TECHNICAL NOTE

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The Explosive Reaction Between Swimming Pool Chlorine and Brake Fluid

ABSTRACT: Granular swimming pool chlorine (calcium hypochlorite) and brake fluid (polyethylene glycol) react violently when mixed together, producing a fierce fireball. This paper proposes a mechanism which explains the production of the flammable products of the reaction by means of a radical fragmentation of polyethylene glycol.

KEYWORDS: forensic science, calcium hypochlorite, polyethylene glycol, explosives, incendiary preparations

Improvised explosive and incendiary preparations are often encountered by forensic scientists, and the circumstances of their use can be both criminal and accidental. The basic components of such mixtures are a fuel and an oxidizing agent. Probably the best known is gunpowder, in which potassium nitrate is the oxidizing agent, and charcoal and sulfur are the fuels. Often a major factor deciding the composition of improvised mixtures appears to be whether the chemicals are readily available. For example, potassium chlorate is sold as a rat poison in some parts of the world and can form an effective incendiary or explosive mixture in combination with sugar or another fuel.

An oxidizing agent that is commonly available in Australia is calcium hypochlorite. It is sold commercially as a granular powder for use as an algicide and bactericide in the treatment of water in domestic swimming pools and, hence, is commonly referred to as swimming pool chlorine. Calcium hypochlorite will react violently with motor vehicle brake fluid of the polyethylene glycol type, producing a fierce fireball. Since brake fluid is also easily available, it is not surprising that this mixture has occurred in a number of criminal and accidental explosions. Calcium hypochlorite will also react violently and exothermically with other fuels, such as moistened sugar and cellulose products. However, a fireball is not produced with these fuels. Although the explosive nature of the mixture is known [1,2], a search of the literature proved fruitless in providing an explanation of the fireball. This paper reports the results of an investigation to explain the cause of it.

Experimental Procedure

The Reaction

Commercial granular pool chlorine (calcium hypochlorite, HTH brand) and commercial brake fluid (DOT4 grade, Mobil) were used. About 2 to 2.5 g of pool chlorine was placed in an open Pyrex evaporating dish in a fume cupboard. About 1 mL of brake fluid was added rapidly from a Pasteur pipette.

Collection of Reaction Products

A 50% solution of brake fluid in water was added dropwise to about 2 g of pool chlorine at a rate sufficient to initiate the reaction but slow enough to prevent ignition. Gas generated by the reaction was swept by nitrogen into an infrared gas cell.

Analysis of Reaction Products

Infrared Spectroscopy—The products collected in the gas cell (6.75-m path length) were analyzed using a Digilab FTS-50 Fourier transform infrared spectrometer operating at 8 cm^{-1} resolution for 16 scans.

Chemicals Spot Tests—The following tests were performed.

1. A solution containing equal volumes of a 20% aqueous morpholine solution and a 5% aqueous sodium nitroprusside solution was used to test the evolved gas for the presence of acetaldehyde. A positive reaction produced a blue color [3].

2. Two millilitres of 12N sulfuric acid (H_2SO_4) plus two drops of chromotropic acid was used to test the gas for the presence of formaldehyde. A positive reaction produced a bright violet color [3].

Results and Discussion

The Reaction

When the brake fluid was added to the pool chlorine, the two reagents did not react instantaneously. Instead, the mixture lay dormant for between 5 and 30 s (depending upon how "fresh" the pool chlorine was); it then emitted a hiss and, within 1 s, the mixture erupted into a ball of flame (see Fig. 1). The flame lasted for no more than a few seconds, but in this time, the amount of heat produced was sufficient to shatter the Pyrex vessels in which the experiments were performed.

When using small quantities of material (see the section on experimental procedure), the reaction is quite safe to perform if simple precautions are taken. A safety face shield should be worn, and one should stand clear of the reaction vessel as soon as the brake fluid has been added. Do not be tempted into careless inspection of the vessel because of the initial dormant period.

When the reaction had ceased, it was observed that the brake fluid had been totally consumed and a large amount of inorganic material remained. X-ray microanalysis and chemical spot tests indicated that this was a mixture of calcium chloride and unreacted calcium hypochlorite. This suggested that the flammable products were not the result of thermal decomposition of the calcium hypochlorite.

Brake fluid could not be ignited using a Bunsen burner, and hence, it is not possible that the cause of the fireball was ignition of brake fluid vapor. The heat produced by the reaction, and the total consumption of the organic material, suggests that brake fluid undergoes molecular fragmentation to produce volatile organic substances of high flam-
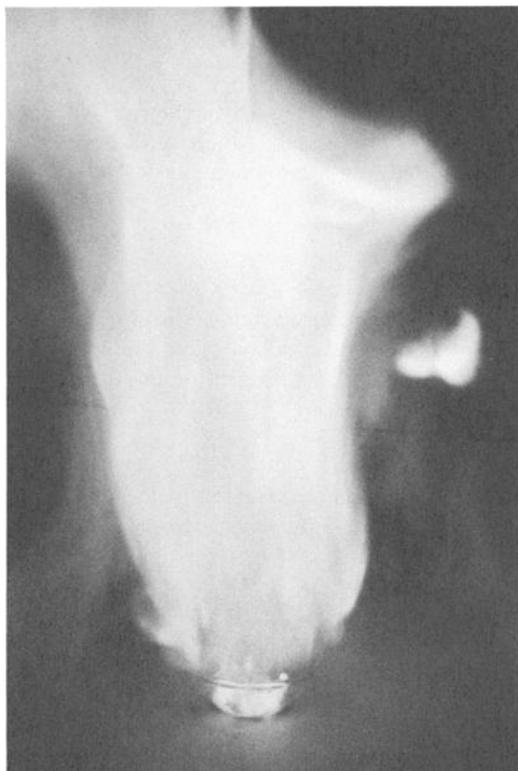
FIG. 1—*Fireball produced by the reaction between swimming pool chlorine and brake fluid.*

mability. Molecular fragmentations are favored by there being a large negative ΔS in the reaction.

The rate of the reaction was not influenced (accelerated or retarded) by the presence of acid catalysts [concentrated hydrochloric acid (HCl)] or base catalysts [ammonium hydroxide (NH_4OH)]. This observation suggests that the reaction takes place by means of a radical fragmentation and does not involve anion or cation fragmentations.

The infrared spectrum of the gaseous products (Fig. 2) suggested the presence of acetaldehyde, a trace of carbon monoxide, and a polyether (possibly paraformaldehyde), as is shown in Table 1. The chemical spot tests gave further support for the presence of acetaldehyde and also indicated the presence of formaldehyde.

The Mechanism

From these observations, the authors concluded that the explosion proceeds by means of the mechanism outlined in Fig. 3. The alkoxy radical ($RO^\bullet$) generated by this reaction might then catalyze further decomposition of brake fluid in a manner analogous to that of the chlorine radical. We do not have experimental evidence for the formation of ethylene during the course of the reaction. It is possible that the heat produced by the reaction, and by the exothermic polymerization of formaldehyde, is sufficient to ignite the gaseous products.

Assuming complete decomposition of the brake fluid in the manner described, in theory, 1 mol of brake fluid can give rise to 4 mol of flammable gas, as is summarized in Fig. 4.
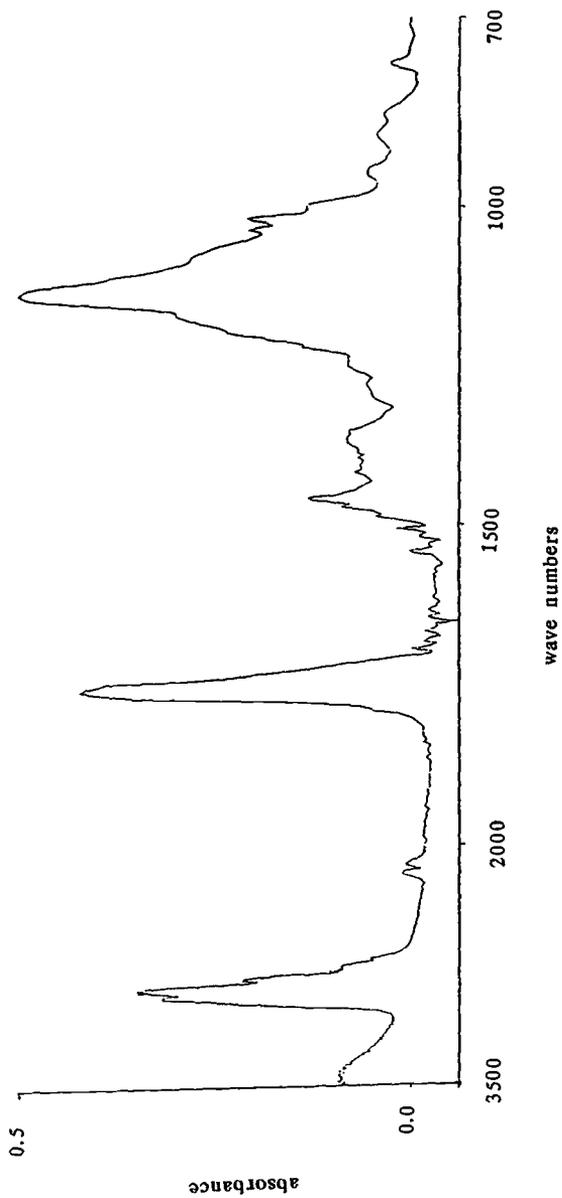
FIG. 2—*Infrared spectrum of the gaseous products produced from the reaction between swimming pool chlorine and brake fluid.*

TABLE 1—*Interpretation of the infrared spectrum of the gaseous products.*

| Absorption Maxima, cm^{-1}	Assigned to
1026	acetaldehyde
1134 (s)	paraformaldehyde
1373	acetaldehyde
1459	acetaldehyde
1755 (s)	acetaldehyde
2180 (w)	carbon monoxide
2701	acetaldehyde
2730	acetaldehyde
2881 (s)	. . .
2897 (s)	. . .
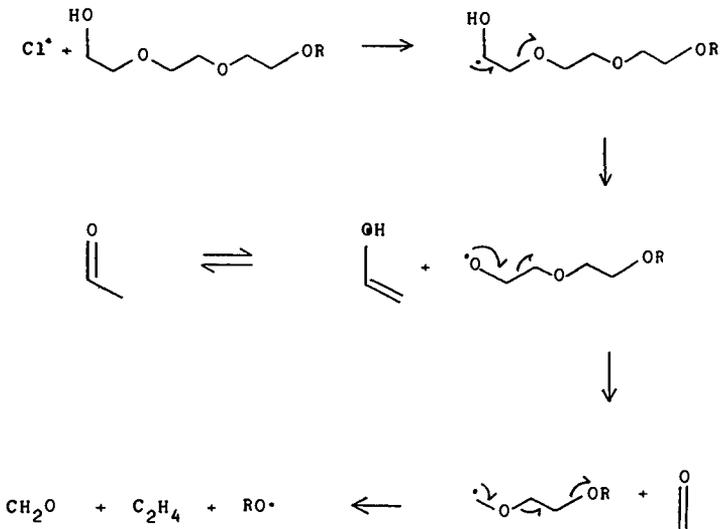
FIG. 3—*Proposed mechanism for the molecular fragmentation of brake fluid.*
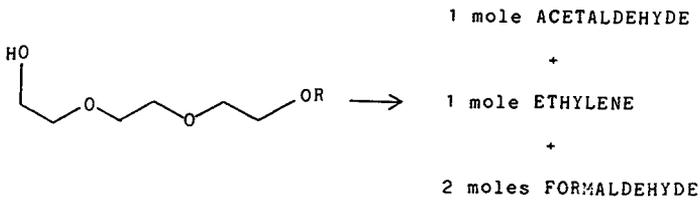
FIG. 4—*Theoretical stoichiometry for the decomposition of brake fluid.*

TABLE 2—*Flammable properties of the gaseous products.*

Substance	Flash point, °C	Autoignition Temperature, °C	Explosive Limits, % in air
Ethylene	−136	160	3 to 36
Acetaldehyde	−38	180	4.5 to 60.5
Formaldehyde	. . .	300	7 to 72

From this stoichiometry it was estimated that 10 mL of brake fluid can yield over 4 L of flammable gas at standard temperature and pressure. Some data describing the potential hazards of the reaction products are presented in Table 2.

Conclusions

The molecular fragmentation mechanism appears to explain the production of volatile products from the oxidation of brake fluid by calcium hypochlorite. This appears to be in agreement with the experimental data, although it is appreciated that identification of the reaction products might not be conclusive. Because of the free availability of these compounds, their misuse is likely to continue to occur. The uncontrolled nature of the reaction makes it difficult to use successfully in criminal applications. An improvised delay device, such as that described in Ref 2, might reduce the hazards involved.

References

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