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The Kinetics of the β-Cyclodextrin-catalyzed Decarboxylation of Trichloroacetic Acid in an Alkaline Solution

Yoshiaki Motozato, Yoshiaki Furuya,* Toshikazu Matsumoto,
and Tsukasa Nishihara
Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860
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The rate of the decarboxylation of trichloroacetic acid (abbreviated as TCAH) in the presence of β-cyclodextrin(βCD) in an aqueous solution of sodium hydroxide has been followed by the determination of the remaining TCAH. The rate equation was given by

$$\text{Rate} = (k_{1\text{T}}+k_{1\text{TC}}C_{\beta\text{CD}})C_{\text{TCAH}}{}^{1/2} + (k_{2\text{T}}-k_{2\text{TC}}C_{\beta\text{CD}})C_{\text{TCAH}}.$$

A probable bimolecular decarboxylation mechanism which involves the unionized molecule of TCAH rather than the anion was proposed and discussed.

Since it was pointed out that TCAH was split quantitatively into chloroform and carbon dioxide when heated in organic bases,[1] the decarboxylation mechanism has been studied by many chemists. Verhoek and his co-workers have suggested that the reaction is a unimolecular reaction of the anion.[2] In opposition to this, Clark has assumed that the reaction is a bimolecular decomposition of the anion.[3]

Some facts of interest were found when we were dealing with the decarboxylation of TCAH as a part of the studies of βCD-catalyzed reactions. We should like to note that the title reaction involves a bimolecular reaction of the unionized TCAH with the solvent water molecule. We will also discuss the catalysis of βCD.

Experimental

Materials. Guaranteed reagents of TCAH (Wako Pure Chemical Industries), βCD (Tokyo Kasei Kogyo Co.), and the sodium hydroxide were used without further purification. The molarities (denoted by M, 1 M = 1 mol dm^{-3}) of an aqueous solution of TCAH and of sodium hydroxide were determined by titration with aqueous solutions of sodium hydroxide or hydrochloric acid of known concentrations. The molecular weight of βCD was measured vapor pressure-osmometrically. M_n 1078; calcd 1135.

Typical Rum for the Rate Measurements. Aqueous solutions of TCAH (0.4961 M, 59.97 ml) and sodium hydroxide (0.2957 M, 100.46 ml) were kept separately in a thermostatted water bath of a specified temperature. After appropriate temperature equilibration, the two solutions were mixed together. Aliquots (9.99 ml each) were taken out at appropriate intervals of time, and to each one was added a 9.94 ml portion of a 0.4833 M aqueous solution of hydrochloric acid. Then, they were titrated by 0.4912 M aqueous sodium hydroxide, with Methyl Orange as an indicator. The initial concentration and concentration at time *t* are given by the following equations:

$$C^0_{\text{TCAH}} = ad_1/(d_1+d_2+w)$$

$$C^t_{\text{TCAH}} = \{bV+9.99bd_2/(d_1+d_2+w)-9.94c\}/9.99.$$

Here, C^0_{TCAH} and C^t_{TCAH} denote the concentrations of TCAH at time 0 and *t*, and *a* and *b* are the molarities of, and d_1 and d_2 are the quantities (in ml) of aqueous solutions of TCAH and sodium hydroxide respectively. The character, *w*, is the volume of water added, and *c* and *V* are the molarity of an aqueous solution of hydrochloric acid and a titer (at time *t*) of an aqueous solution of sodium hydroxide respectively.

Measurement of Dissociation State for TCAH in an Aqueous Solution. The degree of dissociation for TCAH in an aqueous solution containing about an equimolar amount of sodium hydroxide was measured by means of a Yanagimoto Conductivity Outfit, model MY-7, in pH 9.0 at 60 °C. The molar conductivities are plotted against the square root of the TCAH concentrations in Fig. 1. From Fig. 1, the degrees of dissociation may be found to be 0.7038—0.8694 in the range of 0.25—0.06 M TCAH at 60 °C. Therefore, it was concluded that the trichloroacetate anion may coexist with the unionized TCAH molecule.

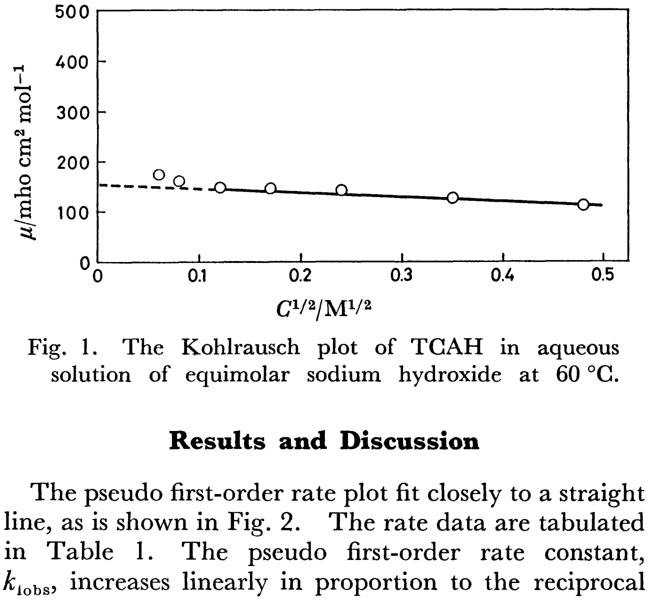


Fig. 1. The Kohlrausch plot of TCAH in aqueous solution of equimolar sodium hydroxide at 60 °C.

Results and Discussion

The pseudo first-order rate plot fit closely to a straight line, as is shown in Fig. 2. The rate data are tabulated in Table 1. The pseudo first-order rate constant, $k_{1\text{obs}}$, increases linearly in proportion to the reciprocal of the square root of the initial concentration of TCAH, as is shown in Fig. 3. Thus, the following equation can be derived:

$$k_{1\text{obs}} = k_1 C_{\text{TCAH}}{}^{-1/2} + k_2. \tag{1}$$

The values of $k_{1\text{obs}}$ in the decarboxylation of 0.05 M TCAH ($6.21\times10^{-5}\,\text{s}^{-1}$ and $1.33\times10^{-4}\,\text{s}^{-1}$) at 80 °C in the absence or the presence of 0.02 M βCD agreed well with those ($7.00\times10^{-5}\,\text{s}^{-1}$ and $1.36\times10^{-4}\,\text{s}^{-1}$) calculated from the half-life periods given by Cramer and Kampe.[4]

The rate constant k_1 increases, while k_2 decreases, with an increase in the βCD concentration, as is shown in Figs. 4 and 5. Therefore, each constant can be divided into two terms:

TABLE 1. RATE DATA AND ACTIVATION PARAMETERS FOR THE DECARBOXYLATION OF TRICHLOROACETIC ACID

		βCD-catalyzed				Non-catalyzed	
		$10^5 k_{1T}$ / $M^{1/2} s^{-1}$	$10^4 k_{1TC}$ / $M^{-1/2} s^{-1}$	$10^5 k_{2T}$ / s^{-1}	$10^4 k_{2TC}$ / $M^{-1} s^{-1}$	$10^5 k_1$ / $M^{1/2} s^{-1}$	$10^5 k_2$ / s^{-1}
Temp/°C	75	0.18	5.90	2.70	7.40	0.18	2.67
	80	0.40	10.67	5.80	15.73	0.41	5.60
	83	0.65	14.43	7.94	21.13	0.66	7.85
$\Delta H^{\neq}$ kcal/mol		39.4	28.5	33.8	32.5	39.4	33.8
$\Delta S^{\neq}$ e.u.		28.1	18.3	17.5	20.2	28.1	17.4
$\Delta G^{\neq}$ kcal/mol		29.5	25.6	27.6	25.3	29.5	27.6

1 cal = 4.184 J.

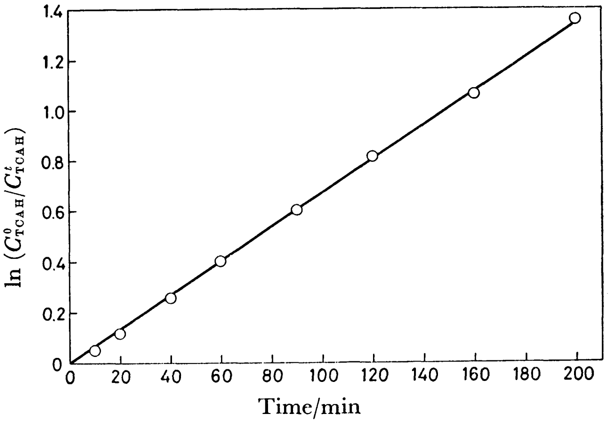


Fig. 2. The first-order rate plot for the decarboxylation of TCAH in aqueous solution of sodium hydroxide at 83 °C.
Initial concn of TCAH: 0.238 M, Concn of βCD: 0.02 M.

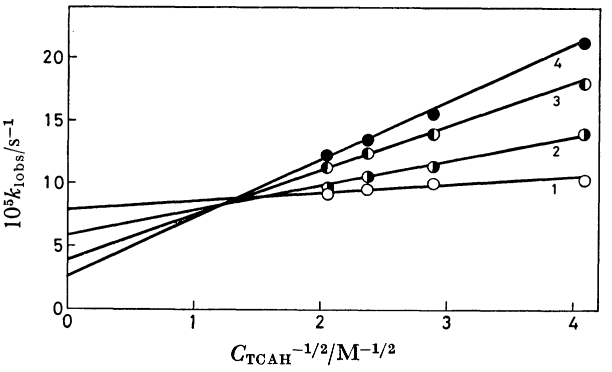


Fig. 3. The plot of k_{1obs} vs. $C_{TCAH}^{-1/2}$ for the decarboxylation of TCAH in aqueous solution of sodium hydroxide at 83 °C.
Concn of βCD: 1, none; 2, 0.01 M; 3, 0.02 M; 4, 0.03 M

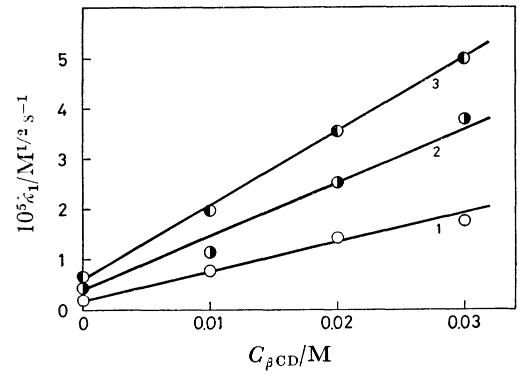


Fig. 4. The plot of k_1 vs. βCD concentration for the decarboxylation of TCAH in aqueous solution of sodium hydroxide. Reaction temp: 1, 75 °C; 2, 80 °C; 3, 83 °C.

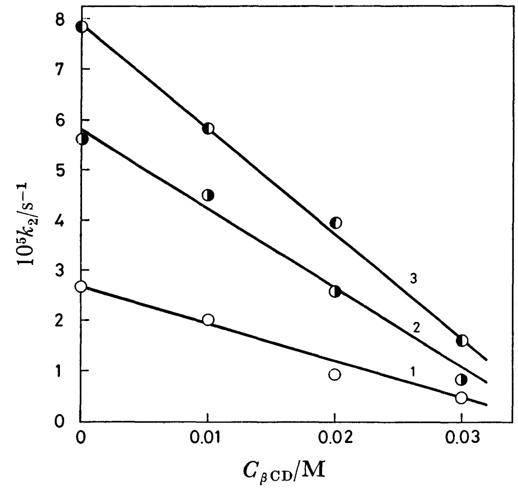


Fig. 5. The plot of k_2 vs. βCD concentration for the decarboxylation of TCAH in aqueous solution of sodium hydroxide.
Reaction temp: 1, 75 °C: 2, 80 °C; 3, 83 °C.

$$k_1 = k_{1T} + k_{1TC}C_{\beta CD} \tag{2}$$

$$k_2 = k_{2T} - k_{2TC}C_{\beta CD}. \tag{3}$$

From these relationships, the overall kinetics of this reaction is given by the following equation:

$$\text{Rate} = (k_{1T} + k_{1TC}C_{\beta CD})C_{TCAH}^{1/2} + (k_{2T} - k_{2TC}C_{\beta CD})C_{TCAH}. \tag{4}$$

The first and second terms represent the decarboxylation of the anion, for $C_{TCAH}^{1/2}$ is expressed by $K^{-1/2}C_{TCA^-}$ under our reaction conditions (Equivalent of TCAH$\simeq$ Equivalent of NaOH).[2] Here, K and C_{TCA^-} are the dissociation constant of TCAH and the anion concentration respectively. The third and fourth terms express the decomposition of the unionized molecule and concecutive reactions. In spite of its strong acidity, a measurable amount of TCAH still remains un-

TABLE 2. A COMPARISON OF THE KINETIC DATA FOR THE DECARBOXYLATION OF MALONIC ACID AND TRICHLOROACETIC ACID IN VARIOUS SOLVENTS[6] AT 100 °C

	Malonic acid			Trichloroacetic acid		
	$\Delta H^{\neq}$ kcal mol	$\Delta S^{\neq}$ e.u. mol	$10^4 k$ s^{-1}	$\Delta H^{\neq}$ kcal mol	$\Delta S^{\neq}$ e.u. mol	$10^4 k$ s^{-1}
1) Aniline	26.9	−4.46	1.3	24.5	−2.57	78
2) *o*-Toluidine	25.7	−7.05	2.0	23.8	−6.82	29
3) Quinoline	26.74	−2.37	5.0	23.98	−2.41	214
4) 8-Methylquinoline	24.4	−10.47	2.1	22.31	−8.43	100
5) Hexanoic acid	32.5	3.2	0.037	39.3	22.1	0.065

1 cal=4.184 J.

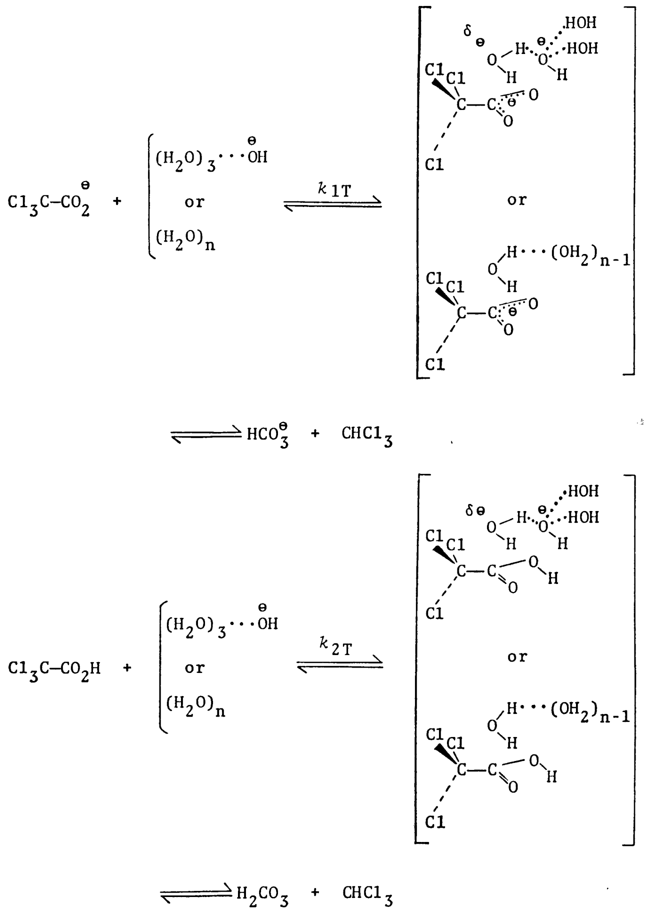
ionized, as has been mentioned above. Accordingly, it seems reasonable to assume that the chemical species which takes part in the decarboxylation is not only the anion, but also the unionized molecule.

The loss of a proton to form the anion increases the electron density on the oxygen of the carboxylate residue, thus decreasing the effective positive charge on the polarized carboxyl carbon atom. This leads to a weakening of the attraction between the nucleophile and the carboxylate carbon; this may account for the observed increase in the enthalpy of activation[5] of the first term as compared with that of the third term. On the other hand, a comparison of the kinetic data for the decarboxylation of malonic and trichloroacetic acids in various amines[6] showed that the steric effect hinders the approach of the nitrogen of amine to the carboxyl carbon, thus decreasing the probability of the formation of the activated complex. This leads to the decrease in the entropy of activation in the formation of the activated complex, as is shown in Table 2. Analogously to this, the smaller entropy of the activation of the third term than that of the first term, as is found in Table 1, may be ascribed to the hindrance of the approach of the oxygen of water to the carboxylic carbon of TCAH caused by the free-rotating carboxylic hydroxyl group. As a result of these findings, the pathways of the decarboxylation of TCA^- and of TCAH will be expressed by the first and the third terms respectively.

Furthermore, the kinetic behavior of TCAH bears some resemblance to that of malonic acid, as is shown in Table 2. Malonic acid apparently does not ionize not only in water and/or alcohol and dioxane containing water,[7] but also in aromatic amines and in acid solvents.[6] Therefore, an un-ionized TCAH molecule will probably take part in a decarboxylation reaction. This pathway, to be expressed as the first-order kinetics, seems to correspond to the third term, which constitutes the main part of the decarboxylation reaction (70—90%).

The values of the overlap population between two carbons in both TCAH and TCA^- were calculated by means of the CNDO/2 method in a closed system.[8] The geometries of the chemical species are cited from Sutton's Tables[9] and are fixed. When the oxygen of water, which is parallel to the $\mathrm{Cl{-}C{-}\overset{O}{\overset{/}{C}}{-}O}$ plane, approaches the carboxylic carbon of TCAH or TCA^- up to 0.2 nm on its p_z-axis, the diminution degree of the value of Mulliken's population between C–C in the free acid (0.0052) is larger than that in its anion (0.0008). Thus, the anion seems to be less liable to decarboxylate than the free acid.

The value of $\log k_{1T}$ decreases slightly and linearly with an increase in the pH, whereas $\log k_{2T}$ increases slightly and linearly with an increase in the pH value. It seems reasonable to assume that there are two kinds of water as the attacking species in a basic aqueous solution; one is the water affected by the hydroxide anion, and the other is the one unaffected by the anion. The hydroxide anion is hydrated by three molecules of water.[10] The oxygen of such water may have a larger negativity. As the ratio of the participation of such water increases with an increase in the pH,



the rate constants, k_{1T} and k_{2T}, will decrease and increase respectively with an increase of the pH value.

The value of k_{1T} decreases, and that of k_{2T} increases, with a decrease in the pH value in this acidic range. The former still has some value (0.173×10^{-5} M$^{1/2}$ s^{-1}) even at pH 1.30, however, the concentration of the anion will decrease remarkably, but not to zero. The latter phenomenon is considered to be due to the formation of the protonated TCAH, which is liable to be attacked by the oxygen of water.

The second and fourth terms constitute a βCD-catalyzed mechanism. The value of log k_{1TC} is affected to a small extent by the pH. On the other hand, log k_{2TC} is independent of the basicity of the reaction medium. In the reaction catalyzed by βCD, the activated complex formed by the attack of the water molecule on the TCA$^-$ anion included in βCD will be more stable than that in the case of free TCA$^-$, but the approach of the water molecule will be controlled by the severe steric factor. Therefore, both the enthalpy and the entropy of activation of the second term will have smaller values than those of the first term, as may be found in Table 1.

The fourth term of Eq. 4 may be a βCD-catalyzed hydrolysis of the trichloromethyl anion formed:[11]

$$\underset{}{\mathrm{TCAH}} + \beta\mathrm{CD} \rightleftharpoons \underset{[\mathrm{I}]}{\beta\mathrm{CD}\cdots\mathrm{TCAH}} \tag{5}$$

$$\mathrm{I} + \mathrm{H_2O} \rightleftharpoons \underset{[\mathrm{II}]}{\beta\mathrm{CD}\cdots\mathrm{Cl_3C^-}} + \mathrm{H^+} + \mathrm{H_2CO_3} \tag{6}$$

$$\mathrm{II} + \mathrm{H^+} \xrightarrow{\text{slow}} \beta\mathrm{CD} + \mathrm{HCl} + \mathrm{CCl_2} \tag{7}$$

$$\mathrm{CCl_2} + 2\mathrm{H_2O} \longrightarrow 2\mathrm{HCl} + \mathrm{HCO_2H}. \tag{8}$$

In a reaction mixture, both the chloride and formate anions are detected. As the concentrations of formic and hydrochroric acids are added to the remaining TCAH concentration, the fourth term should have a minus sign.

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