<sup>1</sup>, А.И. Малеева<sup>1</sup>, В.А. Куропатов<sup>2</sup>**

<sup>1</sup> Нижегородский государственный университет им. Н.И. Лобачевского,  
г. Нижний Новгород

<sup>2</sup> Институт металлоорганической химии РАН им. Г.А. Разуваева, г. Нижний Новгород

Дикротонат трифенилвисмута Ph<sub>3</sub>Bi(O<sub>2</sub>CCH=CHCH<sub>3</sub>)<sub>2</sub> в присутствии 2-метил-2-нитрозопропана на свету распадается в бензоле. Образующиеся в результате распада Ph<sub>3</sub>Bi(O<sub>2</sub>CCH=CHCH<sub>3</sub>)<sub>2</sub> фенильные радикалы подтверждены методом спиновых

ловушек и способны инициировать полимеризацию метилметакрилата при комнатной температуре. В отсутствие света распада не наблюдается.

*Ключевые слова:* ЭПР, дикротонат трифенилвисмута, 2-метил-2-нитропропан.

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## Химия элементоорганических соединений

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**Гущин Алексей Владимирович** – доктор химических наук, профессор, декан химического факультета, Нижегородский государственный университет им. Н.И. Лобачевского. 603950, г. Н. Новгород, пр. Гагарина, 23. E-mail: gushchin@chem.unn.ru

**Калистратова Ольга Сергеевна** – аспирант химического факультета, Нижегородский государственный университет им. Н.И. Лобачевского. 603950, г. Н. Новгород, пр. Гагарина, 23. E-mail: olga.kalistratova@yandex.ru

**Малеева Алевтина Игоревна** – аспирант химического факультета, Нижегородский государственный университет им. Н.И. Лобачевского. 603950, г. Н. Новгород, пр. Гагарина, 23. E-mail: Alevtinamaleeva@mail.ru

**Куропатов Вячеслав Александрович** – кандидат химических наук, старший научный сотрудник, Институт металлоорганической химии РАН им. Г.А. Разуваева. 603137, г. Нижний Новгород, ул. Тропинина, 49. E-mail: viach@iomc.ras.ru

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### ОБРАЗЕЦ ЦИТИРОВАНИЯ

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