

# A STUDY OF THE DECARBOXYLATION OF TRICHLOROACETIC ACID IN SOLUTIONS OF WATER AND DIMETHYLSULFOXIDE<sup>1</sup>

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## ABSTRACT

The decarboxylation of trichloroacetic acid has been found to occur readily at temperatures as low as 25.0°C in the presence of dimethylsulfoxide in water solutions, a fact not previously reported in chemical literature. The reaction rate is dependent upon the concentration of the dimethylsulfoxide. The reaction rate constant increases about sixty percent as the concentration of dimethylsulfoxide (DMSO) is increased from c. 50 percent to c. 86 percent. The reaction is first order and the rate is also influenced by the actual concentration of the trichloroacetate ion. An effect of the DMSO is to increase the concentration of this ion. The paper presents density curves at 20.00°C and 25.00°C (each=0.05°C) for solutions of DMSO in water.

## INTRODUCTION

Since 1955 this laboratory (Denison University) has been concerned with the studies pertaining to the relative strengths of trichloroacetic acid (HB), trifluoroacetic acid (HA), and hydrochloric acid. Inman, Barringer, and Ronneberg (1955) measured the rate constants for the hydrolysis of sucrose in water with varying concentrations of HA, HB, and hydrochloric acid. Considering structure and properties, HA, HB, and hydrochloric acid might be expected to differ in strength in solution of comparable concentrations of suitable solvents. In water, however, the leveling effect is great enough to make them essentially equally strong, indicating complete ionization of dilute solutions of all three acids in water.

In 1963 the authors attempted to differentiate the relative strengths of hydrochloric acid, HA, and HB. The object was to find a solvent with a dielectric constant sufficiently low as compared with water to permit the differentiation of the relative strengths of these three acids. The solvent chosen to test this hypothesis was dimethylsulfoxide [(CH<sub>3</sub>)<sub>2</sub>SO] in water solution, hereafter referred to as DMSO. It was chosen because it has a dielectric constant of about 46, as compared with 78 for water. DMSO is an active proton acceptor.

The pH's of various concentrations of HA and HB in 50 percent and 75 percent by weight DMSO and water solutions were measured. From the experimentally measured pH's, the apparent ionizations were calculated by comparing the measured hydronium-ion concentration with the hydronium-ion concentration, assuming complete ionization. In concentrations greater than 0.025 N, a definite difference was found in the relative strengths of HA, HB, and hydrochloric acid in various concentrations of DMSO in water solutions.

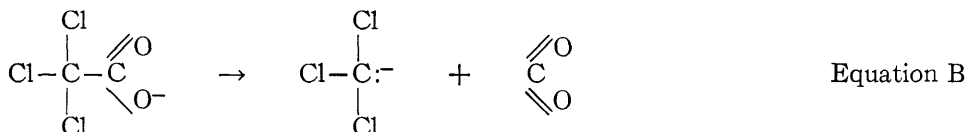
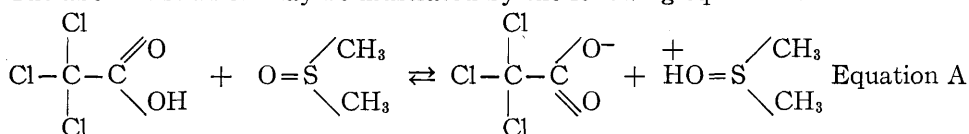
While determining the pH of solutions of the acids, no difficulty was met in obtaining reproducible results for HA, HB, and hydrochloric acid in water. Similarly no difficulty was met in determining the pH of HA in any of the DMSO solutions. But the measured pH of HB in a DMSO solution was appreciably higher than the calculated pH. This was quite unexpected in view of the assumption that, in water solutions, HB is as strong an acid as HA. It was then observed that DMSO solutions of HB were slowly effervescing. This could possibly mean that carbon dioxide was being given off. If decarboxylation was occurring, the unexpectedly high pH values could be explained. While attempting to measure the pH of solutions of HB in 75 percent DMSO and water, the rate of evolution of gas was very noticeably increased. The pH of the solution increased more

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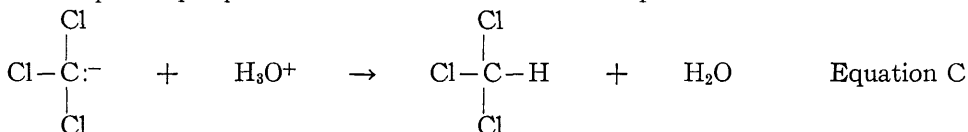
rapidly than when using 50 percent DMSO and water solution. A barium hydroxide test indicated that the gas was carbon dioxide.

All reports in the literature on the decarboxylation of trichloroacetic acid or its salts have been at elevated temperatures. Verhoek (1934) studied this reaction in various water, alcohol, and aniline solutions at high temperatures. Clark (1955, 1956, 1957) reported on the decarboxylation of trichloroacetic acid at temperatures considerably above room temperature in solvents such as glycerol and DMSO. He also studied the decarboxylation of malonic and oxalic acids in DMSO and in glycerol, but this work was also at high temperatures (100° C to 166° C). He showed, for example, that malonic acid decarboxylates seven times as fast in DMSO as in glycerol.

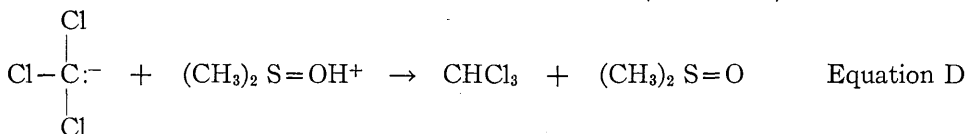
According to Verhoek (1934), and as verified by Clark (1955), the decarboxylation of HB at elevated temperatures is monomolecular. A mechanistic interpretation (Fieser and Fieser, 1961) is based on the fact that a chlorine atom linked to a carbon atom is electron-attracting. The three chlorine atoms of the anion cause an inductive pull on the electron pair shared by the two carbon atoms to the extent that this pair is captured by the chlorinated carbon, as a lone pair of electrons on the ionic oxygen moves in to be shared with the oxygenated carbon. The result is the liberation of carbon dioxide and the formation of a transient carbanion, which combines with protons from various possible sources to form chloroform. The above discussion may be illustrated by the following equations:



Equation B is the rate-determining reaction in this decarboxylation (the carbanion may have other resonance forms). Finally, as shown below, the carbanion picks up a proton to form chloroform and complete the reaction.



DMSO in acid solutions is highly protonated. It appeared therefore that DMSO should likewise react with the intermediate ion, as follows,



and thus accelerate the decarboxylation of HB even at room temperatures. This paper is concerned with the verification of this hypothesis.

#### EXPERIMENT A

Before the decarboxylation of HB studies could proceed, certain information pertaining to DMSO and its solutions not available in the literature was necessary. The density of various concentrations of DMSO and water solutions was necessary. Two density curves were made, one at 20.00°C and the other at 25.00°C. This

was accomplished by finding the mass and volume relationships of solutions ranging in concentrations from 0.0 to 100 percent DMSO by weight.

The method of preparing the solutions was as follows. Known amounts of DMSO and water weighed to the closest drop on a balance accurate to  $\pm 0.002$  g were mixed. Herewith is an example:

To prepare 25 g of 87.50 percent by weight DMSO, use

21.88  $\pm$  0.06 g (1 drop) DMSO  
 3.12  $\pm$  0.05 g (1 drop) water, or  
 25.00  $\pm$  0.07 g solution ( $\pm 0.3\%$ ).

Densities were determined by using a calibrated pycnometer. The following examples illustrate the procedure:

Composition of solution	87.5 percent $\pm 0.3\%$
Volume of pycnometer (20°C)	10.1088 ml $\pm 0.004\%$
Mass of solution in pycnometer (20°C)	11.1750 g $\pm 0.004\%$
Density of solution (20°C)	1.1037 g/ml $\pm 0.0007$ g/ml

The temperature of the water bath was kept constant to  $\pm 0.05^\circ\text{C}$ . The precision with which the densities were determined was of the order of 0.10 percent. The densities of the various solutions of DMSO in water at 20°C and 25°C are shown in Table 1, and the graphs of these data are shown in Figure 1. The inflection in the curve at about 75 percent can be accounted for by the very polar natures of both solvent and solute.

TABLE 1  
*Data for densities of DMSO solutions*

Percent DMSO Solution Precision 0.3%	Density 20.00°C $\pm 0.05^\circ\text{C}$ Precision $\pm 0.10\%$	Density 25.00°C $\pm 0.05^\circ\text{C}$ Precision $\pm 0.10\%$
0.00	0.9982 g/ml	0.9970 g/ml
12.50	1.0147	1.0134
25.00	1.0331	1.0308
37.50	1.0534	1.0502
50.00	1.0729	1.0704
62.50	1.0899	1.0859
68.75	1.0954	1.0931
75.00	1.1003	1.0966
81.25	1.1024	1.0995
87.50	1.1037	1.1003
93.75	1.1027	1.0984
100.00	1.1014	1.0962

#### EXPERIMENT B

The apparatus finally devised to follow the rate of evolution of carbon dioxide from samples of HB in the presence of DMSO is shown in Figure 2. The reaction vessel, labelled No. 1 in Figure 2, was a 250 ml round-bottom flask. To this a 90° connecting tube with a stopcock was fitted; the connecting tube led to a large test tube, labelled No. 2, filled with distilled water. The purpose of the water was to collect any DMSO vapor that might escape from the reaction vessel. It should be noted that DMSO is extremely soluble in water. The vapor pressure of pure DMSO at 25°C is only 0.06 mm of mercury. The DMSO solution, as well as the water, in tube No. 2 was saturated with carbon dioxide from a tank before any experimental run. From tube No. 2 the displaced carbon dioxide was directed to another large test tube, labelled No. 3 in Figure 2, which was filled with drierite. Here the moisture was removed. The exit gas was then assumed to be dry carbon dioxide, equivalent in amount to that produced in the reaction vessel.

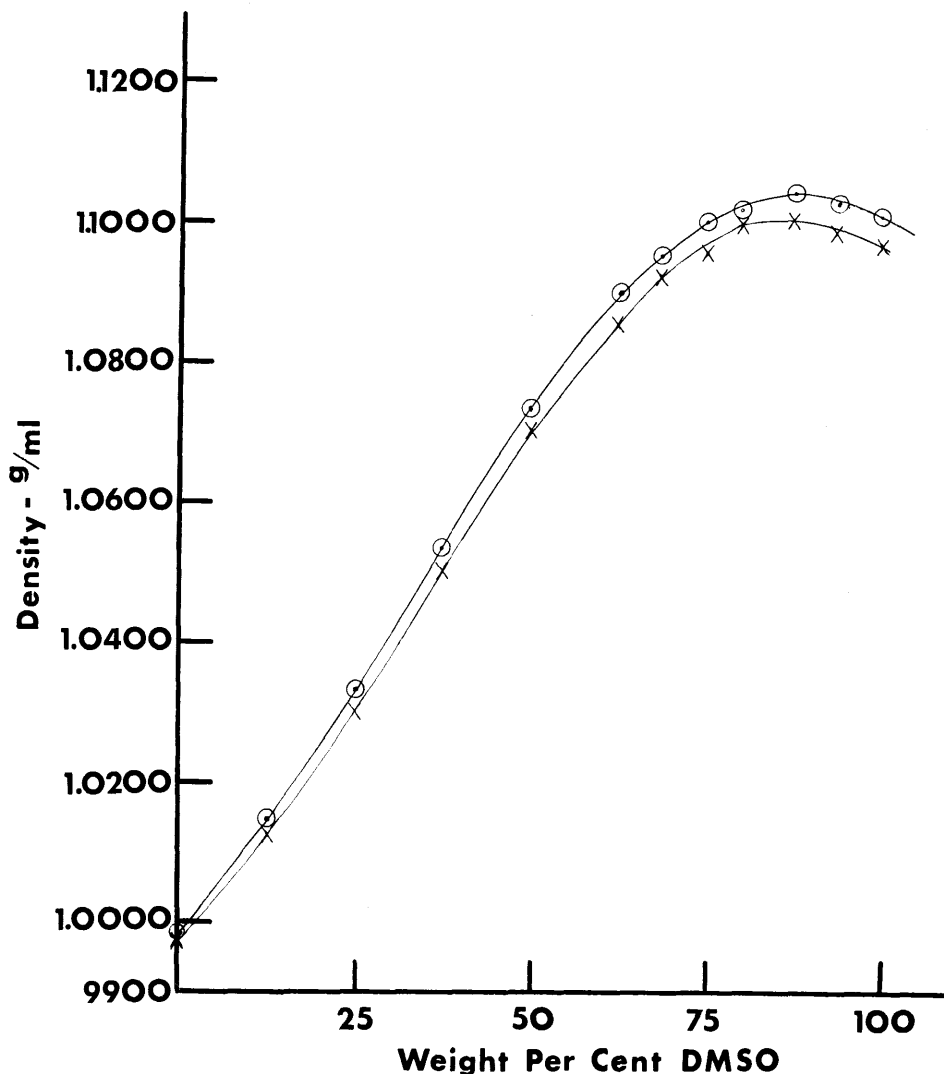


FIGURE 1. Density of DMSO solutions. Circled dots— $-20^{\circ}\text{C}$   
Crosses — $-25^{\circ}\text{C}$

These first three vessels were immersed in a constant temperature bath ( $25.00^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$ ).

From the drying tube, the carbon dioxide was passed to a Schwartz U tube (No. 5 in Figure 2) filled with ascarite, where it was collected and weighed. Between the collecting tube and the drying tube was an open manometer (No. 4) connected to the system by means of a three-way stopcock. This was included to check occasionally on the pressure within the system. On the other end of the collecting tube were two smaller tubes. One (No. 6) was filled with ascarite to insure against the absorption of carbon dioxide from the atmosphere. The other (No. 7) was filled with drierite to prevent the entrance of water vapor from the atmosphere.

Trichloroacetic acid is extremely hygroscopic. It was dried before using by placing in a small glass-stoppered weighing bottle with cap removed in a vacuum

desiccator over concentrated sulfuric acid. After being desiccated overnight, the bottle was removed, capped, and weighed. When ready for a run, the acid was dropped into the reaction vessel No. 1 (fig. 2). The empty vessel, with stopper in place, was then weighed. This gave the weight of the added HB. The effect of adding as much as 2.0 grams of HB in 100 ml of DMSO plus water solvent did not result in a noticeable volume change.

The sequence of operations for an experimental run on the rate of evolution of carbon dioxide was as follows. One hundred milliliters of DMSO solution of

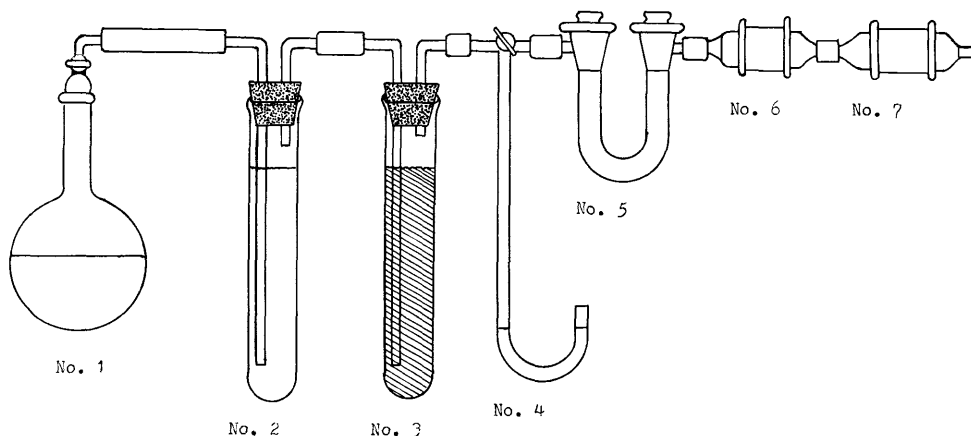


FIGURE 2. Experimental set up.

- No. 1—reaction vessel
- No. 2—DMSO vapor collector
- No. 3—gas drier
- No. 4—pressure check, open manometer
- No. 5—gas collecting tube
- No. 6—outside carbon dioxide interceptor
- No. 7—outside water vapor interceptor

known composition was transferred to the reaction vessel (No. 1 in Figure 2). Carbon dioxide (from a tank) was slowly bubbled through the system until saturation of the solution in vessels 1 and 2 was assured, and all air in the system was displaced. The time necessary for this operation was about one and one half hours. The weighed sample of HB was introduced at a known time. The pressure of the system was checked with the manometer and a weighed collecting tube (No. 5) put into place. Two collecting tubes were used in each run. A weighed tube was always in place. The tubes were changed at known time intervals and the increases in weight ascertained. The change in weight was the weight equivalent to the weight of carbon dioxide produced in the reaction vessel.

The data from a typical run using 80 percent DMSO solution in water is presented in table 2. The calculations for  $k$ , the specific-rate constant, indicated that the reaction was first order. The equation for the first-order reaction was used in the following form:

$$k = \frac{2.303}{t} \cdot \log \left( \frac{a}{a-x} \right)$$

The value of "x" was calculated from the known weight of carbon dioxide collected; "a" was the original molar concentration of HB. From the individual reaction rate constants, the average  $k$  was determined. The constant was also determined

TABLE 2

Total CO <sub>2</sub> collected to time t	Time Hours	Mols CO <sub>2</sub> /l collected to time t	Mols HB/1 decarboxylated to time t	$\log \left( \frac{a}{a-x} \right)$	Reaction rate constant k hr <sup>-1</sup>
0.1832	7	0.0417	0.0417	0.1673	0.0552
0.3053	11	0.0694	0.0694	0.3308	0.0693
0.4104	17	0.0930	0.0930	0.5478	0.0742
0.4485	20	0.1018	0.1018	0.6637	0.0764
0.4710	22	0.1065	0.1065	0.7702	0.0806

k (average)—0.0711 hr<sup>-1</sup>  
k from graph—0.0753 hr<sup>-1</sup>

from the slope of the curve obtained by plotting the  $\log \left( \frac{a}{a-x} \right)$  against time t.

From the slope of the curve for 80 percent DMSO, for example, k was determined as follows.

$$k = \frac{2.303}{35 \text{ hrs.}} \times 1.15 = 0.0755 \text{ hr}^{-1}$$

The half time of the reaction is given by

$$T_{\frac{1}{2}} = \frac{0.693}{k}$$

Using the reaction-rate constant for the 86 percent concentration, the half time is calculated to be 9.2 hrs. It should be noted that the values of k obtained from averaging the individual experimental reaction-rate constants and the value for k from the slope of the curve are in satisfactory agreement ( $\approx 5.00$  percent).

TABLE 3  
*Experimental results*

Solution Percent DMSO	Initial Concentration HB mols/l	Conditions	Reaction-Rate Constant k-hr <sup>-1</sup>	Shown on Fig. 3 by:	Reaction-Rate Constant from Curve k-hr <sup>-1</sup>	Reaction Half Time t <sub>1/2</sub>
86%	0.1352	25.0°	0.577	..	0.553	1.2 hrs
86%	0.1460	25.0°	0.578	x		1.2 hrs
80%	0.1301	25.0°	0.0728	..	0.0755	9.5 hrs
80%	0.1556	25.0°	0.0789	..		8.9 hrs
80%	0.1316	25.0°	0.0732	†		9.5 hrs
50%	0.1346	25.0°	0.00890	x	0.00837	77.5 hrs
75%	0.1350	25.0°	0.246	on Fig. 5 by:	..	2.8 hrs
		0.06505 molar B <sup>-</sup> ion		..		
75%	0.1459	25.0°	0.396	x		1.7 hrs
		0.06505 molar B <sup>-</sup> ion				
80%	0.1159	35.0°	0.738			0.94 hrs

From Fig. 3 and Fig. 5—

$$\text{Reaction Rate Constant } k = \frac{2.303}{t} \cdot \log \left( \frac{a}{a-x} \right)$$

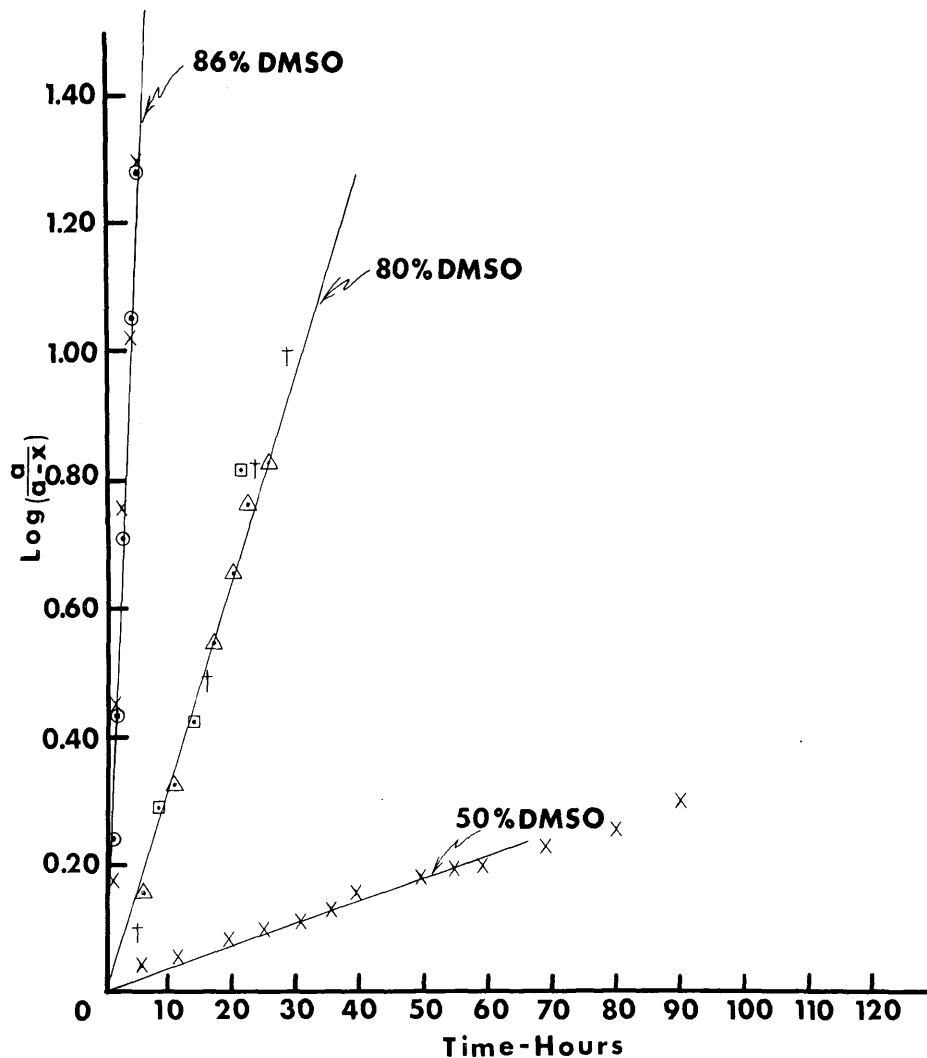


FIGURE 3. Rates of Decarboxylation.

The experimental results obtained in the entire set of runs are shown in Table 3 and in Figures 3 and 5. These data indicate that the reaction of decarboxylation is first order and is markedly influenced by the concentration of DMSO. The reaction-rate constants increase by a factor of 6-7 with a change in concentration of DMSO from 50 to 86 percent. A comparison of the reaction-rate constants as influenced by the mol-fraction of DMSO is shown in Table 4 and in Figure 4. It is reasonable to believe that DMSO becomes highly protonated in the presence of HB, and in this form reacts with the carbanion  $(Cl_3C^-)$  to accelerate the decarboxylation (refer to Equations A, B, C and D).

As hypothesized before, the rate of the reaction is also dependent upon the concentration of  $B^-$  ions. Added trichloroacetate ions therefore should also accelerate the decomposition of trichloroacetic acid. This was verified by adding the anion in the form of sodium trichloroacetate. These solutions were prepared by

TABLE 4  
 Collected data for runs of all HB at 25.0°C and various  
 concentrations of DMSO

Percent DMSO	Mole Fraction DMSO	k-hr <sup>-1</sup>	T <sub>1/2</sub>
50.	0.1971	0.00890	77.9 hrs
80.	0.4970	0.0749	9.3 hrs
86.	0.6053	0.577	1.2 hrs

first neutralizing a known amount of HB with sodium hydroxide. Two runs were made with 75 percent DMSO solution plus 0.06505 molar B<sup>-</sup> ions and 0.1350 molar HB, and one with 0.1459 HB. The comparative results are shown in Table 3 and Figure 5. The rates of decarboxylation shown in Curves 5 and 6 are 6–10 times faster than when no trichloroacetate ions (Curve 4) were present. These curves (5 and 6) deviate somewhat from each other, but the rate constants are of the same order of magnitude and considerably greater than for Curve 4 where there were no B<sup>-</sup> ions present as added trichloroacetate. The data for

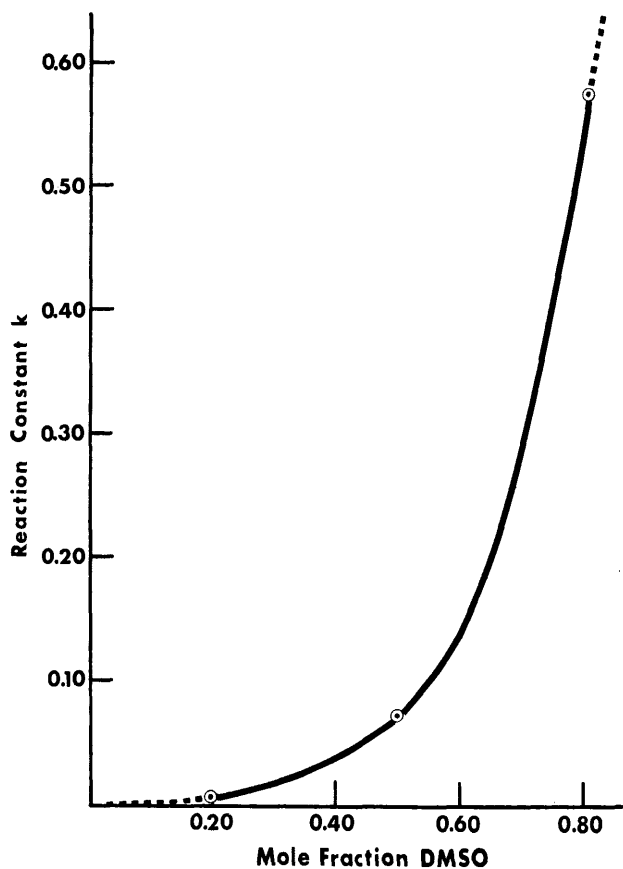


FIGURE 4. Reaction constant  $k$  plotted against mole fraction of DMSO.



Curve No. 5 were determined twenty-four hours after determining the data for Curve No. 6. The decrease in rate of decarboxylation was attributed to two factors: namely, (1) the concentration of HB was somewhat less, and (2) some of the trichloroacetate ions had decomposed during the twenty-four-hour interval between these runs.

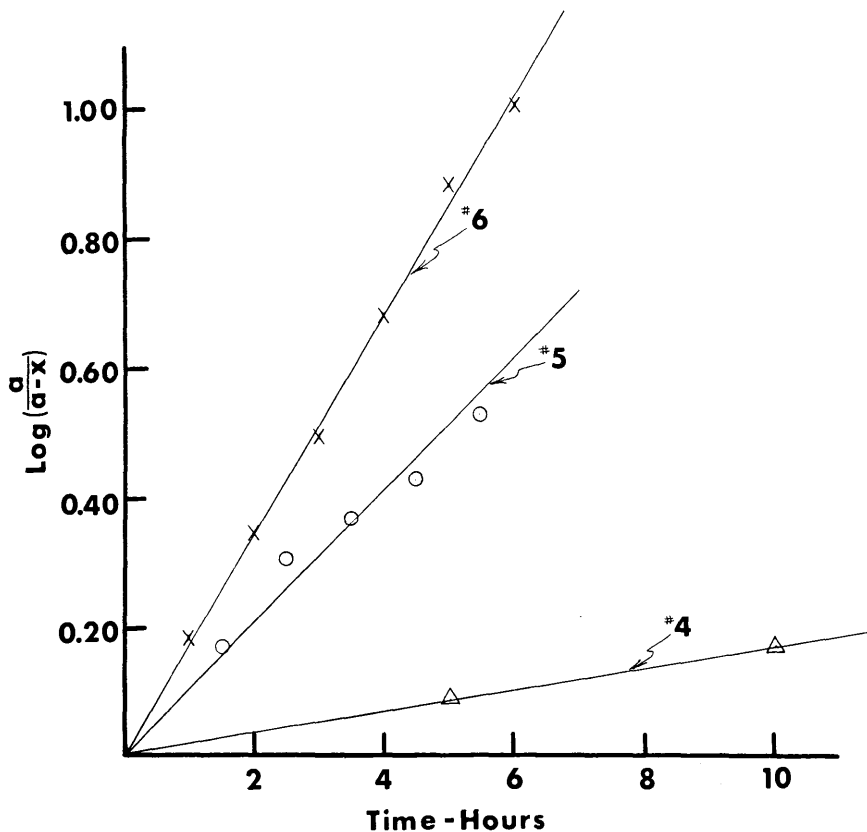


FIGURE 5. Effect of Trichloroacetate ions.  
 dots in triangles—75 percent DMSO,  
 dots in circles —75 percent DMSO,  
 0.1350 molar HB  
 0.0655 molar B<sup>-</sup> ions  
 crosses  
 —75 percent DMSO  
 0.1450 molar HB  
 0.0655 molar B<sup>-</sup> ions.

An indication of the magnitude of the energy of activation for the decarboxylation of HB was obtained by determining the rate constant at 35.0°C and then applying the Arrhenius equation. One run was made in 80 percent DMSO and 0.1159 molar HB (Table 4). The rate constant at 35.0°C was found to be 0.738 hr<sup>-1</sup>. The rate constant for a comparable concentration of HB in 80 percent DMSO at 25.0°C was found to be 0.0777 hr<sup>-1</sup>. Using these values in the Arrhenius equation gave  $\Delta E$  of activation of about 42.3 kcal/mole. More precise values for the  $\Delta E$  of activation must await further experimental work. The rate constant appears to increase by a factor of about 10 in going from 25.0°C to 35.0°C.

## SUMMARY

1. The decarboxylation reaction of HB in the presence of DMSO in water solutions proceeds with significant rates at a temperature of 25.0°C, which is far below any temperature reported in the literature.
2. The reaction rate for decarboxylation of trichloroacetic acid in solutions of dimethylsulfoxide in water at 25.0°C increases rapidly with increasing concentration of DMSO.
3. The reaction rate is determined by the speed with which the carbanion  $[\text{Cl}_3\text{C}]^-$  is broken down to form chloroform.
4. The addition of trichloroacetate ion to the reaction significantly increases the rate of the reaction.
5. The rate of decarboxylation increased by a factor of about 10 with a 10-degree rise in temperature.
6. It would appear that the energy of activation of the decarboxylation reaction is on the order of 42 kcal/mole.

## ACKNOWLEDGMENT

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