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Letters to the Editor

Oxidation of molecular nitrogen with hydrogen peroxide*

A. E. Gekhman,[a]* ***I. P. Stolyarov,***[a] ***A. F. Shestakov,***[b] ***A. E. Shilov,***[b] ***and I. I. Moiseev***[a]

[a]*Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: iimois@igic.ras.ru
[b]*Emanuel´ Institute of Biochemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 117977 Moscow, Russian Federation.
E-mail: shilov@icp.ac.ru

Molecular nitrogen is among the most inert to oxidation substrates. Under close to standard conditions, the oxidation of molecular nitrogen to nitrogen(I or II) oxides with dioxygen in its ground ($^3O_2$) and excited $^1O_2(^1\Delta_g)$ states is thermodynamically unfavourable. However, the oxidation of molecular nitrogen with hydrogen peroxide is allowed thermodynamically**:

$$2\,H_2O_{2(l)} + N_{2(g)} = 2\,NO_{(g)} + 2\,H_2O_{(l)}, \qquad (1)$$

$$\Delta G^\circ_{298} = -58.3\ \text{kJ mol}^{-1},$$

$$H_2O_{2(l)} + N_{2(g)} = N_2O_{(g)} + H_2O_{(l)}, \qquad (2)$$

$$\Delta G^\circ_{298} = -13.1\ \text{kJ mol}^{-1},$$

$$3\,H_2O_{2(l)} + N_{2(g)} = N_2O_{(g)} + 3\,H_2O_{(l)} + {}^3O_{2(g)}, \qquad (3)$$

$$\Delta G^\circ_{298} = -185.5\ \text{kJ mol}^{-1}.$$

For instance, N_2O formation has been detected in the high-temperature decomposition of hydrogen peroxide in a nitrogen atmosphere,[2—4] which fact is in accord to the thermodynamic data.

In the work[5] theoretical aspects of molecular nitrogen oxidation have been considered in the relation to biomimetic processes.

The data[6] showed that vanadium(V) complexes in the catalytic $V^V/H_2O_2/CF_3COOH$ system are capable of transferring to various substrates not only such oxygen-containing active species as $^1O_2(^1\Delta_g)$[6—8] but also an $O(^1P)$ atom or $[O^{\bullet +}]$ radical cation.[9] Two latter species are strong acids in terms of the Usanovich theory[10,11] and therefore should exhibit acidic properties even toward such a weak base as N_2 to oxidize this substrate.

In our study we found the first example of involving molecular nitrogen in the hydroperoxide-catalyzed oxidation.

The oxidation of N_2 (special purity grade) was carried out in a gas flow reactor passing N_2 flow (30—60 mL min^{-1}) through a solution of H_2O_2 (1 mol L^{-1}) and $VO(acac)_2$ (10^{-2} mol L^{-1}) in trifluoroacetic acid at 0—20 °C. The outgoing gas was collected above an aqueous solution of NaCl or NaOH during 5—20 min and then analyzed by chromato-mass spectrometry (Automass

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* Dedicated to Academician I. P. Beletskaya on occasion of her anniversary.

** Thermodynamic parameters for compounds in reactions (1)—(3) are taken from the Handbook.[1]

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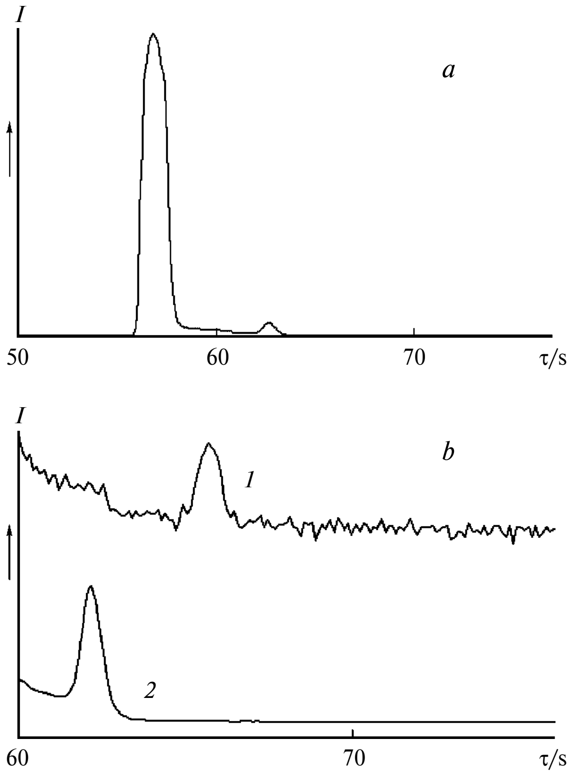


Fig. 1. Chtomatogram of gaseous products of N_2 oxidation in the $V^V/H_2O_2/CF_3COOH$ system: *a*, chromatogram of total ionic current; and *b*, part of the chromatogram (*1*) and fragmentogram (*2*) for $m/z = 30$.

150 (Delsi-Nermag) chromato-mass spectrometer, column Supel-QPlot (Supelco), 30 m×0.32 mm, -10 °C, $P_{inj} = 0.5$ bar, flow splitting 1 : 40, probe volume 100 L, electron impact 70 eV, mass interval 25—100 amu, spectrum sweep time 50 ms).

The chromatogram of the collected gas contains the unseparated $N_2—O_2$ peak (retention time 57 s) and the CO_2 peak (retention time 63 s) (Fig. 1, *a*), along with a low-intensity chromatographic peak with a retention time of 67 s (Fig. 1, *b*). The mass spectrum of the component corresponding to the latter chromatographic peak, which was obtained by subtraction of the averaged background before and after the chromatographic peak, contains ions with masses (intensities are in parentheses) 44 (100), 30 (27), and 28 (14) *m/z* (Fig. 2, *a*). This spectrum is in good agreement with the literature mass spectrum of N_2O, *m/z*: 44 (100), 30 (31), and 28 (13) (Fig. 2, *b*), as follows from a close to zero intensity of the lines in the difference spectrum (Fig. 2, *c*). The concentration of N_2O estimated from the ratio of the ionic currents of the components is at most 0.1%. The chromatograms of gaseous nitogen used in the runs and those of the gaseous products of hydrogen peroxide decomposition in the presence of $VO(acac)_2$ in a solution of trifluoroacetic acid in helium atmosphere contain no peaks close in the retention time and shape to the chromatographic signals found in the spectrum of the products of nitrogen oxidation. In the runs performed in the absence of $VO(acac)_2$, no chromatographic peaks corresponding to N_2O were found.

The data obtained give evidence that molecular nitrogen is oxidized in the $V^V/H_2O_2/CF_3COOH$ catalytic system to form N_2O. Analysis of the reaction solutions for the presence of other products of nitrogen oxidation was not carried out.

The data available does not allow for definite conclusions on the nature of the active intermediate responsible for dinitrogen oxidation and the mechanism of formation of nitrogen(I) oxide. However, the above thermodynamic

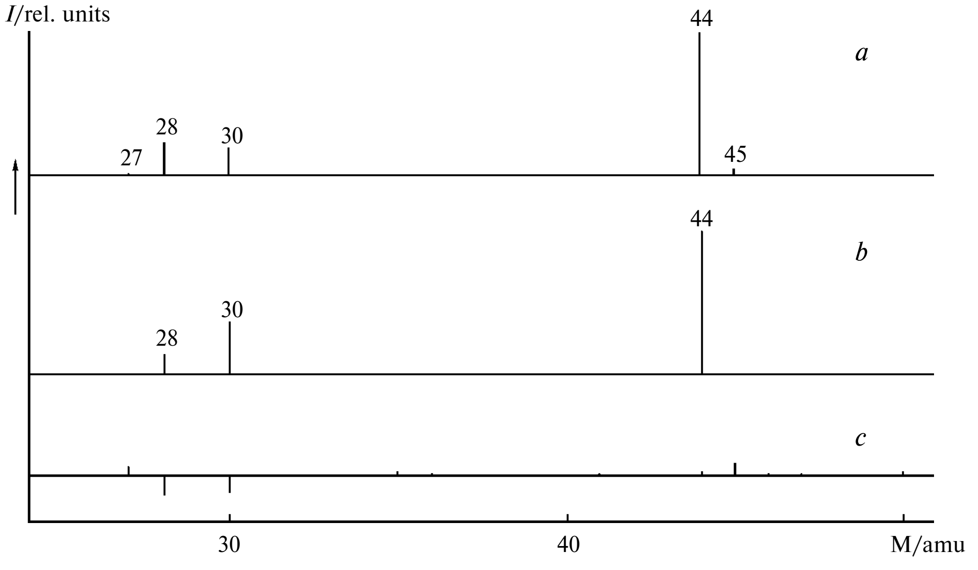
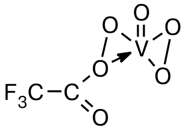


Fig. 2. Oxidation of molecular nitrogen: *a*, mass-spectrum of the component with a retention time of 67 s in the chromatogram of gaseous products of N_2 oxidation in the $V^V/H_2O_2/CF_3COOH$ system; *b*, the literature electron impact (70 eV) mass spectrum of nitrogen(I) oxide; and *c*, difference between mass spectra *a* and *b*.

data unambiguously rule out the participation of free ozone and singlet dioxygen in the reaction under question.



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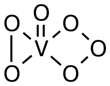

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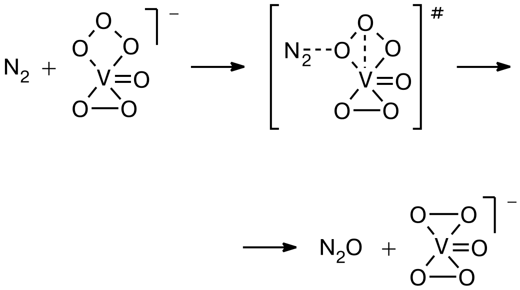
Studies of the oxidation of perfluoroalkenes, alkanes, and arenes with hydrogen peroxide showed[6—8] that the intermediate vanadium (V) complexes like **1** and **2** can be formed in a solution of trifluoroacetic acid containing vanadium compounds. These complexes can transfer an oxygen atom and/or radical cation $O^{\bullet +}$ to a substrate, in our case to the N_2 molecule, to form nitrogen(I) oxide or its radical cation. However, the formation of $N_2O^{\bullet +}$, which could be expected in the $N_2 + O^{\bullet +}$ reaction, is improbable because of a rather high N_2O ionization potential. It seems that the found product of N_2 oxidation is formed through a transfer of the oxygen atom to the nitrogen molecule, for example



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