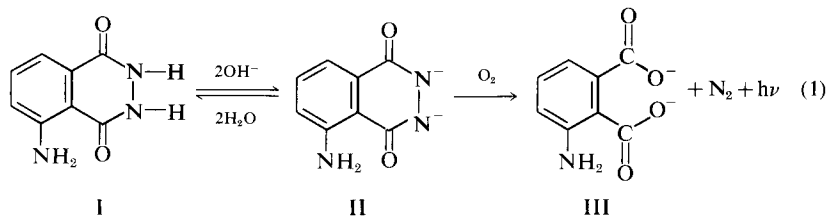


## NOTES

### 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:



The luminol reaction has been used for the determination of oxidizing agents, such as peroxide, and for metal ions, such as Cu or Co, which catalyze the chemiluminescence (Guilbault, 1967; Lavee and Siegel, unpublished).

Clay minerals have been shown to catalyze reactions of various kinds in molecules sorbed on their surface (Grim, 1968). Although most of the work on catalytic reactions at the surface of clay minerals has been on systems extensively dehydrated and at high temperatures, more recent work has demonstrated catalysis at relatively low temperatures and appreciable hydration levels (Mortland, 1970). In the present study we have examined the ability of several clay minerals, especially montmorillonite, to catalyze the chemiluminescence of luminol in aqueous solution.

The montmorillonite used was Fisher bentonite B235 either in the raw form or as Na-bentonite described earlier (Lahav and Raziell, 1971). The other clay minerals were: Nontronite H-33b Manito, Spokane, Wash. (Ward's Natural Science Est.); Fithian illite No. 36 (Ward's Natural Science Est.) saturated with Ca; colloidal kaolin, Bollus alba; and attapulgite (Attagel 30). In addition, precipitated CaCO<sub>3</sub> (AR) was also used.

Several preliminary observations were carried out in a dark room by adding the basic luminol solution to either the clay suspension or the clay powder. The solution was prepared by dissolving the yellow powder in 1 N NaOH solution.

Accurate measurements of the chemiluminescent light were carried out in Packard Tri-Carb Liquid Scintilla-

tion Spectrometer model 3003 at 0°C. The luminol solution in these experiments was prepared by dissolving the luminol powder in 0.1 N NaOH solution and titrating with HCl to the desired pH. Both the luminol solutions and the clay suspensions at the desired pH and concentration were brought into the instrument chamber and left for more than half an hour before mixing. The measurements started about 20 sec after mixing. The reaction rate is given as counts per minute above the background given by pure luminol solution.

At pH values above about 10 and at luminol concen-

trations higher than about 10<sup>-3</sup> 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<sup>-2</sup> M. At luminol concentration of 10<sup>-4</sup> 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

Mineral	Luminescence rate (counts per min)
Bentonite	205,550
Illite	9,500
Kaolinite	9,500
Attapulgit	4,550
Nontronite	1,520
$\text{CaCO}_3(\text{AR})$	5,300

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 pro-

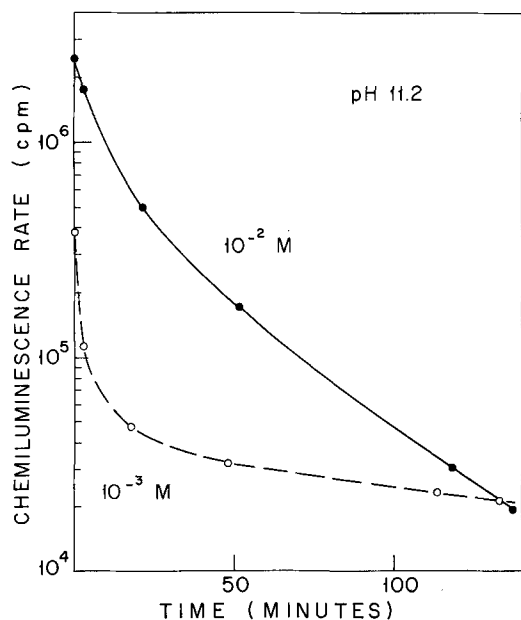


Fig. 1. Chemiluminescence rate of luminol in the presence of Na-bentonite (2 mg/ml) as a function of time at two luminol concentrations and pH 11.2. The background of pure luminol was about 1 per cent of the catalyzed reaction.

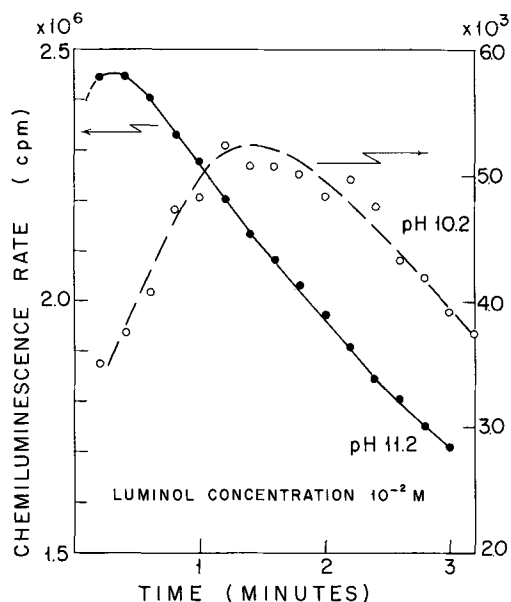


Fig. 2. Chemiluminescence rate of luminol in the presence of Na-bentonite (2 mg/ml) as a function of time at two values of pH and a luminol concentration of  $10^{-2}$  M.

duced 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

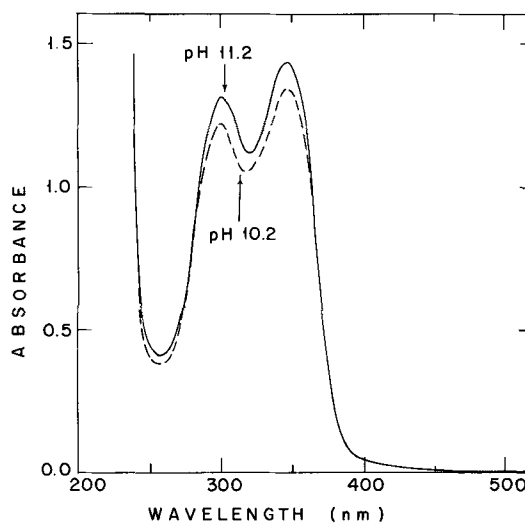


Fig. 3. The absorbance spectrum of  $10^{-4}$  M luminol solution at two pH values.

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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