Oxidation of organic compounds by ozone on a surface
1. Ozonization of adamantane on silica gel

E. V. Avzyanova, N. N. Kabal'nova, and V. V. Shereshovets*

Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 356 066

Adamantanol was obtained by the ozonization of adamantane, at −78 °C, adsorbed on silica gel. Ozone does not decompose on silica gel in the absence of a substrate.

Ozonization of adamantane on silica gel is accompanied by chemiluminescence in the IR region. The chemiluminescence quenching is of first-order with the effective rate constant k'. In the range from 0.4 to 5 mmol, k' depends linearly on the amount of adamantane adsorbed on the silica gel. The activation energy $E_a = 9.97\pm1.89$ kcal mol^{-1} and the pre-exponential factor $A = (2.76\pm0.52)\cdot10^6$ were calculated from the temperature dependence of k'.

Key words: ozone, "dry" ozonization, chemiluminescence, rate constants.

It is known that ozone is an efficient oxidant capable of oxidizing organic compounds under mild conditions. This opens wide possibilities for the application of ozone in technology. However, in many cases, reactions involving ozone are not selective. Ozonization on a surface is one of the methods for increasing the selectivity of the process.[1]

In this work, ozonization of adamantane adsorbed on silica gel was used as an example to study the effect of amounts of adsorbed substrate and adsorbed ozone on the yield of a target product, adamantanol. The kinetic regularities of this process were studied by the chemiluminescence (CL) method.

Experimental

Adamantane (0.1—0.5 g) was ozonized on freshly calcinated silica gel (≈8.3 g) at −78 °C in a 40-mL cylindrical Pyrex reactor. A preliminarily cooled ozone-oxygen mixture (90 mL min^{-1}, 1—2 % O_3) was fed for 10—120 min through a porous membrane in a reactor containing silica gel with an adsorbed substrate. After switching off the ozonator, unreacted ozone was removed with the oxygen flow. The amount of absorbed ozone was determined spectrophotometrically by measuring the optical density of ozone at λ = 310 nm at the inlet and outlet of the reactor.[2] The reaction mass was thawed out for 3 h to room temperature, moved to a chromatographic column, and eluted with ethyl acetate (50 mL). Unreacted adamantane and oxidation products were analyzed by GLC on a Chrom-5 chromatograph (column 370×0.3 cm, stationary phase SE-30, working temperature 50—300 °C, flame-ionization detector, argon as the carrier gas, lauryl alcohol as the internal standard).

CL was registered on a photometric installation with a cooled FEU-83 photoelectron amplifier and an IKS-7 light filter in the range of 1000—1300 nm.[3] In order to register luminescence, 12 g of silica gel with adsorbed adamantane (0.05—0.6 g) was placed into a thermostated 15-mL glass reactor. The reactor was thermostated to the specified temperature (−28÷+20 °C). A cooled ozone-oxygen mixture (40 mL min^{-1}, 1—2 % O_3) was admitted through a porous membrane sealed into the reaction wall. When the specified luminescence intensity was achieved, the letting of ozone was stopped, and the change in the intensity of CL in time was measured.

Adamantane (Fluka) was purified by sublimation. Adamantanol was obtained by the known procedure.[4] Silica gel (Chemapol, L 40/100 μm (particle size 0.063—0.2 nm)) was calcinated at 600 °C (content of H_2O ≈ 7 %) prior to use in TLC.

Adamantane (0.1 g) dissolved in pentane was poured to freshly calcinated silica gel (8.3 g) with rigorous stirring. The solvent was evaporated at room temperature in a rotary evaporator by a water-jet pump. It was shown by the special experiments that adamantane was completely adsorbed on the surface under these conditions.

Results and Discussion

Typical curves of a change in the concentration of ozone at the inlet and outlet of the reactor are presented in Fig. 1. The surface areas S_1 and S_2 correspond to the amounts of ozone absorbed in the reactor before switching off the ozonator and of desorbed ozone after switching off the ozonator, respectively. Curves of adsorption of O_3 by silica gel in the absence of adamantane are shown in Fig. 2, demonstrating that at −78 °C maximum saturation of silica gel with ozone is achieved in 40—50 min and equals ~3 mmol of ozone per 8.3 g of silica gel. No decomposition of the ozone adsorbed on silica gel

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 375—378, February, 1996.

1066-5285/96/4502-0360 $15.00

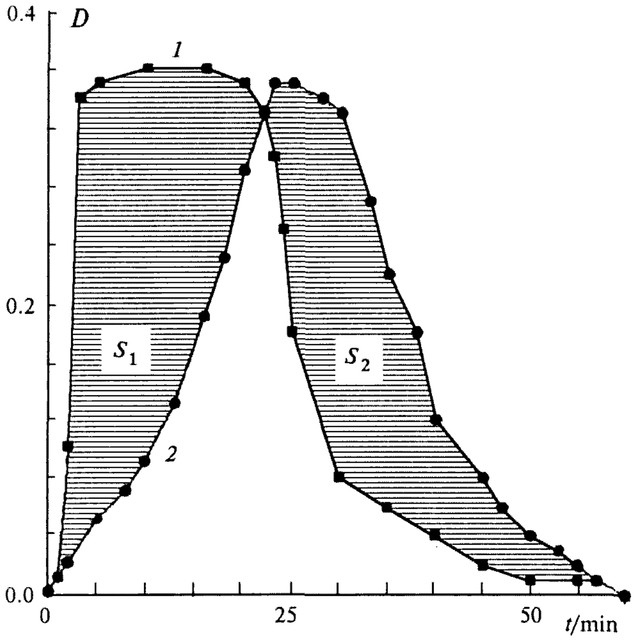

Fig. 2. Kinetic curves of adsorption of ozone in the absence (*1*) and presence of 0.9 mmol of substrate (*2*) on silica gel (−78 °C, mass of silica gel is 8.3 g).

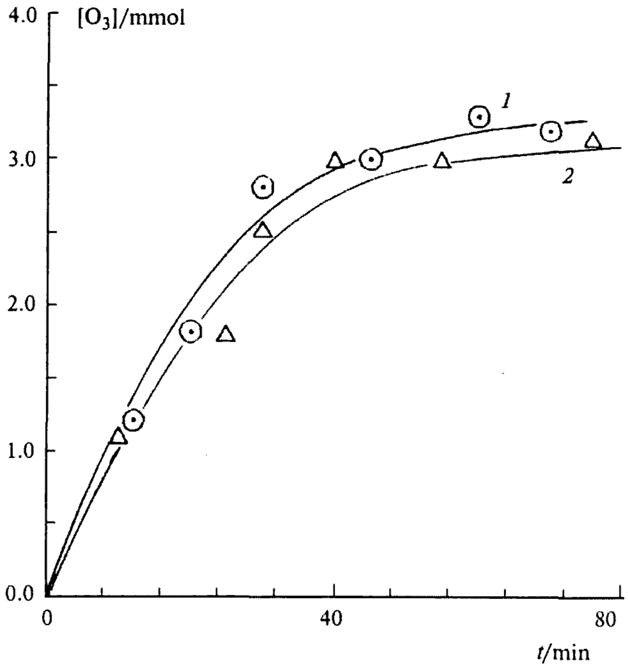

Fig. 1. Curves of the change in the optical density of ozone at the inlet (*1*) and outlet (*2*) of the reactor (λ = 310 nm, −78 °C, Ad_0 = 0.8 mmol, mass of silica gel is 8.3 g).

occurs, which is confirmed by the equality of S_1 and S_2.

The curve of adsorption of ozone in the presence of adamantane has a similar character, and the limiting saturation is also achieved in 40—50 min (see Fig. 2). However, in this case, the adsorption of ozone is accompanied by its consumption. The amount of ozone consumed in the reaction (ΔO_3) was calculated as the difference between S_1 and S_2.

1-Adamantanol is practically the sole oxidation product, which is confirmed well with the previous results.[4,5] According to the data in Table 1, the stoichiometry of the ozone consumption is close to unity, and the conversion of the substrate is ~90 %. The yield of the product per adamantane converted is ~90 % (see Table 1). It is of interest that the rate and selectivity of the liquid-phase ozonization of adamantane at −78 °C in CCl_3F are considerably lower. For example, the ozonization of 7.3 mmol of adamantane for 6—8 days resulted in the formation of 3.3 mmol of adamantanol and 0.54 mmol of adamantanone with the conversion of 52 %. Moreover, a solvent was involved in the process in several cases, which resulted in a considerable decrease in selectivity.[6]

Table 1. Consumption of adamantane and ozone (mmol) in the reaction at −78 °C

Ad_0	Ad_∞	ΔO_3	AdOH
0.83	0.11	0.78	0.67
0.81	0.01	0.82	0.77
0.81	0	1.04	0.78
0.74	0.01	0.94	0.73
0.97	0	0.93	0.84
0.96	0.01	1.39	0.79
0.97	0.11	1.14	0.79
3.63	—	1.06	0.92
3.75	—	1.87	2.24

Note. Ad_0 is the initial amount of adamantane; Ad_∞ is the amount of adamantane after the reaction; ΔO_3 is the amount of ozone adsorbed in the reaction.

The ozonization of adamantane adsorbed on silica gel is accompanied by the intense CL in the IR spectral range (1000—1300 nm). It can be supposed that CL is caused by the radiation of singlet oxygen, because this radiation has the maximum at 1270 nm.[3] The appearance of $^1O_2$ can be explained in the following way:

$$Ad + O_3 \rightarrow AdOOOH \rightarrow AdOH + {}^1O_2.$$

The formation of hydrotrioxides upon ozonization of organic compounds in the liquid phase and generation of singlet oxygen upon their decomposition have been reliably established previously.[7—9] The kinetic curves of a change in the intensity of CL upon the admitting of ozone have the limiting character and reach a plateau (Fig. 3, *a*). When the admitting of ozone is stopped, the first-order decay of CL is observed (see Fig. 3, *b*). The rate constants *k*′ were determined from the semilogarithmic anamorphoses of chemiluminescence decay. It is established that at the constant mass of silica gel and $[Ad]_0 \gg \Delta O_3$, the *k*′ rate constant depends linearly on

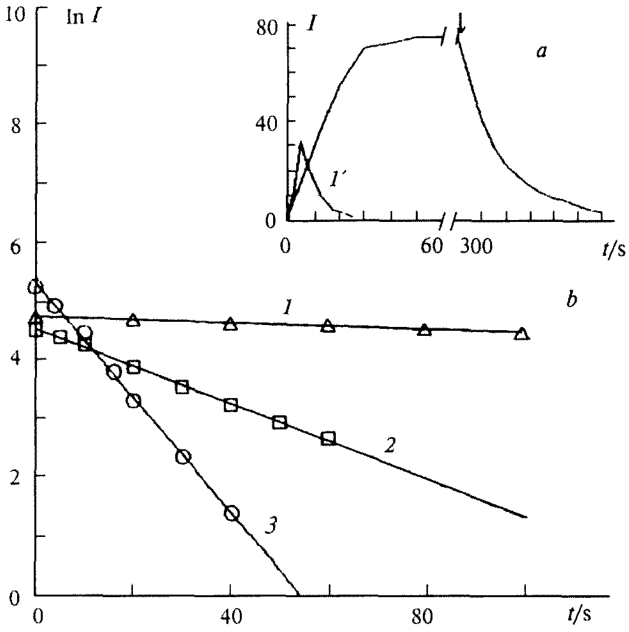

Fig. 3. *a*, Typical kinetic curves of the change in the intensity of CL; the moment when the admission of ozone was stopped is marked by the arrow (20 °C, Ad_0 = 1.5 mmol, mass of silica gel is 12 g); *1'*, blank experiment (20 °C, mass of silica gel is 12 g). *b*, Semilogarithmic anamorphoses of kinetic curves of CL decay (Ad_0 = 2.5 mmol, mass of silica gel is 12 g): −28 °C (*1*); 0 °C (*2*); 10 °C (*3*).

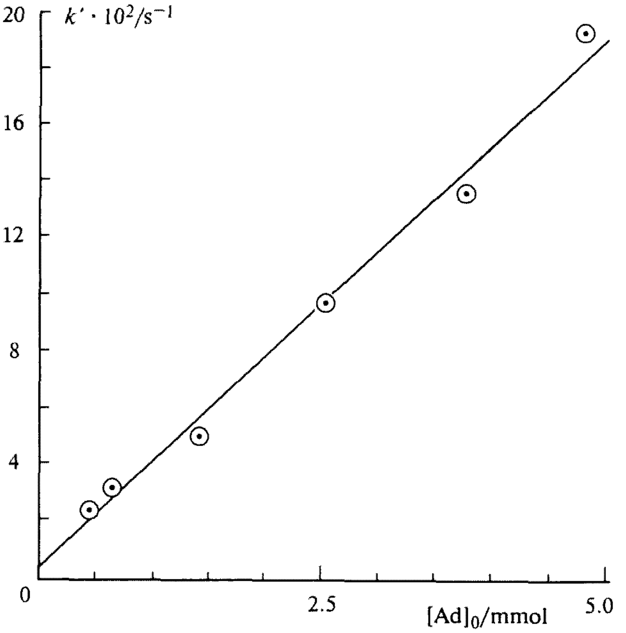

Fig. 4. Dependence of the effective rate constant k' of CL decay on the amount of adamantane (20 °C, mass of silica gel is 12 g).

the amount of adamantane adsorbed on the surface (Fig. 4) and is almost independent of the amount of ozone adsorbed. The activation energy E_a = 9.97±1.89 kcal mol^{-1} and the pre-exponential factor A = $(2.76\pm0.52)\cdot10^6$ (r = 0.995) were calculated from the temperature dependence of k':

T/°C	−28	−10	0	10	20
$k' \cdot 10^2/s^{-1}$	0.31	1.70	3.13	4.87	9.74
	±0.03	±0.14	±0.73	±0.52	±0.80

It is noteworthy that CL (probably, adsorboluminescence[10,11]) is also observed upon ozonization of silica gel in the absence of a substrate. This CL is less intense and decays rapidly according to the first-order law, despite the continuous flow of ozone (see Fig. 3, *a*). No CL flash is observed upon the repeated ozonization of silica gel in the blank experiment.

Thus, the CL found makes it possible to understand the process of ozonization on the surface and can be used for study of the kinetic regularities of this process.

References

1. P. S. Bailey (ed.), *Ozonation in Organic Chemistry*, Academic Press, New York, 1978, **2**, 136.
2. V. V. Shereshovets, V. D. Komissarov, and E. T. Denisov, *Neftekhimiya* [*Petrochemistry*], 1980, **20**, 245 (in Russian).
3. A. A. Krasnovskii, *Izv. Akad. Nauk SSSR, Ser. Fiz.* [*Bull. Acad. Sci. USSR, Div. Phys. Sci.*], 1978, **42**, 343 (in Russian).
4. Z. Cohen, H. Varkony, E. Keinan, and Y. Mazur, *Org. Synth.*, 1979, **59**, 176.
5. Z. Cohen, E. Keinan, Y. Mazur, and H. Varkony, *J. Org. Chem.*, 1975, **40**, 2141.
6. M. C. Whiting, A. J. N. Bolt, and J. H. Parish, *Adv. Chem. Ser.*, 1969, **77**, 4.
7. R. W. Murray, W. C. Lumma, and J. W. P. Lin, *J. Am. Chem. Soc.*, 1970, **92**, 3205.
8. V. V. Shereshovets, G. L. Sharipov, and N. N. Kabal'nova, *Zh. Org. Khim.*, 1986, **22**, 2549 [*J. Org. Chem. USSR*, 1986, **22** (Engl. Transl.)].
9. W. A. Pryor, N. Ohto, and D. F. Church, *J. Am. Chem. Soc.*, 1982, **104**, 5813.
10. F. F. Vol'kenshtein, A. I. Gorban', and V. A. Sokolov, *Radikaly rekombinatsionnye — lyuminestsentsiya poluprovodnikov* [*Recombination of Radicals and Luminescence of Semiconductors*], Nauka, Moscow, 1976, 214 (in Russian).
11. A. I. Voloshin, G. L. Sharipov, and V. P. Kazakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2613 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 2397 (Engl. Transl.)].

Received June 8, 1995