CARBON-13 KINETIC ISOTOPE EFFECT OF THE DECARBONYLATION OF OXALIC ACID

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Carbon-13 intramolecular kinetic isotope effects in the decarbonylation of oxalic acid dihydrate of natural isotopic composition by SO₃ and by fuming sulphuric acid at room temperature and decarbonylation of oxalic acid dihydrate by 100% H₃PO₄ in the temperature interval 80-150 °C have been determined. The obtained isotopic and kinetic results have been compared with the earlier ¹³C experimental and theoretical studies in other solvents.

There are extensive kinetic data concerning the decomposition of solid and melted¹-⁴ oxalic acid and solutions of this acid in water,⁵,⁶ in concentrated and fuming sulphuric acids⁷-¹⁰ and in organic solvents,⁴,¹¹,¹² as well as in vapour phase.¹³,¹⁴ The decomposition of oxalic acid is kinetically a first-order reaction with respect to oxalic acid in all the above systems. The solid acid and its solutions in organic solvents decompose to carbon dioxide and to formic acid:

\[
\text{HOOC-COOH} \rightarrow \text{CO}_2 + \text{HCOOH}
\]  

(1)

The formic acid is about half dehydrated to carbon monoxide in aqueous solution. In concentrated sulphuric acid solvents the oxalic acid decomposes quantitatively to carbon dioxide and monoxide:

\[
\text{HOOC-COOH} \rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O}
\]  

(2)

The different ¹³C kinetic isotope effects (KIE) found in decompositions proceeding according to Eqs (1)¹⁵-¹⁷ and (2)¹⁸-²⁰ indicate that the transition states and mechanisms of decompositions shown are also different. The ¹³C intramolecular kinetic isotope effects in the decomposition of oxalic acid in gas phase to carbon dioxide and formic acid [Eq. (1)] were found to be relatively small, strongly temperature dependent and
inverting within the experimental range at higher temperatures (at about 145 °C). Intramolecular $^{13}$C KIE in the decomposition of oxalic acid in glycerine solution increases with increasing temperature being about 1.2% at 98 °C and about 2.4% at 135 °C. The observed abnormalities have been thoroughly discussed but no satisfactory explanation has been found for the “cross-over phenomenon” in the temperature dependent factors of the isotopic rate constant ratios determined. The $^{13}$C intramolecular KIE in the decarbonylation of oxalic acid of natural isotopic composition in concentrated sulphuric acid, reinvestigated by us recently, was found to be in good agreement in the temperature interval 80–135 °C with simplified calculations taking into account the $^{13}$C isotopic shifts of fundamental vibrations of carboxylic group only and assuming that the carbon monoxide is produced directly in the fast decomposition of the charged fragment HOOC–$^{12}$O, formed in the rate determining step and not in the fast dehydration of the stable intermediate, formic acid, produced as shown in Eq. (1). Single experiment in which anhydrous oxalic acid was decomposed by fuming sulphuric acid at room temperature indicated that the simple structure of the transition state proposed by FRY and CALVIN for the decomposition of oxalic acid in 100% sulphuric acid predicts well the intramolecular $^{13}$C KIE, $k_2/k_3$, in the decarbonylation of this bifunctional acid for the reaction temperature equal 20 °C providing the value of $k_2/k_3 = 1.0381$:

$$
\begin{align*}
^{12}\text{COOH} & \xrightarrow{2k_1} ^{12}\text{CO}_2 + ^{12}\text{CO} + \text{H}_2\text{O} \\
^{12}\text{COOH} & \xrightarrow{k_2} ^{13}\text{CO}_2 + ^{12}\text{CO} + \text{H}_2\text{O} \\
^{12}\text{COOH} & \xrightarrow{k_3} ^{12}\text{CO}_2 + ^{13}\text{CO} + \text{H}_2\text{O}
\end{align*}
$$

In the present investigation we describe the results of the determination of $^{13}$C intramolecular KIE in the decarbonylation of oxalic acid dihydrate of natural isotopic composition proceeding at room temperature under the mild conditions in the course of absorption of sulphur trioxide vapours in closed vacuum reaction vessel:

$$
\text{HOOC--COOH} \cdot 2\text{H}_2\text{O}_{(solid)} + 3\text{SO}_3_{(vapours)} = \text{CO} \uparrow + \text{CO}_2 \uparrow + 3\text{H}_2\text{SO}_4
$$

We report also the results of the determinations of intramolecular $^{13}$C kinetic isotope effect in the decarbonylation of oxalic acid by 100% phosphoric acid covering the temperature interval 80–150 °C. This study was intended to determine the intramolecular $^{13}$C KIE (observed at complete decarbonylation because of bi-