J. Phys. Chem. A **2006,** *110,* 3383−3387

Investigation of the Primary Photodynamics of the Aqueous Formate Anion

Christian Petersen,* Jan Thøgersen, Svend Knak Jensen, and Søren Rud Keiding

Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Received: October 19, 2005; In Final Form: December 22, 2005

We have investigated the primary photodynamics of the aqueous formate anion using femtosecond transient absorption spectroscopy. The formate anions are excited at 200 nm, and the resulting products are probed in the region 200−650 nm. The ultraviolet part of the transient spectrum compares favorably with that of O^-(aq). However, its counter radical, HCO(aq), is not observed. In the visible region hydrated electrons are observed. The electrons are produced from photodetachment of the formate anions and from two-photon ionization of water.

1. Introduction

The (n,π*) transition is common to all species containing a carbonyl group, including the carboxylic acids. The low extinction coefficient of the (n,π*) transition has complicated the study of the primary photodynamics of the carboxylic acids and their derivatives. An important subgroup of the carboxylic acids is the amino acids. It has been suggested that asymmetric photolysis of amino acids is linked to the homochirality of naturally occurring amino acids.[1] A detailed understanding of the photolysis of the aqueous carboxylic acids and their anions could be a useful step toward an understanding of the primary photodynamics of amino acids. In this light, it is not surprising that the dissociation of formic acid has been studied extensively experimentally in the gas phase and by theoretical calculations. A recent paper by He et al. gives a good overview of the theoretical results.[2] It is believed that excitation of the (n,π*) band leads to a wavelength-dependent dissociation into five different channels.[3−8] At wavelengths below 240 nm, the main photodissociation channel is the production of the formyl radical, HCO, and the hydroxyl radical, OH, via direct dissociation from the first excited singlet state. Minor channels include the formation of H + COOH, $CO_2 + H_2$, and H_2O + CO.

In an earlier experiment we studied the primary photodynamics of aqueous formic acid following excitation at 200 nm.[9] In accordance with the gas-phase measurements and the calculations, it was found that the transient spectrum for the photolysis of formic acid in aqueous solution could be reproduced quite accurately by the spectrum of the hydroxyl radical. From the temporal dynamics it was found that the concentration of hydroxyl radicals decays on a nanosecond time scale concurrent with the formation of formic acid. However, the geminate partner of the hydroxyl radical, HCO, could not be identified. On the basis of a theoretical investigation, we proposed that the lack of HCO in the spectral data is caused by solvent interactions shifting the spectrum of HCO outside the range covered in the experiment. Alternatively, HCO reacts rapidly with the surrounding water molecules producing undetectable fragments. It was concluded on the basis of the experiment that excitation in the carbonyl group with an (n,π*) transition in formic acid results in the cleavage of the C−OH bond.

In this work we turn our attention to the deprotonated form of formic acid, the formate anion. The photolysis of simple aqueous deprotonated carboxylic acids is scarcely reported in the literature, mainly owing to the complexity of operating in the deep UV. To our knowledge, no studies exist with a time resolution better than a few microseconds. A flash-photolysis study has been carried out on aqueous formate at 200 nm by Arvis et al.[10] Hydrated electrons and CO_2^-(aq) were detected by means of their absorption spectra, and it was concluded that excitation at 200 nm of the formate anion can result in the breaking of the carbon−hydrogen bond as well as photodetachment. The corresponding hydrogen atoms were not identified because this species has negligible absorbance above 225 nm and thus lay outside the spectral range of the experiment. A photodissociation experiment on aqueous formate with excitation at 184.5 nm was carried out by Zechner and Getoff.[11] Their method relied on the identification of gaseous products resulting from secondary or tertiary reactions of the primary photoproducts. They concluded that the channel resulting in the formation of the formyl radical, HCO(aq) and O^-(aq), was accessible at the applied wavelength because carbon monoxide, resulting from the reaction of the formyl radical with hydroxyl radicals, could be identified. Mittal et al. conducted a flash-photolysis experiment using a flash-lamp emitting light with wavelengths longer than 200 nm. No hydrated electrons were detected, and it was not possible to identify photoproducts absorbing in the UV.[12] In the gas phase the photodetachment of the formate anion and the subsequent decomposition of the formyloxyl radical has been investigated by Clements et al.[13] The main decomposition channel of the formyloxyl radical resulted in the formation of hydrogen atoms and carbon dioxide.

In the present work we study the primary photodynamics of the aqueous formate anion with femtosecond transient absorption spectroscopy. We detect formation of hydrated electrons resulting from photodetachment of the anions and additional photofragments absorbing in the range 200−350 nm. We will in this work discuss the possible assignment of this absorption; the most likely being that it pertains to O^-(aq).

2. Absorption Spectra of Relevant Species

The experimental technique of transient absorption spectroscopy identifies the species involved in the photolysis by their absorption spectra. This section presents the spectra that are

---

* Corresponding author. E-mail chrp@chem.au.dk.

10.1021/jp055976i CCC: $33.50

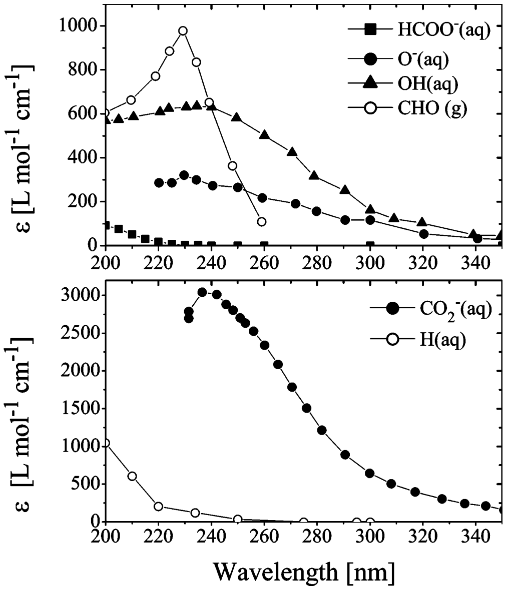

Figure 1. Absorption spectra of relevant species taken from refs 18−24.

expected to be relevant for the photolysis of aqueous formate, see Figure 1.

The formate anion has a weak absorption starting at 250 nm and rising toward shorter wavelengths. Using an Agilent 8453 spectrometer, we have determined the extinction coefficient to be $\epsilon = 93 \pm 6$ M^{-1} cm^{-1} at 200 nm. It has been suggested that the absorption around 200 nm is caused by an (n,π*) transition,[14,15] possibly in connection with a CTTS band,[10] although it has also been assigned as being a (π,π*) transition.[16]

O$^-$(aq) is formed if the photolysis results in a cleavage of the carbon−oxygen bond. This species has previously been identified in pulse radiolysis experiments. It may be produced as a result of the scavenging of hydrated electrons by N_2O. To our knowledge, the only two reports on measurements of the spectrum of O$^-$(aq) are those by Rabani[17] and Czapski and Bielski.[18] The measurement of the spectrum of O$^-$(aq) is complicated by the fact that several spectra have to be subtracted to produce the pure O$^-$(aq) spectrum. Consequently, it has not been possible to produce a reliable spectrum below 240 nm. We will limit ourselves to present only the most recent spectrum measured by Czapski and Bielski. This spectrum shows an increase in absorption starting from 340 nm and rising toward shorter wavelengths. The extinction coefficient at 250 nm is 250 M^{-1} cm^{-1}. The spectrum shown for H(aq) is taken from the work of Pagsberg et al.[19] and from the work of Nielsen et al.[20] The spectrum of OH(aq) is taken from the pulse radiolysis experiments of Pagsberg et al.[19] and Boyle et al.[21] If the photolysis results in electron photodetachment, the radical produced will be the formyloxyl radical, HCOO(aq). To our knowledge, the spectrum of HCOO(aq) has not been reported, although there have been speculations that this species could be produced along with COOH(aq) in pulse radiolysis experiments of aqueous formic acid and on saturated aqueous solutions of carbon dioxide.[22] If, instead, the C−H bond is cleaved, the resulting radicals will be the carboxyl radical anion, CO_2^-(aq), and hydrogen atoms. The spectra of CO_2^-(aq) is taken from ref 23. We note that the spectra of COOH(aq) and CO_2^-(aq) are believed to be essentially identical.[23] The CO_2^-(aq) radical has a maximum absorption at 235 nm with an extinction coefficient of 3000 M^{-1} cm^{-1}. The formyl radical has only been identified in the gas phase.[24] We show the reported spectrum with the comment that there is no indication that this spectrum can be applied to aqueous solutions.

3. Experimental Setup

A 1 kHz titanium-sapphire laser system emitting 100 fs pulses with a pulse energy of 0.75 mJ is frequency quadrupled in three consecutive BBO crystals to generate the 200 nm pulse used to initiate the photolysis. The ~8 μJ pump pulse is modulated at 0.5 kHz by a mechanical chopper synchronized to the 1 kHz pulse repetition rate and sent through a scanning delay line before it is focused through the sample by a $f = 50$ cm concave mirror. The probe pulses covering the interval from 460 to 650 nm are generated by a two-stage optical parametric amplifier (OPA) pumped at 400 nm. Probe pulses in the interval from 230 to 350 nm are produced by frequency doubling the pulses from the OPA in a 0.2 mm BBO crystal. The wavelengths between 200 and 235 nm are covered by sum frequency mixing the frequency-doubled output from the OPA with the residual of the fundamental 800 nm pulses. Alternatively, probe wavelengths in the region from 215 to 250 nm are generated by frequency mixing the output from the OPA with the second harmonic of the residual 800 nm pulses. The probe beam is then split into a signal beam and a reference beam. The signal beam is focused onto the sample using a CaF_2 lens with $f = 50$ mm. The spot size of the probe beam is ~6 times smaller than the spot size of the pump pulse. Signal and reference pulses are then detected by matched photodiodes and boxcar integrators. The time resolution of the spectrometer is 300 fs. The sample is a ~0.15 mm thick jet of 1 M aqueous NaCOOH. At these concentrations the amount of formic acid and hydroxide ions in the solution is negligible. The flow through the jet was adjusted so that a fresh sample was supplied for each laser pulse. We observed no degradation of the solution during the measurements, but to avoid the potential accumulation of photoproducts, the solution was changed regularly. The reproducibility of the transient absorption data was tested by repeated measurements on different days using different samples.

4. Results

The temporal evolution of the transient absorption of aqueous formate was measured from 200 to 650 nm. Common to all curves is a sharp initial peak that predominantly originates from the coherent absorption of one pump and one probe photon in water. The peak strongly resembles the one observed in neat water. On the basis of the prompt response of this two-photon absorption signal, we take the position and width of the initial peak to mark the point of zero delay and temporal resolution (300 fs), respectively. The two-photon absorption of water produces hydrated electrons that absorb from the vacuum ultraviolet to far into the infrared region. The transient spectrum recorded between 460 and 650 nm closely resembles the spectrum of the hydrated electron. There is no sign of other species in this region. Therefore, we have estimated the concentration of hydrated electrons from the transient spectrum and its contribution has been subtracted from the transient spectrum presented for wavelengths below 400 nm in Figure 2. The induced absorption increases after 360 nm toward 200 nm with a steep rise in absorption in the spectral range between 250 and 200 nm.

The temporal evolution of the transient absorption is shown for three characteristic wavelengths in Figure 3. At 205 nm we observe a fast rise of the transient absorption within the first picosecond followed by a decay to a level of 10% of the initial absorption after 120 ps. The time constant of the decay is 25

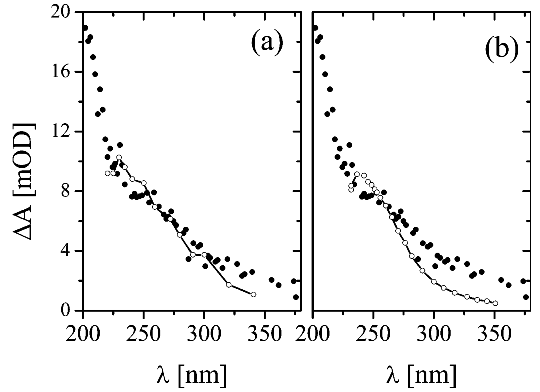

Figure 2. (a) Formate transient spectrum recorded at 10 ps probe delay (●) and absorption spectra of O^- assuming a concentration of 3.2 mM (○). (b) Formate transient spectrum (●) and normalized absorption spectra of CO_2^- assuming a concentration of 0.3 mM (○).

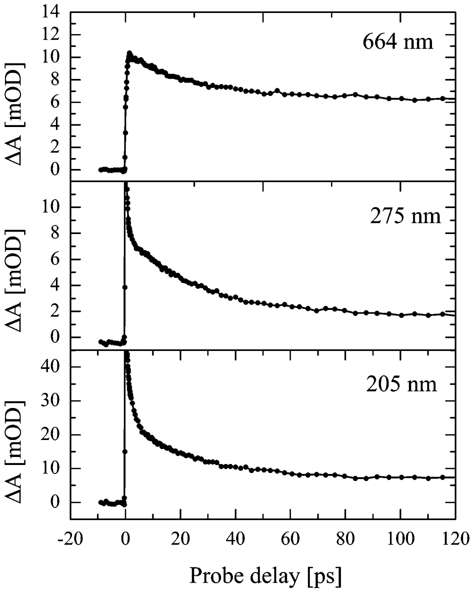

Figure 3. Transient absorption traces at three characteristic wavelengths for the aqueous formate anion.

ps. The dynamics of the scans at 205 and 275 nm are essentially equivalent after 3 ps. At wavelengths longer than 575 nm the initial absorption is no longer dominated by the coherence peak and the transient absorption rises in 0.75 ps (10% → 90%). The initial rise is followed by a decay to a constant level of absorption of 75% of the initial value. The time constant of the decay is roughly 25 ps.

We have measured the intensity dependence of the induced absorption at 235 and 665 nm at 10 and 100 ps probe delay, respectively. At 235 nm, $\Delta A \propto I^{1.2\pm0.2}$ indicating no, or only a minor contribution from products pertaining to two-photon ionization of water. At 625 nm, $\Delta A \propto I^{1.7\pm0.2}$ revealing a significant contribution from hydrated electrons formed by ionization of water. At 205 nm probe wavelength we have measured the transient absorption for both perpendicular and parallel pump–probe polarizations. The data were identical within the experimental uncertainty, thus showing no sign of rotational anisotropy.

5. Discussion

In this section we discuss the identification of the photofragments that appear in the measured transient spectrum. The most likely interpretation of our data is that excitation of the formate anion at 200 nm leads to photodetachment of the excess electron and cleavage of a C–O bond. The literature on the photolysis of the aqueous formate anion is scarce but may be summarized by the following reactions

$$HCOO^- + h\nu \rightarrow HCO + O^- \qquad (1)$$

$$\rightarrow HCOO + e_{aq}^- \qquad (2)$$

$$\rightarrow CO_2^- + H \qquad (3)$$

In addition to reactions 1–3, we expect that hydrated electrons will be produced by two-photon ionization of the water solvent[25,26]

$$2h\nu + 2H_2O \rightarrow e_{aq}^- + H_3O^+ + OH \qquad (4)$$

A comparison of the absorption spectrum of O^- with the transient spectrum of the formate anion depicted in Figure 2a shows a satisfactory agreement. The formation of O^- implies the formation of the geminate radical, HCO. So far, HCO has not been identified in an aqueous environment whereas gas-phase HCO has been reported to absorb below 250 nm. Hence, one could speculate that the abruptly rising absorption in the range 200–235 nm is due to this radical. However, if HCO does possess such an absorption, it would have been detected in our earlier studies.[9] The fact that HCO was not observed indicates that the 200–235 nm absorption pertains to the absorption spectrum of O^-. Assuming this holds true, the present measurement is an improvement of the spectral range of this spectrum. The decay of the transient absorption in the ultraviolet takes place on a time scale on the order of 25 ps. The source of this decay is unlikely to be due to the reaction of O^- with water[27]

$$O^- + H_2O \rightarrow OH + OH^- \qquad k_5 = (9.2 \pm 2.0) \times 10^7\ M^{-1}\ s^{-1} \quad (5)$$

because the extinction coefficient of OH from 200 to 350 nm is larger than that of O^-. Hence, reaction 5 would result in an increase in the transient absorption contrary to observation. Similarly, O^- is also known to react with hydrated electrons according to the reaction[28]

$$O^- + e_{aq}^- + H_2O \rightarrow 2OH^- \qquad k_6 = (2.2 \pm 0.6) \times 10^{10}\ M^{-1}\ s^{-1} \quad (6)$$

but the concentrations of O^- and e_{aq}^- are much too small for reaction 6 to occur within the experimental window of 500 ps, let alone 30 ps. Likewise, other bimolecular reactions involving reaction products from different ionization sites are safely excluded. Therefore, assuming that photodissociation leads to formation of O^- and HCO we attribute the decay of the absorption to a geminate recombination of these two species, or species formed in the reaction of HCO with water.

The transient spectrum after 100 ps at visible probe wavelengths is very similar to that of the hydrated electron. We find that the transient absorption in this region decays on two distinct time scales. One decay occurs on a time scale of 25 ps whereas a slower decay takes place on a time scale longer than the range covered by our setup. A comparison of the temporal evolution of hydrated electrons produced in the formate solution and in neat water under identical conditions is shown in Figure 4 (see also ref 25).

The time evolution displays a distinct difference between the two situations indicating that the hydrated electrons produced

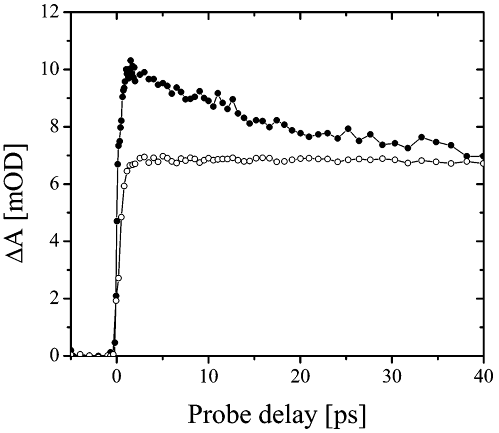

Figure 4. Normalized traces for the formate solution at 630 nm (●) and for bi-photonic ionization of neat water at 625 nm (○).

in our experiment originate from two different photoprocesses. The fast decay is caused by geminate recombination of electrons and formyloxyl radicals formed by photodetachment. Calculations at the CIS(D)/AUG-cc-pVDZ//B3LYP/6-311+G(d,p) level of theory of the vertical ionization energy of the formate anion in a water cluster consisting of eight water molecules yield a ionization energy of 6.3 eV. This is slightly higher than the energy supplied by the pump photons and suggests that the detached electrons are formed in a charge-transfer-to-solvent process rather than by direct ionization. The absorption spectrum of the counter radical, the formyloxyl radical, is not known in aqueous solution, and therefore, its presence cannot be verified directly. The slowly decaying part of the transient absorption is due to the hydrated electrons produced by two-photon ionization of the water solvent. A more thorough analysis of the transient absorption traces shows that there is good agreement between the decay of the hydrated electron absorption pertaining to photodetachment and the decay rate of the transient absorption observed at wavelengths below 350 nm. We estimate that the time scales are identical within 5 ps. This correspondence suggests that the species absorbing at the low wavelengths are associated with the process responsible for the generation of the photodetached electrons. In turn, this may imply that the species absorbing below 350 nm are the formyloxyl radicals resulting from the photodetachment. However, the following estimate of the extinction coefficient needed for HCOO to match the observed absorption shows that this interpretation is unlikely: On the basis of the measured total transient absorption of the hydrated electron and the spectrum from ref 29, we calculate the concentration of hydrated electrons to $[e_{aq}^-] \sim 0.08$ mM. The number of electrons originating from the detachment and from the two-photon ionization of water may be deduced from the ratio between the transient absorption of the fast and the slowly decaying contributions to the absorption. The resulting concentration of electrons photodetached from formate ions is about 0.03 mM. We then calculate the expected extinction coefficient of the radicals produced in the photodetachment assuming that the transient absorption below 350 nm is entirely due to absorption by the formyloxyl radical and assuming there is an equimolar relation between the number of radicals and the number of photodetached electrons. This estimate yields an extinction coefficient for the formyloxyl radical of $\sim$20 000 M^{-1} cm^{-1} at 200 nm. The extinction coefficient of the formyloxyl radical has not been established experimentally, but theoretical calculations using CIS(D)/AUG-cc-pVDZ//B3LYP/6-311+G(d,p) on the formyloxyl radical in a water cluster consisting of eight water molecules give no indication that significant UV absorption takes place at wavelengths longer than 200 nm. To the extent that this calculation provides accurate results, the absorption in the deep UV is not due to the formyloxyl radical. Consequently, the similar decay rates of the concentration of detached electrons and the UV absorption would have to be the result of two separate photoprocesses exhibiting nearly identical reaction rates.

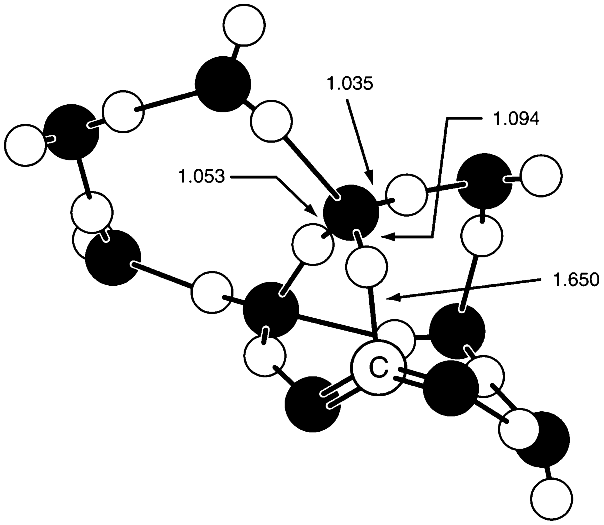

Figure 5. Structure of a potential minimum obtained by geometry optimizations on a cluster consisting of the HCOO radical and eight water molecules. The structure is derived at the B3LYP/6-311+G(d,p) level of theory. The distances are in Å. ● indicates an oxygen atom and ○ indicates a hydrogen atom.

Theoretical calculations at the B3LYP/6-311+G(d,p) level on the formyloxyl radical placed in a water cluster consisting of 8 water molecules show that the dissociation of the formyloxyl radical into a proton and a carboxylic radical anion is energetically favorable. The energy difference being of the order of tens of kJ/mol and presumably with a small energy barrier on the same order of magnitude. The result of the calculations are shown in Figure 5. In the gas phase the formyloxyl radical is known to dissociate as a result of photodetachment from the formate anion.[13] Therefore, we consider the possibility that the species dominating the transient spectrum in the ultraviolet region result from the fragmentation of the formyloxyl radical. This means that we consider a process, which in addition to reaction 2 and the recombination of the formyloxyl radical and the detached electrons, contains the steps,

$$\mathrm{HCOO} \rightarrow \mathrm{H}^+ + \mathrm{CO_2}^- \tag{7}$$

$$e_{aq}^- + \mathrm{H}^+ \rightarrow \mathrm{H} \tag{8}$$

The estimated concentration of H-atoms in reaction 8 is too low to allow for production of H_2 in a Kolbe-like reaction[30] within our observation time of 500 ps. The carboxylic radical anion, CO_2^-, has a strong ultraviolet absorption in aqueous solution. A comparison of the transient spectrum measured in this experiment and the spectrum of CO_2^-, assuming a concentration of 0.3 mM of CO_2^-, is shown in Figure 2b. The spectrum from the literature deviates substantially from the measured transient spectrum. Moreover, if one assumes that CO_2^- is produced in the same concentration as photodetached electrons by a rapid fragmentation of the formyloxyl radical, the induced absorption due to CO_2^- is an order of magnitude lower than the observed transient absorption in the UV. We therefore conclude that a rapid dissociation of the formyloxyl radical cannot exclusively account for the transient absorption in the UV. Alternatively, it is possible that the fragmentation of the formyloxyl radical competes with the recombination of detached electrons and formyloxyl radicals. If reaction 8 is fast compared to the fragmentation in reaction 7, the removal of the formyloxyl radicals and the detached electrons will be determined by the rate of fragmentation as well as the recombination rate. This means that the decay rates of the transient absorption in the ultraviolet and in the visible range will be identical. Unfortunately, our experimental results cannot validate or exclude these speculations. The alternative fragmentation of HCOO into $CO_2 + H$ (which is observed in the gas phase) is ruled out by the presence of the ultraviolet absorption; carbon dioxide has no significant absorption for the wavelength interval investigated in this experiment. The breaking of a carbon−hydrogen bond in reaction 3 is yet another possible photodissociation channel resulting in the production of CO_2^- and hydrogen atoms. Hydrogen atoms in an aqueous environment absorb only below 225 nm. Therefore, the absorption of hydrogen could explain the steeply rising absorption setting in at 230−225 nm. However, this cannot be verified experimentally, because the absorption spectrum of CO_2^- is not known below 230 nm. As previously described, the spectrum of the measured transient absorption does not agree with the spectrum of CO_2^- and there is no indication in our results that this dissociation channel is dominant.

6. Conclusion

We have investigated the primary photodynamics of the aqueous formate anion following excitation at 200 nm using femtosecond transient absorption. We find that hydrated electrons are produced through photodetachment of the anion and we observe a photoproduct absorbing in the ultraviolet. The most likely interpretation of our data is that this species is O^- produced by a dissociation of the anion, although more work is needed to draw unambiguous conclusions.

Note Added in Proof. A new measurement of the absorption spectrum of O^-_{aq} has been reported after the submission of our manuscript (Alam, M. S.; Janata, E. *Chem. Phys. Lett.* **2006**, *417*, 363). This new spectrum resembles the spectrum measured by Czapski apart from a higher extinction coefficient and a clear decrease in absorbance below 225 nm.

References and Notes

(1) Jorissen, A.; Cerf, C. *Origins Life Evol. Biosphere* **2002**, *32*, 129.
(2) He, H.-Y.; Fang, W.-H. *J. Am. Chem. Soc.* **2003**, *125*, 16139.
(3) Langford, S. R.; Batten, A. D.; Kono, M.; Ashfold, M. N. R. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3757.
(4) Su, H.; He, Y.; Kong, F.; Fang, W.; Liu, R. *J. Chem. Phys* **2000**, *113*, 1891.
(5) Brouard, M.; Simons, J. P.; Wang, J. X. *Faraday Discuss.* **1991**, *91*, 63.
(6) Ebata, T.; Fujii, A.; Amano, T.; Ito, M. *J. Phys. Chem.* **1987**, *91*, 6095.
(7) Lee, K. W.; Lee, K. S.; Jung, K. H.; Volpp, H.-R. *J. Chem. Phys* **2002**, *117*, 9266.
(8) Brouard, M.; Wang, J. X. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3511.
(9) Thøgersen, J.; Jensen, S. K.; Christiansen, O.; Keiding, S. R. *J. Phys. Chem A* **2004**, *108*, 7483.
(10) Arvis, M.; Lustig, H.; Hickel, B. *J. Photochem.* **1980**, *13*, 223.
(11) Zechner, J.; Getoff, N. *Int. J. Rad. Phys. Chem.* **1974**, *6*, 215.
(12) Mittal, L. J.; Mittal, J. P.; Hayon, E. *J. Phys. Chem.* **1973**, *77*, 1482.
(13) Clements, T. G.; Continetti, R. E. *J. Chem. Phys* **2001**, *115*, 5345.
(14) Basch, H.; Robin, M. B.; Kuebler, N. A. *J. Chem. Phys* **1968**, *49*, 5007.
(15) Johnson, L. W.; Maria, H. J.; McGlynn. *J. Chem. Phys* **1971**, *54*, 3823.
(16) Szyper, M.; Zuman, P. *Anal. Chim. Acta* **1976**, *85*, 357.
(17) Rabani, J. *Adv. Chem. Ser.* **1968**, *81*, 131.
(18) Czapski, G.; Bielski, B. H. J. *Rad. Phys. Chem.* **1993**, *41*, 503.
(19) Pagsberg, P.; Christensen, H.; Rabani, J.; Nilsson, G.; Fenger, J.; Nielsen, S. O. *J. Phys. Chem.* **1969**, *73*, 1029.
(20) Nielsen, S.; Michael, B. D.; Hart, E. J. *J. Phys. Chem.* **1976**, *80*, 2482.
(21) Boyle, J. W.; Ghormley, J. A.; Hochanadel, C. J.; Riley, J. F. *J. Phys. Chem.* **1969**, *73*, 2886.
(22) Keene, J. P.; Raef, Y.; Swallow, A. J. In *Pulse radiolysis*; Ebert, M., Keene, J. P., Swallow, A. J., Baxendale, J. H., Eds.; Academic Press: New York, 1965; p 99.
(23) Neta, P.; Simic, M.; Hayon, E. *J. Phys. Chem.* **1969**, *73*, 4207.
(24) Hochanadel, C. J.; Sworski, T. J.; Ogren, P. J. *J. Phys. Chem.* **1980**, *84*, 231.
(25) Lian, R.; Oulianov, D. A.; Shkrob, I. A.; Crowell, R. A. *Chem. Phys. Lett.* **2004**, *398*, 102.
(26) Lian, R.; Crowell, R. A.; Shkrob, I. A. *J. Phys. Chem A* **2005**, *109*, 1510.
(27) Buxton, G. V. *Trans. Faraday. Soc.* **1970**, *66*, 1656.
(28) Matheson, M. S.; Rabani, J. *J. Phys. Chem.* **1965**, *69*, 1324.
(29) Jou, F.-Y.; Freeman, G. R. *J. Phys. Chem.* **1977**, *81*, 909.
(30) Fieser, L. F.; Fieser, M. *Organic Chemistry*, 3rd ed.; Reinhold Publishing Corp.: New York, 1956.