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Mechanism of Ozone Decomposition in Water. The Role of Termination

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The radical-chain mechanism of ozone decomposition in water is suggested. Addition of an extra chain termination step, i.e., reaction between superoxide and ozonide radicals, allowed the author to account for various reaction kinetic orders with respect to ozone and hydroxide ion concentrations reported in the literature, in particular the transition from 1.5 to 1 kinetic order for $[O_3]$ at neutral pH. The rate constant of the proposed new termination reaction has been estimated to be between 2×10^2 and 1×10^4 $dm^3 \cdot mol^{-1} \cdot s^{-1}$.

The purpose of this publication is to suggest a realistic mechanism of ozone decomposition in water which would account for a variety of different reaction kinetic orders with respect to ozone and hydroxide ion concentrations reported in the literature.

Ozone decomposition reaction has been the subject of numerous kinetic studies since 1913 (Rothmund and Burgstaller, 1913). A number of different, sometimes contradictory, kinetic expressions for the reaction rate were derived both theoretically and experimentally, the last publication on the topic being by Sotelo et al. (1987). The radical-chain nature of the ozone decomposition is probably universally recognized by now. The effects of radical scavengers, including certain buffers (Staehelin and Hoigne, 1982), as well as direct observations of radical species in the system (Forni et al. 1982) have been reported in the past. Several kinetic schemes based on radical reactions were proposed, starting with the pioneering work of Weiss (1935).

The overall reaction kinetic orders with respect to O_3 and OH^- concentrations have been previously compiled in

the form of tables by Peleg (1976), by Gurol and Singer (1982), and lately by Sotelo et al. (1987).

The variety of kinetic expressions in those tables does not necessarily call for a singular choice among them but may in fact represent a set of limiting cases of a more general formula.

According to the majority of studies, the kinetic order of the brutto reaction with respect to ozone changed from 1.5 at acidic pH into 1 at alkaline pH, while the kinetic order with respect to hydroxide ion concentration varied from 0 to 1.

The first radical-chain reaction sequence suggested by Weiss (1935), includes the ozone attack on the hydroxide ion as the initiation step, two chain propagation reactions involving $OH^\bullet$ and $HO_2^\bullet$ radicals with ozone, and two recombination reactions between the two radicals. Of course, either the rates of elementary processes or relative thermodynamic stability of the radicals involved was practically not known at the time. Virtually the same scheme, supplemented by a second initiation reaction between ozone and water, was suggested by Sotelo et al. (1987) to

Table I. Elementary Steps of Ozone Decomposition in Water in the Range from 3 to 12

eq no.	reaction	rate const, k, dm^3·mol^{-1}·s^{-1}	equilib. const, k, mol·dm^{-3}	ref
		Initiation		
1	$O_3 + OH^- \rightarrow HO_2^{\bullet} + O_2^{\bullet-}$	48; 70		Forni et al., 1982; Staehelin and Hoigne, 1982
2	$O_3 + H_2O \rightarrow 2HO_2^{\bullet}$			Sotelo et al., 1987
		Propagation		
3	$HO_2^{\bullet} \leftrightarrow H^+ + O_2^{\bullet-}$		1.3×10^{-5}	Behar et al., 1970
4	$O_2^{\bullet-} + O_3 \rightarrow O_2 + O_3^{\bullet-}$	1.5×10^9		Sehested et al., 1983
5	$O_3^{\bullet-} \rightarrow O^{\bullet-} + O_2$	3×10^3 s^{-1}		Gall and Dorfman, 1969
6	$OH^{\bullet} \leftrightarrow O^{\bullet-} + H^+$		1.6×10^{-12}	Rabani and Matheson, 1966
7	$OH^{\bullet} + O_3 \rightarrow HO_2^{\bullet} + O_2$	3×10^9		Bahnemann and Hart, 1982
		Termination		
8	$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	0.76×10^6		Behar et al., 1970; Bielski and Allen, 1977
9	$HO_2^{\bullet} + O_2^{\bullet-} \rightarrow HO_2^- + O_2$	8.7×10^7		
10	$O_3^{\bullet-} + O_2^{\bullet-} \xrightarrow{H_2O} 2OH^- + 2O_2$	$2 \times 10^2 < k < 1 \times 10^4$		this work

explain an apparent independence of the rate on pH in the acidic region.

Results

All subsequent discussion will be based solely on the sequence of elementary reactions represented by eq 1–10 in Table I. The processes considered thus far correspond to eq 1, 2, 4, 7, and 8 in the overall scheme. The whole scheme has been constructed using additional information available from different sources, in particular propagation reactions involving ozonide ion, $O_3^{\bullet-}$, studied by Gall and Dorfman (1969) and Sehested et al. (1983) and discussed by Staehelin and Hoigne (1982) and Forni et al. (1982). The acid–base equilibria involving perhydroxyl, $HO_2^{\bullet}$, and hydroxyl, $OH^{\bullet}$, radicals were added, eq 3 and 6. In addition we took into consideration a new crossover termination reaction involving a strong oxidant $O_3^{\bullet-}$ and an electron donor $O_2^{\bullet-}$, eq 10. The latter reaction was crucial in providing the explanation for the change in the brutto reaction kinetic order with respect to ozone concentration that has been observed at neutral pH.

The right-hand side of eq 1, 2, and 8–10 in Table I, describing the initiation and termination processes, does not necessarily have to correspond to the actually produced primary species. This does not affect the kinetic formula obtained from the overall scheme, for it is sufficient to know only that two chain carriers are produced or consumed per each elementary act of chain initiation or termination. For example, the same overall O_3 decomposition rate expression as given by eq 11 below would be obtained if one assumes an alternative mechanism of reaction 2, $O_3 + OH^- \rightarrow O_3^{\bullet-} + OH^{\bullet}$, as proposed by Forni et al. (1982).

If one temporarily excludes from consideration the strongly alkaline (pH > 12) and strongly acidic (pH < 3) regions, the reaction equations of Table I are expected to adequately describe the main processes in the system. Otherwise, it would be necessary to take into account possible, but less known, reactions of protonated forms of chain carriers at low pH and completely deprotonated forms, such as $O^{\bullet-}$, at high pH.

At pH above 3.0, the rate of reaction 9 is always higher than that of reaction 8 from Table I. The overall ozone decomposition rate derived by using the steady-state approximation for the pH range of 3–12 is then given by the following expression:

$$-\frac{d[O_3]}{dt} = 2k_4 \left(\frac{k_1[H_2O] + k_2[OH^-]}{k_9[H^+]/K_3 + k_4k_{10}[O_3]/k_5} \right)^{0.5} [O_3]^{1.5} \quad (11)$$

Let us examine now the expression in parentheses.

At low pH, when $k_1[H_2O] > k_2[OH^-]$ and $k_9[H^+]/K_3 > k_4k_{10}[O_3]/k_5$, the overall rate expression can be approximated as follows:

$$-d[O_3]/dt \simeq 2k_4(k_1[H_2O]K_3/(k_9K_w))^{0.5}[OH^-]^{0.5}[O_3]^{1.5} \quad (12)$$

where $K_w = [OH^-][H^+] \simeq 10^{-14}$ mol^2·dm^{-6}.

At high pH, the reverse relations between rates of reactions 1 and 2 and 9 and 10 would hold; i.e., $k_1[H_2O] < k_2[OH^-]$ and $k_9[H^+]/K_3 < k_4k_{10}[O_3]/k_5$. The ozone decomposition rate at high pH then is given by the approximate equation

$$-d[O_3]/dt \simeq 2(k_4k_5k_2/k_{10})^{0.5}[OH^-]^{0.5}[O_3] \quad (13)$$

At neutral pH, one of two possibilities exists, i.e., either $k_1[H_2O] > k_2[OH^-]$ and $k_9[H^+]/K_3 < k_4k_{10}[O_3]/k_5$ or $k_1[H_2O] < k_2[OH^-]$ and $k_9[H^+]/K_3 > k_4k_{10}[O_3]/k_5$.

In the former case the rate of ozone decomposition would be independent of $[OH^-]$,

$$-d[O_3]/dt \simeq 2(k_1k_4k_5[H_2O]/k_{10})^{0.5}[O_3] \quad (14)$$

while in the latter case the rate would be given by

$$-d[O_3]/dt \simeq 2k_4(k_2K_3/(k_9K_w))^{0.5}[OH^-][O_3]^{1.5} \quad (15)$$

Apparently the experimentally observed rate dependence on pH allows us to make our choice in favor of the latter situation, i.e., eq 15. As has been reported by a number of workers, the kinetic order with respect to ozone concentration becomes 1 above pH $\geqslant$ 8 (Forni et al., 1982). In terms of the scheme of Table I, this transition corresponds to the shift in the dominating chain termination process from $O_2^{\bullet-} + HO_2^{\bullet}$ recombination (eq 9) to the $O_2^{\bullet-} + O_3^{\bullet-}$ crossover recombination (eq 10). Mathematically this corresponds to the following relation:

$$k_9[H^+]/K_3 \simeq k_4k_{10}[O_3]/k_5 \quad (16)$$

relation 16 should be valid in the pH interval between 7 and 8. The typical initial ozone concentration range was between 1×10^{-4} and 6×10^{-4} M as used by Gurol and Singer (1982) or Sotelo et al. (1987). One can now estimate the value of crossover recombination reaction 10 as follows: $2 \times 10^2 < k(O_2^{\bullet-} + O_3^{\bullet-}) < 1 \times 10^4$ dm^3·mol·s^{-1}.

Discussion

Generally speaking, overall rate of the radical-chain process, R_t, in which the compound of interest participates in the initiation and propagation steps, is equal to the sum of the initiation, R_i, and propagation, R_p, rates, i.e.,

$$R_t = R_i + R_p$$

Table II. Reactions of Superoxide Anion with Other Anionic Species

reaction	rate const, k, $dm^3 \cdot mol^{-1} \cdot s^{-1}$	ref
$O_2^{\cdot -} + Br_3^{\cdot -}$	3.8×10^9	Sutton and Downes, 1972
$O_2^{\cdot -} + CO_3^{\cdot -}$	1.5×10^9	Adams et al., 1966
$O_2^{\cdot -} + Fe(CN)_6^{3-}$	2.7×10^2	Zehavi and Rabani, 1972
$O_2^{\cdot -} + KFe(CN)_6^{2-}$	6.2×10^3	Zehavi and Rabani, 1972

This relation was originally used by Weiss (1935) and then by Sotelo et al. (1987) to arrive at a rate expression containing a linear member with respect to $[O_3]$. However, as has been demonstrated by several researchers, such as Forni et al. (1982) and Staehelin and Hoigne (1982), the rate of noninhibited ozone decomposition in water can be an order of magnitude faster than that in the presence of free-radical scavengers. Therefore, the rate of initiation (R_i) in our system must be negligible as compared to the chain propagation rate (R_p); i.e., $R_t \cong R_p$. Accordingly, a simple, apparent first-order rate expression should be a result of a peculiar combination of conditions and elementary reactions rate constants as shown in the previous section of this paper.

Careful formal analysis of the available experimental data on the elementary reactions and their rate constants ((1)–(9) in Table I) shows that probably the only simple way to explain the change in the ozone kinetic order from 1.5 to 1.0 in terms of a chain-radical mechanism would be to introduce a crossover termination reaction. The reaction between ozonide and superoxide radicals suggested in the beginning of the paper should be a relatively fast electron-transfer process, being between a strong one-electron acceptor, ozonide, and a strong one-electron donor, superoxide radicals. The anionic nature of the two reacting species does not usually prevent such processes from occurring at a fairly high rate as evidenced by similar reactions listed in Table II.

Direct verification of the suggested reaction 10 requires experimental techniques not accessible for this author, although an attempt is made to estimate its elementary rate constant on the basis of previously established experimental facts.

The question which remains to be addressed is an apparent second kinetic order with respect to $[O_3]$ repeatedly observed by a number of investigators over the whole range of the solution pH, the latest report being by Gurol and Singer (1982). Apparently some adjustments of the general mechanism of Table I would have to be made in order to arrive at that rate law. The easiest way would be the introduction of "linear" termination step, where only one chain carrier is consumed per one elementary act of chain termination. For example,

$$OH^{\cdot} + X \rightarrow \text{inactive species} \qquad (17)$$

Here X is a free-radical trap such as organic molecule or even buffer component such as HCO_3^-, acetate, or PO_4^{3-} (Gurol and Singer, 1982; Staehelin and Hoigne, 1982). If reaction 17 dominates the termination process as may happen in the buffered system, then

$$-d[O_3]/dt \propto [O_3]^2$$

Conclusions

Within framework of radical-chain reaction mechanism of ozone decomposition in water, we took into account two initiation and two termination elementary processes. The overall rate kinetic expression can be delineated in various pH regions as follows:

$$-d[O_3]/dt \propto \begin{cases} [O_3]^{1.5}[OH^-]^{0.5} & 3 < pH < 7 \\ [O_3]^{1.5}[OH^-] & pH \cong 7 \\ [O_3][OH^-]^{0.5} & 7 < pH < 12 \end{cases}$$

In the presence of $OH^{\cdot}$ radical scavengers, including certain buffers, the second kinetic order with respect to $[O_3]$ may be observed.

Acknowledgment

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