

## Kinetic and Equilibrium Studies of the Thermal Decomposition of 2-Methyl-2-Propanol

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The thermal decomposition of 2-methyl-2-propanol has been studied at 153°C with a semi-automatic pyrolysis apparatus. The initial rate constants at various pressures of the butanol (20 to 0.15 mm Hg) usually mixed with argon, in some experiments with oxygen, have been measured. The change of the reaction order depending on the reactant pressure has been observed. The equilibrium constant for the reaction:



has been determined and the free energy change at 153°C calculated to be  $-3.21 \pm 0.04$  kcal mole<sup>-1</sup>.

The kinetics of the thermal decomposition of organic substances has been studied extensively over a period of about thirty years.<sup>1</sup> Methods used can be roughly divided into static and flow methods. In both cases the introduction of GLC as an analytical tool represents a major step forward allowing the simultaneous quantitative analysis of a number of components using very small samples. Together with a static method the use of GLC was first described in 1961 by Purnell *et al.*<sup>2</sup> It was made possible by the construction of a leak-proof gas injection valve.<sup>3</sup>

The present research was planned back in 1961 and was directed towards the study of the thermal decomposition of organic compounds using GLC for analysis. It was realized that with the use of a suitable flame ionization detector satisfactory analyses could be performed at as low initial pressure of reactant as 10<sup>-2</sup> mm Hg and on a sampling volume as small as 0.1 ml. By adding an inert gas like argon sampling procedures could be much simplified. The high dilution was believed to be favorable, leading to more ideal conditions. Also the collision frequency between reactant and reactant-product molecules should be low compared to the frequency with which colli-

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sions occur with rare gas atoms. At constant partial pressure of reactant the number of collisions with the walls of the vessel is of course independent of the partial pressure of the added inert gas.

In kinetic studies of gas-phase reactions the presence of the phase boundary,<sup>1</sup> *i.e.* the walls of the reaction vessel, presents a difficult problem. Parallel to the homogeneous gas-phase reaction a reaction occurs at the phase boundary. Usually the activation energy of the reaction at the wall is much less than that of the homogeneous reaction. Therefore the method of conditioning the reaction vessel has long been used as a standard procedure by numerous workers.<sup>1</sup> Either the surface of the vessel is coated in one way or another or the reaction is allowed to take place repeatedly until the reaction rate becomes constant (due to the formation of a layer of pyrolysis products?). If the rate is invariant to the ratio surface/gas volume it is generally believed that the amount of reaction at the wall is negligible.

Hydrocarbons and alkyl halides have been subject to extensive studies using this method.<sup>1</sup> Kinetic measurements on alkyl halides recently made in shock-tube experiments are in accordance with pyrolysis data in conditioned vessels.<sup>4,5</sup> The influence of the wall-effect in pyrolysis of hydrocarbons has been demonstrated and the results show that it is possible to get reproducible rates in clean pyrex vessels.<sup>6</sup>

The thermal decomposition of alcohols has not previously been studied with special attention paid to the wall-effect. In earlier studies the conventional static system has been used in which the decomposition is followed manometrically. — In all cases the reaction vessel has been thoroughly conditioned. The decomposition of 2-methyl-2-propanol and 1,1-dimethyl-1-propanol was investigated by Schultz and Kistiakowsky<sup>7</sup> and the decomposition of methanol by Fletcher.<sup>8</sup> Barnard *et al.*<sup>9-13</sup> studied some alcohols: 2-methyl-2-propanol, 1-butanol, ethanol, 1-propanol and 2-propanol.

The first part of this paper describes the kinetics of the thermal decomposition of 2-methyl-2-propanol at a relatively low temperature and at low pressures. The second part describes the use of the same apparatus for determining the equilibrium constant for the dehydration of 2-methyl-2-propanol.

## EXPERIMENTAL

*Materials.* 2-Methyl-2-propanol (Baker Analyzed Reagent) was dried over Linde Molecular Sieves, 4 A, and distilled. The middle fraction, b.p. 82.3–82.5°C, was finally purified by preparative gas chromatography using an Aerograph Autoprep model A-700, with Carbowax 20 M as stationary phase on Chromosorb W.

*Apparatus.* The pyrolysis system consists of a reaction vessel inside a thermostat, a vacuum line with pumps and pressure measuring devices, and two gas systems, one for the reactant and one for argon or oxygen. The gas chromatograph consists of an air thermostat accommodating the columns, a flame ionization detector with electrometer, Aerograph, a recorder with disc integrator, Texas, and controlling valves for the carrier gas (nitrogen), hydrogen, and air. The pyrolysis and GC-systems are joined by a gas injection valve.

The total pressure of the gas (gas mixture) was measured outside the reaction vessel by a wide-bore mercury manometer. The readings could be done with an accuracy of  $\pm 0.1$  mm Hg. The initial butanol pressure was usually *ca.* 20 mm Hg, thus the error in the pressure determination amounted to *ca.*  $\pm 0.5$  %. By an expansion procedure at accurately known volume ratios samples were obtained at successively lower pressures

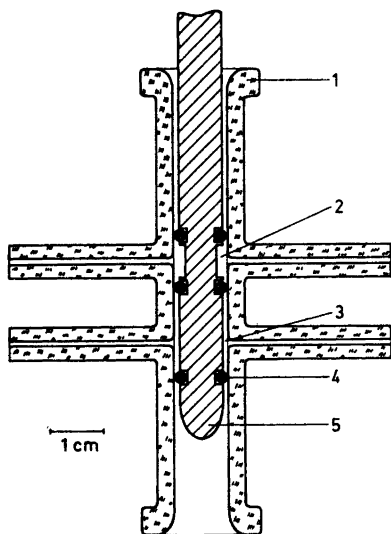


Fig. 1. Section through the gas injection valve. 1. Glass tube of Pyrex. 2. Cavity. 3. Cavity. 4. Viton O-rings. 5. Steel plunger.

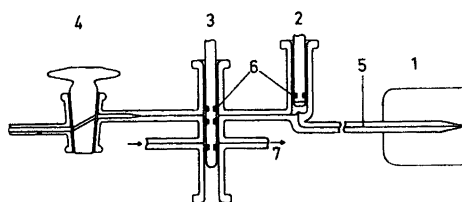


Fig. 2. Arrangement of sampling system. 1. Reaction vessel. 2. Greaseless vacuum valve. 3. Gas injection valve. 4. Conventional stopcock lubricated with silicone high vacuum grease. 5. 1 mm capillary tube. 6. Viton O-rings. 7. GLC carrier gas, nitrogen.

with almost retained pressure accuracy. The evacuated reaction vessel was filled from a storage container and the pressure was either calculated from the known volume ratio and the temperatures outside and inside the furnace (low pressure of reactant) or measured directly (high pressure of reactant + inert gas).

The construction of the furnace follows a conventional pattern. The reaction vessel is made of Pyrex or Vycor glass and placed inside an aluminium block, which can be heated by two separate heaters wound around the block. One of the heaters gives a constant energy supply that keeps the furnace temperature at *ca.* 20 degrees below the desired thermostating temperature. The input to the second heater is controlled from the platinum resistance thermometer situated in the air gap. The resistance thermometer is one arm of the Wheatstone bridge with an electronic null-detector operating the heater *via* a relay. The temperature fluctuations measured by an iron-constantan thermocouple are  $\pm 0.05$  at 200°C and  $\pm 0.1$  at 440°C. The gas chromatography column was maintained at constant temperature; variation less than 0.1°C.

The details of the gas injection valve are given in Fig. 1. The tube (1-1) is made of Pyrex-glass and cavities (1-2), (1-3) are enclosed by Viton O-rings (1-4) on a steel-plunger (1-5). It is possible to evacuate the sample volume (1-2) to better than  $10^{-4}$  mm Hg. The plunger has two operating positions; the cavity (1-2) in position one, as shown in Fig. 1, can be moved into the GLC carrier gas stream, position two. The plunger can be operated without any grease on the O-rings but a very thin layer of vacuum grease facilitates the operations. By using silicone high vacuum grease no discrepancies were observed with gases used in this work. The gases were in contact with O-rings and grease for 5–10 sec. The cavity (1-2) had a volume of 180  $\mu$ l and the carrier gas stream a pressure of 1.3 atm.

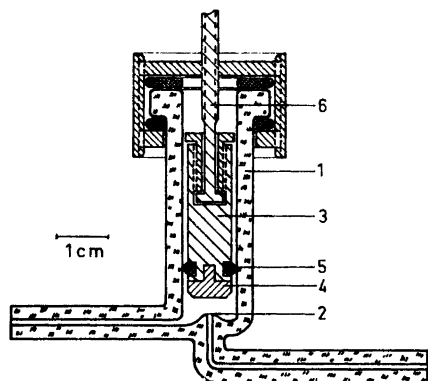


Fig. 3. Section through greaseless vacuum valve. 1. Glass tube of Pyrex. 2. Fire-polished seat. 3. Stainless steel plunger. 4. Teflon plug. 5. Viton O-ring. 6. Threaded spindle.

The gas injection system is schematically represented in Fig. 2. The volume between stopcocks (2-2) and (2-4) is 2 ml. The capillary tube between the reaction vessel has a volume of 0.3 ml. The volume between the plunger and stopcock (2-4) is 1.8 ml. When the gas sample fills the evacuated space between (2-2) and (2-4) the cavity in the plunger will be flushed thoroughly and the sample taken should represent the true composition of the gas mixture in the reaction vessel.

In gas-phase reactions it is difficult to predict the effects of the lubricants in the stopcocks which limit the reaction zone. The lubricant can adsorb gases and introduce impurities and thus interfere with the analytical results. Various solutions of this problem have been suggested in the literature,<sup>14-18</sup> each with its special advantages. A greaseless vacuum-stopcock made of pyrex glass has been developed in this laboratory, Fig. 3. It consists of a house (3-1) with a fire-polished seat (3-2), a stainless steel plunger (3-3) with a teflon plug (3-4) and a Viton O-ring seal (3-5). The plunger can be moved up and down by turning the threaded spindle (3-6). The spindle moves freely in the plunger in such a way that the plunger does not rotate when the spindle is operated. With this valve the reactant in the reaction vessel (attached to the capillary tube in connection with the seat) comes into contact only with glass and *ca.* 1 mm<sup>2</sup> teflon. The valve can be operated up to 200 deg. Time for opening and closing the valve is approximately 4 sec. The valve is vacuum tight and the only parts that can be worn out are the easily replaceable teflon plug and O-ring.

*Procedure.* The reactant alone or with oxygen or argon was introduced into the evacuated reaction vessel which has one inlet and one outlet tube. At predetermined time intervals the greaseless stopcock between reaction vessel and gas injection valve was opened for about 3 sec and the plunger was pushed down, injecting the gas mixture into the carrier gas stream. The sampling procedure consumes 2 ml and the volume of the reaction vessel is 200 ml. A series of 10 consecutive determinations can be made without decreasing the pressure in the reaction vessel by more than 10%. The minimum time between two determinations is approximately 4 min (time for evacuation).

*Treatment of preliminary data.* According to the literature, thermal decomposition of 2-methyl-2-propanol



gives only two products: 2-methyl-propene and water.<sup>7,9</sup> This was confirmed in the present work: no products other than 2-methyl-propene were observed even at the highest sensitivity of the flame ionization detector. The sensitivity ratio of the detector to the alcohol and the alkene was determined by letting the reaction proceed in the presence of octane as a reference. Samples were withdrawn at reaction time zero and at complete conversion, Fig. 4. Division

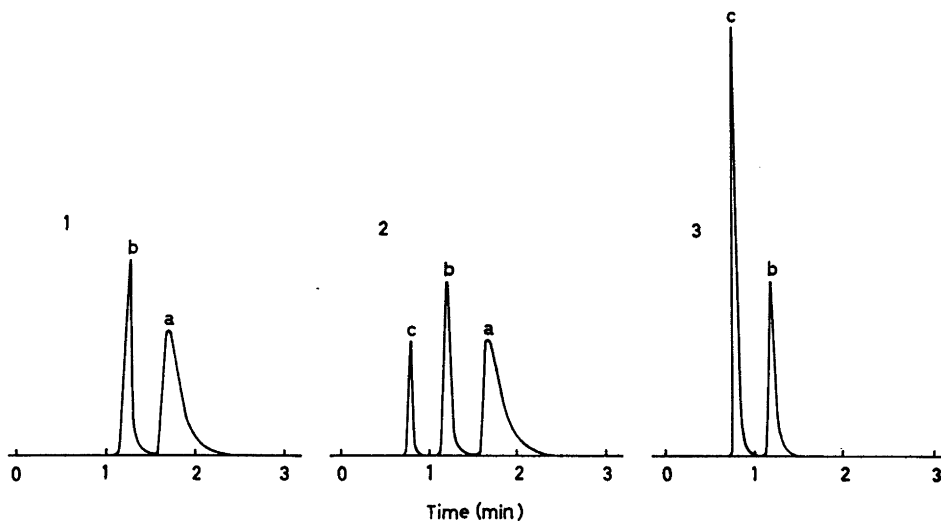


Fig. 4. GLC-analysis of samples from the pyrolysis of 2-methyl-2-propanol (a) to isobutene (c) with octane (b) present as a reference. 1. At reaction time zero. 2. At about 30 % decomposition. 3. Complete conversion. Conditions: 0.80 m aluminium tube packed with 9 % Carbowax 1500 on Chromosorb W-HMDS treated, 60–80 mesh, temperature 42°C, nitrogen flow rate 20 ml min<sup>-1</sup>, hydrogen flow rate 20 ml min<sup>-1</sup> and air flow rate 200 ml min<sup>-1</sup>.

of the peak area ratios between 2-methyl-2-propanol:octane and 2-methyl-propene:octane gave then the sensitivity ratio of the system between 2-methyl-2-propanol and 2-methyl-propene. As expected this ratio was found to be close to unity or  $0.974 \pm 0.01_3$ . When at time  $t = t$  a sample is taken the area under the alcohol peak is  $Y_{ol}$  and under the 2-methyl-propene peak is  $Y_{en}$ . If this sample is converted to unreacted alcohol it should give a 2-methyl-2-propanol peak area of  $Y_{ol} + 0.97 Y_{en} = Y_0$ . The reproducibility of  $Y_0$  was found to be 7 %, corresponding to the uncertainty in the sampling procedure, and thus  $Y_0$  had to be calculated for every sample.

For a first and zero order reaction the rate expressions define additional symbols used:

First order:

$$\begin{aligned} -dP/dt &= k_1 P \\ P &= a Y_{ol} \\ P_0 &= a Y_0 \end{aligned}$$

$$\begin{aligned} &\text{gives} \\ &\ln(Y_0/Y_{ol}) = k_1 t \end{aligned}$$

Zero-order:

$$\begin{aligned} -dP/dt &= k_0 \\ P &= a Y_{ol} \\ P_0 &= a Y_0 \end{aligned}$$

$$\begin{aligned} &\text{gives} \\ &P_0[1 - (Y_{ol}/Y_0)] = k_0 t \end{aligned}$$

At 150°C the equilibrium lies to the extreme right and thus the given expressions are valid at least up to 90 % conversion.

## RESULTS

*Conditioning experiments.* A series of consecutive test experiments were carried out in a Vycor glass reaction vessel at 300–350°C. The initial pressure of the 2-methyl-2-propanol was 15 mm Hg. In each run the decomposition was followed until *ca.* 70 % conversion was reached. The reaction rate decreased continuously, rapidly in the beginning and more slowly with increasing number of runs. After about 100 runs the decrease in first order reaction rate was small although still recognizable. It was assumed that the reaction vessel had been “almost conditioned” and the temperature was raised to 462°C. Twentyfive runs were made. The calculated first order rate constant value varied between 9 and  $32 \times 10^{-4} \text{s}^{-1}$ . In 5 of the runs octane was added at 10 mm Hg to the butanol, but no significant change in rate of decomposition was observed. The smallest rate constant observed was still approximately 50 times larger than would be expected from the literature data.<sup>7,9</sup> The reaction vessel was then cleaned using chromic acid, rinsed very thoroughly with distilled water and dried in vacuum at 462°C for 2 days. The rate of decomposition was now much higher, complete conversion was reached within less than 3 min compared with 12 min to 70 % before the cleaning operation.

The results from the above experiments were highly unsatisfactory. It seems that, under prevailing conditions, no reproducible conditioning of the walls of the reaction vessel could be achieved by thermal decomposition of the butanol. Also, the results indicate that even after 125 experiments in the same vessel the reaction rate is far too high compared to literature data. It is believed that one reason could be the low butanol pressure which does not allow the walls of the vessel to be properly “conditioned”. Kistiakowsky *et al.* state<sup>7</sup> “Another precaution we found necessary in the efforts to obtain homogeneity was the practice of “poisoning” a clean reaction flask by letting a high pressure of alcohol react and remain in contact with the flask for about twelve hours. When this was not done the constants were high and irreproducible”.

The main *raison d'être* for developing the present method was to enable work at low reactant pressure and it was felt desirable to keep this condition in the continuation of the research. Purnell's approach was therefore followed (compare above) by which the rate constant was determined in a clean pyrex vessel at low conversion.

*Measurements in a clean Pyrex vessel.* A Pyrex vessel washed with warm concentrated nitric acid and distilled water and thoroughly dried in vacuum was used to study the initial decomposition at 153°C. Forty runs were made with randomly distributed initial butanol pressure between 20 and 0.15 mm Hg. In all experiments with initial butanol pressure  $P_0 > 1$  mm Hg (26 runs) the decomposition was not allowed to exceed 5 %, at lower pressures the reaction proceeded faster and when 4 analyses had been taken as fast as possible the decomposition had reached 10 to 15 % (in 2 experiments 20 %). It was found that within the limits of error  $(dP/dt)_{t=0}$  was independent of the pressure in the interval 20–1 mm Hg, *i.e.* that the reaction was of zero order. The rate constant was calculated to  $11 \pm 1 \times 10^{-5} \text{ mm Hg s}^{-1}$ . Below 1 mm

Hg the rate constants were lower than for pressures above 1 mm Hg. The average value for 10 runs at  $P_0 < 0.5$  was found to be  $4 \times 10^{-5}$  mm Hg  $s^{-1}$ .

The rate constant  $k_0$  showed a significant decrease throughout the series ( $P_0 > 1$  mm Hg). For the first 10 runs  $k_0$  averaged  $14 \times 10^{-5}$  mm Hg  $s^{-1}$ , for the last 10 runs  $7 \times 10^{-5}$ . Addition of oxygen (2–250 mm Hg) or argon (100–450 mm Hg) to the butanol did not change the decomposition rate significantly.\* It seems that at low degree of conversion and/or the low temperature used in this series of experiments the reaction vessel was very little although slowly "conditioned".

The reaction vessel was left fully evacuated for 4 days at 153°C. A second series of 5 experiments was then carried out in the presence of  $350 \pm 2$  mm Hg argon and the reaction was allowed to proceed to 60 % or more.

From Table 1 is seen that the reaction rates in these experiments apparently behave irregularly compared to what could be expected from the former series.

Table 1. Thermal decomposition of 2-methyl-2-propanol at 153°C to a high degree of conversion.

Date(s)	$P_0$ (mm Hg)	Assumed zero order reaction		Assumed first order reaction		Maximum conversion plotted %
		Good linear plot up to conversion %	$k_0 \times 10^{-6}$ (mm Hg $s^{-1}$ )	Good linear plot up to conversion %	$k_1 \times 10^{-6}$ ( $s^{-1}$ )	
8/9–8/23**	15.2	54	56	23	(4)	70
8/29–9/1	2.8	80	9.0	30	(3)	80
9/7–9/8	0.5 <sub>3</sub>	86	5.1	45	(11)	86
9/10	0.2 <sub>0</sub>	65	3.3	42	(19)	65
9/15	0.05	30	(1.2)	60	29	65

\*\* The reaction was allowed to reach equilibrium.

The zero order reaction constant decreased very significantly with decreasing pressure between experiments. In contrast each run internally followed a zero order plot over the whole region for  $P_0 = 2.8, 0.53,$  and  $0.20$  mm Hg. The run at  $P_0 = 0.05$  mm Hg showed a closer fit to a first order reaction. (The best fit was in fact obtained for reaction order 0.9.) The first experiment behaved internally unsatisfactorily — no adjustment to any possible reaction order could be made. That the rate of reaction changed during the fortnight run may be due to a change in surface activity during the experiments. The slowing down of the reaction between consecutive runs indicates a "poisoning" in Kistiakowsky's sense.

\* Degassing the alcohol up to three times did not change the decomposition rate.

*Equilibrium measurement.* The equilibrium constants shown in Table 2 were calculated from the formula:

$$P_{\text{H}_2\text{O}}P_{\text{en}}/P_{\text{ol}} = K_p$$

From the areas under the GC-peaks the  $P_{\text{en}}:P_{\text{ol}}$ -ratio was obtained. As the conversion was close to 99.9 % the water pressure,  $P_{\text{H}_2\text{O}}$ , could be taken equal to the known initial pressure of the butanol,  $P_0$ , corrected for the number of samplings which reduce the total pressure in the reaction vessel.

In Table 2 column 1 gives the corrected  $P_{\text{H}_2\text{O}}$ , column 2 the  $Y_{\text{en}}:Y_{\text{ol}}$ -ratio and column 3 shows the equilibrium constant at 153°C.

Table 2.

$P_{\text{H}_2\text{O}} \times 10^3$ (atm)	$\frac{Y_{\text{en}} \times 10^{-2}}{Y_{\text{ol}}}$	$K_p$ (atm)
17.5	21.7	38.0
17.4	31.2	54.3
17.1	24.5	41.9
17.0	27.5	46.8
16.7	22.3	37.2
16.4	24.4	40.0
15.8	34.0	53.7
15.7	29.2	45.8
15.5	28.2	43.7
15.1	32.1	48.5
14.7	27.3	40.1

Mean  $44.5 \pm 1.8$

From the mean  $K_p$ -value the free energy change for the reaction at 153°C was calculated:

$$\Delta G^\circ = -RT \ln K_p = -3.21 \pm 0.04 \text{ kcal mole}^{-1}$$

The agreement is excellent with the datum,  $-3.08 \text{ kcal.mole}^{-1}$ , obtained by interpolation of standard free energy data for 2-methyl-2-propanol,<sup>19</sup> 2-methylpropene,<sup>20</sup> and water vapor.<sup>21</sup>

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