Gas Phase Properties of ONOO-anion and ONOO-radical

Leo Klasinc, Dunja Srzić, Ljiljana Paša-Tolić, and Suzana Martinović

Ruđer Bošković Institute, Bijenička 54, HR-10001 Zagreb, Croatia

We report calculated *ab initio* energies and barriers to internal rotation for ONOO-anion and ONOO-radical species at the 6-31G** level. The anion is 48 kJ/mol more stable than the radical in its lowest ^{2}A" (*trans*) state. The difference between the more stable *trans* and less stable *cis* conformations of the ONOO-anion and ONOO-radical is small, amounting to 4.6 and 3.9 kJ/mol, respectively. However, the energy of the 90° *skew* form is 68 kJ/mol above the *trans* form in the ONOO-anion, but only 40 kJ/mol in ONOO-radical. Several ways to produce the ONOO-anion for FTMS analysis and determination of its thermodynamic properties are presented.

Peroxynitrite (ONOO$^-$) is a toxic compound[1] formed in solution from the reaction of the radical species superoxide and nitric oxide. Both radicals are produced by activated macrophages and neutrophils. The product is not stable and isomerizes to nitrate. The anion or the protonated form (ONOOH, pKa = 6.8) oxidizes biomolecules through presently poorly understood pathways. Much effort is recently put in investigating how peroxynitrite or its protonated form carry out these deleterious reactions. Only a few thermodynamic parameters have been measured: the enthalpy of formation of ONOO$^-$,[2] the pKa of ONOOH and enthalpy of ionization.[3] For a better understanding of the reactivity of peroxynitrite and peroxynitrous acid more thermochemical data are essential.

The oxoperoxonitrate radical (ONOO·) is considered a transient species formed in the trimolecular reaction of nitric oxide and oxygen in the gas phase and which could be important for biological systems.

Nitric acid and halogennitrates (particularly $ClONO_2$), which are formed in the stratosphere by radical recombination reactions, play an important role in the stratospheric ozone layer chemistry, acting as temporary reservoirs for radicals. Recently, formation of ONOOH by radical recombination upon nitric acid photolysis in solid argon was observed and its spectrum reported.[4-6] Such photolysis is not currently considered in the atmospheric models, nor any reaction involving ONOOH. McGrath and Rowland[7] investigated theoretically the conformational potential energy surfaces of ONOOH and ONOOCl and found that conformers of ONOOH may well be formed by reactions of OH with NO_2 in the atmosphere while formation of ONOOCl from ClO with NO_2 is thermodynamically unfavourable.

Preliminary *ab initio* calculations at the 6-31G** level yielded the structural parameters described in Ref. 8. At this level, peroxynitrous acid in the *cis*- configuration is more stable than that in the *trans* – form by 3.9 kJ/mol, which is nearly identical to the result obtained by McGrath *et al.*[9] of 3.8 kJ/mol, at the RMP2/6-31G* level. A calculation by the same authors at the RMP2/6-311++G** level resulted in a difference of 5.4 kJ/mol.

Our *ab initio* calculations, also at the 6-31G** level for the 90° *skew* forms of the anion and radical species indicate that this form is 68 kJ/mol above the trans form in ONOO-anion but only 38.9 kJ/mol in ONOO⁻ radical (Table I). Thus, it is understandable if one observes that this latter energy corresponds to the difference in total energies between the *trans* – form and the sum of O_2 (–149.532997H) and NO (–129.247883H) energy.

The HF/6-31G**level calculations were performed using the GAUSSIAN system of programs[10] at the Computing Centre of the University of Düsseldorf, Germany.

Gas phase reactions of negative ions with neutral molecules are of great interest for several reasons. They enable determination of gas phase acidities, electron affinities and thermochemical data. Gas phase studies of reactions important in solution yield information on solvation effects and intrinsic reactivity. In particular, reactions of superoxide anions have received attention through their importance in ionospheric and stratospheric ion chemistry, chemical ionization mass spectrometry and the chemistry of plasmas. Studying the reactivity of superoxide towards halocarbons, McDonald and Chowdhury[11] found superoxide to be an excellent intrinsic gas phase nucleophile. Streit[12] used a flowing afterglow apparatus to study the reactions of O^- and O_2^- with a number of compounds, but the technique did not allow the ionic products to be assigned particularly to O^- and O_2^-. Morris[13] used a variable temperature selected ion flow tube instrument to determine the rate constants and product branching fractions of O^- and O_2^- with halocarbons. He produced superoxide from a mixture of N_2O and O_2 in the source, as follows: the O^- produced from electron attachment to N_2O reacts with another N_2O to form NO^-, which transfers its electron to O_2. Thus, the reaction

TABLE I

Distances and bond angles for ONOO⁻ and ONOO·

| | ONOO⁻ | | | ONOO· | | | | |
| | *cis* | *trans* | *skew* | *cis* | | *trans* | | *skew* |
				A'	A"	A'	A"	A"
O=N	1.188	1.198	1.177	1.150	1.140	1.444	1.148	1.137
N-O	1.270	1.264	1.321	1.354	1.422	1.383	1.402	1.467
O-O	1.428	1.446	1.515	1.372	1.296	1.367	1.297	1.294
O=N-O	118.5	113.2	114.0	115.1	113.8	109.5	108.9	109.7
N-O-O	118.2	111.3	102.8	113.1	107.3	107.2	108.6	107.3
E(H)	−278.81051	−278.81224	−278.78629	−278.77126	−278.79241	−278.769062	−278.79386	−278.77909
rel. E (kJ/mol)	4.6	0	68.1	(0)	3.8	(5.8)	0	38.9

of NO^- with O_2 seems to involve only charge transfer without formation of an ($O_2 \cdot NO^-$) adduct. However, already in 1970 Adams and coworkers[14] noticed that, among the superoxide clusters with dinitrogen, dioxygen, water, carbon dioxide and nitrogen monoxide, the ($O_2 \cdot NO$) cluster is the most stable and, when formed in Reaction 1:

$$O_4^- + NO \rightarrow NO_3^- + O_2 \tag{1}$$

yields a product which is different from that formed by Reaction 2:

$$NO_2^- + NO_2 \rightarrow NO_3^- + NO \tag{2}$$

because the former reacts with nitrogen monoxide, whereas the latter does not. Although the authors explained this by claiming that the reactive NO_3^- is in an electronically excited state, it seems that this NO_3^- is actually gaseous peroxynitrite. Therefore, we propose to form peroxynitrite from reactive collisions of presorted $O2 \cdot^-$ with $\cdot NO$ gas in the mass spectrometer. It is possible to remove all but the desired ionic species using special procedures in a Fourier transform mass spectrometer.

$$O_2^- + NO \rightarrow ONOO^- \qquad \text{(with FTMS detection)} \tag{3}$$

$$O_2 \cdot O_2^- + NO \rightarrow ONOO^- + O_2 \quad \text{(with FTMS detection)} \tag{4}$$
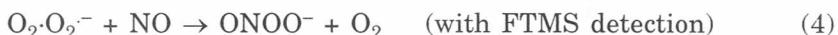
The first proposed synthesis (Reaction 3) is exothermic and may not be successful. In the second synthesis (Reactions 4) there a is inert reaction partner that can carry away the excess energy. In general, a problem exists if a single compound is formed by collision of two reactants in the gas phase, because there is no additional product, wall or solvent over which the excess energy of the reaction could be distributed.

If $O_2 \cdot O_2^-$ is the reaction partner (Reaction 4), it can be formed by flowing an O_2/He mixture past an electron gun. Dioxygen will capture an electron and, at higher pressure, $O_2 \cdot O_2^-$ is the dominant ion. This species can be introduced by differential pumping into the Fourier transform mass spectrometer and, reacting with NO introduced through pulsed valves, yield $ONOO^-$ which can be analysed and measured.

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SAŽETAK

Svojstva ONOO-aniona i ONOO-radikala u plinskoj fazi

Leo Klasinc, Dunja Srzić, Ljiljana Paša-Tolić i Suzana Martinović

Određene su energije i barijere interne rotacije ONOO-aniona i ONOO-radikala na temelju *ab initio* 6-31G** računa. Anion je 48 kJ/mol stabilniji no radikal u svom najnižem ^{2}A" (*trans*) stanju. Razlika između stabilnije *trans* i manje stabilne *cis* konformacije ONOO-aniona i ONOO-radikala je mala i iznosi 4,6 kJ/mol odnosno 3,9 kJ/mol. Međutim energija konformacije zakrenute za 90° je 68 kJ/mol iznad energije *trans* konformacije ONOO-aniona, ali samo 40 kJ/mol iznad energije ONOO-radikala. Prikazano je nekoliko načina dobivanja ONOO-aniona za FTMS analizu i određivanja njegovih termodinamičkih svojstava.