

Notes on chlorinated rubber and some other chlorine donors

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Abstract: *A brief review is given of the history and technology of chlorinated rubber. The empirical formula is approximately $(C_{10}H_{11}Cl_7)_n$ corresponding to 65.4% Cl. The structure is complex, and includes partially chlorinated cyclohexane rings. All the Cl is released as HCl on pyrolysis. The enthalpy of formation was estimated from the reported heat of combustion as -395 kJ mol^{-1} . For comparison, the enthalpy of formation of solid polyvinyl chloride $(C_2H_3Cl)_n$ was reported to be $-94.6 \text{ kJ mol}^{-1}$ and that of solid polyvinylidene chloride $(C_2H_2Cl_2)_n$ was reported to be $-100.4 \text{ kJ mol}^{-1}$.*

Keywords: *chlorinated rubber, Parlon, enthalpy of formation, chlorine donors, PVC, polyvinyl chloride, polyvinylidene chloride.*

Introduction

Thermodynamic modelling of the combustion of pyrotechnic mixtures is hindered by the lack of information on the enthalpy of formation of some commonly used ingredients.

In an effort to find values for the enthalpy of formation of various chlorine donors, the writer found some information on chlorinated rubber that may be of interest. This information includes the heat of combustion, which permits the enthalpy of formation of this important chlorine donor to be estimated.

Discussion

Natural rubber is poly(2-methyl-1,3 butadiene), $(C_5H_8)_n$, also called polyisoprene.¹ Chlorination of rubber was studied as long ago as 1888, but commercial production did not start until 1918.² By the early 1930s it was being made by ICI in the UK (brand name “Alloprene”) and by several German firms (brand names “Pergut”, “Tegofan”, “Tornesit”).² In 1945 the Hercules Powder Co. of Wilmington, Delaware (later Hercules, Inc.) began marketing an improved version of “Tornesit” in the United States as “Parlon”.²

The original use of chlorinated rubber was as a lacquer for the protection of chemical plant.² Later, it became an important ingredient in a wide range of corrosion-resistant and wear-resistant paints and wood finishes.² It is also used in adhesives and in printing inks. The first mention that the writer could find of its use as a

chlorine donor in pyrotechnics was in a report by Eppig, who lists it as one of the materials tested by German researchers during the Second World War “in an effort to obtain a chlorine carrier which would be more effective than polyvinyl chloride” in green light compositions for military signaling. The report indicates that it was considered less effective than a chlorinated polyvinyl chloride containing about 63% chlorine.⁴ Chlorinated rubber is mentioned in Lancaster’s 1972 book.³ Ellern refers to “Parlon” in his 1968 book⁵ but says that it is “chlorinated polyisopropylene”, that it contains 67% Cl, and that is apparently not used as a chlorine donor. Lancaster points out that Parlon, (chlorinated rubber), is not the same as “Parlon P, which is chlorinated polypropylene, and which is not used as a colour intensifier”.³ Parker says that “chlorinated polypropylene in most respects resembles chlorinated rubber”,² but current commercial grades (such as “Superchlone” made by Nippon Paper Industries of Tokyo, Japan) contain only 20-40% Cl.⁶ This probably explains why it is not used as a colour intensifier. If there ever were a grade that contained 67% Cl, as stated by Ellern,⁵ there seems no obvious reason why it would not have been a useful chlorine donor.

Chlorinated rubber was one of the chlorine donors studied by Shimizu in his 1979 article on blue and purple flames,⁷ and he mentions it in his 1981 book.⁸ In 1981 Fish⁹ discussed the use of chlorinated rubber in metal-fuelled coloured flame compositions.

It is unfortunate that the name “Parlon”, a

trademark that evidently referred to two different products (chlorinated natural rubber and chlorinated polypropylene),⁴ should have become the common name for chlorinated rubber in the firework literature. The US National Institute for Occupational Safety and Health lists 38 synonyms for chlorinated rubber.¹⁰ It would be better to follow Dr Shimizu's example and use the term "chlorinated isoprene rubber"⁸ or just "chlorinated rubber".

The chlorine content of chlorinated rubber is in the range 65–68%, but is usually specified as ">65%". Various grades are available, differing principally in the viscosities of their solutions in toluene and presumably corresponding to different chain lengths in the polymer.

Chlorinated rubber was made by passing chlorine into a solution of natural rubber in carbon tetrachloride (tetrachloromethane, CCl₄).² Both ICI and Hercules have stopped making chlorinated rubber, possibly because of concern about the use of CCl₄ and the presence of low concentrations of CCl₄ in the product. Carbon tetrachloride is carcinogenic to various laboratory mammals and is classified by the US Environmental Protection Agency as a "probable human carcinogen".¹¹ Residual CCl₄ in chlorinated rubber is liberated when the product is dissolved, so appropriate care has to be taken. Chlorinated rubber is still made by Bayer MaterialScience AG at Dormagen, Germany ("Pergut")¹² and by Rishiroop Rubber (International) Limited of Mumbai, India ("Chlorub"),¹³ to name just two manufacturers. The CCl₄ content of the Pergut brand chlorinated rubber manufactured by Bayer is no more than 0.005%.¹²

Chlorinated rubber is soluble in many solvents "including aromatic hydrocarbons, chlorinated hydrocarbons, ketones higher than acetone and some alcoholic ethers. It is not soluble in water, simple alcohols or aliphatic hydrocarbons".²

According to Dodson and McNeill¹⁴ "chlorinated rubber may have a very complicated structure with many variations". The empirical formula given by Dodson and McNeill is C₁₀H₄Cl₇ (65.4% Cl).¹⁴ This formula corresponds to 66.7% Cl, not 65.4%, and is obviously a typographical error. The formula corresponding to 65.4% Cl is C₁₀H₁₁Cl₇, and this is the formula given by Bloomfield.¹⁵ Fish⁹ gives

the empirical formula as C₅H₆Cl₄, corresponding to a chlorine content of 68.2%.

Parker² notes that there is evidence that the structure contains partially chlorinated cyclohexane rings – the chlorination process involves cyclization of parts of the polyisoprene chain as well as substitution and addition at double bonds. If only the latter two processes were involved, the empirical formula would be C₅H_{10-x}Cl_x. The formula given by Fish⁹ corresponds to this formula with $x = 4$.

Dodson and McNeill¹⁴ studied the thermal decomposition of Allopren chlorinated rubber and found that the major volatile product was hydrogen chloride. Five sevenths of the total available HCl "is lost with great ease, and complete dehydrochlorination is very much easier than in poly (vinylidene chloride)".

In a temperature programmed thermogravimetric analysis experiment 95% of the total chlorine was lost as HCl below 400 °C. All the chlorine was lost as HCl, accompanied by hydrogen, methane and ethylene, leaving a "carbonaceous residue". These authors also studied the thermal degradation of polyvinylchloride (PVC) and polyvinylidene chloride. PVC lost all its chlorine as HCl between 250 and 300 °C. Polyvinylidene chloride very readily lost half of its chlorine as HCl, but loss of the remaining HCl required high temperatures. Polyvinylidene chloride is the only one of the three polymers that contains equal numbers of Cl and H atoms and evolves only HCl on pyrolysis.¹⁶ The others have an excess of H that is lost as "tar" and as simple gases such as H₂, CH₄ and C₂H₄.¹⁶ Dr Shimizu⁷ found that both PVC and chlorinated rubber can function as fuel in pyrotechnic mixtures when KClO₄ is the oxidizer, but the burning times for the fastest-burning chlorinated rubber mixtures were roughly twice as long as those of the corresponding PVC mixtures, showing that PVC was the better fuel.

No information about the enthalpy of formation of chlorinated rubber could be found, but values for PVC and polyvinylidene chloride were reported by Sinke and Stull from their measurements of the heats of combustion.¹⁷ The calorimetric measurements required special precautions to prevent attack of the calorimeter by the products of combustion and to ensure that all the chlorine

Table 1. Chlorine content, chemical formulas heats of combustion and enthalpy of formation of three chlorine donors.

Material	Common/Trade Names	Chlorine Content (% by Mass)	Empirical Formula	Heat of combustion/ MJ kg ⁻¹	Enthalpy of Formation/kJ mol ⁻¹
Chlorinated natural rubber	Parlon, Alloprene, Chlororub, Pergut	65–68, typically 65.4	(C ₁₀ H ₁₁ Cl ₇) _n approximately	13.91 ± ? ¹⁸	–395 ±? see text
Polyvinyl chloride	PVC	56.7	(C ₂ H ₃ Cl) _n	18.31 ± 0.03 ¹⁷	–94.6 ± 1.3 ¹⁷
Polyvinylidene chloride	Saran	73.1	(C ₂ H ₂ Cl ₂) _n	10.52 ± 0.03 ¹⁷	–100.4 ± 1.7 ¹⁷

was converted to aqueous HCl of known concentration.¹⁷ Similar precautions would be needed to obtain reliable values for chlorinated rubber. Barton et al. reported the heat of combustion of Alloprene,¹⁸ but it is not clear from their report that they took the precautions specified by Sinke and Stull.¹⁷ The value for the heat of formation of chlorinated rubber was calculated by the writer from the heat of combustion given by Barton et al.¹⁸, following the procedure given by Sinke and Stull¹⁷ and using their values for the heats of formation of the combustion products. In view of the uncertainty about the method followed in the determination of the heat of combustion, this estimate of the enthalpy of formation is very much less reliable than the results for the other two chlorine donors, but none the less should be useful for thermodynamic modeling of the combustion of pyrotechnic mixtures containing chlorinated rubber. Data for the three chlorine donors are summarized in Table 1.

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