Carbon-13 Isotope Fractionation in the Decarboxylation of Phenylpropiolic Acid in Orthophosphoric Acid and in Diphosphoric Acid

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(Received December 20th, 1999)

C-13 isotope fractionation in the decarboxylation of phenylpropiolic acid (PPA) in the 10% solution of diphosphoric acid (H₄P₂O₇) in orthophosphoric acid (H₃PO₄) and in the solution of diphosphoric acid in metaphosphoric acid (HPO₃) has been studied between 20–140°C (293.16–413.16). The initial ¹³C fractionation observed in the decarboxylation of PPA in 10% solution of H₄P₂O₇ in H₃PO₄ in the temperature interval 20–30°C coincides with \((k_{12}/k_{13})_{KIE} = 1.045\), calculated assuming the “full” C–C bond rupture in the decarboxylation transition state. The subsequent carbon dioxide probes collected between 40–70°C are depleted in carbon-13 by about 1% more than the carbon-13 isotope effects calculated for this higher temperature interval. The total yield of carbon dioxide was 96% only. The fast polymerization of phenylpropiolic acid accompanying the decarboxylation of this acid in the solution of pyrophosphoric acid in metaphosphoric acid decreased the total yield of carbon dioxide probes, collected between 40–140°C (so far investigated) to 33%. The mass spectrometric determinations of the isotopic compositions of these probes \((R_{pf})\) showed that they are enriched in ¹³C with respect to the “initial ¹³C/¹²C carbon isotope ratio \(R_{io}\)” for carboxylic carbon of the starting PPA used in the decarboxylation experiments. The last small fractions of CO₂, collected at higher temperatures, were produced with the apparent reversed ¹³C KIE, \((k_{12}/k_{13}) < 1.0\).

Key words: phenylpropiolic acid, phosphoric acids, decarboxylation, kinetics, C-13 fractionations, polymerization, isotope effect

The first introductory study of the decarboxylation of phenylpropiolic acid (PPA) in 85% orthophosphoric acid medium [1] indicated that this reaction proceeds between 323–343 K in orthophosphoric acid, H₃PO₄, diluted with water in 1:1, (H₃PO₄)/(H₂O), molar ratio, with Arrhenius activation energy \(Q_{Arrh} = 30.1\) kcal/mol (126.1 kJ/mol) and with Arrhenius preexponential factor \(A_{Arrh} = 6.96 \times 10^{14}\) s⁻¹. Both, the Arrhenius plot, \(ln(k_{exp}) vs (1/T)\), and Eyring plot, \(ln(k_{exp}/T) vs (1/T)\), have correl.coef. very close to 1 between 323–354 K investigated so far and the decarboxylation of PPA occurs, according to one mechanism characterized by loose, not tied up transition state (\(\Delta S^° = +30.0\) e.u. SI). Phenylpropiolic acid decarboxylates in 85% H₃PO₄ with negligible

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$^{13}$C KIE, $k_{12}/k_{13} = 1.004–1.005$, thus suggesting that not the carbon–carbon bond rupture but protonation of the triple bond and subsequent carbon–hydrogen bond formation in the transient “sp$^2$” system are rate and isotope effect determining steps in orthophosphoric acid diluted with water similarly as it has been observed in the decarboxylation of PPA in sulphuric acid diluted with water [2].

In the present studies of the decarboxylation of phenylpropiolic acid in phosphoric acids media, the effort has been made to disclose the eventual dependence of the rate of decarboxylation itself and of the decarboxylation $^{13}$C KIE on the concentration of $P_2O_5$ in aqueous phosphoric acid solutions. Such dependence was observed in the decarboxylation of formic acid in different phosphoric acid media [3]. The stable distribution of $P_2O_5$ and water between coexistent different species, $H_2O$, $H_3PO_4$, $H_4P_2O_7$, $HPO_3$, $P_2O_5$, in the reaction medium upon addition of excess $P_2O_5$ to 85% $H_3PO_4$ has to be achieved before initiation of the proper decarboxylation of PPA. This has been done by prolonging the heating of the mixture of calculated amount of $P_2O_5$ (Merck, anal. reagent) and given volume of commercial 85% $H_3PO_4$ (anal. reagent).

The kinetic and carbon-13 isotopic results, presented in this investigation, fully confirmed our expectations. They revealed the deep chemical changes, taking place in the course of decarboxylation of PPA in phosphoric acid media, which increase with the increase of the $P_2O_5$ content in orthophosphoric acid medium and increase the magnitude of the $^{13}$C KIE from the negligible value of 1.004 to the “full” one observed, when complete rupture of the C–C bond proceeds in the decarboxylation transition state. This complicates the temperature dependence of the $^{13}$C KIE at large excess of $P_2O_5$ in $H_3PO_4$ and at higher temperatures due to polymerization of the substrate acid, PPA, and of the product of decarboxylation, phenylacetylene.

**EXPERIMENTAL**

The kinetic and $^{13}$C KIE experiments have been carried out by transferring into the vacuum reaction vessel about 5 mmol of Aldrich phenylpropionic acid and then the phosphoric acid of known $P_2O_5$ content obtained by homogenization of 30 cm$^3$ of 85% $H_3PO_4$ with the weighed amount of $P_2O_5$ at 220°C during 15–20 hours. The evacuated reaction vessel has been placed at 18.6°C for slow dissolving of the PPA in phosphoric acid. The reproducible decarboxylation of phenylpropionic acid proceeds already at 20°C in concentrated phosphoric acids, therefore, the first portions of carbon dioxide have been isolated and analyzed mass spectrometrically. The subsequent portions of carbon dioxide collected at temperatures indicated in columns (1) of the Tables, have been purified by cryogenic methods, flame sealed in glass tubes under vacuum and analyzed using the Europa Scientific 20–20 mass spectrometer with ANCA-TG preparation modul, operating at the “J.Stefan” Institute in Ljubljana-Slovenia. The corresponding delta (PDB) values of the CO$_2$ samples, listed in columns (2), are given in columns (4). The precision of the measurements was better than ±0.1‰.
Table 1. Carbon-13 kinetic isotope effect for decarboxylation of 5.269 mmol phenylpropiolic acid (PPA) in solution of 156.7 mmoles of P$_\text{2}O_5$ in 30 cm$^3$ of 85% H$_3$PO$_4$.

<table>
<thead>
<tr>
<th>Temp. K</th>
<th>mmol CO$_2$ (mmol PPA)</th>
<th>PPA fraction f of decarboxylation</th>
<th>(PDB)</th>
<th>$R(13C/12C)$ carbon isotope ratio for carboxylic carbon</th>
<th>$k^{13}k^{13}$ exp. theor.$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Exp. No)</td>
<td>(1) (2) (3) (4) (5)</td>
<td>(6) (7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>291.76</td>
<td>0.0731</td>
<td>0.0139</td>
<td>–84.99(pf)</td>
<td>0.0102822(pf)$^a$</td>
<td>1.0429 1.0451/20$^c$</td>
</tr>
<tr>
<td>(PP-1)</td>
<td>(5.2694)</td>
<td></td>
<td></td>
<td>0.0107204(so)$^b$</td>
<td></td>
</tr>
<tr>
<td>303.21</td>
<td>0.1286</td>
<td>0.0247</td>
<td>–86.81(pf)</td>
<td>0.0102617(pf)</td>
<td>1.0459 1.0438/30$^c$</td>
</tr>
<tr>
<td>(PP-2)</td>
<td>(5.1963)</td>
<td></td>
<td></td>
<td>0.0107265(so2)</td>
<td></td>
</tr>
<tr>
<td>303.21</td>
<td>0.2521</td>
<td>0.0497</td>
<td>–85.80(pf)</td>
<td>0.0102731(pf)</td>
<td>1.0465 1.0438/30$^c$</td>
</tr>
<tr>
<td>(PP-3)</td>
<td>(5.0677)</td>
<td></td>
<td></td>
<td>0.0107383(so3)</td>
<td></td>
</tr>
<tr>
<td>313.36</td>
<td>0.3974</td>
<td>0.0825</td>
<td>–78.50(pf)</td>
<td>0.0102539(pf)</td>
<td>1.0518 1.0425/40$^c$</td>
</tr>
<tr>
<td>(PP-4)</td>
<td>(4.8156)</td>
<td></td>
<td></td>
<td>0.0107627(so4)</td>
<td></td>
</tr>
<tr>
<td>292.86</td>
<td>0.0974</td>
<td>0.0221</td>
<td>–86.68(pf)</td>
<td>0.0102632(pf)</td>
<td>1.0537 1.0451/20$^c$</td>
</tr>
<tr>
<td>(PP-5)</td>
<td>(4.4182)</td>
<td></td>
<td></td>
<td>0.0108084(so5)</td>
<td></td>
</tr>
<tr>
<td>323.46</td>
<td>0.7967</td>
<td>0.1844</td>
<td>–79.85(pf)</td>
<td>0.0103399(pf)</td>
<td>1.0516 1.0414/50$^c$</td>
</tr>
<tr>
<td>(PP-6)</td>
<td>(4.3208)</td>
<td></td>
<td></td>
<td>0.0108207(so6)</td>
<td></td>
</tr>
<tr>
<td>292.86</td>
<td>0.1748</td>
<td>0.4960</td>
<td>–74.95(pf)</td>
<td>0.0103950(pf)</td>
<td>1.0551 1.0451/20$^c$</td>
</tr>
<tr>
<td>(PP-7)</td>
<td>(3.5241)</td>
<td></td>
<td></td>
<td>0.0109535(so7)</td>
<td></td>
</tr>
<tr>
<td>333.16</td>
<td>0.7767</td>
<td>0.2319</td>
<td>–64.45(pf)</td>
<td>0.0105130(pf)</td>
<td>1.0511 1.0403/60$^c$</td>
</tr>
<tr>
<td>(PP-8)</td>
<td>(3.3493)</td>
<td></td>
<td></td>
<td>0.0108926(so8)</td>
<td></td>
</tr>
<tr>
<td>343.56</td>
<td>1.0422</td>
<td>0.4051</td>
<td>–43.39(pf)</td>
<td>0.0107496(pf)</td>
<td>1.0457 1.0393/70$^c$</td>
</tr>
<tr>
<td>(PP-9)</td>
<td>(2.5726)</td>
<td></td>
<td></td>
<td>0.0111245(so9)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$(pf) corresponds to product carbon dioxide; $^b$(so) corresponds to carboxylic carbon of PPA before decarboxylation; $^c$calculated values for complete break of the C–C* bond in the T.S.

Table 2. Carbon-13 isotope fractionation in the decarboxylation of phenylpropiolic acid (1.6874 mmol) in the solution of 28 g of P$_2$O$_5$ in 10 cm$^3$ of 85% H$_3$PO$_4$ corresponding to (H$_4$P$_2$O$_7$)/(HPO$_3$) = 1/4 molar ratio.

<table>
<thead>
<tr>
<th>temp.$^\circ$C</th>
<th>mmoles CO$_2$</th>
<th>(PDB)</th>
<th>$R(13C/12C)$ carbon isotope ratio for carboxylic carbon</th>
<th>$R_{pf}/R_{so}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.No</td>
<td>(1) (2) (3)</td>
<td>(4) (5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.8/P-1</td>
<td>0.2840</td>
<td>–36.73</td>
<td>0.0108245(pf)$^a$</td>
<td>1.0097</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0107204(sa)$^a$</td>
<td></td>
</tr>
<tr>
<td>40.8/P-2</td>
<td>0.1550</td>
<td>–34.82</td>
<td>0.0108459 (pf)</td>
<td>1.0117</td>
</tr>
<tr>
<td>20.9/P-3</td>
<td>0.0072</td>
<td>–35.00</td>
<td>0.0108439(pf)</td>
<td>1.0115</td>
</tr>
<tr>
<td>60.1/P-4</td>
<td>0.0385</td>
<td>–33.53</td>
<td>0.0108604(pf)</td>
<td>1.0131</td>
</tr>
<tr>
<td>80.1/P-5</td>
<td>0.0294</td>
<td>–28.32</td>
<td>0.0109190(pf)</td>
<td>1.0185</td>
</tr>
<tr>
<td>113.3/P-6</td>
<td>0.0204</td>
<td>–23.09</td>
<td>0.0109777(pf)</td>
<td>1.0240</td>
</tr>
<tr>
<td>140.4/P-8</td>
<td>0.0135</td>
<td>–26.65</td>
<td>0.0109377(pf)</td>
<td>1.0203</td>
</tr>
</tbody>
</table>

$^a$(pf) corresponds to product carbon dioxide; $^b$(so) corresponds to carboxylic carbon of PPA before decarboxylation.
RESULTS AND DISCUSSION

The carbon isotope ratios $R( ^{13}\text{C}/^{12}\text{C})$, related with delta (PDB) by (1), used for calculation of $(k_{12}/k_{13})$ KIE’s by equation (2), are given in columns (5) of the Tables.

\[
\delta (\%) = [(R_{\text{sample}}/R_{\text{standard}}) – 1] \times 1000
\]  

\[
(k_{12}/k_{13}) = \frac{\ln[1 – f(1 + R_{\text{so}})/(1 + R_{\text{pf}})]}{\ln[1 – f(R_{\text{pf}}/R_{\text{so}})(1 + R_{\text{so}})/(1 + R_{\text{pf}})]}
\]

where as usually [4]: “f” is the fraction of decarboxylation of phenylpropionic acid (PPA), “R_{\text{so}}” is the initial $R(\text{C-13/\text{C-12})}$ ratio for carboxylic carbon of PPA, “R_{\text{pf}}” is the $R(\text{C-13/\text{C-12})}$ ratio of carbon dioxide collected at fraction “f” of decarboxylation of the acid respectively. The best internally consistent kinetic data have been obtained in the decarboxylation of 5.27 mmol of phenylpropionic acid in homogenized at 220°C solution of 22.244 g of P2O5 (Merck, p.a.) in 30 cm³ of 85% H3PO4 (Loba, Austria) corresponding to H3PO4 containing 11% of H4P2O7 (value calculated from the solution of phosphoric acid composed of 665 mmol of H3PO4 and 46 mmol of H4P2O7). The decarboxylation rate constants corresponding to $^{13}\text{C}$ isotopic experiments listed in Table 1, equal to: 8.656 $\times 10^{-3}$ min⁻¹/at 343.56 K, 2.638 $\times 10^{-5}$/at 333.16 K, 7.993 $\times 10^{-4}$/at 323.46 K, 2.309 $\times 10^{-5}$/at 313.36 K and 5.532 $\times 10^{-5}$/at 303.21 K provide the Arrhenius plot characterized by correl.coef. of 0.99995, slope of 13.0050 (Q_{\text{Arrh}} = 25.83 kcal/mol, 108.14 kJ/mol), intep. of 33.098 (A_{\text{Arrh}} = 2.369 $\times 10^{14}$ min⁻¹ or 3.95 $\times 10^{12}$ s⁻¹), and the Eyring plot of the ln$(k_{\exp}/T)$ vs $(1/T)$, corresponding to (3):

\[
(k_{\exp}/T) = (k_{b}/h)\exp(\Delta S^{\star}/R)\exp(-\Delta H^{\star}/RT)
\]

correl.coef. = 0.99995, slope = 12.6812 ($\Delta H^{\star}$ = 105.4 kJ/mol), intep. = 26.3173 ($\Delta S^{\star}$ = –12.8 e.u. (J/K) or –3.07 e.u. (cal/deg.)). Thus, the increase of the P2O5 in phosphoric acid medium resulted in the acceleration of the decarboxylation of PPA, due to decrease of the activation energy by $Q = (31.310 – 25.831) = 5.48$ kcal/mol or (131.0 – 105.4) = 25.6 kJ/mol, but the effect of the decrease of the enthalpy of activation $\Delta H^{\star}$ by (123.3–105.4) = 17.7 kJ/mol is compensated partly by the decrease of the entropy of activation $\Delta S^{\star}$ from the positive value of 30.0 e.u. (SI) to negative value of –12.8 e.u. (SI) (or from +7.2 cal/deg to –3.1 cal/deg respectively). The pyrophosphoric acid, H4P2O7, is the strongest phosphoric acid able to protonate the triple bond of PPA better than H3PO4, but the decarboxylation transition state in its presence is more restricted than in 85% H3PO4. The “protonation” mechanism of the decarboxylation of phenylpropionic acid implies the highest rate of decarboxylation of PPA to be observed at concentrations of P2O5 in phosphoric acid medium corresponding to diphosphoric acid, H$_3$P$_2$O$_7$. Dissociation constant for the first hydrogen of diphosphoric acid equals 1.4 $\times 10^{-1}$, for the second hydrogen 1.1 $\times 10^{-5}$; dissociation constant of H$_3$PO$_4$ equals 1.1 $\times 10^{-2}$ for the first hydrogen, 7.5 $\times 10^{-8}$ for the second, and
4.8 \times 10^{-13} for the third hydrogen respectively. But the investigation of the dependence of the rate of the decarboxylation of PPA on the acidity of the phosphoric acids is obscured by the increase of the side reactivity of the PPA with the increase of the concentration of pyrophosphoric acid in the phosphoric acid medium. The concentration of PPA diminishes, both due to decarboxylation and polymerization. This is clearly demonstrated by kinetic results of decarboxylation of PPA in water deficient phosphoric acid medium, prepared by heating at 250°C during 16 h the mixture of 10 cm$^3$ of 85% H$_3$PO$_4$ and 27.8 g of P$_2$O$_5$, corresponding to calculated final molar ratio (HPO$_3$)/(H$_4$P$_2$O$_7$) = (4/1). The total yield of carbon dioxide after prolonged lasting decarboxylation experiments was 32.3% only in this medium. The polymerization “side” compound was found to be resistant for the decarboxylation at 140°C. The initial rate of decarboxylation of PPA at 40.8°C (313.96 K), determined by collecting carbon dioxide during first 19.83 hours, equals $1.55 \times 10^{-4}$ min$^{-1}$ at this temperature. The rate of decarboxylation, calculated by collecting CO$_2$ during the subsequent 44.5 h at this temperature, equals $4.38 \times 10^{-5}$ min$^{-1}$. Assuming that this apparent decrease of the rate of decarboxylation of PPA is caused by the simultaneous disappearance of this acid in the parallel condensation reaction path, providing decarboxylation resistant product, one obtains the indication, that about 73% of PPA polymerized during the first 20 h decarboxylation period. The change of the mechanism of decarboxylation of PPA, in water deficient orthophosphoric acids, is also strongly documented by $^{13}$C fractionations and by the $(k_{12}/k_{13})$ KIE data presented in columns (4)–(7) of Table 1 and in columns (3)–(5) of Table 2. In accordance with the “protonation” mechanism of decarboxylation of PPA proposed in studies of this decarboxylation in sulphuric acid media [2], the decarboxylation $^{13}$C KIE’s increased in 10% solution of diphosphoric acid in H$_3$PO$_4$ to normal “full” $^{13}$C KIE values expected, when one carbon stretching vibration disappears in the transition state. Moreover, the isotopic decarboxylation experiments in concentrated phosphoric acid media permitted to separate in one internally related experimental series the pure kinetic $^{13}$C KIE values (Exp. No PP1–PP3), where the initial low temperature experimental KIE, and pure kinetic theoretical isotope effects overlap each other, from the subsequent, higher temperature interval data, where the change of the structure of the solute–solvent interactions caused an increase of the observed $^{13}$C fractionation above the expected pure kinetic $(k_{12}/k_{13})$ values. At high decarboxylation temperatures (for 10–20% H$_3$P$_2$O$_5$ in H$_2$PO$_4$ solution) and in all 40–140°C decarboxylations of PPA in diphosphoric acid solutions in HPO$_3$ (metaphosphoric acid) medium, the fast polymerization of PPA disfigure the normal temperature dependence of the experimental $^{13}$C KIE and apparent “negative” $^{13}$C KIE’s are observed. The listed in Table 2 ($^{13}$C/$^{12}$C) isotopic ratios for all carbon dioxide probes, collected in experiments (P-1)–(P-8), are larger than the R($^{13}$C/$^{12}$C) carbon isotope ratio of the carbon dioxide collected at the complete decarboxylation of the known portion of PPA taken from the bottle. The polymerized polyene carboxylic acids are resistant for the low temper-
ature lost of carbon dioxide and the low 33% total decarboxylation yield was achieved after the prolonged heating at 140°C.

At the present "state of art", the quantum chemistry is able to provide a gross description of the chemical reaction paths only. The detailed kinetic and especially kinetic isotope effect studies serve to establish the actual reaction mechanism and to determine with great accuracy the activation parameters, particularly in condensed systems. For instance, different quantum mechanical calculations of addition reactions of olefins, including acetylene, to small zeolite models gave the spectrum of activation energy values, which differ in many cases from the experimentally estimated values [5], but provided essentially the same zwitterionic like transition states in the case of acetylene, ethylene and propene adsorbates: ZO × ′CH2CH2, and ZO × ′HC(CH3)2 [6,7]. A nearly complete proton transfer at the transition state is occurring before addition of ZO moiety to the unsaturated bond. Concerted theoretical descriptions of the TS, in which proton transfer and C–O bond formations are taking place simultaneously in the transition state, resulted the same activation energies and geometrical parameters of the TS [5]. Calculated activation energies for the reaction of acetylene are more irregular and depend on the method used. There are no precise KIE studies concerning the additions of unsaturated hydrocarbons to acidic site, ZOH, in zeolites which could provide unambiguous data for TS structure. The qualitative observations, regarding deuterium isotope exchanges with ethylene, acetylene and benzene with H-ZSM5, are used as the reference experimental data [8,9]. The approximate kinetic data are available for CH₄/CD₄, H/D exchanges with protonated zeolites only [5,6]. Besides the critical O–H, C–H, and C–O bond distances, the degree of partial sp² hybridization of the linear acetylene carbon has been theoretically predicted also [5].

No advanced quantum mechanical study of the addition of formic acid to triple bond of phenyl acetylene (4) has been carried out, but we assumed [10] also that protonation of the triple bond is the rate determining step in the methyl phenyl ketone (acetophenone) formation [12–15].

\[
\text{PhC≡CH} + \text{HCOOH} \rightarrow \text{[PhC≡CH, } ^{13}\text{OOCH}] \rightarrow \text{PhC} = \text{CH} \quad (4)
\]

In the present study, the decarboxylation of phenylpropionic acid has been investigated in different phosphoric acid media. Both, kinetics and $^{13}$C kinetic isotope effects have been determined. In condensed systems, the kinetic parameters do not indicate directly the rate controlling step. The magnitudes of D- and $^{13}$C-KIE’s point directly the bonds in the reacting molecules, which remain unchanged in the TS and the bonds which underwent large changes in the TS in the course of chemical transformation.

In the case of decarboxylation of PPA in 85% $\text{H}_3\text{PO}_4$, very negligible $^{13}$C KIE of 1.004 has been found [1]. This implies that the isotopic carbon–carbon bond is not ruptured in the decarboxylation TS and the first process, protonation of the triple
bond, followed by the formation of the carbon–hydrogen bond, is the rate determining one (5).

\[
\begin{align*}
\text{PhC}≡\text{C}−\text{COOH} + \text{H}_2\text{O}^\circ & \rightarrow ( \text{PhC}≡\text{C}−\text{COOH}) \rightarrow \left[ \begin{array}{c}
  \text{PhC}≡\text{C}−\text{COO}^a \\
  \text{H} \\
 \end{array} \right] \\
\text{H}_2\text{O}^\circ & \rightarrow
\end{align*}
\]

(5)

\[
\begin{align*}
\text{Ph}≡\text{CH} + \text{CO}_2 + \text{H}_2\text{O}^\circ
\end{align*}
\]

The above “protonation” mechanism of decarboxylation is assumed to operate both in sulphuric acid diluted with water and in 85% orthophosphoric acid. In 85% H\textsubscript{2}PO\textsubscript{4}, the presence of one water molecule per one H\textsubscript{2}PO\textsubscript{4} species is sufficient to prevent the addition of H\textsubscript{2}PO\textsubscript{4}− anion to the protonated triple bond (or zwitter ion) and formation of the enol ester, as in the case of the formate enol ester synthesis (4) [11,12]. The decarboxylation of PPA in 85% H\textsubscript{2}PO\textsubscript{4} medium may be presented explicitly by (6).

\[
\begin{align*}
\text{PhC}≡\text{C}−\text{C} & \rightarrow \left( \begin{array}{c}
  \text{PhC}≡\text{C}−\text{C} \\
  \text{O} \\
 \end{array} \right) \rightarrow \left[ \begin{array}{c}
  \text{PhC}≡\text{C}−\text{COO}^a \\
  \text{H} \\
 \end{array} \right] \\
\text{H}_2\text{O} & \rightarrow
\end{align*}
\]

(6)

\[
\begin{align*}
\text{CO}_2 + \text{PhC}≡\text{CH} + \text{H}_2\text{O}\cdot\text{H}_2\text{PO}_4
\end{align*}
\]

A partial sp\textsuperscript{2} character of carbon in the T.S. may be responsible for small but not “zero” \textsuperscript{13}C KIE, observed in the decarboxylation of PPA in diluted with water mineral acids. The gas phase proton affinity of water, equal 166.5±2 kcal/mol (697±8 kJ/mol), is higher than the gas phase proton affinity of acetylene, equal 155.3 kcal/mol (641 kJ/mol) [8]. In solutions the above difference of proton affinities, changed by solvation effects, leads to experimental activation energy of decarboxylation of 30.12 kcal/mol (126.09 kJ/mol). In water deficient 100% orthophosphoric acid, the decarboxylation of PPA is occurring with activation energy Q\textsubscript{Arr} = 105.40 kJ/mol (25.19 kcal/mol) and with slightly negative entropy of activation \Delta S\textsuperscript{f} = −12.8 e.u. (J/K, SI) or −3.05 e.u. (cal/deg) between 30–70°C (303.2–343.6 K). Thus, the direct protonation
of the triple bond by the orthophosphoric acid, avoiding the intermediary water, proceeds with activation energy by 5 kcal smaller than in the 85% H₃PO₄ medium and with a negligible decrease of the entropy of activation (contrary to the large increase of entropy of activation in 85% H₃PO₄). The transition state may also be preceded by the molecular complex, which is protonated by the pyrophosphoric acid species present in 100% H₃PO₄ due to the definite excess of P₂O₅.

\[
(\text{PhC}≡\text{C}–\text{H}) \quad \xrightarrow{\text{molecular complex}} \quad \begin{array}{c}
\text{PhC}≡\text{C}–\text{H} \\
\hat{\text{O}}\quad \hat{\text{O}} \\
\text{O}–\text{P}–\text{OH} \\
\text{O}–\text{OH}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{PhC}≡\text{C}–\text{O}–(\text{H}_3\text{PO}_4) \\
\hat{\text{O}}\quad \hat{\text{O}}\quad \hat{\text{O}} \\
\text{O}–\text{P}–\text{OH} \\
\text{O}–\text{OH}
\end{array} \quad \xrightarrow{\text{T.S.}} \quad \begin{array}{c}
\text{PhC}≡\text{C}–\text{O}–(\text{H}_3\text{PO}_4) \\
\hat{\text{O}}\quad \hat{\text{O}}\quad \hat{\text{O}} \\
\text{O}–\text{P}–\text{OH} \\
\text{O}–\text{OH}
\end{array}
\]

\(7\)

CO₂ + (polymerization and addition products produced when large excess of P₂O₅ is present in the phosphoric acid medium)

Some decrease of the entropy of activation, found in decarboxylation of PPA in water deficient H₃PO₄ containing 10% H₄P₂O₇, suggests that the interactions and ordering in the T.S. are slightly better pronounced than in the “molecular complex” preceding T.S. The negatively charged H₄P₂O₇ anion might interact directly with the positive charge on carbon atom in the T.S. (8). In the absence of the second unsaturated acetylene derivative at the reaction center, the T.S. loosing carbon dioxide might transform into phenylacetylene or stabilize as the enol ester, which is solvated by H₃PO₄ molecules.

\[
(\text{molecular complex}) \quad \xrightarrow{\text{molecular complex}} \quad \begin{array}{c}
\text{PhC}≡\text{C}–\text{H} \\
\hat{\text{O}}\quad \hat{\text{O}} \\
\text{O}–\text{P}–\text{OH} \\
\text{O}–\text{OH}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{PhC}≡\text{C}–\text{H} + \text{CO}_2 + \text{H}_3\text{PO}_4 \\
\hat{\text{O}}\quad \hat{\text{O}} \\
\text{O}–\text{P}–\text{OH} \\
\text{O}–\text{OH}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{PhC}≡\text{C}–\text{H} \\
\hat{\text{O}}\quad \hat{\text{O}} \\
\text{O}–\text{P}–\text{OH} \\
\text{O}–\text{OH}
\end{array} \quad \text{PhC}≡\text{C}–\text{H} + \text{CO}_2 + \text{H}_3\text{PO}_4 \\
\hat{\text{O}}\quad \hat{\text{O}} \\
\text{O}–\text{P}–\text{OH} \\
\text{O}–\text{OH}
\]

\(8\)
In the presence of large excess of 100% H₃PO₄, the decarboxylation of PPA, avoiding the polymerization, is the dominant process reaching 96% yield or more. But with the increase of the concentration of P₂O₅ in 100% H₃PO₄ to values corresponding to a solution of HPO₃ in H₄P₂O₇ the polymerization prevails (9).

\[
\text{PhC=CCOOH} + \text{H}^+ \rightarrow \text{PhC}=\text{C}^{\text{OOH}} + \text{H}^+ \\
\text{PhC}=\text{CCOOH} + \text{Ph} = \text{C}^{\text{C}=\text{C}} \rightarrow \text{PhC}=\text{C}^{\text{C}=\text{C}} (\text{R})
\]

\[ R=\text{H}_3\text{P}_2\text{O}_7 \text{ or } (\text{OOCC=CPh}) \]

Carbon dioxide, produced in the minor decarboxylation process accompanying polymerization, is enriched in carbon-13 in comparison with the initial ratio R\(^{13}\text{C}/^{12}\text{C}\) of the carboxylic carbon in PPA used in experiments. The polyenepolycarboxylic acid does not decarboxylate measurably below 140°C as tested in this study.

Acknowledgments

This study has been supported by the Polish State Committee for Scientific Research, Grant No C44/99, by the Ministry of Science and Technology of the Republic of Slovenia, by the J. Stefan Institute of Ljubljana and by the Faculty of Chemistry of the Jagiellonian University. The valuable help given by the Central Technical Library of the University of Ljubljana is also acknowledged.

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