

ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

Improvement of a Process for Synthesis of Thioglycolic Acid

V. R. Islamgulova, E. N. Shitova, S. G. Akhmerova, and A. P. Tomilov

Research and Technological Institute of Herbicides and Plant Growth Regulators with Pilot Plant,
Ufa, Bashkortostan, Russia

State Research Institute of Organic Chemistry and Technology, Moscow, Russia

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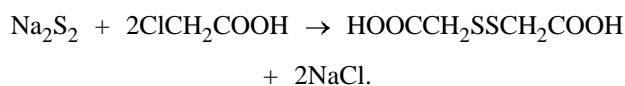
Abstract—An environmentally clean process was proposed for synthesis of thioglycolic acid by condensation of monochloroacetic acid with sodium disulfide, followed by electrochemical reduction of the resulting mixture.

Thioglycolic acid (TGA) and its derivatives are used in production of polymers, drugs, pesticides, dyes, flotation agents, and perfumes [1].

The known routes to TGA are based on reactions of monochloroacetic acid (MCAA) in the form of sodium salt with various sulfur derivatives. MCAA reacts with sodium hydrosulfide in one stage under H_2S pressure of 5–50 atm; yield of TGA 81.0–90.8% [2–5]. The reaction of MCAA with sodium thiosulfate yields sodium 5-carboxymethyl thiosulfate; its hydrolysis in the presence of oxidants affords TGA, yield 92–96% [6–8]. The reaction is sensitive to oxidants, whose presence results ion formation of dithiodiglycolic acid (DTDGA) as impurity [8]. DTDGA can be prepared in a reasonable yield by the reaction of sodium disulfide with sodium monochloroacetate [9] and can be subsequently reduced to TGA (yield 98–99%) on hydrogenation catalysts at 140°C and hydrogen pressure of 50 atm [10]. DTDGA can also be reduced electrochemically (yield 80%) [11].

Thus, the known procedures for preparing TGA either involve the use of high pressures or require thorough protection of the reaction mixtures from atmospheric oxygen. Taking into account published data and the availability of starting compounds for commercial synthesis, we chose the route based on the reaction of MCA with sodium disulfide, followed by electrochemical reduction of the resulting DTDGA.

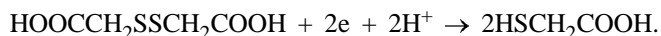
MCA reacts with sodium disulfide as follows:



First, we determined the optimal conditions for this reaction: 70–80°C, 30 min. Below 70°C the reaction

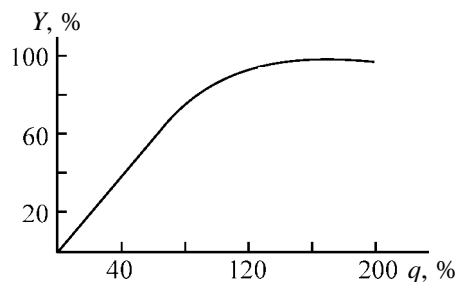
takes much longer time, and above 80°C by-products start to form. Under the optimal conditions, the yield of DTDGA is nearly quantitative.

Electrochemical reduction of DTDGA occurs with the consumption of $2F$ of electricity per mole:



According to published data, the reaction occurs with a high yield in a sulfuric acid solution on a lead anode; however, the process was not optimized.

For the success of the electrochemical synthesis, TGA should be stable under the electrolysis conditions. We have studied the behavior of pure TGA in aqueous sulfuric acid at 25–30°C and current density of 200 A m^{-2} . The amount and purity of TGA remained unchanged after passing $2F$ of electricity per mole. Similar results were obtained when a double amount of electricity was passed in the course of electroreduction of DTDGA (see figure). The maximal amount of TGA formed remains unchanged after passing 200% amount of electricity relative to the stoichiometry, with the optimal amount being 140–150%.



TGA yield Y as a function of the amount of electricity passed q (relative to stoichiometry). 20–25°C; current density 200 A m^{-2} .

Table 1. Influence of the current density on the yield and quality of TGA. 20–25°C; 0.3 mol of DTDGA loaded; amount of electricity passed 11.3 A h (140% relative to stoichiometry)

Run no.	i , A m ⁻²	Obtained, mol		DTDGA conversion, %	TGA yield, %	Current efficiency, %	Content in isolated product, %	
		TGA	DTDGA				TGA	DTGA
1	100	0.291	0.003	99.0	96.9	69.2	96.0	1.0
2	300	0.288	0.008	97.3	96.1	68.6	95.3	2.7
3	500	0.286	0.010	96.7	95.2	68.0	94.7	3.3
4	700	0.283	0.014	95.3	94.3	67.4	93.3	4.7
5*	500–600	0.290	0.005	98.3	96.7	69.1	96.0	1.7

* Gradual decrease in the current density.

Table 2. Influence of temperature on the TGA yield and DTDGA conversion. Current density 200 A m⁻²; 0.3 mol of DTDGA loaded; amount of electricity passed 140% relative to stoichiometry

Run no.	T , °C	Obtained, mol		TGA yield, %	Current efficiency, %	DTDGA conversion, %
		TGA	DTDGA			
1	20–23	0.289	0.008	96.3	68.8	97.71
2	40–43	0.290	0.007	96.7	69.0	97.3
3	60–62	0.288	0.007	96.0	68.6	97.7
4	70–75	0.285	0.005	95.1	67.9	98.3

To find the optimal parameters of the electrochemical synthesis of TGA, we studied the cathodic reduction of pure DTDGA in 2 N sulfuric acid. The influence of the current density on the yield of TGA is illustrated by Table 1.

As seen from Table 1, with increasing current density the DTDGA conversion and the current efficiency by TGA decrease, which is due to water decomposition with the release of hydrogen. Electrolysis at a low (100 A m⁻²) or gradually decreased (from 500 to 100 A m⁻²) current density affords higher yield and purity of TGA. At low current density, the electrolysis takes longer time; therefore, the gradual decrease of the current density is preferable.

We have studied how the reaction temperature affects the process parameters and the quality of TGA in the range 20–80°C (Table 2).

Table 2 shows that variation of temperature in the range 20–75°C has no appreciable effect on the TGA yield. Slightly decreased yield at elevated temperatures may be due to self-esterification of TGA. Thus, the optimal conditions for the electrochemical reduction of DTDGA are as follows: $i_c = 100–400$ A m⁻², $T = 20–40$ °C, and amount of electricity 140–150% relative to stoichiometry.

We have studied under the same conditions the electrochemical reduction of mixtures from the reaction of MCA sodium salt with sodium disulfide. The yield of TGA in the process was 92–97% based on MCA, and the purity, 94–98%; the amount of wastewater was 2–2.5 times lower as compared to published procedures for TGA synthesis.

EXPERIMENTAL

The content of TGA in the reaction mixture and finished product was determined by iodometric titration, and the total content of TGA and DTDGA, by bromatometric titration in the presence of KBr in acid solution. The DTDGA content in reaction mixtures and isolated products was determined from the difference.

Electrochemical reduction was performed in a glass electrolyzer with a ceramic diaphragm, equipped with a stirrer and a heat-exchange jacket. A lead cathode was used; working surface area 120 cm². Solutions were prepared in double-distilled water.

A solution of 11 g (0.1 mol) of sodium disulfide in 60 ml of water was added to an aqueous solution of 23.3 g (0.2 mol) of sodium monochloroacetate in 26 ml of water, heated to 70–80°C. The resulting

solution was stirred for 30 min, according to [9]. To the cooled reaction mixture, 19.6 g (0.2 mol) of concentrated sulfuric acid was added, and the solution was subjected to electrochemical reduction at 20–45°C and current density gradually decreased from 500 to 100 A m⁻²; 8 A h of electricity was passed. After the electrolysis completion, the catholyte was extracted with ethyl acetate, and the solvent was evaporated; 17.8 g of 95.2% pure TGA was obtained. Yield 92.0%. The waste was a solution of 11.7 g (0.2 mol) of NaCl and 14.9 g (0.1 mol) of Na₂SO₄ in 80 ml of water.

CONCLUSION

The optimal parameters were determined and a process was developed for the synthesis of thioglycolic acid from sodium monochloroacetate and sodium disulfide without isolation of intermediates. The yield

of the target product is as high as 92–97%, with the amount of wastewater being considerably reduced.

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