Detection of Gaseous Products in the Radiolysis of Aqueous Solutions¹

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A new technique for the direct determination of radiolytically produced gaseous products is discussed. The method consists of continuously bubbling a gas through a sample cell and monitoring the effluent with a mass spectrometer. It has been applied to the determination of H₂ and CO₂ produced in various aqueous solutions irradiated with ⁶⁰Co γ radiation. The yield of H₂ is found to be 0.51 molecules/100 eV in aerated ferrous sulfate solutions and in deaerated KBr solutions. The effect of saturating the ferrous sulfate solution with oxygen or addition of KNO₂ to the KBr solution is the same with a yield of H₂ of 0.43 molecules/100 eV. The yield of OH radicals as determined by the production of CO₂ in dilute oxygen-saturated formic acid solutions is 2.5 molecules/100 eV.

Introduction

A variety of gaseous products such as H_2 , O_2 , N_2 , and CO_2 can be formed in the radiolysis of water and aqueous solutions.² Determining the yields of these products is usually performed by freezing the sample after irradiation and pumping the volatile gases off. Analysis is then done by volumetric methods, gas chromatography, or mass spectrometry. These methods are time-consuming, and contamination or loss of products during handling is a problem. It is also very difficult to detect a particular product in the presence of a large excess of another gas. Large doses must be given or the gases separated by distillation or other methods. For this reason the detection of H_2 in aerated solutions is very difficult.

A few methods have been developed for the detection of gaseous products directly. The use of an electrolytic oxygen detector (Hersch cell) has been successfully used for determining the production of O_2 in ferrous sulfate-cupric sulfate solutions.³⁻⁵ Burns has used a Hersch cell in a subtractive manner to detect hydrogen, and he has also used an infrared detector for determining the production of CO_2 in the radiolysis of formic acid solutions.⁵ However, the last two techniques are cumbersome and the sensitivity and accuracy, especially for hydrogen, are poor. In this paper a new technique for the on-line determination of radiolytic gases is described. It involves bubbling a gas through a sample cell and monitoring the effluent with a mass spectrometer. By continuously monitoring the parent peak of the desired product, quantitative analysis can be readily accomplished. A mass spectrometer is versatile so that many different gasses can be monitored, even simultaneously, and it is very sensitive. The apparatus has been applied to the measurement of H_2 produced by ⁶⁰Co γ radiation in a variety of solutions and the production of CO₂ in oxygen-saturated formic acid solutions, and the results are discussed.

Experimental Section

The apparatus consisted of a well-regulated gas stream that continuously bubbled through a sample cell made from a 1-cm quartz cuvette. An electrolysis cell and a septum for the injection of calibration gases were placed upstream from the sample cell. Although the electrolysis cell was not used for calibration (see below), it was left in place to moisturize the gases. The effluent of the sample cell was monitored by a Balzers Model QMS 311 quadrupole mass spectrometer. The mass spectrometer ion source was coupled to the gas stream directly by a $50-\mu$ m diameter fused silica capillary tubing (Chrompack, Inc.) ~30 cm long. A 170 L/s turbomolecular pump was able to maintain a pressure of 1×10^{-5} Torr in the ion source region. The gas flow through the capillary was 0.1 mL/min resulting in a transit time of 0.4 s so that gases eluting very quickly could be detected without bias and with very little distortion due to eddy effects. The main gas stream was maintained at a flow rate of 25 mL/min, which in the present case represented a good compromise between a low split ratio and fast evolution of gases from the liquid samples. The output of the mass spectrometer detector (17-stage electron multiplier) was coupled to an integrating linear recorder. The mass spectrometer was set to monitor the parent peak of the product of interest (i.e., mass 2 for H₂ and 44 for CO₂).

The irradiations were performed by using a Shephard ⁶⁰Co γ source with a dose rate of 26 krad/min. The source was calibrated by observing the oxidation of ferrous ions in the Fricke dosimeter using the same sample cell and configuration as in gas analysis. The production of Fe³⁺ was determined spectrophotometrically at 304 nm and 25 °C with an extinction coefficient of 2194 M⁻¹ cm⁻¹ and 15.45 molecules/100 eV for the yield of Fe^{3+,6} The ratio of the absorption coefficient of 0.8 N sulfuric acid to water was taken to be 1.025.⁷ Typical energy input was 2 × 10¹⁸ eV in 4 mL of solution (dose of 8 krad).

The purging gas was dry oxygen, dry compressed air, or oxygen-free nitrogen. The solutions were 1 or 10 mM formic acid, 1 mM KBr, or 1 mM KBr with 1 mM KNO₂ and no added acid. The Fricke solutions were 10 mM ferrous ammonium sulfate in 0.8 N sulfuric acid with no added chloride. The electrolysis cell contained 0.5 M NaOH. All solutions were made with triply distilled water.

Results and Discussion

The response of the mass spectrometer to H_2 was linear throughout the range studied ($\sim 0.02-1 \ \mu mol$) with a sensitivity of at least a few ppm. However, the response was different for each purging gas. The production of H_2 using an electrolysis cell was within a few percent of that found by direct injection of H₂ only with nitrogen as the purging gas. With aerated solutions the efficiency of the electrolysis cell was 76% and dropped to about 16% with oxygen-saturated solutions. The presence of oxygen appears to lead to intermediates that need an excess of electrons for the production of molecular hydrogen. Throughout this work a gas-tight syringe was used to inject H₂ or CO₂ for calibration of the mass spectrometer. The gas stream bubbled continuously through the sample, and although the radiolysis times were short (6-24 s), there was some delay before the radiolytic products were purged from the solution. The evolution of both H_2 and CO_2 from the solutions was complete within ~ 6 min following irradiation, and the error in determining their yields is estimated to be less than 2%.

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⁽²⁾ Allen, A. O. The Radiation Chemistry of Water and Aqueous Solutions; Van Nostrand: Princeton, NJ, 1961.

⁽³⁾ Burns, W. G.; May, R.; Baverstock, K. F. Radiat. Res. 1981, 86, 1.
(4) LaVerne, J. A.; Schuler, R. H.; Burns, W. G. J. Phys. Chem. 1986, 90, 3238.

⁽⁵⁾ Burns, W. G.; Sims, H. E. J. Chem. Soc., Faraday Trans. 1 1981, 77, 2803.

⁽⁶⁾ Schuler, R. H.; Allen, A. O. J. Chem. Phys. 1956, 24, 56.

⁽⁷⁾ Schwarz, H. A.; Losee, J. P., Jr.; Allen, A. Ó. J. Am. Chem. Soc. 1954, 76, 4693.

TABLE I: H₂ Formation in Various Solutions

solution	<i>G</i> (H ₂)	ref	
Fricke, deaerated	3.84	this work	
calcd from Fricke ^a	4.11	15	
Fricke, aerated	0.51	this work	
calcd from Fricke ^a	0.50	15	
Fricke, O_2 saturated	0.43	this work	
Fricke, O_2 saturated	0.43	11	
Fricke, O_2 saturated	0.38	9	
KBr, O_2 saturated	0.41	10	
KBr, deaerated	0.52	this work	
KBr, deaerated	0.50	11	
KBr, deaerated	0.45	12	
KBr, deaerated	0.46	9	
KBr, deaerated	0.46	13	
KNO_2 , deaerated	0.46	13	
KBr, KNO ₂ , deaerated	0.43	this work	
KBr, KNO_2 , deaerated	0.41	13	
KBr, KNO_2 , deaerated	0.42	5	
KNO_2 , N_2O , deaerated	0.43	7	
KNO_2 , N_2O , O_2 saturated	0.41	this work	

^a In aerated solutions $G(H_2) = G_{H_2} = G(Fe^{3+})_{deserated} - \frac{1}{2}G-(Fe^{3+})_{serated}$. In deaerated solutions $G(H_2) = G_{H_2} + G_H = \frac{1}{2}G-(Fe^{3+})_{serated}$. (Fe³⁺)_{deaerated}

The production of H_2 has been determined in a variety of solutions,^{5,7-14} and the results are shown in Table I. In deaerated ferrous sulfate solutions the measured yield of H_2 is equal to the sum of the molecular H_2 yield and the H atom yield. It is seen that the present results are slightly lower than that expected using mass balance and the observed yields of Fe^{3+} in aerated and deaerated ferrous sulfate solutions.¹⁵ In aerated ferrous sulfate solutions the observed yield of H_2 is equal to the molecular yield and is found to be 0.51 molecules/100 eV in good agreement with the expected yield. This value decreases to 0.43 molecules/100 eV in oxygen-saturated solutions because of increased intraspur scavenging of H atoms.

There is more variation in the reported H_2 yields in deaerated KBr solutions as seen in Table I, but in general the yields are about the same as in aerated ferrous sulfate solutions. However, the addition of KNO_2 decreases the yields to values similar to that found in oxygen-saturated ferrous sulfate solutions. This result suggests that 1 mM solutions of NO₂⁻ or oxygen are equally

- (12) Schwarz, H. A. J. Am. Chem. Soc. 1955, 77, 4960.
- (13) Schwarz, H. A.; Caffrey, J. M., Jr.; Scholes, G. J. Am. Chem. Soc. 1959, 81, 1801.
 - (14) Appleby, A.; Schwarz, H. A. J. Phys. Chem. 1969, 73, 1937.
 (15) Barr, N. F.; Schuler, R. H. J. Phys. Chem. 1959, 63, 808.

TABLE II: Production of CO₂ and H₂ in Oxygen-Saturated Formic Acid Solutions

solution	$G(CO_2)$	$G(H_2)$	ref	
1 mM HCOOH	2.47 2.46 2.53	0.39 0.42 0.42	this work 17 18	
10 mM HCOOH	2.69 2.76 2.86	0.44 0.41 0.40	this work 17 18	
1 mM HCOONa	2.65		5	

efficient in scavenging intraspur hydrogen atoms. There is very little additional H atom scavenging when KBr-KNO₂ solutions are saturated with oxygen.

The production of CO_2 from oxygen-saturated formic acid solutions has been thoroughly studied, and it is well-known that $G(CO_2) = G_{OH}$.¹⁶⁻¹⁸ Table II shows the yields of CO₂ found in formic acid and sodium formate solutions. The reaction of sodium formate with OH radicals is approximately an order of magnitude greater than formic acid,¹⁸ which is supported by the results in Table II. With increasing formic acid concentration the yield of CO₂ increases because of increased scavenging of OH radicals in the spur. It appears that the yield of H_2 is also found to increase with increasing formic acid concentration, although the differences are very close to experimental error. This increase is expected because if fewer OH radicals are available to recombine with H atoms, the yield of H₂ should increase. These results show that at low scavenger concentrations the yield of OH radicals is about 2.5 molecules/100 eV.

It has been shown in these examples that it is now possible to accurately and easily determine the yield of gaseous products in the radiolysis of aqueous solutions. The technique should also work with other systems such as determining the yield of aqueous electrons by monitoring the production of N₂ in N₂O-saturated solutions, although the high background N_2^+ peak from N_2O may cause some difficulty. It should also be possible to directly measure production of gaseous products in the radiolysis of hydrocarbons. This will be especially useful in determining isotopic ratios such as H_2 :HD:D₂. With suitable instrumentation these yields can be measured simultaneously. Direct determination of gaseous products will be very useful where instantaneous feedback is very desirable such as in heavy ion radiolysis studies. Preliminary heavy ion experiments using this technique have been very successful. Further development may make this technique even more useful to radiation chemistry.

Registry No. H₂, 1333-74-0; CO₂, 124-38-9; KBr, 7758-02-3; H₂O, 7732-18-5; O₂, 7782-44-7; KNO₂, 7758-09-0; OH, 3352-57-6; HCOOH, 64-18-6; HCOONa, 141-53-7; ferrous sulfate, 7720-78-7.

⁽⁸⁾ Johnson, E. R.; Allen, A. O. J. Am. Chem. Soc. 1952, 74, 4147.
(9) Hochanadel, C. J. J. Phys. Chem. 1952, 56, 587.

⁽¹⁰⁾ Ghormley, J. A.; Hochanadel, C. J. J. Am. Chem. Soc. 1954, 76, 3351

⁽¹¹⁾ Miller, N.; Wilkinson, J. Trans. Faraday Soc. 1954, 50, 690.

⁽¹⁶⁾ Hart, E. J. J. Phys. Chem. 1952, 56, 594.

⁽¹⁷⁾ Hart, E. J. J. Am. Chem. Soc. 1954, 76, 4312

⁽¹⁸⁾ Draganic, I. G.; Nenadovic, M. T.; Draganic, Z. D. J. Phys. Chem. 1969, 73, 2564.