into each flask. Incubate the solutions for 3-10 min to complete oxidation of the sugars. Using the pipette, add 2.0 mL of the 1 M HCl solution and titrate the excess of iodine with the thiosulfate solution until pale-yellow coloration. Then add 3-5 drops of 1 % starch solution and continue the titration with shaking until disappearance of blue coloration.

Repeat the titrations as necessary. Write down the titration results and the accepted titrant volumes.

Questions and assignments

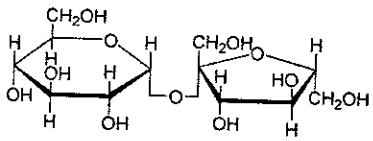
9. Derive the formula for calculation of the molecular mass of a sugar depending on the mass of the weighed amount and the titration results. Explain the symbols used.

10. Write down the equation of iodine reaction with an alkali.

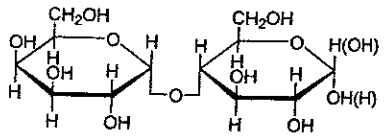
11. Write down the equation of the reaction of a sugar oxidation by iodine (give the sugar formula in any abbreviated form, pay attention to the reaction stoichiometry).

12. Using the formula derived in *i.* 9, calculate the molecular mass *M* (g/mol) of each of the given sugars.

13. *Identification of sugars.* For titrimetric determination of the molecular masses, you could have been provided with the following sugar types: tetrose, pentose, hexose, heptose, and a disaccharide (either *D*-sucrose or *D*-lactose).



D-sucrose



D-lactose

Analyze the calculated molecular masses and decide about the sugar types you have been actually given. If a disaccharide is one of you answers, indicate whether it was *D*-sucrose or *D*-lactose.

14. Comparing the results obtained in Parts 1 and 2, decide which of the sugar samples studied by titration was also given for the ozazone synthesis.

15. Titration of iodine with thiosulfate must be carried out in a neutral or weakly acidic medium (pH≤6.5), since side reactions are observed in an alkaline medium as well as in an acid excess. Write down equations of the side reactions.

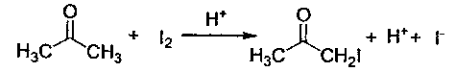
16. Oxidizing properties of divalent copper are behind another widespread method of saccharides determination, which ends up with iodometric titration. Write down the reaction of a reducing saccharide with Cu(II) and the reaction entered by the excess of unreacted copper.

The 41st Mendeleev Olympiad (2007)

Kinetics of iodination of acetone in acidic medium

(authors Khvalyuk V.N., Beklemishev M.K., Golovko Yu.S.)

The irreversible reaction between dimethyl ketone and iodine in aqueous solution is catalyzed by protons:



The corresponding kinetic equation can be written as:

$$w = -\frac{d[I_2]}{dt} = k \cdot [CH_3COCH_3]^x \cdot [I_2]^y \cdot [H^+]^z$$

The initial rate is measured in order to determine the rate constant k and the reaction orders x, y, and z with respect to every reacting substance. The initial rate can be determined by following the decrease of iodine concentration in the reaction mixture during a definite period of time (15 min in the present experiment) after the reaction start. The curvature of the kinetic curve can be neglected, when the conversion degree of reagents is low. Thus, it is possible to treat the average rate during a short period as the initial reaction rate w_0:

$$w_0 = -\frac{d[I_2]_0}{dt} = k \cdot [CH_3COCH_3]_0^x \cdot [I_2]_0^y \cdot [H^+]_0^z,$$

where $[CH_3COCH_3]_0$, $[I_2]_0$, and $[H^+]_0$ are the initial concentrations of dimethyl ketone, iodine and hydrogen ions, respectively.

Sodium acetate is added to the reaction mixture in order to stop the reaction at the required time point. Acetate reacts instantly with H^+ resulting in formation of acetic acid and decreasing the concentration of H^+ ions to the values, when the reaction takes place at a negligibly low rate. Since the reaction of iodination is not completely stopped (it is just slowed down), the reaction mixture must be titrated as fast as possible, once sodium acetate is added.

The excess of unreacted iodine in the reaction mixture is determined by titration with sodium thiosulfate using starch as an indicator. Calculate the initial molar

concentrations of iodine, dimethyl ketone and HCl in flasks **A**–**D**, hypothetically taking the dimethyl ketone concentration in the 100 mL flask as 1 M.

Reagents, labware and equipment

Item	*Quantity*	*Label*
For each participant		
250 mL volumetric flask	1 pc.	
100 mL conical flask with stopper	4 pcs.	A, B, C, D
5.00 mL graduated pipette	1 pc.	
10.00 mL graduated pipette	1 pc.	
Pipette filler	1 pc.	
Stopwatch	1 pc.	
Distilled water in wash bottle	0.5 L	H_2O
Spatula	1 pc.	
Glass rod	1 pc.	
100 mL beaker	1 pc.	
Laboratory stand with burette clamp	1 pc.	
Burette	2 pcs.	
50 mL beaker (to be used under the burette)	2 pcs.	
Funnel for filling the burette	2 pcs.	
150 mL titration flask	2 pcs.	
20 mL measuring cylinder	1 pc.	
100 mL measuring cylinder	1 pc.	
Hydroxylamine hydrochloride, 0.2 M solution	50 mL	$NH_2OH \cdot HCl$
Dimethyl ketone, in 100 mL volumetric flask (concentration to be determined)	-	Acetone
On the table of common use		
Analytical balance	1 pc.	
Iodine, aqueous solution (concentration to be determined)	1 L	I_2
Sodium acetate	250 g	CH_3COONa
Sodium hydroxide, aqueous solution (concentration to be determined)	1 L	NaOH
Sodium thiosulfate, standard solution (see the exact concentration on the label)	1 L	$Na_2S_2O_3$ (___M)
Hydrochloric acid, 0.1000 M aqueous solution	1 L	HCl
Starch, 1 % solution (in the dropper)	25 mL	Starch
Methyl Orange, alcohol solution (in the dropper)	25 mL	Methyl Orange

Part 1.

Standardization of iodine solution

a) Using the pipette, transfer a 5.00 mL aliquot of the iodine aqueous solution into the 100 mL conical flask labeled **A**. Using the measuring cylinder, add 10 mL of distilled water.

b) Titrate the obtained iodine solution with the standard sodium thiosulfate solution to the pale-yellow coloration. Then add 3 drops of the starch solution and continue titrating until the blue coloration disappears (fig. 1/2007).

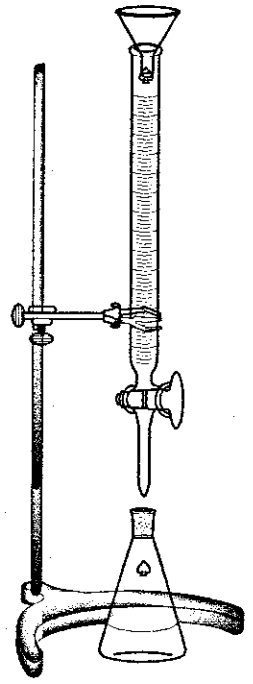


Fig. 1/2007. A typical titration setup.

c) Repeat the titration as needed. Write down the titration results and the accepted titrant volume, mL.

d) Wash the flask **A**.

Questions and assignments

1. Calculate the iodine concentration in the given solution.

Part 2.

Study of dimethyl ketone iodination kinetics in acidic medium

e) Bring up the dimethyl ketone solution to the mark in the 100 mL volumetric flask with distilled water and mix well. *Caution*: the solution warms up upon mixing. Hold the stopper tightly, periodically taking it out to release the pressure inside the flask.

f) Pour a portion of dimethyl ketone solution into the beaker. Add the hereunder given volumes of distilled water, 0.1000 M hydrochloric acid and dimethyl ketone solution to the conical flasks labeled **A**, **B**, **C**, and **D** (stopper the flasks after adding the solutions).

Flask	Volume, mL			
	Water	HCl	Dimethyl ketone solution	Iodine solution
A	5.00	5.00	5.00	5.00
B	0	5.00	5.00	10.00
C	0	5.00	10.00	5.00
D	0	10.00	5.00	5.00

g) Using the pipette, transfer a 5.00 mL aliquot of the iodine solution into the flask **A**. Switch on the stopwatch exactly when you start adding the iodine solution. Stopper the flask tightly, mixt the flask contents well and incubate for 15 min.

h) Meanwhile, prepare the sodium acetate solution. Weigh ~5.0 g of sodium acetate in the 50 mL beaker. Using the measuring cylinder, add 80 mL of water and stir the mixture to completely dissolve the salt.

i) In 15 min, add 10 mL of the sodium acetate solution to the reaction mixture using the cylinder and stir.

j) Titrate the iodine excess in the reaction mixture with the standard thiosulfate solution. Write down the titration results.

k) Repeat i. f), g), i), and j) for the flasks **B**, **C**, and **D**, adding the solutions in the amounts shown in the above table.

Questions and assignments

2. Calculate the initial rate of iodine consumption $-\frac{d[I_2]}{dt}$ (in $mol \cdot L^{-1}s^{-1}$).

3. Using the initial reaction rates and initial concentrations, calculate the reaction orders x, y, and z.

$$w = -\frac{d[I_2]}{dt} = k \cdot [CH_3COCH_3]^x \cdot [I_2]^y \cdot [H^+]^z$$

4. Write down the kinetic reaction.

Part 3.

Standardization of the alkali

l) Fill the second burette with the alkali solution. Titrate a 10.00 mL aliquot of 0.1000 M HCl solution in the presence of Methyl orange with the alkali solution. The titration endpoint is determined by the color transition of the indicator from pink to yellow.

m) Repeat the titration as needed. Write down the titration results and the accepted titrant volume, mL.

Questions and assignments

5. Calculate the concentration of the alkali solution.

Determination of the dimethyl ketone concentration

n) Transfer a 4.00 mL aliquot of the dimethyl ketone solution into the 250 mL volumetric flask and bring up to the mark with water.

o) Transfer a 10.00 mL aliquot of the obtained dimethyl ketone solution from the 250 mL flask into a 100 mL conical flask. Add 10 mL of 0.2 M hydroxylamine hydrochloride solution, stopper the flask, stir the obtained mixture and store it for 5 min.

p) Titrate the mixture with the alkali solution in the presence of Methyl orange until the indicator color changes from pink to yellow.

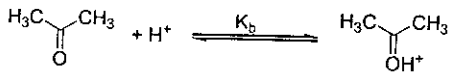
q) Repeat the titration as needed. Write down the titration results and the accepted titrant volume, mL.

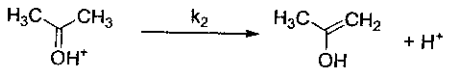
Questions and assignments

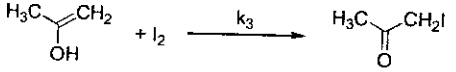
6. Calculate the dimethyl ketone concentration in the initial solution.

7. Knowing molar concentrations of all the reagents, calculate the rate constant k for the flasks **A** – **D** using the kinetic equation you have derived earlier.

8. The catalytic iodination of dimethyl ketone you have studied includes the following steps:


(1) (rapidly)


(2) (rate-limiting stage)


(3) (rapidly)

The rate of the entire process is determined by that of enol formation (2).

Use the above scheme to derive the theoretical kinetic equation of dimethyl ketone iodination (show dimethyl ketone as A).

9. Write down the condition when the derived equation coincides with the experimental kinetic equation $w = k'[A][H^+]$ that you had to obtain doing when the experimental parts.

10. Iodination of dimethyl ketone can be also carried out in an acid-free medium, the initial rate being considerably lower in this case than in an acidic medium. Draw the kinetic curves in the acid-containing and acid-free media.

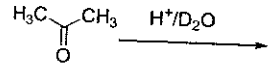
11. Compare the rate constants of bromination and iodination of dimethyl ketone with Br_2 and I_2 under the conditions of your experiment (encircle one of the following):

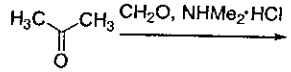
a) $k_{Br} < k_I$; b) $k_{Br} > k_I$; c) $k_{Br} \cong k_I$; d) $k_{Br} >> k_I$

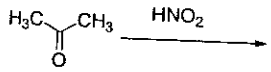
12. Messinger's method is another procedure for dimethyl ketone determination. The method involves addition of an excess of iodine to the alkaline aqueous solution of dimethyl ketone with subsequent titrimetric determination of the unreacted iodine after acidification of the mixture. Write down the equation of the reaction occurring upon iodine addition to dimethyl ketone.

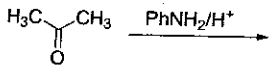
13. Is the Messinger's method selective towards dimethyl ketone? Write down the reaction supporting your answer.

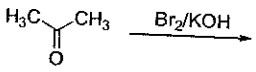
14. Write down the structures of the products of the following reactions.

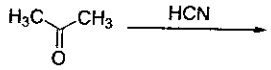












The 42nd Mendeleev Olympiad (2008)

Identification of organic compounds

(author Beklemishev M.K.)

The task consist of two parts: identification of organic compounds, some of which are common medicines, and quantitation of analgin in tablets.

Reagents, labware and equipment

Item	*Quantity*	*Label*
For each student		
Laboratory stand with clamp and ring	1 pc.	
250 mL Erlenmeier flask, for titration	3 pcs.	
100 mL volumetric flask, for the sample	1 pc.	
25 mL burette	1 pc.	
10 mL pipette	3 pcs.	
Pipette filler	1 pc.	
100 mL beaker	1 pc.	
50 mL measuring cylinder	1 pc.	
Spatula	3 pcs.	
Glass rod	3 pcs.	
Eyedropper	6 шт.	
Paper towels	1 pack	
Distilled water in wash bottle	0.5 L	H_2O
p-Nitrophenol (for analysis, in a vial)	1 g	One of **A-G**
Benzoic acid (for analysis, in a vial)	1 g	One of **A-G**
Salicylic acid (for analysis, in a vial)	1 g	One of **A-G**
Acetylsalicylic acid (for analysis, in a vial)	1 g	One of **A-G**
Paracetamol (for analysis, in a vial)	1 g	One of **A-G**
Streptocide White (for analysis, in a vial)	1 g	One of **A-G**
Analgin (for analysis, in a vial)	1 g	One of **A-G**
Analgin (for determination, in a beaker)	weighed amount	**H**
Potassium permanganate, 0.04 M aqueous solution	15 mL	$KMnO_4$
Iron(III) chloride, 0.01 M aqueous solution	15 mL	$FeCl_3$
Sodium nitrite, 0.1 M aqueous solution	15 mL	$NaNO_2$