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Reaction of chloride anion with atomic oxygen in aqueous solutions: Can cold plasma help in chemistry research?

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Materials.

The gases He (99.999%) and O_2 (>99.5%) were supplied by Praxair.

Ethanol (99.5%) and NaOCl (5% chlorine) were obtained from Acros Organics. NaNO₂ (98%) was from Alfa Aesar. ClO_2^- , ClO_3^- and ClO_4^- standards (1000 mg/L) were purchased from Carl Roth. The Griess Reagent Nitrite Measurement kit was from Cell Signalling Technology.CH₃COONa (\geq 99.5%), NaCl (>99.5%), KCl (99%), KH₂PO₄ (99.5%) and Na₂HPO₄•2H₂O (\geq 98.5%) were from Merck. 5-Diethoxyphosphoryl-5-methyl-1-pyrroline *N*-oxide (DEPMPO; 99%) was from Focus Biomolecules. 3,3',5,5'-Tetramethylbenzidine (TMB; \geq 99%), 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPOL; 97%), 2,2,6,6tetramethylpiperidine (TEMP; \geq 99%), NaN₃ (\geq 99.5%), H₂O₂ (30 wt% in H₂O), K₂TiO(C₂O₄)₂•2H₂O (\geq 98% Ti basis), H₂SO₄ (95-98%) and CH₃COOH (\geq 99%) were from Sigma Aldrich.

De-ionised H₂O was used to prepare all solutions.

Plasma operation.

Plasma was operated with a feed gas of He with or without O_2 admixtures of 0.1-1%. 1% O_2 was the maximum O_2 content with which He+O₂ plasma could be ignited under the used conditions. The flow of each gas was regulated using mass flow controllers equipped with a microcomputer controller (Brooks Instruments 0254). The total flow rate of the feed gas was 1 L/min in all cases. Prior to ignition, the plasma jet was flushed with the feed gas for 15 min.

A Pico Technology PicoScope PC Oscilloscope voltage probe was used to measure the time-resolved root mean square voltage (V_{RMS}). In all experiments, the plasma in the COST jet was sustained at 250 V_{RMS} and a frequency of 13.56 MHz as described elsewhere.^{1, 2}

Solutions preparation and exposure.

10 mM phosphate buffer saline (PBS, pH 7.4) was prepared in H_2O with NaCl, KCl, KH_2PO_4 and $Na_2HPO_4 \bullet 2H_2O$, as described elsewhere.³ PB (pH 7.4) was prepared the same way, but without KCl and NaCl.

In the plasma exposure experiments, 200 μ L of PB or PBS were put in a well in a 96 well plate (Greiner) under the COST plasma jet. The distance from the jet nozzle to the top of the well was 5 mm, while the total distance to the surface of the liquid sample was 10 mm. The exposure time was 60 s unless stated otherwise.

UV-Vis and EPR equipment and methods.

UV-Vis measurements of ClO⁻ and H_2O_2 were performed using a ThermoFischer Genesys 6 spectrophotometer. Quartz cuvettes were used with a 10 mm path length (internal width 2 mm) and a volume of 700 mL.

UV-Vis measurements of NO_2^- were performed on a Tecan Infinite F Plex 200 Pro microplate reader in transparent 96 well plates (Greiner).

EPR measurements were carried out on a Magnettech MiniScope MS 200 spectrometer as follows: frequency 9.4 GHz, power 3.16 mW, modulation frequency 100 kHz, modulation amplitude 0.1 mT, sweep time 40 s, time constant 0.1, sweep width 17 mT.

In all EPR measurements, the analysed samples were contained in 50 μ L glass capillaries (Hirschmann). The concentrations reported were obtained via double integration (SpectrumViewer ver. 2.6.3⁴) of the respective simulated spectra (NIH P.E.S.T. WinSIM software ver. 0.96⁵) of the formed nitroxide radical adducts. The hyperfine coupling constants used in the simulations were obtained from literature.⁶ The calibration of the EPR signal was done using solutions of stable nitroxide radical TEMPOL as described elsewhere.^{1, 2}

Detection of $O/{}^{1}O_{2}/O_{3}$ by EPR.

We used the TEMP spin trap, which is oxidised to TEMPO (a stable nitroxide detected by EPR) by $O/^{1}O_{2}/O_{3}$.^{1, 7, 8} Sodium azide was added as a scavenger for $^{1}O_{2}$.⁹ 20 mM solutions of TEMP (with or without 40 mM NaN₃) in PBS or PB were exposed to plasma as described above. Immediately after plasma exposure, the samples were contained in glass capillaries and analysed using EPR spectrometry. The time between the plasma exposure and the analysis was 1 min.

Detection of H₂O₂.

The measurements of H_2O_2 were done using colourimetry with the Ti(IV) reagent.^{1, 2, 10} 100 mM Ti(IV) reagent was prepared by dissolving $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ in a mixture of H_2SO_4 and H_2O (2:5). For the measurement, 150 µL of the plasmatreated solution were mixed with 50 µL of 80 mM NaN₃ in H_2O , shaken for 10 s, and followed by addition of 150 µL of the Ti(IV) reagent. The resulting mixture was incubated for 2 min and analysed on a UV-Vis spectrophotometer. The calibration of the method was done using H_2O_2 solutions of known concentrations as described in our previous works.^{2, 10} The concentrations of H_2O_2 were calculated from the peak maximum at 402 nm. The analysis was performed 1 min after plasma exposure.

Detection of •OH and O_2^{\bullet} / •OOH radicals.

The radicals were measured using spin trapping with the DEPMPO spin trap.^{1, 2, 7} 100 mM solution of DEPMPO in PBS or PB was exposed to plasma as described above. Immediately after plasma exposure, the samples were contained in glass capillaries and analysed using EPR spectrometry. The time between plasma exposure and analysis was 1 min.

Detection of NO₂⁻.

 NO_2^- was detected by colourimetry in a reaction with Griess reagent, provided as the Griess Reagent Nitrite Measurement kit.^{1, 10} For the measurements, 100 µL of the Griess reagent (1:1 sulfanilamide and *N*-(1-naphthyl)-ethylenediamine) were mixed in a well plate with 100 µL of the plasma-treated solution. The resulting mixture was incubated for 5 min before it was analysed on a microplate reader. The calibration of the method was performed with NO_2^- solutions within the kit. The peak maximum at 540 nm was used to measure the concentration of NO_2^- .

Detection of CIO⁻ with TMB by UV-Vis spectrophotometry.

The method was adapted from literature.¹¹ A 5 mM solution of TMB was prepared in a mixture of EtOH:H₂O (1:1). 0.2 M acetate buffer (AB) in H₂O was prepared using CH₃COONa and CH₃COOH.³

For the detection of CIO⁻, 600 μ L of the TMB solution were mixed with 750 μ L of AB. To this mixture, 150 μ L of plasma-treated PBS were added and the solution was shaken for 10 s. Then, 1.5 mL of H₂O were added, giving a total volume of 3 mL. The pH of each sample was measured using Metler Toledo FiveEasy F20 pH meter, and found to be 3.95-4.00. The resulting solution was incubated for 1 min prior to UV-Vis measurements. The calibration was performed using commercial NaOCI in the range of concentrations 1.3 μ M – 1.3 mM (see Fig. S2). The concentration of CIO⁻ was determined from the peak maximum at 660 nm.

The analysis was performed 1 min after plasma exposure.

Detection of $ClO_2^{-}/ClO_3^{-}/ClO_4^{-}$ by ion chromatography.

For the ion chromatography measurements,¹² we used a Metrohm 883 Basic IC Plus equipped with 863 Compact IC Autosampler and a Metrosep A 5 Supp 250/4.0 column. An H₂O solution containing 1 mM NaHCO₃ and 3.2 mM Na₂CO₃ in H₂O was used as eluent. Flow and pressure were 0.8 L/min and 120 bar, respectively. The retention times were: Cl⁻ 8.9 min, ClO_2^- 7.5 min, ClO_3^- 13.0 min, ClO_4^- 85.0 min.



Figure S1. Experimental setup of an air-free reactor with an O₃-containing exhaust.

Table S1. Oxidation of the solution of TMB with PB by the O_3 -containing exhaust of the air-free reactor. In these experiments, 600 µL of the TMB solution were mixed with 750 µL of AB and 1.5 mL of H₂O. Then, 150 µL of PB (to avoid any possible formation of ClO⁻) were added. The resulting liquid was put in a well in a 24 well plate and exposed to the reactor exhaust. The results are shown with standard deviations of 3 measurements.

In as little as 30 s, we observed very intense oxidation of TMB, as shown by the absorbance at 660 nm. For comparison, hypothetical concentrations of CIO⁻ which could give the same oxidation of TMB are given in the right-most column (see CIO⁻ detection details).

Plasma	Exposure time (s)	Absorbance at 660 nm (a.u.)	Corresponding potential concentration of CIO ⁻ (μ M)
He+0.2% O ₂	30	0.405±0.04	277±27
He+0.8% O ₂	30	1.565±0.066	1070±45

Chemical kinetics model.

A zero-dimensional chemical kinetics model was developed to study the reaction chemistry occurring in the gas phase, both inside the COST-jet as well as in the plasma effluent. In each time step, we solve the balance equations for all species investigated, based on their corresponding source and loss terms. The chemistry set used, described in more detail in our previous work,¹⁰ comprises 91 different species and a total of 1390 reactions. It is a combination of the chemistry sets developed by Murakami et al. and Van Gaens et al.^{13, 14} Besides heavy species reactions, the chemistry set also contains reactions of energetic electrons, which are very important inside the jet. To determine the rate of such reactions, the ZDPlasKin code¹⁵ used in this study has a built-in Boltzmann solver that calculates the electron energy distribution function (EEDF).¹⁶ This EEDF, in combination with a set of cross-sections taken from literature, determines the reaction rates of the electron impact reactions.

In the 0D-approach of a plasma jet, a cylindrical volume element is followed along the jet stream, assuming a homogeneous plasma along the radial axis of the jet. Furthermore, by implementing the velocity profile of the feed gas, the time dependence typically predicted in 0D simulations can be correlated with the distance along the axis. We calculated the velocity profile using 2D flow simulations for the experimental geometry (see also Fig. S2) as described elsewhere.² The initial velocity, calculated based on the flow rate of the feed gas and the dimensions of the plasma jet, is kept constant inside the jet. Due to expansion of the effluent when mixing with ambient air surrounding the jet, this velocity decreases in the effluent.

Besides the velocity profile and the chemistry set, a few more input parameters are needed in the model, including the profile of the applied power and the gas temperature. A constant power is applied inside the plasma jet, and immediately removed once the nozzle of the plasma jet is reached (i.e., no power is applied in the effluent). The initial gas temperature is set at 293 K, which increases throughout the jet to 323 K due to gas heating. Once outside the jet, this temperature decreases again steadily due to cooling by ambient air.²

A schematic representation of the geometry and dimensions considered in the chemical kinetics model is shown in Fig. S2, which also includes the applied power, gas temperature and axial velocity profiles.



Figure S2. Geometry and parameters assumed in the 0D model used to calculate the densities of the reactive species in the gas phase immediately above the liquid solution.



Figure S3. Formation of TEMPO in PBS as measured by EPR. The error bars the represent the standard deviation of three measurements.



Figure S4. Concentrations of •NO, •NO₂ and N₂O₅ (left), •OH, •OOH and O₂•⁻ (right) in the gas phase, as predicted by the 0D chemical kinetics model. The trends of •OOH and O₂•⁻ agreed well with the experimental data (see Fig. 2c in the main paper): in aqueous media, DEPMPO-OOH adduct may represent adducts with both •OOH and O₂•⁻ radicals.^{1,17}

While very good agreements between the model and the experiments were achieved for $\bullet OOH/O_2 \bullet^-$, for $\bullet OH$ the model predicted a low amount of DEPMPO-OH at 0% O_2 in He. The experiments showed a higher concentration of DEPMPO-OH at 0% O_2 in He (see Fig. 2c). We tentatively speculate that this was probably because plasma generates a large amount of He^{*} metastables in the absence of admixtures to the feed gas. These metastables can reach the liquid and generate additional

•OH from H_2O , probably from a dense layer of vapour above the liquid solution.⁷ The latter process could not be accounted for in the model.



Figure S5. Calibration of the TMB method using a commercial solution of NaOCI. The error bars represent the standard deviation of three measurements.



Figure S6. Induction of the absorbance peak with a maximum at 660 nm with PBS samples containing 1 mM ClO_2^- (left) and 52 μ M ClO^- (right) as a function of incubation time.



Figure S7. Induction of the absorbance peak with a maximum at 660 nm with PBS samples containing various concentrations of NO_2^- as a function of incubation time. NO_2^- was added as $NaNO_2$.



Figure S8. Formation of CIO⁻ in plasma-treated solution as a function of treatment time. The near-linear concentration trend at treatment times as long as 2 min agrees with no $CIO_2^-/CIO_3^-/CIO_4^-$ detected (see main text).



Figure S9. Decay of CIO⁻ in PBS in the presence of H_2O_2 (left) and NO_2^{-} (right). NO_2^{-} was added as NaNO₂.



Figure S10. Stability of pre-added CIO⁻ in PBS (left), and CIO⁻ formed by He+O₂ plasma in PBS 1 min after treatment (right).

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