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# **SCHOOL SCIENCE REVIEW**

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*A Journal of the Association  
for Science Education*

## How do pupils perceive the concept of energy in chemical situations?

IP Martins and AF Cachapuz

### THE PROBLEM

In the last decade much research has been done on pupils' ideas of different aspects of the energy domain [1, 2, 3, 4, 5]. Surprisingly, most of the investigations have been undertaken in the domain of physics and little is known [6, 7] of the substantive nature of pupils' ideas about energy in chemical systems, even though the subject has been rated very difficult [8]. However, chemical systems do have their own specificity and usual demonstrations aiming to differentiate the concepts of heat and temperature in physics classes, (eg through the variation of the mass of a hot substance) are probably not easily transferable to chemistry contexts in which students are required to appreciate what happens at the intramolecular level.

This article investigates how pupils use ideas of energy and temperature to interpret energy changes when  $\text{NH}_4\text{Cl}$  crystals (10 g) are added to  $\text{H}_2\text{O}$  (50  $\text{cm}^3$ ) at room temperature. The study is part of an action-research project aiming at building useful strategies to teach elementary chemistry thermodynamics in Portuguese schools. The results obtained should be understood as provisional as this investigation is no more than a pilot study. More extensive work should be done with larger samples in order to make results more definitive.

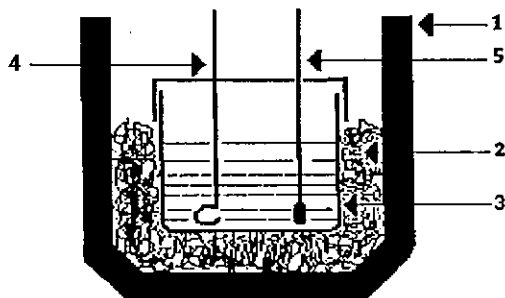


Figure 1 Apparatus for the reaction between  $\text{NH}_4\text{Cl}$  and  $\text{H}_2\text{O}$

#### Legend

- 1 polystyrene vessel
- 2 cotton
- 3 glass container with cover
- 4 glass stirrer
- 5 thermometer (0.1°C)

### METHOD

The endothermic reaction ( $\Delta t = 12.9^\circ\text{C}$ ) took place in a 100  $\text{cm}^3$  insulated glass container covered with a non-insulating material (Figure 1).

To investigate whether alternative ideas might persist for different degrees of instruction the sample included 15 subjects from grade 9 (age 15) and 15 subjects from grade 11 (age 17) randomly selected from a group of volunteers drawn from mixed-ability classes of a high school located in an urban area of Portugal. The subjects were individually interviewed (40 mins) to explain 'why the temperature fall?' and 'where does the energy of the reaction come from?' in the experiment. The interview protocols followed the Erickson's method [3] and the extracted ideas were independently validated by two experienced teachers.

### RESULTS

Grade 9 pupils were expected to equate temperature fall with a decrease in the kinetic energy of the particles in the final system though without specifying its transformation into potential energy. These pupils had been previously taught basic ideas of energy conservation in the physics course (mechanical energy). Grade 11 pupils were expected to use a formal model of chemical reaction involving ideas of bond breaking ( $\text{NH}_4^+/\text{Cl}^-$ ) and bond forming ( $\text{NH}_4^+/\text{H}_2\text{O}$ ;  $\text{Cl}^-/\text{H}_2\text{O}$ ) with the total internal energy being conserved.

The results (Table 1) reflect different ways used to resolve the cognitive conflict between ideas students brought to the task (eg not differentiating the notions of temperature and energy, non-energy conservation), and perceived aspects of the experiment. Three other pupils used idiosyncratic ideas.

'Sequential transfer' was the explanation closest to the expected answer:

...the bonds (of reactants) break apart and there is energy absorption. Then, the atoms which come from the water are linked with those coming from the ammonium chloride and energy is evolved...this (energy evolved) is smaller than the energy absorbed...during the reaction there is energy consumption (grade 11).

These subjects equated temperature fall with amount of 'energy scattered between the water molecules' which 'was absorbed by the newly formed bonds'.

Both 'Dissipation' and 'Absorption' re-

Table 1

IDEA	DESCRIPTION	GRADE	
		9	11
'Sequential transfer'	Energy associated with chemical change results from two-step process with structural and energetic components articulated; endothermic net effect	0	2
'Dissipation'	Temperature fall associated with energy transferred to outside solution	3	6
'Adsorption'	The system being insulated, energy was absorbed by one or both reactants	3	1
'I can't explain it'	No reconciliation between observation of temperature fall and ideas about energy conservation; temperature should remain constant	7	5

sponses reflect views of energy changes as the result of processes involving the reactants only. In both cases energy conservation was not used as a guiding model. Temperature decrease was explained using energy transfer models of two types:

(i) to the surroundings:

...the energy comes out (of the solution) to that small space...to that area (under the cover)...energy must have been released because the temperature is like that (decreases) ('Dissipation')

(ii) 'absorbed' by one or both reactants:

...well, the container is insulated and energy can't get through it, thus may be the substance, that substance (ammonium chloride) kept the energy (grade 9) ('Absorption').

In the case of the most popular answer ('I can't explain it') conceptual conflict was not resolved:

...the energy remains the same inside the container. It can't come out because it's a thermal insulator...the temperature should also be the same! I am confused, the temperature decreases and the energy is constant...I don't see how it works! (grade 11).

To sum up, when faced with difficulties in interpreting the experiment most students revert to the same everyday notions of heat. Notions of temperature and energy were not clearly differentiated. In particular, grade 11 students were not able to use kinetic theory as an explanatory model.

The results suggest that the role of some standard experiments and examples commonly

used to introduce elementary thermodynamic concepts should probably be carefully scrutinized. Mechanistic models used to depict inter-conversion between kinetic and potential energy (up/down hill) may not be easily transferable to chemistry contexts in which the conversion of one form of energy into another lies beyond personal experience. This may be the reason for the adoption by these students of energy transfer models based on simple ideas about energy conduction.

#### CONCLUDING REMARKS

The present experiment was tailored as part of a strategy aiming to help pupils to differentiate the notions of temperature and energy in chemical contexts. This goal can only be achieved if pupils are encouraged to express and explore their interpretations through discussion with other pupils. In this phase the teacher should adopt the role of a 'resource' which simply helps different views to emerge. The explanations identified in this experiment may be used as diagnostic questions with this in mind. In a second, restructuring phase, teachers should give appropriate informative feedback to help pupils to identify inconsistencies in their explanations. For instance, in the 'Dissipation' explanation pupils should be aware that the temperature doesn't rise in the immediate surroundings. It is in this phase that careful use of analogical models for energy changes may be most useful. In a third, developmental phase, other varied examples could be used in a step-by-step manner to facilitate conceptual expansion (eg open systems; exothermic processes). Hopefully, in this way, a closer connection between research and school practice will reduce difficulties in the teaching

and learning of topics related to energy.

#### ACKNOWLEDGEMENT

The authors wish to thank Dr R Maskill for his most valuable comments.

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## Project work with thionyl chloride

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Over the past few years Caterham School has developed quite close links with a number of chemical companies. The Chemical Industry is

keen to help teachers to encourage students to study chemistry, especially to degree level. One way to do this is by the development of a 'chemistry club', that operates at lunch times or after school. Another possible approach is by offering a 'general studies' course, based on a practical project, for the sixth form.

We have found that if an industrial concern is approached with a well researched, well presented request for help, on a practical project, they nearly always respond positively. Mostly help is given in three areas:

- 1 Literature studies and advice on the best way to proceed
- 2 Samples of chemicals
- 3 Analytical services

This article describes a project carried out by a sixth form 'general studies' group. Analysis of the products was carried out using the services of a large chemical company.

#### INTRODUCTION

There is an extensive literature on the use of thionyl chloride in organic chemistry. Most advanced level textbooks outline a number of uses for this compound. These include:

#### 1 The production of alkyl halides by reaction of thionyl chloride with hydroxy compound

Reactions of this type were first reported by Carius in 1859 [1].

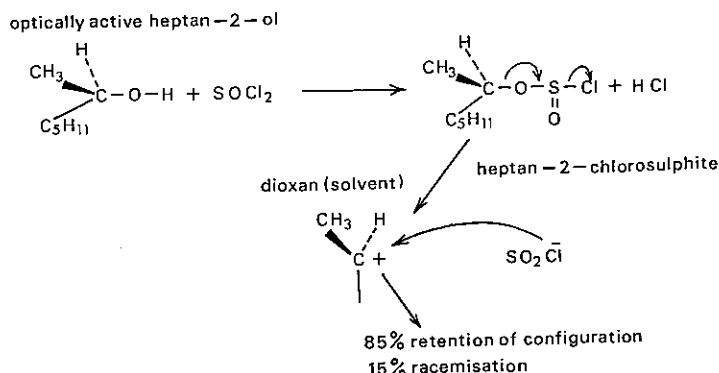


Thionyl chloride is refluxed with the alcohol in the presence of pyridine (in a molar ratio 1:1:1). This is known as the Darzens procedure [2] and high yields (>80%) are normally obtained.

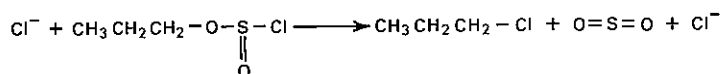
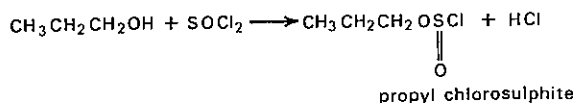
One of the advantages of using thionyl chloride is that the sulphur dioxide and hydrogen chloride formed are gases and so easily removed. In the Darzens procedure the pyridine reacts with the hydrogen chloride, so removing it from the system.

Thionyl chloride is on the whole superior to phosphorus pentachloride as this compound gives variable yields depending on the alcohol used. Phosphorus trichloride gives poor yields of alkyl halides except with alcohols which tend to react by an  $\text{S}_{\text{N}}1$  mechanism.

All the above reagents firstly convert the hydroxyl group to inorganic esters together with the production of hydrogen chloride. Substitution of chloride ions for the new complex leav-

Figure 1 A substitution nucleophilic internal reaction (S<sub>ni</sub>)

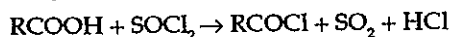
ing group then occurs.



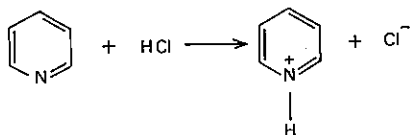
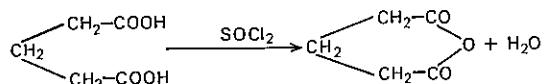
Reactions of thionyl chloride with alcohols frequently result in substitution with predominant retention of configuration. During solvolysis the complex leaving groups decompose to produce nucleophilic species that react with the carbonium ion before it can become symmetrical. Such mechanisms are known as S<sub>ni</sub>, or *substitution nucleophilic internal* (Figure 1).

If the solvent is basic, such as pyridine, inversion of configuration results. Hydrogen chloride, produced in the first step, reacts to form chloride ions. These are sufficiently nucleophilic to decompose the chlorosulphite ion by an S<sub>N2</sub> mechanism (Figure 2).

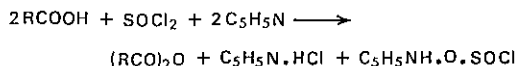
## 2 The production of acid chlorides by reaction with carboxylic acids



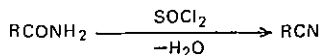
Yields are normally high eg reaction with benzoic acid is often in excess of 80%. Whether phosphorus pentachloride or thionyl chloride is used depends upon the boiling point of the acid chloride formed. Usually thionyl chloride is the most convenient for all monocarboxylic acids - due to its ease of removal if in excess - but not always for all dicarboxylic acids. Phthalic acid reacts with thionyl chloride, in the presence of zinc chloride at 220 °C, to form the acid chloride, with high yield (90%). On the other hand pentan-1,5-dioic acid reacts to form the anhydride, although the yields are low (40%).

Figure 2 An S<sub>N2</sub> decomposition in the presence of pyridine

In the presence of an ethereal solution of a mixture of an acid and pyridine, thionyl chloride reacts to form an acid anhydride.



3 Amides may be converted into nitriles by heating with thionyl chloride



During the 1920s reactions between thionyl chloride and anthraquinoid dyes were extensively studied. It was found that when alizarin, 1,2-dihydroxyanthraquinone (Figure 3), reacted with thionyl chloride both hydroxyl groups were substituted while in quinizarin (Figure 3) only one hydroxyl group is substituted [3].

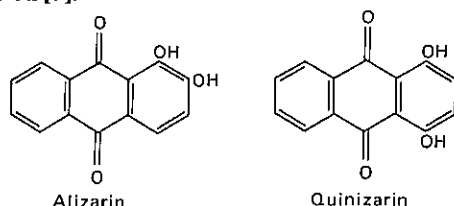
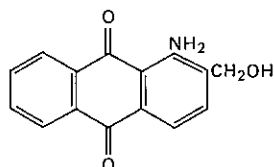


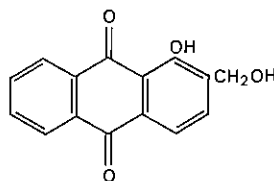
Figure 3 The structures of alizarin and quinizarin

Alizarin is one of the most important anthraquinoid dyes; it is the chief constituent of the madder root. It forms ruby red crystals, sparingly soluble in water but quite soluble in alcohol. Purple solutions are produced when it is dissolved in alkali. Being a mordant dye the colour produced depends on the metal used to form the 'lake'. With aluminium a red colour is formed, this is commonly employed for dyeing cotton and wood.

It was decided to investigate the reactions of thionyl chloride on derivatives of hydroxymethylanthraquinone as a suitable project for the chemistry club. Two compounds were



A 1-amino-2-hydroxymethylanthraquinone



B 1-hydroxy-2-hydroxymethylanthraquinone

Figure 4 The structures of 1-amino-2-hydroxymethylanthraquinone and 1-hydroxy-2-hydroxymethylanthraquinone

chosen, 1-amino-2-hydroxymethylanthraquinone and 1-hydroxy-2-hydroxymethylanthraquinone (Figure 4).

#### EXPERIMENTAL DETAILS

The reactions between the thionyl chloride and the hydroxymethylanthraquinone derivatives were carried out by mixing and leaving for 24 hours at room temperature. Any excess thionyl chloride was removed by heating under reduced pressure to dryness.

The solid products were purified by recrystallization, using petroleum ether (60-95°C) as solvent.

The melting points and reaction yields were determined.

Samples were sent for analysis to the 'analytical department' of a large chemical company. The results are presented as element composition for the product (Table 1). Visible and infrared spectra were recorded and details of these were used to confirm the structure.

All reactions were carried out in a fume cupboard. Students wore protective clothing and face masks while working on the project.

#### RESULTS

It appears that 1-amino-2-hydroxymethylanthraquinone reacted with thionyl chloride at room temperature to form 1-amino-2-chlorosulphinylmethylanthraquinone (Figure 5). This was not as expected so the reaction was repeated by refluxing the original solution for 5 hours. The product for this reaction appeared to be 1-amino-2-chlorosulphinylmethyl-4-chloroanthraquinone (Figure 5). This compound on heating above its melting point lost sulphur dioxide and gave 1-amino-2-chloromethyl-4-chloroanthraquinone.

The reaction of thionyl chloride on 1-hydroxy-2-methylanthraquinone appears to result only in the formation of the 2-chloromethyl derivatives (Figure 5).

#### DISCUSSION

The effects of thionyl chloride seemed to be

Table 1 Element composition of products obtained by reaction with thionyl chloride

Compound A	1-amino-2-chlorosulphonylmethylanthraquinone							
Compound B	1-amino-2-chloro-sulphonylmethyl-4-chloroanthraquinone							
Compound C	1-amino-2-chloromethyl-4-chloroanthraquinone							
Compound D	1-hydroxy-2-chloromethylanthraquinone							
Compound	Melting point (°C)	Yield (%)	Calc (Observed)(%)	C	H	N	Cl	S
A	166	82	53.65(53.38)	2.98(3.125)	4.17(4.20)	10.58(10.65)	9.53(9.81)	
B	192	76	48.66(48.68)	2.72(2.48)	3.78(3.89)	19.15(19.25)	8.66(8.84)	
C	213	80	58.85(59.30)	2.97(3.09)	4.57(4.65)	23.15(23.20)	—	
D	154	79	66.07(66.19)	3.33(3.50)	—	13.00(13.29)	—	

dependent on the substitution pattern of the ring as well as the reaction temperature.

The presence of the amino group decreases the acidic character of the hydroxyl group, the result of this is the formation of the chlorosulphonylmethyl derivatives. These compounds lose sulphur dioxide when heated above their melting point. How thermally stable they are is an interesting question. Perhaps with prolonged refluxing they would decompose and liberate sulphur dioxide? The product here was relatively stable under the conditions used.

The chlorination of the aromatic nucleus is interesting. The most likely explanation is that of substitution of the ring by an electrophile. An electrophile is a reagent with an empty orbital that is able to form covalent bonds to a substrate, using the latter's electrons. Just as a base is a nucleophile so a Lewis acid is an electrophile. Thionyl chloride can function as a weak Lewis base using lone-pairs of electrons from the oxygen. It can also function as weak Lewis acid using vacant *d*-orbitals.

As is true in most electrophilic substitutions the actual reagent is produced by a complex ionization reaction. The initial product being unstable may undergo an S<sub>N</sub>i reaction to form

the chloride.

The presence of the hydroxyl group on the ring obviously increases the acidic character of the methylhydroxyl group. This appears to facilitate the substitution by chlorine. The chlorosulphonylmethyl derivative here is obviously less stable and so decomposes quickly after formation.

There is a great danger when teaching organic chemistry to be too simplistic. Often reactions are taught without any reference to the yield, and at time to the conditions employed. What often appears to be a straightforward reaction produces some quite stable intermediate that requires prolonged heating to form the final product.

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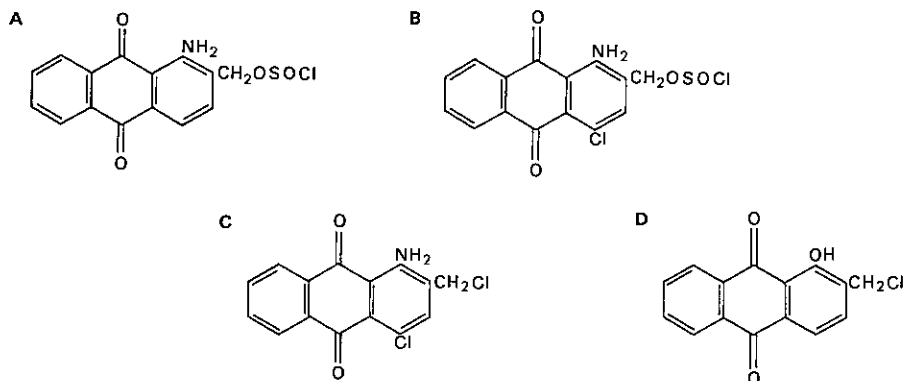


Figure 5 The structures of the compounds A to D in Table 1