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Tropospheric Photolysis Rates of the Acetaldehyde Isotopologues CD$_3$CHO and CD$_3$CDO Relative to CH$_3$CHO Measured at the European Photoreactor Facility

Elna J. K. Nilsson,*,[†] Jimmy Heimdal,[‡] Lihn Bache-Andreassen,[§] Matthew S. Johnson,[‡] and Claus J. Nielsen[§]

[†]Division of Combustion Physics, Department of Physics, Lund University, Professorsgatan 1, SE-22363 Lund, Sweden

[‡]Copenhagen Center for Atmospheric Research, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen OE, Denmark

[§]Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, Pb. 1033 − Blindern, 0315 Oslo, Norway

S *Supporting Information*

ABSTRACT: Acetaldehyde is a hazardous pollutant found in indoor and ambient air. Acetaldehyde photolysis is pressure- and wavelength-dependent with three distinct product channels. In this study, the photolysis rates of CH$_3$CHO, CD$_3$CDO, and CD$_3$CHO are studied in natural tropospheric conditions using long path FTIR spectroscopy, at the European Photoreactor Facility (EUPHORE) in Valencia, Spain. The average relative photolysis rate as an average of four experiments for the fully deuterated isotopologue is $j_{CH3CHO}/j_{CD3CDO} = 1.75 \pm 0.04$, and as a result of a single experiment $j_{CH3CHO}/j_{CD3CHO} = 1.10 \pm 0.10$. These results, combined with our previous determination of $j_{CH3CHO}/j_{CH3CDO} = 1.26 \pm 0.03$, provide mechanistic insight into the photodissociation dynamics of the photoexcited species. Despite the extensive isotopic scrambling in photoexcited acetaldehyde that has recently been reported, the position of the substitution has a clear effect on the relative photolysis rates.
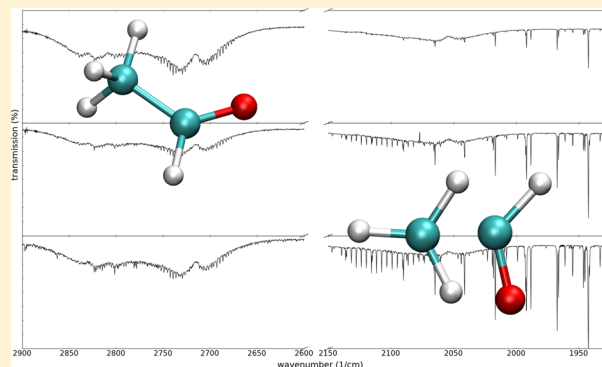
1. INTRODUCTION

Acetaldehyde, CH$_3$CHO, was first observed by the Swedish chemist Carl Wilhelm Scheele in 1774.[1] It is a hazardous air pollutant and potential carcinogen found in indoor and ambient air and influences concentrations of ozone and peroxyacetyl nitrates (PAN).[2] The tropospheric lifetime of acetaldehyde has recently been determined to be about 0.8 days using 3D model analysis and comparison with atmospheric measurements.[3] Earlier analysis of the global tropospheric acetaldehyde budget indicated a gap in understanding because the atmospheric models were not able to correctly predict atmospheric measurements.[4] The apparent imbalance was resolved when it was shown that in situ production from chemical oxidation of hydrocarbons is a dominant source contributing 60% of the total; other important sources include emissions from vegetation and from the oceans.[3] The anthropogenic sources of acetaldehyde contribute only a few percent of the total direct emission, but in addition, some of the acetaldehyde produced by oxidation in the atmosphere will originate from hydrocarbons with an anthropogenic origin. One example is that the use of ethanol as a vehicle fuel has increased direct acetaldehyde emissions as well as in situ formation of acetaldehyde from ethanol oxidation.[5,6] Photochemical processes dominate

removal of acetaldehyde from the atmosphere. Of these, reaction with OH and photolysis contribute 88 and 11%, respectively.

Insight into atmospheric photochemical processes, sources, and transport can be obtained by measuring the concentrations of several isotopologues of a given compound and combining them with the isotopic signatures of production and loss processes. The photolytic kinetic isotope effect for CH$_3$CDO, $j_{CH3CHO}/j_{CH3CDO} = 1.26 \pm 0.03$, was determined under natural sunlight conditions in the same experimental campaign as the results presented in the present paper.[7] The hydrogen/deuterium isotope effects for the formaldehyde[8−10] and acetaldehyde[9−11] reactions with OH, Br, Cl, and NO$_3$ have been determined. The most important of these oxidants is the OH radical, which has an isotope effect (light/heavy) of 1.65 ± 0.08 for the fully deuterated isotopologue, as determined by D'Anna et al.[9] The same group determined a kinetic isotope
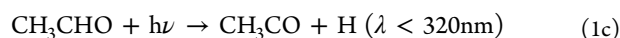
effect for CD$_3$CHO of 1.13 ± 0.04, while Taylor et al. determined a conflicting value of 0.88.[11] D'Anna et al.[9] present theoretical calculations in agreement with their experimental results, which can be taken as a support for their experimental result that the light isotopologue reacts faster than the heavy.

Photolytic excitation of acetaldehyde in the actinic wavelength region (approximately 300−330 nm) can lead to isomerization or dissociation. For atmospheric conditions, the overall photodissociation quantum yield is about 0.14, ranging from close to unity at shorter wavelengths and decreasing to below a percent at the long wavelength end of the range.[12−14] Andrews et al.[14] report that for collision-free conditions about one-fifth of the reactions of photoexcited acetaldehyde proceed via keto−enol tauteromization and isomerize to form vinyl alcohol, which is a precursor to formic acid formation in the troposphere. The authors have drawn attention to the lack of good experimental data on a range of prototypical carbonyls under atmospheric conditions; acetaldehyde is the simplest carbonyl that can undergo keto−enol tautomerization.

The photodissociation of acetaldehyde is pressure- and wavelength-dependent and has three distinct product channels:

$$CH_3CHO + h\nu \rightarrow CH_3 + HCO \ (\lambda < 337 nm) \tag{1a}$$

[13]

$$CH_3CHO + h\nu \rightarrow CH_4 + CO \tag{1b}$$

$$CH_3CHO + h\nu \rightarrow CH_3CO + H \ (\lambda < 320 nm) \tag{1c}$$

[13]

For tropospheric conditions, channel 1a is dominant and channel 1c contributes with about 10% according to the most recent IUPAC evaluation.[13] Channel 1b, giving molecular products, is energetically accessible over the whole wavelength range, but the quantum yield is insignificant at atmospheric wavelengths.[12,13,15] The molecular channel has been extensively studied in recent years, since it occurs via the so-called "roaming" mechanism.[16−18]

Isotopes are used in reaction kinetics to obtain otherwise inaccessible information about reaction mechanisms. A recent study of CD$_3$CHO found that there is a significant amount of H/D scrambling in the photodissociation process of the molecule,[19] so that almost one-fifth of the radical channel products have the composition CD$_2$H+DCO, instead of the expected CD$_3$+HCO. The main mechanism involves sequential hydrogen (H or D) shifts to form CD$_2$HCDO, and at the lowest photolysis energies, the system undergoes an average of 20 hydrogen shifts, giving rise to significant isotopic scrambling. It was argued that this type of photoinduced isotopic isomerization will be important for atmospheric photodissociation when the barrier to exchange is lower than the dissociation limit.[20]

The UV absorption cross section of acetaldehyde has been described many times and has been critically reviewed.[12,13,21] The n → π* band in acetaldehyde is broad with some vibrational structure and a maximum around 290 nm. The band is a superposition of the S$_0$-S$_1$ (240−290 nm) and the spin forbidden S$_0$-T$_1$ (255−337 nm) transitions.[22] The single report on the n → π* band in the acetaldehyde isotopologues CH$_3$CDO and CD$_3$CDO shows large isotope effects in the region below 300 nm; the heavy isotopologues have smaller cross sections at all wavelengths.[23]

In the present work, we report the results for isotope effects in the tropospheric photolysis of the two acetaldehyde isotopologues CD$_3$CHO and CD$_3$CDO relative to CH$_3$CHO.

2. EXPERIMENT AND ANALYSIS

2.1. Reference Spectra. IR-spectra of the three deuterated acetaldehyde isotopologues CH$_3$CDO, CD$_3$CHO, and CD$_3$CDO were recorded in the photochemical reactor system at University of Copenhagen. The system consists of a 100 L quartz chamber equipped with White type multipass optics allowing the beam from a FTIR spectrometer (Bruker IFS 66v/s) to pass through the gas mixture. The setup is described in detail by Nilsson et al.[24] Gas mixtures were prepared by introducing the acetaldehyde into a calibrated volume equipped with a pressure gauge. The gas was expanded into the quartz chamber, and the calibrated volume was flushed with nitrogen gas into the chamber. The chamber was then filled with nitrogen to a total pressure of 980 mbar, which resulted in partial pressures of about 0.01 mbar of the acetaldehydes. The reference spectra were recorded at an optical path length of 64 m, using an MCT detector, at a resolution of 0.125 cm^{-1}, coadding 128 scans. The reference spectra of CD$_3$CDO and CD$_3$CHO are available as Figures S1 and S2 of the Supporting Information and are also available for download from the Eurochamp database (http://euphore.es/FTIRReferences2/index.php).

2.2. Photolysis Experiments. The photolysis experiments were part of a campaign carried out in the period of June 17 − July 7, 2006, in chamber B at the European Photoreactor Facility (EUPHORE) in Valencia, Spain (longitude −0.5, latitude 39.5). The present experiments are similar to those described in our previous publications concerning photolysis of the acetaldehyde isotopologue CH$_3$CDO[7] and the formaldehyde isotopologues.[25−27] A typical experiment starts around 06:00 UT (local time = UT + 2) when reagents are added to the chamber. The canopy of the chamber is kept closed for 1−2 h, during which the reagents mix and a series of spectra of the reaction mixture in the dark chamber are recorded. When the gas mixture was considered well-mixed, FTIR spectra were used to quantify reactants starting at least 30 min before exposing the mixture to sunlight to check for dark reactions. After the chamber canopy is opened, the experiment lasts for up to 4 h, after which the chamber is closed and flushed overnight with scrubbed air. The chamber is always at the same pressure as the ambient atmosphere, 1 bar.

Approximately 0.5 g (1.5 ppm) of each of the acetaldehyde isotopologues, CH$_3$CHO (Fluka, >99.0% purity) and CD$_3$CDO (CDN, 99.9% purity, 99 atom % D) or CD$_3$CHO (CDN, 99.9% purity, 98 atom % D), were evaporated and flushed into the chamber. Throughout the duration of the experiment, the actinic flux (290−520 nm) was measured by a Bentham DM300 spectroradiometer, while IR spectra were recorded every 10 min by coadding 230 interferograms obtained at a resolution of 0.5 cm^{-1} (Nicolet Magna 550 FTIR spectrometer coupled with a White-type multireflection mirror system with an optical path length of 553.3 m). In addition to the FTIR analysis, the gas mixture is analyzed for variations in pressure, temperature, solar flux, j_{NO2}, [NO], [NO$_2$], [O$_3$], and [CO]. An example of these data for 1 day during the campaign, June 19, is reported in the previous publication.[7] Figure 1 shows how the composition changes in the chamber throughout an experiment. The top panel shows an IR spectrum recorded when the canopy is opened, and the
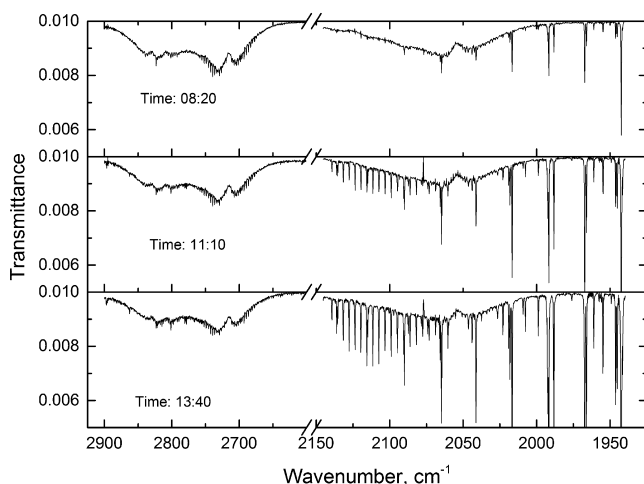
Figure 1. Time series for experiments on June 30, 2006. The top panel shows the initial mixture when the canopy was opened, including CH_3CHO, CD_3CDO, and CD_3CHO. As the day progresses, shown in the middle and lower panels, reaction products CO and H_2O build up.
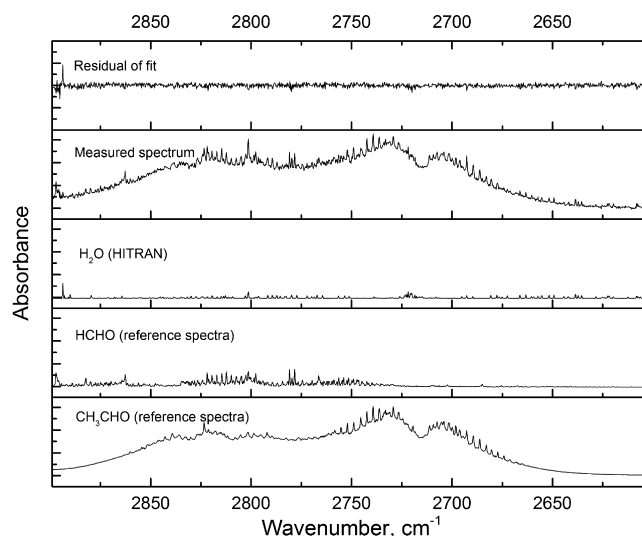

Figure 2. Example of spectral fit of normal acetaldehyde, formaldehyde, and water to an experimental spectrum, and residual of fit during the photolysis experiment in the EUPHORE chamber B on June 30, 2006. See text for information on the spectral fitting procedure.

middle and lower panels show spectra recorded at later times in the day. As time passes, one can see the buildup of CO and H_2O.

Purified air is constantly added to compensate for leakage, loss through connections, and continuous sampling by ozone and NOx monitors. This is corrected for in the data analysis using the FTIR record of the loss of the inert SF_6, of which about 20 ppb is added to the chamber together with the other reactants. The apparent dilution rate coefficient of the chamber, $k_{dilution}$, is determined:

$$\ln\{[SF_6]_0/[SF_6]_t\} = k_{dilution} \times t \qquad (2)$$

where $[SF_6]_0$ and $[SF_6]_t$ are the SF_6 concentrations at times zero and t, respectively. Typical values of $k_{dilution}$ of the EUPHORE Chamber B during the present experiments are in the range of $5-7 \times 10^{-6}$ s^{-1}.

2.3. Analysis of the Spectra. The experimental spectra were analyzed using a nonlinear least-squares spectral fitting program, MALT.[28] The program uses HITRAN line parameter data or high-resolution reference spectra to simulate a spectrum from an initial guess of concentrations of the components. An iterative fitting follows, using the Levenberg−Marquardt algorithm to adjust the calculation parameters (absorber concentrations, continuum level, and instrument line-shape parameters). A least-squares minimum residual between measured and simulated spectra is normally achieved in 5 to 10 iterations.

The spectral features used in the analysis of the acetaldehyde removal from the chamber were the C−H stretching bands in the 2900−2600 cm^{-1} region and the C−D stretching bands in the 2145−1940 cm^{-1} region. The reference spectra for acetaldehyde isotopologues CD_3CDO and CD_3CHO are presented in Figures S1 and S2 of the Supporting Information. Formaldehyde isotopologues were produced during experiments, and since they have spectral features in the analyzed regions, they need to be included in the spectral fitting. For this purpose, IR absorption cross sections from Gratien et al.[29] were used. For H_2O, HDO, CO, and CO_2, the spectral data needed in the fitting procedure were taken from the HITRAN 2008 database.[30] Figure 2 shows an example of an experimental spectrum in the region 2900−2600 cm^{-1}, the spectra of the

three components included in the analyses, and the residual in the spectral fitting. Looking at the residual, one can conclude that all components are accounted for correctly. Figure 3 shows
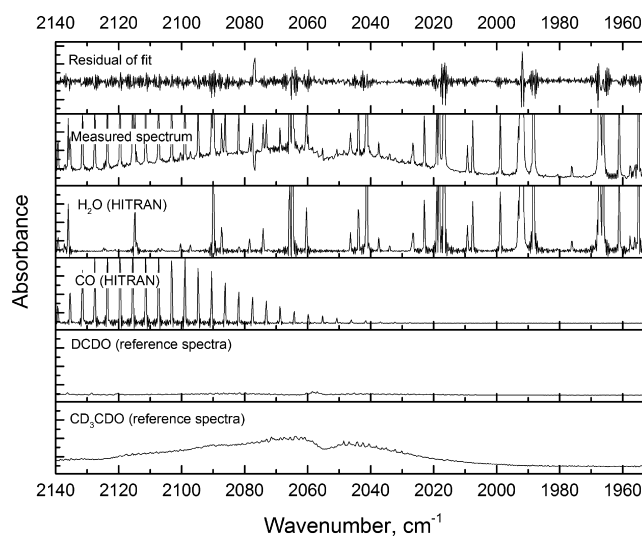

Figure 3. Example of spectral fit of deuterated acetaldehyde and formaldehyde, carbon monoxide, and water to an experimental spectrum and residual of fit during the photolysis experiment with CD_3CDO in the EUPHORE chamber B on June 30, 2006. See text for information on the spectral fitting procedure.

an analysis in the 2140−1950 cm^{-1} region, where CO also absorbs. The residual in this case shows some spectral features resulting from difficulties in accurately fitting the water lines. The other components are, however, well-determined, and this fit is considered to be of high quality for the acetaldehyde bands.

The concentration of SF_6 was determined from the integrated intensity of its $\nu_3(F_{1u})$ band around 947.5 cm^{-1}, the shape of which is sensitive to temperature variations. The

spectral overlap with acetaldehyde isotopologues in this region is negligible.

3. RESULTS

With the chamber canopy open, OH radicals are formed as hydrogen atoms and formyl radicals from acetaldehyde photolysis react with O_2 to generate HO_2 and eventually H_2O_2, OH, and O_3. As there is always a small amount of NO_x present, depending in part on outside conditions, enough OH could be generated to make the OH + CH_3CHO reaction competetive to photolysis. It is obviously important to quantify the fraction of the aldehydes that react with OH as this is not only an additional loss process but also associated with a kinetic isotope effect[9] that must be considered in the analyses. The reaction system was therefore examined using a FACSIMILE kinetic model based on the Master Chemical Mechanism and specially designed for the EUPHORE chamber in order to examine the extent of the competing chemical reaction of the aldehyde with OH.[31] The model uses the temperature and the photolysis rate of NO_2 recorded in the chamber each day, and the initial concentrations of NO_x, O_3, and (in the present case) CH_3CHO to simulate the OH concentration throughout the day for each day of experiments. The j_{NO2} values are used to scale the photolysis rates of all species in the model to match the specific conditions of a given day. Figure 4 shows an
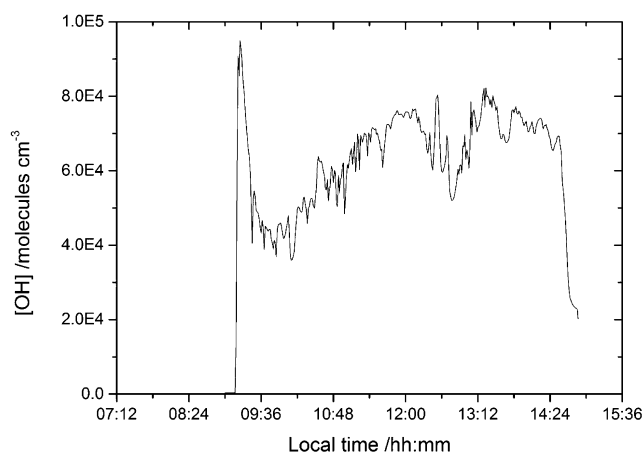

Figure 4. Example of modeled OH concentration as a function of time. The model considers temperature, j_{NO2}, and the initial concentrations of NO_x, O_3, and acetaldehyde isotopologues.

example of the calculated OH radical concentration as a function of time. The calculated OH concentrations, ca. 5×10^4 cm^{-3}, in the reaction chamber during experiments are not high enough to make a significant contribution to the removal of acetaldehyde. However, as the OH concentration could reach as much as 10^5 cm^{-3} during the middle of the day, corrections are made in the data analyses (see later). Thus, the average OH concentration is lower than the tropospheric average of ca. 1×10^6 cm^{-3}.

The relative rate method was used to determine the photolysis rates of CD_3CHO and CD_3CDO relative to that of CH_3CHO. The decays in concentration of the species undergoing photolysis are measured simultaneously as a function of reaction time. Consider an experiment with two simultaneous photolysis processes with the rates j_{RH} and j_{RD}, where RH denotes the normal species and RD the deuterated species:

$$RH + h\nu \xrightarrow{j_{RH}} products$$

$$RD + h\nu \xrightarrow{j_{RD}} products \tag{3}$$
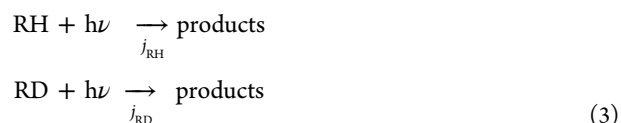
Assuming that there are no loss processes other than these reactions and that there are no other processes producing the reactants, the following relation is valid:

$$\ln\left\{\frac{[RH]_0}{[RH]_t}\right\} = \frac{j_{RH}}{j_{RD}} \ln\left\{\frac{[RD]_0}{[RD]_t}\right\} \tag{4}$$

where $[RH]_0$, $[RH]_t$, $[RD]_0$, and $[RD]_t$ denote the concentrations of the aldehydes at times zero and t, respectively. A plot of $\ln([RH]_0/[RH]_t)$ versus $\ln([RD]_0/[RD]_t)$ will thus give the relative photolysis rate coefficient $j_{rel} = j_{RH}/j_{RD}$ as the slope.

In the present cases, however, three loss processes for the aldehyde isotopologues in the chamber have to be taken into account, photolysis, reaction with OH, and dilution:

$$\frac{d[RH]}{dt} = -(j_{RH} + k_{dilution} + k_{OH+RH} \times [OH]) \times [RH]$$

$$\frac{d[RD]}{dt} = -(j_{RD} + k_{dilution} + k_{OH+RD} \times [OH]) \times [RD] \tag{5}$$

The photolysis rates, j_{RH} and j_{RD}, have time-dependencies determined by the variation in actinic flux. These are assumed to be identical for the two isotopologues, as done previously by Feilberg et al.[25,26] Eq 5 gives:

$$\ln\frac{[RH]_0}{[RH]_t} - k_{dilution} \times t - \int_0^t k_{OH+RH} \times [OH]_t \times dt$$

$$= \frac{j_{RH}}{j_{RD}}\left(\ln\frac{[RD]_0}{[RD]_t} - k_{dilution} \times t - \int_0^t k_{OH+RD} \times [OH]_t \right.$$

$$\left. \times dt\right) \tag{6}$$

The analysis of the FTIR spectra produced accurate values for the relative change in concentrations, which were subsequently analyzed according to eq 6, using a weighted least-squares procedure which includes uncertainties in both the dependent and independent variables. The uncertainty assigned each data point includes conservative estimates of a 10% relative error in the dilution contribution and a 20% relative error in the calculated loss due to reaction with OH radicals.

Plots for the acetaldehyde experiments are shown in Figure 5. The results from weighted least-squares analyses are summarized in Table 1, where the quoted error represents 2σ from the statistical analysis, including propagation of uncertainties in the individual measurements.

4. DISCUSSION

As mentioned, a number of recent reports show that acetaldehyde subject to tropospheric ultraviolet excitation explores a significant region of its configuration space. Due to the complex topography of the potential energy surface, this involves a significant amount of hydrogen exchange. In addition, it has been proposed that acetaldehyde may be a significant source of atmospheric acids, helping to explain the
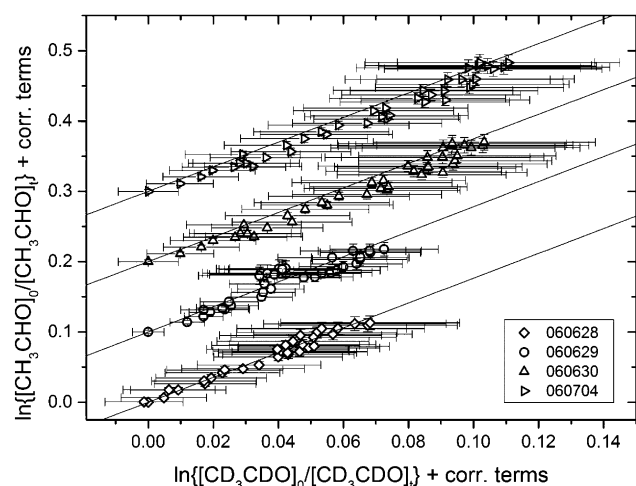
Figure 5. Decay of CH_3CHO versus CD_3CDO during photolysis experiments in the EUPHORE reactor as measured by FTIR; error bars include the 1σ error from the spectral analysis and the estimated uncertainties in the correction terms given in eq 5. The average relative photolysis rate from 4 independent experiments is 1.75 ± 0.04 (2σ). Data offset by 0.1, 0.2, and 0.3 for June 29 and 30 and July 4, respectively.

Table 1. Summary of Relative Photolysis Rates of Acetaldehyde Measured by FTIR[a]

date of experiment[b]	$[CH_3CHO]_0/[CD_3CDO]_0$ (ppb)	$k_{dilution}$ (s^{-1})	$j_{rel} = j_{CH3CHO}/j_{CD3CDO}$
060628	580/690	4.9×10^{-6}	1.75 ± 0.06
060629	690/1380	6.2×10^{-6}	1.78 ± 0.05
060630	710/670	5.2×10^{-6}	1.65 ± 0.06
060704	440/1750	5.5×10^{-6}	1.77 ± 0.03
weighted average			1.75 ± 0.04
date of experiment	$[CH_3CHO]_0/[CD_3CHO]_0$ (ppb)	$k_{dilution}$ (s^{-1})	$j_{rel} = j_{CH3CHO}/j_{CD3CHO}$
060706	600/470	5.4×10^{-6}	1.10 ± 0.10

[a]Errors represent 2 sigma derived from the statistical analyses. [b]Dates are in the format of year, month, day (i.e., yymmdd).

gap between measurements and models. Examination of the absorption cross sections of the acetaldehyde isotopologues[23] shows that only a few percent of the observed photolytic kinetic isotope effects ($j_{CH3CHO}/j_{CD3CHO} = 1.10 \pm 0.10$, $j_{CH3CHO}/j_{CH3CDO} = 1.26 \pm 0.03$ (see ref 7) and $j_{CH3CHO}/j_{CD3CDO} = 1.75 \pm 0.04$) is due to the differing rates of photoexcitation. The explanation seems rather to involve isotope-dependent changes in the unimolecular lifetimes of the isotopologues and their rates of collisional quenching, resulting in pressure and isotopologue-dependent changes in the photolysis quantum yields. This is shown for example in the effect of deuterating the methyl group, which has a primary effect on the density of states but a secondary effect on the chromophore. While scrambling is apparently very important, there is also a key role for the position of the hydrogen, with deuterium in the aldehydic position significantly slowing photolysis. As noted by Heazlewood et al., while the acetaldehyde isotopologues share the same potential energy surface, there are differences in the vibrational frequencies and rotational constants.[16,19] Recent studies of the atmospheric photolysis of formaldehyde isotopologues have found that some of the deuterium kinetic isotope effect is due to changes in the unimolecular lifetime of

the excited molecule.[32] A simple quantum chemistry-RRKM model shows that the density of states of HCDO is higher than that of HCHO, with DCDO being highest of all, due to the lower vibrational frequencies of the substituted species. A similar trend is seen in the acetaldehyde data. However, studies show that only about half of the photolytic kinetic isotope effect can be attributed to the change in unimolecular lifetime. Isotope-dependent changes in rate of S_1 to S_0 intersystem crossing also play a role.[32,33] A similar dynamical process may also be at work in the photolysis of acetaldehyde, which would be an interesting case to study using a dynamics/trajectory surface hopping calculation.[34]

■ ASSOCIATED CONTENT

⑤ Supporting Information

IR spectra of the acetaldehyde isotopologues CD_3CDO and CD_3CHO. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: elna.heimdal_nilsson@forbrf.lth.se. Fax: +46462224542.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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