

**MORE THAN A CENTURY AFTER THE FREE RADICALS DISCOVERY:
TRIPHENYLMETHYL – THE FIRST KNOWN FREE RADICAL
(An undergraduate lecture experiment)**

Vladimir M. Petruševski, Metodija Ž. Najdoski

*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University,
P.O. Box 162, MK-1001 Skopje, Republic of Macedonia
vladop@iunona.pmf.ukim.edu.mk*

Triphenylchloromethane (TPCM) is reduced by zinc in a benzene solution, giving an intense yellow solution of triphenylmethyl (TPM), the first known stable free radical. In the solution, the free radical is in equilibrium with the dimer – 3-diphenylmethylidene-6-triphenylmethylcyclohexa-1,4-diene. The reactivity of TPM is demonstrated in reactions with oxygen and iodine, using a purpose built reaction chamber. The products are triphenylmethylperoxyde and triphenyliodomethane (both are colorless).

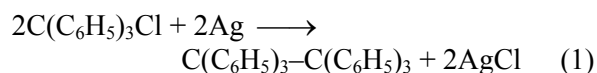
Key words: free radicals; triphenylmethyl; triphenylchloromethane; hexaphenylethane;
3-diphenylmethylidene-6-triphenylmethylcyclohexa-1,4-diene

INTRODUCTION

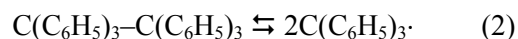
In the second half of the 19th century it became clear that chemical compounds consist of groups which were named radicals by Lavoisier (in Latin *radicalis*, means one that has roots). Some attempts to isolate these radicals seemed to be successful: thus, Berzelius in 1808 isolated ‘free’ ammonium as amalgam, Gay-Lussac reported in 1815 the isolation of free radical cyan, and Frankland believed that ethyl radical was isolated in the reaction of ethyl iodide with zinc metal, as reviewed by Noller [1]. However, Cannizzaro’s persistence that molecular weights must be determined as an independent identity check of the chemical nature of the newly synthesized materials, revealed that Gay-Lussac’s cyan is actually cyanogen – (CN)₂, and Frankland’s ethyl is simply its dimer – butane gas. Soon after this it was generally adopted that compounds with di- or trivalent carbon can not exist (apart from only a few simple carbon compounds, one of which is carbon monoxide, CO).

Free radicals are considered as atoms or groups of atoms (i.e. atomic or molecular species) that are neutral (this is important distinction from ions), and contain unpaired electrons. The true

existence of free radicals was first confirmed in 1900 by Gomberg [2]. His goal was the synthesis of hexaphenylethane, following the success in syntheses of various alkanes (Würtz), and aromatic hydrocarbons (Fittig) (see. Noller [3]). Adding finely powdered metals to a benzene solution of triphenylchloromethane (TPCM), would yield (he reasoned) the desired C(C₆H₅)₃–C(C₆H₅)₃ according to the chemical equation:

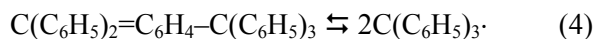
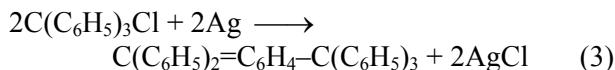


The so-called hexaphenylethane appeared to be a colorless crystalline solid. However, its solution in benzene was intense yellow and highly reactive. Gomberg assumed that dissociation takes place and that free triphenylmethyl (TPM) radicals are obtained:



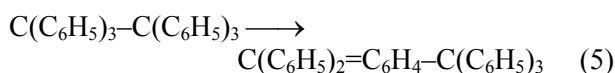
While Gomberg’s conclusion that the yellow solution contains TPM appeared to be correct, the

notion that the product of eq. 1 is hexaphenylethane was wrong [4,5], as first pointed by Lancamp in 1968. Therefore, instead of eqs. 1 and 2, the following equations are the correct ones:



The equilibrium mixture (eq. 4) contains both the free radical and the dimer, which is (according to eq. 3) 3-diphenylmethylidene-6-triphenylmethylcyclohexa-1,4-diene*. One may wonder, why this rather complex dimer appears instead of the much simpler hexaphenylethane? Further, what are the reasons behind the unexpected stability of the TPM free radical? A brief answer that may be offered to both questions is the increased stabilization (resonance) energy.

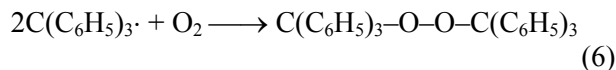
Therefore, an instantaneous isomerization occurs:



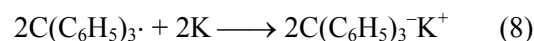
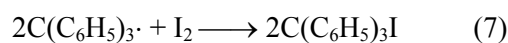
as a result of extended conjugation (π -electron delocalization) from a single benzene ring (any of the

benzene rings in hexaphenylethane) to a $C(C_6H_5)_2=C_6H_4-$ group in 3-diphenylmethylidene-6-triphenylmethylcyclohexa-1,4-diene.

As mentioned, the benzene solution of TPM is highly reactive. Thus, in a reaction with oxygen gas, a colorless solution was obtained, containing triphenylmethylperoxide:



while, reactions with I_2 and metallic potassium gave triphenyliodomethane, and potassium triphenylmethylide, respectively:



There are not many lecture demonstrations showing the properties of free radicals. In the present paper, we describe an experiment with a benzene solution of 3-diphenylmethylidene-6-triphenylmethylcyclohexa-1,4-diene, containing, as already mentioned, the free radical TPM.

MATERIALS AND EQUIPMENT

Cylinders with oxygen and nitrogen, TPCM (see Appendix 1), dry benzene, zinc (or silver) powder, benzene solution of iodine, 2 rubber balloons with stopcocks, purpose built reaction cham-

ber (see Appendix 2), a small separatory funnel with a suitable stopper, a medium size test-tube, a bent glass tube with a stopper, and a stand with clamps and screws have been used.

THE DEMONSTRATION

The demonstration can easily be performed in 10–15 min, thus making it ideal as a lecture demonstration on free radicals (it strengthens the assertions offered and makes the lesson more vivid). It can be performed with very simple equipment (a test-tube and a bent tube would work for the whole demonstration, cf. Fig. 1), but as mentioned above,

we prefer to perform the second part of it in a purpose built chamber (cf. Fig. 2 and Appendix 2).

First, the balloons are filled with oxygen and nitrogen, respectively. The test-tube is filled with ≈ 10 mL benzene and about 0.5 g of TPCM is added. The tube is agitated, until the crystals dissolve, and splashed with gaseous nitrogen from the balloon. Zinc powder is quickly added, the test-tube is stoppered and shaken. In less than a minute the liquid turns intense yellow (see eqs. 3 & 4). Here the instructor gives an explanation of the processes (it is important to mention Gomberg's misconception about the nature of the product; the possible

*In a benzene solution containing $1 \text{ mol}\cdot\text{dm}^{-3}$ of 3-diphenylmethylidene-6-triphenylmethylcyclohexa-1,4-diene, only about 2 % of the dimer dissociate into radicals. However, in a $10 \text{ mmol}\cdot\text{dm}^{-3}$ solution – about 10 % is dissociated. Increasing the temperature has the same effect as dilution.

reasons for the isomerization of hexaphenylethane; the remarkable stability of TMP etc.). The yellow solution is quickly poured into the reaction chamber, and the chamber is stoppered (cf. Fig. 2), the separation funnel being half-filled with the iodine solution. A slow stream of oxygen is passed through the chamber, until complete loss of color (formation of peroxide, eq. 6). The balloons are now switched and a fast stream of nitrogen is passed through the chamber. The color soon recovers (see eq. 4). The procedure may be repeated.

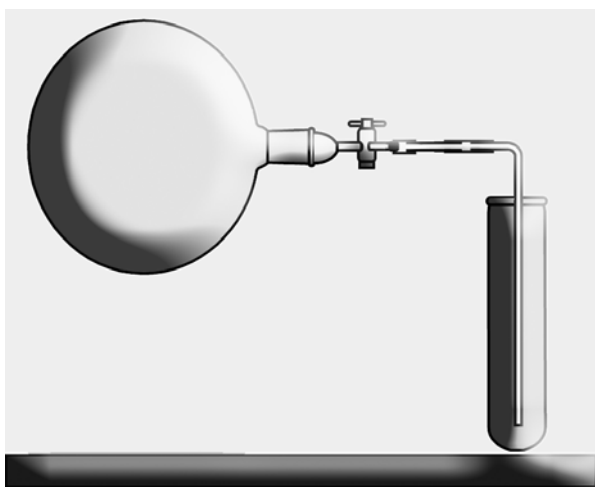


Fig. 1. Simple equipment used to synthesize triphenylmethyl

Some iodine solution is added to the TMP solution in the reaction chamber, until the color changes to one 'between yellow and violet'. Again, a fast stream of nitrogen is passed. Soon the color due to iodine disappears (cf. eq. 7).

A reader may think about an extension of the demonstration, including reactions with potassium or sodium. The product of eq. 8, potassium triphenylmethylide, has an intense red color, hence the whole demonstration could be made even more vivid and attractive.



Fig. 2. Setup for demonstration of the free radicals' properties: (left) balloon filled with oxygen or nitrogen; (right) purpose built reaction chamber, partly filled with benzene solution containing triphenylmethyl (on the top of the chamber is the separation funnel containing benzene solution of iodine)

CONCLUSION

Little effort is needed to build the chamber (actually to make a drawing according to which the chamber should be assembled by a glassblower)

and to synthesize TPCM. The result is – a beautiful demonstration of the phenomenon that is known for more than 100 years.

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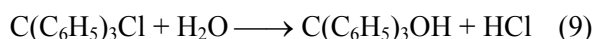
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APPENDIX 1

Synthesis of TPCM. TPCM is usually obtained by Friedel-Crafts synthesis. The synthesis was performed according to a method given in literature [6], which will be given here for reasons of completeness (ref. [6] is neither widely known, nor readily available). One starts with 57 mL benzene and 13 mL, CCl_4 that are placed in a 250 mL reaction flask. After that, 15 g of powdered aluminium chloride (AlCl_3) are added to the mixture in small portions (if the reaction is very vigorous, cooling with cold water is recommended). After the required quantity of AlCl_3 has been added, the reaction mixture is placed for about 30 min on a hot water bath (a condenser is mounted on the flask during this operation). The reaction mixture (which by this time turns brown) is cooled and poured (while vigorously agitated) into a mixture of 50 g ice and 50 mL concentrated HCl. 20–30 mL of pure benzene is further added to the mixture, which is immediately transferred to a separation

funnel. After few minutes shaking, the upper (benzene) layer is collected and dried by CaCl_2 . Benzene is distilled off on a water bath, the flask is cooled and diethyl ether is added until the mixture is homogeneous. The solution is placed on an ice bath for several hours, and is vacuum filtrated (during filtration it may be washed with a tiny amount of ice-cooled ether).

The raw product is pale yellow. Recrystallization is performed in the following way: the raw product is dissolved in a small amount of benzene, petrol ether is added (four times the volume of the used benzene) and the crystals are vacuum filtrated. These crystals are colorless ($T_m \approx 385 \text{ K}$). The crystals should be kept in a dry, tightly closed container. They are sensitive to moisture, due to slow hydrolysis:



APPENDIX 2

The reaction chamber was assembled by glassblower of the Chemistry Department. All parts should be made of the same type of glass, otherwise the joints may be apt to crack. It is a good idea, after the chamber is ready to leave it overnight, to see whether it will 'survive'. Of course, it may be built of a good-quality hard glass, but for this purpose (no heating, cooling or abrupt temperature changes occur using the chamber) this is really not necessary. The way the chamber is assembled is shown in Fig. 3.

Chambers of basically similar construction may be used for vivid demonstration of many other 'well-known' experiments [7].

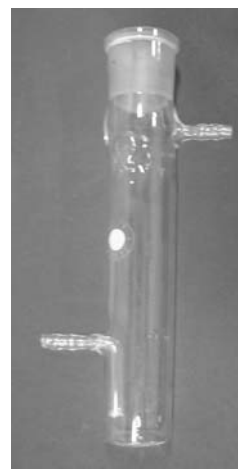


Fig. 3. The purpose built reaction chamber (a closer look)

SAFETY TIPS

Wear safety goggles when performing the demonstration. Wear safety goggles (or face shield) and disposable plastic gloves, while doing the synthesis. Benzene is used both in the demonstration and during the synthesis of triphenylchloromethane. CCl_4 , AlCl_3 and petrol ether are used during the synthesis. **Benzene and**

petrol ether are highly flammable! Avoid any use of open flame during the synthesis/demonstration. **Benzene and CCl_4 are suspected to cause cancer!** Never inhale any of these substances even for a short period of time. The synthesis must be done in a hood. **AlCl_3 may cause burns in contact with skin.**

Резиме

**ПОВЕЌЕ ОД ЕДЕН ВЕК ПО ОТКРИТИЕТО НА СЛОБОДНИТЕ РАДИКАЛИ:
ТРИФЕНИЛМЕТИЛ – ПРВИОТ ПОЗНАТ СЛОБОДЕН РАДИКАЛ
(Демонстрационен експеримент за студенти)**

Владимир М. Петрушевски, Методија Ж. Најдоски

*Институт за хемија, Природно-математички факултет, Универзитет "Св. Кирил и Методиј",
и. фах 162, МК-1001 Скопје, Република Македонија
vladop@iunona.pmf.ukim.edu.mk*

Клучни зборови: слободни радикали; трифенилметил; трифенилхлорометан; хексафенилетан;
3-дифенилметилен-6-трифенилметилциклохекса-1,4-диен

При редукција на трифенилхлорометан со цинк во бензен како медиум се добива интензивно жолто обоен раствор од трифенилметил, првиот познат стабилен слободен радикал. Во растворот слободниот радикал е во рамнотежа со димерот – 3-дифенилметилен-6-трифенилметилциклохекса-1,4-диен. Реактив-

носта на трифенилметилот е демонстрирана при реакциите со кислород и јод, во реакциона комора што е конструирана специјално за демонстрациони цели. Продуктите на реакцијата се трифенилметилпероксид и трифенилјодометан (двата се безбојни).