Solvated Electrons

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A Non-Exploding Alkali Metal Drop on Water: From Blue Solvated Electrons to Bursting Molten Hydroxide

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Abstract: *Alkali metals in water are always at the brink of explosion. Herein, we show that this vigorous reaction can be kept in a non-exploding regime, revealing a fascinating richness of hitherto unexplored chemical processes. A combination of high-speed camera imaging and visible/near-infrared/infrared spectroscopy allowed us to catch and characterize the system at each stage of the reaction. After gently placing a drop of a sodium/potassium alloy on water under an inert atmosphere, the production of solvated electrons became so strong that their characteristic blue color could be observed with the naked eye. The exoergic reaction leading to the formation of hydrogen and hydroxide eventually heated the alkali metal drop such that it became glowing red, and part of the metal evaporated. As a result of the reaction, a perfectly transparent drop consisting of molten hydroxide was temporarily stabilized on water through the Leidenfrost effect, bursting spectacularly after it had cooled sufficiently.*

It is high-school chemistry that sodium reacts vigorously with water.[1,2] Upon contact between the reagents, electrons move from the alkali metal to water, forming hydrogen and hydroxide in a strongly exothermic process nominally written as $2\,M+2\,H_2O \rightarrow 2\,MOH+H_2$ (M = alkali metal), which often leads to explosions.[1,3] In our previous study,[4] we showed that a hitherto unrecognized precondition for the explosive behavior is a massive positive charging of the metal drop upon exit of the valence electrons from the alkali metal to water. This can create an electrostatic instability, which leads to metal spikes shooting into water, ensuring efficient reactant mixing. We have also demonstrated that such an electrostatic Coulomb explosion[5–9] can be quenched by limiting the contact between the alkali metal and water, for example by adding a small amount of surface active species such as hexanol. This raised the idea to keep the reaction just below the explosive threshold and follow the individual stages of the process, which is all but impossible if explosion occurs. In this work, we reached the non-explosive regime in a controlled way by carefully placing a sodium/potassium alloy drop on water rather than dropping it from a considerable height (which always leads to explosion). We then used a combination of high-speed camera imaging and visible/near-IR/IR spectroscopy to fully characterize a sequence of unique chemical processes, starting with strong formation of solvated electrons, which is visible to the naked eye despite their extremely short lifetime in water,[10–13] and ending with a bursting drop of molten hydroxide. The fact that a hot drop of hydroxide, which is heavier than water and well miscible with it, can be temporarily supported at the water surface is a remarkable demonstration of the Leidenfrost effect (which also keeps water drops stable on a hot stove).[14,15]

After much experimentation, we found that a robust and reproducible way to the non-explosive regime of alkali metal reactions in water is to deposit a drop of a sodium/potassium alloy, which is liquid at room temperature, from a syringe directly on the aqueous surface (see Figure 1 for a photograph and a schematic illustration of the experimental setup). This limits the contact between the reactants compared to our previous setup, where the alloy was dropped from about one meter above the water surface and always exploded.[4] When gently placed on water, the sodium/potassium alloy drop (which has a lower density than water) starts reacting vigorously (Figure 1 A). However, owing to its buoyancy and immediate gas production, the contact with water is limited such that the reaction towards hydrogen and hydroxide proceeds in a non-explosive way. Also, there is no ignition of the hydrogen gas formed as we are continuously flushing the reaction vessel with argon gas. When properly designed, the argon flow is a double blessing as it also carries with itself the produced smoke, which would otherwise completely obscure the view for the camera. A fascinating richness of hitherto unexplored chemical processes then unravels in front of the lens of the camera (for a Movie, see the Supporting Information). Here, we may only show static snapshots (Figure 1) and do our best to re-enact the impressions from the moving pictures by adding an accurate verbal description supported by spectroscopic evidence.

Shortly after the beginning of the reaction, the metal drop starts turning blue (Figure 1 B), with the color getting progressively darker and the drop eventually turning black. We confirmed spectroscopically that the blue color, which is visible to the naked eye (and also caught on high-speed camera within our previous explosive setup),[4] is due to

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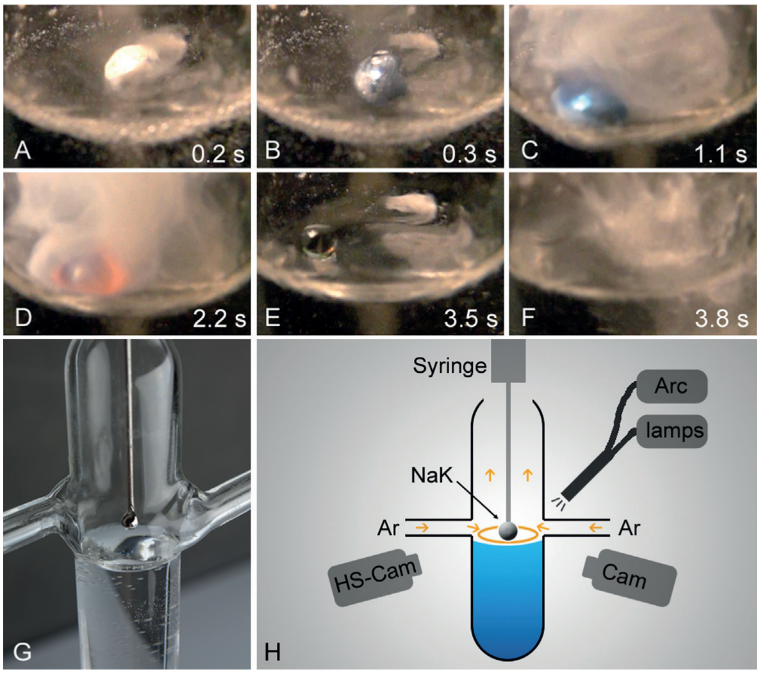

Figure 1. Images of a sodium/potassium alloy drop reacting on water, showing individual stages of the process: A) Onset of the reaction in a non-explosive mode. B) Occurrence of blue solvated electrons at the surface of the drop. C) Evaporation of hot alkali metal (blue/turquoise) from the drop. D) Continuous heating leading to a glowing red drop. E) Formation of a transparent alkali metal hydroxide drop. F) Bursting of the transiently stable alkali metal hydroxide drop after breakdown of the supporting Leidenfrost vapor layer. G, H) Photograph and schematic representation of the experimental setup.

solvated electrons. Figure 2 shows a spectrum that has been recorded in a slightly modified setup where a drop of water was placed on the sodium/potassium alloy drop (Figure 2, right). This setup both spatially limits and efficiently cools the alloy drop, thus increasing the concentration of the solvated electrons and providing a visually spectacular blue spot at the surface of the metal drop and its aqueous surroundings, the color of which can be easily dispersed by a standard Vis/near-IR spectrometer. The obtained spectrum is overlaid in Figure 2 with previously recorded spectra of hydrated electrons prepared at various temperatures through pulse radiolysis of water.[16] The agreement with the reference measurements[16] is convincing despite the different ways of preparing the solvated electrons, demonstrating also that our system is heating up from the initial ambient conditions. Being far from thermodynamic equilibrium, the reacting system can hardly be assigned a well-defined temperature. Nevertheless, it is clear from Figure 2 that already at this early stage, the exoergic chemical process heats the surface of the metal drop well above room temperature, up to at least 100 °C in the present setup.

In the setup presented in Figure 1, the drop continues to heat up, and at a certain point, strong alkali metal evaporation begins (Figure 1 C). The recorded visible spectrum of the alkali metal vapor is presented in Figure 3. We see the presence of both potassium and sodium gas, as indicated by characteristic lines in the absorption spectrum at around $\lambda = 770$ nm (potassium) and 580 nm (sodium). Also, a strong near-IR tail, which is due to the heating of the drop, is clearly visible. It is precisely this spectral tail that masks the spectrum of the hydrated electrons to a significant extent within this setup, and we therefore developed the modified setup shown in Figure 2 to record its spectrum. The continued heating of the alkali metal drop, which is due to the ongoing exoergic chemical processes, eventually renders it glowing red (see Figure 1 D). Using a remote thermometer, we estimated

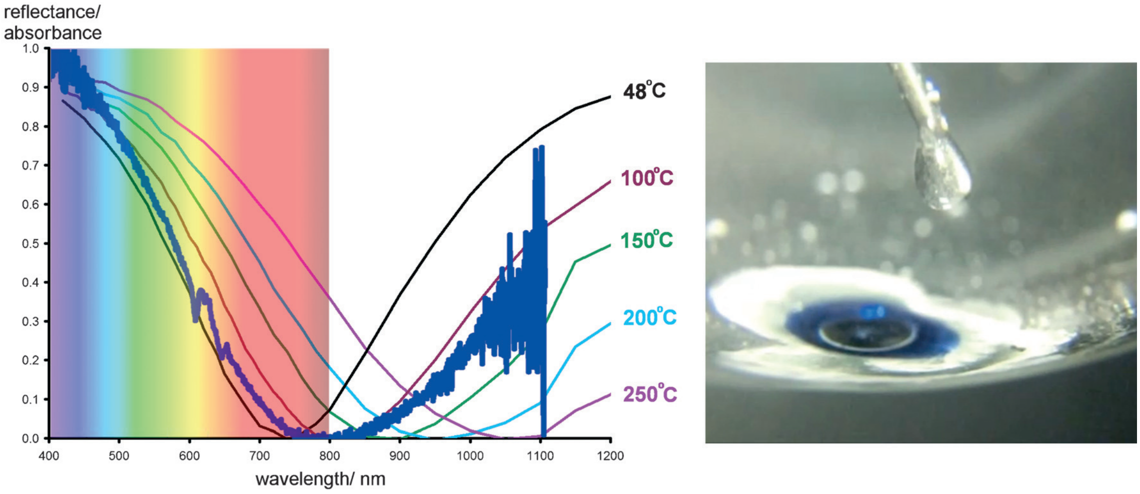

Figure 2. Visible/near-IR spectrum of the solvated electrons recorded in the reflection mode, overlaid with previous spectra of electrons obtained from pulse radiolysis of water at various temperatures (data from Ref. [16] taken in the absorption mode are presented here horizontally inverted for direct comparison). The background rainbow roughly indicates the visible range. The snapshot on the right shows the modified experimental setup (corresponding to stage B in Figure 1) that yielded the clearest signature of the solvated electrons seen as the blue spot at and around the alkali metal drop.

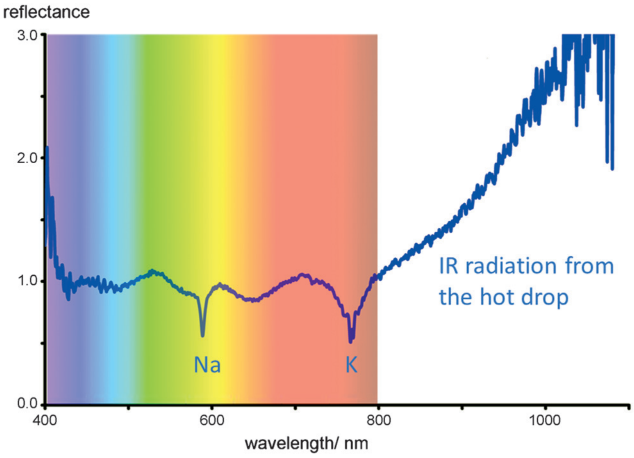

Figure 3. Visible/near-IR spectrum from stage C in Figure 1 recorded in the reflection mode. The sodium and potassium atomic lines in the spectrum demonstrate the presence of alkali metals evaporating from the hot drop, while the presence of a strong IR tail to a large extent obscures the spectral signature of the solvated electrons in the setup from Figure 1. The background rainbow roughly indicates the visible range.

the temperature of the droplet at this stage to be around 600 °C.

A most amazing thing happens after the chemistry is essentially over. When the smoke clears, the drop cools and suddenly becomes completely transparent (Figure 1 E). This transparent drop lives at the aqueous surface for about one second before it bursts spectacularly. Several questions arise immediately. First, what is the transparent drop made from? It is clearly not metallic anymore, and the fact that the vigorous reactivity has ceased already indicates that it may be dominantly composed of the key non-gaseous product of the reaction, that is, molten alkali metal hydroxide (likely also containing other products such as sodium oxide). This was indeed confirmed by IR spectroscopic analysis of this drop (see Figure 4), which revealed characteristic fingerprints of molten or solid hydroxides, in particular the OH stretch between 3480 and 3620 cm^{-1}, and at around 900 cm^{-1}.[17–19] The next intriguing question is how a drop of molten alkali metal hydroxide, which is significantly heavier than water and perfectly miscible with it, can be supported at the aqueous surface. The answer lies in invoking the Leidenfrost effect.[14,15] In its conventional realization, it is the effect behind the stabilization of water drops on a hot stove via a separating hot steam layer. Here, we have an analogous situation, but in an inverse mode, with a hot drop of molten hydroxide stabilized by a vapor layer on water at room temperature. Finally, as the drop cools down, the hot vapor layer separating it from water becomes destabilized. Eventually, this layer ceases to be able to effectively separate the two species, which leads to a vigorous mixing of the hydroxide drop with water proceeding in a dramatic burst.

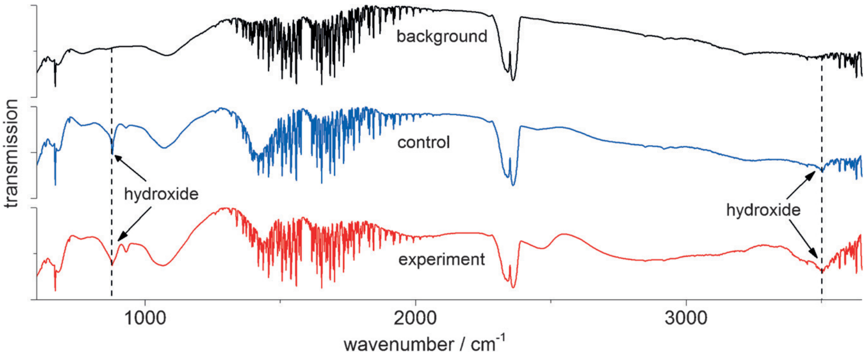

Figure 4. IR spectrum recorded in the transmission mode showing clear signatures confirming the presence of hydroxide in the transparent drop at stage E in Figure 1 (red line). The black line shows the background spectrum whereas the blue line corresponds to a control measurement for molten sodium/potassium hydroxide.

In summary, we have shown that the non-explosive regime of the textbook reaction of alkali metals with water offers even richer and less explored chemistry and physics than the explosions that we recently characterized and rationalized in detail.[4] When a sodium/potassium alloy is gently placed on a water surface, the vigorous reaction of the drop proceeds in distinct stages, which were spectroscopically characterized. With a bit of temperature control, the broad spectrum of solvated electrons could be recorded using a standard continuous-wave Vis/near-IR spectrometer. Moreover, the characteristic blue color of solvated electrons could be clearly seen with the naked eye, which was thought to be all but impossible owing to their extremely short (sub-millisecond) lifetime in water.[20,21] The trick here is to establish a steady-state regime for hundreds of milliseconds with a massive influx of electrons from the alkali metal to the water. Continued reaction leads to further heating of the drop along with alkali metal evaporation and burning in the water vapor with the drop becoming glowing red. When the chemistry eventually ceases, the metal drop is transformed into a transparent ball of molten hydroxide, which is transiently stabilized at the water surface through the Leidenfrost effect[14,15] until it cools down and bursts spectacularly.

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