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COMMENTS

Comment on “Spontaneous Reactions and Reduction by Iodide of Peroxynitrite and Peroxynitrate: Mechanistic Insight from Activation Parameters”

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In a previous report,[1] the activation parameters for the decomposition of O_2NOO^- were determined to be $A = 1 \times 10^{12}$ s^{-1} and $E_a = 16.3$ kcal/mol using the pulse radiolysis technique for generation of O_2NOO^-. These values are considerably lower than $A = 7.7 \times 10^{20}$ s^{-1} and $E_a = 28.7$ kcal/mol, which were estimated by Régimbal and Mozurkewich[2] by following the decomposition of O_2NOOH as a function of pH at pH < 5.

Peroxynitric acid (pK(O_2NOOH) $= 5.9 \pm 0.1$[3,4]) is relatively stable in aqueous solution,[2,3,5] whereas O_2NOO^- decomposes into nitrite and oxygen[6] with $k_d = 1.35$ s^{-1} at 25 °C.[7]

$$O_2NOO^- \rightarrow NO_2^- + O_2 \qquad (1)$$

We have recently[7] shown that O_2NOO^- dissociates into $^{\bullet}NO_2$ and $O_2^{\bullet -}$ and that the contribution of this reaction to the decomposition of O_2NOO^- is ca. 50%. Two alternative mechanisms were suggested to account for this observation. According to the first mechanism, O_2NOO^- decomposes into O_2 and NO_2^- and in parallel homolyses into $^{\bullet}NO_2$ and $O_2^{\bullet -}$ via two different transition states. This mechanism predicts on grounds of spin conservation the formation of $^1O_2$. According to the second mechanism (the cage mechanism), $^{\bullet}NO_2$ and $O_2^{\bullet -}$ are formed in a solvent cage, and ca. 50% of the radicals escape the cage and the remaining undergo electron transfer in the cage to form NO_2^- and $^3O_2$. We tried to resolve the discrepancy in the activation parameters as they could point toward the most probable mechanism for the decomposition of O_2NOO^-.

Peroxynitric acid was prepared through the reaction of nitrite with an excess of acidified H_2O_2 as described previously.[7] Bio SX-17MV sequential stopped-flow from Applied Photophysics with a 1 cm long mixing cell was used for kinetic measurements. Peroxynitric acid was diluted with 0.01 M $HClO_4$ and mixed in a 1:1 ratio with 0.2 M iodide in 0.2 M acetate buffer or 20 mM borate buffer. The reaction of O_2NOO^- with I^- was followed at 351 nm ($\epsilon(I_3^-) = 25\,800$ M^{-1} s^{-1})[8] and that of the decomposition of O_2NOO^- at 285 nm.[3,4,7] The pH of the mixture was measured at the outlet of the flow system.

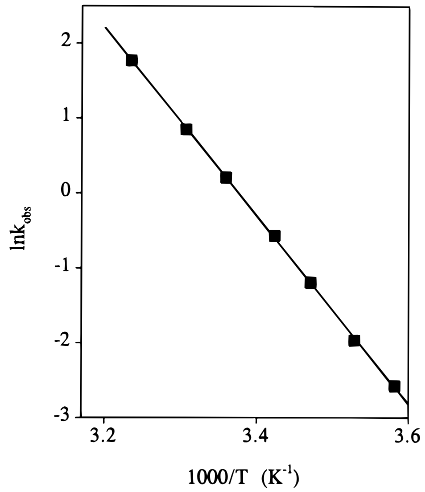
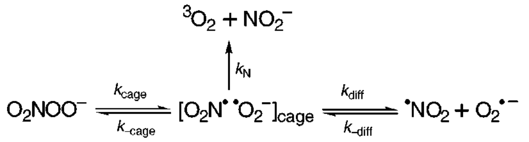


Figure 1. Arrhenius plots for the decomposition rate constant of 0.1 mM O_2NOO^- at pH 8.9.

SCHEME 1



The decomposition of 0.1 mM O_2NOO^- at pH 8.9 was followed at 6.2−36.1 °C. The Arrhenius plot is given in Figure 1, and the extracted activation parameters are $A = 3 \times 10^{18}$ s^{-1} and $E_a = 25.2 \pm 0.4$ kcal/mol. These values are higher than those determined previously using the pulse radiolysis technique.[1] However, k_d at ambient temperature was found to be identical with both the stopped-flow and pulse radiolysis methods.[1,7] We therefore suspected that the pulse radiolysis setup in Jerusalem is not well thermostated. Indeed, we found that the temperature inside the irradiated cell is higher than that of the thermostated bath below room temperature, and vice versa above room temperature. In our previous report[1] we also determined $A = 1.5 \times 10^9$ M^{-1} s^{-1} and $E_a = 8.4$ kcal/mol for the reaction of O_2NOOH with iodide. Therefore, we repeated the experiment using the stopped-flow technique where the temperature is well-defined. The reaction of 20 μM O_2NOOH with 0.1 M I^- at pH 4.1 was followed at 6.2−25.9 °C, and the extracted activation parameters were found to be $A = 7.2 \times 10^9$ M^{-1} s^{-1} and $E_a = 10.7 \pm 0.1$ kcal/mol (results not shown).

The very high preexponential factor ($A = 3 \times 10^{18}$ s^{-1}) implies that the decomposition of O_2NOO^- does not produce $^1O_2$ via a concerted elementary reaction, as such a reaction is expected to have a tight transition state in comparison with a homolysis reaction. Therefore, the cage mechanism, which is given in Scheme 1 appears more probable.

According to this mechanism, k_d and the observed rate constant for the formation of an oxidized product via the reaction of a scavenger with the radicals, k_f, are given by

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$$k_d = k_{cage}k_N/(k_{-cage} + k_N) = 1.30 \pm 0.08\ s^{-1}$$
(this study, ref 7) (2)

$$k_f = k_{cage}(k_N + k_{diff})/(k_{-cage} + k_N + k_{diff}) = 2.4 \pm 0.2\ s^{-1}$$
(ref 7) (3)

As ca. 50% of the radicals escape the cage, $k_N \approx k_{diff}$, and hence $k_N < 0.3k_{-cage}$. The latter result agrees well with the experimental observations where the reaction of $^{\bullet}NO_2$ with $O_2^{\bullet-}$ yields 85 ± 15% O_2NOO^-.[3,4,7] The cage mechanism excludes the formation of $^1O_2$ during O_2NOO^- decomposition, as electron transfer in the cage, which yields $^3O_2$, is both spin-allowed and favored on energetic grounds.

The activation parameters, estimated by Régimbal and Mozurkewich,[2] are higher than those determined directly in this study. They got a temperature dependence of $k_1K_a(O_2NOOH)$, and assumed −22 eu for the entropy of dissociation of O_2NOOH.[2] We note, however, that the enthalpy of dissociation of ONOOH was found to be ca. 4 kcal/mol.[9] As the ONOOH and O_2NOOH have similar pK_a's, we adopt 4 kcal/mol for O_2NOOH, and calculated ca. −14 eu for the entropy of dissociation of O_2NOOH. Utilizing this value and the data in ref 2, we derive $A \approx 10^{19}\ s^{-1}$ and $E_a = 26$ kcal/mol, in good agreement with our values. However, even $A = 3 \times 10^{18}\ s^{-1}$ would seem to be too high for a homolysis reaction, as according to eq 2, k_{cage} exceeds k_d by more than a factor of 4, and thus the A factor of k_{cage} is even higher than $10^{19}\ s^{-1}$. The A value for homolysis of neutral species is expected to be close to $10^{16}\ s^{-1}$, about the same as in the gas phase. Consequently, an increase by a factor of 10^3 or more must be ascribed to ionic solvation in water. It is thus reasonable to assume that the entropy of solvation of the incipient $O_2^{\bullet-}$ in the cage is significantly more positive than that of O_2NOO^-. This would be consistent with a delocalization of charge on $O_2^{\bullet-}$ as opposed to charge concentration on the terminal oxygen of O_2NOO^-.[10]

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