

Electrogenerated Chemiluminescence with Ruthenium Trisbipyridine and TATP

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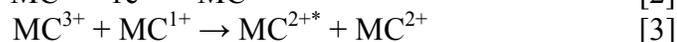
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Interaction of the explosive triacetone triperoxide (TATP) with the electrogenerated chemiluminescence (ECL) of Ru(bpy)₃²⁺ in acetonitrile was studied. The analyte greatly reduces the light made during the annihilation mechanism yielding ppb level detection. The mechanism is thought to be EEC' during reduction which reduces the light by oxidizing the Ru(bpy)₃⁺ before it can react with Ru(bpy)₃³⁺.

Introduction

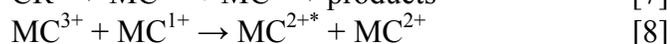
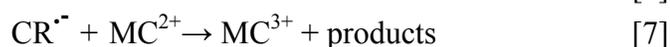
In light of multiple events over the last decade, there is a clear need for new and more sensitive methods of detecting explosives, especially those made by easily available materials. In fact, it was this kind of threat that led to the banning of liquids in containers larger than 3 ounces on flights in the United States and most of the world.¹ Triacetone triperoxide (TATP) is one of these explosives, as it has been used in multiple terrorist attacks both unsuccessful² and successful.³

Since TATP is a peroxide, it should be possible to detect it by electrogenerated chemiluminescence (ECL). ECL at its simplest, is a process that involves the annihilation of redox generated species produced when a complex such as a transition metal chelate (MC) is oxidized and then then reduced rapidly⁴ as shown in equations 1-4



The process will produce visible light if the energy difference between the oxidized and reduced species falls in the range $> 2\text{eV}$.⁵

Alternately, light may also be produced from what is known as the co-reactant scheme⁶ as shown in equations 5-8. Here, the reduction process makes an energetic enough oxidizing agent [5] to directly produce the oxidized metal chelate so the follow-on annihilation reaction [3] can occur.



This is how the project hoped to detect the explosive. Other, more elaborate mechanisms are possible in these schemes which are thought to occur in parallel. Additionally, the

most studied of this kind of scheme is actually on the oxidation side and these are discussed at length in other references so will not be belabored here.⁷

This process can then be exploited to determine the concentration of the photon emitting molecule, in much the same way as fluorescence. The advantage over fluorescence, however, is a greatly reduced background due to the lack of an excitation source which allows the sensitivity to be greatly improved.⁸

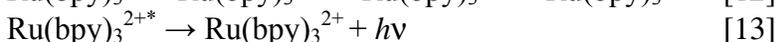
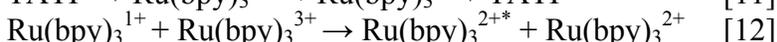
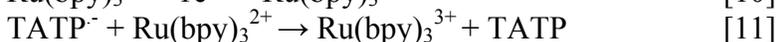
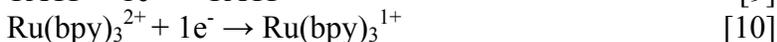
Experimental

A CHI 770 potentiostat (CH Instruments, Austin, TX) was used for all experiments. Light was detected by an Oriel photo multiplier tube scavenged from an unused SPEX UV/Visible spectrophotometer. Voltammetry and chronoamperometry were conducted in a glass cell located directly above the PMT in a standard three electrode arrangement with a Pt electrode used as the working electrode, Pt wire as the counter, and a Ag wire as the reference. The working electrode faced directly down into the PMT and foil was placed above this arrangement to reflect scattered light back down. This cell and PMT were placed under concentric black boxes to minimize background light. PMT current was measured by a picoamp capable meter (Kiethley, Cleveland, OH) and its analog output sent to the CHI 770 auxiliary input via 9 pin serial port.

Ru(bpy)₃Cl₂ (ACROS) was recrystallized with 3M NaBF₄ (Baker) to swap the counter ion prior to making a 1mM stock solution in HPLC grade, 99.5% acetonitrile (ACROS). Tetrabutyl ammonium phosphate (Baker) was used as background electrolyte. ECL experiments were performed under both atmospheric and degassed (Ar) conditions. Sweep voltammetry was used to verify the oxidation and reduction potentials prior to conducting the chronoamperometry experiments. TATP solutions (0.1 mg/mL in MeCN) were purchased from AccuStandard (New Haven, CT) via Fisher.

Results and Discussion

At the outset of the project, the expectation was that light would be generated via a co-reactant scheme where the TATP radical anion would lead to excited state production as demonstrated with benzoyl peroxide and rubrene by Akins et. al.⁹ This is shown by equations 9 – 12.



However, mixed results soon revealed the moisture content of the solvent made a great deal of difference. A more detailed analysis of this has been published elsewhere.¹⁰ The conclusion is that water aids the decomposition of TATP^{·-} to hydroxyl radicals which are energetic enough to produce light.¹¹

In solvent dried over molecular sieves and the cell degassed by Ar bubbled through MeCN (also over molecular sieves) no light is produced. The radical should, however, still be an oxidizing agent which leads to the conclusion that if TATP^{·-} reacts with Ru(bpy)₃⁺ it is just not energetic enough to produce the excited state. Evidence of

this can be seen in Figure 1 by looking at the effect on light made using the annihilation scheme (equations 1-4). The plot shows both Faradaic and PMT output current as there is information in both sets of data. The first obvious effect is that adding TATP dramatically reduces light made. Of note, in the experiment shown, the first pulse was negative and did not produce light.

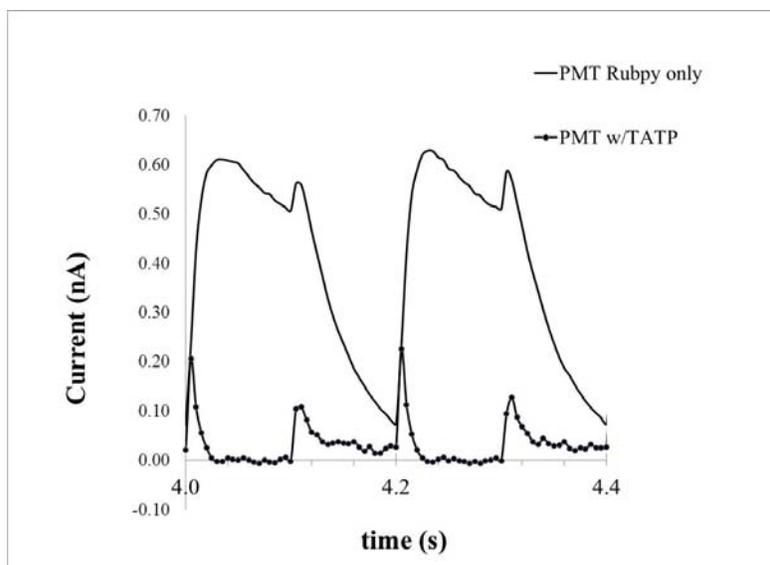


Figure 1. ECL of 250 μM $\text{Ru}(\text{bpy})_3^{2+}$ in MeCN with 0.1M TBAP before and after addition of TATP at 10 nM. The potential was pulsed between -0.9V and 1.3V vs. an Ag wire with a pw of 100 msec for 12 seconds.

Faradaic Current Analysis

Preliminary studies in a dry box using square wave voltammetry indicated TATP undergoes a one electron, irreversible reduction at $< 1\text{V}$ vs. Fc. Thus, stepping the potential to 0.9V vs. an Ag wire is negative enough to produce the anion radical. That is also negative enough to produce $\text{Ru}(\text{bpy})_3^+$, just not the diffusion controlled amount making that the limiting reagent of the reaction with $\text{Ru}(\text{bpy})_3^{3+}$ to make light. That is why the cathodic pulse is making less current than the anodic in the experiment with the complex only.

Adding TATP has no effect on the peak current of the negative potential step but does show a slower decay current than the $\text{Ru}(\text{bpy})_3^{2+}$ only experiment. This can be more clearly seen in Figure 2. Given the very low TATP concentration, one reasonable explanation is that the reaction is catalytically regenerating the $\text{Ru}(\text{bpy})_3^{2+}$ near the electrode, leading to more reduction current. The same trend in the decay is seen on the oxidation side as well. However, note the peak of the oxidative pulse is greater after TATP has been added. If the TATP radical anion is in fact reacting with the $\text{Ru}(\text{bpy})_3^+$ as expected, these data make sense. During the negative pulse, the amount of $\text{Ru}(\text{bpy})_3^{2+}$ initially at the electrode is essentially the same with or without TATP since the analyte is there in such a small concentration. However, the expected product of this homogeneous reaction would be to regenerate $\text{Ru}(\text{bpy})_3^{2+}$, thus increasing its concentration at the electrode when the potential is stepped back to produce $\text{Ru}(\text{bpy})_3^{3+}$ (compared to the complex only experiment). That results in the larger faradaic peak current in the oxidative step vs. reduction. The current was analyzed at early times in the experiment,

in the middle and late pulses as well. The trend was consistent throughout, though scatter in the data was larger at early times.

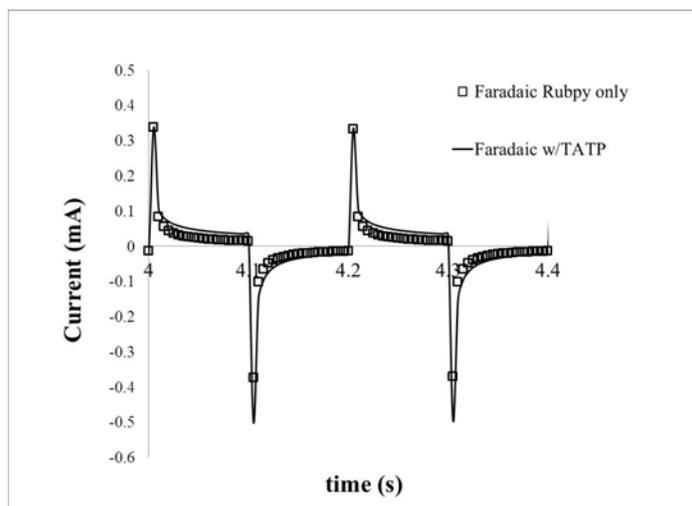


Figure 2. ECL of 250 μM $\text{Ru}(\text{bpy})_3^{2+}$ in MeCN with 0.1M TBAP and 10 nM TATP.

PMT Current Analysis

The theory that, on the negative pulse, $\text{TATP}^{\cdot-}$ is consuming $\text{Ru}(\text{bpy})_3^+$ by converting it back to $\text{Ru}(\text{bpy})_3^{2+}$ is borne out by the light traces as well. Light pulses on the cathodic step decay sharply to background vs. the anodic step. The subtleties of where the light is produced spatially must be considered to adequately explain this observation. Commencing with the negative step (eq 1 and 2), newly produced $\text{Ru}(\text{bpy})_3^+$ and $\text{TATP}^{\cdot-}$ diffuse away from the electrode due to their high concentration there. When the positive step occurs one pulse width later, $\text{Ru}(\text{bpy})_3^{2+}$ present is immediately converted to $\text{Ru}(\text{bpy})_3^{3+}$ (eq 3), changing the concentration gradient. $\text{Ru}(\text{bpy})_3^{3+}$ diffuses outward while the $\text{Ru}(\text{bpy})_3^+$ and $\text{TATP}^{\cdot-}$ begin to diffuse back. All species meet at some distance in front of the electrode. However, if $\text{TATP}^{\cdot-}$ has been converting $\text{Ru}(\text{bpy})_3^+$ back to $\text{Ru}(\text{bpy})_3^{2+}$ in the time it takes for the diffusion out and back to occur (pulse width + diffusion back), less of it is available to react with $\text{Ru}(\text{bpy})_3^{3+}$ in the light production step. Thus, weaker light is detected.

However, on the succeeding negative step, when fresh $\text{Ru}(\text{bpy})_3^+$ and $\text{TATP}^{\cdot-}$ are produced, they will collide with the $\text{Ru}(\text{bpy})_3^{3+}$ diffusion field similarly coming back to the electrode. Now, $\text{Ru}(\text{bpy})_3^+$ has only had the diffusion time to react with $\text{TATP}^{\cdot-}$ before coming in contact with $\text{Ru}(\text{bpy})_3^{3+}$ left over from the preceding step. Significantly more light is thus made. There will still be plenty of $\text{Ru}(\text{bpy})_3^{3+}$ left because the potential used for producing $\text{Ru}(\text{bpy})_3^{3+}$ is sufficient to produce a mass transfer limited amount of material vs. the $\text{Ru}(\text{bpy})_3^+$ step whose potential is only negative enough to produce a kinetically controlled amount which is further reduced by the $\text{TATP}^{\cdot-}$ reaction.

Concentration Effects

Adding more TATP to this experiment only serves to consume more $\text{Ru}(\text{bpy})_3^+$ before the light generating step, causing even less light to be produced as shown in Figure 3. The effect is most pronounced by analyzing the anodic pulses. Data for the entire 12 second experiment was analyzed at three different time intervals as well to look for possible variations both in time and for the two different pulses.

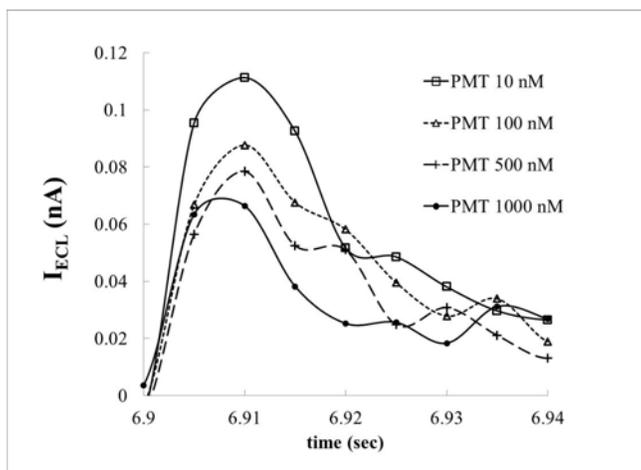


Figure 3. Effect of great TATP concentration on the ECL of $250 \mu\text{M Ru}(\text{bpy})_3^{2+}$.

Figure 4 shows the trend for peaks on the anodic step. Error bars indicate the standard deviation of five sampled pulses in the time interval indicated. There are some differences at early times which are attributable to the fact that a steady state condition has not quite been established, but the data converges within the error bars at later times.

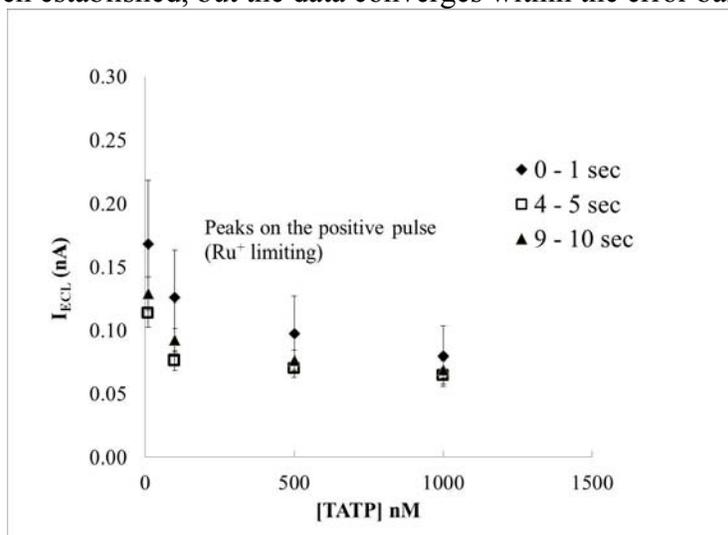


Figure 4. Analysis of peak light intensity for anodic pulses at various times during the experiments shown in Figure 3.

The light generated by this pulse can be thought to be limited by the amount of $\text{Ru}(\text{bpy})_3^+$ available which is why their peaks are smaller than the peaks on the negative pulse.

The trend for the anodic peaks is shown in Figure 5 which can be thought of as TATP limited. These peaks are higher in intensity and the variations from pulse to pulse less than the cathodic step. It also shows a slight deviation from the continuous

downward trend in light production with increasing concentration of TATP. There is a peak in the data at 100 nM which is not surprising given it occurs at a concentration 2500 times smaller than the $\text{Ru}(\text{bpy})_3^{2+}$. This effect has been shown before in the study of hydrogen peroxide as a co-reactant (ref 11) where follow-on fluorescence experiments showed hydroxyl radicals to be actual excited state quenchers. We have not undertaken that analysis as of this writing, but since the TATP stability in dry solvent appears to be key to the effect, the expectation is that hydroxyl radicals are not being produced. If that is the case, then a reasonable assumption is that TATP is not providing a non-radiative pathway for $\text{Ru}(\text{bpy})_3^{2+*}$ to return to the ground state, rather one of the reactants that produces the excited state is being consumed.

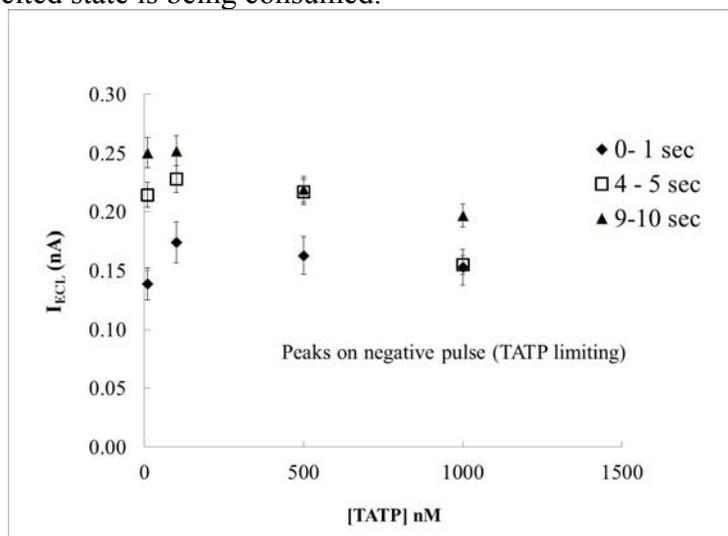
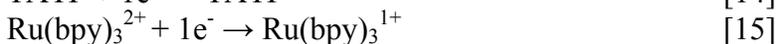


Figure 5. Analysis of peak light intensity for cathodic pulses at various times during the experiments shown in Figure 3.

Proposed Mechanism

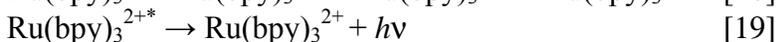
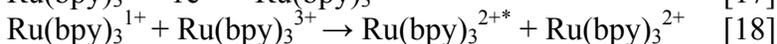
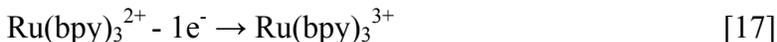
Based on the above analysis, the proposed mechanism begins as expected:



on the negative pulse which does not produce light. Then for the time duration of the pulse, the following occurs:



which has a rate constant kc . Then, on the positive pulse:



but light is reduced when TATP has been added, because there is less $\text{Ru}(\text{bpy})_3^{1+}$ available since it is being converted back to $\text{Ru}(\text{bpy})_3^{2+}$ via [16]. The additional reduction in light produced on the anodic vs. cathodic pulse is attributed to the fact that

[16] will have been taking place longer within a cycle before the light generating reactants come together.

Given [16] is a catalytic following reaction, an analysis as described in Bard and Faulkner¹² yields a reasonable estimate for the rate constant of the homogeneous reaction by comparing the faradaic current both with and without TATP. Substituting values obtained from the current/time plots gives a ratio of 2.0 which puts this reaction in the 'intermediate kinetic' region, meaning the reaction proceeds with a mix of diffusion and kinetic control. Solving for kc gives a value of $4.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the bimolecular rate constant, but fitting to simulation is currently being undertaken to refine the estimate.

Conclusions

In dry solvent, the TATP radical anion is sufficiently stable to react with $\text{Ru}(\text{bpy})_3^{1+}$, but this reaction is not energetic enough to produce light directly. However, this reaction competes with normal annihilation mode ECL and reduces light made by this route. A rough estimate of the bi-molecular rate constant for the competition reaction is $4.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ based on analysis of the faradaic current both with and without TATP. Detection of TATP concentrations as low as 10nM (~ 2 ppb) has been shown by focusing on the light reduction effect. Given that even 10nM TATP results in a significant light reduction, a lower detection limit is possible.

Acknowledgments

My thanks to Dr. Wujian Miao who not only inspired and helped with this study, but has also been a mentor. Funding was provided by the U.S. Naval Academy and the Defense Threat Reduction Agency.

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