

Brief Communications

Formation of triphenylmethyl radicals upon alkaline hydrolysis of diphenyl sulfophthalide

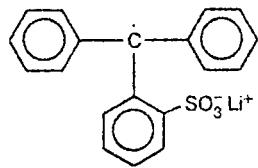
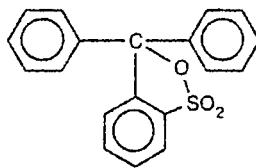
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Triphenylmethyl radicals (TPMR) with an *o*-positioned sulfonate group are generated by alkaline hydrolysis of diphenyl sulfophthalide in DMSO. Electronic and ESR spectra of these radicals are characterized. It is suggested that the radicals result from one-electron transfer reactions. Triarylmethyl radicals are also formed in alkaline hydrolysis of poly-arylenesulfophthalides.

Key words: alkaline hydrolysis, triphenylmethyl radicals, diphenylenesulfophthalide, electronic spectra, ESR spectra, polyarylenesulfophthalides.

Nucleophilic opening of the sulthone and sulthine cycles is considered to be a heterolytic process,¹⁻³ and the appearance of radicals in these reactions was not reported. However, it is assumed that many heterolytic reactions occur through a one-electron transfer stage⁴ or compete with one-electron transfer.⁵ The study of alkaline hydrolysis of compound **1** showed the appearance of paramagnetic species (PMS), with spectral properties attributable to triphenylmethyl radicals (TPMR).



Argon was bubbled through nine parts of a solution of **1** in DMSO ($C = 0.3 \text{ mmol L}^{-1}$) and 1 part of a 1 M solution of LiOH in a DMSO+H₂O (5 : 1) mixture. Then the electronic spectrum and ESR spectrum of the mixture exhibit an absorption band (AB) with $\lambda_{\text{max}} = 339 \text{ nm}$ and a multicomponent ESR signal (45–51 lines) with a splitting of ~ 0.7 –1 Oe, $g = 2.0026 \pm 0.0003$, and overall extension of ~ 26 Oe (Fig. 1). Three groups (each containing 15–17 lines) with a splitting between the groups of ~ 7 Oe can be distinguished in the ESR spectrum. Similarly ill-defined ESR spectra were observed for radicals obtained from some triphenylmethane dyes.⁶ The presence of splitting of ~ 7 Oe, which is unusually high for TPMR, is probably due to the effect of the negative charge of the sulfonate group at the *o*-position of the radical.

A weak AB of a forbidden transition of the radical is also detected at 518 nm in the optical spectrum.

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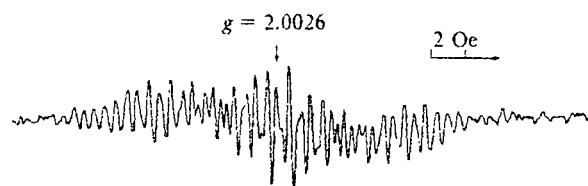


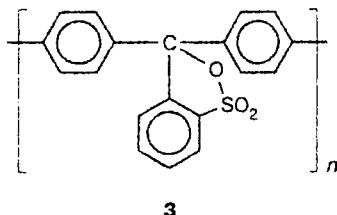
Fig. 1. ESR spectrum of the paramagnetic product of alkaline hydrolysis of compound **1** in DMSO 40 min after mixing the reagents (a planar quartz tube, argon bubbling).

Based on the published data,^{7,8} the AB and ESR signal observed can be assigned to TPMR with, most likely, structure **2**.

The highest concentration of the radicals ($\sim 0.2 \text{ mmol L}^{-1}$) is achieved approximately 40 min after pouring together the reagents. This implies that more than 60% of compound **1** is transformed into the radical form. The presence of air oxygen in the system retards increase in the concentration of the radicals and somewhat decreases their highest yield.

It is known that TPMR are formed through carbocations under combined treatment with alkalies and oxidants.⁹ In our case, no AB of carboanions and carbocations are observed, and it is not clear yet at which step of the reaction of **1** with LiOH that TPMR are formed. In addition to the direct cleavage of C—O during the electron transfer from the hydroxide ion to a molecule of **1**,⁵ the stage of formation of zwitterions cannot be ruled out,¹¹ for example, by analogy with the mechanism of opening of the sulfophthalide cycle accepted for sulfophthalein dyes.¹¹ Then an electron can be transferred from the hydroxide ion to carbocationic centers, whose stationary concentration is lower than the sensitivity of the spectrophotometric method of analysis. The electron transfer can be facilitated by an increase in the donating ability of the hydroxide ion in aprotic solvents.¹⁰

Relatively stable hydrocarbon radicals appear during alkaline hydrolysis in DMSO of several polyarylenesulfophthalides, the structure of its monomeric units being similar to that of compound **1**. For example, the formation of radicals of the triarylmethyl type (TAMTR) was detected in alkaline hydrolysis of polydiphenylenesulfophthalide **3**. These radicals give AB at 410 nm in the electronic spectrum and a poorly resolved ESR signal with $\Delta H = 10 \text{ Oe}$ and $g = 2.0028$.



In addition to TAMTR, hydrolysis of **3** also gives blue centers of coloring (CC) with two AB at 345 and

566 nm in the electronic spectrum. Taking into account the polymer structure and based on the published data,^{12,13} we preliminarily ascribed these CC to quinoid structures of the Chichibabin hydrocarbon, which can appear due to the interaction of two lone electrons localized at adjacent quaternary carbon atoms.

Alkaline hydrolysis of polyterphenyl sulfophthalide generates TAMTR that have AB of the allowed transition in the region of 410 nm and a poorly resolved ESR signal with $\Delta H = 10 \text{ Oe}$.

As a whole, PMS and CC formed due to alkaline hydrolysis of polyarylenesulfophthalides are similar to species that appear upon dissolution of these polymers in aniline—cyclohexanone mixtures.¹⁴

Thus, the appearance of TPMR and TAMTR during alkaline hydrolysis of compounds containing the sulfophthalide cycle indicates a possibility of one-electron transfer during opening of this cycle, although it cannot be ruled out that these radicals result from secondary reactions. Secondary reactions are favored by the excess of alkali used in our experiments.

Experimental

Diphenyl sulfophthalide was synthesized by the known procedure¹⁵ from *ortho*-sulfonylbenzoic acid dichloride. Product **1** recrystallized from ethanol is a white crystalline powder with m.p. 162 °C. Synthesis of polyarylenesulfophthalides has been described previously.¹⁴ DMSO and LiOH (reagent grade) were used without additional purification. Oxygen was removed from solutions by 20-min bubbling of argon. Deionized water was used for the preparation of alkaline solutions. ESR spectra were recorded on a Radiopan SE/X-2544 ESR spectrometer in thin glass tubes and in a planar quartz tube for polar solvents. Electronic spectra were obtained on a Specord spectrophotometer in 2- and 5-mm quartz cells. When solutions were bubbled with argon, cells were closed with sealed caps. All spectra were recorded at room temperature. The concentration of triphenylmethyl radicals was estimated from the intensity of an ESR signal determined for a solution of the stable imidazole radical in DMSO with a known concentration.

References

1. D. W. Roberts and D. L. Williams, *Tetrahedron*, 1987, **43**, 1027.
2. O. B. Bondarenko, L. G. Saginova, and N. V. Zyk, *Usp. Khim.*, 1996, **65**, 156 [*Russ. Chem. Rev.*, 1996, **65** (Engl. Transl.)].
3. T. Okuyama, H. Takano, K. Ohnishi, and Sh. Nagase, *J. Org. Chem.*, 1994, **59**, 472.
4. O. Yu. Okhlobystin, *Perenos elektrona v organiceskikh reaktsiyakh* [Electron Transfer in Organic Reactions], Izd-vo Rostov Univ., Rostov, 1974 (in Russian).
5. R. A. Marcus, *J. Phys. Chem. A*, 1997, **101**, 22, 4072.
6. H. Langbein, M. Friedrich, and R. Paetzold, *Z. Phys. Chem., Neue Folge*, 1982, **133**, 99.
7. T. L. Chu and S. I. Weismann, *J. Chem. Phys.*, 1954, **22**, 21.
8. W. P. Neumann, W. Uzick, and A. K. Zarkadis, *J. Am. Chem. Soc.*, 1986, **108**, 3762.
9. V. D. Sholle and E. G. Rozantsev, *Usp. Khim.*, 1973, **52**, 2176 [*Russ. Chem. Rev.*, 1973, **52** (Engl. Transl.)].

10. K. Umemoto, Y. Nagase, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 12, 3245.
11. Yu. K. Mikhailovskii, V. A. Azarko, and V. E. Agabekov, *Vestsi AN Belarusi [Bull. Belorussian Acad. Sci.]*, 1992, 27 (in Belorussian).
12. L. K. Montgomery, J. C. Huffman, E. A. Jurczak, and M. P. Grendze, *J. Am. Chem. Soc.*, 1986, **108**, 6004.
13. N. M. Shishlov, Sh. S. Akhmetzyanov, M. G. Zolotukhin, I. V. Novoselov, G. I. Nikiforova, A. P. Kapina, and F. G. Valyamova, *Dokl. Akad. Nauk SSSR*, 1992, **322**, 304 [*Dokl. Chem.*, 1992 (Engl. Transl.)].
14. N. M. Shishlov, Sh. S. Akhmetzyanov, and V. N. Khrustaleva, *Izv. Akad. Nauk, Ser. Khim.*, 1997 389 [*Russ. Chem. Bull.*, 1997, **46**, 377 (Engl. Transl.)].
15. R. List and M. Stein, *Ber.*, 1898, **31**, 1648.

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IR spectroscopic investigation of structural hydroxyl groups in W—Si heteropolycompound supported on Al_2O_3

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Structural hydroxyl and deuterioxy groups within the $\text{K}_4[\text{SiW}_{12}\text{O}_{40}]/\text{Al}_2\text{O}_3$ and $\text{K}_6[\text{SiW}_{11}\text{PdO}_{39}]/\text{Al}_2\text{O}_3$ systems were studied by diffuse-reflectance FTIR spectroscopy in a spectral range of fundamental stretching vibrations, first overtones, and combination bands of stretching and bending vibrations. For hydroxyl groups, the region of combination vibrations is the most informative. The calculated frequencies of bending vibrations of hydroxyl groups (865 and 730 cm^{-1}) are characteristic of acidic OH groups.

Key words: diffuse-reflectance FTIR spectroscopy, hydroxyl groups, W—Si heteropolycompound, combination vibrations, bending vibrations of OH groups.

Heteropolycompounds (HPC) are widely used as catalysts.^{1,2} Activity of these systems is usually explained by the presence of Brönsted acid sites, OH groups associated with oxide polyhedra that form Keggin structure.³

IR spectroscopy remains the most informative method for studying structural OH groups in heterogeneous catalysts. In studies of the acidic properties of oxide systems, IR spectra are usually recorded in the region of fundamental stretching vibrations of the O—H bond. IR spectra of supported HPC and other catalysts with strong acid properties⁴ are, as a rule, a superposition of broad lines, and the problem of differentiation of sites of different nature and strength is often difficult. Measurements of IR spectra in the region of combination bands of stretching and bending vibrations of structural OH groups (4000 — 5000 cm^{-1}) or overtones of stretching vibrations of the O—H bond (6500 — 7500 cm^{-1}) were found to be more efficient.⁵ This approach is especially

applicable for heterogeneous catalysts that are characterized by broad unresolved IR spectra in the region of fundamental stretching vibrations of OH groups.

This method has previously been successfully used for studying structural OH groups of laminated clays pillared by Al_2O_3 and SiO_2 columns⁶ and some unstable forms of zeolites.⁷ In this work, a similar approach was extended to tungsten-silicon HPC: $\text{K}_4[\text{SiW}_{12}\text{O}_{40}]$ and $\text{K}_6[\text{SiW}_{11}\text{PdO}_{39}]$ supported on aluminum oxide.

Experimental

Tungsten-silicon HPC were used for the preparation of samples: $\text{K}_4[\text{SiW}_{12}\text{O}_{40}]$ (reagent grade, Krasnyi Khimik Co., St. Petersburg) and $\text{K}_6[\text{SiW}_{11}\text{PdO}_{39}]$ synthesized by the known procedure.⁸ Chemical analysis of potassium palladium-11-tungstosilicate was performed by atomic-absorption spectrophotometry. Found (%): WO_3 , 78.95; SiO_2 , 1.74; PdO , 3.7; K_2O , 8.61; H_2O , 7.0. Calculated (%): WO_3 , 79.36; SiO_2 , 1.87;