INTRODUCTION

It was shown in [1] that the reaction of CO\(_2\) with anhydrous trifluoroacetic acid (TFA) in the presence of molecular oxygen leads to the formation of a resinous substance, the molecular formula of which according to the data of elemental analysis is \((C_4H_7O_9)_n\). The product yield with reference to CO\(_2\) was no less than 68.5%. The obtained resinous product was not soluble in water, alkanes, benzene, and CCl\(_4\), but it was partially soluble in acetone and isopropanol.

The decrease in the yield of reaction products after a substantial increase in the surface area of a glass reactor and the increase in the yield upon changing to a Teflon reactor could indicate the presence of radical stages in the product formation processes.

The formation of C–C bonds upon the conversion of CO\(_2\) in aqueous solutions of trifluoroacetic acid, which leads to the formation of a range of products with different molecular weights and is proven experimentally in this work, has never been described in the literature.

EXPERIMENTAL

The conversion of CO\(_2\) in aqueous solutions of TFA was investigated at room temperature and atmospheric pressure. CO\(_2\) was obtained in a Kipp’s apparatus via the reaction of marble chips with a dilute solution of hydrochloric acid. The evolved CO\(_2\) was passed at flow rates of 15, 22, and 30 mL/min through a bubbler that contained 15 mL of TFA solutions with various concentrations (1–10 M); the flow rate of the passed gas was controlled by a valve for fine adjustment and measured by a rheometer. Unreacted CO\(_2\) in the system outlet was absorbed in removable traps with a 0.427 M NaOH solution, the pH value of which was continually monitored by a glass electrode. The flow rate of unreacted CO\(_2\) in the outlet (mmol/min) was calculated from the results of titration with regard to bubbling time of the effluent gas through the trap. This method for experimental determination of the value of carbon dioxide absorption by TFA is characterized by the condition that, depending on the feed flow rate (from 2 to 30 mL/min), the gas flow at the system outlet is not detected at all for 5–25 min, due to the complete absorption of carbon dioxide in the bubbler, since a flow of pure CO\(_2\) feeds the reaction system. The results from titration of the content of the traps with NaOH in the initial period of the experiment therefore exactly match the molar rate of carbon dioxide entering the bubbler. The initial TFA solution before bubbling with CO\(_2\) contained no less than 0.65 mol/L of dissolved oxygen [2].

The amount of the sodium hydrocarbonate and carbonate formed when the CO\(_2\) reacted with a NaOH solution was determined by potentiometric titration with a 1 M HCl solution on an Expert-001-3 titrator using a pH glass electrode. The error of determination was ±0.03%.

TFA was distilled off (bp 72.4°C) from the obtained mixture of products after the reaction with CO\(_2\) at atmospheric pressure. The distillate was collected in a flask placed into a container with ice. In order to destroy the esters and peroxo groups, a solution containing TFA and CO\(_2\) was refluxed and then evaporated into the air at 40°C. The produced substance was dissolved in water. The yield of oxalic acid was determined from the results of potentiometric titration.

The oxalic acid in the reaction products was analyzed qualitatively and quantitatively. The appearance of a white precipitate after adding several drops of a 0.1 M CaCl\(_2\) solution to the analyzed solution in the pH range of 5 to 8 that was insoluble in organic acids but soluble in a dilute sulfuric acid points to the forma-
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Quantitative determination was performed via titration of the reaction product with a 0.1 M NaOH solution on an ATP-02 automatic potentiometric titrator with an ESL-43-07SP glass electrode and EVL-1M3.1 reference electrode.

The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance-600 spectrometer at a temperature of 303 K; the chemical shifts, $\delta$, were determined in ppm with reference to the solvent signals (DMSO-$d_6$: $\delta_H = 2.50$ and $\delta_C = 39.5$ ppm).

The MALDI-TOF spectra of positive ions were registered on a Bruker Ultraflex spectrometer; dithranol (1,8-dihydroxydihydroanthracene-9-on) and anthracene were used as matrices.

RESULTS AND DISCUSSION

Experimental dependences of the absorption rate of carbon dioxide on time of passing the CO$_2$ flow through the fixed amount (15 mL) of TFA solutions with various concentrations are shown in Fig. 1 (the feed flow rate of CO$_2$ is 15 mL/min). The initial linear parts on each curve that were obtained at different gas flow rates correspond to the initial rate of carbon dioxide absorption by fresh solution, which remains constant for 10–15 min and almost equals the flow rate of CO$_2$ entering the system. This testifies to the nearly instant absorption value of carbon dioxide in the initial period of the experiment.

The total amounts of absorbed carbon dioxide, $N_{CO_2}$, at different pH values of the TFA solution are given below:

<table>
<thead>
<tr>
<th>pH</th>
<th>2.4</th>
<th>3.6</th>
<th>4.2</th>
<th>6.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{CO_2}$, mol/L</td>
<td>0.23</td>
<td>0.27</td>
<td>0.33</td>
<td>0.29</td>
</tr>
</tbody>
</table>

As can be seen from the given data, the amount of the absorbed CO$_2$ increases to some extent (from 0.23 to 0.33 mol/L) when the pH value is increased by 2 units, i.e., at a 100-fold reduction in the proton concentration.

Even though the solubility of CO$_2$ in an acidic media declines, the amount of absorbed CO$_2$ for 10 M TFA solutions is greater in acidic media (pH 2) than in neutral media (pH 6). This could be associated with an increase in the oxidative ability of TFA in acidic media [3] and the absence of this ability in neutral media.

The amounts of the absorbed CO$_2$ for 0.1 and 10 M TFA solutions are in fact the same in acidic media (pH 2). These results differ from the data obtained in investigations of the oxidation of SO$_2$ in solutions of alkali trifluoroacetates. As was shown in [3], the amount of the oxidized SO$_2$ increases by 20–30 times at a pH value of ~2, in comparison to oxidation in neutral media.