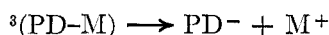


the role of the complex CT triplet state in the photoionization process.

Experiments were carried out at various temperatures down to 77°K, in 2:1 ether-isopentane deaerated solutions. Flash absorption experiments employed a conventional low-temperature flash photolysis setup.^{5b} Correlated flash absorption and emission measurements were made using an AVCO-EVERETT 3371-Å N₂ laser as the exciting source in a front face irradiation setup. The PD negative ion was followed in deaerated PD-M solutions, excited in the CT band, by recording its absorption at 660 nm. At sufficiently low temperatures a distinct growing-in stage of the radical anion absorption was observed (Figure 1a). Simultaneously, we have also followed the decay of the PD-M charge-transfer triplet state by recording the phosphorescence intensity at 500 nm² as a function of time (Figure 1b). (We have not been able to detect an absorption in the 350–800-nm range which could be assigned to a T-T transition of the CT complex.) The kinetic analysis in Figure 1c indicates that both processes are of first order, exhibiting a common rate constant: $k \sim 800 \text{ sec}^{-1}$ at $-156 \pm 1^\circ$. In oxygen-saturated solutions the formation of PD⁻ does not take place. In solutions of low O₂ content ($\sim 10^{-4} M$) the photoionization process can still be detected. It is then found that the O₂ effect is one of reducing the PD⁻ yield as well as that of decreasing the half-life of the growing-in process (both by a factor of ~ 50) relatively to deaerated systems. Simultaneously a quenching of the CT phosphorescence by O₂ takes place.

All these observations lead to the conclusion that the charge-transfer triplet, ³(PD-M), undergoes spontaneous ionization according to⁶



The process competes with deactivation of the triplet state in alternative paths, such as emission or the reaction with oxygen. Although predicted long ago from theoretical considerations,^{1a} this is the first experimental detection of the spontaneous ionization of a complex CT triplet state. In a rigid glass at 77°K only the phosphorescence, but not the PD⁻ absorption, could be detected. The ionization process is then suppressed, probably by sterical or thermal restrictions.

The physical picture involved in the dissociation of the complex CT triplet is closely related to that recently suggested⁶ for the quenching of the triplet state of an organic donor (diphenyl-*p*-phenylenediamine) by a ground-state acceptor (diphenyl-*p*-phenylenediimine). From kinetic considerations a mixed triplet excimer of CT character was suggested as intermediate in the charge-transfer quenching process. In the present system, where the CT triplet is populated by direct excitation of the ground-state donor-acceptor pair, the dissociation process can be directly observed by absorption and emission spectroscopy. The results re-

ported above bear on the mechanism of deactivation of molecular complexes in their CT triplet state as well as on that of the closely related mixed triplet excimers. They also suggest a general path for photoionization of organic CT systems. The applicability of the same mechanism to other complexes is now being investigated.

(5) (a) H. Linschitz, M. Ottolenghi, and R. Bensasson, *J. Amer. Chem. Soc.*, **89**, 4592 (1967); (b) M. Ottolenghi and R. Bensasson, *J. Phys. Chem.*, **72**, 3774 (1968).

(6) No distinct absorption which can be attributed to M⁺ was detected in the 350–800-nm range.

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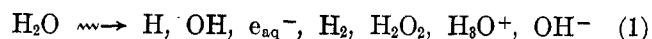
RECEIVED MAY 7, 1969

Absorption Spectrum of the Hydrated Electron from 200 to 250 nm

Sir: The theory of the excess electron state in liquid water associated with the hydrated electron, e_{aq}⁻, is of considerable current interest. A successful model of e_{aq}⁻ must account for its unusually broad, structureless absorption band (maximum at 720 nm) that extends into the uv to 220 nm, the shortest wavelength examined.¹ Here we report new pulse-radiolysis measurements down to 200 nm. Our results, given in Figure 1, demonstrate the inception of a new absorption band with a maximum below 200 nm. This band is similar to the recently reported bands of the H and OH radicals in aqueous solutions^{2,3} and should prove useful in constructing models of e_{aq}⁻.

Whereas Fielden and Hart¹ were limited in their work to wavelengths of 220 nm and above by the optical absorption of OH⁻ in solutions containing $5 \times 10^{-2} M$ NaOH, we have been able to monitor the pulse radiolytic absorbance transients down to 200 nm in solutions of $2 \times 10^{-5} M$ NaOH + 0.027 M H₂ [$p(\text{H}_2) = 35 \text{ atm}$] using the 7.1-cm pressure cell and pulse-radiolysis techniques already described.^{3,4} The 11-MeV Risø Linac delivered the 1.3-μsec single-electron pulses used (dose ca. 10^{20} eV/l.).

Of the primary radiolytic products in reaction 1



(1) E. M. Fielden and E. J. Hart, *Trans. Faraday Soc.*, **63**, 2975 (1967).

(2) S. O. Nielsen, P. Pagsberg, J. Rabani, H. Christensen, and G. Nilsson, *Chem. Commun.*, 1523 (1968).

(3) P. Pagsberg, H. Christensen, J. Rabani, G. Nilsson, J. Fenger, and S. O. Nielsen, *J. Phys. Chem.*, **73**, 1029 (1969).

(4) H. Christensen, G. Nilsson, P. Pagsberg, and S. O. Nielsen, *Rev. Sci. Instrum.*, **40**, 786 (1969).

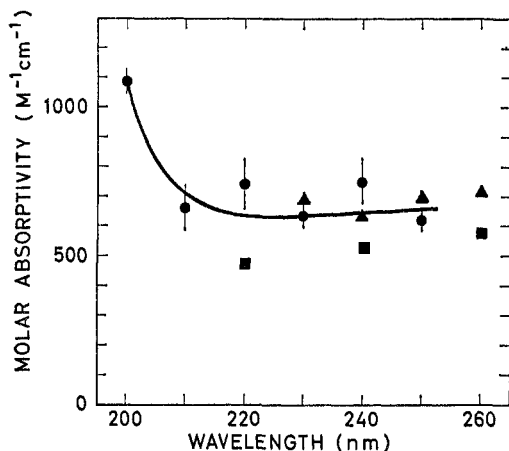


Figure 1. Absorption spectrum of the hydrated electron at 25° from pulse radiolysis of: ●, $2 \times 10^{-5} M$ NaOH + $0.027 M$ H_2 (vertical bars give standard deviation and the curve gives best fit); ▲, $10^{-2} M$ NaOH + $0.027 M$ H_2 (after radiation clean-up); ■, from ref 1.

only H, e_{aq}^- , H_2 , H_2O_2 , and OH^- could still be present a few microseconds after the electron pulse. Under our conditions OH reacts with H_2 to form H (half-time $0.5 \mu\text{sec}$) and H_3O^+ reacts with OH^- (half-time $0.3 \mu\text{sec}$). The pulse-radiolytic absorbance transients were extrapolated back to the end of the electron pulse (disregarding essentially the first $2 \mu\text{sec}$ after the electron pulse) and corrected for radical recombination during the pulse. The absorbances obtained were corrected for those due to H ,^{2,3} H_2O_2 ,⁵ and OH^- ⁵ using $G(H) = 3.2$, $G(H_2O_2) = 0.7$, and $G(-OH^-) = 2.6$. The calculated molar decadic absorptivity, ϵ_e , of e_{aq}^- using $G(e_{aq}^-) = 2.6$ is given by the curve and the points ● in Figure 1. The values of ϵ_e determined similarly by pulse radiolysis of $10^{-5} M$ NaOH + $0.027 M$ H_2 (not purified) after radiation clean-up at low dose rates were in good agreement with the points ● in Figure 1 except at 200 nm where ϵ_e values were found to be consistently higher than those in Figure 1. The values of ϵ_e given by the curve in Figure 1 agree fairly well with those of Fielden and Hart above 220 nm (points ■ in Figure 1) and with ϵ_e obtained by repeating their experiments with nonpurified H_2 and radiation clean-up at pH 12 (points ▲ in Figure 1).

It has previously been shown³ that only very weak pulse-radiolytic absorbance transients at 200–250 nm are present in the pressure cell windows used. If new transients produced from soluble impurities were the cause of the increased absorptivity at 200 nm shown in Figure 1, they would have to be present in concentrations of at least $5 \times 10^{-5} M$ in order to have reacted substantially with H, OH, and e_{aq}^- in a few microseconds after the pulse. Such high concentrations of impurities are unlikely in view of the triply distilled water, analytical grade NaOH (diluted from a concentrated, stored solution), and purified H_2 (passage through 2 m of molecular sieve at -196°) used. Fur-

thermore, after 15 identical electron pulses were given to the same solution it was found that the transient absorbance following the 15th pulse was identical within experimental error with the absorbance following the first pulse. The assignment of the increased absorptivity at 200 nm in Figure 1 to e_{aq}^- is consistent with the observation that the reaction $e_{aq}^- + H_3O^+ \rightarrow H + H_2O$, when monitored at 200 nm in dilute $HClO_4$, is accompanied by only a relatively small change in absorbance. ϵ_H at 200 nm was previously measured to be $900 \pm 30 M^{-1} \text{ cm}^{-1}$.^{2,3} We therefore assign the new absorption band with maximum below 200 nm in Figure 1 to e_{aq}^- rather than to some unknown species not listed on the right-hand side of reaction scheme 1.

The proposed new uv absorption band of the hydrated electron is similar in appearance around 200 nm to an absorption band associated with H atoms in aqueous solution^{2,3} and a similar interpretation of it may be offered. We attribute this new absorption band of e_{aq}^- to a red shift of the liquid water absorption band beginning at ~ 200 nm caused by the presence of e_{aq}^- . The perturbation may involve a partial electron transfer from the first excited singlet of water to a "neighboring" e_{aq}^- . The uv absorption band of e_{aq}^- here proposed is analogous to the β bands associated with F centers in alkali halides.^{6,7} A similar band may exist in metal-ammonia solutions.⁸ We wish to thank Professor J. Jortner for calling these β bands to our attention.

(5) Landolt-Börnstein Tables, 6th ed, Vol. I, "Atomic and Molecular Physics," Part 3 "Molecules II," Springer-Verlag, Berlin, 1951, p 231.

(6) C. J. Delbecq, P. Pringsheim, and P. Yuster, *J. Chem. Phys.*, **19**, 574 (1951); **20**, 746 (1952).

(7) J. J. Markham, *Solid State Phys., Suppl.*, **8**, 106 (1966).

(8) J. J. Lagowski and P. Rusch, private communication.

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Paramagnetic Resonance and Phosphorescence of Chromia-Silica Catalyst with Chemisorbed Oxygen¹

Sir: Electron paramagnetic resonance (epr) techniques have revealed the presence of several distinct states of chromia adsorbed on high surface area alu-

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.