

at absorption zones of different complexes), some conclusions concerning the kinetics of different complexes formation may be reached.

Spectroscopic examination of the emitted light were also performed, using a spectrograph, which analyses the outgoing beam of light. A similar technique has also been adopted from time to time in absorption measurements. For that purpose the source of light (tungsten bulb, flash burner, etc.) is provided to be installed in the irradiation chamber.

A recent application of the device described here is the illumination of certain solutions with high-intensity filtered or monochromatic light (visible, ultra-violet) of the  $\gamma$ -irradiated sample. By using this technique some interesting effects have been observed.

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S. MINC  
Z. P. ZAGÓRSKI

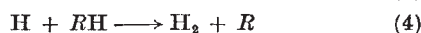
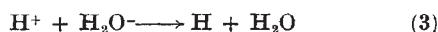
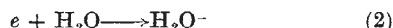
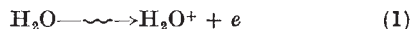
Department of Radiation Chemistry,  
Institute of Nuclear Research,  
Warsaw.

<sup>1</sup> Zagórski, Z. P., and Nev, W., *Nukleonika*, **5**, 219 (1960).

<sup>2</sup> Dainton, F. S., *Disc. Farad. Soc.*, **12**, 44 (1952).

### pH Effects in the Radiolysis of Aquo-Organic Systems

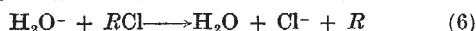
RECENT studies of pH effects in the radiolysis of aqueous solutions have demonstrated the existence of two types of reducing species in irradiated water. The indications are that these species correspond to the solvated electron,  $H_2O^-$ , and the H atom<sup>1,2</sup>. Hayon and Weiss have proposed that the marked pH dependence of hydrogen yields in the radiolysis of air-free solutions of organic compounds is consistent with:



where (3) and hence (4) become less important at the higher pH values as competing reactions lead to removal of  $H_2O^-$  through:



or through capture by solute, for example:



Now, in the radiolysis of air-free formic acid solutions, the yield not only of hydrogen but also of carbon dioxide decreases with increasing pH, and the yield of carbon dioxide becomes essentially zero at pH 7 and above<sup>3</sup>. This latter phenomenon has been interpreted elsewhere<sup>4</sup> in terms of an effect of pH on the relative rates of the two reactions:



Allan and Scholes<sup>5</sup>, on the other hand, have recently proposed that carbon dioxide is produced under all conditions of pH (through an unspecified mechanism), and that it is afterwards removed through a back reaction between carbonate and the solvated electron



followed by 7a or the equivalent. Although carbon dioxide in aqueous solution is known to be reduced to formic and/or oxalic acid under various conditions

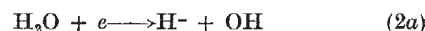
of radiolysis<sup>5,6</sup>, there is a question as to whether or not reaction 8 could account for the fact that the 'steady-state' concentration of carbonate in alkaline formate solutions is essentially zero<sup>3</sup>. To obtain information on this point, we have investigated the products labelled with carbon-14 formed in the  $\gamma$ -ray radiolysis of the systems (I) 0.1 M HCOONa-0.01 M NaH<sup>14</sup>CO<sub>3</sub>, (II) 0.1 M H<sup>14</sup>COONa-0.01 M NaHCO<sub>3</sub>.

The radiometric and analytical techniques were those developed in an earlier radiation-chemical study of aqueous formic acid solutions labelled with carbon-14 (ref. 4). Both H<sup>14</sup>COOH and (<sup>14</sup>COOH)<sub>2</sub> were determined because of the possibility of the step:



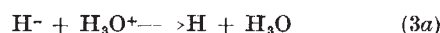
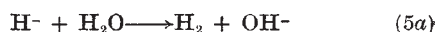
At a dose of  $9 \times 10^{18}$  eV./ml., we obtained with solution (I) the values  $G(H{}^{14}COOH) \approx 0.14$ ,  $G({}^{14}COOH)_2 \approx 0.01$ . Solution (II) under the same conditions of irradiation gave  $G({}^{14}COOH)_2 \approx 1.5$ . It is concluded, therefore, that the reductive reaction (8) is relatively unimportant even at carbonate concentrations as high as one-tenth that of the formic acid. Presumably, the solvated electron is removed in alkaline formic acid solutions through reaction (5).

In this connexion it is of interest to note that a reaction mechanism formally equivalent to the sequence (1) to (5) can be derived on the assumption that the electron formed in step (1) undergoes dissociative capture to yield the hydride ion:



The appearance of H<sup>-</sup> at an electron-impact potential of 5.6 eV. has been associated by Laidler<sup>7</sup> with a repulsive state of the H<sub>2</sub>O<sup>-</sup> molecule ion. Factors influencing the relative yields of processes 2 and 2a have been treated by Magee and Burton<sup>8</sup>.

Disposition of H<sup>-</sup> may be formulated in terms of the competing steps:



Reaction (5a) has recently been identified experimentally in electron-impact studies of Muschlitz and Bailey<sup>9</sup>. The proposal that H atoms could be liberated in the bulk of the solution through step (3a) is predicated on the hypothesis that electron transfer in aqueous solution may occur at large separations<sup>10</sup>.

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WARREN M. GARRISON  
BOYD M. WEEKS  
SIBYL COLE

Lawrence Radiation Laboratory,  
Crocker Laboratory,  
University of California,  
Berkeley 4, California.

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<sup>9</sup> Muschlitz, E. E., and Bailey, T. L., *J. Phys. Chem.*, **60**, 681 (1956).

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