Pulse Radiolysis Studies. XV. Reactivity of the Oxide Radical Ion and of the Ozonide Ion in Aqueous Solution[1,2]

Bonnie L. Gall and Leon M. Dorfman

*Department of Chemistry, The Ohio State University, Columbus, Ohio.
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Abstract: The reactivity of the oxide radical ion, O^-, and the decay kinetics of the ozonide ion, O_3^-, have been investigated in aqueous solutions at pH >13, containing methanol, ethanol, or benzoate ion, by the pulse radiolysis method. The decay of O_3^- occurs through the thermal dissociation reaction, $O_3^- = O_2 + O^-$, for which the absolute rate constant at 25° is $(3.3 \pm 0.3) \times 10^3 \, sec^{-1}$, and the activation energy is 11 ± 2 kcal/mole. The reactive species in the over-all decay of ozonide is O^-, which is in equilibrium with OH, and which reacts with additives such as methanol and ethanol. Absolute rate constants for these reactions are: $(5.2 \pm 1.0) \times 10^8 \, M^{-1} \, sec^{-1}$ for $O^- + CH_3OH$ and $(8.4 \pm 1.6) \times 10^8 \, M^{-1} \, sec^{-1}$ for $O^- + C_2H_5OH$. The reactivity of O^- with benzoate ion is at least three orders of magnitude lower than that of OH. The reactivity of O^- in several types of reactions is compared with that of OH, the normal form of the hydroxyl radical.

The chemical behavior of two reactive forms of oxygen, the oxide radical ion, O^-, and the ozonide ion, O_3^-, represents one of the two principal features of the radiolysis of oxygenated aqueous solutions at high pH. The oxide ion is introduced into the system, in very strongly basic solutions, by the dissociation of the hydroxyl radical.[3,4] This primary oxidizing species produced in the radiolysis behaves like a weak acid

$$OH \rightleftharpoons O^- + H^+ \qquad (1)$$
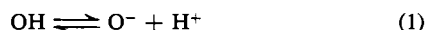
with published values for the pK of this equilibrium of 11.9 ± 0.2[3] and 11.8 ± 0.2.[4] The ozonide ion, which exhibits an optical absorption band[5-7] with a maximum at 430 nm, is formed by the reaction

$$O^- + O_2 = O_3^+ \qquad (2)$$
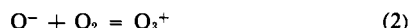
The rate constant[8,9] for this reaction is $2.5 \times 10^9 \, M^{-1} \, sec^{-1}$ at 25°.

There have been several recent investigations of the reactivity of the ozonide ion by the pluse radiolysis method.[6-10] The decay kinetics of this species is very complex and there has not been a satisfactory understanding of its reactivity and the mechanism of its decay. This paper presents the results of a study not only of O_3^- (formed in oxygenated solutions), but also of O^- (formed in deaerated solutions) and of the detailed dependence of the behavior of O_3^- upon the chemical reactivity of O^-.

Experimental Section

The general methods of pulse radiolysis[6,11-13] and the particular electron source and irradiation arrangement used in this laboratory[5] have been described previously. A few specific details, unique to the present investigation, follow.

Pulse Irradiation. A Varian V-7715A linear accelerator was used as the electron source. For the present investigation 3–4-MeV electrons at a current of 300–350 mA were used. The pulse width was varied from 0.1 to 0.5 μsec. The dose per pulse of a 0.4-μsec pulse at 300 mA was approximately 1×10^{17} eV/g. The electron beam had a cross-sectional area of approximately 3 cm $\times$ 2.5 cm incident on the solution. Energy deposition varied by approximately 15% through the depth of the cell as determined using a He–Ne laser as an optical probe to measure the optical density of reactive species produced at various positions in the solution. The observed kinetics was not affected by this small change, however. Dose per pulse was found to be reproducible to within ± 3% so that no pulse monitoring was necessary.

Optical Detection. Transient species were detected by observing the optical absorption spectrophotometrically. RCA photomultiplier tubes 1P28 and 7200 were used to monitor the light passing through the reaction cell. The light source was a 500-W Osram xenon lamp, Type XBO 450W. A Bausch and Lomb grating monochromator, Type 33-86-02, $f/3.5$, dispersion 6.4 nm/mm, was used. The exit slit was usually set at less than 0.2 mm so that the band width of the light monitored was less than 1.3 nm.

Reaction Cells. Rectangular cells made of fused quartz for the body and high-purity silica optical windows were used. The internal dimensions of the cells were 8 mm in the direction of the electron beam $\times$ 12 mm $\times$ 20 mm in the direction of the light beam.

Several arrangements for sample introduction were used. For runs at atmospheric pressure the cell had two entry ports and the solutions were prepared and handled using the syringe technique.[14] For solutions pressurized with oxygen, the cell was arranged as illustrated previously[7] except that break-seals were replaced by Fischer Porter Teflon stopcocks. Enough solution could be introduced to allow for irradiation of 10–15 fresh samples of solution. For solutions to be irradiated at temperatures other than at room temperature, the cell was arranged so that it could be positioned in a thermostatic box.[15] A copper–constantin thermocouple was cemented to the cell with indium metal. For temperatures below ambient, the temperature was controlled in the thermostatic box by a flow of cooled nitrogen gas. For temperatures above ambient, the entire solution and the cell were heated in a constant-temperature bath. Irradiation occurred within 1 min after removal of the solution from the constant-temperature bath. Some cooling occurred in this time interval, but the temperature was measured at the time of irradiation.

(1) This work was supported by the U. S. Atomic Energy Commission.

(2) From the Ph.D. thesis of B. L. Gall, who was an NSF Summer Fellow in 1966, and a Lubrizol Fellow in 1967.

(3) J. Rabani and M. S. Matheson, *J. Phys. Chem.*, **70**, 761 (1966).

(4) J. L. Weeks and J. Rabani, *ibid.*, **70**, 2100 (1966).

(5) J. W. Boag and G. E. Adams, 18th Annual Symposium on Cellular Radiation Biology, Houston, Texas, 1964.

(6) G. Czapski and L. M. Dorfman, *J. Phys. Chem.*, **68**, 1169 (1964).

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(13) I. A. Taub and L. M. Dorfman, *J. Am. Chem. Soc.*, **84**, 4053 (1962).

(14) C. B. Senvar and E. J. Hart, *Proc. Intern. Conf. Peaceful Uses At. Energy*, **29**, 19 (1958).

(15) S. Arai, E. T. Tremba, J. R. Brandon, and L. M. Dorfman, *Can. J. Chem.*, **45**, 1119 (1967).

Materials. Water was triply distilled in a quartz still. Baker Analyzed Reagent sodium hydroxide and benzoic acid were used. Concentrated solutions, 19 M, of sodium hydroxide were prepared. Sodium carbonate is insoluble in concentrated sodium hydroxide and can be filtered out. The concentrated base was diluted with triply distilled water to obtain the desired hydroxide ion concentration. U.S.I. Chemical Co. ethanol was used without further purification. Baker Analyzed Reagent methanol was refluxed with added sulfuric acid and 2,4-dinitrophenylhydrazine and distilled.[16]

Analytical. Solutes were weighed and dissolved in triply distilled water. Hydroxide ion concentrations were determined by titration with a standardized acid to phenolphthalein end point. Oxygen concentrations were determined in one of three methods. The first method was to calculate the concentration assuming Henry's law at the specific pH. The solubility data of Seidell were used.[17] For the second method, samples of known volume of the solutions were degassed by pumping with a Toepler pump. The gas was dried by passing it through Dry Ice–acetone cooled traps and its pressure measured with a gas buret. The third method was modification of the second in that the gas buret was replaced by an Aerograph gas chromatograph, Model A-350-B, with thermoconductivity detectors. The gases pumped off from the solutions were separated on a Porapak Q column, mesh 150–200, cooled to Dry Ice temperatures. The column would separate nitrogen and oxygen and would retain water vapor until it was warmed to room temperature.

Results and Discussion

The decay kinetics of the reactive intermediates in the system was investigated, as in the earlier work,[5–9] by observing the ozonide ion spectrophotometrically at 430 nm. It was found[6] that at low concentrations ($<5 \times 10^{-6}$ M) of ozonide ion the decay of this species was first order. Czapski[10] extended this study to show that the rate constant for the first-order decay exhibited an inverse dependence upon the oxygen concentration. At higher initial concentration ($>10^{-5}$ M) of ozonide ion the decay is no longer first order. Adams, et al.,[9] reported second-order decay in oxygenated alkaline solutions containing N_2O, which they attributed to the reaction

$$O_3^- + O_3^- = \text{products} \tag{3}$$
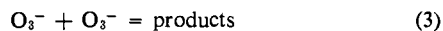
The nitrous oxide converts the system almost completely to a one-species system by the reaction

$$e_{aq}^- + N_2O = N_2 + O^- \tag{4}$$
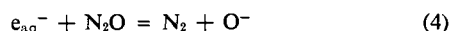
which forms the oxide radical ion and ultimately the ozonide ion. It was shown, however, by Felix, et al.,[7] that the decay of the ozonide ion at concentrations even as high as 2×10^{-4} M in N_2O–O_2 solutions was mixed first and second order. More important, they found that the second-order rate constant also depended on some inverse function of the oxygen concentration.

The decay of ozonide ion has also been studied in solutions containing excess hydrogen peroxide[7,10] in which case the decay is pseudo first order. In the present investigation, as in concurrent work of Behar and Czapski on the flash photolysis of H_2O_2 solutions,[18] it was found that the decay in solutions containing H_2O_2 also shows an inverse dependence on the oxygen concentration. It appears, therefore, that oxygen shows an inhibiting effect for all the reactions studied. This complexity raises a serious question about the simple interpretation of the ozonide decay kinetics.

To explain the oxygen effect, Behar and Czapski[18] have suggested a reaction sequence, the central feature of which is the unimolecular dissociation of ozonide ion

$$O_3^- = O_2 + O^- \tag{5}$$

which occurs along with the formation, reaction 2. The reactive species is the oxide ion.

$$O^- + H_2O_2 = OH^- + HO_2 \tag{6}$$

The decay of ozonide ion in this system then occurs through reactions 5 and 6, reflecting the reactivity of O^- rather than O_3^-. Our data, as will be shown, support this mechanism through investigation of several reactants such as benzoate ion, methanol, and ethanol, as well as hydrogen peroxide. Furthermore, these data provide information about the reactivity of the oxide ion, about which very little is presently known.

A good deal more is now known about the reactivity of the normal form of the hydroxyl radical, OH, and rate constants have been determined in this laboratory[19] for its reactions with benzoate ion, methanol, and ethanol. A comparison between the reactivity of O^- and OH may then be made.

Benzoate Ion. Rate constants for reactions such as

$$OH + C_6H_5COO^- = (OH)\dot{C}_6H_5COO^- \tag{7}$$

have been determined by observing the formation rate curve for the particular cyclohexadienyl radical[19–21] which exhibits a strong uv absorption band. An attempt was made in deaerated solutions to determine the rate constant for

$$O^- + C_6H_5COO^- = (O^-)\dot{C}_6H_5COO^- \tag{8}$$
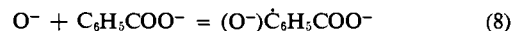
by this direct method. Although rate curves were observed at 330 nm and found to fit a first-order rate law, the "constant" derived from the slopes of the lines showed a complex dependence upon the benzoate ion concentration, indicating that the simple explanation for the reaction represented by (8) was not valid.

We therefore attempted to determine k_8 relative to k_2 from competition kinetics by measuring the decrease in relative yield of the ozonide ion in oxygenated solutions containing benzoate ion. This was done by measuring the optical density at 430 nm. No other species in oxygenated solution absorbing at 430 nm persist into the range of lifetime of O_3^- (>5 μsec). There is thus no interference with this measurement.

The competition equation for reactions 2 and 8 is

$$D^0/D = 1 + \frac{k_8[C_6H_5COO^-]}{k_2[O_2]} \tag{9}$$

where D^0 is the optical density at 430 nm at 5 μsec after the pulse in solutions containing no benzoate ion and D is the optical density under the same conditions with added benzoate ion. A plot of D^0/D against $[C_6H_5COO^-]/[O_2]$ does give a straight line, but the slopes obtained show an inverse dependence on the hydroxide ion concentration. All the data do, however, fit an equation of the form

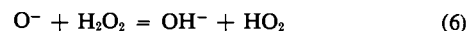(16) I. A. Taub, D. A. Harter, M. C. Sauer, and L. M. Dorfman, *J. Chem. Phys.*, 41, 979 (1964).
(17) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," D. Van Nostrand Co., New York, N. Y., 1941, p 1355.
(18) D. Behar and G. Czapski, *Israel J. Chem.*, 6, 43 (1968).

(19) P. Neta and L. M. Dorfman, "Radiation Chemistry I," Advances in Chemistry Series, No. 81, American Chemical Society, Washington, D. C., 1968, p 222.
(20) L. M. Dorfman, I. A. Taub, and R. E. Bühler, *J. Chem. Phys.*, 36, 3051 (1962).
(21) R. C. Wander, P. Neta, and L. M. Dorfman, *J. Phys. Chem.*, 72, 2946 (1968).

$$D^0/D = 1 + \frac{k'[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{O}_2][\text{OH}^-]} \qquad (10)$$
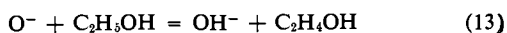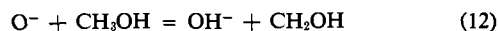
as may be seen from Figure 1, which shows a plot of D^0/D against $[\text{C}_6\text{H}_5\text{COO}^-]/[\text{O}_2][\text{OH}^-]$. The results may be explained on the basis of the dissociation of OH in accord with reaction 1, and the assumption that the equilibrium between the two forms is pH dependent.
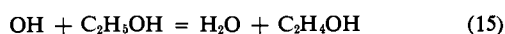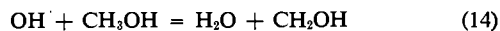
$$\text{O}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{OH}^- \qquad (11)$$
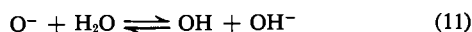
Reaction 8 is then replaced by eq 7. The mechanism consisting of reactions 2, 7, and 11 gives $k' = k_7 K_\text{W}/k_2 K_\text{OH}$, where K_W is the equilibrium constant for the dissociation of water and K_OH is the dissociation constant for OH. Taking $k_7^{19} = 6.0 \times 10^9$ M^{-1} sec^{-1}, $K_\text{W} = 1 \times 10^{-14}$, and $k_2^{8,9} = 2.5 \times 10^9$ M^{-1} sec^{-1} at 25°, the value for k' may be used to calculate $pK_\text{OH} = 11.8 \pm 2$, in excellent agreement with the previously determined values.[3,4] This agreement substantiates the mechanism and indicates that $k_8 \lll k_7$. The data indicate an upper limit of $k_8 \lesssim 6 \times 10^6$ M^{-1} sec^{-1} at 25°, but the true value may, of course, be very much lower.

Two conditions must obtain in the system for the foregoing interpretation to be valid. (a) The maintenance of the equilibrium between O$^-$ and OH must be rapid compared to reactions 2 and 7. (b) The rate of other reactions of O$^-$ (or OH) must be negligible compared to the rates of (2), (7), and (11). The latter condition has been confirmed by demonstrating the absence of any dose rate effect. Condition a is consistent with a value for the forward rate constant $k_{11f} = 2 \times 10^7$ M^{-1} sec^{-1} obtained from K_W/K_OH and the higher of the values in the literature for k_{11r}, namely 3×10^{9} [22] and 4×10^9 M^{-1} sec^{-1}.[23] The latter is recalculated from the author's data[23] using $k_{\text{OH}+\text{I}^-} = 2 \times 10^{10}$ M^{-1} sec^{-1} as the corrected value[19] for the reference rate constant.

Methanol and Ethanol. The rate constants for the reactions

$$\text{O}^- + \text{CH}_3\text{OH} = \text{OH}^- + \text{CH}_2\text{OH} \qquad (12)$$

$$\text{O}^- + \text{C}_2\text{H}_5\text{OH} = \text{OH}^- + \text{C}_2\text{H}_4\text{OH} \qquad (13)$$

are most readily determined from competition kinetics rather than from formation rate curves since the transient product in (12) and (13) is not easily observable. Moreover, the values for k_{12} and k_{13}, as will be seen, are sufficiently high for competition with reaction 2. The rate constants for

$$\text{OH} + \text{CH}_3\text{OH} = \text{H}_2\text{O} + \text{CH}_2\text{OH} \qquad (14)$$

$$\text{OH} + \text{C}_2\text{H}_5\text{OH} = \text{H}_2\text{O} + \text{C}_2\text{H}_4\text{OH} \qquad (15)$$

which may be involved in view of equilibrium 11, have been determined[19] as $k_{14} = 8.4 \times 10^8$ and $k_{15} = 1.83 \times 10^9$ M^{-1} sec^{-1} at 25°. The contribution of reactions 14 and 15 to the decay of O$^-$, which turns out to account for only a few per cent in the competition, need not be neglected in interpreting the data. There is apparently no need to consider the reaction with the ionized form of the alcohols, CH$_3$O$^-$ and C$_2$H$_5$O$^-$, since the pK for methanol and ethanol is slightly higher than that of water.

(22) G. E. Adams, J. W. Boag, and B. D. Michaels, *Trans. Faraday Soc.*, **61**, 492 (1965).

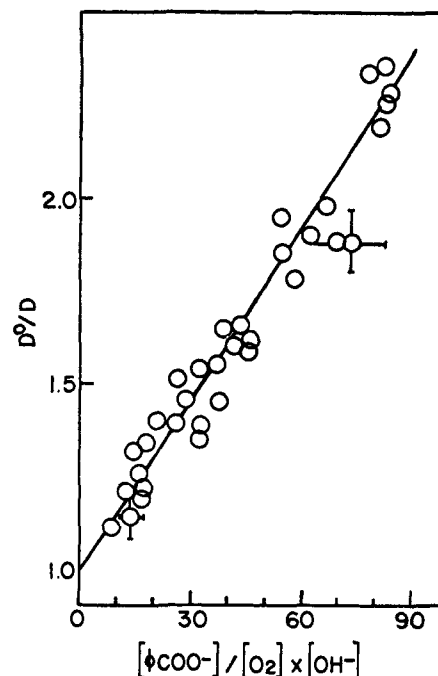(23) F. S. Dainton and S. A. Sills, *Proc. Chem. Soc.*, 223 (1962).

Figure 1. Dependence of the ratio of the optical density of ozonide ion at 430 nm in solutions containing no benzoate ion, D^0, to the optical density at 430 nm in solutions containing benzoate ion, D, as a function of $[\text{C}_6\text{H}_5\text{COO}^-]$, $[\text{O}_2]$, and $[\text{OH}^-]$.

The competition equation, written for methanol, is

$$D^0/D = 1 + \frac{\left\{k_{12} + k_{14} \dfrac{K_\text{W}}{K_\text{OH}[\text{OH}^-]}\right\}[\text{CH}_3\text{OH}]}{k_2[\text{O}_2]} \qquad (16)$$

An analogous expression may be written for the ethanol competition equation. Since $k_{14}(K_\text{W}/K_\text{OH})$ is known, we may determine $k_{12}/k_2 = 0.209 \pm 0.014$ and $k_{13}/k_2 = 0.337 \pm 0.028$, as may be seen in Tables I and II.

Table I. Oxygen and Methanol Competition for Oxide Radical Ion

$[\text{O}_2]$, $M \times 10^4$	$[\text{MeOH}]$, $M \times 10^4$	$[\text{OH}^-]$, M	D^0/D	k_{12}/k_2
3.39	2.34	0.332	2.310	0.181
3.39	4.76	0.326	3.771	0.191
3.39	7.14	0.322	5.688	0.217
2.53	4.80	0.127	1.441	0.217
2.53	9.60	0.125	1.794	0.195
2.53	13.4	0.134	2.169	0.221
2.56	4.80	0.386	1.449	0.234
2.56	9.60	0.338	1.692	0.180
2.48	13.4	0.374	2.165	0.217
2.92	4.80	0.161	1.422	0.245
2.78	9.60	0.152	1.699	0.191
2.75	13.4	0.151	2.164	0.227
8.90	19.5	0.235	1.477	0.208
8.90	29.2	0.218	1.710	0.209
			Av	0.209 ± 0.014

Adams, *et al.*,[22] found $k_{13}/k_2 = 0.35$ from a competition experiment with ethanol and oxygen without correcting for reaction 15. Taking $k_2 = 2.5 \times 10^9$ we obtain $k_{12} = (5.2 \pm 1.0) \times 10^8$ M^{-1} sec^{-1} and $k_{13} = (8.4 \pm 1.7) \times 10^8$ M^{-1} sec^{-1} at 25°. Thus the specific rate of these abstraction reactions by O$^-$ is lower, by roughly a factor of 2, than the specific rates of the analogous
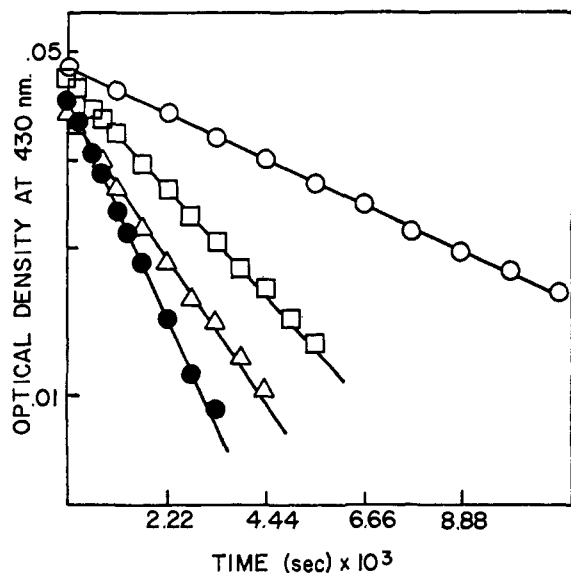
Figure 2. Test of the pseudo-first-order fit for the decay of ozonide ion in oxygenated benzoate ion solutions at pH >13. $[O_2]$ = $2.5 \times 10^{-4}\ M$ and $[OH^-]$ = 0.175 M for all the above curves: O, $[C_6H_5COO^-]$ = 0; $\square$, $[C_6H_5COO^-]$ = $1.04 \times 10^{-4}\ M$; $\triangle$, $[C_6H_5COO^-]$ = $2.08 \times 10^{-4}\ M$; ●, $[C_6H_5COO^-]$ = $3.12 \times 10^{-4}\ M$.

reactions of OH. This difference may result largely from the difference in the thermochemistry of (12) and (14), or (13) and (15), since the O–H bond energy in OH^- is 108 kcal/mole[24] compared with 117 kcal/mole in water.[24]

Table II. Oxygen and Ethanol Competition for Oxide Radical Ion

$[O_2]$, $M \times 10^4$	[EtOH], $M \times 10^4$	$[OH^-]$, M	D^0/D	k_{13}/k_2
2.48	3.37	0.469	1.452	0.323
2.29	6.74	0.394	1.989	0.326
2.29	10.11	0.384	2.560	0.342
2.70	3.37	0.144	1.500	0.379
2.85	6.74	0.148	1.936	0.368
2.19	10.11	0.154	2.608	0.321
2.36	3.36	0.460	1.506	0.346
2.24	6.72	0.450	1.893	0.288
2.51	10.08	0.435	2.614	0.391
			Av	0.337 ± 0.028

Hydrogen Peroxide. Hydrogen peroxide represents a particularly complex case in the region of pH >12. Since the pK for H_2O_2[25] is 11.9, a series of three reactions may occur.

$$O^- + HO_2^- = OH^- + O_2^- \qquad (17)$$

$$O^- + H_2O_2 = OH^- + HO_2 \qquad (18)$$

$$OH + HO_2^- = H_2O + HO_2 \qquad (19)$$
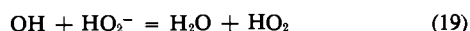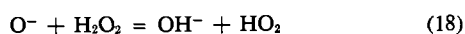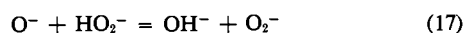
Our earlier determination[7] of $k_{17} = 7 \times 10^8\ M^{-1}\ sec^{-1}$ is, in fact, a complex composite of k_{17}, k_{18}, and k_{19}, and Rabani[26] has reported $k_{17} = 2.74 \times 10^8\ M^{-1}\ sec^{-1}$. He finds also that $(k_{18} + 1.42k_{19}) = 1.18 \times 10^{10}\ M^{-1}\ sec^{-1}$. Present data do not permit a separation of these

(24) V. I. Vedenyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold Ltd., London, 1966.
(25) J. Jortner and G. Stein, *Bull. Res. Council Israel*, A6, 239 (1957).
(26) J. Rabani in ref 19, p 131.

values. Table III summarizes the reactivity of both forms of the hydroxyl radical toward the compounds in this investigation.

Table III. Rate Constants for Reactions of O^- and of OH

	Rate constant, $M^{-1}\ sec^{-1}$	
Compound	OH	O^-
$C_6H_5COO^-$	6.0×10^9 [a] (ref 19)	$<6 \times 10^6$
CH_3OH	8.4×10^8 [a] (ref 19)	5.2×10^8
C_2H_5OH	1.83×10^9 [a] (ref 19)	8.4×10^8
O_2	Unreactive	2.5×10^9 [b]

[a] Reference 19. [b] References 8 and 9.

Dissociation of Ozonide Ion. The observation of decay curves of the ozonide ion in solutions containing various additives permits the determination of the rate constant for the dissociation of O_3^-, namely k_5. The foregoing general mechanism, reactions 2 and 5, the OH–O^- equilibrium 11, and the appropriate reactions of OH and/or O^- with the additive [(7) and (8) for benzoate ion, (14) and (12) for methanol, (15) and (13) for ethanol] together with the first-order natural decay of the oxide ion

$$O^- = \text{products} \qquad (20)$$

is consistent with the decay kinetics for O_3^-. Using the steady-state approximation for $[O^-]$ and [OH], the differential rate expression (written for benzoate ion as the additive) is

$$\frac{-d[O_3^-]}{dt} =$$

$$\left\{ \frac{k_5(k_8 + k_7K_W/K_{OH}[OH^-])[C_6H_5COO^-] + k_5k_{20}}{k_2[O_2] + (k_8 + k_7K_W/K_{OH}[OH^-])[C_6H_5COO^-] + k_{20}} \right\} \times [O_3^-] \qquad (21)$$

Appropriate rate constants for methanol or ethanol will replace k_7 and k_8, when these compounds are used as the added reactant.

Figure 2 shows first-order plots for the decay of ozonide in with benzoate ion present. Good linearity is obtained. The slopes of these lines give the value of the coefficient of $[O_3^-]$ in eq 21 from which k_5 is determined.

For benzoate ion as the additive it has been shown in the competition kinetics that $k_8 \ll k_7$ and may be neglected. k_2 and k_7, along with $K_W/K_{OH}[OH^-]$ are known. k_{20} may be calculated from the first-order decay constant for ozonide ion in the absence of added benzoate, determined from the observed rate curves. Under these conditions the decay rate is given by

$$\frac{-d[O_3^-]}{dt} = \left(\frac{k_5k_{20}}{k_2[O_2] + k_{20}} \right)[O_3^-] \qquad (22)$$

k_5 and k_{20} may then be determined from eq 21 and 22. In practice this was done by successive approximation to determine first k_{20}, and then k_5, the rate constant of interest. Reaction 20, the precise nature of which is not known, may represent more than a single process in that reaction of O^- with impurities may occur along with a natural decay of O^- in water. k_{20} is approximately constant from one solution to another, the value from our work being $k_{20} = (3 \pm 1) \times 10^4\ sec^{-1}$, about

30% lower than the value of Czapski.[8] With this value, the contribution of reaction 20 to the determination of k_5 from eq 21 amounts to only 10%. Table IV shows the results obtained from benzoate ion solutions. The average value is $k_5 = (3.3 \pm 0.3) \times 10^3 \, \mathrm{sec}^{-1}$.

Table IV. Decay of Ozonide Ion in Oxygenated Benzoate Ion Solutions

$[O_2]$, $M \times 10^4$	$[C_6H_5COO^-]$, $M \times 10^4$	$[OH^-]$, M	k_{obsd}	k_5 $\times 10^{-3} \, \mathrm{sec}$
2.66	1.04	0.177	226	3.64
2.55	2.08	0.174	335	3.57
2.48	3.12	0.175	427	3.47
2.46	2.39	0.444	225	3.23
2.41	4.76	0.484	311	3.33
2.46	7.14	0.459	427	3.59
4.83	2.81	0.200	180	2.86
4.45	5.61	0.217	331	3.28
4.83	8.43	0.232	401	3.37
2.70	4.24	0.246	461	3.60
2.70	8.48	0.182	838	3.64
2.81	12.7	0.218	988	3.82
9.19	11.2	0.366	152	2.63
9.53	19.3	0.364	246	2.87
9.41	31.3	0.320	452	3.20
			Av	3.3 ± 0.3

With methanol or ethanol as the additive, the data may be treated similarly. The results are shown in Tables V and VI for methanol and ethanol, respectively. The average value from methanol solutions is $k_5 = (3.2 \pm 0.3) \times 10^3 \, \mathrm{sec}^{-1}$ and from ethanol solutions $k_5 = (3.3 \pm 0.3) \times 10^3 \, \mathrm{sec}^{-1}$ at 25°. The values from all three systems are in excellent agreement with an average of $k_5 = (3.3 \pm 0.3) \times 10^3 \, \mathrm{sec}^{-1}$. Previously determined values, both from peroxide solutions, a rather more complex system, as noted, are $5 \times 10^3 \, \mathrm{sec}^{-1}$, from Behar and Czapski,[18] and $2.8 \times 10^3 \, \mathrm{sec}^{-1}$ from Heidt.[27]

Table V. Decay of Ozonide Ion in Oxygenated Methanol Solutions

$[O_2]$, $M \times 10^4$	$[MeOH]$, $M \times 10^4$	$[OH^-]$, M	k_{obsd}	k_5 $\times 10^{-3} \, \mathrm{sec}$
2.56	4.90	0.173	1183	3.70
2.53	9.80	0.219	1727	3.68
2.53	14.7	0.198	2074	3.67
2.10	4.72	0.482	1177	3.67
2.22	9.44	0.450	1954	3.41
2.41	14.2	0.456	1980	3.54
8.9	9.74	0.230	651	3.30
8.9	19.5	0.218	1162	3.59
8.9	29.2	0.235	1568	3.78
7.4	23.4	0.456	1209	2.99
6.3	46.8	0.424	1859	3.04
7.4	60.2	0.416	1921	3.02
6.2	15.0	0.236	1004	2.88
6.2	30.0	0.235	1467	2.86
6.2	45.0	0.274	1971	3.24
11.5	23.9	0.302	1098	3.06
11.5	47.9	0.331	1869	3.59
11.5	71.8	0.356	2100	3.40
9.3	0.72	0.324	109	3.21
9.4	1.44	0.305	136	2.83
9.4	2.15	0.326	177	2.81
			Av	3.3 ± 0.3

(27) L. J. Heidt, *J. Chem. Educ.*, **43**, 623 (1966).

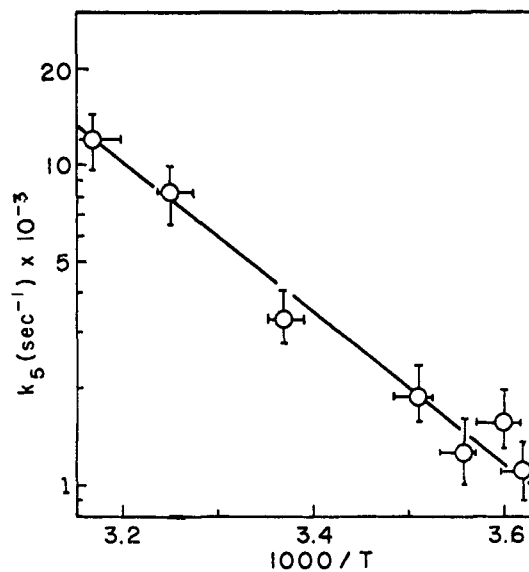
Figure 3. Temperature dependence of the rate constant for the unimolecular dissociation of ozonide ion, $O_3 \rightarrow O^- + O_2$.

With such a low value for k_5 it is of interest to know whether the activation energy is the determining factor. The temperature coefficient of k_5 has been determined over the range 276–318°K. An Arrhenius plot is shown in Figure 3. The value for reaction 5 is $E_a = 11 \pm 2 \, \mathrm{kcal/mole}$.

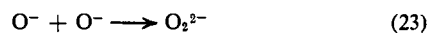**Table VI.** Decay of Ozonide Ion in Oxygenated Ethanol Solutions

| $[O_2]$, $M \times 10^4$	$[EtOH]$, $M \times 10^4$	$[OH^-]$, M	k_{obsd}	k_5 $\times 10^{-3} \, \mathrm{sec}$
2.19	3.30	0.257	1240	3.21
1.94	6.60	0.285	1810	3.21
2.14	1.98	0.248	909	3.20
2.07	1.32	0.238	725	3.14
2.48	0.66	0.252	506	3.69
6.3	6.8	0.253	901	3.13
5.6	13.6	0.256	1676	3.57
5.2	4.08	0.217	686	2.92
5.2	2.72	0.227	459	2.59
5.0	1.36	0.221	332	2.94
2.00	2.72	0.411	1049	3.11
2.19	6.80	0.375	1593	3.02
2.19	13.6	0.374	2489	3.19
2.55	3.35	0.424	1128	3.46
2.53	6.70	0.413	1499	3.09
2.58	10.05	0.434	2041	3.53
2.36	3.36	0.460	1168	3.33
2.24	6.72	0.460	1645	3.13
2.51	10.09	0.435	2033	3.46
			Av	3.2 ± 0.2

The foregoing data indicate that the ozonide ion is unreactive toward various added reactants we have investigated. No such statement can be made concerning the reactivity of the ozonide ion toward other radical species. In solutions containing no additive, the first-order decay rate is given by eq 22. For higher initial $[O_3^-]$, a fourth reaction must be added to the sequence of reactions 2, 5, and 20 to explain the observed second-order component of the decay.[7,9] Reaction 3 cannot account for the second-order decay because of the observed inverse $[O_2]$ dependence. Nor

can the reaction

$$O^- + O^- \longrightarrow O_2{}^{2-} \qquad (23)$$

account for the decay because k_{23}, under our conditions, would be required to be $>10^{12} M^{-1} \sec^{-1}$ as calculated from the data of Felix, et al.[7] The reaction may, however, be

$$O_3{}^- + O^- \longrightarrow O_4{}^{2-} \qquad (24)$$
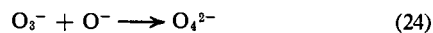
for which we estimate $k_{24} \approx 5 \times 10^8 M^{-1} \sec^{-1}$ using

the sequence of reactions 2, 5, 20, and 24 and the steady-state approximation for [O$^-$] to determine the decay equation for $O_3{}^-$.

Brønsted Catalysis of the Fading Reaction of Flash-Produced Transients from 2,6-Dinitrotoluene

Margaret E. Langmuir, Libera Dogliotti, Edward D. Black, and G. Wettermark

Contribution from the Pioneering Research Laboratory, U. S. Army Natick Laboratories, Natick, Massachusetts 01760. Received October 17, 1968

Abstract: 2,6-Dinitrobenzyl anion, λ_{max} 500 mμ, was produced by flash photolysis of 2,6-dinitrotoluene. A study of the catalysis of the reaction, 2,6-dinitrobenzyl anion + HA → 2,6-dinitrotoluene, with acids whose pK's vary from -1.75 to 16.75 has shown that the Brønsted α varies from 0 to 1 as the pK of the donor is increased. The limiting rate of proton transfer in this system (where $\alpha = 0$) is around 10^5 l. mole^{-1} sec^{-1} at 30°, far below diffusion control. Other factors such as H bonding between anion and donor acid and charge delocalization in the anion must be responsible for the relatively slow proton transfer to carbon. The Arrhenius activation energy for protonation of the anion by H$_2$O is 11.5 kcal mole^{-1}. The transient produced by flashing acid solutions had a λ_{max} of 410 mμ and is the *aci* form of 2,6-dinitrotoluene. Its pK_a was determined to be 1.8. The direct tautomerizm of *aci* to nitro form has a rate of $2 \times 10^3 \sec^{-1}$ at 30° and an Arrhenius activation energy of 10.1 kcal mole^{-1}.

A number of careful studies of the general acid catalysis of nitrobenzyl anions produced from aromatic nitro compounds having alkyl substituents have been made in recent years. In the majority of these studies, the anion was produced by reaction with strong ethoxide in alcoholic solvent and the catalysis of the return reaction studied at low temperature by addition of excess catalyzing acid.[1-4]

It has been shown that similar anions may be produced photochemically by decarboxylation of the corresponding nitrophenylacetate ion,[5] or by ionization of the initial photoproduct from flash photolysis of o-nitrotoluenes. In the latter case the initial photoproducts appear to be the *aci*-nitro species which, because of the low pK_a, are ionized completely to anion in aqueous solutions of pH greater than 2 or 3.[6-8] The latter method offers some advantages for catalysis studies. First, aqueous solutions in which acidity is easily defined are used. This is an advantage since the kinetic constants are ultimately related to the thermodynamic pK's of the catalyzing acids. Second, since flash methods produce the anion homogeneously dispersed in an equilibrated system, rate measurements
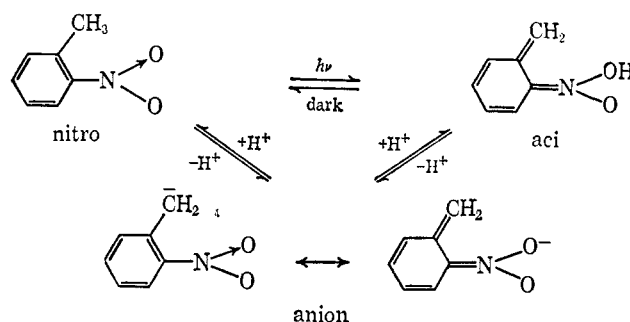
are not limited by speed of mixing and can be made at room temperature using fast oscilloscope recording methods. Third, the catalysis can be studied over a very wide range of pH since the production of anion does not depend on a high initial pH as in photolysis of the carboxylate ion or direct ionization by ethoxide.

Caldin and Long,[2] have shown that catalysis of the protonation of 2,4,6-trinitrobenzyl anion (TNT$^-$) by several substituted acetic acids gives an α value of 0.5 at 20° in a typical Brønsted catalysis plot. More recently, Blake, Evans, and Russell[4] have studied the catalysis of the same anion by phenols and give a value of 0.84 ± 0.07 for α (at $-40°$). In the present paper we attempt to give a more detailed description of the behavior of the catalysis coefficient with the acid strength of the catalyzing acid for 2,6-dinitrobenzyl anion and correlate it with the data of 2,4,6-trinitrobenzyl anion in the light of the comprehensive description of acid–base catalysis given by Eigen and coworkers.[9,10]

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