

Figure 5. Single-exponential fit of absorbance decay at 1726 cm^{-1} (Figure 3) yields decay constant of $0.38 \pm 0.03\text{ s}^{-1}$.

of the intermediate. As shown in Figure 5, a single-exponential fit of the integrated absorbance decay gives a $1/e$ time of $2.6 \pm 0.2\text{ s}$.

In addition to observing formaldehyde (1726 cm^{-1}) and growth of formate at 1625 cm^{-1} , spectra of Figure 3a reveal strong transient absorptions not seen in the single pulse experiments (Figure 2a). The main band at 1679 cm^{-1} is assigned to HCO_2H , the shoulder around 1650 cm^{-1} is assigned to the H_2O coproduct. These assignments are confirmed by observation of transient $\text{H}^{13}\text{CO}_2\text{H}$ at 1638 cm^{-1} (coinciding with H_2O) in rapid-scan runs of $^{13}\text{CH}_3\text{OH} + \text{O}_2$ (Figure 4a), and DCO_2H at 1660 cm^{-1} in experiments with CD_3OD (Figure 4b).^{1,2,9,10} $\text{H}^{13}\text{CO}_2\text{H}$ and DCO_2H convert to $\text{H}^{13}\text{CO}_2\cdots\text{Fe}$ (1578 cm^{-1}) and $\text{DCO}_2\cdots\text{Fe}$ (1615 cm^{-1}), respectively, within 10 s. We conclude that formic acid emerges as an intermediate in rapid-scan experiments but only when irradiating with multiple laser pulses in rapid succession (100 ms between pulses). This points to secondary photolysis of a reaction intermediate as the source of HCO_2H .

According to our recent study of addition products of formaldehyde with various molecules that are present in the $\text{CH}_3\text{OH} + \text{O}_2$ reaction mixture, only hydroxymethylhydroperoxide is photolabile upon irradiation at 355 nm in a FAPO-5 sieve.² To determine the photoproducts, time-resolved experiments of $\text{HO}_2\text{CH}_2\text{OH}$ photodissociation in a FAPO-5 sieve were performed on the millisecond time scale. Because of the thermal instability of the hydroperoxide (half-life 20 min at 296 K),² FT-IR runs were conducted immediately following room-temperature adsorption of $\text{CH}_2=\text{O}$ gas onto the H_2O_2 -loaded sieve. Rapid-scan experiments consisted of acquisition of interferograms of 25 ms duration according to the procedure described in section II. A 200 laser shot experiment lasted 15 s, which guaranteed negligible thermal decomposition of the hydroxymethylhydroperoxide during the rapid-scan experiment. Absorbance spectra were obtained by ratioing and then averaging consecutive single beam spectra.

The resulting spectrum, displayed in Figure 6, shows the photoinduced depletion of $\text{HO}_2\text{CH}_2\text{OH}$ at 1455 cm^{-1} . The predominant product band is at 1676 cm^{-1} and originates from HCO_2H . The depletion in the $1650\text{--}1620\text{ cm}^{-1}$ range (dashed line) is due to a laser-induced thermal effect on the large absorption of residual H_2O (hydrogen peroxide is loaded into the sieve as a 30% aqueous solution). For the same reason, any formation of H_2O upon $\text{HO}_2\text{CH}_2\text{OH}$ photodissociation would not be detectable. Very weak absorptions at 1734 and 1503 cm^{-1} signal the formation of a small amount of $\text{CH}_2=\text{O}$. Hence, two

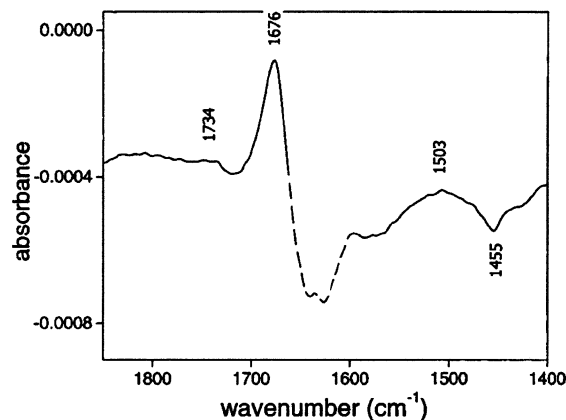
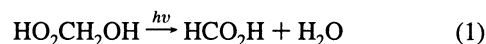
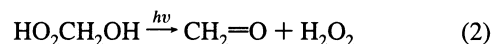


Figure 6. Rapid-scan FT-IR spectroscopy of 355 nm induced $\text{HO}_2\text{-CH}_2\text{OH}$ photodissociation in a FAPO-5 sieve at 25 ms resolution (298 K). Dashed part of the spectrum indicates laser-induced thermal effect on residual water.

photodecomposition channels are operative, namely, the major channel



and the minor path



(Note that the formaldehyde coproduct, H_2O_2 , does not possess an infrared absorption in the $2000\text{--}1300\text{ cm}^{-1}$ region).¹¹ It is interesting to add that both channels are also observed upon photodissociation of the molecule in homogeneous solution.¹² We conclude that the formic acid product observed in Figures 3 and 4 originates most probably from secondary photolysis of hydroxymethylhydroperoxide intermediate. Because no HCO_2H is detected upon single pulse-induced $\text{CH}_3\text{OH} + \text{O}_2$ photolysis and because formaldehyde is only a minor photodissociation product of $\text{HO}_2\text{CH}_2\text{OH}$, the $\text{CH}_2=\text{O}$ growth observed in the rapid-scan experiments is exclusively due to single photon reaction of CH_3OH and O_2 .

To obtain direct evidence for the intermediacy of $\text{HO}_2\text{CH}_2\text{-OH}$, we have measured time-resolved FT-IR spectra on the microsecond time scale by employing the step-scan method. Of the three absorptions observed for an authentic hydroxymethylhydroperoxide sample in the FAPO-5 sieve (1456 , 2884 , and 2948 cm^{-1})², the CH stretching modes are in a region where the sieve scatters strongly, resulting in a noise level that is too high for step-scan measurements. Therefore, we have concentrated the measurements on the absorption in the fingerprint region. Figure 7 shows the $500\text{ }\mu\text{s}$ time slices of step-scan runs of $\text{CH}_3\text{OH} + \text{O}_2$ (trace a) and $\text{CH}_3\text{OH} + \text{N}_2$ (trace b). Aside from the methanol desorption effect around 1475 cm^{-1} , there is positive growth at 1450 cm^{-1} , which we attribute to $\text{HO}_2\text{-CH}_2\text{OH}$. The product band is most clearly evident from the $\text{O}_2\text{-N}_2$ difference spectrum shown in the insert. Note that the observed absorbance growth at 1450 cm^{-1} due to $\text{CH}_3\text{OH} + \text{O}_2$ photoreaction is diminished by simultaneous depletion upon photodissociation of $\text{HO}_2\text{CH}_2\text{OH}$ that remains from the preceding laser pulse.

IV. Discussion

A key result of the rapid-scan experiments is that the rise of the final product $\text{HCO}_2\cdots\text{Fe}$ follows a single-exponential law