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A Facile and Effective Chemiluminescence Demonstration Experiment

In addition to being fascinating phenomena *per se*, chemiluminescent reactions provide a facile and effective means of demonstrating important chemical principles. For example, since the observed intensity of a chemiluminescent system is generally proportional to the rate of the key step which produces a "hot" intermediate (eqn. (1)), factors which affect the rate of reactions (temperature, concentration, catalysis, solvent, etc.) can, in principle, be visually demonstrated by use of an appropriate chemiluminescence system. Furthermore, for an ideal chemiluminescence system, it is usually possible to perform significant experiments relevant to the mechanism of the chemiluminescent system by simply employing visual observations and a clock. Thus, the effect of concentrations, temperature, etc., can be qualitatively measured and a student can readily understand the impact of changes on these experimental variables because of the rather "obvious" nature of the results. We report here a chemiluminescence system which meets the essence of the above ideal chemiluminescence systems. In addition to the above properties, the system described here has the added advantage of being "tunable"; i.e., the light emitted is not an inherent property of the system, but that of a controllable added material, a fluorescent dye.

$$I_{CL} = K \text{ Rate} \quad (1)$$

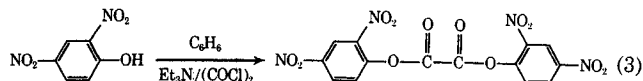
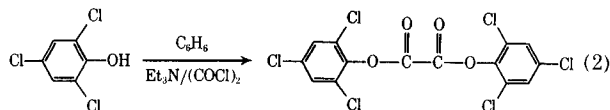
Description of the Peroxyoxalate Chemiluminescence Experiment

The peroxyoxalate system (1) is comprised of a "chemical pump" (e.g., the reaction of an oxalate ester with hydrogen peroxide) and an emitting acceptor (e.g., almost any dye which is highly fluorescent in the visible region). The reaction of the oxalate ester with H_2O_2 is not itself an efficient chemiluminescent system, but requires the addition of a fluorescent molecule, a fluorescent dye, to capture the chemical energy and convert it to visible light. This system was developed by M. M. Rauhut at American Cyanamid and has been described in a number of patents (1b).

The peroxyoxalate chemiluminescent system is conveniently initiated by mixing a solution of an oxalate ester and a fluorescer (Solution A) with a solution of hydrogen peroxide and a weak catalytic base (Solution B). The chemiluminescent emission is usually bright and can be made to last on the order of hours. The materials required for the demonstration are inexpensive and may be purchased or readily synthesized.

Experimental Details

Solution A. Convenient oxalate esters which may be used are bis(2,4-dinitrophenyl) oxalate (DNPO) and bis(2,4,6-trichlorophenyl) oxalate (TCPO) which are prepared as follows (eqns. (2) and (3))



A solution of 19.75 g (0.1 M, mol wt = 197.5) of 2,4,6-trichlorophenol (MCB practical, mp 64–66°C) or 18.4 g (0.1 M, mol wt = 184.1) of 2,4-dinitrophenol (Aldrich, mp 106–108°C) in 250 ml of benzene was dried azeotropically by distillation of 50 ml of benzene.

The solution was cooled to 10°C and 10.1 g (0.1 M) of freshly distilled triethylamine was added. Then, 7 g (0.055 mole of oxalyl chloride) was added dropwise and the reaction mixture was allowed to warm to room temperature and stand overnight. Removal of solvent under reduced pressure leaves a yellow solid. A 50-ml portion of chloroform (DNPO) or petroleum ether (TCPO) was added; the mixture was stirred for 15 min and filtered to give a white solid which was further washed with the solvent. The white solid was dried under vacuum for 1 hr and recrystallized from the indicated solvent.

oxalate ester	recrystallization		mp
	solvent	yield	
TCPO	benzene	14.6 g (65%)	190–192°C (lit (3) 196–8°C)
DNPO	nitrobenzene or ethyl acetate	7.6 g (38%)	192–194°C (lit (4) 192–4°C)

Solution A was made by preparing a stock solution of 0.01 M oxalate, 0.003 M dye in dimethyl phthalate as solvent. The dye may be nearly any strongly fluorescent compound. The following dyes have been employed with satisfactory results: 9,10-diphenylanthracene (blue emission); tetracene or 9,10-bis(phenylethynyl)anthracene (5) (green emission). The stock solution of the trichlorophenyl oxalate lasts for periods of months. The dinitrophenyl oxalate stock solution must be prepared fresh and the solid oxalate tends to decompose if allowed to be exposed to moisture for extended periods.

Solution B consists of 0.4 M hydrogen peroxide in a solvent of 80:20 dimethyl phthalate/*t*-butanol (by volume). This solution is prepared by adding 98% hydrogen peroxide slowly to a cooled stirred solution of the solvent. **Caution:** 98% hydrogen peroxide is a corrosive and caustic acid which, if contaminated, represents an explosive hazard. Never put pipets into the original container nor return unused samples to the original container. Once prepared, the 0.4 M solution of hydrogen peroxide (approximately 1% by weight by H_2O_2) is stable and safe. Solution B may contain 0.001 M sodium salicylate as catalyst if a brighter chemiluminescence is desired.

Both solutions A and B are stable for several months if stored in Teflon or polyethylene containers in the absence of light and moisture.

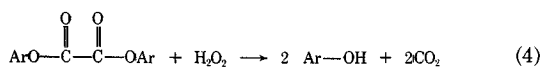
The chemiluminescent reaction is achieved by simply mixing approximately equal volumes of Solution A and Solution B in a glass container (beaker or flask).

Of the two oxalate systems, DNPO is more impressive because it gives a brighter chemiluminescence (but for a shorter period of time) than TCPO. However, DNPO is not as shelf stable as TCPO and often becomes ineffective after several months of storage. TCPO appears to be shelf stable for many months.

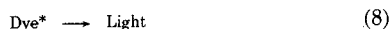
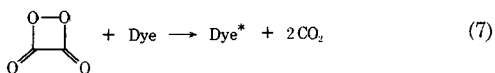
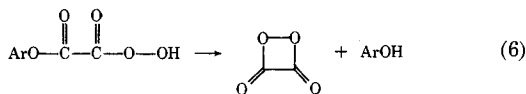
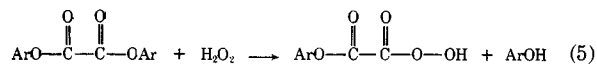
The Mechanism of Peroxyoxalate Chemiluminescence

In fact, the precise nature of the key "hot" intermediate in the peroxyoxalate chemiluminescent reaction is not known. It is, however, almost certainly derived from addition of H_2O_2 on the oxalate ester, since the stoichiometry

of the reaction (eqn. (4)) is quite simple. An interesting exercise for the students is to calculate from energies available in tables, the exothermicity of the reaction. They can then judge the maximum energy of light (shortest wavelength emission) possible from this system.



A working partial mechanism (1) is given below



The instructor and student can profitably consider alternate mechanisms and even devise simple experiments to support or exclude them.

Demonstration of the Effect of Catalysts and Temperature on Reaction Rates

The effect of basic catalysts on the rate of the peroxyoxalate is easily demonstrated by mixing solution A with solution B containing no sodium salicylate in a cylinder or test tube. A low level of chemiluminescent emission will be observed. A small amount of solid sodium salicylate is then sprinkled on the surface of the solution without mixing. As the solid particles sift down from the surface of the solution through the liquid, bright tracks of chemiluminescent emission follow the falling particles, thereby demonstrating that reaction is more rapid in regions where there is a high local concentration of catalyst. The total mixture can now be stirred to dissolve the particles and the occurrence of dissolution of the solid will be con-

comitant with homogeneous brightening of the entire solution.

The effect of temperature on reaction rate is easily demonstrated by immersing a test tube containing a mixture of solutions A and B into an ice bath, and observing the rapid decrease in intensity of emission as the temperature of the sample decreases. Immersing the cooled test tube in a beaker of hot water almost immediately causes restoration and then increases in the original emission intensity.

Conclusion

Chemiluminescent reactions are a handy and effective pedagogical tool for the demonstration of several fundamental chemical principles. A commercial chemiluminescent device is available,¹ and may serve the same purposes as solutions A and B, except that only one type of emission (green light) is observed.

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Literature Cited

- (1) (a) Rauhut, M. M., *Accounts Chem. Res.*, **2**, 80 (1969) and references cited therein; (b) Rauhut, M. M., and Bolyky, L. J., U.S. Patent 3597362, 1971; Bolyky, L. J., U.S. Patent 3704231, 1971; Zweig, A., and Maulding, D. R., U.S. Patent 3729462, 1973; Roberts, B. G., and Rauhut, M. M., U.S. Patent 3700738, 1972.
- (2) For a recent general review of chemiluminescence see: McCapra, F., "Progress in Organic Chemistry," **8**, 231 (1971); Demonstration of chemiluminescence, White, E., *J. CHEM. EDUC.*, **34**, 275 (1957); Schneider, H. W., *J. Chem. Educ.*, **47**, 518 (1970).
- (3) Baker, J. W., and Schumaker, I., *J. Amer. Eng. Data*, **9**, 584 (1964).
- (4) Rauhut, M. M., et al., *J. Amer. Chem. Soc.*, **89**, 6516 (1967).
- (5) Reid, W., Donner, W., and Schlegelmilch, W., *Ber.*, **94**, 1051 (1961).

¹"Cyalume" (Trademark of American Cyanamid Company) chemical light available from the Aldrich Chemical Company and the Edmund Scientific and Chemical Dynamics Corporation.