Water-Accelerated Photo-oxidation of CH$_3$NH$_3$PbI$_3$ Perovskite: Mechanism, rate orders, and rate constants

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1. Experimental Methods

Sample Preparation. Precursor inks were prepared by dissolving stoichiometric amounts of MAI (Dyesol) and PbI$_2$ (Alfa Aesar, ultra dry 99.999%) at 1.0 M concentration in a 1:1 vol:vol mixture of N,N-dimethylformamide (DMF, Sigma Aldrich anhydrous grade) and 1-methyl-2-pyrrolidinone (NMP, Sigma Aldrich anhydrous grade). After leaving the inks to dissolve overnight, films were prepared by spin coating. Soda-lime glass substrates were cleaned by sonication in Alconox, deionized water, acetone, and isopropanol for 10 min in each solvent, then blow-dried with clean N$_2$ and treated for a further 10 min with an Ar plasma. After cleaning, the substrates were immediately transferred into a nitrogen-filled glovebox for film deposition. 50 μL of freshly filtered solution (using a 0.2 μm PTFE filter) was deposited on each substrate, which was then spun at 4000 rpm for 45 s. Immediately afterward, the films were immersed in a bath of diethyl ether (Fisher Scientific, anhydrous) for 1 minute. The films were then annealed on a ceramic hot plate at 100 °C for 10 min. Samples were stored in the dark in N$_2$ until use, with precautions taken against contamination by residual solvent vapors in the storage gloveboxes.

Degradation Experiments. In a typical degradation experiment, a sample prepared as described above was placed in a Linkam Scientific LTSE420-P environmental test chamber, outfitted with an electric heater, gas ports, electrical probes, and windows above and below the sample to allow light transmission. Atmosphere was controlled by connecting a cylinder of the desired gas (N$_2$ (99.998%), dry air, or O$_2$ (technical diving grade); Praxair) through a H$_2$O/glycerol bath to the gas port on the Linkam chamber. Relative humidity was controlled by changing the ratio of H$_2$O to glycerol in the bath and verified using a Fisher Scientific Traceable™ hygrometer (PN #11-661-18). Gas flow was bubbled through the H$_2$O/glycerol bath at 2.0 L/min using twin Omega FMA5400/5500 mass flow controllers connected to dry oxygen, dry nitrogen, and/or dry air gas cylinders (Praxair) to precisely control oxygen content in the Linkam chamber. Sample temperature was maintained at the desired value using the electric heater/thermocouple control loop in the Linkam chamber. Sample illumination was achieved using a calibrated 550 nm LED (Lumencor Retra Light Engine) as the light source in a metallurgical upright microscope (Olympus BX53M, equipped with a 50X Mitutoyo Plan Apo NIR HR objective lens), and adjusted based on the sample band gap to deliver the desired N-sun equivalent flux of above-band gap photons under the AM1.5G spectrum. The excitation light was passed through a band pass filter centered at 550 nm with 30 nm bandwidth and directed onto the sample using a filter cube containing a dichroic mirror (Semrock FL-007042) and long-pass emission filter (Semrock FL-008527). Blue light excitation experiments were performed identically as described utilizing a 395 nm LED (Lumencor Spectra Light Engine) light source through a band pass filter centered at 395 nm with a 25 nm bandwidth, using the same filter cube as above.

Photoluminescence videos were recorded using a Panda PCO camera mounted to the microscope, controlled by MicroManager software$^1$ to automatically record 5-second long 50-frame (10 fps) videos. The raw light intensity in each video frame is obtained from the camera detector counts at each pixel divided by the frame exposure time, yielding a signal with units of counts/s (cps). The frame exposure time is automatically set prior to collecting each video to maximize image signal-to-noise ratio without saturating the detector, and focus is maintained through the experiment by automated autofocus adjustment by a Marzhauser motorized stage (Olympus part #48-54-700-0000, optimized for BX53M microscopes). The camera detector count intensity in cps is converted to photoluminescence intensity (photons/m$^2$/s) by preparing a standard MAPbI$_3$ thin film and measuring its photoluminescence quantum yield (PLQY) using a calibrated
Horiba LabRAM HR-800 confocal PL spectrometer, as described in previous work. Collecting PL images of the thin film standard at the same incident light intensity as the confocal PL spectrum allows the calibration factor to be determined (photons/m²/count). The video data are thereafter averaged over all frames and pixels within them to yield a global measure of the PLQY. Sample transmittance is detected by measuring the amount of light passing through the sample using an OSI Optoelectronics UV-100DQ photodiode positioned beneath the bottom window of the Linkam stage and operated in photovoltaic mode. The photodiode current at short circuit is detected using a Keithley 2400 source/measure unit. PL videos and transmittance measurements are automatically recorded every 5 minutes using a custom-written Python master control program.

**Spectral Reflectance, Transmittance, and Absorptance.** Data were collected using a Perkin-Elmer Lambda 1050 UV/Vis/NIR spectrometer equipped with an integrating sphere. Transmittance, reflectance, and absorbance spectra were each independently measured by placing the sample on the front exterior mount, rear exterior mount, and center mount positions on the integrating sphere, respectively. The absorbance \(A\) is the fraction of incident light that is absorbed by the perovskite on glass sample, denoted by the script capital. There is no emission at the excitation energy, and thus a photon balance requires that the sum of the absorbance, reflectance \(R\), and transmittance \(T\) must be one \((A + R + T = 1)\). The experimentally measured \(A\), \(R\), and \(T\) sum 1.0 ± 0.02. The absorptivity \(a\) is the fraction of absorbed light relative to the component of the incident beam that penetrates the film (the component that is not reflected). In the limit of a thick, highly absorbing film for which interference effects are minimal and the reflectance is dominated by the reflectivity of the front surface, the absorptivity is related to the absorbance by \(a = A/(1-R)\). The absorptivity may be equivalently expressed as \(a = 1 - \exp(-\alpha L)\), where \(\alpha\) is the absorption coefficient of the material in the film, and \(L\) is the optical path length through the film, which at normal incidence is equivalent to its thickness. The absorption coefficient may therefore be calculated from the primary measured quantities (absorbance, reflectance, transmittance) as \(\alpha = -\frac{1}{L} \ln(1 - a) = -\frac{1}{L} \ln \left(1 - \frac{A}{1-R}\right) = -\frac{1}{L} \ln \left(1 - \frac{T}{1-R}\right)\). Finally, the film absorbance \(A\), which is the quantity used to represent the state of degradation in the perovskite film, is calculated as \(A = -\log_{10}(a) = -\log_{10}\left(\frac{T}{1-R}\right)\) from UV-Vis measurements. Thus, we can quantitatively assess the accuracy of approximating the absorbance as \(A = -\log_{10}(T)\), see section 2 and Fig. S1 below.

**XRD and SEM Characterization.** Powder X-ray diffraction (XRD) measurements were collected by Bruker D8 Discover instrument equipped with Pilatus 100K large-area 2D detector and a Cu anode microfocus X-ray source (wavelength 1.542Å, Ka radiation). The X-ray beam size was defined with a 0.5mm collimator. The sample was prepared by scraping off the material deposited on a square 15x15 mm soda-lime glass substrate, collected and compressed with a spatula. Scanning electron microscopy (SEM) micrographs were obtained on Pt coated films using a FEI Sirion XL30. To avoid charging effects, an Pt coating with 4 nm was sputtered onto the perovskite films prior to imaging.

**XRD and SEM Characterization.** Current voltage (I-V) curves of the device were measured under simulated AM 1.5G 1 Sun illumination with 0.02 V/s sweep rate for forward and reverse sweeps. The light source is an Oriel VeraSol-2 AAA Solar Simulator. An OSI Optoelectronics UV-100DQ Si photodiode was used to set the lamp intensity to equal the integrated above-bandgap AM1.5GT photon flux for a 1.6 eV bandgap material. The device area is ~0.06 cm².
2. Estimation of Systemic Error Associated with Neglecting Changes in Reflectance

Neglecting the changes in reflectance, the rate of reaction is estimated to be:

$$ r = -\frac{\rho}{M \cdot \log_{10}(e) \cdot \alpha_0} \cdot \frac{dA}{dt} \approx \frac{\rho}{M \cdot \log_{10}(e) \cdot \alpha_0} \cdot \frac{d}{dt} \left( \log_{10} \left( \frac{T_t}{T_0} \right) \right) $$

where: $\log_{10}(e) = 0.4343$, $\rho_{\text{MAPI}} = 4.2 \text{ g/cm}^3$, $M = 620.0 \text{ g/mol}$, and the absorption coefficient of MAPI at 550 nm is $\alpha_0 = 9.61 \times 10^4 \text{ cm}^{-1}$ as determined from UV-Vis-NIR spectrometry on a pristine film (Figure S3). This equation assumes: (i) the validity of an effective-medium approximation for absorption coefficient, (ii) that wave interference effects are negligible, and (iii) a slowly changing reflectance with time, $\frac{d}{dt} \left( \log(T) \right) >> \frac{d}{dt} \left( \log(1 - R) \right)$. The first assumption is expected to be an excellent approximation at early times (low extent of the degradation reaction), and the latter two assumptions are validated by an ex-situ degradation experiment in which we periodically monitor the reflectance, transmittance, and absorptance of a MAPI film degrading under AM1.5G illumination in ~60% RH air, using a UV-vis spectrometer equipped with an integrating sphere (Figure S1).

The 260 nm-thick MAPbI\(_3\) films in this study are approximately half the wavelength of the 550 nm probe beam and do exhibit some interference effects. These interference effects are evident in oscillations of reflectance data observed in Figure S1c, and are removed to good approximation in the absorptivity, absorbance, and absorption coefficient spectra (Fig. S1 d, e, and f, respectively). However, some effects of interference are observed in the absorptance and transmittance spectra, and thus those errors propagation into $dA/dt$ when the calculation is based on transmittance (without correcting for reflectance). The changes in the interference patterns as a function of the extent of reaction are observed to be relatively small at the 550 nm probe wavelength (Figure S1), and the degradation rate calculated simply from treating absorbance as a function of transmittance alone differs from that calculated while accounting for changes in reflectance by less than 1% for the probe wavelength of 550 nm used in this work (Figure S1j). However, suppose the film thickness were different by enough to shift the interference pattern from a peak to a valley. How much would the error associated with neglecting reflectance change?

To assess this, we compare rates of reaction estimated at three different wavelengths between the PbI\(_2\) and MAPbI\(_3\) bandgaps at 550, 630, and 710 nm (see Fig. S1 j, k, and l). The worst case scenario is an error of about 28%. Different films in this study have very similar interference peaks and valley owing to the constant film thickness, and the systemic error associated this phenomena is much closer to 1% than 28%.
Figure S1. (a) Absorptance $\mathcal{A}$, (b) transmittance $\mathcal{T}$, (c) total reflectance $R$, (d) absorptivity $\alpha = \mathcal{A}/(1 - R)$, (e) absorbance $A$, and (f) absorption coefficient $\alpha$ of a MAPbI$_3$ film degrading under 1 Sun AM1.5G illumination from a solar simulator in ambient lab air (60% RH at the time of experiment), measured ex-situ by periodically removing the sample from the light and collecting data in a UV-vis spectrometer. (g-i) Values of the above quantities in the spectral region of the
microscope probe beam (550 nm), as well as at 630 and 710 nm, are tracked over time, and the amount of perovskite present in the sample is tracked over time. Using measurements at each of the above three wavelengths, we determined the initial degradation rates from linear fits to these absorbance data. Comparing the spectra in this manner enables the evaluation of how sensitive the rate calculations are to interference effects. Between the bandgaps of MAPbI₃ and PbI₂ (approximately 540-770 nm), the absorption coefficient shifts uniformly as the sample degrades, indicating that the material decomposition rate should be insensitive to the probe wavelength. Comparison of the calculated rates at these three wavelengths (using \( A = -\log_{10}(T/(1-R)) \)) yields an average of \( 4.43 \pm 0.34 \times 10^{-8} \) mol/m²/s. Here, the uncertainty is represented by the standard deviation, and is less than 10% of the average rate, demonstrating that the extracted rate indeed does not depend strongly on the choice of probe wavelength. Changes in reflectance over the course of degradation can have a larger influence on the rate when film absorbance is approximated as \( A = -\log_{10}(T) \), as used for in-situ calculation of initial degradation rates in this work. The maximum discrepancy occurs at 630 nm, where the largest excursions in reflections are observed, and the transmittance-only approximation thus underestimates the rate that accounts for reflectance by about 28%. The discrepancy in degradation rates is much smaller at 710 nm (~4%) and even smaller at 550 nm (<1%), the wavelength employed for the in-situ photodiode measurements discussed in the rest of this work. Consequently, neglecting changes in reflectance when calculating rate in this manner should not introduce a large degree of error.

Figure S3. Absorption coefficient of the pristine MAPI films used in this study, determined from UV-vis-NIR spectroscopy.
3. Surface Rate vs Volumetric Rate

In fluid phase reactions where reactants and products undergo collision and thus have opportunity to react, it is conventional to define a reaction rate based on the volume. If the reactants (other than MAPI) such as oxygen and water are able to diffuse throughout the volume, the rate of disappearance of MAPI per unit volume [mol/(cm$^3$·s)] would be:

$$r_{vol} = -\frac{1}{WL} \frac{dN}{dt} \text{ [mol/m}^3\text{s]}$$

where $W$ is the planar area exposed to the incident beam and $L$ is the film thickness. However, if (especially at early times) the other important reactants (O$_2$ and H$_2$O) are limited to the surface, the rate of disappearance of MAPbI$_3$ should be independent of film thickness. In this case, the appropriate rate expression would be:

$$r_{sur} = -\frac{1}{W} \frac{dN}{dt} \text{ [mol/m}^2\text{s]}$$

Experiments performed on MAPbI$_3$ films of varying thickness (Figure S2) in 1 air, 25°C, 60% RH air demonstrate that $\frac{1}{L} \frac{dA}{dt}$ is roughly constant as a function of $L$. Therefore, it is appropriate to use the surface-based rate expression. We note that the effective surface area for reactions may increase or be larger than the planar surface area due to surface roughening (which has been observed experimentally)$^{4,5}$ and potential reactions at the interior surfaces along grain boundaries. This would manifest as an increased rate (when expressed as per unit planar surface area). Here, we assume this effect is small and use the planar surface reaction rate expression above.

![Figure S2](image_url)

**Figure S2.** Rates of degradation of MAPbI$_3$ films in 50% RH air aged under 1 sun at 25 °C. Experiments show that volumetric degradation rate (b) decreases with increasing film thickness, while surface degradation rate (c) is relatively constant below ~500 nm thickness. This demonstrates that the surface degradation rate equation is most appropriate to model early-time degradation of MAPbI$_3$ thin films.
4. Comparison of Degradation Under Illumination and in the Dark

In Table 1, degradation rates are reported in “limiting cases”, or cases where individual degradation stresses such as heat, oxygen content, and water vapor content are introduced to films in isolation. Rates reported in Table 1 are all demonstrated under 1 sun illumination intensity. Table S1 shows degradation rates at both 1 sun and 0 sun illumination intensity. As in Table 1, degradation is shown to only occur in the confluence of humidity and oxygen. Data in Table S1 further demonstrate that degradation only occurs in light as well, consistent with the observation that degradation in humid air is a result of the commonly reported photooxidation process.

Table S1. Degradation rates of MAPbI₃ in various environmental conditions. Rapid degradation only occurs in combinations of light, humidity, and oxygen.

| Degradation Conditions | 25 °C in 1 Sun [mol/(m²·s)] | 25 °C in 0 Sun [mol/(m²·s)] | 85 °C in 1 Sun [mol/(m²·s)] | 85 °C in 0 Sun [mol/(m²·s)] |
|------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Heat Only (0% O₂, 0% RH) | less than 10⁻¹⁰ | less than 10⁻¹⁰ | less than 10⁻¹⁰ | 2 x 10⁻¹⁰ |
| Humid N₂ (0% O₂, 50% RH) | 5 x 10⁻¹⁰ | 2 x 10⁻⁹ | 2 x 10⁻⁹ | less than 10⁻¹⁰ |
| Dry Air (21% O₂, 0% RH) | 1 x 10⁻⁸ | 2 x 10⁻¹⁰ | 1 x 10⁻⁷ | 1 x 10⁻⁸ |
| Humid Air (21% O₂, 50% RH) | 1 x 10⁻⁷ | 5 x 10⁻⁹ | 2 x 10⁻⁷ | 1 x 10⁻⁸ |

Degradation in “dark” conditions is complicated to measure, as optical absorbance is used as a probe of degradation. Therefore, some level of light exposure is necessary to calculate the degradation rates in the “dark” in Table S1. This may lead to conclusions, particularly in 85 °C humid air, that there is a dark oxidation pathway, when this pathway is merely an artifact of light exposure during optical measurements. To characterize whether or not degradation in dark conditions is a reflection of the brief light exposure that occurs during optical measurement, degradation experiments in humid air were performed in the dark utilizing the standard measurement cycle used to collect absorbance measurements for all experiments in this report (8 sun probe intensity for 45-65 s). Absorbance evolution under 1 sun probe intensity and a 5 min measurement cycle period was compared to absorbance evolution under dark stress intensity using two different measurement cycle periods: 15 min, and 2 hrs (humid air degradation rates calculated from the 2 hr period are shown in Table S1). Degradation rate is significantly arrested when the measurement cycle period is increased. Results in Figure S4 demonstrate that calculated nonzero degradation rates in dark conditions are therefore an incident of light exposure during measurement, and likely not due to a parallel dark oxidation pathway.
Figure S4. Degradation in 50% RH air at 25 °C and 85 °C under 1 sun stress with 5 min measurement cycles (1 cycle = 8 sun light exposure for ~50 s), 0 sun stress with 15 min measurement cycles, and 0 sun with 2 hr measurement cycles. Degradation rate significantly decreases in dark conditions at longer measurement cycles, indicating that degradation in dark humid air is likely a result of exposure to the probe beam during optical measurement.

Finally, under certain conditions, degradation rates in dark conditions proceed faster than degradation under 1 sun illumination intensity. While characterizing this is beyond the scope of the present work, it is possible that in humid nitrogen, increased degradation rates in dark conditions may be attributed to water desorption from the MAPbI$_3$ surface, either due to light-induced desorption, or desorption due to local temperature increases that result from illumination. The exact cause of these light-induced stabilization effects are currently still under study in our lab, and results of this work will be published elsewhere.
5. Derivation of Concentration of Electrons from Illumination Intensity

As photoexcited carriers play a significant role in MAPbI$_3$ degradation, the activity of electrons $a_e$ is an important parameter in the rate expression of MAPbI$_3$ degradation. Thermodynamic activity of a species $i$ is formally defined by:

$$a_i = \exp \left( \frac{m_i - m_i^\theta}{k_BT} \right)$$

where $m$ is the molar chemical potential (changed here from convention $\mu$ to avoid confusion with carrier mobility), $m^\theta$ is chemical potential under some set of standard conditions, and $k_B$ is Boltzmann’s constant. The chemical potential of electrons in a semiconductor is identically equal to the Fermi level in the dark, and the quasi-Fermi level of electrons under photoexcitation.

Assuming quasi-thermal equilibrium, electron concentration $n$ and electron quasi-Fermi level $E_{F_n}$ are related by:

$$m_e = E_{F_n} = -k_BT(\ln n - \ln N_C) + E_C$$

where $N_C$ is the effective density of states in the conduction band and $E_C$ is the band energy of the conduction band edge. Combining the two prior equations yields

$$a_e = \exp \left( \frac{-k_BT(\ln n - \ln N_C) + E_C - m_e^\theta}{k_BT} \right)$$

Taking out the constant $c_1 = \frac{1}{N_C} \exp \left( \frac{E_C - m_e^\theta}{k_BT} \right)$ yields

$$a_e = c_1 n,$$

and activity of electrons is proportional to electron concentration.

We then relate $n$ to illumination intensity using photoconductivity measurements. The semiconductor photoconductivity $\sigma_{ph}$ is:

$$\sigma_{ph} = q(\mu_n n + \mu_p p)$$

where $q$ is the fundamental electric charge ($1.6 \times 10^{-19}$ C), $\mu_n$ and $\mu_p$ are electron and hole mobilities, and $n$ and $p$ are the electron and hole concentrations. For an intrinsic material under illumination, the equilibrium electron and hole concentrations are small compared to the excess (photoexcited) carrier populations, and thus $n$ and $p$ are approximately equal to the excess carrier populations. The power law relationship between illumination intensity and $\sigma_{ph}$ is identical to the power law relationship between illumination intensity and $n$; therefore, $n \propto N_{SUN}^{0.4-0.75}$. Given the measured rate order of illumination intensity in Figure 3e is $0.71 \pm 0.14$, within the range of power law relationships between illumination and electron concentration (0.4-0.75), we take for this work $n \propto N_{SUN}^{0.7}$ (see Fig. S5). Given this relationship, we identify that photooxidation in dry air is first order with respect to electron activity $a_e$. 
Figure S5. Photoconductivity of an MAPbI$_3$ film as a function of incident light intensity, demonstrating that photogenerated electron concentration scales $\sim N_{\text{suns}}^{0.7}$. 
6. Derivation of Rate Equation for Dry Photo-oxidation

Potential mechanisms of perovskite degradation proposed in this work and described in Scheme 1 for dry photo-oxidation and Scheme 2 in the presence of water are in the main text and replicated below. Note that reaction pathways involving reactive oxygen species (ROSs) can be quite complex, and the details of the fast reaction steps may differ from what is presented. However, these details have minimal relevance to the overall rate due to the short-lived nature of the ROSs; due to their reactivity, we assume that step D4, which involve a proton abstraction by superoxide from methylammonium is rate-limiting. Note that some studies\[ref\] report water as a product, but others\[ref\] do not. We derive a rate law assuming each case below.

Dry Photo-oxidation with Water Generated as a Product

The following is a plausible reaction mechanism for photo-oxidation that occurs without water as a reactant.

\[ h\nu \rightarrow e^- + h^+ \]  \hspace{1cm} (step D1)
\[ O_2 + [*] \rightleftharpoons O_2^* \]  \hspace{1cm} (step D2)
\[ O_2^* + e^- \rightleftharpoons O_2^{2-} \]  \hspace{1cm} (step D3)
\[ CH_3NH_3PbI_3 + O_2^{2-} \rightarrow HO_2^{*} + PbI_2 + CH_3NH_2 + I^- \]  \hspace{1cm} (step D4)
\[ CH_3NH_3PbI_3 + HO_2^* \rightarrow H_2O_2^* + PbI_2 + CH_3NH_2 + I^* \]  \hspace{1cm} (step D5)
\[ H_2O_2^* + e^- + [*] \rightleftharpoons HO^- + HO^{**} \]  \hspace{1cm} (step D6)
\[ CH_3NH_3PbI_3 + HO^{**} \rightarrow H_2O^* + PbI_2 + CH_3NH_2 + I^* \]  \hspace{1cm} (step D7)
\[ CH_3NH_3PbI_3 + HO^- \rightarrow H_2O^* + PbI_2 + CH_3NH_2 + I^- \]  \hspace{1cm} (step D8)
\[ h^+ + CH_3NH_3PbI_3 \rightleftharpoons CH_3NH_3PbI_3^+ + [*] + I^* \]  \hspace{1cm} (step D9)
\[ CH_3NH_3PbI_2^+ + [*] + I^- \rightleftharpoons CH_3NH_3PbI_3 \]  \hspace{1cm} (step D10)
\[ I^* \rightarrow I_2 \]  \hspace{1cm} (step D11)

The rate of depletion of MAPI in dry air is derived from this mechanism, using the relation that, for a given species X that participates in an \( m \)-step mechanism, the rate of accumulation or generation of X \( r_X \) is given by:\[8\]

\[ r_X = \sum_{i=1}^{m} v_{X,i} r_i \]

where \( v_{X,i} \) is the stoichiometric coefficient of species X participating in reaction step i. From this relation and using the numeric labels given in the reaction scheme, the rate of depletion of MAPI is given by:

\[ r_{MAPI} = -r_{D4} - r_{D5} - r_{D7} - r_{D8} \]
Many intermediates in the reaction are short-lived unstable radical or ionic species, which can be assumed to be in pseudo-steady state, i.e., that during the reaction, there is no accumulation or depletion of these species. Using this assumption, the following system of equations can be derived (note that negative subscripts $i$ in $r_i$ correspond to reverse reactions in equilibrium expressions):

$$
\begin{align*}
r_{O_2^*} &= 0 = r_{D2} - r_{-D2} + r_{-D3} - r_{D3} \\
r_{O_2^{-*}} &= 0 = r_{D3} - r_{-D3} - r_{D4} \\
r_{HO_2^*} &= 0 = r_{D4} - r_{D5} \\
r_{H_2O_2^*} &= 0 = r_{D5} - r_{D6} + r_{-D6} \\
r_{HO^{-*}} &= 0 = r_{D6} - r_{-D6} - r_{D7} \\
r_{HO^{-*}} &= 0 = r_{D6} - r_{-D6} - r_{D8}
\end{align*}
$$

It is from this system of equations that we derive our expressions for dry air MAPbI$_3$ degradation. Derivation of rate expressions begins with assumptions we place on these equations based on experimental conditions. In dry air, the following assumptions are made:

(a) Continuous purge assumption: water generated as a degradation byproduct rapidly desorbs and is carried away by the flowing gas purge before it can accumulate ($[H_2O^*] \equiv 0$).

(b) Reaction step (D4) is rate limiting ($r_{D4} \ll r_{i \neq D4}$).

Combining terms from the set of linear equations generated above creates a simpler set:

$$
\begin{align*}
r_{D2} &= r_{-D2} + r_{D4} \\
r_{D4} &= r_{D5} \\
r_{D5} &= r_{D6} - r_{-D6} = r_{D7} = r_{D8}
\end{align*}
$$

And simplifying the MAPbI$_3$ depletion rate expression yields:

$$
r_{MAPI} = -4r_{D4}
$$

consistent with the result that the rate of a reaction is equal to the rate of the rate-limiting step$^8$ (Note that -4 is a proposed stochiometric coefficient of MAPI for the full photooxidation reaction)$^9$.

Given the MAPbI$_3$ depletion rate expression, and the proposed mechanism, it follows that

$$
r_{MAPI} = -4k_{D4}[O_2^{-*}]a_{MAPI}
$$

where $[O_2^{-*}]$ is the surface concentration of superoxide species, and $a_{MAPI}$ is the activity of MAPbI$_3$. To identify the quasi-steady state superoxide surface concentration, the mechanism is developed as follows (where $a_e$ is electron activity, which is equal to excess carrier concentration $n$):

$$
r_{D2} = r_{-D2} + r_{D4} \approx r_{-D2}
$$
\[
\begin{align*}
    k_{D2}P_{O_2}[*] & = k_{-D2}[O_2^*] \\
    [O_2^*] & = K_{eq,D2}P_{O_2}[*] \\
    r_{D3} & = r_{-D3} + r_{D4} \approx r_{-D3} \\
    k_{D3}[O_2^*]n & = k_{-D3}[O_2^{-*}] \\
    [O_2^{-*}] & = K_{eq,D3}n[O_2^*] \\
    [O_2^{-*}] & = K_{eq,D2}K_{eq,D3}P_{O_2}n[*]
\end{align*}
\]

Yielding
\[
r_{\text{MAPI}} = -4a_{\text{MAPI}}K_{eq,D2}K_{eq,D3}k_{D4}P_{O_2}n[*]
\]

Unoccupied adsorption site concentration [*] is an unknown variable. However, assuming a constant number of total adsorption sites (valid given kinetic fits are taken at early times), this unknown can be calculated based on a site balance:

\[
[*]_T = [*] + [O_2^*] + [O_2^{-*}] + [HO_2^*] + [H_2O_2^*] + [HO^*] + [HO^{-*}]
\]

Each of these occupied site concentrations are redefined based on elementary rates \(r_i\):

\[
\begin{align*}
    [O_2^*] & = r_{-D2}/k_{-D2} \\
    [O_2^{-*}] & = r_{-D3}/k_{-D3} \\
    [HO_2^*] & = r_{D5}/k_{D5}a_{\text{MAPI}} = r_{D4}/k_{D5}a_{\text{MAPI}} \\
    [HO^*] & = r_{D7}/k_{D7}a_{\text{MAPI}} = r_{D4}/k_{D7}a_{\text{MAPI}} \\
    [HO^{-*}] & = r_{D9}/k_{D9}a_{\text{MAPI}} = r_{D4}/k_{D9}a_{\text{MAPI}} \\
    r_{D6} & \approx r_{-D6} = k_{D6}[H_2O_2^*]n[*] = k_{-D6}[HO^*][HO^{-*}]
\end{align*}
\]

\[
[H_2O_2^*] = \frac{[HO^*][HO^{-*}]}{K_{eq,D6}n[*]} = \frac{r_{D4}^2}{K_{eq,D6}k_{D7}k_{D8}n[*]a_{\text{MAPI}}^2}
\]

These simplifications yield the following adjusted site balance:

\[
[*]_T = [*] + \frac{r_{-D2}}{k_{-D2}} + \frac{r_{-D3}}{k_{-D3}} + \frac{r_{D4}}{k_{D5}a_{\text{MAPI}}} + \frac{r_{D4}^2}{K_{eq,D6}k_{D7}k_{D8}n[*]a_{\text{MAPI}}^2} + \frac{r_{D4}}{k_{D7}a_{\text{MAPI}}} + \frac{r_{D4}}{k_{D8}a_{\text{MAPI}}}
\]

Remembering assumption (b), where \(r_{D4}\) is assumed to be very small relative to \(r_{-D2},r_{-D3}\) means that terms in the previous equation that are \(O(r_{D4}) \approx 0\) and \(O(r_{D4}^2) \approx 0\). Re-entering surface concentration expressions and simplifying:

\[
[*]_T = [*] + [O_2^*] + [O_2^{-*}]
\]

\[
[*]_T = [*](1 + K_{eq,D2}P_{O_2} + K_{eq,D2}K_{eq,D3}P_{O_2}n)
\]

\[
[*] = \frac{[*]_T}{1 + K_{eq,D2}P_{O_2} + K_{eq,D2}K_{eq,D3}P_{O_2}n}
\]
Yielding
\[ r_{\text{API}} = -4a_{\text{API}}K_{eq,D2}K_{eq,D3}k_D[\star]_T \frac{P_{O_2}n}{1 + K_{eq,D2}P_{O_2} + K_{eq,D2}K_{eq,D3}P_{O_2}n} \]

Combining constants (surface reaction assumption turns \( a_{\text{API}} \) into a constant):
\[ r_{\text{API}} = -k_{\text{eff}}P_{O_2}n \]

Matching experimental results based on rate orders requires two more simplifying assumptions:
(c) In dry air, reduction of adsorbed oxygen is pushed to the left \( (K_{eq,D3} \ll 1) \)
(d) In dry air, oxygen absorption is pushed to the right \( (K_{eq,D2} \gg 1) \)

Incorporating these assumptions yields the final form of the expression:
\[ r_{DPO} = -k_{DPO}n \]

**Dry Photo-oxidation with *No* Water Generated as a Product**

While earlier derivations describe a degradation pathway that is likely given the reported photooxidation stoichiometry of \( 4\text{MAPbI}_3 + O_2 + h\nu \rightarrow 4\text{PbI}_2 + 4\text{CH}_3\text{NH}_2 + 2\text{I}_2 + 2\text{H}_2\text{O} \),\textsuperscript{13} other groups have contended that no water is generated from photooxidation, and that \( \text{HO}_2^- \) reacts with itself once generated to form \( \text{O}_2 \) and \( \text{H}_2 \), with no product water generated.\textsuperscript{15} If this mechanism is true, then the pathway becomes:

\( \text{hv} \rightarrow e^- + h^+ \) \hspace{1cm} (step DI)

\( O_2 + [\star] \rightleftharpoons O_2^\star \) \hspace{1cm} (step DII)

\( O_2^\star + e^- \rightleftharpoons O_2^- + [\star] \) \hspace{1cm} (step DIII)

\( \text{CH}_3\text{NH}_3\text{PbI}_3 + \text{HO}_2^\star \rightarrow \text{HO}_2^\star + \text{PbI}_2 + \text{CH}_3\text{NH}_2 + \text{I}^- \) \hspace{1cm} (step DIV)

\( \text{HO}_2^\star \rightarrow \frac{1}{2}\text{H}_2 + O_2^\star \) \hspace{1cm} (step DV)

\( h^+ + \text{CH}_3\text{NH}_3\text{PbI}_3 \rightleftharpoons \text{CH}_3\text{NH}_3\text{PbI}_2^+ + [\star] + \text{I}^- \) \hspace{1cm} (step DVI)

\( \text{CH}_3\text{NH}_3\text{PbI}_2^+ + [\star] + \text{I}^- \rightleftharpoons \text{CH}_3\text{NH}_3\text{PbI}_3 \) \hspace{1cm} (step DVII)

\( 2\text{I}^- \rightarrow \text{I}_2 \) \hspace{1cm} (step DVIII)

The rate of depletion of MAPbI\(_3\) becomes:
\[ r_{\text{MAPbI}} = -r_{\text{DIV}} \]

The system of linear equations describing intermediate concentrations in quasi-steady state becomes:
\[ r_{O_2^\star} = 0 = r_{\text{DIV}} - r_{-\text{DII}} - r_{-\text{DIII}} + r_{-\text{DIV}} + r_{DV} \]
\[ r_{O_2^{-}} = 0 = r_{_{III}} - r_{-_{III}} - r_{DIV} \]
\[ r_{HO_2^{*}} = 0 = r_{DIV} - r_{DV} \]

Unlike in the other mechanism, since no water is generated, we only need to make one assumption

(a) Step DIV is the rate limiting step \((r_{DIV} < r_{D[i<IV]})\)

From this, we can simplify the linear equations to:

\[ r_{DIV} = r_{DV} \]
\[ r_{_{III}} = r_{-_{III}} \]
\[ r_{_{III}} + r_{-_{III}} = r_{-_{III}} + r_{IV} + r_{DV} \]
\[ r_{_{III}} = r_{-_{III}} \]

Solving for \(r_{MAPI}\):

\[ r_{MAPI} = -k_{DIV}[O_2^{*-}]a_{MAPI} \]

Solving for \([O_2^{*-}]\):

\[ r_{_{III}} = r_{-_{III}} \]
\[ k_{_{III}}[O_2^{*}]n = k_{-_{III}}[O_2^{*-}] \]
\[ [O_2^{*-}] = K_{eq,_{III}}n[O_2^{*}] \]
\[ r_{_{III}} = r_{-_{III}} \]
\[ k_{_{III}}P_{O_2}[*] = k_{-_{III}}[O_2^{*}] \]
\[ [O_2^{*}] = K_{eq,_{III}}P_{O_2}[*] \]
\[ [O_2^{*-}] = K_{eq,_{III}}K_{eq,_{III}}nP_{O_2}[*] \]

Doing a site balance to solve for \([*]\):

\[ [*]_T = [*] + [O_2^{*}] + [O_2^{*-}] + [HO_2^{*}] \]
\[ [*]_T = [*] + \frac{r_{-_{III}}}{k_{-_{III}}} + \frac{r_{-_{III}}}{k_{-_{III}}} + \frac{r_{DV}}{k_{DV}} \]
\[ [*]_T = [*] + [O_2^{*}] + [O_2^{*-}] \]
\[ [*]_T = [*] \left(1 + K_{eq,_{III}}P_{O_2} \left(1 + K_{eq,_{III}}n \right) \right) \]
\[ [*] = \frac{[*]_T}{\left(1 + K_{eq,_{III}}P_{O_2} \left(1 + K_{eq,_{III}}n \right) \right)} \]

Resulting in:

\[ r_{MAPI} = -r_{DIV} = -k_{DIV}[O_2^{*-}]a_{MAPI} = -k_{DIV}a_{MAPI}K_{eq,_{III}}K_{eq,_{III}}nP_{O_2}[*] \]
\[ r_{\text{MAPI}} = -k_{\text{DIV}} a_{\text{MAPI}} K_{\text{eq,DIH}} K_{\text{eq,DIH}}^{[*]} T \frac{n P_{O_2}}{(1 + K_{\text{eq,DIH}} P_{O_2} (1 + K_{\text{eq,DIH}} n))} \]

As before, matching experimental results based on rate orders requires two more simplifying assumptions:

(b) In dry air, reduction of adsorbed oxygen is pushed to the left \((K_{\text{eq,D3}} \ll 1)\)

(c) In dry air, oxygen absorption is pushed to the right \((K_{\text{eq,D2}} \gg 1)\)

Yielding again the experimental result that

\[ r_{\text{MAPI}} = -k_{DPO} n \]

From this derivation we prove that the same functional form for the dry photooxidation rate expression is derived regardless of whether water is produced from the photooxidation reaction.
7. Derivation of Rate Equation for Water-Accelerated Photo-oxidation

Potential mechanisms of perovskite degradation proposed in this work and described in Scheme 2 in the presence of water are in the main text and replicated below. Note that reaction pathways involving reactive oxygen species (ROSs) can be quite complex, and the details of the fast reaction steps may differ from what is presented. However, these details have minimal relevance to the overall rate due to the short-lived nature of the ROSs; due to their reactivity, we assume that step H5, which involves proton abstraction by superoxide from water is rate-limiting. As developed in the main text, this assumption leads to derived rate expressions that are in excellent agreement with the experimentally measured rates.

\[ 2h\nu \rightarrow 2e^- + 2h^+ \]  \hspace{1cm} \text{(step H1)}

\[ O_2 + [\ast] \rightleftharpoons O_2^\ast \]  \hspace{1cm} \text{(step H2)}

\[ H_2O + [\ast] \rightleftharpoons H_2O^\ast \]  \hspace{1cm} \text{(step H3)}

\[ O_2^\ast + e^- \rightleftharpoons O_2^{\ast\ast} \]  \hspace{1cm} \text{(step H4)}

\[ O_2^{\ast\ast} + H_2O^\ast \rightleftharpoons HO_2^\ast + HO^{\ast\ast} \]  \hspace{1cm} \text{(step H5)}

\[ CH_3NH_3PbI_3 + HO_2^\ast \rightarrow H_2O_2^\ast + PbI_2 + CH_3NH_2 + I^\ast \]  \hspace{1cm} \text{(step H6)}

\[ H_2O_2^\ast + e^- + [\ast] \rightleftharpoons HO^{\ast\ast} + HO^{\ast\ast} \]  \hspace{1cm} \text{(step H7)}

\[ CH_3NH_3PbI_3 + HO^{\ast\ast} \rightarrow H_2O^\ast + PbI_2 + CH_3NH_2 + I^\ast \]  \hspace{1cm} \text{(step H8)}

\[ 2CH_3NH_3PbI_3 + 2HO^- \rightarrow 2H_2O^\ast + 2PbI_2 + 2CH_3NH_2 + 2I^- \]  \hspace{1cm} \text{(step H9)}

\[ h^\ast + CH_3NH_3PbI_3 \rightleftharpoons CH_3NH_3PbI_2^\ast + [\ast] + I^\ast \]  \hspace{1cm} \text{(step H10)}

\[ CH_3NH_3PbI_2^\ast + [\ast] + I^- \rightleftharpoons CH_3NH_3PbI_3 \]  \hspace{1cm} \text{(step H11)}

\[ 4I^\ast \rightarrow 2I_2 \]  \hspace{1cm} \text{(step H12)}

Following the same process as for the dry-air system, the rate of degradation for humidity-accelerated photo-oxidation can be found. From this mechanism, the following system of equations is generated:

\[ r_{MAPI} = -r_{H6} - r_{H8} - r_{H9} \]

\[ r_{O_2^\ast} = 0 = r_{H2} - r_{-H2} + r_{-H4} - r_{H4} \]

\[ r_{H_2O^\ast} = 0 = r_{H3} - r_{-H3} - r_{H5} + r_{-H5} + r_{H8} + r_{H9} \]

\[ r_{O_2^{\ast\ast}} = 0 = r_{H4} - r_{-H4} - r_{H5} + r_{-H5} \]

\[ r_{HO_2^\ast} = 0 = r_{H5} - r_{-H5} - r_{H6} \]

\[ r_{H_2O_2^\ast} = 0 = r_{H6} - r_{H7} + r_{-H7} \]

\[ r_{HO^{\ast\ast}} = 0 = r_{H7} - r_{-H7} - r_{H8} \]
\[ r_{HO^-} = 0 = r_{H5} - r_{-H5} + r_{H7} - r_{-H7} - r_{H9} \]

The following assumptions are implemented as a starting point for rate expression derivation:

(a) Superoxide species abstract protons from water more quickly than they abstract protons from methylammonium \((r_D \ll r_{H5})\).

(b) Proton abstraction by superoxide (step H5) is slow to equilibrium \((r_{H5} \ll r_{H(|i|<5)})\).

Applying these assumptions to the set of linear equations from the quasi-steady-state assumption above yields:

\[ r_{H2} + r_{-H4} = r_{-H2} + r_{H4} \]
\[ r_{H3} + r_{H8} + r_{H9} = r_{-H3} \]
\[ r_{H4} = r_{-H4} + r_{H5} \]
\[ r_{H5} = r_{H6} + r_{-H5} \]
\[ r_{H6} + r_{-H7} = r_{H7} \]
\[ r_{H7} = r_{-H7} + r_{H8} \]
\[ r_{H5} + r_{H7} = r_{H5} + r_{-H7} + r_{H9} \]

Of these, the equation

\[ r_{H5} = r_{H6} + r_{-H5} \]

Is particularly important. From this equation, given nonnegative rates, it is easily concluded that \(r_{-H5} \leq r_{H5} \) and \(r_{H6} \leq r_{H5}\). Given that \(r_{H5}\) is taken to be the rate limiting step, we then conclude that if \(r_{-H5}\) is less than or equal to \(r_{H5}\), assumption (b) becomes: \(r_{-H5} \leq r_{H5} \ll r_{H(|i|<5)}\), which aids in simplification of the system of linear equations. Furthermore, it is important for the derivation of \(r_{MAPI}\) to know the relative rates of \(r_{H6}\) and \(r_{-H5}\). There are of course three possible scenarios: (1) \(r_{H6} \gg r_{-H5}\), (2) \(r_{-H5} \gg r_{H6}\), and (3) \(r_{-H5} \approx r_{H6}\). Applying these three scenarios to \(r_{H5} = r_{H6} + r_{-H5}\) yields the following conclusions, labeled here based on scenario number: (1) \(r_{H6} \approx r_{H5}\), (2) \(r_{H6} < r_{H5}\), (3) \(r_{H6} \ll r_{H5}\). In this derivation, we assume that step H5 is the rate controlling step. However, any assumptions we make in this derivation that result in \(r_{H6} < r_{H5}\) change the rate limiting step of this reaction from step H5 to H6, as this result means there is a rate that proceeds after our initially assumed “rate limiting step” that is calculated to be slower than this step. This is rationally inconsistent. The only way we can maintain the integrity of assumption (b), that step H5 is rate controlling, is to therefore assume that \(r_{-H5} \ll r_{H6} \approx r_{H5}\). If this relation does not hold true, step H6 becomes the rate limiting step in our mechanism. With these conclusions, combining terms gives a simpler system of equations:

\[ r_{H2} = r_{-H2} \]
\[ r_{H3} + r_{H8} + r_{H9} = r_{-H3} \]
\[ r_{H5} = r_{H6} \]
\[ r_{H6} = r_{H8} \]
\[ r_{H6} + r_{H8} = r_{H9} \]

With these, the depletion rate of MAPbI\(_3\) simplifies to:

\[ r_{MAP} = -4(k_r) \]

Again recovering that the rate of degradation is equal to the rate of the rate limiting step. Further:

\[ r_{MAP} = -4(k_r[H_2O][O_2^{-*}]) \]

To calculate the adsorbed surface concentrations of water and superoxide for the degradation rate expression, the system of linear equations derived previously is used:

\[ r_{H3} + r_{H8} + r_{H9} = r_{H3} \]
\[ r_{H3} + 3r_{H5} \approx r_{H3} = r_{H3} \]
\[ k_{H3} P_{H_2O}[*] = k_{-H3}[H_2O^+] \]
\[ [H_2O^+] = K_{eq,H3}P_{H_2O}[*] \]

And similarly:

\[ r_{H2} = r_{-H2} \]
\[ k_{H2} P_{O_2}[*] = k_{-H2}[O_2] \]
\[ [O_2] = K_{eq,H2}P_{O_2}[*] \]
\[ r_{H4} = r_{-H4} \]
\[ k_{H4}[O_2^+]a_e = k_{-H4}[O_2^{-*}] \]
\[ [O_2^{-*}] = K_{eq,H2}K_{eq,H4}P_{O_2}a_e[*] \]

Yielding:

\[ r_{MAP} = -4k_rK_{eq,H2}K_{eq,H3}K_{eq,H4}P_{H_2O}P_{O_2}a_e[\]²

Again, a site balance is required to solve for the unknown variable \[ [*] \]:

\[ [*]_T = [*] + [O_2] + [O_2^{-*}] + [H_2O^+] + [HO_2^+] + [H_2O_2] + [HO^{**}] + [HO^{-*}] \]

Expressing surface concentrations in terms of fundamental rates \( r_i \):

\[ [O_2] = r_{-H2}/k_{-H2} \]
\[ [O_2^{-*}] = r_{-H4}/k_{-H4} \]
\[ [H_2O^+] = r_{-H3}/k_{-H3} \]
\[ [HO_2^+] = r_{H6}/k_{H6}a_{MAP} = r_{H5}/k_{H6}a_{MAP} \]
\[ [HO^{**}] = r_{H6}/k_{H6}a_{MAP} = 2r_{H5}/k_{H6}a_{MAP} \]
\[ [HO^{-*}] = 2r_{H9}/k_{H9}a_{MAP} = r_{H5}/k_{H9}a_{MAP} \]
\[
    r_{H7} \approx r_{-H7} = k_{H7}[H_2O_2^*]a_e[\ast] = k_{-H7}[HO^*][HO^{\ast\ast}]
\]

\[
    [H_2O_2^*] = \frac{[HO^*][HO^{\ast\ast}]}{K_{eq,H7}a_e[\ast]} = \frac{2r_{H5}^2}{K_{eq,H7}k_{H8}k_{H9}a_{MAPI}^2a_e[\ast]}
\]
simplifies the site balance as:

\[
    [\ast]_T = [\ast] + \frac{r_{-H2} - H2}{k_{-H2}} + \frac{r_{-H4} - H4}{k_{-H4}} + \frac{r_{H5}}{k_{H6}a_{MAPI}} + \frac{2r_{H5}^2}{k_{H8}a_{MAPI}} + \frac{2r_{H5}}{k_{H9}a_{MAPI}}
\]

Remembering the rate limiting step assumption, where \( r_{H5} \ll r_{-H2, H3, H4} \), simplifies the expression further:

\[
    [\ast]_T = [\ast] + \frac{r_{-H2}}{k_{-H2}} + \frac{r_{-H4}}{k_{-H4}} + \frac{r_{H5}}{k_{H3}}
\]

\[
    [\ast]_T = [\ast] + [O_2^\ast] + [O_2^{\ast\ast}] + [H_2O^*]
\]

Taking advantage of prior development where explicit terms for these three surface concentrations were derived:

\[
    [\ast]_T = [\ast](1 + K_{eq,H2}P_{O_2} + K_{eq,H2}K_{eq,H4}P_{O_2}a_e + K_{eq,H3}P_{H2O})
\]

\[
    [\ast] = \frac{[\ast]_T}{1 + K_{eq,H2}P_{O_2}(1 + K_{eq,H4}a_e) + K_{eq,H3}P_{H2O}}
\]

And the rate expression becomes:

\[
    r_{MAPI} = -4k_{H5}K_{eq,H2}K_{eq,H3}K_{eq,H4}[\ast]^2 \frac{P_{H2O}P_{O_2}a_e}{(1 + K_{eq,H2}P_{O_2}(1 + K_{eq,H4}a_e) + K_{eq,H3}P_{H2O})^2}
\]

To recover experimental results, one final assumption is required:

(c) At 21 kPa oxygen pressure and 1 sun illumination, water is in the linear region of the Langmuir isotherm such that \((1 + K_{eq,H2}P_{O_2}(1 + K_{eq,H4}a_e)) \gg K_{eq,H3}P_{H2O})\)

Taking this assumption and combining constants yields the expression consistent with experimental data:

\[
    r_{MAPI} = -k_{eff} \frac{P_{O_2}P_{H2O}a_e}{(1 + K_{eq,H2}P_{O_2}(1 + K_{eq,H4}a_e))^2}
\]

Note that this result relies on \(K_{eq,2P_{O_2}}\) and \(K_{eq,4^n}\) being within an order of magnitude of 1, which conflicts with assumptions (4) and (5) in the \(r_{DPO}\) derivation. However, the presence of humidity impacts \(K_{eq,2}\) and \(K_{eq,4}\). A recent DFT study has shown that the presence of atmospheric water can reduce the reduction potential of adsorbed oxygen species, increasing the yield of superoxide at constant illumination. This would be reflected by an increase in \(K_{eq,4}\) in humidity.
Similarly, Haque et. al. demonstrated that MAPbI$_3$ films synthesized in high humidity conditions created less superoxide than identical films synthesized in low humidity conditions, even after both films were taken to an anhydrous environment.$^{11}$ This, combined with the rapid adsorption kinetics of moisture on MAPbI$_3$$^{12}$ is consistent with H$_2$O saturation of favorable O$_2$ adsorption sites (e.g., I$^{-}$ surface vacancies$^{13,14}$), which would in turn lower the equilibrium coefficient of O$_2$ adsorption $K_{eq,2}$. 
8. Iodide Vacancy Generation from Photoexcited Holes and Mass Transport

All mechanisms cited in this work involve reaction of photoexcited electrons as an important initial step. However, photoexcited holes have been shown to increase iodide vacancy concentration. Converting the Kroger-Vink notation in Kim et al., the expression becomes

\[
CH_3NH_3PbI_3 + h^+ \rightleftharpoons I^* + CH_3NH_3Pb(I_2,*)^+ \quad \text{(Step VI)}
\]

Iodide vacancies are the most favorable adsorption sites for both oxygen and water, and as shown in the rate derivations above:

\[
\tau_{MAPI} \propto [\ast]_T
\]

So, iodide vacancies are very important in the degradation process. Importantly, the adsorption site concentration is at steady-state during the degradation since: (i) step VG1 reaches equilibrium, after exposed to illumination, on time scales faster than degradation rate, and (2) accumulation or depletion of adsorption site density would result in rates that vary as a function of time. As discussed in the main text and previously in this document, \( \tau_{MAPI} \) is relatively constant over time at the start of the degradation reaction, meaning degradation is not impacted by changing iodide vacancy generation.

This is supported by the proposed mechanisms. In all mechanisms, consistent with established literature consensus, photogenerated electrons reduce absorb oxygen species to form adsorbed superoxide radical anions. These radical anions then interact with MAPbI3, either directly or indirectly via reaction with water and generation of reactive oxygen species, to degrade MAPbI3 into CH3NH2 and PbI2. Balancing reaction sub-steps involving attack of anionic species on MAPbI3 (e.g. steps D4, H9, DIV, etc.) necessarily involves generation of product I-. All experimental evidence gathered to date unanimously agrees that the volatile iodine-containing degradation byproduct of photooxidation is I2. Therefore, the iodide anion, I-, must undergo an oxidation to retain consistency with these observations. The only oxidizing species generated in this mechanism is the unpaired photoexcited hole; therefore, this hole is taken to be the redox partner for generated I-

This oxidation can theoretically occur two ways: either direct oxidation of I- by unpaired holes (\( h^+ + I^- \rightleftharpoons I^* \)), or by annihilation of iodide vacancies by I-

\[
CH_3NH_3Pb(I_2,*)^+ + I^- \rightleftharpoons CH_3NH_3PbI_3 \quad \text{(Step V2)}
\]

and subsequent regeneration of iodine radicals via step VG1. In either event, it is crucial to note that the oxidation of free iodide anions by unpaired holes is taken to be a fast step occurring after the rate controlling step in all proposed mechanisms. Necessarily this means that neither unpaired holes due to photooxidation nor generated I- are long-lived enough to appreciably impact iodide vacancy generation, and that the constant adsorption site concentration assumption remains valid in the limit of early degradation times.

Instead, iodide vacancy concentration is set by the rate of mass-transport of iodide away from the film. The rapid removal of I3 should decrease the quasi-equilibrium concentration of iodine radical and (in accord with Le Chatelier’s principle) shift the equilibrium in VG1 to the right, increasing the iodide vacancy concentration. To test this hypothesis, a MAPbI3 film degradation was analyzed in stagnant ambient lab air (not in the environmental control chamber)
where conditions at the time were 20 °C, 40% RH air, and 1 sun illumination. After one hour, a fan was turned on, blowing the same 20 °C, 40% RH air over the sample. The degradation rate increased substantially (we believe due to removal of I₂ and increased iodide vacancy formation) and then returned to the initially measured rate when the fan was turned off (Fig. S6). Predictions of degradation rate (\( \eta_{WPO} \)) based on measurements in the environmental control cell (which utilizes flowing air) closely match the degradation rate observed with the fan on, indicating that rate data generated in this paper are in the fast mass-transport limit (rapid removal of high I₂).

![MAPbI₃ Absorbance Evolution at 20 C in 40% RH air](image)

**Figure S6.** Degradation in ambient conditions with and without forced air convection. Degradation happens much more quickly when air is blown over the thin film sample, indicating degradation rate depends on the rate of removal of a volatile specie, proposed here to be iodine.
9. Possible Changes in Species Adsorption Surface Site Concentration

MAPbI$_3$ degradation—and degradation of all halide perovskites—is an inherently surface-mediated process, with degradation products nucleating at grain surfaces, forming a shell around perovskite grains. As degradation proceeds, the reaction front between pristine perovskite and solid degradation products proceeds inwards. However, conversion of the surface of MAPbI$_3$ to PbI$_2$ may result in changing surface adsorption site density $[^*]_T$. This would result in a total surface site density that is changing in time, which as described in the previous section, is inconsistent with the experimental observation of consistently accurate linear fits of $\Delta A$ vs time in the limit of early degradation time.

To explain how surface site concentration remains roughly time-invariant as grain surfaces react, we note that O$_2$ and H$_2$O adsorption in halide perovskites does not merely occur at the interface of the solid film and the environment. Many reports$^{2,20,21}$ have demonstrated that adsorption and/or surface degradation occurs at homogenous perovskite-perovskite grain boundaries as well. The possibility of rapid diffusion of gaseous reactants through homogeneous perovskite-perovskite grain boundaries and subsequent adsorption at nontrivial depths within the thickness of the films opens up the possibility that such diffusion can occur at heterogeneous solid state interfaces as well. Consider gas diffusion through a partially reacted perovskite grain, with an established thin product PbI$_2$ shell surrounding a pristine MAPbI$_3$ core. Rate of reaction between the MAPbI$_3$ core and gaseous species can be limited in two ways. If diffusion of gaseous species through the product PbI$_2$ shell is slow relative to reaction with MAPbI$_3$, then rate is diffusion-limited. Likewise, if diffusion through PbI$_2$ is fast relative to reaction rate, then the overall rate is limited by the latter. In the limit of slow gas diffusion, the relevant adsorption sites are on the PbI$_2$ surface, as concentration of occupied adsorption sites on the PbI$_2$ surface dictates the concentration profile through the PbI$_2$ shell, and by extension the amount of O$_2$ or H$_2$O that is in physical contact with MAPbI$_3$. By contrast, if diffusion through PbI$_2$ is fast relative to reaction, gaseous concentration profiles through the PbI$_2$ shell can be assumed to roughly be constant, and the relevant adsorption site concentration is on the MAPbI$_3$ surface. This latter assumption is equivalent to assuming rapid diffusion of gaseous species along the heterogeneous PbI$_2$-MAPbI$_3$ grain boundary and subsequent absorption onto MAPbI$_3$, akin to what is observed in homogeneous MAPbI$_3$-MAPbI$_3$ grain boundaries. At early times on which we focus in this work, the PbI$_2$ cladding that forms will be thin and likely discontinuous. Thus, diffusion of O$_2$ and H$_2$O through reacted PbI$_2$ shells is indeed expected to be rapid, that adsorption on MAPbI$_3$ grains therefore remains relevant for rate calculations. If we assume that the surface area of MAPbI$_3$ grains is roughly constant in the limit of early times, we can therefore assume total relevant site density $[^*]_T$ is approximately constant as well.
10. Data from Degradation Experiments

**Figure S7.** Absorbance evolution vs time for MAPbI$_3$ degradation runs performed in 0% RH air under 1 sun illumination. The (a,c,e,g) linear fit regions used to extract initial rate and (b,d,f,h) full absorbance evolution curve are shown for degradation runs performed at (a,b) 25 °C, (c,d) 45 °C, (e,f) 65 °C, and (g,h) 85 °C.
Figure S8. Absorbance evolution vs time for MAPbI\textsubscript{3} degradation runs performed in 60\% RH air under 1 sun illumination. The (a,c,e,g) linear fit regions used to extract initial rate and (b,d,f,h) full absorbance evolution curve are shown for degradation runs performed at (a,b) 25 °C, (c,d) 45 °C, (e,f) 65 °C, and (g,h) 85 °C.
Figure S9. Absorbance evolution vs time for MAPbI$_3$ degradation runs performed at 25 °C in 0% RH air. The (a,c,e,g,i,k,m) linear fit regions used to extract initial rate and (b,d,f,h,j,l,n) full absorbance evolution curve are shown for degradation runs performed at (a,b) 0.25 suns, (c,d) 0.5 suns, (e,f) 1 sun, (g,h) 2 suns, (i,j) 4 suns, (k,l) 7 suns, and (m,n) 10 suns illumination.
**Figure S10.** Absorbance evolution vs time for MAPbI$_3$ degradation runs performed at 25 °C in 0% RH conditions under 1 sun illumination. The (a,c,e,g,i,k) linear fit regions used to extract initial rate and (b,d,f,h,j,l) full absorbance evolution curve are shown for degradation runs performed under (a,b) 5% O$_2$, (c,d) 10.5% O$_2$, (e,f) air, (g,h) 50% O$_2$, (i,j) 75% O$_2$, and (k,l) 100% O$_2$ environments (O$_2$/N$_2$ binary mixtures).
Figure S11. Absorbance evolution vs time for MAPbI₃ degradation runs performed at 25 °C in 60% RH air. The (a,c,e,g,i,k,m) linear fit regions used to extract initial rate and (b,d,f,h,j,l,n) full absorbance evolution curve are shown for degradation runs performed under (a,b) 0.25 suns, (c,d) 0.5 suns, (e,f) 1 sun, (g,h) 2 suns, (i,j) 4 suns, (k,l) 7 suns, and (m,n) 10 suns illumination.
Figure S12. Absorbance evolution vs time for MAPbI$_3$ degradation runs performed at 25 °C in 60% RH atmosphere under 1 sun illumination. The (a,c,e,g,i,k,m) linear fit regions used to extract initial rate and (b,d,f,h,j,l,n) full absorbance evolution curve are shown for degradation runs performed under (a,b) N$_2$, (c,d) 5% O$_2$, (e,f) 10% O$_2$, (g,h) air, (i,j) 50% O$_2$, (k,l) 75% O$_2$, and (m,n) O$_2$ atmospheres (O$_2$/N$_2$ binary mixtures).
Figure S13. Absorbance evolution vs time for MAPbI₃ degradation runs performed at 25 °C in air under 1 sun illumination. The (a,c,e,g,i) linear fit regions used to extract initial rate and (b,d,f,h,j) full absorbance evolution curve are shown for degradation runs performed under (a,b) 0% RH, (c,d) 20% RH, (e,f) 40% RH, (g,h) 60% RH, and (i,j) 80% RH atmospheres.
11. Other Data

Figure S14. (a,b) Absorbance evolution vs time for MAPbI$_3$ degradation runs performed in 50% RH N$_2$ under 1 sun illumination. The (a) linear fit regions used to extract initial rate and (b) full absorbance evolution curve are shown for degradation runs performed under 25, 45, 65, and 85 ºC. (c) Arrhenius plot of MAPbI$_3$ degradation in 50% RH N$_2$ under 1 sun illumination, demonstrating an activation energy of 0.21 ± 0.10 eV.
Figure S15. To calculate very small changes in transmittance in nitrogen, a pre-bake condition (aging in dry N$_2$ at 100 °C under 1 sun illumination intensity until observed transmittance values remained stable (within 0.1%) for ~30 min, usually 8-12 hr) was performed on MAPbI$_3$ films to counteract the observation that there was an initial, small (~10% relative) decrease in optical transmittance when films were placed in high temperature inert environments. (a,b) Bright field and (c,d) dark field microscope images of a MAPbI$_3$ film taken (a,c) before and (b,d) after this preconditioning process, showing the film became visibly more textured/rough during this conditioning process. Dark field images do not appear noticeably more intense; however, (f) absorbance taken in an integrating sphere increased. In concert, these results demonstrate this texture decreases transmittance by “trapping” incident light in the sample via waveguiding (akin to a textured piece of silicon), rather than directly increasing diffuse reflectance/scattered light. (e) XRD patterns show that, while small PbI$_2$ contamination peaks emerged during this ~12 hr preconditioning process, the extent of degradation was negligible. (reference patterns: MAPbI$_3$: COD #4124388, PbI$_2$: COD #1010062).
Figure S16. (a,b) Absorbance traces and (c,d) absorbance at 550 nm of 2 identical MAPbI$_3$ thin films aged in 60% RH air in the dark for 3 days. Changes in absorbance over 72 hrs are negligible, demonstrating air and moisture do not rapidly degrade MAPbI$_3$ in the absence of light.
Figure S17. (a-b) The SEM images of an MAPbI$_3$ film; (c) The J-V curve of an MAPbI$_3$ solar cells; (d) The stabilized power output (SPO) measurement on the MAPbI$_3$ solar cell under 1 sun illumination.
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