

COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Tome X
(Série B)

İSTANBUL
ŞİRKETİ MÜRETTİBİYE BASIMEVİ
1962

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara," est une organe de publication englobant toutes les disciplines scientifiques représentées à la Faculté: Mathématiques pures et appliquées, Astronomie, Physique et Chimie théoriques, expérimentales et techniques, Géologie, Botanique et Zoologie.

La Revue, à l'exception des tomes I, II, III, comprend trois séries:

Série A: Mathématiques et Physique.

Série B: Chimie.

Série C: Sciences naturelles.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté. Elle accepte cependant, dans la mesure de la place disponible, les communications des savants étrangers. Les langues allemande, anglaise et française sont admises indifféremment. Les articles devront être accompagnés d'un bref sommaire en langue turque.

Adresse:

Fen Fakültesi Tebliğler Dergisi,

Fen Fakültesi,

Ankara

Comité de Rédaction de la Série B:

O. Gerngross

S. Saracoğlu

S. Aybar

Secrétaire de publication

A. N. Ergun

COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série : B Chimie-Physique

Tome X

1962

Radiation Chemistry Studies of Aqueous Iodine-Iodide Solutions †

Cemil B. ŞENVAR*

(Department of Physical Chemistry, Faculty of Science,
Ankara University)

Özet: Havasız İyodür-İyod çözeltilerinin γ ışınları ile irradasyonunda moleküler ürünler ile serbest radikallerin teşekkül verimlerine pH'in etkisi incelendi. İyod böyle bir ortamda meydana gelen hidrojen atomlarını ve iyodür iyonu ise hidroksil radikallerini yakalamaktadır. Denel neticeler göstermiştir ki iyodun azalma verimi $G(-I_2)$, Hidrojen peroksit'in teşekkül verimi $G(H_2O_2)$ ile hidrojenin teşekkül verimi $G(H_2)$ farkına eşittir. Öte yandan teorik mülâhazalar ise $G(-I_2)$ 'un $G(H)-G(OH)$ farkının bir ölçüsü olduğunu gösteriyor. pH 1 ile 6 arasında arttıkça, $G(H_2O_2)$ değerlerinin $G(H_2)$ değerlerine yaklaştığı bulunmuştur. Bu durumdan faydalanarak $G(H)$ ve $G(OH)$ değerleri hesaplanmış ve bunlar literatürdeki değerlerle karşılaştırılarak münakaşası yapılmıştır.

* *

Abstract: The effect of pH on molecular product and free radical yields is reported for γ -ray irradiated air-free iodine-iodide solutions. Iodine scavenges hydrogen atoms and iodide ion scavenges hydroxyl radicals. As the pH increases in the range from 1 to 6, $G(H_2O_2)$ approaches $G(H_2)$ and the difference $G(H)-G(OH)$ approaches zero. Values of $G(H)$ and $G(OH)$ found in this work are compared with previous values.

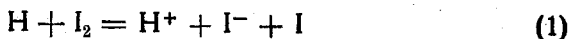
Introduction

Free radical scavengers depress hydrogen and hydrogen peroxide yields in irradiated aqueous solutions.¹⁻⁴ Solutes reducible by hydrogen atoms lower the hydrogen yield and solutes oxidizable by hydroxyl radicals lower the hydrogen peroxide yield. These reactions depend on pH.⁵⁻⁸

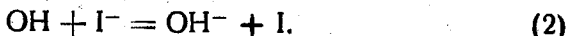
In the present work, the effect of pH on the relative number of hydrogen and hydroxyl radicals escaping from transient

* Address : Fen Fakültesi, Ankara-Turkey

"spurs" resulting from the γ -ray irradiation of water is reported. By using dilute iodine plus iodide solutions the difference between the hydrogen atom yield and hydroxyl radical yield, $G(H) - G(OH)$, is obtained. The iodine scavenges hydrogen atoms by the reaction



and the iodide atoms scavenge hydroxyl radicals by reaction (2)



Then



If $G(H) = G(OH)$, no change is expected in iodine concentration because the iodine consumed in (1) is reformed in (3). However it is found that iodine is consumed and that $G(-I_2)$ and $G(H_2O_2)$ are pH dependent.

Experimental

The solutions prepared with triply distilled water contain 5–60 μ M iodine and 0.13 to 1.0 m M potassium iodide. The pH's are adjusted from 0.61 to 6.0 with sulfuric acid. Pyrex cells of ~ 12 cc. capacity are filled with oxygen-free solutions and irradiated in a Co^{60} γ -irradiation chamber⁹ supplying dosage rates of 1.37×10^{21} and 0.23×10^{20} ev/l. min. as measured by the Fricke Dosimeter using a $G(Fe^{+++})$ yield of 15.6. The total dose given is between 3×10^{20} and 40×10^{20} ev/l. Hydrogen analyses are run in a Van Slyke micro-gas apparatus and the ferric ion concentrations are measured by the optical absorbance at 3020 \AA .

Free iodine and hydrogen peroxide are determined by triiodide ion absorption¹⁰ at 3500 \AA in a 10 cm. absorption cell. The optical density of reagent solutions must be measured at the same time as the irradiated sample. This is a necessary precaution since the optical density of the reagent solutions change appreciably with time.

The following stock reagent solutions are used for determining iodine and hydrogen peroxide: (I) 10 g. of potassium

hydrogen phthalate in 500 ml. of water; (II) 33 g. potassium iodide, 1 g. sodium hydroxide and 10 ml. of 1 % ammonium molybdate in 500 ml. of water; (III) same as (II) without ammonium molybdate.

(i) a 50/50 mixture of (I) and (II) and an equal volume of the sample to be analyzed is used to find total hydrogen peroxide plus iodine.

(ii) a 50/50 mixture of (I) and (III) and an equal volume of sample is used to measure iodine. In both cases the optical density is multiplied by the factor 7.63 (for 10 cm. absorption cells) to obtain the concentrations in units of 10^{-6} M. The difference between (i) and (ii) gives hydrogen peroxide.

Results and Discussion

$G(H_2)$, $G(H_2O_2)$ and $G(-I_2)$ are plotted in Figure 1 as a function of pH. Over the limited ranges studied, all dosage curves are linear. Note from Figure 1 that there is no observable influence of potassium iodide concentration in the range from 0.13 to 1.0 mM. Also there is no effect of iodine concentration in the range from 0.005 to 0.060 mM. These results indicate that all of the radicals diffusing from the spur into the volume of liquid are successfully scavenged. It is clear that the results reported here, particularly for H_2O_2 , are in partial disagreement with previously reported values. The difficulty in the analytical method used is appreciable.

$G(H_2)$ is independent of pH and equals 0.43 in agreement with the results of previous authors.^{9,13} According to the results of this work $G(H_2O_2)$ and $G(-I_2)$ have a flat maxima at a pH of 2.0. Both yields slowly decrease with increasing pH. In slightly acid and unbuffered solutions $G(-I_2)$ becomes very small and $G(H_2O_2)$ parallels the drop in $G(-I_2)$.

Schwarz, Losee and Allen⁷ report an initial increase in $G(H_2)$ at low pH's but as iodine forms in the solution, $G(H_2)$ again decreases to the molecular product yield of 0.39 (in 0.8 N sulfuric acid). The results of this work agree with these. Since iodine is added to the solutions initially one expects, as it is found, that $G(H_2)$ will be independent of pH. This result is explained by assuming that the excess hydrogen forming reaction

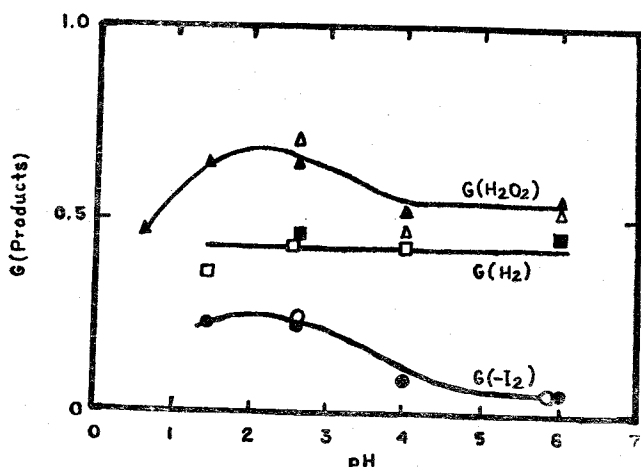


Fig. 1. Effect of pH on $G(\text{H}_2\text{O}_2)$, $G(\text{H}_2)$ and $G(-\text{I}_2)$ in aqueous air-free iodine-iodide solutions irradiated by Co^{60} γ -rays. (Open symbols, 0.13 mM; Dark symbols, 1.00 mM)



is effectively suppressed by reaction (1).

At a pH of 2, in these *oxygen-free* solutions it was found that $G(\text{H}_2\text{O}_2)$ is 0.68, a value somewhat lower than 0.75 reported by Sworski⁴ for aqueous *aerated* potassium bromide solutions.

The results reported here allow to calculate the difference between the hydrogen atom yield, $G(\text{H})$ and the hydroxyl radical yield, $G(\text{OH})$. To do this, assume that all «bulk» hydrogen atoms and hydroxyl radicals react according to reactions (1) and (2), respectively, and that iodine atoms recombine according to (3), then

$$G(-\text{I}_2) = \frac{G(\text{H}) - G(\text{OH})}{2} \quad (5)$$

Here one assumes that the yields, $G(\text{H})$ and $G(\text{OH})$, remain constant over the iodine and iodide concentration ranges studied. From Figure 1 we note that $G(-\text{I}_2)$ equals 0.26 and from equation (5) that $G(\text{H}) - G(\text{OH})$ equals 0.52. This difference in radical yield decreases to 0.1 at pH 6.

Experimentally we find that

$$G(-I_2) = G(H_2O_2) - G(H_2) \quad (6)$$

From the simple reaction scheme 1, 2, 3 shown above and the general equation for material balance in aqueous radiolysis reactions

$$G(-H_2O) = 2G(H_2) + G(H) = 2G(H_2O_2) + G(OH), \quad (7)$$

we may derive equation (6).

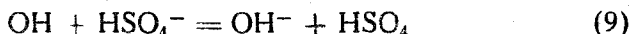
Rearranging (7) to

$$\frac{G(H) - G(OH)}{2} = G(H_2O_2) - G(H_2), \quad (8)$$

then by combining (5) and (8), equation (6) is obtained.

The reason for this decrease in $G(H) - G(OH)$ with pH is not clear. Since $G(-H_2O)$ is independent of pH⁵ it is concluded that OH radicals recombine more readily at low pH's than at higher pH's. At any rate, as the pH increases, $G(H)$ becomes more nearly equal to $G(OH)$ and $G(H_2O_2)$ becomes more nearly equal to $G(H_2)$.

The low pH's are obtained by adding sulfuric acid to the solution. Thus the bisulfate ion may act to scavenge hydroxyl radicals by the reaction:



Capture of another hydroxyl radical by the HSO_4 radical gives Caro's acid. Since Caro's acid cannot be distinguished from hydrogen peroxide by the method of analysis used here the importance of reaction (9) in increasing the molecular peroxide yield is uncertain.

$G(H)$ and $G(OH)$ each may be calculated by combining the present data with that obtained using ferric sulfate-formic solutions with or without cupric sulfate^{12,13,14}. These systems give the sum, $G(H) + G(OH)$.

At a pH of 2, $G(H) + G(OH)$ equals 6.33 in dilute solutions. Combining this results with our value of 0.52 for the difference, $G(H) - G(OH)$, it is found that $G(H)$ equals 3.42 and $G(OH)$ equals 2.88. These yields compare with 3.47 and 2.55 respectively as obtained in the formic acid-oxygen system at pH=2.1.

The author is grateful to ICA AID for a research fellowship, to Argonne National Laboratory for permission to publish this work and finally to Dr. Edwin J. Hart for his great help.

References

- [1] J. W. Boyle, C. J. Hochanadel, J. A. Ghormley and W. F. Kieffer, *Proc. of the International Conf. on Peaceful Uses of Atomic Energy*, Geneva 7, 576 (1955).
- [2] H. A. Schwarz, *J. Am. Chem. Soc.* 77, 4960 (1955).
- [3] J. A. Ghormley and C. J. Hochanadel, *Radiation Research* 3, 227 (1956).
- [4] T. J. Sworski, *J. Am. Chem. Soc.* 76, 4687 (1954).
- [5] E. J. Hart, *Ann. Rev. Phys. Chem.* 5, 139 (1954); *J. Am. Chem. Soc.* 76, 4198 (1954).
- [6] J. Weiss, *Experimentia* 12, 280 (1956); *Nature* 165, 728 (1950).
- [7] H. A. Schwarz, J. P. Losee and A. O. Allen, *J. Am. Chem. Soc.* 76 4693 (1954).
- [8] E. R. Johnson, *J. Chem. Phys.* 21, 1417 (1953).
- [9] R. A. Blomgren, E. J. Hart and L. S. Markheim, *Rev. Sci. Instruments* 24, 298 (1953).
- [10] A. O. Allen, T. W. Davis, G. V. Elmore, J. A. Chormley, B. M. Haines and C. J. Hochanadel, ORNL-130 (October 11, 1949).
- [11] H. Fricke and E. J. Hart, *J. Chem. Phys.* 3, 596 (1935).
- [12] E. J. Hart, *J. Am. Chem. Soc.* 77, 5786 (1955).
- [13] J. H. Baxendale and D. Smithies, *Z. Phys. Chem.* 7, 242 (1956).
- [14] D. M. Donaldson and N. Miller, *Radiation Research*, 9, 487-97 (1958).

(Received 7. 5. 1962.)