2005

- 1. $KH(IO_3)_2$ is the product to be synthesized. Taking into account the Lathimer diagrams and chemical properties of iodine with stable oxidation states of +7, +5, and -1, one can expect that the oxidation product will be iodate, whereas the amount of K_2CO_3 added to the solution containing the product of iodine oxidation suggests that the iodine: potassium ratio equals 2:1.
- 2. The first step must be conducted in an acidic medium. Since the difference of $E^{\circ}(\text{ClO}_3^{-}/\text{Cl}^{-})$ and $E^{\circ}(\text{HIO}_3/\text{I}_2)$ potentials is maximal in an acidic medium, using pH 0 at the first step of the synthesis would contribute to a higher yield. Protonation of anions of oxygen-containing acids contributes to higher reactivity due to the fact that an electron transfer onto a neutral particle happens easier than than onto an anion. Thus, the process rate will be higher in an acidic medium.
- 3. Comparison of potentials at the Lathimer diagram suggests that chlorate is the oxidizer.
- 4. The side processes accompanying the first synthesis step are: iodine evaporation, evolution of Cl_2 and ClO_2 :

5. Equations of the reaction of the target product synthesis:

$$5KClO_3 + 3I_2 + 3H_2O \rightarrow 6HIO_3 + 5KCl;$$

 $4HIO_3 + K_2CO_3 \rightarrow 2KH(IO_3)_2 + H_2O + CO_3.$

- 6. Concentrated HCl is a catalyst, since it adjusts the required pH value (see above), not being consumed in the reaction.
- 7. As it is seen from item 2, the reaction rate should increase at higher hydrochloric acid concentrations. Most probably this will be accompanied by a lowered yield due to enhanced formation of by-products (Cl₂ μ ClO₂), whereas the neutralization of acid with potassium carbonate will lead to a great amount of KCl in the precipitate.
- 8. Equation of the reaction between KI and $KH(IO_3)_2$ in the hydrochloric acid-containing medium is:

$$KH(IO_3)_2 + 10KI + 11HCI \rightarrow 11KCI + 6I_2 + 6H_2O.$$

9. Equation of the reaction between I₂ and Na₂S₂O₃:

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI.$$

- The ratio of H^{\dagger} to oxidizer in X must be equal to 1:12.
- . KH(IO₃)₂.
- 15. KH(IO₃)₂ is an acid salt.
- 16. The product is a salt of iodic acid HIO₃.

- 17. Iodine was the limiting reagent. It was necessary to constantly add new portions of iodine, as it was being consumed by an excess of potassium chlorate during the first synthetic step.
- 18. The reasons for a lower product yield:
 - losses of iodine due to sublimation;
 - chlorine evolution in the course of the reaction;
 - mechanical losses.
- 19. The initial crystallization allows purification of the product from all the listed substances: HCl, KCl, KIO₃, K₂CO₃, KClO₃, but not the product itself.
- 20. Substances with poor solubility in water and those present in an excess in the mother waters (KCl, KIO₃, KClO₃) are removed by recrystallization.
- 21. According to Pauling's rule, iodic acid is strong, since there are two oxo (=O) and only one hydroxyl (-OH) groups. Thus, iodic acid should be close to nitric and perchloric acids by strength.

The estimated pK_{α} value for $(OH)_m XO_n$ acids equals 8-5n; n=2 in the case under consideration, thus $pK_{\alpha} \approx -2$. According to the literature data, $pK_{\alpha}(HIO_3) \approx 0.8$.

22. Let us write down equations of the processes and calculate the corresponding ΔG values:

$$\Delta_{r}G^{\circ}$$
(1) HIO₃ + 5H⁺ + 6e⁻ \rightarrow Γ + 3H₂O
$$-6F \cdot E^{\circ}_{1}$$
(2) IO₃⁻ + 3H₂O + 6e⁻ \rightarrow Γ + 6OH⁻

$$-6F \cdot E^{\circ}_{2}$$
(3) HIO₃ \rightarrow IO₃⁻ + H⁺

$$-RT \cdot \ln K_{\alpha}$$
(4) H₂O \rightarrow OH⁻ + H⁺
Thus,

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$$\Delta_r G^{\circ}_{1} - \Delta_r G^{\circ}_{2} = \Delta_r G^{\circ}_{3} - 6\Delta_r G^{\circ}_{4},$$

$$-6F(E_{1}^{\circ}-E_{2}^{\circ})=-RT\ln K_{\alpha}+6RT\ln K_{W},$$

After the expression conversion:

$$pK_a = 6 \cdot 14 - 6 \cdot (E_1^o - E_2^o) / 0.059 = 6 \cdot 14 - 6 \cdot (1.192 - 0.204) / 0.059 = -16.44$$

23. For instance, hydrofluoric acid HF forms an acid salt (KHF₂).

and: