

RADIOLYTIC AND RADIOLYTICALLY INDUCED GENERATION OF GASES IN SIMULATED WASTE SOLUTIONS

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ABSTRACT

The radiolytic generation of gases in simulated mixed waste solutions was studied. Computer modeling of the non-homogeneous kinetic processes in these highly concentrated homogeneous solutions was attempted. The predictions of the modeling simulations were verified experimentally. Two sources for the radiolytic generation of H₂ are identified: direct dissociation of highly energetic water molecules and hydrogen abstraction from the organic molecules by hydrogen atoms. Computer simulation of the homogeneous kinetics of the NO_x system indicate that no N₂O will be produced in the absence of organic solutes and none was experimentally detected. It was also found that long term pre-irradiation of the simulated waste solutions leads to enhanced thermal production of these two gases.

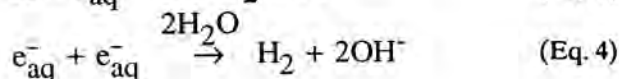
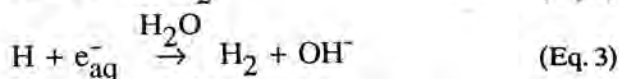
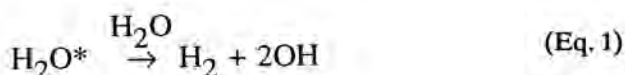
INTRODUCTION

The accumulation of high level liquid wastes in large temporary storage tanks raise concerns due to the gases generated in the tanks. Some of the mixed wastes were found to generate mixtures of gases which may approach flammability under certain conditions. (1) The waste solutions originally contained high concentrations of nitric acid as well as medium level concentrations of organic additives (often chelating agents) and trace amounts of transition metals. To minimize corrosion to the storage tanks the solutions are brought to high level of basicity. Sodium nitrite, at high concentrations, is also added or is present in the mixed waste as a radiolytic degradation product (2) of the nitrate. The generation of gases in simulated waste solutions of similar composition are the focus of this report.

The radiation chemistry of nitrate solutions, over a wide concentration range and mostly at acidic pH's, has been extensively studied. (2-12) Recent observations show efficient radiolytic generation of H₂ and N₂O from these solutions. (13,14) While H₂ could be expected as a radiolysis product of the aqueous solutions (albeit at low yields), generation of N₂O is somewhat surprising. It is evident from the above mentioned reports that organic components are necessary for the production of N₂O.

MODELING APPROACH

The radiolysis of pure water primarily creates H, OH, H⁺, and e_{aq}⁻. In high concentrations of salts, some of the radiation energy may be directly deposited in the salt and the salts can then be directly ionized. The primary reactions for hydrogen production in water are: (15)



Reactions 2-4 occur in competition with scavenging reactions that do not lead to H₂ production.



In the presence of organic additive, hydrogen abstraction reactions can also produce dihydrogen.



Reactions 1-7 take place, at early times, in "spurs", the high local concentration domains of ions and radicals that are created by the radiolysis. It is necessary, therefore, to take into account the non-homogeneous distribution of radicals and ions created by the ionizing event.

To model the generation of H₂, we have used the continuum diffusion kinetics model. (16-19) In this model, we assume that the ionizing event will generate the reactive fragmentation products in a spherically symmetric distribution. The diffusive and reactive processes are modeled using the coupled partial differential equations of the form:

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i - \sum_j k_{ij} c_i c_j + \sum_{j,k} k_{jk} c_j c_k$$

where k_{ij} are the rate constants for reactions that deplete species i and k_{jk} are the rate constants for reactions that will form species i . D_i is the diffusion coefficient for species i . Whereas more rigorous computational techniques have shown that there are errors in this approach, the errors are small and are primarily in reactions between two similar entities. Such reactions do not contribute strongly to the chemistry that occurs in the system under study. This technique is modest in computational needs and is easily modified to accommodate the multiple reactions that occur in the chemical system of interest here.

EXPERIMENTAL

All irradiated solutions contained 2.27 M NaOH, 2.22 M NaNO₂, 2.79 M NaNO₃, and 0.86 M NaAlO₂. This composition will be referred to as the "base solution". Appropriate amounts of the organic solutes (in the form of their sodium salts) were dissolved, with stirring at room temperature, in the

required amount of the base solution in volumetric flasks. Samples in syringes were irradiated in a ^{60}Co source. For runs at 60°C , the syringes were placed in a thermostatted bath. Dose rates (in krad/min) were determined using Fricke dosimetry. Appropriate corrections for density and electron density were made in calculating the dose absorbed by the samples. Yields are quoted as G values in units of 100 molecules per 100 eV. Unless otherwise stated, solutions deaerated by bubbling argon through the syringes. The gases produced in the samples were extracted using a Van Slyke apparatus connected to a gas chromatograph. All gas analyses were done with the syringes and the gases equilibrated at ambient temperature. A "molecular sieve 13x" column was used for most of the analyses. For N_2O analysis, the column was kept at 153°C .

RESULTS AND DISCUSSION

Modeling Results

Effect of Model Parameters. The model parameters that were used in the present calculations are given in Table I. Two different distributions of spur sizes were used for the calculations. One set employs the distribution defined by Trumbore and co-workers (20) which gives a good representation of the decay of the hydrated electron and the OH radical. A second set of parameters was based on calculations by Kuppermann and modified as suggested by him to give better agreement with experimentally observed decay rates. (17,18) The initial radiolytic yields of ions and radicals used for the calculation are also given in Table I. Initial H and H_2 yields given by Schwarz are too large to agree with the experimental data given in section B. A few calculations were done using a modified set of radiolytic yields. The initial yield of H atoms was assumed to be directly proportional to the electron fraction of the water in the concentrated solution. The mechanism for the instantaneous production of H_2 is not known so its dependence on the direct effect is difficult to predict. The initial H_2 yield was assumed to be proportional to the square of the electron fraction of water in the solution - i.e., two water molecules in the same region must interact to produce H_2 . The

oxidizing radical was assumed to be OH. Clearly this will not be the case when the direct effect becomes significant, but as long as the reaction scheme does not depend on the specific oxidizing radical there will be little dependence on the identity of the oxidizing radical.

The calculated yields are only slightly different for the two extreme calculations of Table I. The yields of H_2 are, thus, only weakly affected by the selection of spatial spur parameters. This lack of sensitivity to the spur parameters is, at least partially, due to the dominance of the scavenging reactions by the nitrate and nitrite systems. However, hydrogen peroxide yields will be strongly affected by the spur parameters because of the shorter separation distances between the OH radicals.

Effect of Nitrate and Nitrite. Figure 1 shows the computed yield of H_2 as a function of $[\text{NO}_2^-]$ and $[\text{NO}_3^-]$ in a system with an organic additive, RH, present. These results show that the yield is virtually independent of $[\text{NO}_3^-]$ in the concentration range examined. The effect of nitrate in reducing H_2 yields is largely due to scavenging of e_{aq}^- (reaction 6, in competition with reactions 3 and 4). None of the other solutes can significantly compete with nitrate for e_{aq}^- , therefore, the effect of nitrate is maximized at relatively low concentrations. The dependence of $G(\text{H}_2)$ on $[\text{NaNO}_2]$, however, is quite substantial over the concentration range shown in Fig. 1. This is because reaction 5 competes with reaction 2 for the H atoms and the rate constant for the former is *ca.* an order of magnitude slower than that of nitrate with e_{aq}^- . It seems clear from these results that the concentration of nitrite in the simulated waste solution is more important than that of nitrate if minimization of radiolytic H_2 generation is desired. It also follows that if the nitrite concentration is already at the 2.0 M level (and nitrate is at the ≤ 1.0 M level), further increase in its concentration, or addition of any other H atom scavenger, could hardly reduce the yield of H_2 generation.

Effect of Organic Solutes. An increase in the concentration of the organic solute, RH, will increase the rate of reaction 7 and thus increase the yield of H_2 . The calculated dependence of yield of H_2 on $k_7 \times [\text{RH}]$, i.e., on the total

TABLE I

Diffusion-Model Parameters Used in the Calculations of Yields

Species	$D \times 10^{-5a}$ cm^2/sec	Initial Radius (r_0 or r_e) ^b Å			No. of Fragments Molecules/spur		
		Big spur	Trumbore	Modified	Big spur	Trumbore	Modified
e_{aq}^-	4.5	60.00	23.10 ^c	23.10 ^c	6.000	2.820	2.820
H_3O^+	10.0	20.00	21.21	21.21	6.000	2.820	1.260
OH^-	2.0						
OH	2.0	20.00	21.21	21.21	7.400	3.480	3.120
H_2O_2	1.4						
H	8.0	20.00	21.21	21.21	1.300	0.6000	0.4400
H_2	2.0	20.00	21.21	21.21	0.074	0.035	0.018

^a The values quoted were used in the calculations. They are not precise experimental values.

^b The concentration of radicals is $C_0 e^{-r^2/2r_0^2} dV$ where the given initial radius is r_0 .

^c The distribution is $C_e r^3 e^{-r^2/2r_e^2} dV$ where the given initial radius is r_e .

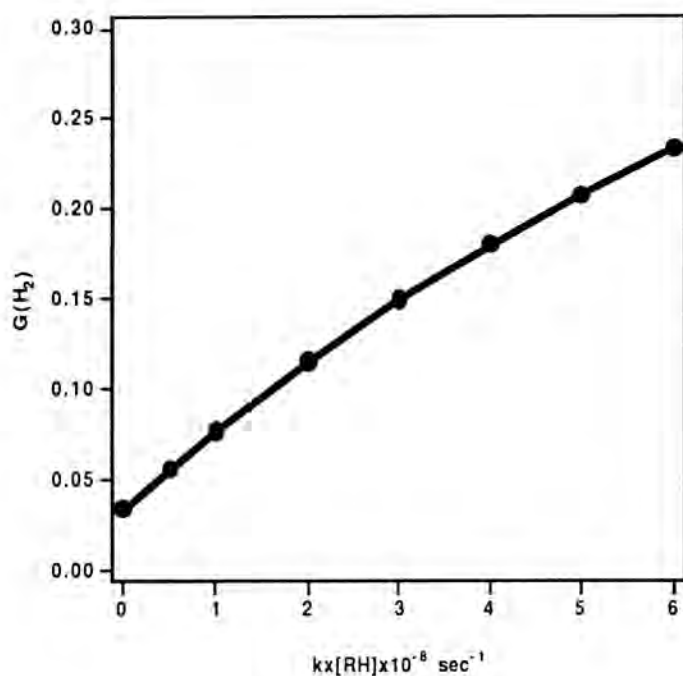


Fig. 1. Calculated effect of nitrite and nitrate on the yield of H_2 . Assumed concentrations are 1.0 M NaOH for both; 0.5 M NaNO_2 for the nitrate effect; 1.0 M NaNO_3 for the nitrite effect; $k \times [RH] = 4 \times 10^7 \text{ s}^{-1}$ for both.

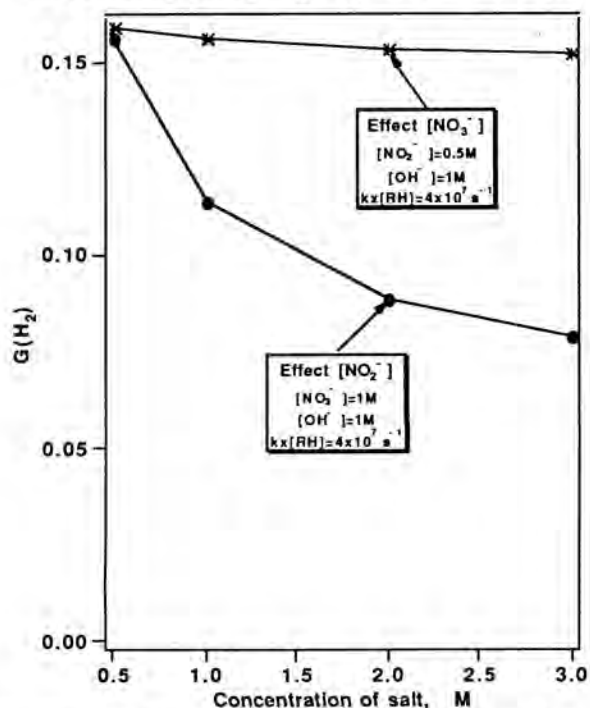


Fig. 2. Yield of H_2 as a function of rate for the H-atom abstraction reaction from the organic solute. All concentrations of the inorganic solute are the same as in the base solution. Also includes the "direct effect".

reactivity of the organic additive, is given in Fig. 2 where the concentration of the inorganic species OH^- , NO_2^- , and NO_3^- were chosen to mimic the base solution described in the Experimental section. The yields of H and H_2 were modified as discussed above to take into account the direct effect in the solution. The results show that the yield of H_2 will increase linearly with the concentration and reactivity of RH at low total reactivity, in agreement with the experimental observations. At higher concentrations the yield increases sublinearly upon increasing total reactivity.

Determination of Radiolytic Yields

Yields of H_2 . No effect of dose (30-1000 krad) on $G(\text{H}_2)$ was found in the irradiated base solution with or without the organic additives. Within experimental error, there is also no

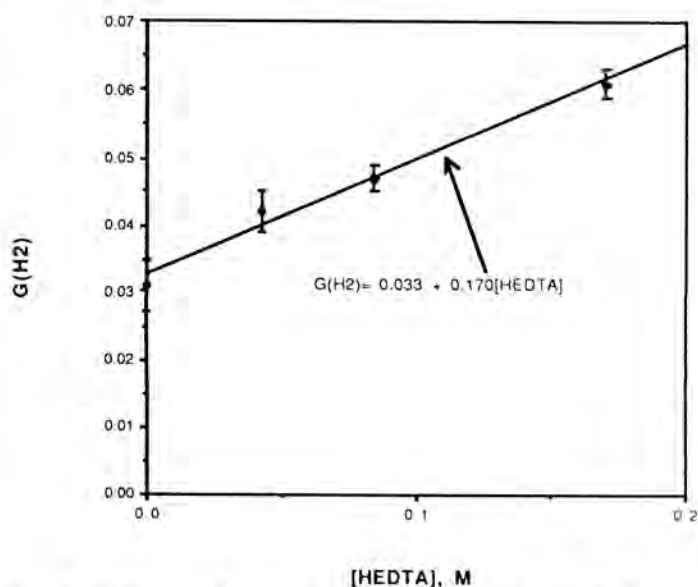
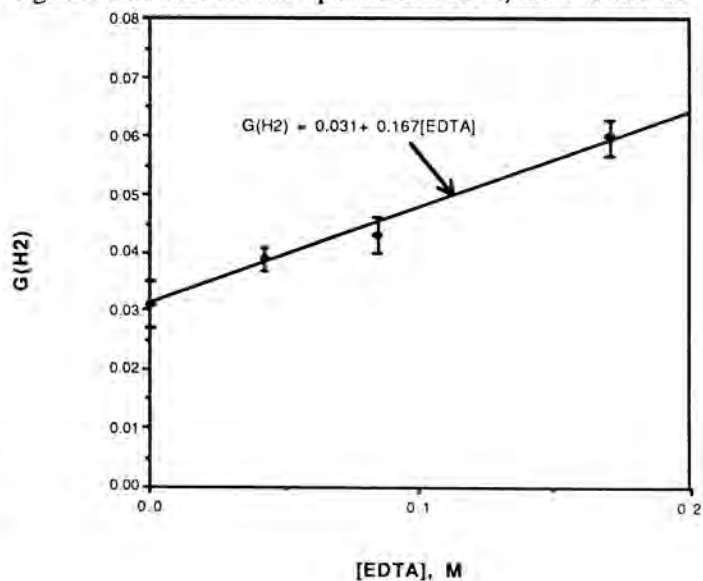


Fig. 3. $G(\text{H}_2)$ vs. the concentration of the organic chelators [EDTA] (left) and [HEDTA] (right) in the base solution. Solutions irradiated at 4.4 krad/min to 130 krad dose at 30°C .

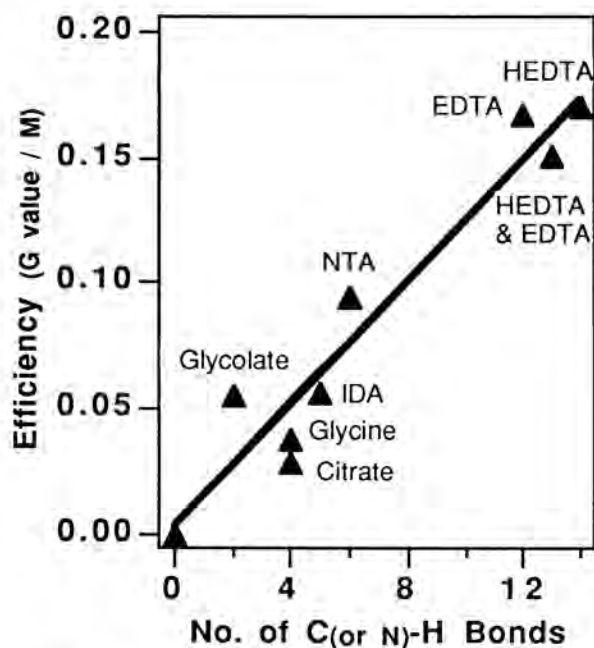


Fig. 4. The dependence of the efficiency, R , of H_2 generation (in G values per mole) of the various organic solutes on the hydrogen content of the compound.

effect of dose rate on $G(H_2)$ for the base solution. No effect of dose rate on $G(H_2)$ was observed in any of the other solutions either. Figure 3 shows the effect of the concentration of two organic solutes, EDTA and HEDTA, in the base solution on $G(H_2)$ for irradiations at $30^\circ C$. The G value seems to increase linearly with concentration of the organic chelator. No theoretical significance is attached to this linear dependence on organic solute concentration, which was observed for all organic solutes added. It can, however, be rationalized based on the mechanism proposed below.

The slopes of the lines describing $G(H_2)$ vs. the concentration of the organic solutes were determined, and are referred to as R values. They represent an empirically determined efficiency of the organic solute in increasing the hydrogen yield. In Fig. 4 we show a correlation between the R -values and the number of C-H or N-H bonds in the molecule. It is seen that a qualitative correlation of R with the hydrogen content in the molecule exists. The correlation suggests that the probability of a molecule serving as a source for H_2 increases with the number of hydrogen atoms (bound to a C or N atom only; labeled below N_{X-H}) in that molecule. From the straight line in Fig. 4, and using the experimentally determined $G(H_2) = 0.031$ in the base solution without organic additives, the yield in the presence of organic solutes can be represented by:

$$G(H_2) = 0.031 + 0.013 \times N_{X-H} \times [RH].$$

It should be emphasized that this equation is only of empirical value; it will be followed only for a background solution of the same composition as the base solution. Deviations from the linear dependence are expected with variations of the rate constant for the H atom abstraction reaction. These deviations will be more pronounced for small molecules where the specificity of the particular X-H bond toward the abstraction reaction will be of major impact. For large molecules, the

TABLE II

Experimental Results for $G(H_2)$ at $60^\circ C$ and Comparison with Results at $30^\circ C^a$.

Additive	[RH] M	$G(H_2)$ $60^\circ C$	$G(H_2)$ $30^\circ C$	Ratio $\frac{G(60^\circ C)}{G(30^\circ C)}$
None	0	0.033	0.031	1.06
EDTA	0.085	0.053	0.045	1.18
HEDTA	0.085	0.054	0.045	1.15
NTA	0.17	0.054	0.047	1.15
IDA	0.17	0.045	0.041	1.10
Citrate	0.17	0.037	0.036	1.03
Glycine	0.3	0.045	0.042	1.07
Glycolate	0.3	0.055	0.048	1.15

^a Samples received approximately 140 krad in 30 min irradiations.

abundance of hydrogen content will mask the specific rates and the total rate constant of the molecule will approach the diffusion control limit.

In Table II we compare the results of $G(H_2)$ determinations at 30 and $60^\circ C$; values are given for the single concentration shown in the table for each organic solute. The value of $G(H_2)$ is seen to be larger at $60^\circ C$ in all cases. Values of $G(H_2)$ at $60^\circ C$ were measured only at the concentration shown in Table II. The table indicates that the yield of H_2 production by the organic solutes increases at $60^\circ C$ for all of the organic additive except for citrate. In the framework of the mechanism for radiolytic hydrogen production (reaction 7), this result indicates that the rate of the hydrogen abstraction reaction increases on increasing the temperature more than the increase in the rate of the other reactions of H atoms (reaction 5; most dominating is the reaction with nitrite). This is reflected in the rate constants for the abstraction reaction.

We now turn to the mechanistic aspects of the generation of dihydrogen in the simulated waste solutions. It is clear that small yields of H_2 are obtained from the base solution in the absence of organic additives. This yield probably results from the dissociation of an excited water molecule that is produced by the absorption of radiation energy. The fact that this yield is lower than Schwarz's estimate of $G(H_2)_0 = 0.15$, (16) and that it is dependent on nitrate concentration indicates that these excited water molecules can be scavenged by high concentrations of solutes. The other source of H_2 involves the organic solutes and we propose that reaction 7 is the pathway to this yield.

The yield of H_2 under these conditions will be given by Eq. (1),

$$G(H_2) = G(H_2)^0 + G(H) \cdot \frac{k_7[RH]}{k_7[RH] + k_5[S]} \quad (\text{Eq. 1})$$

where $G(H_2)^0$ is the limiting yield of H_2 at zero concentration of RH. Equation (1) also predicts the apparently linear dependence of $G(H_2)$ on [RH]; because reaction 7 represents a side reaction in the solutions studied, $k_7[RH] \ll k_5[S]$ and a linear dependence is expected. Obviously, both reactions 5 and 7 are competing with intra-spur reactions and spur

expansion and thus considerations from homogeneous kinetic arguments are not rigorously applicable. Nonetheless, scavenging reactions dominate in a system of such high concentrations and therefore these non-homogeneous effects are small. Our modeling results completely agree with this observation.

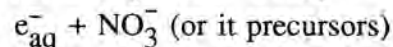
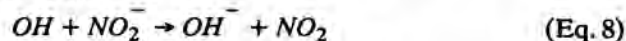
Yields of N_2O . No N_2O was detected from irradiated samples of the base solution in the absence of organic solutes. In the presence of organic solutes, N_2O is produced in a sequence of processes which seem to follow a complex mechanism. For $30^\circ C$ irradiations, pronounced effects of dose rate on $G(N_2O)$ were observed. The yield of N_2O increases as the dose rate decreases. Furthermore, in the case of IDA, N_2O formation persisted after the irradiation had been terminated. For irradiations at $60^\circ C$, no postirradiation production of N_2O was observed. Presumably, this means that the slow reactions producing N_2O are markedly accelerated at $60^\circ C$. For irradiations at $60^\circ C$, no effect of dose rate on $G(N_2O)$ was observed for IDA in the base solution. The yield of N_2O in most cases is higher at $60^\circ C$. While the presence of the organic solute is required to obtain N_2O , the dependence of $G(N_2O)$ on the concentration or the identity of the particular organic solute is rather weak. Although we do not have a specific mechanism for the generation of N_2O our results below allow us to eliminate some pathways.

The effect of dose rate on $G(N_2O)$ suggests that a precursor to N_2O has two competing pathways. One is the pathway that leads to the formation of N_2O and involves only one radiolytically produced precursor. The other pathway does not lead to the production of N_2O and involves two radiation-produced species (the two might be identical species). At present we do not attempt to attach chemical identity to these precursors. The absence of the dose-rate effect at $60^\circ C$ requires that the pathway involving two radiation-produced species is unimportant at that temperature, and the pathway that involves only one precursor, and leads to N_2O , dominates. The temperature dependence implies that the latter pathway has a higher energy of activation than the former.

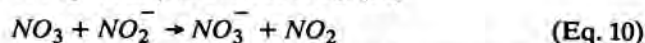
Origin of Nitrogens in N_2O . Experiments with ^{15}N -labeled glycine have been performed to determine what part of N in N_2O , if any, comes from the organic solutes. Samples were $0.3 M$ ^{15}N -glycine (98 atom %) in the base solution, irradiated at $30^\circ C$ at 4.5 krad/min to a dose of 540 krad. The ratios of m/e 45 to m/e 44 obtained for replicate samples were 0.0333 and 0.0336. These results indicate that less than 2.6% of the N_2O molecules formed contain an N from the glycine. Hence, the nitrogen in the N_2O must come overwhelmingly from the inorganic ions, NO_2^- NO_3^- . Nonetheless, the organic component is essential for the production of N_2O . The conclusion from the isotopic labeling experiments is in agreement with other observations. N_2O is produced in irradiated base solution containing glycolate; as glycolate contains no N, it is clear that the organic nitrogenous moiety is not important.

Yields of Other Gases. Oxygen generation was observed in the base solution in the absence of organic additives; we estimate $G(O_2) = 0.08 \pm 0.03$ over the intensity range studied. The generation of O_2 in this solution is commonly believed to result from the direct absorption of irradiation by the nitrate and/or nitrite ions. (12) When an organic solute is present in the base solution, O_2 is not observed as a product. In fact, analysis of the gases remaining in irradiated solutions containing $0.085 M$ each of EDTA and HEDTA, which were satu-

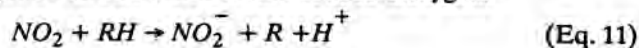
rated with air prior to the irradiation, showed that O_2 was consumed. The value obtained for the destruction of O_2 is $G(-O_2) = 7 \pm 1$. This high yield for dioxygen consumption in the presence of organic additives indicates that the majority of the primary radicals engender a sequence that produces organic radicals. The majority of the primary radicals (OH , e_{aq}^-) are converted to NO_2 radicals in the base solution studied here via the sequence of reactions (only the major pathways are shown):



In addition, NO_3 radicals produced by the direct effect will most probably convert to NO_2 . (21)



Thus a yield of $G(NO_2) \approx 15$ may be expected. Since the destruction of O_2 requires two reduction equivalents, a $G(-O_2) \approx 7$ will be obtained if all NO_2 radicals generate reducing organic radicals which in turn reduce dioxygen.



Thermal Generation of Gases in Preirradiated Solutions

For the various organics dissolved in the base solution, no thermal gas generation was detected at $30^\circ C$. The rate of thermal generation of H_2 and N_2O at $60^\circ C$ was also negligible (less than 1%) as compared to the rate of the radiolytic generation at the dose rates used in our experiments. However, much higher rates of thermal production of these gases were obtained at $60^\circ C$ from the base solution containing the sodium salts of EDTA (0.065 M), HEDTA (0.065 M), and citrate (0.1 M), which had been preirradiated to a dose of 31.5 Mrad at 0.51 krad/min. This solution was degassed after the preirradiation by bubbling with argon. An identical solution was not preirradiated but was otherwise treated identically as a control to check that no changes in the rate of gas generation took place in the solution due to standing for long periods of time, identical to the preirradiation times. The control solution was found to produce the gases at a very slow rate. However, the preirradiated solution thermally generated H_2 at a rate of about 3% of the radiolytic rate, and N_2O at a rate of about 15% of the radiolytic rate (compared to the rate of generation at 4.5 krad/min dose rate). Results from the thermal generation of H_2 from these preirradiated solution are shown in Fig. 5. The rates obtained from these experiments are summarized in Table III. Results quoted in earlier sections for the radiolytic generation of the gases were corrected, when necessary, for the thermal generation using the rates in Table III. These results show that the preirradiation leads to the formation of relatively long lived products that substantially enhance the thermal production of H_2 and N_2O . Formaldehyde or glyoxalate, known radiolytic degradation products of the chelators used here, may well constitute these products. (22)

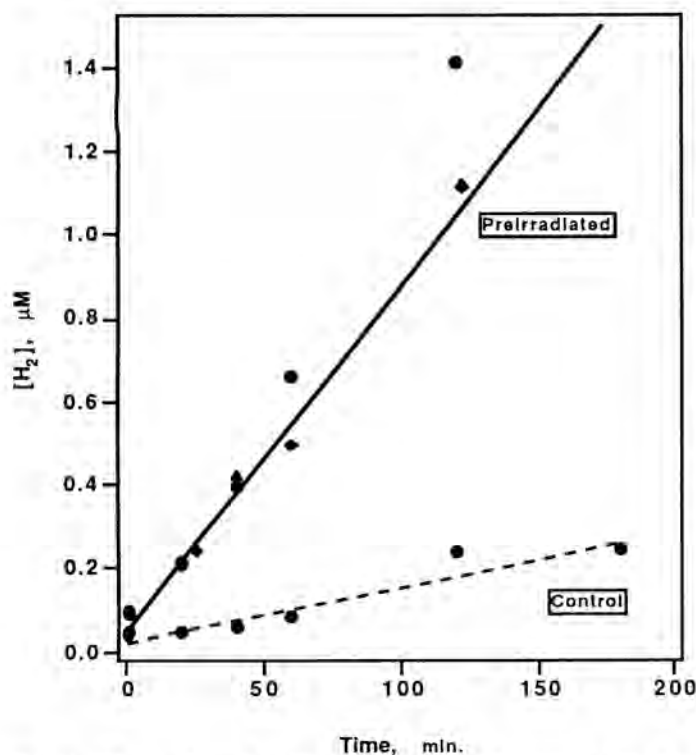


Fig. 5. Thermal production of H₂ at 60°C from several solutions. The preirradiated solution contained 0.065 M of each EDTA and HEDTA and 0.1 M citrate and was preirradiated to 31.5 Mrad at 0.51 krad/min. The control solution was identical except for the preirradiation.

TABLE III

Rates of Thermal and Radiolytic Generation of H₂ and N₂O at 60°C

Solution	10 ⁹ xH ₂ M min ⁻¹	10 ⁷ xN ₂ O M min ⁻¹	G(H ₂) ^a at 60°C	G(N ₂ O) ^a at 60°C
Preirradiated ^b	8.3	5.1	0.080	1.06
Control ^b	1.2	0.2	0.063	0.87
Base with 0.17 M IDA	1.3	not detected	0.045	0.94
Base with 0.085 M HEDTA	0.7	not detected	0.054	0.77

^a Samples received approximately 130 krad in 30 min irradiations.

^b Base solution with 0.065 M EDTA, 0.065 M HEDTA (sodium salts), and 0.1 M sodium citrate preirradiated to 31.5 Mrad at 0.51 krad/min at 30°C. The control solution was aged at 30°C for the same period of time.

The results in Table III also show the effect of preirradiation on the radiolytic yields of H₂ and N₂O. The preirradiation did not significantly alter the yields of H₂ when irradiated at 30°C, i.e. the yields from the preirradiated and control solutions were about the same. The yield of H₂ from irradiation of the control solution at 60°C is very near to what is expected based on the yields from EDTA, HEDTA, and citrate at 60°C. However, the yield from the preirradiated solution following further irradiation at 60°C is significantly higher than that from the control solution. Thus, the preirradiation causes a 20-25% increase in the radiolytic yield of H₂.

CONCLUSIONS

The radiolytic generation of H₂ and N₂O in highly concentrated solutions of nitrate, nitrite, and hydroxide and moderate concentrations of organic chelators has been investigated. Two sources for the generation of H₂, direct dissociation of water molecules to produce dihydrogen and hydrogen abstraction from the organic solutes, have been positively identified. Much larger yields of N₂O than of H₂ were observed when organic additives were present. The yield of N₂O is dose rate dependent but depends only weakly on the concentration or identity of the organic component. A significant observation in this study is the radiolytically induced thermal generation of both these gases. At temperature as low as 60°C, the efficient thermal, but radiolytically induced, generation of the gases may produce as much H₂ and N₂O as the radiolysis, or even more, depending on dose rates deposited in the mixed waste.

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