Adamantylhydrotrioxide formation during ozonation of adamantane on silica gel

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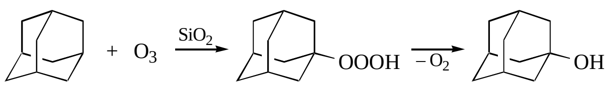
Previously unknown adamantylhydrotrioxide has been shown to be a key intermediate in the ozonation of adamantane on silica and is not obtained in solution.

Dry ozonation, *i.e.* low-temperature ozonation of adsorbed on silica surface substrates is known to be highly selective and fast.[1] In the case of tertiary hydrocarbons the only products were found to be tertiary alcohols.[2] There are almost no data on the mechanism, intermediates and kinetics of this process. The low-temperature ozonation of adamantane has been studied rather better than that of other substances. It was shown that this reaction gave selectively adamantan-1-ol and was accompanied by chemiluminescence in the IR and visible spectral range.[3,4] We have recently suggested that the reaction involves formation of a hypothetical hydrotrioxide intermediate:[3]



In this work we wish to report on the isolation and identification of adamantylhydrotrioxide (AdOOOH) by low-temperature elution of the products of adamantane ozonation on silica gel.

Adamantane (1 mmol) was adsorbed on silica gel (8 g, Chemapol, L 40/100, particle size 0.063–0.2 mm, precalcined at 250 °C) as described elsewhere.[2] The sample was saturated with ozone at –90 °C (1.5 mmol) and kept for 4–5 h at the same temperature to ensure the reaction was complete. Unreacted ozone was then blown out by oxygen flow. The ozonation products were eluted with 10–20 ml of a precooled [$^2H_6$]acetone–Freon-11 (1:1) mixture.

The low-temperature ^{1}H NMR spectra[†] of the eluate shows absorption at δ 12.85 ppm disappearing after heating to ambient temperature. The position of the proton signals of the adamantane skeleton did not change upon heating, whereas the H_2O absorption became significantly broad and shifted downfield from 3.01 to 3.28 ppm. As already reported, the absorption at δ 13±1 ppm is typical of an ROOOH species,[5–7] thus there is no doubt that the singlet at 12.85 ppm can be assigned to hydrotrioxide AdOOOH. The hydrotrioxide concentration determined using triphenylphosphine[8] was 0.01–0.07 M. GLC analysis of the warmed eluate showed that adamantan-1-ol is the only product of hydrotrioxide decomposition.

Chemiluminescence in the IR (1000–1300 nm) and visible (400–500 nm) spectral regions in the thermal decomposition of AdOOOH is observed.[‡] Apparently the IR chemiluminescence is emitted by singlet oxygen $^1O_2$. The dependence of IR intensity *vs.* time has a complex character and to explain it further investigations are required.

Table 1 The temperature dependence of the rate constant.

T/°C	k/10^3 s^{-1}
18	13.30
15	7.89
11	4.95
6.5	3.31
3.5	1.95

The visible chemiluminescence decay follows first-order kinetics; the rate constants k were determined from semi-logarithmic plots of the kinetic curves. From the temperature dependence of k (error does not exceed 10%, Table 1) the activation parameters of the process were calculated lg A = 12.9±1.4 s^{-1}, E_A = 19.6±1.9 kcal mol^{-1}.

Visible chemiluminescence decay reflects hydrotrioxide decomposition kinetics.[9,10] Its activation parameters are close to those experimentally obtained[6,10,11] and theoretically calculated[12,13] for the decomposition of various trioxides, and indicate radical decomposition of adamantylhydrotrioxide. The disappearance of chemiluminescence with addition of *tert*-butylhydroperoxide to an AdOOOH solution confirms our suggestions. In this case hydroperoxide exchanges the radicals which are precursors of chemiluminescence since $Bu^tOO^\cdot$ radicals do not lead to chemiluminescence-emitters.

Addition of silica gel to an AdOOOH solution increases chemiluminescence intensity and rate of chemiluminescence decay apparently due to catalysis by the silica surface.

Thus, the low-temperature ozone–adamantane reaction on a silica surface involves the formation of labile hydrotrioxide. It should be noted that adamantylhydrotrioxide was isolated for the first time and is not formed during ozonation of adamantane in solution. Furthermore, low-temperature ozonation of adamantane in solution is very slow (6–9 days at –78 °C) and is not selective.[14]

Oxygen-containing compounds readily give hydrotrioxides during their reaction with ozone: many hydrotrioxides of alcohols, ethers, acetals, aldehydes *et al.* have been described.[5] On the contrary, for hydrocarbons only hydrotrioxides of cumene[6] and some hydrocarbons with cyclopropane fragments have been synthesized.[7] Apparently, hydrotrioxide formation occurs through a polar mechanism for the ozonation of C–H bonds. This could explain the existence of hydrotrioxides for the substances mentioned above which contain cation-stabilizing fragments.[15] Due to this fact hydrocarbons without such stabilization do not form hydrotrioxides in solution.

The silica surface is known to be a highly polar and anisotropic medium which stabilizes ionic intermediates.[16] Evidently, this explains the hydrotrioxide formation under ozonation of adamantane on silica gel. Thus, dry ozonation is found to be a promising method of hydrotrioxide synthesis.

[†] ^{1}H NMR spectra of hydrotrioxide and its decomposition products were recorded on a Bruker AM 300 instrument at –60 °C. The δ scale was relative to the acetone signal (2.10 ppm). Decomposition products were analysed by GLC on a Chrom-5 chromatograph (370×0.3 cm column, SE-30, 50–300 °C, FID, helium carrier gas, dodecan-1-ol internal standard).

[‡] Chemiluminescence was detected on a photometric unit with a cooled FEU-83 photomultiplier in the IR region (corresponding light filter recording range is 1000–1300 nm) and a photomultiplier FEU-148 in the visible region. Kinetic runs were carried out as follows: to 2.5 ml acetone in a thermostatted reactor (10 ml) was added AdOOOH (0.5 ml, 0.013 M) solution and the chemiluminescence intensity was recorded after achieving thermal equilibrium (*ca.* 10 s).

References

1 P. S. Bailey, *Ozonation in Organic Chemistry*, Academic Press, New York, 1978, vol. 2, p. 136.

2 Z. Cohen, E. Keinan, Y. Mazur and T. H. Varkony, *J. Org. Chem.*, 1975, **40**, 2141.
3 E. V. Avzyanova, N. N. Kabal'nova and V. V. Shereshovets, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 375 (*Russ. Chem. Bull.*, 1996, **45**, 360).
4 Q. K. Timerghazin, E. V. Avzyanova, A. F. Khalizov, N. N. Kabalnova and V. V. Shereshovets, *React. Kinet. Catal. Lett.*, 1996, **58**, 403.
5 B. Plesnièar, in *Organic Peroxides*, ed. W. Ando, Wiley, New York, 1992, ch. 10, pp. 179–553.
6 W. A. Pryor, N. Ohto and D. F. Church, *J. Am. Chem. Soc.*, 1983, **105**, 3614.
7 M. Zarth and A. de Meijere, *Chem. Ber.*, 1985, **118**, 2429.
8 V. V. Shereshovets, N. Ya. Shafikov and F. A. Galieva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1177 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, 1051).
9 E. J. Corey, M. M. Mehrotra and A. U. Khan, *J. Am. Chem. Soc.*, 1986, **108**, 2472.
10 S. L. Khursan, A. F. Khalizov and V. V. Shereshovets, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 924 (*Russ. Chem. Bull.*, 1997, **46**, 884).
11 V. V. Shereshovets, F. A. Galieva, R. A. Sadykov, V. D. Komissarov and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2208 (in Russian).
12 P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, 1980, **102**, 3105.
13 S. L. Khursan, A. F. Khalizov and V. V. Shereshovets, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1129 (*Russ. Chem. Bull.*, 1996, **45**, 1068).
14 M. S. Whiting, A. J. N. Bolt and J. H. Parish, *Adv. Chem. Ser.*, 1969, **77**, 59.
15 J. March, *Advanced Organic Chemistry*, Wiley, New York, 1985, vol. 1, ch. 5.
16 J. E. Leffler, J. T. Barbas and G. C. Flowers, *J. Org. Chem.*, 1982, **47**, 2286.

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