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Pulse Radiolytic Investigation of O_{aq}^- Radical Ions

by Dov Zehavi and Joseph Rabani*

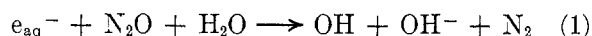
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The reactivity of the oxidizing radicals in N_2O saturated aqueous solutions was measured by pulse radiolysis. Competition experiments between methanol, ethanol, and other solutes such as ferrocyanide, iodide, bromide, thiocyanate, ferrous, and cerous ions were carried out. Comparison with results in the alkaline pH range indicates that O^- is formed as an intermediate in the reaction of e_{aq}^- with N_2O . O^- reacts quickly with water, $k_{(O^-+H_2O)} = 9.6 \times 10^7 \text{ sec}^{-1}$. At high solute concentrations, competition for O^- (generated from N_2O) was carried out. The following reaction rate constants (in $M^{-1} \text{ sec}^{-1}$) were determined: $k_{(O^-+I^-)} = 2.2 \times 10^9$; $k_{(O^-+CNS^-)} = 1.4 \times 10^9$; $k_{(O^-+methanol)} = 5.3 \times 10^8$; $k_{(O^-+ethanol)} = 9.8 \times 10^8$; $k_{(O^-+ferrocyanide)} \leq 3 \times 10^7$; $k_{(O^-+Br^-)} = 1.8 \times 10^8$; $k_{(O^-+ferrous)} = 3.1 \times 10^9$; $k_{(O^-+cerous)} = 5.9 \times 10^8$. The reactivity of O^- as compared with that of OH is discussed. An upper limit ($\sim 10^7 \text{ sec}^{-1}$) is estimated for $k_{(N_2O^- \rightarrow N_2+O^-)}$.

Introduction

The use of nitrous oxide in radiation chemistry of aqueous solutions was introduced by Proskurnin and Kolotyrkin.¹ Dainton and Peterson² have shown that N_2O converts hydrated electrons into hydroxyl radicals according to eq 1



There is a controversy regarding the mechanism of process 1. A negative ion, N_2O^- , has been proposed as an intermediate capable of reacting with solutes.³⁻⁶ In several systems⁷⁻¹² there was evidence that N_2O^- is converted quickly⁷ into OH radicals; several papers indicated half-lives less than 0.2–0.3 μsec .⁸⁻¹² Adams¹³ has put an even lower limit on the lifetime of N_2O^- . His limit is based on competition between methanol and CNS^- for OH radicals. From the deviations in the relative reactivity of CNS^- and methanol, Adams' semiquantitative treatment resulted in an upper limit for the N_2O^- lifetime of $\sim 1 \text{ nsec}$. Czapski¹⁴ pointed out that O^- , and not N_2O^- , may be the reactive species in some aqueous systems in which high solute concentrations were used. He concluded, from the pK of OH radicals (assuming that $k_{(OH+OH^-)} = 10^{10} M^{-1} \text{ sec}^{-1}$), that O^- may live as long as 10^{-8} to 10^{-9} sec at $pH > 2$.

The purpose of this work is to investigate the mechanism according to which N_2O converts hydrated electrons into OH radicals and to obtain information on the nature, lifetime, and reactivities of the intermediates (O^- , N_2O^-).

Experimental Section

The pulse radiolysis apparatus and syringe technique were essentially the same as described elsewhere.¹⁵⁻¹⁷ The linear accelerator at the Hebrew University was used as an electron pulse source at 5 MeV and 200 mA. A rectangular silica cell ($1 \times 2 \times 4 \text{ cm}$) with a light

path of 12.2 cm was used (3 passes) unless otherwise stated. The electron beam was perpendicular to the light beam, and was absorbed in the 1-cm thick water medium after passing through 0.5-mm thick quartz windows. The cell filling method was based on the method developed previously at Risö,¹⁸ except that magnetic valves with photodiode relays were used for both filling and emptying the irradiation cell.

- (1) M. A. Proskurnin and V. M. Kolotyrkin, *Proc. U. N. Int. Conf. Peaceful Uses At. Energy*, 2nd, 29, 52 (1958).
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- (3) M. Anbar, R. A. Munoz, and P. Rona, *J. Phys. Chem.*, **67**, 2708 (1963).
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- (16) L. M. Dorfman, I. A. Taub, and R. E. Bühler, *ibid.*, **36**, 3051 (1962).
- (17) (a) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *Discuss. Faraday Soc.*, **36**, 193 (1963); (b) E. J. Hart, S. Gordon, and J. K. Thomas, *J. Phys. Chem.*, **68**, 1271 (1964).
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The electron pulse intensity was constant within $\pm 5\%$. We used the inductive current obtained by the electron beam in a coil to monitor the pulse intensity. Whenever comparison of optical densities was needed they were first corrected for the differences in pulse intensity as measured by the monitor. The reproducibility of corrected optical densities was better than 3%.

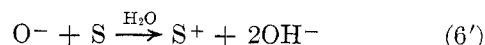
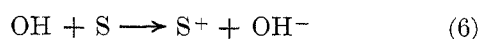
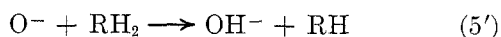
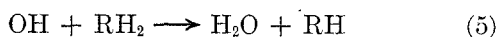
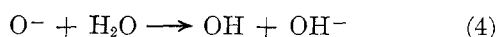
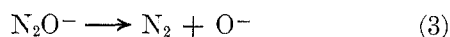
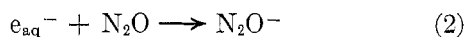
An IP28 photomultiplier, a Bausch and Lomb high intensity monochromator, and Tektronix 556 double beam and 454 single beam oscilloscopes were used in all the experiments. An Osram xenon 150-W lamp with water cooling was used as a light source. Appropriate light filters were employed in order to avoid second-order light signals through the monochromator, as well as to minimize photochemistry of the solutions (especially when ferrocyanide was used as a solute). To minimize photochemistry of the solutions and to protect the photomultiplier system from excess illumination, a shutter operated mechanically by air pressure was used between the irradiation cell and the light source.

Ultrahigh purity argon and O_2 (Matheson Co.) were used for the preparation of the solutions. N_2O (Matheson Co.) was purified by the procedure described before.⁸ Triple distilled water was used in all the experiments; 20 M NaOH (Merck analytical reagent) was used as a stock solution for the preparation of alkaline solutions. $K_4Fe(CN)_6 \cdot 3H_2O$ and methanol (Mallinckrodt AR), KI and KBr (Baker analyzed reagent), KCNS and CCl_4 (Hopkin and Williams, Analar), ethanol (Merck reagent), $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (Riedel-de Haën analytical reagent), and $Ce_2(SO_4)_3 \cdot 8H_2O$ (Fluka puriss reagent) were used without further purification. The temperature was $23 \pm 2^\circ$.

Results

We carried out competition experiments in which two solutes, RH_2 and S, competed for OH radicals and their equivalents, in the presence of N_2O . As RH_2 we used ethanol and methanol, which are known to undergo dehydrogenation by OH radicals, forming free radicals of the type RH which have optical absorptions in the uv region.¹⁹ As S, we chose ferrocyanide, iodide, bromide, thiocyanate, ferrous or cerous salts.

Let us assume the following mechanism ($3.5 < pH < 10$)



In all the systems investigated, S^+ was a relatively stable product, compared with the radical species taking part in reactions 2–6. Usually, S^+ could further react with another S^+ radical, with H atoms, or with RH radicals. However, under our conditions these reactions were slow enough to enable the determination of “initial” (extrapolated to the middle of the pulse) optical densities of S^+ . The reaction of H atoms with N_2O was neglected ($k < 3 \times 10^5 M^{-1} sec^{-1}$).²⁰ These optical densities could be a measure of the total amount of oxidizing radicals which reacted with S in competition with their reactions with RH_2 .

Let us define the following: G_X , the “primary” yield of X; $G_{(Y)}$, the experimental yield of Y; R_i , the rate of reaction i; $G_{(i)}$, the yield of reaction (i).

From the above mechanism (reactions 2–6') it is evident that $G_{(S^+)} = G_{(6)} + G_{(6')}$. RH_2 and S compete for the OH radicals. Such a competition can be described by the relation

$$G_{(6)} = G_{(OH)} / (1 + R_5/R_6)$$

where $G_{(OH)}$ represents the total yield of OH formed both primarily and *via* reaction 4.

$$G_{(OH)} = G_{OH} + G_{(4)}$$

Similarly

$$G_{(4)} = G_e / (1 + (R_{5'} + R_{6'})/R_4)$$

and

$$G_{(6')} = G_e / (1 + (R_1 + R_{5'})/R_{6'})$$

(the last two equations are based on the assumption that all the hydrated electrons are converted into O^- radical ions due to reactions 2 and 3). Combining the above relations leads to formula I

$$G_{(S^+)} = \frac{G_{OH} + G_e / [1 + (R_{5'} + R_{6'})/R_4]}{1 + R_5/R_6} + \frac{G_e}{1 + (R_4 + R_{5'})/R_{6'}} \quad (I)$$

Equation I can be modified into (II)

$$D/D_0 = \frac{1 - G_R / [1 + R_4/(R_{5'} + R_{6'})]}{1 + R_5/R_6} + \frac{G_R}{1 + (R_4 + R_{5'})/R_{6'}} \quad (II)$$

where D and D_0 are the extrapolated optical densities of S^+ , in the presence and in the absence of RH_2 , respectively, and G_R is defined as the ratio $G_e/(G_e + G_{OH})$. Equation II can be used to determine relative rate constants, as will be seen later.

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(20) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967).

Determination of G_R . Primary G values are known to depend on the nature of the solutes and on their concentrations. In Table I we demonstrate the effect of [ferrocyanide] on D_0 . The ratio D_0 (O_2 , 1 atm)/ D_0 (N_2O , 0.1 atm) = $0.50 \simeq (1 - G_R)$ is practically independent of the ferrocyanide concentration. In similar experiments, carried out with negative ions other than ferrocyanide, values of G_R ranging from 0.50 to 0.48 were obtained. The value $G_R = 0.50$ was used whenever eq II has been applied in all the systems containing negative ions S. G_R was assumed to be independent of $[N_2O]$ and $[RH_2]$.

Table I: Calculation of G_R for Ferrocyanide^a

$[K_4Fe(CN)_6]$, M	D_0 (O_2 , 1 atm)	D_0 (N_2O , 0.1 atm)	$\frac{D_0 (O_2, 1 \text{ atm})}{D_0 (N_2O, 0.1 \text{ atm})}$
1×10^{-3}	0.076	0.148	0.51
1×10^{-2}	0.083	0.168	0.49
1×10^{-1}	0.097	0.192	0.51

^a Results measured at 1.5- μ sec pulses.

Determination of k_5/k_6 . Both k_5 and k_6 have been measured before.^{8,10,21,22} We measured directly the ratio k_5/k_6 , using solutions of S-ethanol and S-methanol. Two sets of experiments were carried out for each solute S. (a) In one set, O_2 saturated solutions of relatively high S concentrations were used. The concentrations of S were chosen so that they were about equal to those used later in the competition experiments for O_{aq}^- radical ions. (b) N_2O -saturated O_2 -free solutions with relatively low solute concentrations were used, so that $R_4 \gg (R_5 + R_6)$. In both cases, eq II reduces to (III)

$$D_0/D = 1 + R_5/R_6 \quad (III)$$

From eq III, k_5/k_6 can be obtained using appropriate plots. Such plots are presented in Figure 1. The k_5/k_6 ratios are summarized in Table II.

Table II: k_5/k_6 for Negative Ions^d

S	[S], M	D_0	Pulse duration, μ sec	k_5/k_6	
				Ethanol	Methanol
$K_4Fe(CN)_6$	0.05 ^a	0.0752	0.5	0.199	0.087 ^c
$K_4Fe(CN)_6$	2×10^{-4} ^b	0.0612	0.35	0.186	0.081
CNS^-	0.2 ^a	0.0762	0.075	0.157	0.075 ^c
CNS^-	3×10^{-4} ^b	0.164	0.1	0.181	0.086
I^-	0.1 ^a	0.102	0.075	0.141	
I^-	1×10^{-4} ^b	0.217	0.1	0.181	
Br^-	1.0 ^a	0.188	0.13	0.250	
Br^-	1×10^{-3} ^b	0.186	0.1	1.57	

^a Saturated with oxygen. ^b Saturated with N_2O . ^c Based on the ethanol results assuming k_5 is independent of solute concentrations. ^d Ferrocyanide ions, $(CNS)_2^-$, I_2^- , and Br_2^- were detected at 4200, 4750, 3800, and 3600 Å, respectively.

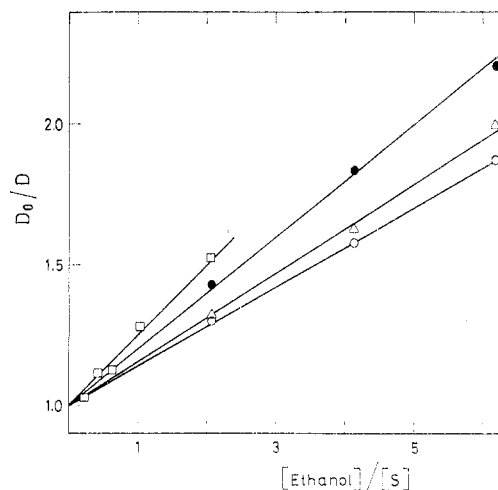


Figure 1. Determination of k_5/k_6 in oxygenated solutions of negative ions: ●, $K_4Fe(CN)_6$ (0.05 M); Δ, $KCNS$ (0.2 M); ○, KI (0.1 M); □, KBr (1.0 M).

The results obtained in the N_2O saturated solutions agree with the known absolute reaction rate constants.^{8,10,21,22} At the relatively high solute concentrations (O_2 saturated), the ratios k_5/k_6 are not identical with the ratios obtained at low solute concentrations. In the case of ferrocyanide, the small difference, if real, may be due to ion association. We have no explanation for the small (but definitely outside experimental error) concentration effects in the thiocyanate and iodide systems. The discrepancy in the case of bromide is especially large. It is probably connected with the particular oxidation mechanism of Br^- by OH radicals.¹⁰ In our experiments, the overall reaction rate of Br^- with OH is measured. If the intermediate¹⁰ $BrOH^-$ is capable of reacting with Br^- to yield OH^- and Br_2^- , an effect of $[Br^-]$ on the competition is expected.

Reaction of Br^- with H_2O^+ can also account for our observations. However, there is no conclusive evidence for reactions of H_2O^+ with solute in irradiated aqueous solutions, and we believe that the observed effect is specific to the intermediates of the solute.

Determination of k_4 . The ferrocyanide system has the advantage that it has been studied extensively.^{8,21} It is known that ferrocyanide is not reactive towards O^- radical ions.⁸

We extended this work⁸ and studied the rate of oxidation of ferrocyanide in solutions containing $[NaOH] = 0.366$ and 1.11 M. The apparent reaction rate constants of hydroxyl radicals with ferrocyanide (10^{-3} M) were 2.57×10^8 and 1.06×10^8 $M^{-1} \text{ sec}^{-1}$, respectively. From this, an upper limit $k_6 \leq 3 \times 10^7$ M^{-1}

(21) (a) J. Rabani and M. S. Matheson, *J. Amer. Chem. Soc.*, **86**, 3175 (1964); (b) G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, **61**, 492 (1965).

(22) (a) J. K. Thomas, *ibid.*, **61**, 702 (1965); (b) G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael, "Pulse Radiolysis," M. Ebert, *et al.*, Ed., Academic Press, London, 1965, p 117; (c) J. H. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, **64**, 2389 (1968); (d) G. V. Buxton, *ibid.*, **65**, 2150 (1969).

sec^{-1} was obtained. This justifies the neglect of R_6 in eq II, in both ferrocyanide-ethanol and ferrocyanide-methanol experiments under our conditions. Equation II is then modified into (IV)

$$D/D_0 = \frac{1 - G_R/(1 + R_4/R_5)}{1 + R_5/R_6} \quad (\text{IV})$$

Measurements of D/D_0 , under conditions where R_4 is equal to R_5 , (within a factor of 2-3), make it possible to obtain the ratio k_4/k_5 , from which k_4 can be calculated if k_5 is known. Using competition experiments we found (Table VI) $k_5 = 5.3 \times 10^8$ and $9.8 \times 10^8 M^{-1} \text{sec}^{-1}$ for methanol and ethanol, respectively, in good agreement with Gall and Dorfman^{7a} and Wander, Gall, and Dorfman.^{7b} In Table III we present k_4 , calculated from eq IV, using our values of G_R , k_5/k_6 , k_5 , and neglecting k_6 . Table III shows that results based on the ethanol system are practically identical with those based on the methanol system, yielding $k_4 = (9.6 \pm 2.3) \times 10^7 \text{sec}^{-1}$. (The value 2.3×10^7 is the standard deviation.)

Table III: Determination of the $\text{O}^- + \text{H}_2\text{O}$ Rate Constant (k_4) (pH 8-8.8)

$[\text{K}_4\text{Fe}(\text{CN})_6],$ M	$[\text{RH}_2],$ M	D^a	$k_4 \times 10^{-8}$ sec^{-1}
0.01		0.174 (4)	
0.01	0.025 ^b	0.104 (6)	0.90
0.01	0.05 ^b	0.075 (5)	1.30
0.025		0.184 (10)	
0.025	0.05 ^b	0.111 (9)	1.08
0.025	0.10 ^b	0.077 (6)	0.98
0.025	0.0495 ^c	0.134 (3)	0.61
0.025	0.099 ^c	0.114 (9)	1.05
0.05		0.194 (10)	
0.05	0.05 ^b	0.134 (5)	0.92
0.05	0.10 ^b	0.098 (7)	0.68
0.05	0.099 ^c	0.134 (8)	0.86
0.05	0.198 ^c	0.115 (7)	1.54
0.10		0.199 (6)	
0.10	0.05 ^b	0.146 (4)	0.76
0.10	0.25 ^b	0.084 (6)	0.85
0.10	0.0495 ^c	0.169 (4)	0.87
0.10	0.099 ^c	0.151 (10)	0.97
0.10	0.198 ^c	0.128 (5)	1.10

^a Average optical density extrapolated to the middle of the pulse duration. Numbers in parentheses represent the number of parallel determinations from which the average optical density was calculated. ^b Ethanol. ^c Methanol.

In Table IV we present data on the sensitivity of the calculated k_4 (average values) to errors in optical densities, solute concentrations, and various parameters (G_R , k_5/k_6 , k_5 , and k_6).

From Table IV it is evident that the results are most sensitive to the accuracy of the optical densities. Other parameters have a relatively small effect.

Table IV: Sensitivity of the Calculated k to Errors

Parameter	Error in parameter, %	Deviation in k , %			
		$\text{K}_4\text{Fe}(\text{CN})_6$	CNS^-	I^-	Br^-
D_0	+3	-18	-20	-20	-28
D	+3	+24	+20	+30	+30
[S]	+3	-4	-5	-5	-5
[RH ₂]	+3	+11	+5	+5	+5
G_R	+4	+7	+6	+5	+16
k_5/k_6	+10	+14	+15	+11	+11
k_4	+30		-5	-5	-16
k_5	-10	-7	-10	-10	-17
k_6	5×10^7 ^a	-4			

^a Absolute reaction rate constant in units of $M^{-1} \text{sec}^{-1}$.

Reaction Rate Constants for O^- Radical Ions. (a) *Neutral pH (6-7 before Pulse).* Equation II was used to obtain ratios of R_5/R_6 , at high solute concentration, where the contribution of reaction 4 may be neglected. In Table V we present reaction rate constants for O^- radical ions in neutral solutions. The k_5/k_6 values obtained at high solute concentrations (Table II) were used for the calculations of the O^- reaction rate constants.

From Table V, $k_6 = (1.5 \pm 0.5) \times 10^9$, $(2.3 \pm 0.4) \times 10^9$, and $(1.8 \pm 0.2) \times 10^8 M^{-1} \text{sec}^{-1}$ for CNS^- , I^- , and Br^- , respectively.

The effect of errors on the calculation of k_6 is demonstrated in Table IV.

The significance of k_6 in the case of bromide is not clear in the light of the complications discussed in connection with the reactivity of Br^- towards OH radicals. If Br^- reacts with H_2O^+ (presumably the precursor of OH), the net result is an apparent increase in the scavenging efficiency of OH by Br^- at high concentration. Such an effect was taken into account by using the results at the high Br^- concentration for the calculations of k_6 . However, the apparent effect of $[\text{Br}^-]$ on k_6 may indicate complications due to the intermediate BrOH^- as discussed above. It is likely that such an intermediate is formed also when Br^- reacts with O^- radical ions. In this case, the apparent reaction rate constant of O^- may also depend on $[\text{Br}^-]$. At present we can only conclude that O^- seems to be less reactive than OH towards Br^- . Further work is in progress in order to elucidate the reaction mechanism of OH with Br^- .

(b) *Alkaline Solutions.* In the alkaline medium, rate constants were measured either directly, following the formation of the product S^+ by its optical absorption, or by competition with other solutes. In the case of iodide, thiocyanate, and ferrocyanide, the formation of the product S^+ [I_2^- , $(\text{CNS})_2^-$, and $\text{Fe}(\text{CN})_6^{3-}$, respectively] could be followed directly. In the case of iodide and thiocyanate, it is known that the oxidation of these ions is followed by a reaction to form the X_2^-

Table V: Reaction Rate Constants for O^- Radical Ions in Neutral Solutions Saturated with N_2O^a

[S], M	[RH ₂], ^b M	<i>D</i> ^c	<i>k</i> × 10 ⁻⁹ , M ⁻¹ sec ⁻¹
CNS ⁻			
0.049		0.280 (3)	
0.049	0.05	0.213 (3)	0.7
0.049	0.10	0.178 (3)	1.1
0.196		0.182 (12)	
0.196	0.5	0.108 (13)	2.0
0.196	1.0	0.0735 (9)	1.5
0.196	0.99 ^d	0.111 (6)	2.6
0.196	1.98 ^d	0.073 (6)	1.5
0.49		0.192 (10)	
0.49	0.5	0.141 (9)	1.4
0.49	1.0	0.114 (11)	1.4
0.49	0.99 ^d	0.140 (9)	1.5
0.49	1.98 ^d	0.109 (7)	1.2
I ⁻			
0.1		0.279 (7)	
0.1	0.103	0.230 (6)	3.0
0.1	0.206	0.185 (7)	2.0
0.1	0.412	0.143 (7)	2.2
0.2		0.282 (6)	
0.2	0.103	0.248 (6)	2.1
0.2	0.206	0.222 (7)	2.1
0.2	0.412	0.189 (6)	2.4
Br ⁻			
0.5		0.303 (12)	
0.5	0.103	0.242 (10)	0.20
0.5	0.515	0.155 (10)	0.15
0.5	1.03	0.119 (7)	0.17
1.0		0.314 (9)	
1.0	0.103	0.264 (9)	0.15
1.0	0.515	0.195 (7)	0.19
1.0	1.03	0.158 (8)	0.19
2.0		0.335 (9)	
2.0	0.103	0.302 (7)	0.18
2.0	0.515	0.240 (10)	0.20
2.0	1.03	0.202 (8)	0.20

^a (CNS)₂⁻, I₂⁻, and Br₂⁻ were detected at 4750, 3800, and 3600 Å, respectively. ^b Ethanol, except if marked *d*. ^c The pulse intensity was constant in all the experiments of any particular solute S, except for the results with 0.049 M thiocyanate which were carried out with a pulse intensity different from the other thiocyanate experiments. The numbers in parentheses represent the number of parallel measurements, from which an average value was calculated. ^d Methanol.

radical ion.²² The rate of formation of X₂⁻ can be used to determine *k*₆ at neutral pH's and *k*₆' in alkaline solutions provided that reaction 6 or 6' is rate determining. In earlier work this point has been disregarded both in the iodide^{22a} and in the thiocyanate^{22b} systems. Baxendale, Bevan, and Stott^{22c} pointed out that in both the iodide and the thiocyanate systems, the formation of X₂⁻ from X and X⁻, and not reaction 6, was actually the rate determining step. However, in alkaline solutions the formation of CNS and I radicals is much slower and the rate of X₂⁻ formation is determined by reaction 6'.

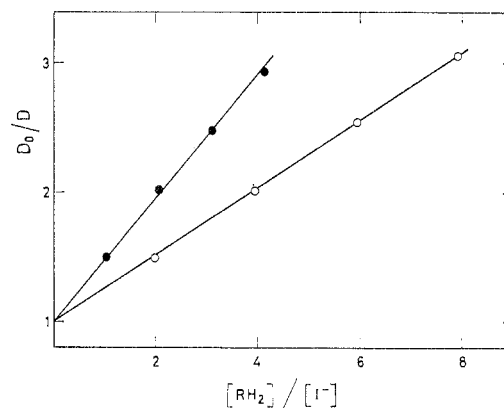


Figure 2. Determination of *k*₅'/*k*₆' in N_2O saturated alkaline iodide solutions: $[NaOH] = 0.58 M$; $[I^-] = 5 \times 10^{-4} M$; $D_0 = 0.263$; 0.1-μsec pulse; ●, ethanol solutions; ○, methanol solutions.

In the alkaline range, plots of $\log (D_\infty - D)$ vs. *t* for both I₂⁻ and (CNS)₂⁻ are linear. *D*_∞ is the optical density measured after all the oxidizing radicals react, and before [X₂⁻] decreases due to recombination. The reaction rate constant of O^- with Br⁻ could not be determined in the alkaline pH range because of the reverse reaction²³ and the complications in the oxidation of Br⁻ in alkaline solutions.¹⁰

The reactivity of O^- towards methanol and ethanol in alkaline solutions has been determined by competition with iodide in N_2O saturated alkaline solutions (Figure 2). In Table VI the results in the alkaline pH range are summarized.

Table VI: The Reactivity of O^- in Alkaline Solutions

S	[S], M	[NaOH], M	" <i>k</i> " _(OH+S) × 10 ⁻⁹ , ^a M ⁻¹ sec ⁻¹	<i>k</i> _(O⁻+S) × 10 ⁻⁹ , M ⁻¹ sec ⁻¹
I ⁻	5 × 10 ⁻⁴	0.58	2.1	2.0
I ⁻	1 × 10 ⁻⁴	0.11	2.4	1.9
CNS ⁻	1 × 10 ⁻³	0.36	1.3	1.1
CNS ⁻	1 × 10 ⁻³	1.08	1.4	1.3
Ethanol		0.58	0.99 ^b	0.98
Methanol		0.58	0.54 ^b	0.53

^a Apparent rate constant for the oxidation of the solute by (OH + O^-) radicals. ^b From competition with iodide ions.

Positive Ions. Ferrous and Cerous Ions (as Sulfates). The identification of O^- as an intermediate in the reaction of N_2O with e_{aq}^- was used to investigate the reactivity of O^- with positive ions which are usually unstable in alkaline media. Again, as with negative ions, high solute concentrations have been employed to suppress reaction 4.

The Ratio *k*₅/*k*₆. The ratio *k*₅/*k*₆ was measured in

(23) V. J. Linnenbom, C. H. Cheek, and J. W. Swinnerton, NRL Quarterly on Nuclear Science and Technology, April 1962, p 46.

both dilute solutions saturated with N_2O and relatively concentrated (0.1 M) deaerated solutions, in a way similar to that described before. The products of the oxidation of S, S^+ , are ferric and ceric ions. Initial optical absorptions of these products were measured at 3050 and 3200 Å, respectively. Ferrocyanide saturated N_2O solutions (1×10^{-3} M) were used for the determination of the pulse doses. As the optical absorptions were relatively small, we could not neglect the optical absorptions of ethanol radicals (only ethanol was used as RH_2). The correction for the ethanol radical absorption was made by successive approximations, using extinction coefficients of 170 and 110 $M^{-1} \text{ cm}^{-1}$ at 3050 and 3200 Å, respectively. These values, measured in N_2O solutions containing no S, are in agreement with those previously reported.^{19a} The formation of reduction products, S^- , by the reaction of the hydrated electrons with S was considered. The extinction coefficient of S^- was determined in Ar saturated 1 M ethanol solutions containing 5×10^{-3} M ferrous sulfate or cerous sulfate. The extinction coefficients ~ 500 and $\sim 40 M^{-1} \text{ cm}^{-1}$ were found for Fe^+ at 3050 and Ce^{2+} at 3200 Å, respectively. Rate constants for $e_{aq}^- + S$ reactions were taken from previous work.²⁴

In Figure 3 we present the competition data for OH radicals. We obtained k_5/k_6 values of 5.45 and 6.5 for ferrous and cerous ions, respectively, in agreement with previous results.^{25,26}

Reactivity of O^- Radical Ions. To obtain the reactivity of O^- radical ions towards ferrous and cerous ions, $G_{R'}$, defined as the ratio $G_{O^-}/(G_{OH} + G_{O^-})$ had to be determined. Unlike the negative ions, here the solutes S reacted with e_{aq}^- in competition with N_2O . In addition, a fraction of the e_{aq}^- reacted with H^+ , which was present as a result of partial hydrolysis of S. We assumed $G_{R'} = D_{CCl_4}/D_{N_2O}$; D_{CCl_4} and D_{N_2O} are the corrected optical densities obtained in solutions saturated with CCl_4 and N_2O , respectively. CCl_4 has a high reaction rate constant with e_{aq}^- .²⁰ The CCl_3 radicals formed did not oxidize the positive ions used. (We determined the extinction coefficients of CCl_3 as 130 and 115 at 3050 and 3200 Å, respectively.) The reactivity of O^- towards ferrous and cerous ions was calculated from initial corrected optical densities using a modified eq II, in which G_R was substituted by $G_{R'}$. The results are presented in Table VII.

From Table VII, $k_6 = (3.1 \pm 1.2) \times 10^9$ and $(5.9 \pm 2.2) \times 10^8 M^{-1} \text{ sec}^{-1}$ for ferrous and cerous ions. The value of $k_6 = 7.6 \times 10^8 M^{-1} \text{ sec}^{-1}$ was calculated for cerous ions if k_4 was $3 \times 10^8 \text{ sec}^{-1}$ instead of $1 \times 10^8 \text{ sec}^{-1}$ (in order to account for the possibility of the reaction $O^- + H^+$).

Discussion

(a) O^- as an Intermediate in Process 1. Reaction rate constants for O^- radical ions from two sources were compared and found identical within experimental

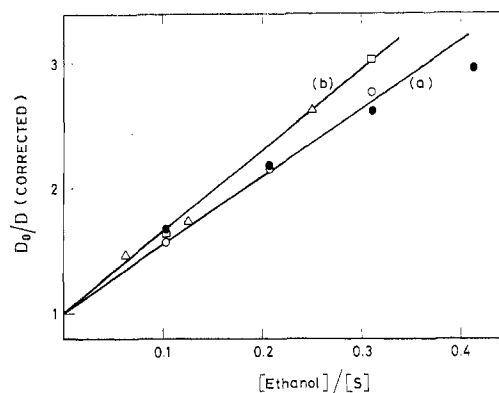


Figure 3. Determination of k_5/k_6 for ferrous and cerous ions: (a) S = $FeSO_4$, 0.5- μsec pulse; \bullet , $[Fe^{2+}] = 5 \times 10^{-3}$ M, N_2O saturated, pH 6.2, $D_0 = 0.167$; \circ , $[Fe^{2+}] = 0.1$ M, Ar saturated, pH 4.5, $D_0 = 0.097$; (b) S = $Ce_2(SO_4)_3$, Δ , $[Ce^{3+}] = 4 \times 10^{-3}$ M, N_2O saturated, pH 2.95 (H_2SO_4 was added), $D_0 = 0.0387$, 0.3- μsec pulse; \square , $[Ce^{3+}] = 0.1$ M, Ar saturated, pH 2.6, $D_0 = 0.130$, 0.6- μsec pulse.

Table VII: Reactivity of O^- Radical Ions toward Ferrous and Cerous Ions

[S], M	[Ethanol], M	pH	$G_{R'}$	D^a (cor)	$k \times 10^{-8}$, $M^{-1} \text{ sec}^{-1}$
Fe^{2+}					
0.05		4.8	0.52	0.176 (7)	
0.05	0.515			0.022 (6)	35
0.05	1.03			0.018 (5)	51
0.1		4.6	0.50	0.174 (5)	
0.1	0.515			0.028 (5)	24
0.1	1.03			0.0225 (6)	35
0.2		4.4	0.47	0.169 (5)	
0.2	0.515			0.033 (5)	15
0.2	1.03			0.030 (3)	28
Ce^{3+}					
0.1		2.6	0.47	0.173 (5)	
0.1	0.25			0.0164 (8)	4.8
0.1	0.5			0.0133 (6)	8.5
0.2		2.3	0.42	0.229 (6)	
0.2	0.25			0.0332 (8)	3.5
0.2	0.5			0.0264 (6)	6.8

^a See footnote a in Table III.

error: (a) O^- radical ions obtained *via* process 1; (b) O^- radical ions obtained by the ionic dissociation of OH radicals. This strongly indicates the identity of the two species as tentatively suggested by Czapski¹⁴ on the basis of the results of Adams.¹³ Moreover, our results in the ferrocyanide system give $k_{(O^-+H_2O)} = 9.6 \times 10^7 \text{ sec}^{-1}$. Combining this with $pK_{OH} = 11.85$ ^{8,9} gives $k_{(OH+OH^-)} = 1.3 \times 10^{10} M^{-1} \text{ sec}^{-1}$. Adams,

(24) (a) J. H. Baxendale, *et al.*, *Nature*, **201**, 468 (1964); (b) J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Roy. Soc. Ser. A*, **286**, 320 (1965).

(25) W. G. Rothschild and A. O. Allen, *Radiat. Res.*, **8**, 101 (1958).

(26) (a) T. J. Sworski, *ibid.*, **6**, 645 (1957); (b) Oak Ridge National Laboratory Annual Report, ORNL-3832 (1965).

Boag, and Michael²¹ reported $k_{(\text{OH}+\text{OH}^-)} = 3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, based on $k_{(\text{OH}+\text{ferrocyanide})} = 5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. If the directly⁸ measured value of $k_{(\text{OH}+\text{ferrocyanide})} = 1.07 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ is used, $k_{(\text{OH}+\text{OH}^-)} = 6.4 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ results. Since $k_{(\text{OH}+\text{OH}^-)}$ was obtained indirectly, using several rate constant ratios for the cross examination, we consider the results as being in agreement. This provides further support for the identification of O^- as an intermediate in process 1.

(b) *The Reactivity of O^- Radical Ions.* The appearance of O^- as an intermediate in process 1 may be used to investigate the reactivity of O^- in neutral and even in moderately acid solutions including solutes such as positive metal ions that are not stable in alkaline solutions. The ratio $k_{(\text{O}^-+\text{reactant})}/k_{(\text{OH}+\text{reactant})}$ increases with the increase in the amount of positive charge of the reactant. The ferrous and cerous positive ions react with O^- faster than with OH . While negative ions react faster with OH , the relative reactivity towards OH increases with the amount of negative charge.

(c) *The Lifetime of N_2O^- .* In previous publications,⁸⁻¹² 0.2–0.3 μsec has been set as an upper limit

for the lifetime of N_2O^- . We have assumed in all the calculations that N_2O^- does not react with any of the solutes, but forms exclusively O^- by reaction 3. The consistency of the rate constant ratios obtained in different systems supports this assumption. In order to determine the lifetime of N_2O^- , we carried out experiments at relatively high $[\text{S}]$ (I^- or ferrocyanide ions were used as S). Under our conditions, e_{aq}^- reacted with N_2O with a half-life of less than 10 nsec, O^- was converted into OH with a half-life of 7 nsec, and OH reacted with the solute (half-lives were calculated as 2–20 nsec depending on the solute concentrations). The time resolution in these experiments was about 50 nsec. Optical absorption was formed within 50 nsec and increased by 10–20% with a half-life of 50–100 nsec. If this increase is due to the conversion of N_2O^- into O^- radical ions, our results suggest that $k_3 \approx 10^7 \text{ sec}^{-1}$.

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Distorted Hydrogen Bonds Formed by Carbonyl Compounds

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Molecular orbital calculations have been carried out on the open formamide dimer and the formaldehyde-water system to examine the effects of deviations from the lone-pair approach and from the linearity of the hydrogen bond. While deviations from the lone-pair approach do not markedly affect the properties of the hydrogen bonds formed by these carbonyl donors, bending the hydrogen bond beyond $\sim 20^\circ$ causes a large decrease in the dissociation energy.

It is generally believed that hydrogen bonds formed by carbonyl compounds should be along the sp^2 lone-pair direction of the carbonyl group.^{1,2} Thus, the angle between an X–H bond and the axis of the carbonyl bond would be expected to be 60° . However, experimental molecular structure studies indicate that the angle, ϕ , between the X–H bond and the lone-pair direction of the carbonyl oxygen (Figure 1) varies anywhere between 0 and 60° in amides, amino acids, and other systems.^{1,3,4} Further, hydrogen bonds in most of these systems are bent,^{1,3,4} the angle of bending, θ , (Figure 1) being as large as 20 or 25° . We considered it interesting to investigate the effect of ϕ and θ on the

properties of the hydrogen bonded systems involving carbonyl donors. For this purpose, we have carried out semiempirical molecular orbital calculations on the formaldehyde-water system and the open trans dimer of formamide. In the case of formaldehyde-water, we

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