

Photobromination (S_R) and Corresp. S_N1 Reactions – Key Reactions for the Development and the Application of the Concept of Hyperconjugation

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Abstract This article first describes photochemical bromination reactions of two different reactants proceeding via electron septet intermediates according to the radical substitution reaction mechanism (S_R). The case comparison is intended to enable learners – high school or university first-year organic chemistry students – to work out the concept of hyperconjugation, which is very significant for organic chemistry, by intertwining experimental results and theoretical interpretation (of free radical intermediates) closely. Since students often do not succeed in transferring concepts they have already learned from one mechanism to another, the second step will be to transfer and apply the concept of hyperconjugation to carbenium ions as reactive intermediates by means of an analogous experimental case comparison of first-order nucleophilic substitution reactions (S_N1).

Keywords: hyperconjugation, concept development, concept transfer and application, contrasting cases, reaction mechanisms

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1. Introduction

The development of a student’s abilities of concept-based process-oriented mechanistic reasoning is one of the most challenging goals in teaching organic chemistry [1]. By contrast, the majority of students often use inadequate learning strategies, as shown by many recent studies [2-10]. Instead of using relevant concepts, they focus on surface features of Lewis structures of reactants and products [2,12]. Finally, their ‘strategy’ is often pure rote memorization without taking any conceptual reasoning strategy into account [1,13,14]. Furthermore, they are often unable to transfer conceptual knowledge from one content to another. Their knowledge about electronic substituent effects, for example, is often not transferable from electrophilic aromatic substitution reactions, where it is usually acquired, to the reactivity of carbonyl compounds against nucleophiles or to the acidity of organic compounds with functional groups [15].

In order to overcome this deficiency and learn to use strong basic concepts of organic chemistry across mechanistic borders, novel tasks for educational purposes seem to be suitable, using contrasting experimental and theoretical cases (‘CCs’) [15]. The key feature of contrasting cases is similar reactions differing only in one structural feature. Comparing the experimental results in a

‘vertical’ case comparison (Case 1 and 2 in Figure 1: the same mechanism A in both cases but different reactants) should explain the differences observed regarding a new concept which is developed based on this case comparison.

We take a step forward in this paper by adding another contrasting case, creating a kind of ‘horizontal’ case comparison with the first couple of cases, Case 3 and 4 in Figure 1. They run over the new mechanism B, but with different reactants having similar structural features compared with cases 1 and 2 and allowing the transfer and application of the concept developed into another mechanistic context (Figure 1).

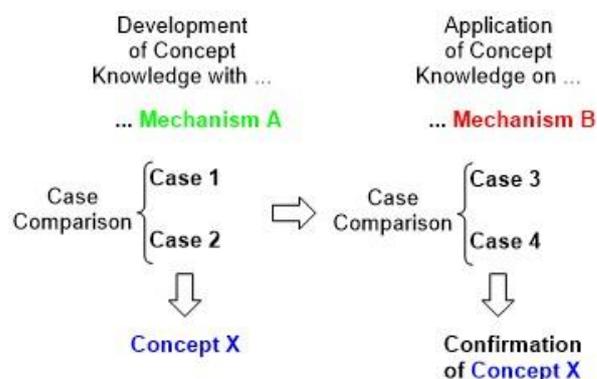
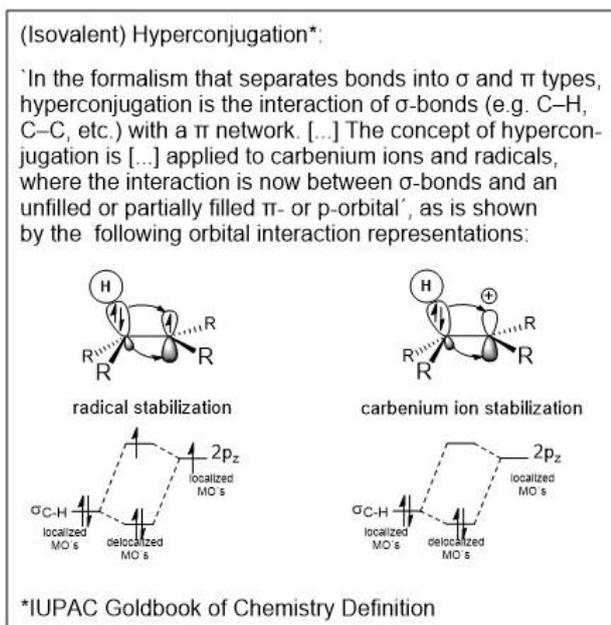


Figure 1. Concept development and transfer/application by double case comparisons, crossing mechanistic borders

2. Subject Analysis and Educational Reconstruction

The concept of hyperconjugation, used to explain the stabilities of electron septet species, such as free radicals (in radical substitution reactions), and electron sextet species, such as carbenium ions (in first order nucleophilic substitution reactions), is very suitable for concept development and transfer across mechanistic borders in learning situations (see Box).



Box 1. (Isovalent) Hyperconjugation stabilizing radicals and carbenium ions

Typical examples of radical substitution reactions in chemistry education are halogenations, and are also the most important ways to introduce functional groups to alkanes. Photobromination reactions play a prominent role among these in organic chemistry education, as they proceed less vigorously and with higher selectivity compared to chlorination reactions. Furthermore, they show the analytical and educational advantage of being observable by continuous decolorization of the solution and by the formation of the by-product hydrogen bromide (HBr). Additionally, the latter is detectable by the lowering of the pH value, increasing the electrical conductance of the solution and by proof of bromide ions. Abundant substitution and elimination products are available through S_N1 , S_N2 , E1 and E2 mechanism reactions via bromoalkanes as the products of these radical mechanism reactions, and thus, they could be characterized as a gate to various organic substance classes. The answer to the question of the regioselectivity of photobromination reactions is closely connected to the most important concepts of organic chemistry. In addition to resonance, hyperconjugation is one of the strongest concepts for explaining the pathways, selectivity, reaction rates and products of organic chemical reactions, especially, if they proceed via reactive intermediates, such as free radicals or carbenium ions. Regarding these entities, hyperconjugation characterizes a stabilizing effect by binding the interaction of filled σ_{C-H} orbitals (or σ_{C-C}

orbitals) with partially filled or empty p_z orbitals (see Box). In all these cases, the first step of explanation for experts and learners is to estimate and compare the thermodynamic stabilities of the entities with each other. The more (stabilizing) hyperconjugative effects that exist, the lower the reactive intermediate in energy. A secondary radical, for example, with six possibilities of hyperconjugation is more stable than a primary radical with only three possibilities, just as a secondary carbenium ion being more stable than a primary one. The similarity of the effect of hyperconjugation on both kinds of reactive intermediates could be used for mechanistic case comparisons, developing a concept based on one mechanistic context and transferring and applying it to another (cf. Figure 2), confirming its usefulness in the explanation.

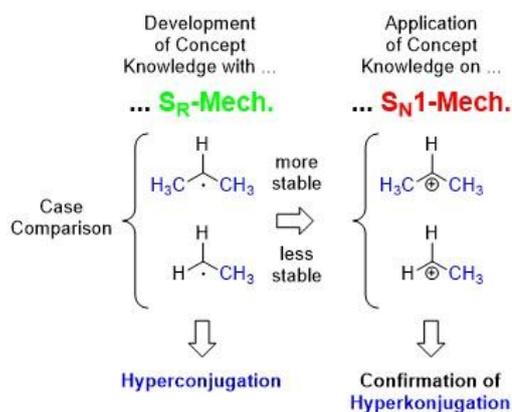


Figure 2. Development of the concept of hyperconjugation by case comparison and application in a new mechanistic field

The relative thermodynamic stability of reactive intermediates (cf. Figure 2) reflects the relative reaction rates of the formation steps compared. According to the BELL-EVANS-POLANYI PRINCIPLE and HAMMOND'S POSTULATE, more stable reactive intermediates (cf. Figure 3, "second.") in rate-determining endergonic steps with product-like transition states are formed faster than less stable ones (cf. Figure 3, "prim."). In other words, the relative energies of the transition states reflect the relative energies of the corresponding reactive intermediates (Figure 3)¹.

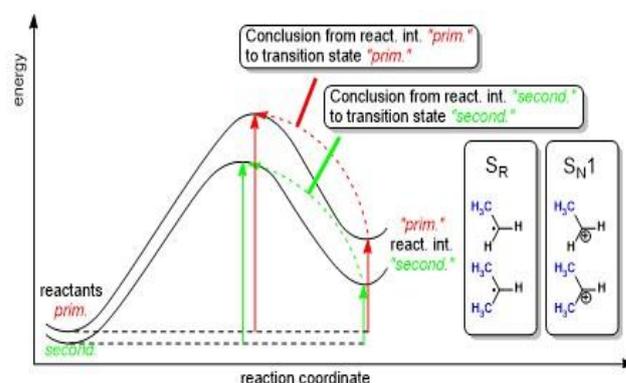


Figure 3. Qualitative reaction energy profiles in comparison to electron-deficient reactive intermediates of radical and nucleophilic substitution reactions

¹ All subject matter, including that described here on the BELL-EVANS-POLANYI PRINCIPLE and HAMMOND'S POSTULATE, can be found in good OC textbooks if needed, for example, "Organic Chemistry" by Clayden, Warren, Greeves, and Wothers, Oxford University Press.

Understanding the relationship between thermodynamic stabilities of products (here: reactive intermediates) and the relative reaction rates is one of the most important goals in organic chemistry education regarding reactions under kinetic control.

3. Conception of a Hands-on Learning Opportunity of Photobromination Reactions

Simply using ethane and propane for the case comparison of reactions via primary and secondary radicals, as described in Figure 2, would have implied working with gaseous reactants, being very unfavorable for educational purposes. Among a plenitude of possible reactants, using toluene and ethylbenzene, as liquid and cheap compounds with high reactivity, seems to us to be the best examples for an experimental case comparison, although a few safety problems still had to be solved (see 3.4).

In parallel approaches, solutions of bromine in dichloromethane were added to solutions of the reactants in dichloromethane as an inert solvent, followed by irradiation of the reaction solutions with UV light. Consequently, the resulting bromine radicals split off the weakest bonded hydrogen atoms from each of the reactants, finally generating brominated products and gaseous HBr. In order to prove the resulting gas is, in fact, the (acidic) HBr generated in a radical substitution reaction (S_R), the gas is introduced into a reaction vessel with a weak alkaline aqueous solution with phenolphthalein as the pH indicator for the visible evidence of a changing pH value. Both the resulting brominated products and hydrogen bromide are lachrymatory. They cannot be disposed of directly but must be treated specially (see 3.4). The concentration of ions in the solution increases as a function of the reaction rate by resorption of the

by-product hydrogen bromide in the alkaline solution. This can be easily recorded as electrical conductance of the solution and represented graphically. The observations confirmed the expected effects of hyperconjugation on the stabilities of the intermediates and the resulting different reaction rates according to the BELL-EVANS-POLANYI PRINCIPLE and HAMMOND'S POSTULATE. The conductance measurement has to be carried out in a separate flask (cf. Figure 5), otherwise bromine attacks the electrodes and passivates them, thus, introducing iron ions into the solution, which have an undesirable catalytic effect of promoting an electrophilic aromatic substitution (S_EAr). A blank sample was also carried out in order to exclude a S_EAr mechanism (with substitution of a hydrogen atom at the phenyl ring) and emphasize the role of light in bromination reactions. Exclusion of light here means working with a closed cardboard box with blackened inner walls, darkened windows, switched off artificial light sources and only as much residual light as is required for safe work. This results in the reaction being completely inhibited by light exclusion (Figure 4b). Furthermore, the expected brominated products benzyl bromide and (1-bromoethyl)benzene of the radical substitution reactions could be confirmed by 1H -NMR measurements.

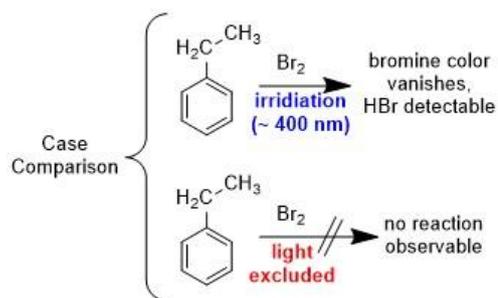


Figure 4a. Reaction of ethylbenzene with molecular bromine under irradiation of UV light (~ 400 nm) and exclusion of any light irradiation

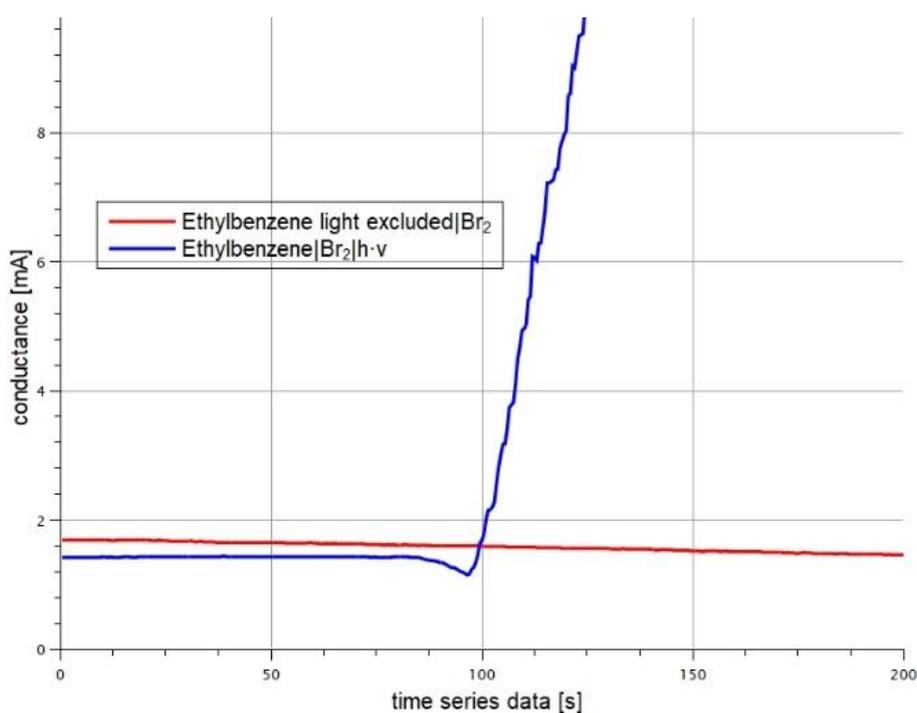


Figure 4b. Conductance values of the solutions in the test flask

3.1. The Role of UV-vis Light in Radical Bromination Reactions

Before starting to compare different reactants, a well-known experimental case comparison using only one reactant but different reaction conditions should be considered, providing hints regarding the initiation step of the reaction and the radical mechanism and underlining the role of (UV-vis) light: Ethylbenzene is treated with bromine, on the one hand, under irradiation with light (~ 400 nm) and, on the other hand, under strict light exclusion (cf. Figure 4a). The visible, unchanged color of the bromine and the result of the conductance measurement (no change in conductance, cf. Figure 4b, red curve) allow the conclusion that no reaction has occurred under light exclusion, while irradiation leads to a rapid increase of the conductance (cf. Figure 4b, blue curve), corresponding to the formation of hydrogen bromide (ionized in solution), and the decolorization of the reaction solution as well.

As a result of this experiment, learners should conclude that energy, in the form of light, is necessary to perform bromination reactions with these organic compounds. A further conclusion could be that the weakest of all bonds of each of the reactants are broken first by supplying this special form of energy. As C-H and C-C bonds are much stronger than the Br-Br bond of molecular bromine, only the latter is broken by irradiation with (UV-vis) light in two radicals. The wavelength required for the cleavage of Br-Br bonds could be calculated by the students using the value of standard dissociation enthalpy (~ 194 kJ · mol⁻¹) at about 621 nm [16]. Therefore, light with a maximum of this wavelength is required to perform photobromination reactions.

3.2. Construction of the Experimental and Measurement Apparatus of the Photobromination Reactions

A digital multiple measuring device ('multimeter'), a VOLT-CRAFT[®] VC 850 model, with an optical interface for data analysis in combination with a commercial available PC was used to measure the conductance. Accordingly, stainless steel electrodes were immersed through a drilled Teflon stopper in an indicator solution and connected to the digital multimeter by crocodile clamps. A conventional alternating voltage source of power of 6 V and a maximum output current of 6 A, available in most high school laboratories, was used. The electrode surface was kept constant by partial isolation with heat-shrink tubing to realize consistent measurement conditions. All reactions were carried out in a cardboard box (simply packaging carton), edge length ~ 500 mm, with a blackened inside and under light exclusion. The cardboard box is equipped with (cut) openings in the outer walls for passing through the UV light source and the gas hose, sealing any slits by using aluminum foil. A reclosable door was cut in the ceiling of the cardboard box for adding reactants. A conventional UV flashlight, which can be bought online, with a power output of 5 W at a wavelength of ~ 400 nm, served as the light source for the homolytic bond cleavage of the bromine. It is necessary that air from outside can flow into the flask to allow the

convection of the gaseous by-product hydrogen bromide. Accordingly, it is advantageous to connect a straight adapter to the flask by a drilled rubber stopper, into which a dropper pipette is inserted, with the tip pointing up, so that the raised position does not allow the gas to leak, while air flows in continuously (cf. Figure 5). The gas hose is connected to the flask containing the indicator solution by a rubber stopper with a gas inlet tube inserted. In this process, the gas inlet tube has to be placed slightly above the solution surface to allow a good absorption.

3.3. Experimental Comparison of Toluene and Ethylbenzene

Laboratory equipment: 2 three-necked round-bottom flasks (1×NS²29, 2×NS14, 50 mL), 2 stainless steel electrodes (150 mm, Ø 2 mm, isolated by heat-shrink tubing (PE)), 2 Teflon stoppers (one with 2 drillings for the electrodes, Ø 2 mm), 1 ground glass stopper (NS14), 1 rubber stopper with drilling, 3 straight connecting adapters (NS14), 2 gas hoses (Ø 6 mm, length 300 mm), glass tube for introducing gas (AR-GLAS[®], Ø 7 mm, length 100 mm), 3 magnetic stirrer bars (5 mm), 3 magnetic stirrers, stand material, 2 volumetric pipettes (25 and 5 mL), 1 graduated pipette (5 mL), suction ball, 2 dropper pipettes, glass funnel (Ø 150 mm), crystallization dish (250 mL), manual pump, UV flashlight (LED, 5 W, 395 nm [20]), alternating voltage source (6V), 2 crocodile clamps, 3 connecting cables, 1 interface cable, digital multimeter with USB interface, PC.

Chemicals: dichloromethane (Warning: GHS07, GHS08), bromine (Danger: GHS05, GHS06, GHS09), actually used: bromine in dichloromethane w = 0.09 (Warning: GHS07), toluene (Danger: GHS02, GHS07, GHS08), ethylbenzene (Danger: GHS02, GHS07, GHS08), potassium hydroxide solution c = 0.002 mol, phenolphthalein < 1 % in ethanol (Danger: GHS07, GHS08), sodium thiosulphate solution saturated, ethanol (Danger: GHS02, GHS08), silver nitrate 0.01 mol in water (Warning: GHS05, GHS09).

Experimental procedure: Firstly, a blank sample of the initial solutions is performed. For this purpose, 2–3 mL of each reactant is made available in 25 mL beakers and mixed with aqueous silver nitrate solution while swiveling. Next, the indicator solution is prepared: 25 mL of a 2 mmol potassium hydroxide solution is put into a 50 mL three-necked round-bottom flask and 3–4 drops of phenolphthalein are added. The indicator solution has to be stirred continuously on the magnetic stirrer at approx. 500 rpm. The reaction vessel, also a 50 mL three-necked round-bottom flask, is then placed in the black box and connected using a gas hose to the flask that contains the indicator solution. On the one hand, it must be ensured that the reaction vessel is mounted at a higher position, so that the gas transition is facilitated by the resulting slope. On the other hand, the gas must pass via a glass tube (inserted through a rubber stopper) that ends slightly above the solution surface (Figure 5) (Warning! It is important to ensure that the glass tube does not dip into the solution. Because of the excellent water solubility of

² The abbreviation 'NS' stands for the German 'Normschliff', in English it is 'ground glass joint'.

the resulting HBr, a negative pressure will be set and, therefore, some reaction solution can come off the apparatus.). Afterwards, 0.03 mol of the reactants is solved in 5 mL dichloromethane in the reaction vessel in the black box. The room now has to be darkened and all artificial light sources have to be turned off. Then, 5 mL of a solution of bromine in dichloromethane ($w = 0.09$) is added and the conductance measurement is started simultaneously (work in pairs, measurement range: mA). The box is closed immediately after adding the bromine solution. After 30 s, the UV flashlight is turned on. The measuring can be stopped on reaching a measured value of ≥ 10 mA. Finally, a few drops of the silver nitrate solution are added to the reaction solution, while swiveling. - For disposal, see 3.4.

Observation: The pH value of the alkaline solution in the case of ethylbenzene as the reactant decreases earlier as in the case of toluene, and the conductance value of the former increases earlier as well (Figure 6). In both cases, decolorization of the indicator solution (outside the card box, Figure 5) takes place nearly simultaneously to the increase of the conductance values. When adding aqueous silver nitrate solution to the indicator solution after completing the reaction, a white compound (silver bromide) is precipitated. By contrast, the blank sample of the reactants does not show any precipitation. Under the exclusion of light, there is no decolorization of the output solution observable and, as is to be expected, no increase of the conductance value and no decolorization of the phenolphthalein indicator solution either.

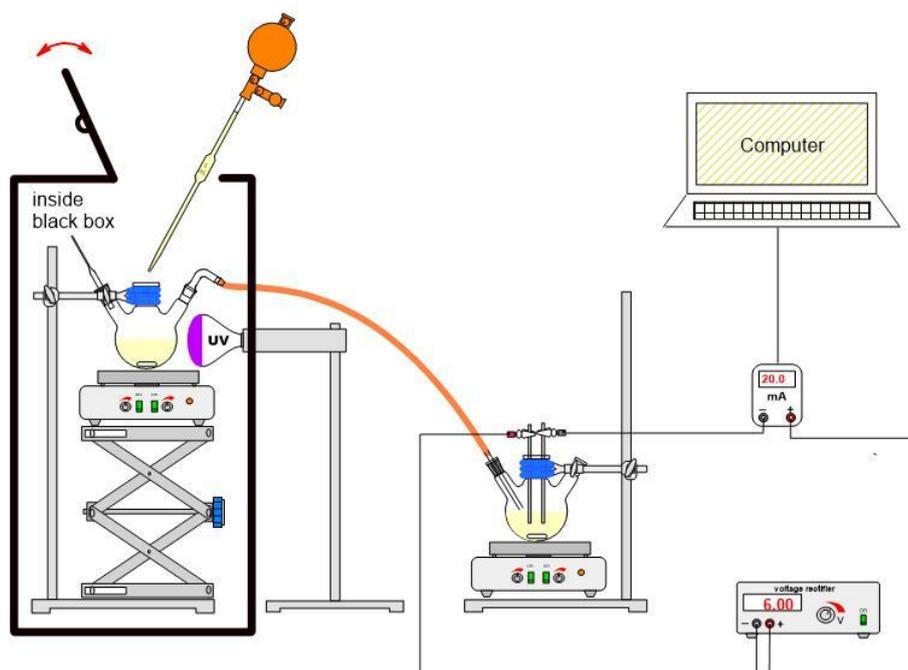


Figure 5. Experimental and measurement apparatus of the photobromination reactions

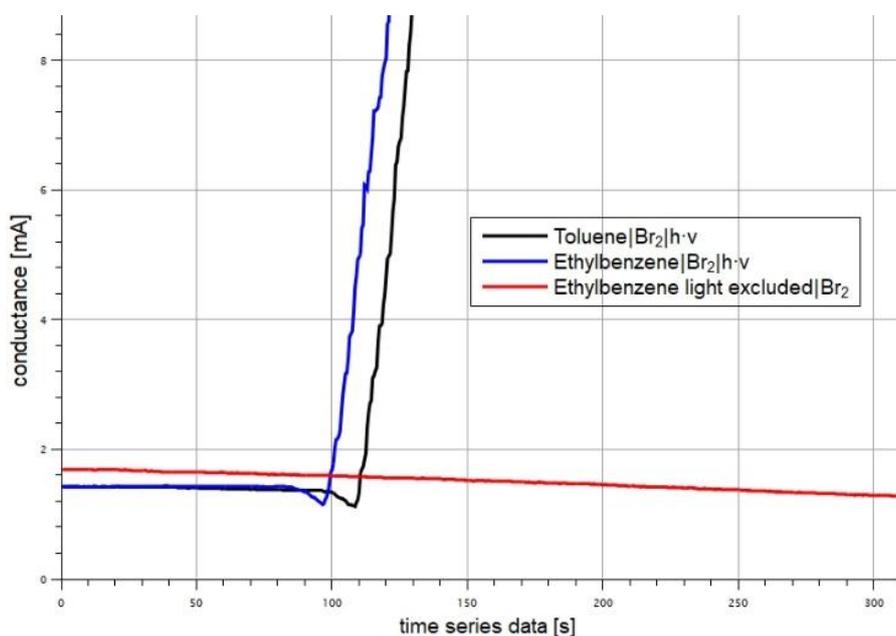


Figure 6. Conductance values of the reaction solutions of toluene and ethylbenzene with bromine under irradiation with UV light (black and blue curve) and of ethylbenzene with bromine under the exclusion of light (red curve)

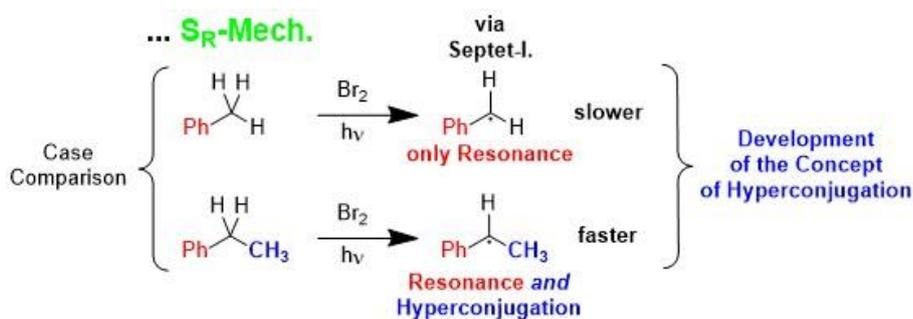


Figure 7. Comparing free radicals as septet intermediates of the radical substitution reaction of toluene and ethyl benzene with bromine under irradiation with UV light

Explanation: Bromine radicals, (theoretically) formed in both reactions with equal rates and in equal concentrations, split off hydrogen atoms from the reactants toluene and ethylbenzene as well. This step, in which hydrogen bromide is formed as the observable by-product, is endothermic in both cases and, therefore, is the rate-determining one: the homolytical cleavage of C-H bonds requires much more energy than the energy set free by the formation of the H-Br bond (cf. Figure 3). However, in the case of toluene, this step is a little more endothermic than in the case of ethylbenzene, leading to a slower reaction of toluene compared to ethylbenzene. The reason is the latter forming a free radical stabilized not only by resonance (through the aromatic ring) but also by hyperconjugation through the adjacent C-H bonds of the methyl group. Considering all possibilities, those H atoms with the weakest bonds to carbon atoms are split off, concurrently leaving the best stabilized radicals. Therefore, in both cases, the benzyl positions (the positions α to the aromatic ring) are the most reactive ones (cf. Figure 7), and finally, are the positions becoming substituted. This predictable regioselectivity was confirmed by $^1\text{H-NMR}$ analyses of the final bromination products [17].

In order to explain the diagrams of the measurements appropriately, it is important to initially recognize the first steps of the reactions compared (the 'H-abstraction') starting at different moments, in accordance with the (slightly) different activation energies. However, the following radical chain reactions (of the alkyl radicals with molecular bromine) show similar reaction rates in both cases, and thus, the electrical conductance of the solutions increases with similar slopes. Corresponding to that, learners in organic chemistry could explain the earlier start of the ethylbenzene bromination reaction by the better stabilized radical intermediate, caused by the adjacent methyl group (Figure 7). Utilizing these experimental results, teachers could introduce hyperconjugation as a basic concept of organic chemistry and, depending on the previous knowledge, suitable representations of it (see box).

As pictured in the box, radical centers of alkyl radicals have electron septets and are usually sp^2 hybridized, owning an unshared electron in a p_z orbital. As such, radicals are electron-deficient particles, stabilized by electron-donor neighbor groups. One important example of such 'neighbors' are adjacent alkyl groups with $\sigma_{\text{C-H}}$ orbitals, donating electron density to the electron-deficient

radical center. The additional stabilizing effect, given in the case of the ethylbenzene reaction but not of the toluene reaction, is based on the binding lateral interaction of electron-donating $\sigma_{\text{C-H}}$ bonds with the single occupied p_z orbital (see box).

3.4. Safety Aspects, Environmental Protection and Disposal

All experiments described under 3 and 4 have to be carried out in the fume hood. This is important to ensure especially in the experiment described under 3, as both the gaseous reaction product HBr and the lachrymatory alkyl aromatics benzyl bromide and (1-bromoethyl)benzene are dangerous to health. Furthermore, all activities have to be performed by using lab coats, nitrile gloves and safety glasses. The preparation of the bromine solution provided may only be carried out by the teacher. The apparatus is preferably assembled over a catch basin that can be quite easily poured over with saturated thiosulphate solution in case of a bromine solution leakage.

Using a gas hose, the apparatus (Figure 8) is connected to a gas trap that consists of a crystallization dish containing an ethanolic potassium hydroxide solution. The solution is stirred on the magnetic stirrer (approx. 500 rpm). The gas introduction takes place by using an inverted funnel, with its larger diameter ending slightly above the solution surface, so that the gas stream can be absorbed. After completion of the reaction, the rest of the HBr always remains in the apparatus. To remove this remainder completely, a manual pump has to be connected with the pressure compensation to pump the gas into the gas trap entirely, where it will be absorbed and neutralized immediately. Subsequently, the reaction solution is also poured into the crystallization dish, where the brominated products directly in a solvolysis ($\text{S}_{\text{N}}1$) are converted to the corresponding ethers. All glassware contaminated with bromine should be thoroughly rinsed with the saturated thiosulfate solution.

Introducing the gas is not necessary in the solvolysis described under 4 as the majority of the HBr remains in the reaction solution. After completing the reaction, the reaction solution is treated analogously and poured into the crystallization dish provided, with the ethanolic potassium hydroxide solution.

All accruing solutions can now be disposed of in the organic solvent waste, after neutralization.

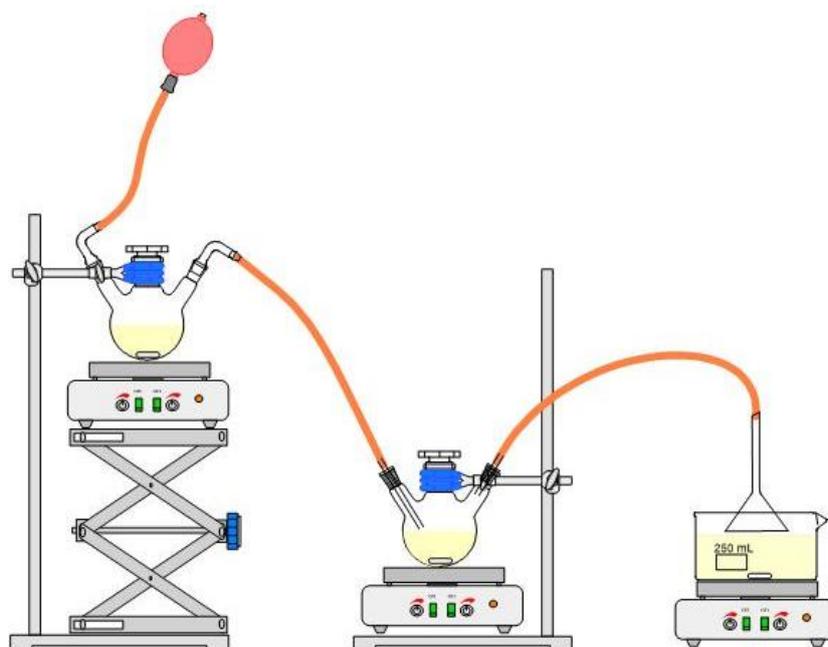


Figure 8. Apparatus for disposal

4. Conception of a Practical Learning Opportunity of Nucleophilic Substitution Reaction by S_N1

The second contrasting case in our learning opportunity consists of the solvolyses of the (formal) products of the photobromination treated under 3 with ethanol. Accordingly, ethanol will be added in parallel approaches to the initial solutions, and the changing of the pH value by the HBr formed is measured using a pH-reactive strip. Simultaneously, the conductance of the reaction solutions will be measured and analyzed in two ways: 1) graphically and 2) by utilizing a Chemophon, a measuring device with an acoustic output. The frequencies of the sounds it sends out depend on the values of the electrical conductance (and, thus, differences between the two cases are also audible by visually impaired students). The higher the frequency is, the higher the conductance of the solution [18].

4.1. Construction of the Experimental and Measurement Apparatus of the solvolyses by S_N1

The construction of the apparatus for measuring the electrical conductance of the reaction solution of the solvolysis by S_N1 reaction, using a digital multimeter again, is carried out by analogous procedure (Figure 9) as that described for the radical substitution reaction under 3.3, except the measuring now takes place directly in the reaction solution and not in a separate indicator solution. This not only reduces the work effort reasonably, as it is not necessary to introduce HBr in a second flask, but also the quantity of the by-product HBr is much lower and immediately solved totally in the reaction solution. The measurement using the Chemophon is associated by an even lower work effort, since the voltage source, connected in series, is also eliminated.

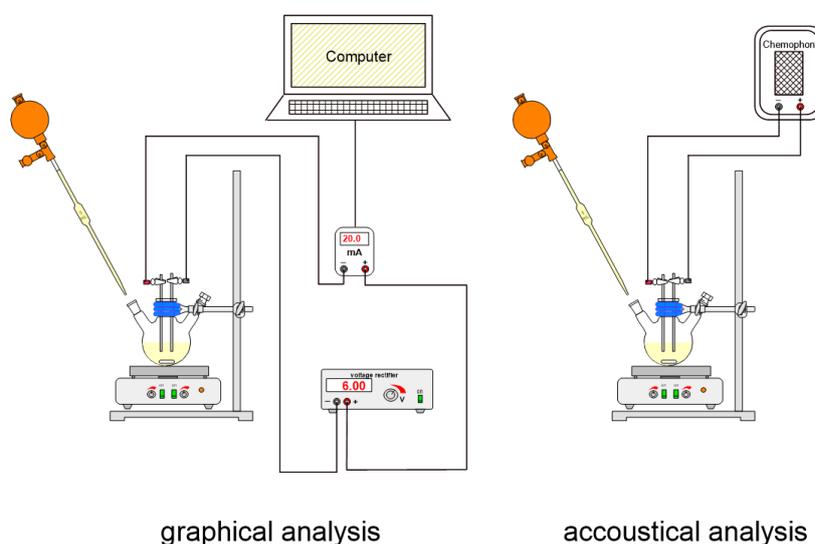


Figure 9. Experimental and measurement apparatus of the solvolysis by S_N1 reaction

4.2. Experimental Comparison of Benzyl Bromide and (1-bromoethyl)benzene

Laboratory equipment: 2 three-necked round-bottom flasks (1×NS29, 2×NS14, 50 mL), 2 stainless steel electrodes (150 mm, \varnothing 2 mm, isolated by heat-shrink tubing (PE), 2 Teflon stoppers (one with 2 drillings for the electrodes, \varnothing 2 mm), 2 ground glass stopper (NS14), 1 rubber stopper with drilling, 3 straight connecting adapters (NS14), magnetic stirrer bar (5 mm), magnetic stirrer, stand material, volumetric pipette (5 mL), 1 graduated pipette (5 mL), suction ball

For graphical (quantitative) analysis: alternating voltage source (6V), 2 crocodile clamps, 3 connecting cables, 1 interface cable, digital multimeter with USB interface, PC

For acoustical (qualitative) analysis: 2 crocodile clamps, 2 connecting cables, Chemophon [18]

Chemicals: benzyl bromide (Warning: GHS07), (1-bromoethyl)benzene, (Warning: GHS07), ethanol (Danger: GHS02, GHS07), silver nitrate 0.01 mol in water (Warning: GHS05, GHS09)

Experimental procedure: At first, similar to the experimental procedure described under 3.1, a blank sample of the initial solutions has to be performed. Accordingly, a few drops of aqueous silver nitrate solution are added to approx. 2–3 mL of each reactant, each in a 25 mL beaker, while swiveling.

For graphical (quantitative) analysis using the digital multimeter: 0.03 mol of the brominated alkyl aromatics will be made available in a 50 mL three-necked round-bottom flask and stirred by the magnetic stirrer at 500 rpm. The electrodes are then placed in the reaction vessel and connected as shown in Figure 9. The measuring range of the multimeter must now be set to μ A and the voltage source (analogously to 2.2) to 6 V at a max. of 6 A. Before starting the reaction, the pH value of the initial solution is

measured. Afterwards, 5 mL of ethanol is added by a volumetric pipette and the measuring started immediately (working in pairs). After approx. 5 min, the measuring can be stopped. The pH value is now measured again. Finally, a few drops of silver nitrate solution are added to the reaction solution while swiveling.

For the acoustical (qualitative) analysis using the Chemophon: The procedure is carried out analogously to the graphical analysis. - For disposal, see 3.4.

Observation: In accordance with the literature data of analogous solvolyses in a methanol/water solution in a 4:1 ratio [19], (1-bromoethyl)benzene, as seen by the varying slopes of the electrical conductance (Figure 10), reacts much faster than benzyl bromide [19]. Regarding the initial solution, the pH value, measured with a pH-reactive strip, is neutral, and after the reaction it is approx. pH= 3. When aqueous silver nitrate solution is added after completing the reaction totally (with no further reactants remaining observable by no further rise of conductance; ~ 15 min), a white compound is precipitated. By contrast, the blank sample of the reactants only show slight hazes of the solutions.

Explanation: Under conditions of solvolysis, both reactants dissociate into a carbenium ion and a bromide ion. Both ions are stabilized by the protic polar solvent ethanol, the carbenium ions by a Lewis acid-base-interaction and the bromide ions by hydrogen bonding. The higher dissociation rate of the (1-bromoethyl)benzene compared to benzyl bromide is grounded in the effect of the 'additional' methyl group of the former. As in the case of free radical stabilization, the methyl group with its C-H bonds stabilizes the electron sextet centers of the carbenium ions by hyperconjugation. As the electron deficiency of electron sextet centers is higher than that of septet centers, hyperconjugation of carbenium ions is even more pronounced compared to that of radicals.

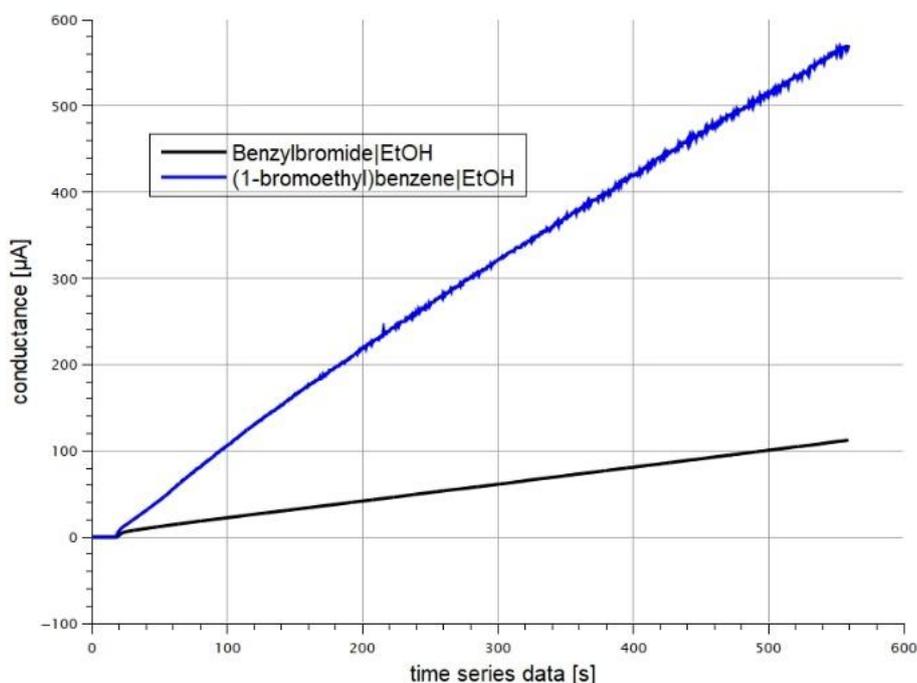


Figure 10. Electrical conductance of the solvolyses of benzyl bromide (black curve) and (1-bromoethyl)benzene (blue curve) with ethanol in comparison

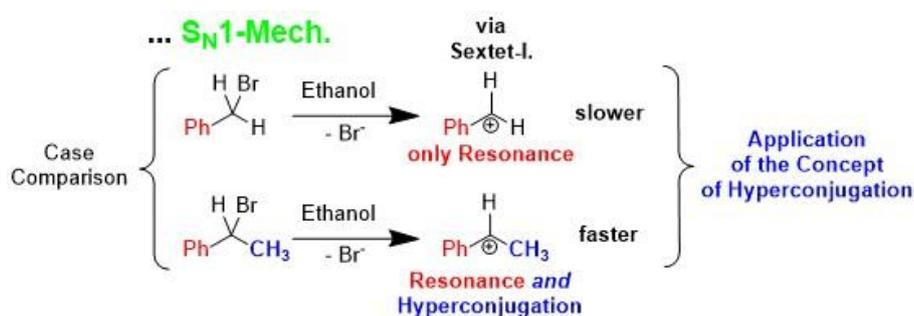


Figure 11. Comparing carbenium ions as sextet intermediates of S_N1 solvolyses of benzyl bromide and (1-bromoethyl)benzene with ethanol: application of the concept of hyperconjugation

5. Discussion

The experimental learning opportunity presented here initially represents a theoretical concept that has been thoroughly investigated for its general experimental feasibility and for unambiguous and reproducible results, but has not yet been tested by a real learning group.

However, we assume that the entire experiment, starting with the photobromination reaction and with guided reflection of the material at appropriately chosen time points, can realistically be carried out in three time hours,

which usually corresponds to two double lessons in school.

Radical substitution should already have been covered fundamentally in class. In addition, the influence of substituents on the stability of electron-deficient centers via I or M effects should have been covered.

The central motivation of the entire learning proposal is the exemplary transfer of an important concept in organic chemistry from one known mechanism to another, with learners developing the new mechanism argumentatively by applying simple basic organic chemistry concepts. For our part, however, it is perfectly conceivable to conduct the two parts of the experiment separately if necessary, since their respective key messages stand on their own.

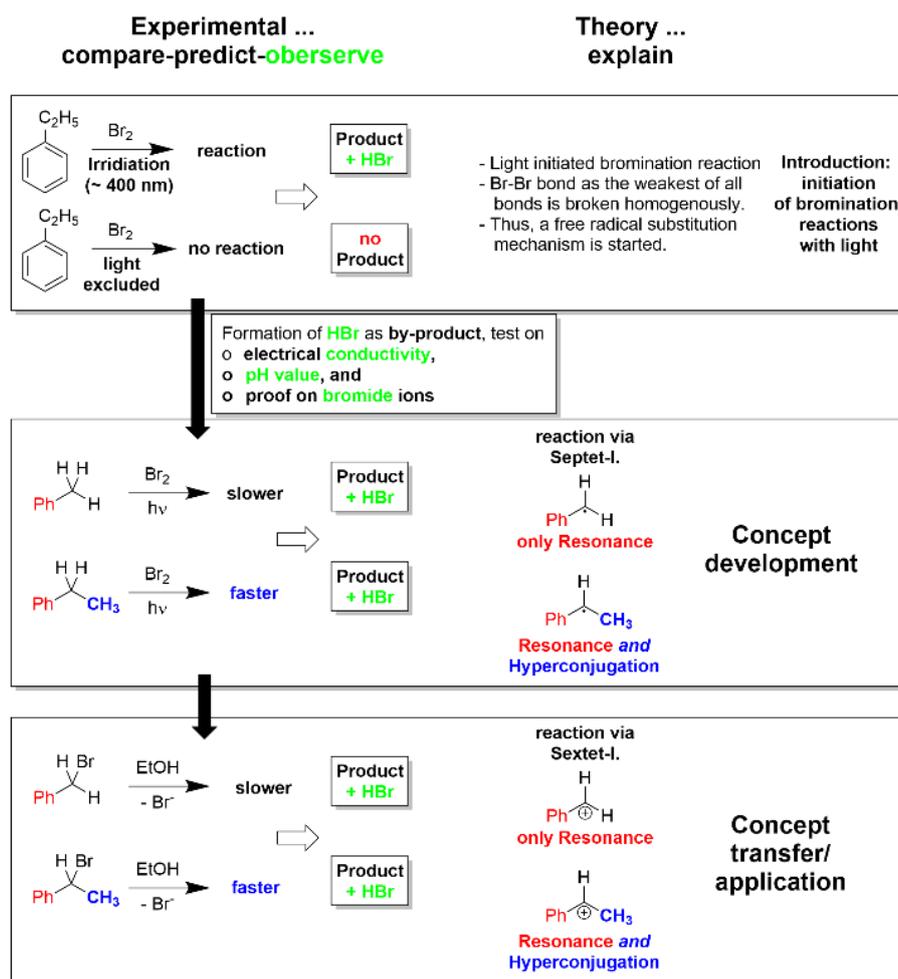


Figure 12. Learning Environment for the development and the transfer of the concept of hyperconjugation with entangled experimental and theory phases

6. Conclusion and Outlook

The experimental and theoretical case comparison of photobromination reactions presented here, designed as a task of contrasting cases (corresponding to the compare-predict-observe-explain cycle (CPOE)) [15], seems to be suitable for learners developing the concept of hyperconjugation. Being a subconcept of the donor-acceptor concept as a basic concept in general chemistry, hyperconjugation is connectable to typical ways of thinking in chemistry. The additional case comparison of nucleophilic substitution reactions (S_N1) creates an opportunity for learners to transfer and apply the concept of hyperconjugation in another mechanistic field. Due to the structural feature of the phenyl ring, all reactants show a good reactivity, leading to high reaction rates. As liquids or solids, they are manageable much better than gaseous reactants if all safety advice is observed. The analytical methods (without any large-scale spectroscopy) are suitable for high school education, but could also be used for first-year organic chemistry students and in teacher training in university labs as well.

According to Figure 12, in the future, we plan to work out a new learning environment with entanglement of experiment and theory and test it with groups of high school students. By means of an interview study, we want to find out whether student's ability to transfer concepts across mechanistic borders is improved by it.

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