

THE REDUCTION POTENTIAL OF THE COUPLE O_3/O_3^-

Consequences for mechanisms of ozone toxicity

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Received 12 January 1982

1. Introduction

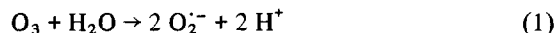
The toxicity of ozone, a major constituent of photochemical smog is well documented [1]. According to the Handbook of Chemistry and Physics [2], the ozone molecule is a powerful two-electron oxidant with a standard reduction potential of 2.07 V. The products of this reaction are oxygen and water. Since two-electron reactions are normally slow, it might be relevant to investigate the thermodynamics of two consecutive electron transfers, to determine whether other reactive oxygen species could be intermediates. Secondary oxidizing agents might be formed [3] as suggested by the decrease of glutathione in red blood cells upon exposure to ozone. One might suspect $\cdot OH$ radicals for this rôle since O_3 in alkaline solution were proposed to lead to the formation of the superoxide anion [4], which upon reaction with a second ozone molecule yields the $\cdot OH$ radical and oxygen.

It is shown here that this reaction sequence is unlikely at pH 7. Instead, the ozone molecule is thermodynamically a powerful one-electron oxidant by itself, and the ozonide anion, O_3^- can be a precursor of the hydroxyl radical. These reactions might take place in addition to the well-characterized reactions of ozone with double bonds in unsaturated lipid molecules [5,6].

2. Thermodynamics

The following reaction at alkaline pH [4]:

* Thermodynamic values for these and other oxygen radicals are discussed elsewhere, together with various interconversion reactions (W. H. K., A. Singh, in preparation)



At pH 7 Gibbs energies of formation ($\Delta G_f^{\circ'}$) for O_3 , H_2O and $O_2^{\cdot -}$ are 39.1 [1], -37.6 and 7.6 kcal/mol*. The latter two values follow via $\Delta G^{\circ'} = -nF\Delta E^{\circ'}$ from the reduction potential at pH 7 of the couples O_2/H_2O , 0.82 V and $O_2/O_2^{\cdot -}$, -0.33 V [7]. From these data it is calculated that at this pH reaction (1) is most unlikely to occur, having a Gibbs energy change of 13.7 kcal. At alkaline pH, however, the reaction becomes thermodynamically possible, because the Gibbs energy of formation for water is less negative.

To calculate the reduction potential of the couple O_3/O_3^- one needs to know the Gibbs energy of formation of the ozonide anion, O_3^- . This quantity can be estimated as follows. From radiation and flash photolysis studies it is known that $O^{\cdot -}$, the anion of the hydroxyl radical, reacts with oxygen to form O_3^- [8-10]. The pK of equilibrium (2) is 11.9 [11]:



At this pH, reaction (3) takes place:



The rate constants k_3 and k_{-3} are $(3.0 \pm 0.5) \times 10^9 M^{-1} \cdot s^{-1}$ and $(5.0 \pm 0.5) \times 10^3 s^{-1}$, respectively [12], leading to a Gibbs energy of -7.8 ± 0.1 kcal for this reaction in the forward direction via the relation $\Delta G^{\circ'} = -RT \ln k_3/k_{-3}$ in which R is the gas constant and T the temperature in Kelvin. Based on a reduction potential of 1.4 ± 0.1 V [13] at pH 14 for the couple $\cdot OH/OH^-$ and a $E^{\circ'}$ of 0.82 V (pH 7) for the couple O_2/H_2O , one calculates a $\Delta G_f^{\circ'}$ of 4 ± 2 kcal/mol for the hydroxyl radical at pH 7. Thus, at pH 7:

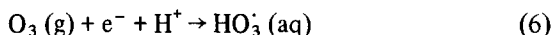
$$\Delta G^{\circ'}_f(\text{O}_3^-) = \Delta G^{\circ'}_f(\text{OH}) + 2.3 RT (11.9-7) + \Delta G^{\circ'} \quad (\text{reaction 3})$$

$$= 3 \pm 2 \text{ kcal/mol} \quad (4)$$

Combining the data for O_3 and O_3^- , it follows that the standard reduction potential for the reaction:



is 1.6 ± 0.1 V. If at $\text{pH} < 10.4$ the ozonide radical is protonated ([14] (but see [12])) the standard potential at $\text{pH} 7$ for the reaction:



would be higher, 1.8 ± 0.1 V and the Gibbs energy of formation of HO_3^- is calculated to be -2 ± 0.2 kcal.

At this point there are thermodynamically 3 possibilities:

(1) The ozonide radical (O_3^-) dissociates into the hydroxyl radical and oxygen:

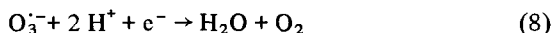


Since the error in $\Delta G^{\circ'}_f(\text{O}_3^-)$ originates from that of the hydroxyl radical, it follows that this reaction has a standard ($\text{pH} 7$) Gibbs energy change of $+1.1 \pm 0.2$ kcal. For reaction (7b):



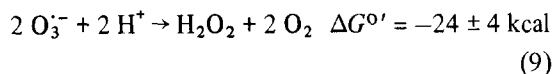
$\Delta G^{\circ'}$ is 5.7 kcal. Conversely, the reaction of oxygen with the hydroxyl radical should be favorable. Since no such reaction has been reported, it might be that it proceeds much slower than the reaction of OH with other solutes and/or itself, or that the ozonide anion is protonated at $\text{pH} \ll 10.4$. The oxygen formed in reaction (7a) cannot be in an excited state, since the production of $^1\Delta_g \text{O}_2$ would require an additional 22.6 kcal/mol.

(2) O_3^- oxidizes another molecule:



The standard reduction potential at $\text{pH} 7$ of this reaction is 1.8 ± 0.1 V, as calculated from the Gibbs energies of formation given above.

(3) O_3^- reacts with another O_3^- :



Pulse radiolysis studies in alkaline solutions indicate that the ozonide anion itself does not react, but first dissociates in O_2 and O^- (see [12]). If this also occurs at lower pH , reaction (7a) would be the predominant way of decay of the ozonide radical.

These thermodynamic data are plotted in an oxidation state diagram of the system O_2 – H_2O_2 (fig.1) [15]. The slopes of the lines in fig.1 represent reduction potentials (legend). Ozone appears to be a very strong one-electron oxidant as follows from the slope of the line joining O_3 and O_3^- .

An attempt can now be made to calculate the Gibbs energy of hydration for the ozonide radical.

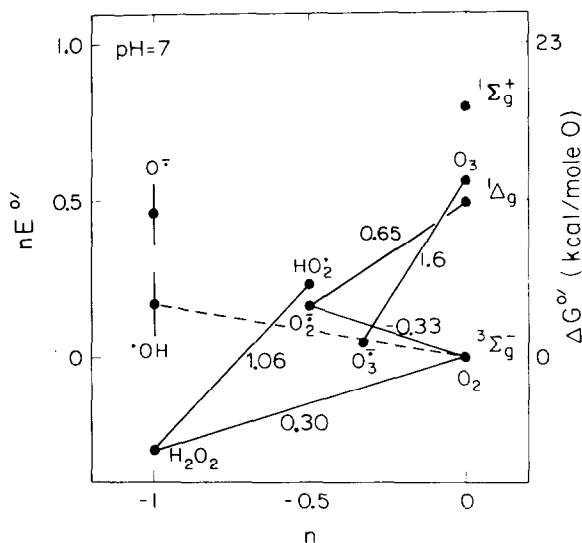


Fig.1. Oxidation state diagram of the system O_2 – H_2O_2 ($P_{\text{gases}} = 1 \text{ atm}$, $T = 25^\circ\text{C}$) at $\text{pH} 7$: abscissa, formal charge, n , per oxygen atom; ordinate (left) n times reduction potential, $E^{\circ'}$, (right) Gibbs energy of formation per gramatom of oxygen. The numbers refer to the gradients. The two ordinates are related by $\Delta G^{\circ'} = -F\Delta E^{\circ'}$, which represent reduction potentials, relative to the normal hydrogen electrode. This diagram was constructed as in [15]. The Gibbs energy of formation of the ozonide radical (O_3^-) calculated here, enables one to calculate the reduction potentials of the couple O_3/O_3^- . O_3^- is located just below the dashed line which indicates that, at equilibrium, an appreciable part of the ozonide anions will be converted to hydroxyl radicals. Since the latter disappear rapidly due to its reactivity, O_3^- might function as a source of OH radicals.

Table 1
Gibbs energies of ozone and ozonide radicals

Species	ΔG°_f (kcal/mol)	$\Delta G^\circ_f(\text{pH } 7)$ (kcal/mol)	$\Delta G^\circ_{\text{hydr.}}$ (kcal/mol)
O_3	39.1	39.1	—
O_3^-	3 ± 2	3 ± 2	-90 ± 2
HO_3^{a}	-11 ± 2	-2 ± 2	—

^a Values are based on $\text{p}K = 10.4$ [14]

Taking the electron affinity (EA) of ozone to be 2.14 ± 0.15 eV [16], and the Gibbs energy of formation of H^\bullet to be 102.5 kcal [17], a value of -90 ± 2 kcal is calculated according to eq. (10):

$$\Delta G^\circ [\text{O}_3 (\text{g}) + 1/2 \text{H}_2 \rightarrow \text{O}_3^- (\text{aq}) + \text{H}^\bullet] = -EA + \Delta G^\circ_{\text{hydr.}} (\text{O}_3^-) + \Delta G^\circ_f (\text{H}^\bullet) \quad (10)$$

Gibbs energies of formation and hydration are collected in table 1.

3. Discussion

The reduction potential of the couple O_3/O_3^- depends on the value for E°' ($\text{OH}/\text{H}_2\text{O}$). The theoretical values for this couple derived from Born-Haber type considerations [18,19] are typically 0.6 V higher than the value derived from 3 independent expt [13]. Such a theoretical value would result in reduction potentials for the couples $\text{O}_3/\text{HO}_3^\bullet$ and O_3/O_3^- which would be correspondingly lower, 1.2 V and 1.0 V, respectively, but still considerably higher than that of the couple $^1\Delta_g \text{O}_2/\text{O}_2^-$, 0.65 V [15]. Such values are likely to have harmful implications, since singlet oxygen was already found to oxidize NADH, producing O_2^- and NAD^\bullet [20].

The value of 1.6 V for the reduction potential of the couple O_3/O_3^- is supported by the following considerations. Ozone and nitrogen dioxide are similar in shape and have electron affinities which are the same within the error, 2.14 ± 0.15 and 2.3 ± 0.2 eV, respectively (see [20]). Assuming that the Gibbs hydration energies are also similar, one would expect the couples $\text{NO}_2/\text{NO}_2^-$ and O_3/O_3^- to have reduction potentials which are comparable. This is indeed the case, the value for the couple $\text{NO}_2/\text{NO}_2^-$ being smaller, 0.91 V, as calculated from the value for the couple

$\text{N}_2\text{O}_4/2 \text{NO}_2^-$ and the Gibbs dissociation energy of N_2O_4 [2].

It is concluded that the ozone molecule is a very strong oxidizer by itself, and that the reaction product, the ozonide radical can thermodynamically yield the hydroxyl radical, or be a strong oxidizer itself. The hydroxyl radical, and most likely the ozone molecule itself [22] are capable of abstracting a hydrogen atom from biomolecules, which will lead to various chain reactions in the presence of oxygen. These reactions amplify the damage, yielding other radicals such as O_2^- , ROO^\bullet and RO^\bullet [23], and take presumably place concomitant with the reaction of ozone with unsaturated lipid molecules, which might also produce various radicals [6].

Acknowledgement

I thank Dr J. Liebman for suggesting the analogy between ozone and nitrogen dioxide.

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