

Figure 4. Experimental difference absorption signal normalized to the square of the laser power, data points; spectrum for 300 K Boltzmann distribution in the singly excited exciton components, solid curve; spectrum for Boltzmann distribution of excitations localized on single chromophores, dashed curve. Data are from ref 6.

loalized on the individual chromophores. (When the excitation localizes on a particular chromophore, the computed ESA arises from exciton states delocalized over the remaining chromophores in the subunit.) The resulting spectrum, shown in Figure 3, is very similar to the thermalized coherent spectrum in Figure 2. For comparison, the experimental spectrum<sup>6</sup> is shown in Figure 4. This was normalized in the earlier work by dividing the observed signal at each wavelength by the corresponding BChl *a*-protein optical density at that wavelength. A more detailed normalization, taking into account the wavelength dependence in the total probe beam attenuation and in the pump beam attenuation in the sample region before the beam intersection, has been applied in Figure 4. The localized spectrum (Figure 3) yields superficially better agreement with the experimental spectrum than the thermalized coherent spectrum (Figure 2); for example, the 795-nm zero-crossing point predicted in the coherent spectrum appears to be inconsistent with the experimental spectrum. However, these two calculated spectra are so similar in our view that they do not form a basis for judging the extent of coherence in this antenna.

In summary, our exciton calculations of absorption difference spectra in *P. aestuarii* lead to the following conclusions: (1) ESA transitions drastically influence the absorption difference spectra in the presence of strong exciton couplings, even in antennae whose monomers do not exhibit strong ESA at wavelengths near the  $Q_y$ static spectrum. (2) Model calculations of the absorption difference spectra, performed under assumptions of coherence over the FMO trimer versus localization on individual chromophores, yield similar agreement with the experimental spectrum.

A more incisive experimental test for coherence may be afforded by a dynamic pump-probe experiment using 100-200-fs laser pulses. For example, Figure 3 offers a prediction of the spectral evolution accompanying relaxation between exciton components in the FMO trimer following excitation at 800 nm. Here, most of the spectral metamorphosis is predicted to occur at probe wavelengths shorter than  $\sim$ 800 nm if exciton coherence is maintained; the photobleaching/stimulated emission peak at 807-814 nm would shift in position and broaden symmetrically. Localization of excitation followed by thermalization, however, would broaden this peak asymmetrically toward the red side (Figure 3). The required time scale for observing these spectral changes is suggested by the zero-phonon hole widths measured by Johnson and Small,<sup>19</sup> who reported that relaxation between exciton componnets occurs within 100 fs in this antenna.

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## COMMENTS

## Influence of Chloride on the Chlorine–Formic Acid Reaction in Sulfuric Acid

Sir: In our article<sup>1</sup> "Kinetics of the Reaction of Chlorine with Formic Acid in Aqueous Sulfuric Acid", we assumed that chlorine is the species that oxidizes formic acid and did not consider the possibility of oxidation by hypochlorous acid. We have completed experiments that explore this possibility. This paper discusses our experiments and results.

A scheme involving oxidation of HOCl consists of an equilibrium step followed by a rate-determining step

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^-$$
 (1)

$$\text{HCOOH} + \text{HOCl} \rightarrow \text{CO}_2 + \text{H}^+ + \text{Cl}^- + \text{H}_2\text{O} \qquad (2)$$

which leads to the rate expression

$$\mathbf{r}_{\rm CO} = kK[\rm HCOOH][\rm Cl_2]/[\rm H^+][\rm Cl^-]$$
(3)

In our original article, we showed that  $r_{CO_2}$  approximately equals  $(1/2) d[Cl^-]dt$ . Substitution of this expression in eq 3 leads to the integrated form

$$[Cl^{-}]^{2} - [Cl^{-}]_{0}^{2} = 2kK[HCOOH][Cl_{2}]/[H^{+}]t$$
(4)

To test for negative order dependence in chloride, we ran two chlorine-formic acid reaction experiments under identical conditions. In one experiment, sodium chloride was added initially to the reaction solution. In the other, sodium chloride was not added; however, some chloride formed initially because of the equilibrium, eq 1. Both experiments were run in triplicate. The experiments were conducted at 298 K with 1 M sulfuric acid and 0.59 M formic acid concentrations. Both of these reactants were present in large excess so that their concentrations remained constant. Chlorine concentration was maintained essentially constant and was monitored continuously by a UV spectrophotometer at 322 nm. Chlorine was continuously added to the solution from a cylinder through a fritted glass gas sparging tube. Chloride concentration was continuously monitored by a chloride-sensitive probe.

Table I shows concentration data collected in the experiments. In experiment 2 (a, b, and c) the initial chloride concentration is, on the average, 10 times greater than that in experiment 1 (a, b, and c). Figure 1 is a plot of chloride concentration versus time

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<sup>(1)</sup> Hoq, M. F.; Indu, B.; Ernst, W. R.; Neumann, H. M. J. Phys. Chem. 1991, 95, 681.

TABLE I: Influence of Chloride on Chlorine-Formic Acid Reaction Rate<sup>a</sup>

time,	expt 1a		expt 1b		expt 1c		expt 2a		expt 2b		expt 2c		
S	[Cl <sub>2</sub> ]	[Cl <sup>-</sup> ]	[Cl <sub>2</sub> ]	[C1-]	[Cl <sub>2</sub> ]	[CI-]	[Cl <sub>2</sub> ]	[CI <sup>-</sup> ]	[Cl <sub>2</sub> ]	[Cl-]	[Cl <sub>2</sub> ]	[C1 <sup>-</sup> ]	
0	1.31	0.40	1.33	0.20	1.38	0.21	1.32	2.80	1.59	2.93	1.34	3.08	
60	1.37	0.55	1.34	0.29	1.43	0.30	1.38	3.07	1.36	3.14	1.23	3.38	
120	1.24	0.76	1.34	0.42	1.46	0.44	1.34	3.36	1.26	3.44	1.56	3.72	
180	1.36	1.00	1.31	0.57	1.34	0.61	1.30	3.62	1.51	3.76	1.43	3.96	
240	1.42	1.25	1.31	0.75	1.37	0.79	1.26	3.93	1.36	4.09	1.26	4.19	
300	1.28	1.50	1.29	0.94	1.27	0.97	1.37	4.22	1.26	4.39	1.47	4.49	
360	1.34	1.76	1.30	1.11	1.37	1.18	1.34	4.59	1.48	4.77	1.44	4.78	
420	1.30	2.03	1.30	1.32	1.29	1.39	1.39	4.93	1.41	5.08	1.38	5.12	
480	1.34	2.29	1.31	1.52	1.35	1.60	1.34	5.25	1.36	5.40	1.33	5.48	
540	1.40	2.55	1.28	1.75	1.32	1.83	1.30	5.57	1.33	5.75	1.38	5.83	
600	1.32	2.80	1.29	1.98	1.28	2.05	1.33	5.87	1.42	6.05	1.43	6.24	
660	1.35	3.06	1.35	2.23	1.30	2.29	1.32	6.23	1.31	6.41	1.38	6.48	
720	1.34	3.33	1.49	2.50	1.28	2.49	1.34	6.57	1.17	6.71	1.38	6.82	
780	1.30	3.59	1.40	2.76	1.39	2.76	1.35	6.90	1.20	7.18	1.44	7.27	
840	1.34	3.86	1.36	3.03	1.36	3.03	1.36	7.22	1.45	7.64	1.36	7.66	
900	1.35	4.13	1.35	3.32	1.32	3.28	1.36	7.55	1.41	7.92	1.41	8.03	

<sup>a</sup>All experiments at 298 K, 1 M H<sub>2</sub>SO<sub>4</sub>, and 0.59 M HCOOH. All species concentrations are in M × 100.



Figure 1. Effect of chloride concentration on the rate of the chlorineformic acid reaction.

for the experiments. Linear least-squares analysis leads to the average rate  $3.7 \times 10^{-5}$  M/s (±0.4 × 10<sup>-5</sup>) for experiment 1 and  $5.4 \times 10^{-5}$  M/s (±0.1 × 10<sup>-5</sup>) for experiment 2. Figure 2 shows a plot of the function  $[Cl^{-}]^{2} - [Cl^{-}]_{0}^{2}$  versus time for the two experiments.

These results are in conflict with the above reaction scheme. Figure 1 shows that the addition of chloride slightly increased rather than decreased the rate. This increase represents a small positive order dependence on chloride of about 0.16. Equation 4 requires that a plot of the square of chloride concentration should be linear. Figure 2 shows that the data of the two experiments do not conform to eq 4.

The small, but significant, positive order effect of chloride may simply reflect an ionic strength effect. However, another possible explanation lies in the fact that the trichloride species  $Cl_3^-$  is a stronger oxidizer than chlorine.

$$Cl_2 + 2e^- \rightarrow 2Cl^-; \quad E_0 = 1.358 \text{ V}$$
 (5)

$$Cl_3^- + 2e^- \rightarrow 3Cl^-; \quad E_0 = 1.415 \text{ V}$$
 (6)

It forms by the equilibrium reaction

$$Cl_2 + Cl^- \leftrightarrow Cl_3^-$$
 (7)



Figure 2. Experimental results plotted in accordance with eq 4.

and therefore would have higher concentration in experiment 2 than in experiment 1. There is the possibility that trichloride reacts with formic acid faster than chlorine.

These experiments and those reported in our original article show that, under the conditions of the two studies, chlorine rather than hypochlorous acid is the species that reacts with formic acid.

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