



Photo-Tautomerization of Acetaldehyde to Vinyl Alcohol: A Potential Route to Tropospheric Acids Duncan U. Andrews *et al. Science* **337**, 1203 (2012); DOI: 10.1126/science.1220712

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The ability to probe electron small polarons is a first step toward experimentally distinguishing the multiple steps that comprise redox transformations of iron (oxyhydr)oxides and measuring their rates. The small-polaron hopping rate is a fundamental mineral phase-dependent limit on the kinetics of many iron redox reactions. As shown in Fig. 4B, we additionally observed iron(II) in the nanoparticles at microsecond time scales, representing itinerant electrons that were trapped within the iron oxides before leaving either by dissolution or recombination. Complementing the present measurements of hopping rates with rates of additional steps, such as bond breaking or the nucleation of new mineral phase, will enable more detailed mechanistic descriptions of the reductive dissolution of iron(III) (oxyhydr)oxides and other important environmental reactions. We anticipate that the combination of transient-absorption spectroscopy, conventional kinetics measurements, and ab initio and kinetic modeling offers a framework for this program.

References and Notes

- 1. W. Stumm, B. Sulzberger, *Geochim. Cosmochim. Acta* 56, 3233 (1992).
- 2. H. D. Pedersen, D. Postma, R. Jakobsen, *Geochim. Cosmochim. Acta* **70**, 4116 (2006).
- O. Larsen, D. Postma, Geochim. Cosmochim. Acta 65, 1367 (2001).
- C. M. Hansel, S. G. Benner, S. Fendorf, *Environ. Sci. Technol.* 39, 7147 (2005).
- H. D. Pedersen, D. Postma, R. Jakobsen, O. Larsen, Geochim. Cosmochim. Acta 69, 3967 (2005).

- 6. S. V. Yanina, K. M. Rosso, Science 320, 218 (2008).
- P. A. Cox, Transition Metal Oxides: An Introduction to Their Electronic Structure and Properties (Oxford Univ. Press, New York, 2010).
- 8. T. Holstein, Ann. Phys. 8, 343 (1959).
- 9. K. M. Rosso, M. Dupuis, J. Chem. Phys. 120, 7050 (2004).
- J. Ederth, A. Hoel, G. A. Niklasson, C. G. Granqvist, J. Appl. Phys. 96, 5722 (2004).
- 11. A. S. Alexandrov, N. F. Mott, *Polarons and Bipolarons* (World Scientific, Singapore, 1996).
- 12. I. Djerdj et al., J. Am. Chem. Soc. 130, 11364 (2008).
- 13. N. Mannella et al., Phys. Rev. Lett. 92, 166401 (2004).
- 14. J. E. Katz et al., J. Phys. Chem. Lett. 1, 1372 (2010).
- 15. Ch. Bressler et al., Science 323, 489 (2009).
- G. A. Waychunas, M. J. Apted, G. E. Brown Jr., Phys. Chem. Miner. 10, 1 (1983).
- 17. M. Grätzel, Nature 414, 338 (2001).
- 18. C. Bressler, M. Chergui, Chem. Rev. 104, 1781 (2004).
- 19. L. X. Chen, Annu. Rev. Phys. Chem. 56, 221 (2005).
- 20. A. Cannizzo et al., Coord. Chem. Rev. 254, 2677 (2010).
- 21. J. Chen et al., J. Phys. Chem. A **111**, 9326 (2007).
- 22. F. M. Michel *et al.*, *Science* **316**, 1726 (2007).
- J. M. Cowley, D. E. Janney, R. C. Gerkin, P. R. Buseck, J. Struct. Biol. 131, 210 (2000).
- N. J. Cherepy, D. B. Liston, J. A. Lovejoy, H. Deng,
 J. Z. Zhang, J. Phys. Chem. B 102, 770 (1998).
- G. Benkö, M. Hilgendorff, A. P. Yartsev, V. Sundström, *J. Phys. Chem. B* 105, 967 (2001).
- M. Hilgendorff, V. Sundström, J. Phys. Chem. B 102, 10505 (1998).
- M. Wilke, F. Farges, P.-E. Petit, G. E. Brown Jr., F. Martin, Am. Mineral. 86, 714 (2001).
- U. Colombo, G. Fagheraz, F. Gazzarrini, G. Lanzavecchia, G. Sironi, *Nature* **219**, 1036 (1967).
- E. Tronc, P. Belleville, J. P. Jolivet, J. Livage, *Langmuir* 8, 313 (1992).
- J. Tang, M. Myers, K. A. Bosnik, L. E. Brus, J. Phys. Chem. B 107, 7501 (2003).

- A. L. Ankudinov, B. Ravel, J. J. Rehr, S. D. Conradson, Phys. Rev. B 58, 7565 (1998).
- B. Gilbert *et al.*, *J. Phys. Chem. A* **107**, 2839 (2003).
 N. Iordanova, M. Dupuis, K. M. Rosso, *J. Chem. Phys.* **122**, 144305 (2005).
- 34. A. Manceau, *Clay Miner.* **44**, 19 (2009).
- 35. D. G. Rancourt, J. F. Meunier, *Am. Mineral.* **93**, 1412 (2008).
- 36. W. Xu et al., Am. Mineral. 96, 513 (2011).

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Supplementary Materials

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Photo-Tautomerization of Acetaldehyde to Vinyl Alcohol: A Potential Route to Tropospheric Acids

Duncan U. Andrews,* Brianna R. Heazlewood,*† Alan T. Maccarone,‡ Trent Conroy, Richard J. Payne, Meredith J. T. Jordan,§ Scott H. Kable§

Current atmospheric models underestimate the production of organic acids in the troposphere. We report a detailed kinetic model of the photochemistry of acetaldehyde (ethanal) under tropospheric conditions. The rate constants are benchmarked to collision-free experiments, where extensive photo-isomerization is observed upon irradiation with actinic ultraviolet radiation (310 to 330 nanometers). The model quantitatively reproduces the experiments and shows unequivocally that keto-enol photo-tautomerization, forming vinyl alcohol (ethenol), is the crucial first step. When collisions at atmospheric pressure are included, the model quantitatively reproduces previously reported quantum yields for photodissociation at all pressures and wavelengths. The model also predicts that $21 \pm 4\%$ of the initially excited acetaldehyde forms stable vinyl alcohol, a known precursor to organic acid formation, which may help to account for the production of organic acids in the troposphere.

rganic acids are important trace components of the troposphere, with estimates ranging from 60 to 120 megatonnes formed per year (1, 2). However, the mechanism responsible for producing these acids is incomplete (2-5); current models underpredict their production by about a factor of two (1), implying a missing acid precursor (2). Recently, there has been interest in enols as efficient precursors for the formation of organic acids (4, 5). Archibald *et al.* (4) modeled the atmospheric fate of enols and concluded that the production of formic acid (HCOOH) was significantly enhanced by their inclusion into the model. However, a viable atmospheric source of enols has not been suggested. We present evidence that photo-induced keto-enol tautomerization occurs under atmospheric conditions and provides such a source.

Carbonyl compounds feature centrally in all atmospheric oxidation pathways (6). Their role toward the end of the oxidation pathway is also clear, with measurable concentrations of acetaldehyde and acetone present in smog chambers (7). The atmospheric photochemistry of carbonyls seems uncontroversial. In the case of acetaldehyde, there are only two reactions that are important in the troposphere, where photochemistry is limited to wavelengths $\lambda > 295$ nm (8).

$$CH_3CHO + h\nu \rightarrow CH_3 + HCO$$
 (1)

$$\rightarrow CH_4 + CO$$
 (2)

Under atmospheric conditions, the photolysis quantum yield of acetaldehyde via reactions 1 and 2 is $\phi_{ph} = 14\%$ (vide infra). Atmospheric models assume implicitly that the other 86% of molecules collisionally cool, reverting to thermalized acetaldehyde. We demonstrate experimentally

School of Chemistry, University of Sydney, NSW, 2006, Australia.

^{*}These authors contributed equally to this work.

[†]Present address: Department of Chemistry, University of Oxford, Oxford, OX1 3QZ, UK.

Present address: Department of Chemistry, University of Wollongong, NSW, 2522, Australia.

[§]To whom correspondence should be addressed. E-mail: scott.kable@sydney.edu.au (S.H.K.); m.jordan@chem.usyd. edu.au (M.J.T.J.)

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and theoretically that photo-induced keto-enol tautomerization of acetaldehyde to vinyl alcohol (VA) is significant under collision-free conditions. Under atmospheric conditions, we predict that VA will constitute a significant fraction of the photochemical product yield and propose that photo-tautomerization might be responsible for a significant concentration of organic acids unaccounted for in current models.

A detailed description of the experiments can be found in the supplementary materials. In brief, CH_3CDO , cooled in a supersonic expansion of helium, was photolysed at a variety of wavelengths using a laser. The production of formyl fragments was measured by laser-induced fluorescence. Isotopic labeling allows a more thorough investigation of the reaction mechanism. Specifically, direct photolysis products can be distinguished from indirect products that require isomerization to CH_2DCHO ; for example, reaction 1 manifests direct and indirect channels 1a and 1b, respectively.

$$CH_3CDO + hv \rightarrow CH_3 + DCO$$
 (1a)

$$CH_2DCHO \rightarrow CH_2D + HCO$$
 (1b)

Figure 1A shows two action spectra of the $S_1 \leftarrow S_0 (n, \pi^*)$ electronic transition of CH₃CDO that were obtained by monitoring the production of DCO or HCO photoproducts while scanning the photolysis wavelength. The vibrational structure is the same; however, the intensities are clearly different, reflecting the changing quantum yield for direct (ϕ_{1a}) versus indirect (ϕ_{1b}) products as a function of wavelength. The ratio of indirect to total formyl yields, ϕ_{1b}/ϕ_1 , derived from these intensities is plotted in Fig. 1B, as explained in the supplementary materials.

At $\lambda > 320$ nm, photolysis can only occur on the ground S_0 state, following internal conversion from S_1 , and here ϕ_{1b}/ϕ_1 falls slowly from 20% at 330 nm to 12% at 320 nm. At 320 nm, there is a sudden decrease in ϕ_{1b} , indicated by an exponential function in the figure. This arises because of intersystem crossing from S_1 to T_1 . On the triplet surface reaction 1b cannot occur, whereas reaction 1 a becomes increasingly dominant at higher energy (9–11), with ϕ_{1b}/ϕ_1 falling to ≈ 0 by 312 nm.

The production of HCO and DCO on S_0 was modeled by calculating transition state theory (TST) or variational TST rate constants for every isomerization and dissociation process. These calculations mirror those that we published (9) for another isotopolog of acetaldehyde, CD₃CHO, and so an extensive description of the theoretical methods is left to the supplementary materials. Table S1 lists the critical energies, and table S2 presents a set of rate constants at a typical energy.

A collision-free master equation (ME) analysis was then used to calculate the population of each species as a function of time, with final populations numerically converged to <1%. More details of the ME modeling are provided as supplementary materials. Figure S2 shows the evolution of population with time for photolysis at 320 nm. When the reaction is complete, the main products are CO + CH₃D ($\phi_2 = 15\%$) and formyl + methyl radicals ($\phi_1 = 85\%$) partitioned as direct products ($\phi_{1a} = 70\%$) and indirect products ($\phi_{1b} = 15\%$). Experimentally, at 320 nm, $\phi_1/\phi_2 = 6$ when extrapolated to zero pressure (*12*), in excellent agreement with the 85/15 ratio above. The calculations reveal that the dominant mechanism for reaction 1b, with >90% of the flux, is the isomerization pathway shown in Fig. 2.

The calculated yields ϕ_{1a} and ϕ_{1b} at zero pressure are benchmarked by our experimental data, also under conditions of few collisions. The solid line in Fig. 1B shows the calculated ratio of ϕ_{1b}/ϕ_1 as a function of wavelength. Triplet reaction is not included in the model, so it cannot reproduce the rapid fall-off observed for $\lambda < 320$ nm. The model slightly overestimates ϕ_{1b} ; however, the wavelength dependence is reproduced. ϕ_{1b} is very sensitive to the height of the enol-carbene isomerization barrier shown in Fig. 2. If this barrier is raised by only 2 kJ/mol, φ_{1b} is reduced, as shown by the dotted curve in Fig. 1B, which provides an excellent fit to the experiments at all energies below the T_1 threshold. A correction of 2 kJ/mol is well within the uncertainty in the calculated barrier height, estimated to be ±5 kJ/mol, based on the level of theory of the calculation. Our model for the collision-free decomposition of CH₃CDO now reproduces quantitatively the relative quantum yield of both chemical channels,



The pressure dependence of acetaldehyde photolysis was modeled using a one-dimensional ME simulation, as implemented in the MultiWell program package (13-15), employing an exponential down collisional energy-transfer model and Lennard-Jones collision frequencies with N2 at 300 K. The average downward collisional energy transfer is taken to be $\langle \Delta E_{down} \rangle = 150 \text{ cm}^{-1}$, as described in the supplementary materials and as used previously (16). We assume that vibration to rotational/translational (V-R,T) energy transfer dominates because N2 has a high vibrational frequency. We also assume $\langle \Delta E_{\text{down}} \rangle$ is independent of energy; we are only interested in collisional deactivation above the keto-enol tautomerization barrier (>282 kJ/mol) where the density of vibrational states is large. The rate of energy transfer below this barrier only affects how quickly the stable products are thermalized, not the final distribution of products.

The ME model is benchmarked to experiments of Horowitz and Calvert (HC) (12) and Moortgat *et al.* (MMW) (17). The wavelength dependence of ϕ_{ph} is shown in Fig. 3A, which also shows that the selected $\langle \Delta E_{down} \rangle = 150 \text{ cm}^{-1}$ provides the best fit to experiment. For $\lambda > 300 \text{ nm}$, the model reproduces the experiments well, but it overestimates ϕ_{ph} at $\lambda < 300 \text{ nm}$. At higher photolysis energies, quenching on T_1 should be

Fig. 1. (**A**) CH₃CDO action spectra monitoring HCO and DCO (displaced vertically). HCO intensity has been increased by a factor of 5 with respect to DCO. (**B**) The percentage of HCO to total formyl radical production measured at each dominant peak in the spectra. Representative error bars are provided. The results of a ME model are shown as a solid line. The effect of raising the rate-limiting transition state (TS) energy by 2 kJ/mol is shown by a dotted line.



included (with a different quenching rate). However, the solar flux at $\lambda < 300$ nm is small, and the discrepancies between our ME model and experimental results will be unimportant for atmospheric chemistry.

HC and MMW also report the dependence of ϕ_{ph} on N₂ or CO₂ pressure at specific wavelengths (12, 17). Figure 3B shows their experimental data as a Stern-Volmer (SV) plot of 1/\$\phi_p\$h versus pressure, P (dashed lines). The experimental data at 331.4 nm have considerable uncertainty, and the zero pressure intercept is reported as $1/\phi_{ph} = 18 (\phi_{ph} = 0.06) (12)$. However, at zero pressure, ϕ_{ph} must be ≈ 1 because the radiative quantum yields are very small [< 0.01 at all wavelengths here (18)]. We have replotted all the experimental SV plots in Fig. 3B, assuming a zero pressure intercept of 1, and compared them to our ME model results (solid lines). The ME model provides a good representation of the experimental data, with the largest variation occurring at 331.4 nm, where experimental uncertainties are largest. Indeed our ME model predictions sit between the two independent sets of experimental data at $\lambda = 313$ nm.

We now consider the fate of excited acetaldehyde molecules that do not photodissociate and explore the effect of collisional quenching under atmospheric conditions on keto-enol tautomerization. Figure 4A shows the predicted quantum yield of stable enol, ϕ_{enol} , as a function of wavelength, for $\langle \Delta E_{down} \rangle = 150 \text{ cm}^{-1}$ and 1 atm pressure. The yield is a maximum at ~315 nm; at shorter wavelengths, the increasing φ_{ph} causes a decrease in ϕ_{enol} , whereas at longer wavelengths the molecule cools before keto-enol tautomerization reaches equilibrium. The most sensitive parameter in the model is the height of the keto-enol barrier. Figure 4A also shows the results of the ME model when the barrier is raised and lowered by 5 kJ/mol, an estimate of the theoretical uncertainty. The predicted ϕ_{enol} changes slightly; the maximum quantum yield increases or decreases by about 4%, giving an estimate of the computational uncertainty.

The collision-free ME model has only been strictly validated for $\lambda > 320$ nm (Fig. 1B). However, the collisional ME model appears valid at atmospheric pressure for $\lambda > 300$ nm (Fig. 3A) because quenching on S_1 and T_1 competes with reaction on T_1 . As a worst case, we might assume that the sharp decrease in ϕ_{1b}/ϕ_1 in Fig. 1B also applies at P = 1 atm. The result of this assumption is shown by the dashed curve in Fig. 4A.

The consequences of keto-enol tautomerization for the atmospheric photochemistry of acetaldehyde can now be evaluated. The rate *k* of a photochemical reaction in the troposphere is the product of the actinic flux $J(\lambda)$, the absorption cross section $\sigma(\lambda)$, and the quantum yield $\phi(\lambda)$ for the specific photochemical process, integrated over wavelength.

$$k = \int J(\lambda) \sigma(\lambda) \phi(\lambda) d\lambda \tag{3}$$

Figure 4B shows $\sigma(\lambda)$ (19) and $J(\lambda)$ under typical conditions (albedo = 0.3 and overhead sun) (6) in the spectral region where both are nonzero. Figure 4C shows the right-hand side of Eq. 3, integrated over 1-nm intervals, for absorption of light (i.e., $\phi = 1$) and for photolysis and photo-tautomerization using ϕ_{ph} from MMW (17) in Fig. 3A and ϕ_{enol} from Fig. 4A. The overall photolysis quantum yield is 14%, in agreement with experiments (12, 17). The worst-case scenario for enol production, if the T_1 reaction follows the collision-free quantum yield (Fig. 4A), is 13%, effectively the same as the photolysis yield. Our best estimate of ϕ_{enol} is 21 ± 4%.

Acetaldehyde is the simplest carbonyl compound that can undergo keto-enol tautomerization, and its photochemical properties are typical



Fig. 2. A schematic showing energies (k]/mol) and important structures on the $CH_3CDO S_0$ potential energy surface for the production of DCO and HCO. The green arrows indicate the experimental yields of HCO and DCO at 320 nm under collision-

free conditions. Under atmospheric conditions, we predict that excited acetaldehyde collisionally relaxes into both keto and enol forms, as shown by the blue curvy arrows. All energies are from this work, as defined in the supplementary materials. of smaller carbonyls. The (n,π^*) transition generally lies between 280 and 330 nm, with similar absorption cross sections throughout the family (8, 19). The barrier to tautomerization is also similar (20). Therefore, we expect photo-tautomerization of small aldehydes and ketones to be a general characteristic of their fate in the atmosphere.

Enols have a different atmospheric chemistry from carbonyls; indeed, the atmospheric fate of

Fig. 3. Comparison of photochemical quantum yields from the ME model and available experiment data. (**A**) ϕ_{ph} as a function of wavelength for P = 1 atm. (**B**) Pressure dependence shown as Stern-Volmer plots. The dashed lines are derived from reported SV fits to experimental data. The ME model used $\langle \Delta E_{down} \rangle =$ 150 cm⁻¹. In both panels: HC (12), MMW (17).

Fig. 4. (A) Quantum yield for enol formation according to the ME model for three keto-enol barrier heights. (B) Solar flux, J, and acetaldehyde absorption cross section, σ . (C) Absorption and photochemistry rates. The area surrounding the phototautomerization line represents the computational uncertainty. The dashed lines in (A) and (C) represent a worst-case correction for triplet reaction.

vinyl alcohol is formic acid (4, 5). Despite this, they have not been included in current atmospheric models for two reasons. First, enols have not been observed in the atmosphere. As reactive intermediates, their concentration will be very low. Second, there is no sufficiently large atmospheric source of enols. On the basis of this work, we propose that photo-tautomerization of carbonyls to enols may provide such a source.



It is interesting to speculate about phototautomerization for larger carbonyls. For linear aldehydes with \geq 4 C atoms, the rate of a Norrish type II mechanism dominates even C-C bond cleavage (21), so we expect photo-tautomerization to be less important for these compounds. When chain flexibility is hindered by unsaturation, branching, or cyclization, the Norrish type II mechanism will likely turn off again, whereas tautomerization will always be present. Evaluation of the importance of this new mechanism for enol formation under the complex chemistry of the troposphere requires its inclusion in the relevant atmospheric models. However, good experimental data are first required for a range of prototypical carbonyls under atmospheric conditions.

References and Notes

- A. Ito, S. Sillman, J. E. Penner, J. Geophys. Res. 112, D06309 (2007).
- F. Paulot et al., Atmos. Chem. Phys. 11, 1989 (2011).
- A. H. Goldstein, I. E. Galbally, *Environ. Sci. Technol.* 41, 1514 (2007).
- A. T. Archibald, M. R. McGillen, C. A. Taatjes,
 C. J. Percival, D. E. Shallcross, *Geophys. Res. Lett.* 34, L21801 (2007).
- 5. G. da Silva, Angew. Chem. Int. Ed. 49, 7523 (2010).
- B. J. Finlayson-Pitts, J. N. Pitts Jr., Chemistry of the Upper and Lower Atmosphere (Academic Press, San Diego, CA, 2000).
- 7. A. Lee et al., J. Geophys. Res. 111, D17305 (2006).
 - 8. R. Atkinson *et al.*; IUPAC Subcommittee, *Atmos. Chem. Phys.* **6**, 3625 (2006).
 - 9. B. R. Heazlewood et al., Nat. Chem. 3, 443 (2011).
 - B. R. Heazlewood, S. J. Rowling, A. T. Maccarone, M. J. T. Jordan, S. H. Kable, *J. Chem. Phys.* **130**, 054310 (2009).
- 11. A. C. West et al., J. Phys. Chem. A 113, 12663 (2009).
 - 12. A. Horowitz, J. G. Calvert, *J. Phys. Chem.* **86**, 3105 (1982).
 - MultiWell-2012.1 Software, 2012, designed and maintained by J. R. Barker with contributors N. F. Ortiz *et al.*; University of Michigan, Ann Arbor, MI; http://aoss.engin. umich.edu/multiwell.
 - 14. J. R. Barker, Int. J. Chem. Kinet. 33, 232 (2001).
 - 15. J. R. Barker, Int. J. Chem. Kinet. 41, 748 (2009).
 - 16. L. B. Harding, Y. Georgievskii, S. J. Klippenstein, J. Phys. Chem. A 114, 765 (2010).
 - G. K. Moortgat, H. Meyrahn, P. Warneck, *ChemPhysChem* 11, 3896 (2010).
 - D. A. Hansen, E. K. C. Lee, J. Chem. Phys. 63, 3272 (1975).
 - R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, J. A. Joens, *Atmos. Environ.* 26A, 785 (1992).
 - 20. P. Pérez, A. Toro-Labbe, J. Phys. Chem. A 104, 1557 (2000).
 - 21. J. Tadic, I. Juranic, G. K. Moortgat, J. Photochem.
 - Photobiol. A 143, 169 (2001).

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Supplementary Materials

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