

# Polychlorides—A Safe and Convenient Alternative for Elemental Chlorine in Demonstration Experiments

Sophie Rathmann, Friedrich Braune, Merlin Kleoff, Patrick Voßnacker, Benjamin Pölloth,\*  
Christian Müller,\* and Sebastian Riedel\*



Cite This: *J. Chem. Educ.* 2024, 101, 1394–1401



Read Online

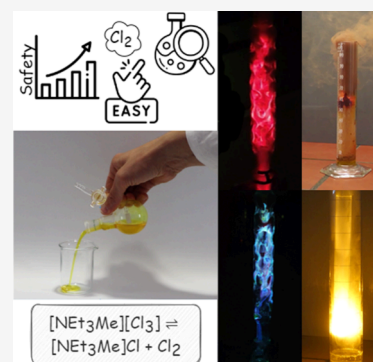
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

**ABSTRACT:** Demonstration experiments involving chlorine are often impressive and can help to understand the reactivity of halogens. However, practical and safety concerns render handling of chlorine difficult in educational settings, particularly in high schools. Recent chemical research has demonstrated the potential of trichloride salts as a much safer and more affordable alternative to chlorine gas. Triethylmethylammonium trichloride,  $[\text{NEt}_3\text{Me}][\text{Cl}_3]$ , is a stable and safe ionic liquid that is easy to use and handle. Upon addition of water, chlorine gas is released in a controlled manner. This process presents a convenient method for conducting chlorine demonstration experiments. Experimental procedures are presented for the production of chlorine gas, the chlorine-initiated formation and subsequent luminescence of singlet oxygen, the synthesis of iron chloride and sodium chloride, and the electrophilic addition to lycopene.



**KEYWORDS:** High School/Introductory Chemistry, First-Year Undergraduate/General, Demonstrations, Inorganic Chemistry, Safety, Main-Group Elements

Chlorine plays a significant role in both the chemical industry and chemistry education. Approximately 55% of all industrial chemicals are estimated to be dependent on chlorine chemistry.<sup>1,2</sup> In 2022, 97 million tons of chlorine were produced worldwide,<sup>3</sup> with the mass of elemental chlorine serving as an indicator of a country's chemical industry development.<sup>4</sup> Chlorine is commonly used to represent the halogen group in many high school chemistry curricula, especially in relation to the properties and reactivity of the respective Group 17 elements, such as oxidation reactions.<sup>5–7</sup>

Unfortunately, elemental chlorine is a highly toxic and corrosive gas.<sup>8</sup> As a tragic consequence, chlorine gas became the first poison gas used in World War I.<sup>9</sup> Today, the storage and transportation of chlorine gas poses significant safety and environmental problems in industrial, academic, and educational settings. In German high schools, for example, the use of compressed chlorine gas cylinders is prohibited.<sup>10</sup> In industry, accidents involving large volumes of chlorine gas have led to severe accidents.<sup>11</sup> In particular, transporting chlorine gas poses significant risks. Figure 1 illustrates the extensive spread of chlorine gas from a train car, as studied in the Jack Rabbit project.<sup>12</sup>

Thus, a safer alternative for the transport and storage of chlorine is necessary. Riedel and co-workers have recently established that alkylammonium trichlorides could be a promising solution.<sup>2,13</sup> In particular, the commercially available triethylmethylammonium chloride  $[\text{NEt}_3\text{Me}]\text{Cl}$  was found to be a suitable chlorine storage material, which forms the



**Figure 1.** Propagation of released chlorine gas from a transport tank (Reproduced with permission from the Jack Rabbit project, ref 12. Copyright 2016 Utah Valley University.).

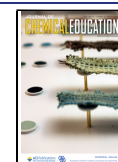
corresponding trichloride  $[\text{NEt}_3\text{Me}][\text{Cl}_3]$  when exposed to an atmosphere of chlorine gas. In recent work, it could be

**Received:** December 4, 2023

**Revised:** January 22, 2024

**Accepted:** February 1, 2024

**Published:** February 29, 2024



demonstrated that the trichloride  $[\text{NEt}_3\text{Me}][\text{Cl}_3]$  shows a similar reactivity as elemental chlorine. However, it is an ionic liquid with a low chlorine vapor pressure (0.9 bar at 20 °C) that is safe and easy to handle.<sup>2</sup>

For demonstration experiments in chemistry education, chlorine is often directly produced, e.g., by the comproportionation reaction of hydrogen chloride and hypochlorites.<sup>14</sup> The ionic liquid  $[\text{NEt}_3\text{Me}][\text{Cl}_3]$  could be another, modern option to facilitate safe handling of chlorine. Consequently, we investigated the use of  $[\text{NEt}_3\text{Me}][\text{Cl}_3]$  in commonly performed demonstration experiments.

## THEORETICAL BACKGROUND

In order to understand how chlorine can be stored in the form of polychloride salts, a brief general overview of polyhalogen anions is given, followed by a more detailed discussion of the most promising representative.

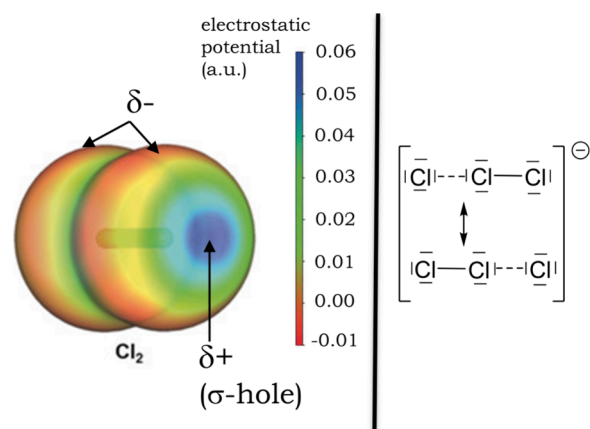
### Polyhalogen Anions and Polychlorides

In principle, all halogens from fluorine to iodine can form polyhalide anions in the presence of halide anions. For instance, the dissolution of elemental iodine in aqueous potassium iodide solutions is best rationalized by the formation of polyiodide anions, such as  $[\text{I}_3]^-$ .<sup>15</sup> In undergraduate laboratories, polyiodide salts are already synthesized and analyzed.<sup>16</sup> Although the formation of polychlorides is energetically less favorable than the formation of polyiodides, a variety of stable polychlorides are known and currently under investigation.<sup>17</sup> For example, the full series of polychlorides from  $[\text{Cl}(\text{Cl}_2)]^-$  to  $[\text{Cl}(\text{Cl}_2)_6]^-$  can be synthesized, and even polychlorides as large as  $[\text{Cl}_{20}]^{2-}$  are known.<sup>18</sup> In addition, many examples of polybromides (e.g.,  $[\text{Br}_9]^-$ ,  $[\text{Br}_{11}]^-$ ) and polyiodides (e.g.,  $[\text{I}_7]^-$ ,  $[\text{I}_{16}]^{2-}$ ) have been reported in the literature.<sup>17</sup> Most generally, these anions are stabilized by conjugation with weakly coordinating cations, e.g., quaternary ammonium or phosphonium cations.<sup>19</sup> Polyhalide salts with asymmetric cations are often room-temperature ionic liquids. The bonding situation in such  $[\text{X}_3]^-$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) anions like  $[\text{Cl}_3]^-$  is rather complex and can be rationalized by assuming donor–acceptor complexes or three-center four-electron bonds.<sup>17</sup> However, the interactions can also be viewed as halogen bonds. These are electrostatic interactions of electropositive areas of a dihalogen molecule (so-called  $\sigma$ -holes) with a chloride anion or electronegative areas of another chlorine molecule (Figure 2).<sup>17</sup> The reference to halogen bonds as a special case of dipole interactions allows for a basic understanding of the bonding situation in polychlorides even in high school.

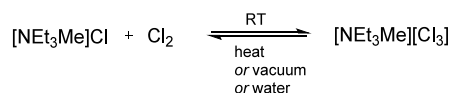
Polychlorides are of great interest in recent chemical research because they open novel synthetic routes to a multiverse of chlorinated substances. For example, they allow the direct synthesis of the base chemical phosgene ( $\text{COCl}_2$ ) from  $\text{CO}$ <sup>20</sup> or the oxidative dissolution of metals.<sup>21</sup> As mentioned above, polychlorides allow the safe storage and transport of elemental chlorine. For this purpose, triethylmethylammonium trichloride ( $[\text{NEt}_3\text{Me}][\text{Cl}_3]$ , TEMACl<sub>3</sub>) was found to be the most promising candidate due to its high stability, high storage capacity, and low viscosity.<sup>13,19</sup>

### TEMACl<sub>3</sub>: A Polychloride-Based Storage for Cl<sub>2</sub>

TEMACl<sub>3</sub> is easily synthesized from readily available chemicals (triethyl amine, chloromethane, and chlorine gas). It is commercially available for reasonable prices (CAS 2460902-02-5). TEMACl<sub>3</sub> is stable for at least 2 years at room temperature.<sup>19</sup> This salt forms an ionic liquid at room



**Figure 2.** (Left) Electrostatic potentials of a chlorine molecule (mapped onto the electron density with an isosurface value of 0.0035 au, calculated at the B3LYP-D3/def2-TZVPP level of theory). The electropositive area ( $\sigma$ -hole, blue) and the electronegative part (red) allow one to explain halogen bonding. Adapted with permission from ref 17. Copyright 2019 Wiley-VCH. (Right) Contributing Lewis structures for the description of the bonding situation in a (symmetric) trichloride ion.



**Figure 3.** Reaction scheme for loading and unloading TEMACl with  $\text{Cl}_2$ .

temperature, making it very easy to handle and to portion. One liter of the loaded ionic liquid can store up to 0.53 kg (7.5 mol) of  $\text{Cl}_2$ . When loaded with chlorine gas, the formed ionic liquid TEMACl<sub>3</sub> appears yellow, while the product, triethylmethylammonium chloride ( $[\text{NEt}_3\text{Me}]\text{Cl}$ , TEMACl), after the chlorine gas is released, is a colorless salt. As shown in Figure 3,  $[\text{NEt}_3\text{Me}]\text{Cl}$  reacts in a chlorine gas atmosphere directly to form the trichloride. Notably, TEMACl<sub>3</sub> is in an equilibrium with TEMACl and  $\text{Cl}_2$  (Figure 3). Therefore, the ionic liquid TEMACl<sub>3</sub> has a chlorine vapor pressure, which is dependent on the temperature and the pressure.

Consequently, chlorine gas can be released from the salt by one of the following operations:

- Heating to approximately 80 °C,
- Applying vacuum,
- Adding water (5 equiv or more).

The release of chlorine gas by the addition of water can be explained by the fact that the hydration energy of the chloride anion  $\text{Cl}^-$  is higher than the bonding energy of the trichloride anion  $[\text{Cl}_3]^-$ : The trichloride anion can be rationalized by assuming a chlorine molecule, which is bound to a chloride anion ( $[\text{Cl}\cdots\text{Cl}_2]^-$ ). When water is added, the chlorine molecules ( $\text{Cl}_2$ ) are displaced by water molecules, resulting in the hydration of TEMACl and the release of chlorine gas.

## USE OF TRICHLORIDES FOR DEMONSTRATION EXPERIMENTS

Due to its properties described above, TEMACl<sub>3</sub> is a very interesting substitute for chlorine gas in industry. In addition, TEMACl<sub>3</sub> offers new possibilities for demonstration experiments.

## Elemental Chlorine in Demonstration Experiments

The reactivity of chlorine is characteristic for halogens. Therefore, reactions of elemental chlorine play a central role in chemical demonstration experiments from high school to the university level, e.g., in the synthesis of sodium chloride from the elements,<sup>22</sup> as a typical oxidant for bleaching,<sup>23</sup> in the combustion reaction of turpentine in a chlorine atmosphere,<sup>24</sup> or for halogenation reactions in organic chemistry.<sup>25</sup> However, working with chlorine gas poses safety risks due to its toxicity and being difficult to handle due to its high corrosiveness and the gas pressure of the cylinder. Hence, in school practice, chlorine is most usually synthesized as needed, e.g., from potassium permanganate and concentrated hydrochloric acid,<sup>26</sup> sodium hypochlorite and hydrochloric acid,<sup>14</sup> or pool disinfectant tablets (e.g., trichloroisocyanuric acid).<sup>24,27</sup> Some of these syntheses require rather complex setups, which can distract students from the essential processes and increase the practical difficulty. Several syntheses involve harmful reactants, produce unwanted byproducts (e.g., oxygen gas) that affect the purity of the released chlorine, and generate heavy metal-containing waste. Finally, the volume of chlorine gas produced is difficult to control, resulting typically in the formation of excessive amounts of this toxic gas. Therefore, it is of great value to teachers and instructors to have another way to safely conduct demonstration experiments with chlorine.

## Polychlorides as an Alternative to Elemental Chlorine for Demonstration Experiments

The use of polychlorides could be a novel, easy, and safer way to conduct experiments with elemental chlorine in educational settings. Commercially available TEMACl<sub>3</sub> is an ionic liquid that is safe to store and easy to portion. The simple addition of water releases chlorine gas and leads to triethylmethylammonium chloride ([NET<sub>3</sub>Me]Cl), which is a relatively harmless chemical.<sup>28</sup> In addition, the color of the ionic liquid allows a direct estimation of the chlorine content in the ionic liquid.

In higher education settings, such as university lab courses, TEMACl<sub>3</sub> could also be used for student experiments. For high school students, experimenting with (compressed) chlorine gas is not recommended; depending on the legal situation, it is not allowed in several countries.<sup>10</sup> Therefore, it seems reasonable to also limit the use of TEMACl<sub>3</sub> to demonstration experiments in high schools.

### GOAL OF THIS WORK

For the reasons discussed above, this work examines to which extent polychloride salts, specifically TEMACl<sub>3</sub>, can be used as a safe alternative to chlorine gas in chemistry demonstration experiments for educational purposes. Therefore, its use in well-known demonstration experiments is described as a proof of concept.

### EXPERIMENTAL SECTION

For all experiments described herein, more detailed information and videos can be found in the [Supporting Information \(SI\)](#). Before describing specific experiments, some general working practices are given.

#### Release of Chlorine Gas

The easiest way to release chlorine gas is to add approximately 0.5 mL of water per 1 mL of TEMACl<sub>3</sub>. Adding 5 equiv of water will release 97% of stored chlorine.<sup>19</sup> Adding more water will

reduce this amount because more chlorine is dissolved in the water.

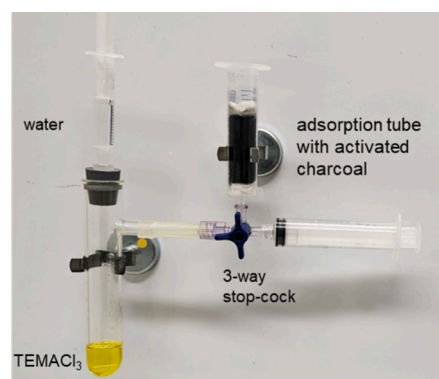
Alternatively, Cl<sub>2</sub> can also be released partially by heating the ionic liquid in a water bath by up to 80 °C.

#### Release of Chlorine Gas in a Microscale Setup

Chlorine gas can also be released from TEMACl<sub>3</sub> in a microscale setup using syringe techniques and test tubes.<sup>22,29,30</sup>

A self-made adsorption tube should be used to prevent the release of chlorine gas into the environment. This is done by removing the plunger from a 10 mL disposable syringe, adding a layer of glass or cotton wool, filling the syringe with activated charcoal, and adding a second layer of wool.<sup>30</sup>

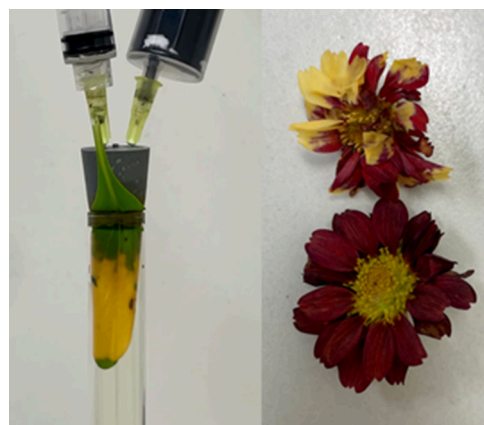
In a typical setup, the required amount of ionic liquid (approximately 1 mL) is transferred into a test tube with side arm. A 3-way stopcock is connected to the side arm. An adsorption tube (see above) and a gastight syringe are connected to the 3-way stopcock. The test tube is closed by a rubber stopper with a hole and a syringe adapter (Figure 4).<sup>31</sup>



**Figure 4.** Microscale setup to produce chlorine gas from TEMACl<sub>3</sub> with a self-made activated charcoal adsorption tube (see [video 1](#)).

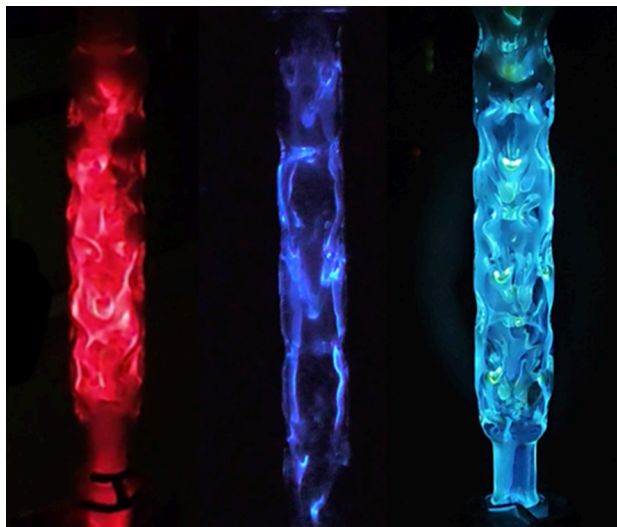
Water (50% of the volume of TEMACl<sub>3</sub>) is added with a syringe into the test tube. After sufficient gas has developed to expel the air from the test tube, chlorine gas can be collected by turning the 3-way stopcock.

Alternatively, a setup using a rubber stopper pierced with two cannulas can be used (Figure 5, for details and videos see the [SI](#)). However, the cannulas corrode very quickly in the chlorine

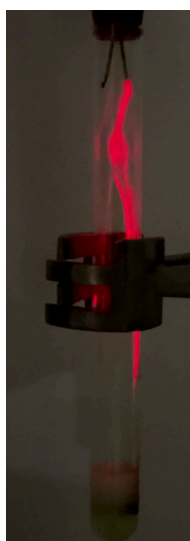


**Figure 5.** Visualization of chlorine gas evolution by bleaching a tree leaf in the alternative microscale setup (left) and bleached flowers (right) (see [video 1](#)).

atmosphere and must be discarded after the reaction. If available, the use of PFA (perfluoroalkoxy alkane) or Teflon tubing is recommended. To visualize the release of chlorine gas, a tree or flower leaf can be inserted into the chlorine atmosphere. Once the chlorine gas reaches the leaf, the leaf will bleach from the bottom up (Figure 5).



**Figure 6.** (Left) Red luminescence of singlet oxygen in the macroscale variant. (Middle) Blue luminescence through addition of luminol. (Right) Green-blue luminescence through addition of luminol/fluorescein (for details see the SI and video 2).



**Figure 7.** Luminescence of singlet oxygen in the microscale variant (see video 1).

### Preparation of Chlorine Water

Chlorine water is considered to be a safe alternative to elemental chlorine for educational purposes.<sup>32</sup> Chlorine water can be prepared by adding a surplus of water to the  $\text{TEMACl}_3$ . The amount of water can be chosen according to the desired concentration (1 mL of  $\text{TEMACl}_3$  is equivalent to approximately 7.5 mmol of  $\text{Cl}_2$ ).

### DEMONSTRATION I: LUMINESCENCE OF SINGLET OXYGEN

Singlet oxygen is the active species in many everyday reactions of oxygen, such as bleaching or decomposition processes.<sup>15</sup> To date, the production of singlet oxygen in demonstrations requires a strong chlorine gas stream.<sup>33</sup>  $\text{TEMACl}_3$  allows to perform this experiment in a much simpler way. First, an impressive demonstration experiment aimed at maximizing the visible effect is presented. Then, a small-scale variation is described.

#### Experimental Procedure—Macroscale

**Caution:** This experiment must be performed in a properly ventilated fume hood. Alternatively, liquids can be added through a dropping funnel connected to tubing that is reaching directly into a fume outlet (for details see SI).

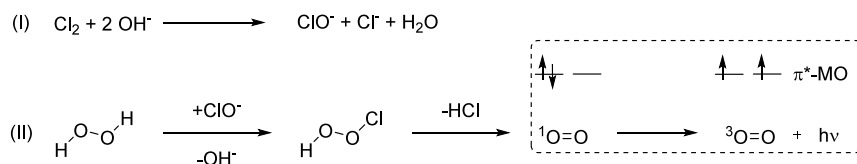
A 9 mL amount of cooled ( $0\text{ }^\circ\text{C}$ ) sodium hydroxide solution ( $c = 3\text{ mol/L}$ ) and 3 mL of cooled hydrogen peroxide solution (30%) are freshly mixed while cooling. Approximately 3 mL of  $\text{TEMACl}_3$  is added to a 25 mL round-bottom flask, and a Vigreux column is attached. Approximately 1.5 mL of water is added through the Vigreux column to create a chlorine atmosphere. In a darkened room, the sodium hydroxide/hydrogen peroxide solution is added dropwise and allowed to run down the inside wall of the Vigreux column. After the demonstration, sodium thiosulfate solution is added to quench the remaining  $\text{TEMACl}_3$ . As soon as the mixed solution comes into contact with the chlorine atmosphere, it begins to glow with a red color (Figure 6, left).

Further colors can be achieved by adding luminol (blue glow) or fluorescein and luminol (green glow) to the sodium hydroxide solution (Figure 6, right).<sup>34</sup> Detailed instructions can be found in the SI.

#### Experimental Procedure—Microscale

Sodium hydroxide solution ( $c = 3\text{ mol/L}$ ) and hydrogen peroxide solution (30%) are freshly mixed in a ratio of 3:1.

A 1 mL amount of  $\text{TEMACl}_3$  is pipetted into a test tube. The test tube is closed with a pierced rubber stopper with an adsorption tube (see above). Through the free cannula, first, 0.5 mL of water is added to release chlorine from  $\text{TEMACl}_3$ , generating a chlorine atmosphere in the test tube; then, the freshly prepared 3:1 mixture of sodium hydroxide and hydrogen peroxide solution is slowly added using a syringe (Figure 7).



**Figure 8.** Reaction scheme for the formation of hypochlorite from chlorine and hydroxide ions (I), and the subsequent formation of singlet oxygen (II). In singlet oxygen, the spin of the two electrons in the  $\pi^*-\text{MO}$  (molecular orbital) is different. In the more stable triplet oxygen, these two electrons have the same spin.<sup>15</sup>

## Results and Discussion

As shown in Figure 8, chlorine first reacts with hydroxide ions to form under disproportionation a mixture of the hypochlorite and the chloride anion. The hypochlorite anion then reacts with hydrogen peroxide to form elemental oxygen. Since the total spin is conserved in this reaction, oxygen is formed in its singlet form, which is higher in energy (approximately 92 kJ/mol) than the triplet form.<sup>15</sup> The unstable singlet oxygen  $^1\text{O}_2$  converts to triplet oxygen  $^3\text{O}_2$ , while red light is emitted.

This experiment not only is impressive but also allows the discussion of atomic structures, especially the role of the electron spin in the electron configuration of atoms and molecules.

### ■ DEMONSTRATION II: SYNTHESIS OF IRON CHLORIDE

The formation of salts from nonmetals and metals is a central reaction in many high school curricula.

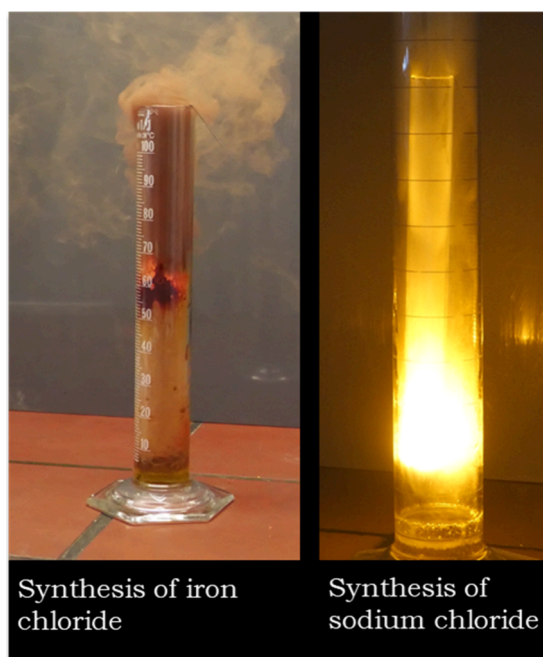
#### Experimental Procedure

**Caution:** This experiment must be performed in a properly ventilated fume hood.

Approximately 5 mL of  $\text{TEMACl}_3$  is added to a glass cylinder. A 2.5 mL amount of water is added to create a chlorine atmosphere. Loosely packed iron wool is attached to a metal hook (e.g., a small spatula can be bent in a z-shape) or to crucible tongs and heated in a roaring flame until glowing. The glowing iron wool is very quickly transferred into the chlorine-filled cylinder, and the metal hook is attached to the edge of the glass cylinder.

#### Results and Discussion

When the glowing iron wool comes in contact with the chlorine atmosphere, its glowing intensifies and a strong red-yellow smoke development takes place (Figure 9, left). Iron and chlorine react to iron(III) chloride  $\text{FeCl}_3$  ( $2 \text{ Fe} + 3 \text{ Cl}_2 \rightarrow 2 \text{ FeCl}_3$ ).



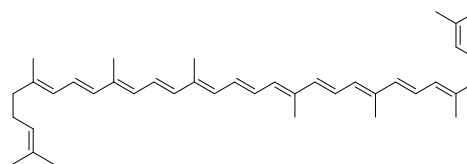
**Figure 9.** (Left) Synthesis of iron chloride. The glowing iron wool and the red-brown smoke is clearly visible. (Right) Synthesis of sodium chloride (for details see the SI and video 3 and 4).

### Alternative: Synthesis of Sodium Chloride

Similarly, sodium chloride can be synthesized from elemental sodium and chlorine (Figure 9, right). Therefore, a test tube with two holes is used to heat the sodium. Detailed instructions are given in the SI. Additional care should be taken when working with elemental sodium.

### ■ DEMONSTRATION III: ELECTROPHILIC ADDITION AT DOUBLE BONDS

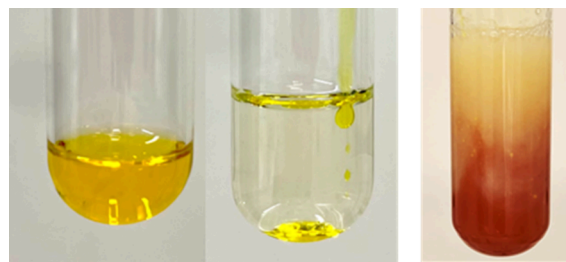
Despite their great importance, electrophilic additions of chlorine are rarely demonstrated in high schools for safety reasons. However,  $\text{TEMACl}_3$  can safely be used to directly chlorinate alkenes without the release of chlorine gas. This can be demonstrated, for example, by the chlorination of lycopene. Lycopene (Figure 10) is a carotenoid with 11 conjugated double bonds and is responsible for the red color of tomatoes.<sup>23,35,36</sup>



**Figure 10.** Structure of lycopene, the main coloring pigment of tomatoes.

#### Experimental Procedure

A 10 mL amount of tomato juice and 10 mL of heptane are filled in a test tube. The test tube is closed with a rubber stopper and well shaken. After separation, a few milliliters of the upper yellow (Figure 11, left) is transferred to another test tube. A few drops of  $\text{TEMACl}_3$  are added. After decolorization, more heptane extract may be added.



**Figure 11.** (Left) Heptane extract of tomato juice. (Middle) After addition of  $\text{TEMACl}_3$ , the upper phase (heptane extract) is decolorized and the lower phase is  $\text{TEMACl}_3$ . (Right) Direct addition of  $\text{TEMACl}_3$  to tomato juice.

#### Results and Discussion

The organic phase turns colorless, while the ionic liquid forms a second phase (Figure 11, middle). In trichlorides, the Cl–Cl bond is prolonged, which facilitates the electrophilic addition of chlorine to double bonds. Hence, the system of conjugated double bonds is destroyed, and thus, the perceived red color disappears.

#### Alternative: Direct Chlorination of Tomato Juice

$\text{TEMACl}_3$  can also be directly added to tomato juice. The upper layer turns white almost instantaneously (Figure 11, right). However, in this case, chlorine gas is released by the reaction with the water in the tomato juice. Accordingly, special precautions (fume hood!) should be taken.

## HAZARDS

TEMACl<sub>3</sub> is an oxidizing agent, corrosive, and harmful.<sup>37</sup> Contact with water or heating produces a toxic, corrosive, and oxidizing gas. All experiments are demonstration experiments and should be performed by experienced experimenters in fume hoods. The use of nitrile gloves is strongly recommended. The reaction product TEMACl causes skin, eye, and respiratory irritations.<sup>28</sup>

Saturated sodium thiosulfate solution should be used to quench all reactions involving chlorine.<sup>32</sup> All reaction vessels and materials used should be thoroughly rinsed with sodium thiosulfate solution. Addition of water releases remaining chlorine that is directly reduced to chloride by thiosulfate solution. Excess chlorine should be bubbled into sodium thiosulfate solution.

Sodium hydroxide causes severe eye damage and skin corrosion. Hydrogen peroxide solution is an oxidizing agent that causes eye damage and is harmful if swallowed or inhaled. Elemental sodium reacts heavily with water. Iron(III) chloride smoke is harmful if swallowed and causes severe skin burn and eye damage.

If metal cannulas are used, they must be discarded after each use. Corroded cannulas can block and create a closed system, which must be avoided.

## RESULTS AND DISCUSSION

The demonstration experiments described illustrate the versatility and the ease of use of trichlorides in chemistry class. The described experiments were tested by 14 preservice teacher students in a lab course. Students were able to perform the experiments with the instructions given above. Eighty-two percent of the students agreed or rather agreed in a survey that they felt safe working with TEMACl<sub>3</sub> (for details and further results, see the SI). Finally, some pedagogical issues are discussed below to facilitate their use in schools.

### Pedagogical Considerations for the Explanation of Trichlorides in High School

Depending on the prior knowledge of the students, trichloride could be used in different complexities in high school.

- As a black box storage of chlorine without further explanation. The bonding situation can be introduced as a general noncovalent interaction:  $X-Cl_2 \rightarrow X + Cl_2$ .
- With a simplified molecular formula. The storage of chlorine can be rationalized by the concept of halogen bonding (see Figure 2):  $R_4NCl-Cl_2 \rightarrow R_4NCl + Cl_2$ .
- By discussing the principles of chemical equilibrium. For more advanced students, the binding and release of chlorine is a prime example for discussing the manipulation of chemical equilibria by heat, pressure, or addition of reactants according to the principle of Le Chatelier.

### Trichlorides and Multidimensional Socioeconomic Issues

Socioscientific problems are multidimensional and complex, yet students tend to oversimplify them.<sup>38,39</sup> The UN defined as goals for sustainable development education that “[t]he learner understands dilemmas/trade-offs related to and system changes necessary for achieving sustainable consumption and production”.<sup>40</sup> Chlorine storage serves as a prime example to discuss the complexities of socioscientific issues and potential solutions.

Ninety-seven percent of chlorine is produced by the energy-intensive chlor-alkali electrolysis of aqueous sodium chloride

solutions.<sup>15</sup> This process cannot be carried out efficiently whenever and wherever electricity from renewable sources is available because “chlorine is difficult to store and to transport economically and is therefore generally produced near consumers”.<sup>4</sup> The magnitude of this problem can be estimated by considering that approximately 2.3% (!) of the electricity consumed in Germany is used for chlor-alkali electrolysis.<sup>2</sup> Thus, a “technical problem” like chlorine storage has serious implications for sustainability. TEMACl<sub>3</sub> is an ionic liquid, which minimizes the risk of uncontrolled release of toxic gases from leaks during transportation and storage (see Figure 1). Such alternative storage and transportation options have the potential to convert chlorine production from chlorine-alkali electrolysis to renewable energy, thereby reducing the environmental impact of chlorine chemistry. From a sustainability perspective, it should be considered that TEMACl has a rather high molecular weight and needs to be synthesized itself. Therefore, one of the main advantages of TEMACl is its reusability. In industry, chlorine loading and release can be easily realized by temperature and pressure changes.<sup>2,19</sup> This allows it to be used as a closed loop chlorine storage medium.

By considering this complex context, students can be made aware of complex problems related to chemical industry. Instead of portraying all chemistry as problematic, it emphasizes the critical role of chemical research in creating a safer and more sustainable future.<sup>41</sup>

## CONCLUSION

In this article, we have described several impressive demonstration experiments using triethylmethylammonium trichloride [NEt<sub>3</sub>Me][Cl<sub>3</sub>] (TEMACl<sub>3</sub>). The experiments illustrate how TEMACl<sub>3</sub> can be used in chemistry education as a safe and convenient substitute for chlorine gas. Compared to other methods of producing chlorine gas, TEMACl<sub>3</sub> is very easy to handle and safe to store, and the release of chlorine gas is as simple as adding water. In addition, TEMACl<sub>3</sub> could be used in a variety of further demonstration experiments and in laboratory courses at the university level.

TEMACl<sub>3</sub> is currently being considered in chemical research and industry as an innovative and safe way to store and transport chlorine gas. Therefore, its use in chemistry education allows for the discussion of real-world challenges in chemistry and provides authentic insights into current chemical research.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available at <https://pubs.acs.org/doi/10.1021/acs.jchemeduc.3c01252>.

Detailed instructions for experimenters (PDF)

Video 1 (Microscale Experiments): gas developer, microscale luminescence, bleaching with chlorine gas (MP4)

Video 2 (Demonstration I): luminescence of singlet oxygen in the macroscale variant (MP4)

Video 3 (Demonstration II): reaction of iron and chlorine (MP4)

Video 4 (Demonstration II): reaction of sodium and chlorine (MP4)

## AUTHOR INFORMATION

### Corresponding Authors

**Benjamin Pöloth** – *Didaktik der Chemie, Eberhard Karls Universität Tübingen, Tübingen D-72076, Germany;*

orcid.org/0000-0001-7777-9903;

Email: benjamin.poelloth@uni-tuebingen.de

**Christian Müller** – *Institut für Chemie und Biochemie, Freie Universität Berlin, Berlin D-14195, Germany;*

Email: c.mueller@fu-berlin.de

**Sebastian Riedel** – *Institut für Chemie und Biochemie, Freie Universität Berlin, Berlin D-14195, Germany;* orcid.org/0000-0003-4552-5719; Email: s.riedel@fu-berlin.de

### Authors

**Sophie Rathmann** – *Institut für Chemie und Biochemie, Freie Universität Berlin, Berlin D-14195, Germany*

**Friedrich Braune** – *Institut für Chemie und Biochemie, Freie Universität Berlin, Berlin D-14195, Germany*

**Merlin Kleoff** – *Institut für Chemie und Biochemie, Freie Universität Berlin, Berlin D-14195, Germany*

**Patrick Voßnacker** – *Institut für Chemie und Biochemie, Freie Universität Berlin, Berlin D-14195, Germany*

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.jchemed.3c01252>

### Notes

The authors declare the following competing financial interest(s): S.R. is an inventor on two pending patents related to this work filed by Covestro Intellectual Property GmbH & Co. KG (no. WO 2019215037 A1, filed 2018, and no. WO2021069757 A1, filed 2021). P.V. and S.R. are inventors on two pending patents related to this work filed by Covestro Deutschland AG (no. WO2022128951 A1, filed 2020, and no. WO2022128950 A1, filed 2020). The authors declare that they have no other competing interests.

## ACKNOWLEDGMENTS

We thank Paul Golz and Thomas Drews (both FU Berlin) for preparative support. The graphical abstract has been designed using images from [Flaticon.com](https://flaticon.com).

## REFERENCES

- Lin, R.; Amrute, A. P.; Pérez-Ramírez, J. Halogen-Mediated Conversion of Hydrocarbons to Commodities. *Chem. Rev.* **2017**, *117* (5), 4182–4247.
- Kleoff, M.; Voßnacker, P.; Riedel, S. The Rise of Trichlorides Enabling an Improved Chlorine Technology. *Angew. Chem., Int. Ed.* **2023**, *62* (17), No. e202216586.
- Market volume of chlorine worldwide from 2015 to 2022, with a forecast for 2023 to 2030. *Statista*, 2023; <https://www.statista.com/statistics/1310477/chlorine-market-volume-worldwide/> (accessed 2023–11–24).
- Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing industry; European Commission-Integrated Pollution Prevention and Control, 2001; [https://eippcb.jrc.ec.europa.eu/sites/default/files/2020-03/superseded\\_cak\\_bref\\_1201.pdf](https://eippcb.jrc.ec.europa.eu/sites/default/files/2020-03/superseded_cak_bref_1201.pdf) (accessed 2023–10–23).
- Bildungsplan des Gymnasiums Chemie (V2); Ministerium für Kultus, Jugend und Sport Baden-Württemberg; <https://bildungsplaene-bw.de/Lde/LS/BP2016BW/ALLG/GYM/CH.V2>.
- Programme de physique-chimie de terminale générale; Ministère de l'Éducation nationale et de la Jeunesse, 2019; [https://www.education.gouv.fr/sites/default/files/imported\\_files/document/spe249\\_annexe\\_1158929.pdf](https://www.education.gouv.fr/sites/default/files/imported_files/document/spe249_annexe_1158929.pdf).

[gouv.fr/sites/default/files/imported\\_files/document/spe249\\_annexe\\_1158929.pdf](https://www.education.gouv.fr/sites/default/files/imported_files/document/spe249_annexe_1158929.pdf).

(7) Next Generation Science Standard Lead States. *Next Generation Science Standards*; National Academies Press, 2013.

(8) Chlorine. *ECHA Chemicals Database*; European Chemicals Agency; <https://echa.europa.eu/de/substance-information/-/substanceinfo/100.029.053> (accessed 2023–11–16).

(9) van der Kloot, W. April 1915: Five future Nobel Prize-winners inaugurate weapons of mass destruction and the academic-industrial-military complex. *Notes Rec. R. Soc. London* **2004**, *58* (2), 149–160.

(10) Stoffliste zur DGUV Regel 113-018 "Unterricht in Schulen mit gefährlichen Stoffen"; DGUV; <https://degintu.dguv.de/> (accessed 2022–12–15).

(11) Moataz, M.; Fahmy, O.; Abdallah, N.; al-Khalidi, S. Chlorine gas leak kills 12, injures 251 at Jordan port. *Reuters Media*, Jun 28, 2022; <https://www.reuters.com/world/middle-east/four-dead-70-injured-toxic-gas-leak-jordans-aqaba-port-state-tv-2022-06-27/> (accessed 2023–11–09).

(12) Utah Valley University. *Jack Rabbit Project*; Utah Valley University; <https://www.uvu.edu/es/jack-rabbit/> (accessed 2023–11–24).

(13) Paven, M.; Schiesser, Y.; Weber, R.; Bramer, W. E.; Yogendra, S.; Hasenstab, R. S.; Steinhauer, S.; Keilhack, T. Method for releasing chlorine gas from polychloride-based storage media by means of chlorine-releasing agents and use in chemical reactions. WO2020EP78768 20201013.

(14) Holmes, L. H., Jr An Easy Way To Make Chlorine Water. *J. Chem. Educ.* **1997**, *74* (11), 1326.

(15) Wiberg, E.; Wiberg, N.; Holleman, A. F. *Anorganische Chemie: Band 1 Grundlagen und Hauptgruppen*; De Gruyter, 2017.

(16) Young, C. G.; Volaric, S. S. Synthesis and Iodometric Analysis of the Polyiodide Salt (NMe<sub>4</sub>)[I<sup>5</sup>]. *J. Chem. Educ.* **2020**, *97* (4), 1117–1119.

(17) Sonnenberg, K.; Mann, L.; Redeker, F. A.; Schmidt, B.; Riedel, S. Polyhalogen and Polyinterhalogen Anions from Fluorine to Iodine. *Angew. Chem., Int. Ed.* **2020**, *59* (14), 5464–5493.

(18) Voßnacker, P.; Keilhack, T.; Schwarze, N.; Sonnenberg, K.; Seppelt, K.; Malischewski, M.; Riedel, S. From Missing Links to New Records: A Series of Novel Polychlorine Anions. *Eur. J. Inorg. Chem.* **2021**, *2021* (11), 1034–1040.

(19) Voßnacker, P.; Schwarze, N.; Keilhack, T.; Kleoff, M.; Steinhauer, S.; Schiesser, Y.; Paven, M.; Yogendra, S.; Weber, R.; Riedel, S. Alkyl Ammonium Chloride Salts for Efficient Chlorine Storage at Ambient Conditions. *ACS Sustainable Chem. Eng.* **2022**, *10* (29), 9525–9531.

(20) Voßnacker, P.; Wüst, A.; Keilhack, T.; Müller, C.; Steinhauer, S.; Beckers, H.; Yogendra, S.; Schiesser, Y.; Weber, R.; Reimann, M.; Müller, R.; Kaupp, M.; Riedel, S. Novel synthetic pathway for the production of phosgene. *Sci. Adv.* **2021**, *7* (40), No. eabj5186.

(21) Li, X.; van den Bossche, A.; Vander Hoogerstraete, T.; Binnemans, K. Ionic liquids with trichloride anions for oxidative dissolution of metals and alloys. *Chem. Commun.* **2018**, *54* (5), 475–478.

(22) Barnard, W. R. A reaction tube for sodium and chlorine. *J. Chem. Educ.* **1963**, *40* (1), A49.

(23) Nemetz, T. M.; Ball, D. W. Bleaching with Chlorine: Another Tomato Juice Demonstration. *J. Chem. Educ.* **1993**, *70* (2), 154.

(24) Panzarasa, G.; Sparnacci, K. The "Mushroom Cloud" Demonstration Revisited. *J. Chem. Educ.* **2013**, *90* (6), 765–767.

(25) Conklin, A. R.; Kramme, A. Free radical chlorination of methane: A demonstration. *J. Chem. Educ.* **1983**, *60* (7), 597.

(26) Alyea, H. N. Chlorine from KMnO<sub>4</sub> + HCl. *J. Chem. Educ.* **1969**, *46* (3), A218.

(27) Hiegel, G. A.; Abdala, M. H.; Burke, S. V.; Beard, D. P. Methods for preparing aqueous solutions of chlorine and bromine for halogen displacement reactions. *J. Chem. Educ.* **1987**, *64* (2), 156.

(28) N,N-diethyl-N-methylethanaminium chloride. *ECHA Chemicals Database*; European Chemicals Agency; <https://echa.europa.eu/de/>

substance-information/-/substanceinfo/100.110.328 (accessed 2023–11–08).

(29) Obendrauf, V. Chlorexperimente mit Kleinstportionen. *Chem. Sch.* **1994**, *41*, 28–33.

(30) Obendrauf, V. More small scale hands on experiments for easier teaching and learning. *Proceedings of the 19th International Conference on Chemical Education*; IUPAC, 2006.

(31) Apparaturen zur Gasentwicklung; <http://www.bhbrand.de/low-cost/medtech-arbeitstechniken/gasentwicklung/index.html> (accessed 2023–11–29).

(32) *Richtlinie zur Sicherheit im Unterricht*; Kultusministerkonferenz, 2019.

(33) Stalke, D. *Lumineszenz von Singulettisauerstoff*; <https://lp.uni-goettingen.de/get/text/2481> (accessed 2023–11–07).

(34) Diekemper, D.; Pölloth, B.; Schwarzer, S. From Agricultural Waste to a Powerful Antioxidant: Hydroxytyrosol as a Sustainable Model Substance for Understanding Antioxidant Capacity. *J. Chem. Educ.* **2021**, *98* (8), 2610–2617.

(35) MacBeath, M. E.; Richardson, A. L. Tomato juice rainbow: A colorful and instructive demonstration. *J. Chem. Educ.* **1986**, *63* (12), 1092–1094.

(36) Pölloth, B.; Piltz, J. Blauer Tomatensaft und elektrophile Addition: Ein Schüler:innenexperiment zum Mechanismus der elektrophilen Addition von Chlorwasserstoff. *NiU-Chem.* **2023**, *34* (195), 17–21.

(37) *AB568861*|CAS 2460902-02-5; [https://abcr.com/de\\_de/ab568861](https://abcr.com/de_de/ab568861) (accessed 2023–10–24).

(38) Sadler, T. D.; Barab, S. A.; Scott, B. What Do Students Gain by Engaging in Socioscientific Inquiry? *Res. Sci. Educ.* **2007**, *37* (4), 371–391.

(39) Solli, A.; Hillman, T.; Mäkitalo, Å. Navigating the Complexity of Socio-scientific Controversies—How Students Make Multiple Voices Present in Discourse. *Res. Sci. Educ.* **2019**, *49* (6), 1595–1623.

(40) UNESCO. *Education for Sustainable Development Goals: learning objectives*; UNESCO; <https://www.unesco.org/en/articles/education-sustainable-development-goals-learning-objectives> (accessed 2023–10–23).

(41) Diekemper, D.; Schnick, W.; Schwarzer, S. Microwave Synthesis of a Prominent LED Phosphor for School Students: Chemistry's Contribution to Sustainable Lighting. *J. Chem. Educ.* **2019**, *96* (12), 3018–3024.