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Simulation of ozone and molecular oxygen oxidation of dinitrogen tetroxide to nitric anhydride

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The oxidations of N_2O_4 to N_2O_5 with ozone or molecular oxygen were simulated using quantum chemistry (DFT) and computer modeling (Gaussian 98 program package) methods.

Nitro compounds are extremely important products of organic synthesis, which are widely used in the military, medical, and other areas. The main method of their synthesis is nitration of organic compounds (arenes, amines, amides, alcohols, *etc.*) using nitric acid (HNO_3) or its mixtures with sulfuric acid. However, nitric acid quickly becomes less active as it is diluted with water generated in the nitration process; moreover, disposal of mixed acid residue is a serious technical problem. In the last decades, nitric anhydride N_2O_5 has been recognized as one of the most powerful and efficient nitrating agents.[1–4] Reactions with N_2O_5 can be efficiently implemented without the use of flammable organic solvents (for example, in liquid or supercritical CO_2[5]), whereas nitric acid, a secondary product of this process, can be converted into N_2O_5, making the method environmentally attractive.

Among the known syntheses of N_2O_5, electrolysis of nitric acid in the presence of dinitrogen tetroxide (N_2O_4) and oxidation of N_2O_4 with ozone (O_3)[3,6] appear the most efficient and suitable for industrial application. Though, in the first case, the product of the reaction is not nitric anhydride *per se* but its solution in HNO_3. Note that N_2O_4 is produced in industrial scale as a side product of nitric acid manufacturing and used as an oxidant in rocket propellants.[7,8] Meantime, theoretical studies on the oxidation of N_2O_4 to N_2O_5 using molecular oxygen O_2 or ozone O_3 are absent. So, the aim of this work was investigation into the mechanism of such an oxidation.

We simulated the nitric anhydride formation from N_2O_4 under the action of ozone and molecular oxygen using quantum chemistry and computer modeling methods. The spatial and electronic structures were calculated within the density functional theory (DFT) with the hybrid potential B3LYP and standard split-valence basis set 6-31G(d) using the Gaussian 98 program package.[9] The positions of stationary points were fixed on the basis of the Hessian matrix by the absence of imaginary frequencies. The charges at atoms were calculated using the method of natural bond orbitals (NBO). Our calculations were also based on the fact that the N_2O_4 in the solid and gaseous states has a covalent structure, whereas the same molecule in liquid phase[10] and especially in nitric acid is dissociated into ions NO^+ and NO_3^-.

Note that the spatial and energetic characteristics of nitrogen oxides were studied[11–13] and reactions of nitrogen oxides with H_2O, N_2, and N_2O were investigated.[13–15] The geometrical characteristics (bond lengths, valence and torsion angles) virtually coincide with the results of our calculations, indicating identical localization of intermediates that were considered in the oxidation of N_2O_4. It is known that N_2O_5 is generated in the atmosphere of Earth from NO_2 and NO_3[16,17] and the enthalpy of this reaction (–22.83 kcal mol^{-1})[16] is in good agreement with the results of our calculations (–22.42 kcal mol^{-1}).

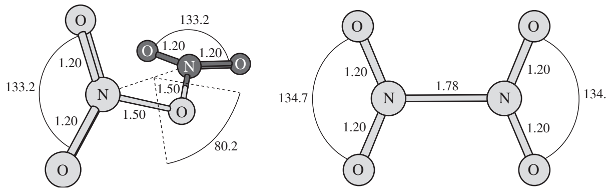

Figure 1 Geometrical characteristics of N_2O_5 and N_2O_4 molecules.

The calculated values of the geometrical parameters of N_2O_4 and N_2O_5 (Figure 1) indicate that the N_2O_4 molecule is planar, whereas the angle between the nitro group planes in the N_2O_5 molecule is 80.19°. Analysis of charges (NBO) reveals that the charge at the nitrogen atom in the N_2O_5 molecule (0.725 a.u.) is higher than in N_2O_4 (0.542 a.u.); this fact is associated with the influence of the ‘additional’ oxygen atom in nitric anhydride.

Since one of the possible ways of N_2O_5 formation is the recombination of free radicals $NO_2^{\cdot}$ and $NO_3^{\cdot}$, we simulated the homolytic route of N_2O_4 decomposition with the formation of a nitro radical ($N_2O_4 \rightarrow 2NO_2^{\cdot}$), which then reacts with NO_3. In our calculations, we assumed that ‘ion’ or radical recombination processes should have low or even zero activation energy[18] and therefore, no activated complex is formed.

The ground states of atomic and molecular oxygen (O and O_2) are triplet rather than singlet.[19,20] Accordingly, the energy of homolytic N–N bond cleavage in N_2O_4 is 14.96 kcal mol^{-1}, whereas the energy of O–O bond dissociation in ozone ($^1O_3 \rightarrow {}^3O_2 + {}^3O$) is 16.19 kcal mol^{-1}. Similar processes of atomic oxygen formation occur in the atmosphere of Earth under the action of UV radiation and do not require much energy.[21] These two stages are rate-limiting (Figure 2). The reaction of $NO_2^{\cdot}$ radical with atomic oxygen and subsequent recombination of $NO_2^{\cdot}$ and $NO_3^{\cdot}$ radicals are exothermic processes. The total thermal effect of the reaction is –43.96 kcal mol^{-1}. Accounting medium (N_2O_4 or HNO_3) does not greatly affect the energy of homolytic oxidation reaction, and

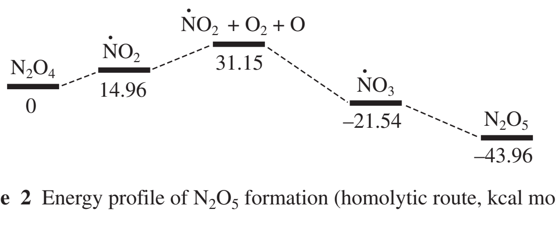

Figure 2 Energy profile of N_2O_5 formation (homolytic route, kcal mol^{-1}).

the change in the calculated energy value of a similar reaction in the gas phase and in the medium is about 1–2 kcal mol^{-1}.

Geometrical calculations of the ozone molecule structure lead one to the conclusion that the oxygen–oxygen bond orders in this molecule correspond to bond multiplicity 1.5, whereas the reported results[22,23] correspond to double bonds.

The reaction of heterolytic nitrogen–nitrogen bond cleavage in N_2O_4 with formation of NO^+ and NO_3^- ions is energetically unfavourable, since the total energy of resultant ions in this case is 189.9 kcal mol^{-1} higher than the energy of N_2O_4 formation (Figure 3). One can assume that, although synthesis of NO_2^+ from NO^+ and atomic oxygen is an exothermic process, as well as interaction of NO_2^+ and NO_3^- ions with formation of N_2O_5, the heterolytic mechanism of N_2O_4 decomposition in the gaseous phase is, as a whole, energetically unfavourable and the free-radical process of nitric anhydride formation must be predominant.

Calculations based on the Polarizable Continuum Model indicate that the activation energy of heterolytic oxidation reaction, unlike the corresponding homolytic process, largely depends on the solvent. Indeed, the activation energy of the reaction in the nitric acid ($\varepsilon = 19.0$) becomes 3–4 times lower and in the dinitrogen tetroxide ($\varepsilon = 2.42$) – 1.5–2 times lower than that in the gas phase.

Further we evaluated the feasibility of N_2O_5 formation from N_2O_4 and molecular oxygen, either directly or *via* the stage of atomic oxygen formation. As is shown above, one of the principal intermediates in this process is the atomic oxygen. Two possible ways of atomic oxygen formation from molecular oxygen have been considered, in particular, *via* ozone generation (then the problem is reduced to the above scheme in Figure 2) and *via* oxygen molecule dissociation into oxygen atoms.

The first scenario takes place in high atmospheric layers, where ozone is accumulated *via* oxygen: two ozone molecules are formed from three oxygen molecules. We considered here just the thermodynamic aspect of the most favourable pathway of this net reaction. The calculated [B3LYP/6-31G(d)] thermal effect of the endothermic reaction (92.4 kcal mol^{-1}) is significantly different from the experimental data (68 kcal mol^{-1})[21] and both values are high enough. The thermal effect (66.69 kcal mol^{-1}) calculated by MP2/6-311++G(d,p) with account of electron correlations is much closer to the experimental value.

For the second variant, we have calculated the energy of molecular oxygen (triplet) dissociation into two atoms ($^3O_2 = {}^3O + {}^3O$) to be even higher, equal to 124.76 kcal mol^{-1} (the experimental value is also very high, 117–119 kcal mol^{-1})[24,25] indicating that the process is thermodynamically unfavourable.

Then we estimated the thermal effect of the hypothetical direct oxidation of N_2O_4 with molecular oxygen ($N_2O_4 + 2\,O_2 = N_2O_5 + O_3$). It turned out to be much lower (48.42 kcal mol^{-1}) than that for the reaction with ozone. Therefore, a practical implementation of this potentially useful process would require the use of high temperatures or other methods of reactant activation (*e.g.*, catalysts, UV radiation, microwave activation, *etc*.). Obviously, further investigations are needed to select the most rational one.

In conclusion, the available experimental data and the results of quantum chemical calculations of reactions between N_2O_4 and ozone or molecular oxygen indicate that current efforts towards the synthesis of N_2O_5 from N_2O_4 should primarily be based on modifications of known procedure using O_3 as a highly reactive oxidant. The development of catalytic oxidation process instead of explosive dangerous ozonolysis method still remains a challenge.

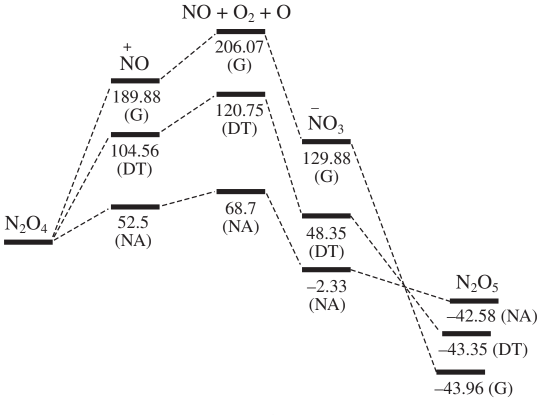

Figure 3 Heterolytic route (kcal mol^{-1}) and the energy profile of N_2O_5 formation in the gas phase (G), in nitric acid (NA) and in dinitrogen tetroxide (DT).

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