Preparation of Cyclohexene (16A/PC)

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1 Introduction

The aim of this experiment was to synthesise cyclohexene through the dehydration of cyclohexanol. Phosphoric acid was used as a catalyst and can be seen to behave catalytically in the reaction mechanism (figure 1) since it is regenerated by the proton donation from the more acidic hydronium ion ($pK_a(H_3O^+) = -0.7$[1], $pK_a(H_3PO_4) = 2.16$[2]) in the final step.

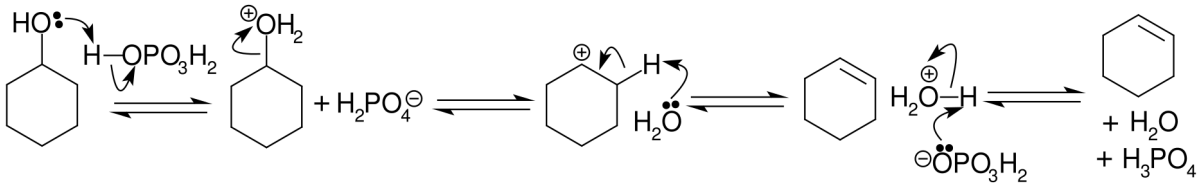

Figure 1: Mechanism for the dehydration reaction.

The overall chemical equation for this reaction is given by equation 1.0.1.

$$C_6H_{11}OH(l) \xrightarrow{H_3PO_4} C_6H_{10}(l) + H_2O(l) \tag{1.0.1}$$

An azeotropic distillation was completed in this experiment with an azeotrope (a mixture of two liquids that boils at constant composition)[3] formed between the water and cyclohexene, hence depressing the boiling temperature of the mixture due to positive excess Gibbs free energy associated with the unfavourable mixing of this liquids relative to an ideal mixture.[4] This distillation removed the products of the reaction from the reaction vessel hence driving the reaction to completion.

2 Experimental Method

A mixture of concentrated (85 %) phosphoric acid (10.0 cm^3) and cyclohexanol (24.00 g) was distilled at 85–95 °C (with collection in a ice-cold flask) until white fumes were evolved from the mixture residue. This produced a colourless, but cloudy distillate containing 3.0 cm^3 of water (69 % of the theoretical maximum volume). The distillate was washed with 15 cm^3 of concentrated sodium chloride solution and then the organic product was dried using anhydrous calcium chloride. After drying the organic product was very slightly cloudy. A further distillation of the dry organic product was completed (boiling temperature 81.5 °C compared to the literature value of 82.9 ± 0.2 °C)[5] and 3.81 g of perfectly clear cyclohexene (19.4 % yield) was collected in a ice-cold flask.

2.1 Calculations

2.1.1 Percentage Yield

From equation 1.0.1, there is a 1:1 molar ratio between the cyclohexanol and the cyclohexene.

$$\text{Amount of Product Synthesised} = \frac{3.81\,\text{g}}{(6(12.011) + 10(1.008))\ \text{g mol}^{-1}} = \frac{3.81\,\text{g}}{82.15\,\text{g mol}^{-1}} = 46.4 \times 10^{-3}\,\text{mol}$$

$$\text{Theoretical Product Yield} = \frac{24.00\,\text{g}}{(6(12.011) + 12(1.008) + 15.999)\ \text{g mol}^{-1}} = \frac{24.00\,\text{g}}{100.2\,\text{g mol}^{-1}} = 0.2396\,\text{mol}$$

$$\therefore \text{Percentage Yield} = \frac{46.4 \times 10^{-3}\,\text{mol}}{0.2396\,\text{mol}} \times 100\,\% = 19.4\,\%$$

[1] Jean-Lewis Burgot. 'New point of view on the meaning and on the values of $K_a^\circ(H_3O^+, H_2O)$ and $K_b^\circ(H_2O, OH^-)$ pairs in water'. In: *Analyst* 123 (1998), pp. 409–410.

[2] W. M. Haynes, ed. *CRC Handbook of Chemistry and Physics*. 97th ed. Boca Raton: CRC Press, 2016, Dissociation Constants of Inorganic Acids and Bases, 5-87.

[3] Richard Rennie, ed. *Oxford Dictionary of Chemistry*. 7th ed. Oxford: Oxford University Press, 2016, pp. 53.

[4] Peter Atkins and Julio de Paula. *Physical Chemistry*. 10th ed. Oxford: Oxford University Press, 2014, Azeotropes, pp. 207.

[5] Haynes, see n. 2, Physical Constants of Organic Compounds, 3-134.

2.1.2 Percentage of Water Obtained Compared to the Theoretical Maximum

Also from equation 1.0.1, there is a 1:1 molar ratio between the cyclohexanol and the water. The density of water at 20.0 °C is $0.998\,\mathrm{g\,cm^{-3}}$.[6]

$$\text{Theoretical Yield of Water} = 0.2396\,\mathrm{mol} \times (2(1.008) + 15.999)\,\mathrm{g\,mol^{-1}} = 4.317\,\mathrm{g}$$
$$\text{Mass of Obtained Water} = 0.998\,\mathrm{g\,cm^{-3}} \times 3.0\,\mathrm{cm^3} = 3.0\,\mathrm{g}$$
$$\therefore \text{Percentage} = \frac{3.0\,\mathrm{g}}{4.317\,\mathrm{g}} \times 100\,\% = 69\,\%$$

3 Analysis

During the experiment both cyclohexanol and water impurities were removed from the product. After the first distillation the product was heavily contaminated with water and hence appeared cloudy due to the emulsion formed. Washing with concentrated sodium chloride solution removed most of this water due to the negative Gibbs free energy change associated with the further solvation of the sodium and chloride ions in the saturated solution. In addition this washing removed any cyclohexanol from the crude product since it is soluble in water,[7] although it is likely that little cyclohexanol was present as an impurity since it has a high boiling temperature of 160.9 ± 0.2 °C.[8] The subsequent drying with anhydrous calcium chloride was intended to remove any remaining water and the final distillation removed byproducts formed from side reactions (e.g. nucleophilic substitution).

3.1 Tests Performed

Three drops of a solution of bromine in dichloromethane (since cyclohexene is insoluble in water,[9] also a different product of (1S,2S)-2-bromocyclohexan-1-ol would result from using an aqueous bromine solution although this is inconsequential since this is also colourless) were added to approximately $1\,\mathrm{cm^3}$ of the collected cyclohexene. This caused the bromine solution to change colour from red-orange to colourless as the reaction shown in figure 2 occurred. This demonstrated the presence of the nucleophilic double bond in the cyclohexene product, hence suggesting the intended product was successfully synthesised.

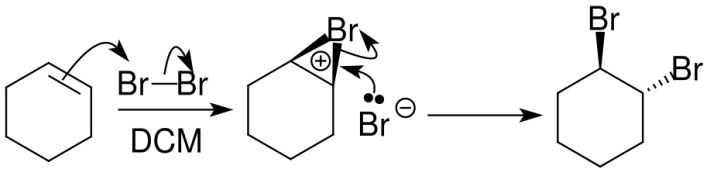

Figure 2: Mechanism for the electrophilic addition reaction between the cyclohexene and bromine.

3.2 Boiling Temperature

The boiling temperature of the distillate collected appears to be close to the published value (1.4 °C lower) and there was no noticeable range of boiling temperatures which suggests that the cyclohexene produced was fairly pure. However the true difference in boiling temperature is slightly greater than this since the air pressure in the laboratory was greater (by approximately 0.575 kPa) than the air pressure for which the literature value is reported at (101.325 kPa). This would have slightly elevated the boiling temperature of the product (since the vapour pressure of the liquid would have to be greater for boiling to occur) thus the true difference in boiling temperatures between pure cyclohexene and the product was instead approximately 1.6 °C. The calculations used to determine these numbers are included in section 3.2.1.

This lower boiling temperature could be due to a combination of factors such as a slight cooling of the vapour as it travelled up the still head and the presence of impurities in the vapour. The product could have been analysed using NMR spectroscopy to definitively identify any impurities in the product, and the thermometer could have been temporarily moved to a position just above the boiling liquid during the distillation in order to obtain a more accurate value for its boiling temperature. An electronic thermometer could also have been used hence giving a more precise temperature reading and allowing the easier establishment of the range of boiling temperatures for the solution.

However it is likely that there was still a little water impurity in the product after the drying since it was very slightly cloudy when compared to the distilled product. This may have been since the solution was not left to dry for 10 minutes as recommended

[6] Haynes, see n. 2, Standard Density of Water, 6-7.
[7] Haynes, see n. 2, Physical Constants of Organic Compounds, 3-134.
[8] Haynes, see n. 2, Physical Constants of Organic Compounds, 3-134.
[9] Haynes, see n. 2, Physical Constants of Organic Compounds, 3-134.

in the laboratory manual due to time constraints, however a possible improvement to the method could be be grind the drying agent into a fine powder to increase its surface area and thus reduce the time required to dry the product.

3.2.1 Boiling Temperature Calculations

The approximate laboratory air pressure was calculated using an adjusted sea-level air pressure of approximately 102.6 kPa[10] and laboratory altitude of 55.30 m above mean sea level[11] with equation 3.2.1.

$$\Delta P = -\rho g \Delta h \tag{3.2.1}$$

Using $\rho = 1.29\,\mathrm{kg\,m^{-3}}$ (obtained by linearly interpolating between given values to 270 K)[12] and $g = 9.81\,\mathrm{m\,s^{-2}}$. While assuming that the temperature of the air is constant at 270 K and the density of the air remains constant.

$$\text{Laboratory Air Pressure} \approx 102.6 \times 10^3\,\mathrm{Pa} - 1.29\,\mathrm{kg\,m^{-3}} \times 9.81\,\mathrm{m\,s^{-2}} \times 55.30\,\mathrm{m} = 102\,\mathrm{kPa}$$

$$\therefore \text{Difference from Published Pressure} \approx 101.325\,\mathrm{kPa} - 102\,\mathrm{kPa} = 0.575\,\mathrm{kPa}$$

The Clausius-Clapeyron equation (equation 3.2.2) and can be rearranged to make T_2 the subject (equation 3.2.3) and hence can be used to determine the boiling temperature elevation caused by this pressure difference.

$$\log_e\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3.2.2}$$

$$T_2 = \frac{T_1 \Delta H_{\text{vap}}}{R T_1 \log_e\left(\frac{P_1}{P_2}\right) + \Delta H_{\text{vap}}} \tag{3.2.3}$$

With $\Delta H_{\text{vap}}(82.9\,^\circ\mathrm{C}) = 30.46\,\mathrm{kJ\,mol^{-1}}$ (assuming this remains constant in the temperature range considered).[13]

$$\begin{aligned}\text{New boiling temperature} &\approx \frac{(82.9 + 273.15)\ \mathrm{K} \times 30.46 \times 10^3\,\mathrm{J\,mol^{-1}}}{8.31\,\mathrm{J\,mol^{-1}\,K^{-1}} \times (82.9 + 273.15)\ \mathrm{K} \times \log_e\left(\frac{101.325\,\mathrm{kPa}}{102\,\mathrm{kPa}}\right) + 30.46 \times 10^3\,\mathrm{J\,mol^{-1}}} \\ &\approx 356\,\mathrm{K} = 83.1\,^\circ\mathrm{C}\end{aligned}$$

$$\therefore \text{Difference in Boiling Temperature} \approx 83.1\,^\circ\mathrm{C} - 81.5\,^\circ\mathrm{C} = 1.6\,^\circ\mathrm{C}$$

3.3 Yield

The overall percentage yield obtained was very low (19.4 %), despite the fairly high percentage of water obtained compared to the theoretical maxima (69 %) after the initial distillation. However this water percentage is likely to be a fairly inaccurate measure of the initial yield since the water which formed an emulsion in the organic layer is not represented in this figure and it doesn't account for any water which was originally contained within the reagents (such as the water in the concentrated phosphoric acid solution) which may have also been collected.

Some of the cyclohexene was lost during transfers both due to some liquid remaining the in previous vessel and due to evaporative losses. To reduce these evaporative losses during transfer the flask containing the product could be cooled in an ice bath at all intermediate stages in the experiment, not just during distillation, hence reducing the temperature of the liquid being transferred. In addition after the distillations some of the cyclohexene remained in the distillation apparatus. To reduce this a 'chaser' solvent with a higher boiling temperature than the cyclohexene – such as toluene – could have been added to the reaction vessel at the end of the first distillation to force any remaining cyclohexene into the collection flask.[14] This solvent would then be removed from the cyclohexene by the second distillation step.

The yield calculated is likely to also have been low since not all of the product was distilled for a second time (due to the small size of the round-bottomed flask used) and the second distillation itself was stopped prematurely due to time constraints.

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[10] TWC Product and LLC Technology. *Weather History for EGNV - February, 2018.* 27th Feb. 2018. URL: `https://www.wunderground.com/history/airport/EGNV/2018/2/27/DailyHistory.html` (visited on 28/02/2018), Pressure at 4:20 PM.

[11] Ordnance Survey. *OS Maps Online.* URL: `https://osmaps.ordnancesurvey.co.uk/54.76830,-1.57110,20` (visited on 28/02/2018), Latitude: 54.7683°, Longitude: −1.5711°.

[12] Haynes, see n. 2, Thermophysical Properties of Air, 6-18.

[13] Haynes, see n. 2, Enthalpy of Vaporization, 6-141.

[14] Peter Samal. *Synthesis of Cyclohexene, The Dehydration of Cyclohexanol.* URL: `https://people.chem.umass.edu/samal/269/cyclohexene.pdf` (visited on 03/03/2018).