Pulse Radiolytic Determination of the Ultraviolet Absorption of Hydrogen Atoms in Aqueous Solution

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PULSE radiolysis of deaerated aqueous solutions of 10^{-3}M-$HClO_4$ + 0·027M-H_2 [$p(H_2)$ = 35 atmos.] has revealed an optical absorption transient at 2000—2300 Å, which we assign to the presence of free hydrogen atoms in the aqueous solution.

The 11 Mev Risø Linac delivered the 1·2 μsec. single-electron pulses used (dose *ca.* 10^{20} ev/l.). The optical detection system, which included a double prism monochromator and a 450 w Xe-lamp with 25 times enhanced luminance in pulsed operation, enabled us to make accurate measurements of the absorption transient ($t_{\frac{1}{2}}$ *ca.* 8 μsec.) (i) down to 2000 Å and (ii) from 0·2 μsec. after the electron pulse.

Of the primary radiolytic products on the right-hand side of reaction scheme (1)[1]

$$H_2O \rightsquigarrow H,\ OH,\ e_{aq}^-,\ H_2,\ H_2O_2,\ H_3O^+,\ OH^- \quad (1)$$

only H, H_2, H_2O_2, and H_3O^+ could still be present a few microseconds after the electron pulse. Thus under our conditions OH reacts with H_2 to form H ($t_{\frac{1}{2}}$ 0·5 μsec.), e_{aq}^- is converted into H atoms ($t_{\frac{1}{2}}$ 0·03 μsec.), and OH^- reacts very fast with H_3O^+: H_3O^+ and H_2 are known not to absorb light at

2000—2300 Å. The primary radiolytic yield of H_2O_2 ($G_{H_2O_2} = 0{\cdot}7$)[1] cannot account for the entire absorbance after the electron pulse. After correcting for the absorbance[2] due to H_2O_2, we assign the corrected optical absorption (disregarding the first two μsec. after the electron pulse) to free H atoms. The calculated molar decadic absorptivity ϵ_H of H is given in the Table. ϵ_H Has been calculated assuming $G(\text{H}) = 5{\cdot}8$ and has been corrected for radical recombination during the pulse. The assignment of the observed optical absorption to H atoms is consistent with the following observations. (1) The absorption was found to decay by second-order kinetics. By using the values of ϵ_H at 2000 and 2100 Å given in the Table, the same value of $2k_{H+H} = (1{\cdot}55 \pm 0{\cdot}10)10^{10}$M^{-1} sec.$^{-1}$ was found at both wavelengths. This value agrees with previous work.[3–6] (2) The absorption transient as measured at 2100 Å was unaffected by substitution of N_2O in a concentration of more than 2×10^{-3}M for 10^{-3}M-$HClO_4$ in the irradiated, H_2-pressurized solution. (3) On addition of 10^{-3}M-O_2, the absorption transient was found to be completely quenched with the formation of a product with the absorption spectrum of HO_2.[7] In a set of experiments with 10^{-3}M-$HClO_4$ containing O_2 in concentrations from zero to $2{\cdot}6 \times 10^{-4}$M (no H_2) the absorbance measured at 2000 Å, $0{\cdot}2$ μsec. after the electron pulse, corresponded to $k(\text{H} + O_2)$ *ca.* 10^{10}M^{-1} sec.$^{-1}$. (The absorbance was assumed to be due only to H, OH, and HO_2. At 2000 Å the absorptivity of HO_2 was found to be smaller than that of H). The value found for $k(\text{H} + O_2)$ is in agreement with previous data.[4–6,8]

ϵ_H *and* $2k_{H+H}$ *in* 10^{-3}M-$HClO_4$ + $0{\cdot}027$M-H_2 *at* 23—25°

Wavelength (Å)	ϵ_H (M^{-1}cm.$^{-1}$)	$2k_{H+H} \times 10^{-10}$ (M^{-1}sec.$^{-1}$)
2500	0	
2400	0	
2300	70	
2200	210	
2100	560	1·51
2000	900 ± 30[a]	1·55 ± 0·10[a]

[a] Standard deviation.

If impurities were the cause of the observed absorption transient assigned to H atoms in 10^{-3}M-$HClO_4$ + $0{\cdot}027$M-H_2 they would have to be present in a concentration of at least 10^{-4}M in order to have reacted completely with H or OH in a few microseconds after the electron pulse. Such a high concentration of impurities is considered unlikely in view of the careful purification of the water (triply distilled) and H_2 (passage through 2 m. of molecular sieve at −196°) used. $HClO_4$ was Merck analytical grade and several different bottles gave the same results. Furthermore, when 10 electron pulses were given to the same solution it was found that the kinetics of the tenth pulse was identical within experimental error with the kinetics of the first pulse.

It might be argued that species other than those listed on the right-hand side of reaction scheme (1) are responsible for the optical absorption at 2000 Å. If this were the case the yield G of such assumed species must be larger than one, otherwise the value of $2k$ for recombination calculated from the slopes of 1/absorbance against time curves would be too large. There is, however, no evidence of any such other primary species with $G > 1$ and with half-life times of several microseconds except those listed in reaction scheme (1).

The absorption spectrum of H atoms in aqueous solution appears to be shifted by several hundred of Å units compared with the gas-phase absorption at 1215·7 Å.[9] We suggest that this enormous red shift is only apparent and is due instead to a much smaller red shift of the water absorption band beginning at 1860 Å. Perturbation of the first excited singlet state of water molecules by neighbouring H atoms involving partial charge transfer is suggested for the interpretation of ϵ_H in the Table.

The absorption spectrum of H atoms at 2000—2300 Å will be shown in a coming paper to account for most of the previous anomalies observed in pulse radiolysis of N_2O, H_2O_2, and $HClO_4$ aqueous solutions.[10]

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