Chemiluminescence of luminol in the presence of bentonite and other clays

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LUMINOL, 5-amino-2,3 dihydro-1,4 phthalazinedione, is one of the best known chemiluminescent compounds (White, 1961). It is stable indefinitely in the absence of oxygen, but light is produced when a basic solution of luminol is treated with an oxidizing agent (Goldenson, 1957). White et al. (1964a, b) showed that the mechanism of chemiluminescence involves first the formation of a negative ion of luminol, II in equation (1) which reacts with oxygen or an oxidizing agent to yield an excited singlet state of the amino phthalate ion, III in equation (1) and the emission of light:

\[
\text{O} \quad \text{N--H} \quad 2\text{H}_2\text{O} \\
\text{NH}_2 \quad \text{O} \quad \text{NHz} \quad \text{O} \\
\text{I} \quad \text{II} \\
\text{III}
\]

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\text{O} \quad \text{N--H} \quad 2\text{H}_2\text{O} \\
\text{NH}_2 \quad \text{O} \quad \text{NHz} \quad \text{O} \\
\text{I} \quad \text{II} \\
\text{III}
\]

At pH values above about 10 and at luminol concentrations higher than about 10^{-3} M, pure luminol solutions produce chemiluminescence without any addition of oxidizing agent. This reaction is temperature dependent and can be detected visually when KOH or NaOH pellets are added to a luminol solution and produce heat upon dissolution. Cold solutions do not produce the visible effect, but their luminescence can be measured by scintillation spectrometer.

Of the minerals studied in the present work, bentonite is by far the most effective catalyst. In Table 1 the six minerals under study are compared as to their effect on light production measured in the scintillation spectrometer. Except for bentonite which has a very significant catalytic effect on the reaction, all the other minerals under study had count rates lower than the background. This decrease below the background is presumably due to absorption of the light by the solid particles. The effects of particle size and flocculation in the mineral suspensions make it impossible to compare accurately the five suspensions under study. Moreover, even if these minerals do have a catalytic effect on the chemiluminescence reaction, under the present conditions it is small and cannot be easily detected. On the other hand, the catalytic effect of bentonite is so large that it can be easily detected in spite of light absorption. It should be noted that light emission from bentonite-luminol systems continues for many days after the mixing of the two compounds.

At pH 9-2 the bentonite had no significant effect on the chemiluminescence even at luminol concentrations of 10^{-3} M. At luminol concentration of 10^{-4} M, the bentonite...
Table 1. Chemiluminescence rate of six raw minerals expressed as counts per min 20 sec after the mixing. Each measurement lasted 12 sec, pH 11.2. Luminol concentration 10⁻³ M. Mineral concentration 10 mg/ml. The background of pure luminol solution was 17,450 cpm

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Luminescence rate (counts per min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>205,550</td>
</tr>
<tr>
<td>Illite</td>
<td>9,500</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>9,500</td>
</tr>
<tr>
<td>Attapulgite</td>
<td>4,550</td>
</tr>
<tr>
<td>Nontronite</td>
<td>1,520</td>
</tr>
<tr>
<td>CaCO₃(AR)</td>
<td>5,300</td>
</tr>
</tbody>
</table>

had no measurable effect even at pH 11.2. In the range of luminol concentration and pH where the bentonite has a catalytic effect, the reaction rate typically first increases and then gradually falls, dependent on the pH and concentration (Figs. 1 and 2). Shaking produces a significant increase in reaction rate, which then falls again after several seconds. The shaking effect is connected to the availability of oxygen as will be shown shortly.

The role of oxygen was studied by bubbling either helium or nitrogen through the luminol solution and the bentonite suspension for more than 3 hr in order to remove oxygen. The treated solutions were then mixed in an oxygen-free atmosphere and the reaction observed in a dark room. The oxygen-free solutions produced no visible effect upon mixing. However, light was detected visually when air was allowed into the reaction vessel. It should be noted that it is not known at present whether the absence of oxygen drastically decreased the reaction rate or stopped it entirely.

Both oxygen adsorbed on the mineral surface and oxidizing sites on the surface (Solomon et al., 1968) can serve as electron acceptors. The possible role of the oxygen as a catalyst rather than as an electron acceptor (Hirschler, 1966) should not be discarded. In both cases

![Fig. 1. Chemiluminescence rate of luminol in the presence of Na-bentonite (2 mg/ml) as a function of time at two luminol concentrations and pH 11.2. The background of pure luminol was about 1 per cent of the catalyzed reaction.](image1)

![Fig. 2. Chemiluminescence rate of luminol in the presence of Na-bentonite (2 mg/ml) as a function of time at two values of pH and a luminol concentration of 10⁻² M.](image2)

![Fig. 3. The absorbance spectrum of 10⁻⁴ M luminol solution at two pH values.](image3)
pumping off the oxygen would reduce the reaction rate.

Adsorption of luminol on Na-bentonite was studied at pH values of 8.5, 9.6, 10.2 and 11.2 by mixing the luminol solution with the bentonite suspension, shaking for half an hour, centrifuging, and measuring the light absorbance of the supernatant. The absorbance spectrum of luminol depends slightly on the pH in the basic range (Fig. 3). The two peaks, at 347 and at 300 nm, can be used for quantitative determination since the Beer–Lambert Law is obeyed for luminol concentrations of at least 0.25 mM/l. No significant adsorption was detected at pH values of 8.5, 9.6 and 10.2. At pH 11.2 a negative adsorption was noted.

The two pK values of luminol are 6 and 13 (Stross and Branch, 1939). Thus, it is an anion in the reaction under study. (See also equation 1). The net electric charge on the montmorillonite surface is negative and pH dependent; it increases with pH and reaches a maximum value at pH 9, above which it decreases considerably (Bergna, 1950). The functional groups at the particle edges are apparently negative at the high pH values used in the present study (Jackson, 1963; Low, 1968) and thus the negatively charged luminol should not be adsorbed, on the clay surface in great quantities. If adsorption of luminol on the montmorillonite surface is the first step in the catalytic reaction, a specific adsorption of the anion is assumed to take place in the system where chemiluminescence was observed. However, if adsorption of luminol on specific sites does take place, it occurs to such a small extent that it cannot be easily measured.

The mechanism of the catalytic reaction has yet to be studied.

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REFERENCES


