Radical formation during ozonation of triphenylmethane on silica gel

Qadir K. Timerghazin, Nikolai M. Shishlov, Natal'ya N. Kabalnova, Sergey L. Khursan and Valerii V. Shereshovets*

Institute of Organic Chemistry, Ufa Scientific Centre of the Russian Academy of Sciences, 450054 Ufa, Russian Federation.
Fax: +7 347 235 6066; e-mail: qadir@chemlum.ufanet.ru

Low-temperature ozonation of triphenylmethane on silica gel is accompanied by generation of peroxy radicals and proceeds *via* formation of ozone–triphenylmethane complexes; without silica the reaction does not proceed at the same temperatures.

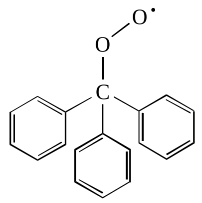
Low-temperature ozonation of tertiary hydrocarbons adsorbed on a silica surface (dry ozonation) leads to the formation of tertiary alcohols with remarkably high selectivity and rate.[1] There are hardly any data on the mechanism, intermediates and kinetics of this process. Here we report on the observation of free-radical intermediates during the dry ozonation of triphenylmethane used as a model substrate.

Silica gel (surface area 540 m^2 g^{-1}) precalcined at 300 °C for 5 h was used in this work. Triphenylmethane was purified by recrystallisation from ethanol. Triphenylmethane (0.04–0.80 g) dissolved in pentane was added to the silica gel (1 g) with intense stirring, then the solvent was removed by rotary evaporation. A glass ampoule charged with silica gel bearing adsorbed triphenylmethane was placed into a cooling bath (–90 °C). A mixture of ozone and oxygen (1–2% O_3) was supplied to the ampoule by glass capillary for 5–10 min. A sample was kept in liquid nitrogen. A SE/X 2544 spectrometer supplied with an optional modulating unit (100 kHz) was used to detect the radicals. The EPR spectra were recorded in the temperature range –196 to –30 °C. The g-factors of the spectra were determined by comparison with those of the spectrum of α,α′-diphenyl-β-picrylhydrazyl (DPPH; $g = 2.0037$).

During the low-temperature ozonation of triphenylmethane on silica gel the sample acquired a green colour. Apparently this is due to the formation of a complex between ozone and aromatic hydrocarbon. The existence of such complexes for a variety of arenes and their derivatives in the liquid phase is well established.[2–4] Without triphenylmethane the silica gel turned blue from accumulating ozone.

The EPR spectrum of the silica–triphenylmethane–ozone system recorded at liquid nitrogen temperature consisted of a single line without hyperfine structure with a pronounced asymmetrical character, Figure 1(*a*). From this spectrum the principal g-factors were determined, $g_{\|} = 2.0353$ and $g_{\perp} = 2.0082$. The isotropic g-factor was calculated as $g = (g_{\|} + 2g_{\perp})/3 = 2.0172$. At higher temperatures the anisotropy of the signal decreases slightly, but still exists in the temperature range over which the signal is observed. With a temperature rise its intensity decreases and at –40 °C the EPR signal almost disappears completely, Figure 1(*b*).

The shape of the EPR signal is an asymmetrical singlet and is typical of alkylperoxy radicals trapped in solid matrices[5] or adsorbed on silica gel at low temperatures.[6] Comparison of the g-factor obtained in this work ($g = 2.0172$) with literature data for peroxy radicals ($g = 2.0120–2.0154$)[5,7] confirms that the spectra observed in our experiments do indeed correspond to peroxy radicals **1**.



1

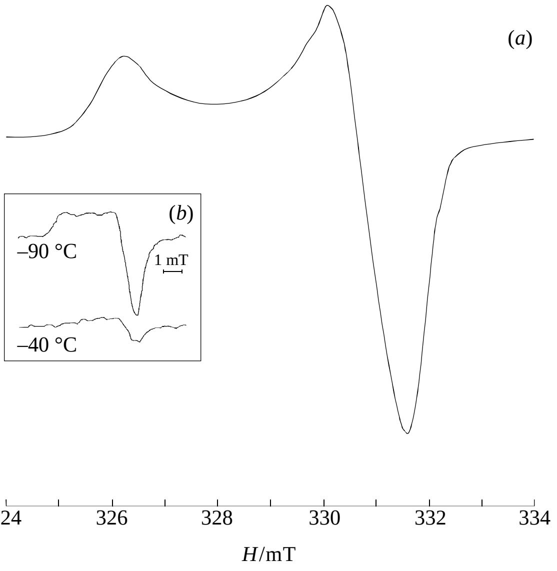


Figure 1 EPR spectra of the silica–triphenylmethane–ozone system: (*a*) in liquid nitrogen; (*b*) at –90 °C and –40 °C.

Conservation of signal anisotropy at fairly high temperatures confirms that radicals are unable to rotate freely on the silica surface. Their translational motion is probably also limited.

It should be noted that during low-temperature ozonation of crystalline triphenylmethane (without silica) neither a change in sample colour nor the EPR signal was observed. Pure silica gel and that with adsorbed ozone or triphenylmethane also do not show signals in the EPR spectra.

The results of this study make it possible to conclude that dry ozonation of triphenylmethane proceeds *via* formation of ozone–triphenylmethane complexes and is accompanied by generation of peroxy radicals.

We are grateful to Dr. B. I. Kutepov for surface area measurements and scientific discussions.

References

1 Z. Cohen, E. Keinan, Y. Mazur and T. H. Varkony, *J. Org. Chem.*, 1975, **40**, 2141.
2 P. S. Bailey, J. W. Ward, T. P. Carter, J. E. Nieth and C. M. Fischer, *J. Am. Chem. Soc.*, 1974, **96**, 6136.
3 V. V. Shereshovets, L. G. Galimova and V. D. Komissarov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2488 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 2055).
4 E. V. Avzyanova, N. N. Kabalnova and V. V. Shereshovets, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 371 (*Russ. Chem. Bull.*, 1996, **45**, 360).
5 J. E. Bennet, D. M. Brown and B. Mile, *Trans. Farad. Soc.*, 1970, **66**, 386.
6 W. J. Maguire and D. M. Pink, *Trans. Farad. Soc.*, 1967, **63**, 1097.
7 W. A. Pryor, N. Ohto and D. F. Church, *J. Am. Chem. Soc.*, 1982, **104**, 5813.

Received: Moscow, 20th August 1997
Cambridge, 13th October 1997; Com. 7/06174I