

Carbon-13 isotope effect for decarboxylation of phenylpropionic acid (PPA) in concentrated phosphoric acids

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Abstract ^{13}C isotope effects on the decarboxylation of phenylpropionic acid (PPA) in 93–97% H_3PO_4 and in 23% diphosphoric acid in orthophosphoric acid have been investigated from 293 to 353 K. The initial ^{13}C fractionations in all three systems are in agreement with the ^{13}C decarboxylation fractionations expected assuming the loss of the one carbon-carbon bond in the transition state. In 100% H_3PO_4 and in 23% diphosphoric acid in orthophosphoric acid later fractions of carbon dioxide are depleted in carbon-13 to a greater degree than expected, probably due to isotopic preequilibria between stable and decarboxylating forms of PPA. At 353 K and higher temperature strong deviations of the experimental rate constants and of the experimental ^{13}C fractionations from the values extrapolated from lower temperature are observed. A tentative decarboxylation scheme operating in concentrated phosphoric acid media is proposed.

Key words carbon-13 • concentrated phosphoric acids • decarboxylation isotope effects • decarboxylation mechanism • phenylpropionic acid

Introduction

Kinetic and carbon-13 isotope effects studies of the decarboxylation of phenylpropionic acid (PPA) in 85% H_3PO_4 indicated that protonation of the triple bond of this acid is the rate and isotope effect determining step [2]. Subsequent isotope effect determinations of the ^{13}C KIE in the decarboxylation of PPA in 10% solution of diphosphoric acid in H_3PO_4 and in a solution of diphosphoric acid in metaphosphoric acid confirmed a suggestion that the act of protonation is a necessary preliminary step preceding decarboxylation of PPA and revealed that polymerization of PPA becomes a very important factor at large concentrations of P_2O_5 in phosphoric acid media. Polymerization is a dominant process in the solution of diphosphoric acid in the metaphosphoric acid taken in $(\text{H}_3\text{PO}_4)/(\text{HPO}_3) = 1/4$ molar ratio [3]. It complicates the investigation of the dependence of ^{13}C fractionation on the acidity of the medium and the temperature dependence of the observed ^{13}C KIE. Polymerization and side reactions become very important at 353 K even in less than 100% H_3PO_4 media. The present investigation of ^{13}C KIE showed that the "full" values of the decarboxylation ^{13}C KIE's are already achieved below 353 K in freshly prepared 93% orthophosphoric acid. In 23% diphosphoric acid in H_3PO_4 the first fraction of carbon dioxide is produced as before [3] with normal full ^{13}C KIE calculated for 313 K, but subsequent fractions of CO_2 collected below 353 K are depleted in ^{13}C to larger degree than follows from simple kinetic consideration. At 353 K and above the ^{13}C fractionation diminishes with time and reverse ^{13}C KIE's are observed ($k_{12}/k_{13} < 1$).

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Methods

The carbon-13 isotope effect experiments in Tables 1 and 2 were carried out by mixing in vacuum 3.1 mmol (and 5.37 mmol, respectively) phenylpropionic acid (PPA) with 92.65 and 97.2% H_3PO_4 (prepared in advance by dissolving at 210°C, 483 K, during two hours 8.52 g and 15.17 g Merck P_2O_5 in 30 cm³ of 85% H_3PO_4 , p.a., Loba, Austria, respectively). The 22.8% solution of $\text{H}_4\text{P}_2\text{O}_7$ in H_3PO_4 (Table 3) was prepared by heating at 250°C, 523 K, 24.68 g P_2O_5 (Merck) in 30 cm³ H_3PO_4 (85%, anal. Loba, Austria) for 16 hours. Full homogeneity of the mixture was obtained already after 30 minutes at 240°C, 513 K. The reaction vessels were placed in thermostats preadjusted to temperatures indicated in column (1) of the Tables. Consecutive fractions of carbon dioxide [column (2)] were quantitatively extracted, purified by cryogenic methods, flame sealed in glass tubes under vacuum, and analyzed using a 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 and carbon isotope ratios, $R(^{13}\text{C}/^{12}\text{C})$, related by equation (1), are presented in columns (4) and (5) of Tables. The precision of measurements was better than 0.1 (‰)

$$(1) \quad \delta_{(0/00)} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) 1000$$

The (k_{12}/k_{13}) kinetic isotope effects, presented in columns (6) of Tables 1, 2 and 3 were calculated using equation (2)

$$(2) \quad (k - 12/k - 13) = \ln \left[\frac{1 - f(1 + R_{\text{so}})/(1 + R_{\text{pf}})}{1 - f(R_{\text{pf}}/R_{\text{so}})(1 + R_{\text{so}})/(1 + R_{\text{pf}})} \right]$$

where: f – is the fraction of decarboxylation of PPA, R_{so} – is the initial $R(^{13}\text{C}/^{12}\text{C})$ ratio for carboxylic carbon dioxide of PPA, R_{pf} – is $R(^{13}\text{C}/^{12}\text{C})$ ratio of carbon dioxide collected at fraction "f" of decarboxylation of the acid, respectively.

The theoretical ($k-12/k-13$) ratios were calculated assuming that one isotopic carbon-carbon stretching vibration is lost in the transition state (TS).

Table 1. The ^{13}C kinetic isotope effect for decarboxylation of phenylpropionic acid (3.094 mmol) in 92.6% orthophosphoric acid (60 mmol of P_2O_5 in 30 cm³ of 85% H_3PO_4).

Temp. K (Exp. No.)	mmol CO_2	PPA fraction f of decarboxylation	$\delta_{(\text{PDB})}$ ($^{13}\text{C}/^{12}\text{C}$)	$R(^{13}\text{C}/^{12}\text{C})$ carbon isotope ratio for carboxylic carbon	k_{12}/k_{13}	
					exp.	theor. ^c
1	2	3	4	5	6	7
333.3 (M-1)	0.4615	0.1492	-78.64 (pf)	0.0103535 (pf) ^a 0.0107204 (so) ^b	1.0385	1.0403/333.2 K
343.2 (M-2)	0.9643	0.3663	-69.42 (pf)	0.0104571 (pf) 0.0107847 (so)	1.0397	1.0393/343.2 K
293.6 (M-3)	0.1923	0.1152	-62.22 (pf)	0.0105380 (pf) 0.0109742 (so)	1.0440	1.0440/293.2 K
353.3 (M-4)	0.7271	0.4926	-36.49 (pf)	0.0108272 (pf) 0.0110310 (so)	1.0269	1.0384/353.2 K

(pf)^a – corresponds to product carbon dioxide; (so)^b – corresponds to carboxylic carbon of PPA before decarboxylation; theor.^c – calculated values for a complete break of the C–*C bond in TS; The experimental (k_{12}/k_{13}) values have been calculated using equation (2).

Results

The initial low temperature ^{13}C fractionations observed in the decarboxylation of PPA in concentrated phosphoric acid media proceed in accordance with theoretical ^{13}C fractionation expected assuming the loss of one C–*C vibration in the (TS).

In 92.6% freshly prepared H_3PO_4 the experimental $^{13}\text{C}/^{12}\text{C}$ fractionations for the first three portions of carbon dioxide collected at 293.2 K, 333.2 K and 334.2 K, respectively overlap well the theoretical ($^{13}\text{C}/^{12}\text{C}$) fractionations: 1.0440_{exp.}/1.440_{theor.}/293.2 K; 1.0397_{exp.}/1.0393_{theor.}/342.3 K. In more concentrated 97.2 freshly prepared orthophosphoric acid medium, the first two carbon dioxide samples obtained in decarboxylations of PPA carried out at 313.5 K are depleted in ^{13}C in agreement with theoretical expectations: ($^{13}\text{C}/^{12}\text{C}$)=1.0440_{exp.}/1.0425_{theor.}, but at 323.4 K a higher experimental value ($^{13}\text{C}/^{12}\text{C}$)=1.0501 is found. In a 23% solution of diphosphoric acid in orthophosphoric acid only the first (though large, 1.5 mmol) fraction of CO_2 is depleted in ^{13}C in agreement with expected simple kinetic fractionation: ($^{13}\text{C}/^{12}\text{C}$)=1.0433_{exp.} vs. 1.0425_{theor.} at 313.2 K. Subsequent fractions are depleted in ^{13}C by about 1% more, similarly as it has been observed in the decarboxylation of PPA in concentrated sulphuric acid [4]. In all three systems the definite chemical changes are taking place at 353 K causing the apparent strong temperature dependence of ^{13}C KIE's which is especially well pronounced in the medium consisting of pyrophosphoric acid and metaphosphoric acid [3]. The chemical changes of decarboxylating phenylpropionic acid taking place in 100% orthophosphoric acid at 353 K must involve both the addition reaction to triple bond and the reaction with the carboxylic group. ^{13}C accumulates in forms which are resistant to low temperature decarboxylations but undergo decarboxylation at higher temperatures.}}}}}}

Discussion

The experimental determinations of the ^{13}C KIE's in phosphoric acid media presented in Tables 1 and 2 indicate that increasing the concentration of P_2O_5 in 85% H_3PO_4 above the nominal content (by dissolving anhydride in commercial 85%

Table 2. The ^{13}C kinetic isotope effect for decarboxylation of phenylpropionic acid (PPA, 5.370 mmol) in 97.2% orthophosphoric acid (107 mmol of P_2O_5 in 30 cm^3 of 85% H_3PO_4).

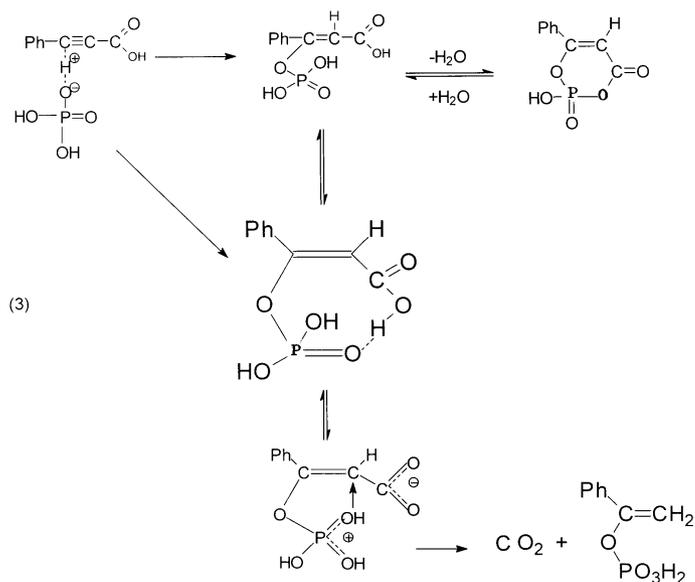
Temp. K (Exp. No.)	mmol CO_2	PPA fraction f of decarboxylation	$\delta_{(\text{PDB})}$ ($^{13}\text{C}/^{12}\text{C}$)	$R(^{13}\text{C}/^{12}\text{C})$ carbon isotope ratio for carboxylic carbon	k_{12}/k_{13}	
					exp.	theor. ^c
1	2	3	4	5	6	7
313.4 (L-1)	0.2594	0.0483	-85.23	0.0102795 (pf) ^a 0.0107204 (so) ^b	1.0440	1.0425/313.2 K
313.5 (L-2)	0.9917	0.1941	-80.75	0.0103298 (pf) 0.0107428 (so)	1.0446	
323.4 (L-3)	0.7807	0.1896	-76.67	0.0103756 (pf) 0.0108423 (so)	1.0501	1.0414/323.2
333.5 (L-4)	1.0461	0.3134	-61.55	0.0105456 (pf) 0.0109515 (so)	1.0467	1.0403/333.2
292.7 (L-5)	0.2336	0.1019	-52.37	0.0106487 (pf) 0.0111369 (so)	1.0484	1.0451/293.2
343.4 (L-6)	0.7296	0.3545	-36.45	0.0108276 (pf) 0.01119238 (so)	1.0423	1.0393/343.2
353.4 (L-7)	0.6483	0.488	-0.35	0.0112333 (pf) 0.0113928 (so)	1.0202	1.0384/353.2

(pf)^a – corresponds to product carbon dioxide; (so)^b – corresponds to carboxylic carbon of PPA before decarboxylation; theor.^c – calculated values for a complete break of the C-*C bond in TS. The experimental (k_{12}/k_{13}) values have been calculated using equation (2).

Table 3. The ^{13}C kinetic isotope effect for decarboxylation of phenylpropionic acid (PPA, 4.747 mmol) in 22.8% solution of $\text{H}_4\text{P}_2\text{O}_7$ in H_3PO_4 (173.9 mmol of P_2O_5 in 30 cm^3 of 85% H_3PO_4).

Temp. K (Exp. No.)	mmol CO_2	PPA fraction f of decarboxylation	$\delta_{(\text{PDB})}$ ($^{13}\text{C}/^{12}\text{C}$)	$R(^{13}\text{C}/^{12}\text{C})$ carbon isotope ratio for carboxylic carbon	k_{12}/k_{13}	
					exp.	theor. ^c
1	2	3	4	5	6	7
314 (PA-1)	1.5534	0.3272	-78.49	0.0103552 (pf) ^a 0.0107204 (so) ^b	1.0433	1.0425/313.2 K
293.5 (PA-2)	0.1306	0.0409	-80.12	0.0103369 (pf) 0.0108981 (so)	1.0555	1.0451/293.2
314 (PA-3)	0.1846	0.0603	-75.17	0.0103925 (pf) 0.0109221 (so)	1.0526	1.0425/313.2
294 (PA-4)	0.0339	0.0118	-75.48	0.0103890 (pf) 0.0109561 (so)	1.0549	1.0451/293.2
333.3 (PA-5)	0.9541	0.03354	-59.50	0.0105686 (pf) 0.0109628 (so)	1.0461	1.0403/333.2
293.5 (PA-6)	0.1861	0.0985	-46.90	0.0107102 (pf) 0.0111619 (so)	1.0445	1.0451/293.2
353.3 (L-7)	1.0464	0.6139	-19.61	0.0110168 (pf) 0.0112112 (so)	1.0294	1.0384/353.2
353.3 (PA-8)	0.3162	0.4805	16.63	0.0114241 (pf) 0.0115205 (so)	1.0119	1.0384/353.2

(pf)^a – corresponds to product carbon dioxide; (so)^b – corresponds to carboxylic carbon of PPA before decarboxylation; theor.^c – calculated values for a complete break of the C-*C bond in TS. The experimental (k_{12}/k_{13}) values have been calculated using equation (2).



orthophosphoric acid) caused tenfold increase of the per cent decarboxylation ^{13}C KIE's determined below 353 K. Probably in 90–100% H_3PO_4 (freshly prepared) exist the water free phosphoric acid species which are able to protonate effectively the triple bond of phenylpropionic acid and the isotopic carbon-carbon bond rupture is the rate determining one. Below 353 K in about 100% and in more concentrated phosphoric acid the decarboxylation ^{13}C fractionation is about 1% higher than the pure kinetic ^{13}C fractionation. This increase of the observed experimentally ^{13}C fractionation is probably caused by equilibrium ^{13}C fractionation between neutral and ionized forms. In all three systems investigated definite chemical changes are taking place at 353 K and above, and this results in drastic deterioration of the Arrhenius plot of rate constants and the ^{13}C KIE temperature dependences. Unfortunately, the high temperature carbon dioxide probes were collected at the end of each experimental series and their isotopic composition might be influenced also by the

partial accumulation in the condensed phase of organic products. Carbon dioxide accumulates preferentially in the gas phase above liquid medium. The decarboxylation scheme (3) is suggested by us to rationalize the observed ^{13}C fractionation in decarboxylation of phenylpropionic acid proceeding in complicated phosphoric acid medium.

This scheme should be corroborated by deuterium isotope effect investigation similarly as it has been done in the case of deuterium isotope effect study of decarboxylation of PPA in 85% D_3PO_4 in D_2O recently [1].

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