

## THE REACTION BETWEEN DIACETYL AND HYDROGEN PEROXIDE: ITS MECHANISM AND KINETIC CONSTANTS

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### ABSTRACT

The reaction between diacetyl and hydrogen peroxide in aqueous solution was investigated using an adiabatic reaction calorimeter. The kinetic constants are calculated using procedures based on the temperature-time behaviour of the reaction system.

The mechanism of the reaction proposed fits very well with the reaction-rate equations used and the observed temperature-time data.

### 1. INTRODUCTION

Diacetyl (2, 3-butanedione) is one of those relatively small molecules with a light absorption in the visible range of the electromagnetic spectrum. Not only its remarkably intense yellow colour but also its flavour makes it an interesting compound.

In 1904, Holleman<sup>1</sup> reported the complete conversion of diacetyl into acetic acid when it reacted with hydrogen peroxide. Weitz and Scheffer<sup>2</sup> proposed, for the first time, a mechanism explaining the rapid cleavage of diketones. They suggested the formation of an unstable diperoxide followed by a ring-shaped superoxide which converted into acetic anhydride. The latter is rapidly hydrolysed to acetic acid in aqueous solution.

However, the investigations of Sauer and Edwards<sup>3</sup> on the reaction between acetone and hydrogen peroxide did not support these steps for the reaction diacetyl and hydrogen peroxide.

From the work of Barnes and Lewis<sup>4</sup> and of Leffler<sup>5</sup>, it is clear that acetic anhydride is always an intermediate product and because of the large amount of water, complete hydrolysis takes place. In Sect. 3.2, a more detailed discussion is presented concerning the possible intermediates.

The objective of this paper is to demonstrate the possibilities in determining the

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kinetic constants of a complex reaction using only the temperature-time relation of the reaction under adiabatic conditions.

In Sect. 2, a description is given of the techniques used in determining the end products of the reaction, the method of realising the adiabatic conditions, and the spectrophotometric experiments used to analyse the diacetyl-water equilibrium. In Sect. 3, an analysis of the mechanism is proposed. In Sect. 4, the results and the method of calculation are discussed.

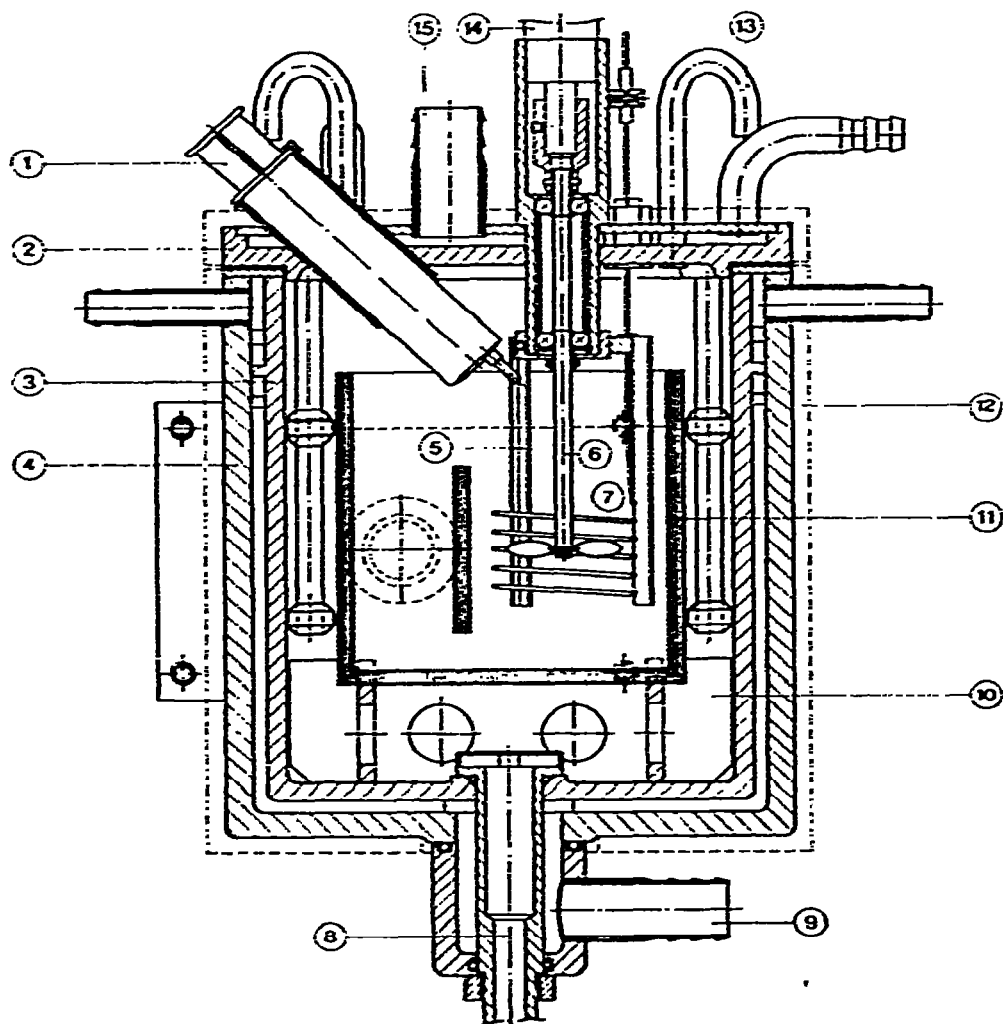


Fig. 1. The spectrophotometric cell compartment assembly. 1, Injection device; 2, cover of cell compartment; 3, inner wall of cell compartment; 4, outer wall of cell compartment; 5, mixing chamber baffles; 6, stirrer; 7, thermocoax for calibration; 8, inlet for thermostatted air; 9, inlet for thermostatted water; 10, cell support; 11, Perspex cell; 12, cork insulation; 13, air outlet; 14, connection for Bowden cable; 15, water outlet; 16, shutter to the detector; 17, glass windows; 18, connection to the photomultiplier; 19, optical axis.

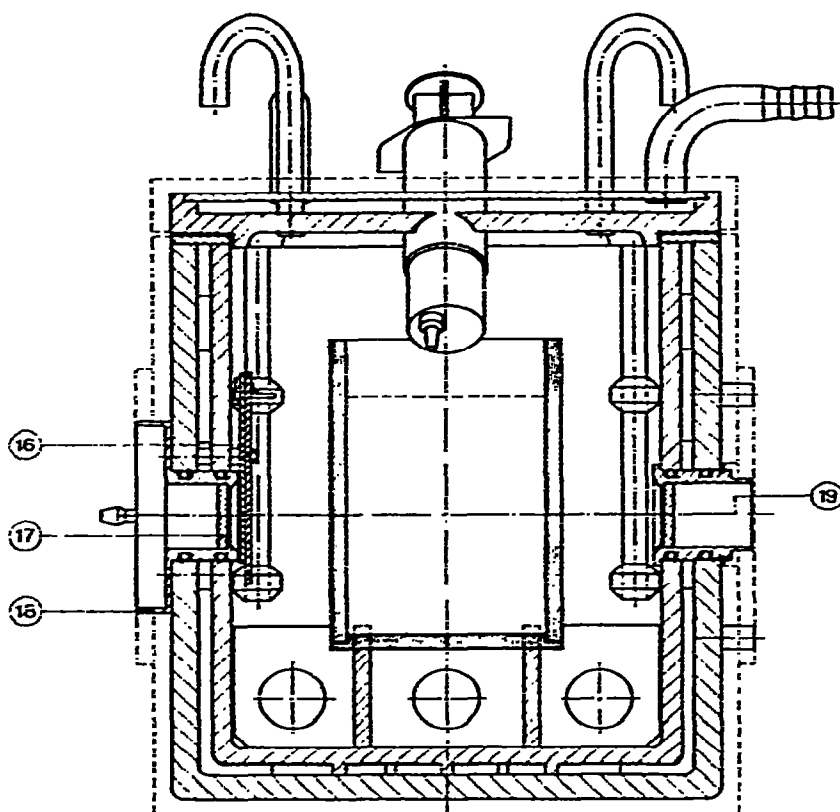


Fig. 2. The spectrophotometric cell compartment assembly parallel to the optical axis. For explanation of numbers, see Fig. 1.

## 2. EXPERIMENTAL

### 2.1 Spectrophotometric experiments

The reaction-rate experiments started with an aqueous mixture of diacetyl to which a known amount of hydrogen peroxide in water was added. There was no reason to expect that the concentration of diacetyl and its hydrate were at equilibrium conditions during the reaction with hydrogen peroxide. So the reaction constants  $k_1$  and  $k_2$  (see Sect. 3.1) and the equilibrium constant  $K$  must be known as a function of temperature.

Visual observation of the change in colour intensity on mixing the diacetyl mixture with hydrogen peroxide gave the impression of a fast equilibrium reaction followed by a slower irreversible reaction. This behaviour is reminiscent of the equilibrium reaction found by Sauer and Edwards for acetone. To get information about the equilibrium constant, preliminary reaction-rate experiments were carried out.

These experiments were all performed with a Model 46 Perkin-Elmer single beam spectrophotometer. The selection criteria are, on the one hand, analogue and digital output and, on the other, high stability and modular construction. Reaction

experiments over a longer period in this spectrophotometer are rather insensitive to drift and change in zero readings.

Commercially available spectrophotometers are, in general, not well suited for reaction-rate experiments but the modular construction of Model 46 presents the opportunity of constructing a suitable cell compartment.

Figures 1 and 2 are sectional drawings of the reaction chamber with the separate parts identified. Only the major design points will be discussed in detail. The construction is such that a constant environment with a high stability can be achieved. To realize this, the wall of the cell compartment consists of an inner compartment (3) and an outer wall (4) with circulating thermostatted water in between. Both walls of the compartment and of the cover (2) are of solid copper. In cases of heat-producing systems in the inner cell compartment, a thermostatted air stream, entering at the bottom (8), will keep the temperature of the cell surroundings constant.

The Perspex cell (11), with plan parallel windows, consists of a stirrer (6) and thermocoax for calibration purposes. The liquid mixture is circulated by the stirrer in the light path of the spectrophotometer in the other part of the cell. Complete mixing is established in about one second. The light path in the reaction mixture is 60.15 mm.

One of the components was kept in the syringe assembled in the thermostatted cover to ensure equal temperatures on mixing. In the experiments for the determination of the equilibrium constants of the diacetyl and water reaction, the syringe contained the diacetyl. In the preliminary reaction-rate experiments, a known amount of hydrogen peroxide was injected via the syringe.

The spectrophotometer data were recorded with the data-logging system, described by Frankvoort and Dammers<sup>16</sup>, on magnetic tape to be processed by suitable computer programmes. Besides transmission-time data, temperature-time and, if necessary, pH-time data were simultaneously recorded.

## 2.2 Reaction products

From different experiments with an initial concentration ratio of diacetyl to hydrogen peroxide from 10:1 to 1:10, the final reaction mixture was analysed by gas chromatography. All mixtures used were completely reacted and stable in chemical composition.

A Packard-Becker Model 427 with a Chromosorb P-120 mesh (20% coating of compound 82) column was used, accepting aqueous mixtures without tailing and bleeding.

The results of the experiments are summarized in Table 1.

The presence of diacetyl, acetic acid and 2-butanone in the mixture was positively demonstrated. A very small peak at a retention time of 482 s was not identified. Analysis of fresh diacetyl showed the presence of diacetyl, 2-butanone and the unknown compound. This means that the only product of the reaction between diacetyl and hydrogen peroxide was acetic acid. The precision of the experiments was about  $\pm 0.5\%$  relative, both for the retention times and the concentrations.

TABLE I

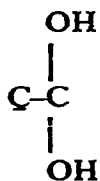
COMPOSITION OF THE FINAL REACTION MIXTURE

<i>Absolute retention time (s)</i>	<i>Compound</i>
0	Injection of 1 $\mu$ l mixture
95	< 1% 2-Butanone
111	Diacetyl
482	$\leq$ 1% Unknown
740	Acetic acid

### 2.3 NMR experiments

In Fig. 3, the NMR spectrum of diacetyl in  $D_2O$  shows three peaks. The two adjacent peaks fall in the range characteristic of methyl protons next to a carbonyl group. The third peak falls in the range of methyl protons adjacent to a hydrated carbonyl group. This spectrum is thus a superposition of the lines of monohydrated and unhydrated diacetyl.

The identification of the three peaks in Fig. 3 is based on intensity measurements as a function of temperature. The area under one of the two adjacent peaks is proportional to the contribution of two  $C-C=O$  groups in diacetyl and the other line with one  $C-C=O$  group in the monohydrate. The third line has an area proportional to one



group in the monohydrate. The peak from the adjacent pair which shows the same temperature behaviour as the single peak belongs to the same molecule, in this case to the monohydrate. The conclusions as to which line belongs to which compound are shown in Fig. 3.

Greenzaid et al.<sup>6</sup> arrived at the same conclusions as found here in the NMR experiments.

Although the experimental set-up in the NMR experiments is not very useful in following intensities as a function of time, reaction experiments have been carried out to confirm the intermediate acetic anhydride.

In Fig. 4, a typical example of a NMR spectrum of the reaction mixture is given. The spectrum showed two extra peaks; the one with a high intensity is acetic acid and the other one belongs to one of the intermediates. The latter decreased with time and disappeared completely after some time. One remarkable point is the pronounced shifting of all the lines in the spectrum as a function of an increasing acetic acid

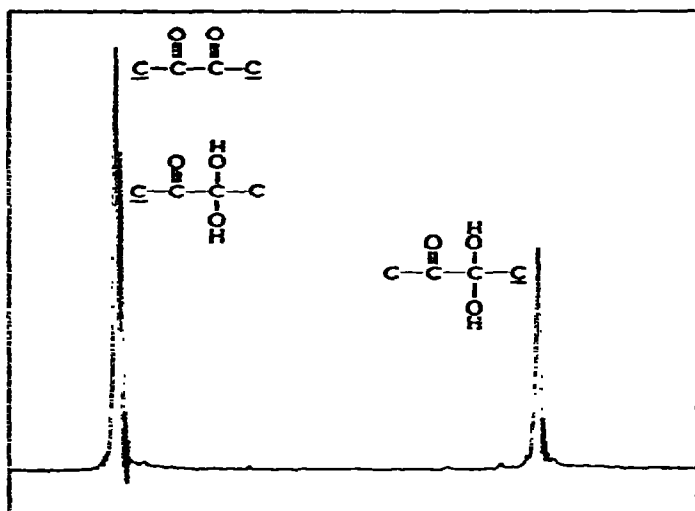


Fig. 3. The NMR spectrum of diacetyl in  $D_2O$ .

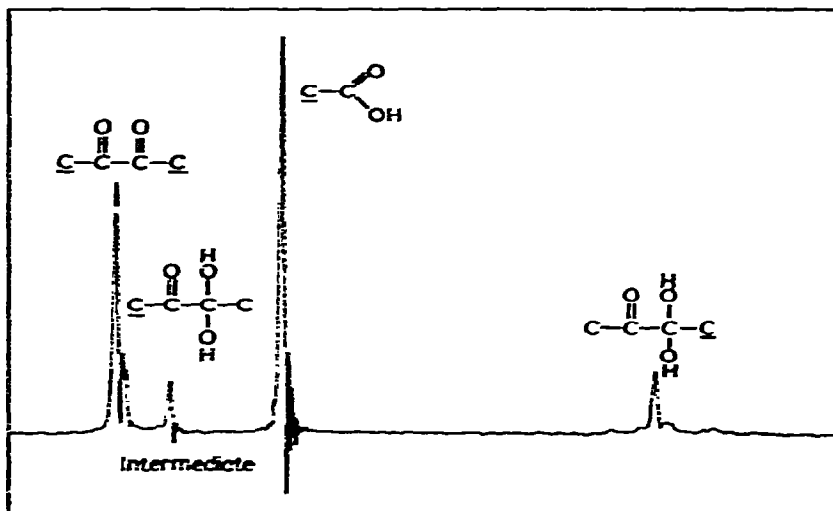


Fig. 4. The NMR spectrum of the reaction mixture of diacetyl and  $H_2O_2$  in  $D_2O$ .

concentration. This prevented an absolute determination of the "intermediate" peak. Using a mixture of diacetyl, acetic acid and acetic anhydride in  $D_2O$ , a position of the acetic anhydride line relative to those of diacetyl and acetic acid was compared with the one of the intermediate in the reaction mixture. A good agreement (better than 3%) in position was found.

Although the assignment of the intermediate as acetic anhydride is not completely certain, the experiments of Leffler<sup>5</sup> and of Barnes and Lewis<sup>4</sup>, together with our results, give a good basis for this assumption.

#### 2.4 Reaction rate experiments

The use of an adiabatic reaction calorimeter has been fully described by

Frankvoort<sup>15</sup>. The experimental conditions have been described in detail in realising the calorimeter.

To achieve the various ratios of diacetyl to hydrogen peroxide in the different experiments, hydrogen peroxide mixtures were sometimes in the inner cell and sometimes in the outer.

The aqueous hydrogen peroxide mixtures were made from a 35wt. % solution. The exact value of the concentrations were determined titrimetrically.

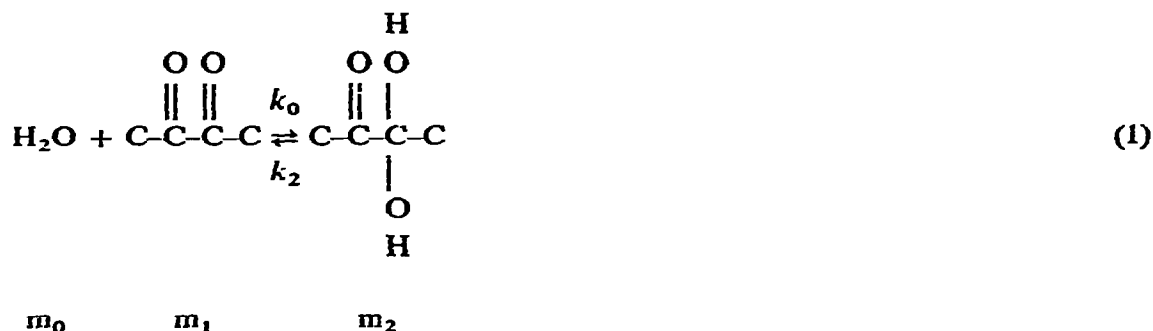
### 3. ANALYSIS OF THE REACTION MECHANISM

#### 3.1 Equilibrium of diacetyl and water

Aqueous solutions of diacetyl, like many aldehydes and ketones, show a high degree of hydrolysis.

Initial reaction mixtures of diacetyl with water were spread over a wide range of temperatures, so that it was necessary to know the equilibrium behaviour of diacetyl in water. Moreover, the rate constants of the forward and reverse reactions had to be known as will be explained later.

The equilibrium, extensively studied by Bell and McDougall<sup>7</sup>, is given by



In excess water, the reaction-rate equation can be written as

$$\frac{dm}{dt} = -k_0 m_0 m_1 + k_2 m_2 \quad (2)$$

and the equilibrium constant  $K$  is defined as

$$K = \frac{k_1}{k_2} = \frac{m_{2,e}}{m_{1,e}} \quad (3)$$

where  $k_1 = k_0 m_0$  and  $m_{i,e}$  is the equilibrium concentration of species  $i$ .

Bell and McDougall<sup>7</sup> determined the equilibrium constant by UV techniques in the temperature range 25–54°C. Both Greenzaid et al.<sup>8</sup> and Bell and McDougall<sup>7</sup> used a wavelength of 420 nm which is, as they showed, specific for diacetyl.

Neither the value for the molar extinction coefficient used by Bell and McDougall<sup>7</sup> ( $\epsilon = 23.0 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) nor the one determined by Greenzaid et al.<sup>8</sup> ( $\epsilon = 16.0 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) seems to be correct. The calculated enthalpy of hydration,

$\Delta H_{298\text{K}} = -29 \pm 3 \text{ kJ mol}^{-1}$ , based on the extinction coefficient determined by Greenzaid et al.<sup>3</sup>, is about 30% higher than our calorimetric value of  $\Delta H_{298\text{K}} = -20.9 \pm 0.5 \text{ kJ mol}^{-1}$  [see text following eqn. (16)].

Because of the fact that only  $K$ , but also  $k_1$  and  $k_2$  should be known as a function of temperature, the following reaction-rate experiments have been carried out.

At various temperature levels, the reaction between diacetyl and water was followed spectrophotometrically at a wavelength of 420 nm. The reaction-rate equation given in eqn. (2) has, as initial and final conditions

$$\begin{aligned} t = 0: m_1 &= m_{1,0} & t = \infty: m_1 &= m_{1,e} \\ m_2 &= 0 & m_2 &= m_{2,e} \end{aligned} \quad (4)$$

Integration of eqn. (2) using the initial and final conditions and the fact that  $m_{1,0} = m_{1,e} + m_{2,e}$ , leads to

$$(m_1 - m_{1,e}) = (m_{1,0} - m_{1,e}) \exp\left(-\frac{k_1 m_{1,0} t}{m_{1,0} - m_{1,e}}\right) \quad (5)$$

Lambert-Beer's law gives the relationship between the concentration of a compound and its measured absorption. Substitution of

$$\begin{aligned} m_1 &= A_i(l\varepsilon) \\ m_{1,0} &= A_{0i}(l\varepsilon) \\ m_{1,e} &= A_{ei}(l\varepsilon) \end{aligned} \quad (6)$$

where  $A$  is the measured absorption, gives

$$(A - A_e) = (A_0 - A_e) \exp\left(-\frac{k_1 A_0 t}{A_0 - A_e}\right) \quad (7)$$

Using an exponential curve fit given by

$$Y = p \exp(qt) \quad (8)$$

the rate constants are determined without using the value of  $\varepsilon$ .

$$k_1 = -\frac{q p}{A_e + p} \quad k_2 = -\frac{q A_e}{A_e + p} \quad (9)$$

$$K = \frac{k_1}{k_2} \quad \varepsilon = \frac{A_e + p}{l m_{1,0}}$$

The equilibrium reaction between diacetyl and water was carried out at various temperatures and fitted using eqn. (8). The temperature relationship for  $k_1$  and  $k_2$  is of the Arrhenius type

$$k_1 = Z_1 \exp\left(-\frac{E_1}{RT}\right) \quad (10)$$

$$k_2 = Z_2 \exp\left(-\frac{E_2}{RT}\right)$$



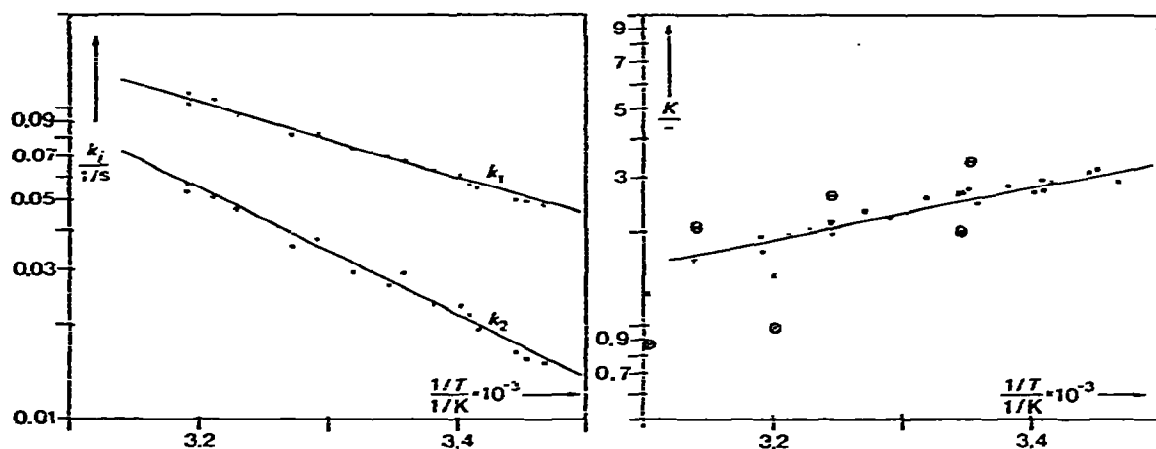


Fig. 5. The temperature function of  $k_1$  and  $k_2$ .

Fig. 6. The temperature function of  $K$ .  $\circ$ , Data from this investigation;  $\dagger$  ( $\epsilon = 19.5$ ),  $\oplus$  ( $\epsilon = 23.0$ ), data from Bell and McDougall<sup>7</sup>;  $\times$  ( $\epsilon = 19.5$ ),  $\otimes$  ( $\epsilon = 16.0$ ), data from Greenzaid et al.<sup>8</sup>;  $*$ , data from Hooper<sup>9</sup>.

resulting in the followings values for the kinetic constants.

$$\begin{aligned} Z_1 &= (7.60 \pm 0.90) \times 10^2 \text{ s}^{-1} & E_1 &= (2.31 \pm 0.07) \times 10^4 \text{ kJ mol}^{-1} \\ Z_2 &= (1.69 \pm 0.85) \times 10^5 \text{ s}^{-1} & E_2 &= (3.88 \pm 0.13) \times 10^4 \text{ kJ mol}^{-1} \end{aligned}$$

The value for  $\epsilon$  in all these experiments appears to be  $\epsilon = 19.5 \pm 0.5$ . All constants determined are valid in the range 285–315 K, the experimentally used range for the reactions. Figure 5 shows the results for  $k_1$  and  $k_2$  as a function of temperature.

Using  $\epsilon = 19.5$  for the data of Bell and McDougall<sup>7</sup>, a good agreement is found. Also, the value given by Hooper<sup>9</sup> fits very well with these experiments as can be seen in Fig. 6. From the data of Greenzaid et al.<sup>8</sup>, those values for  $K$  falling within our temperature range are plotted in Fig. 6 to show the greater discrepancy with the other data values.

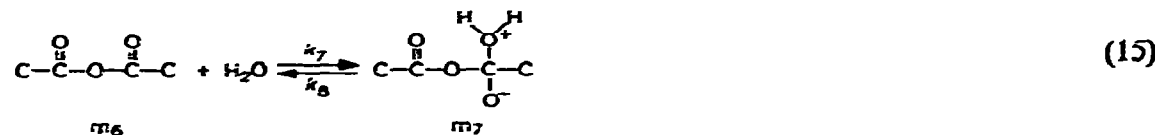
### 3.2 The complete reaction mechanism

From the investigations of Barnes and Lewis<sup>4</sup> and Leffler<sup>5</sup>, the oxidation of diketones with hydrogen peroxide always proceeds via acetic anhydride ( $\text{in}_6$ ). This is confirmed by the NMR experiments in Sect. 2.3.

Using the principles for the oxidation of acetone in this case, the equilibrium reaction (12) will be a good description.

Before discussing the possible intermediates and reactions, the following set of reaction equations might be a good alternative to those proposed by the authors previously mentioned.

Equation (11) is extensively discussed in Sect. 3.1 and the values of  $k_1$  and  $k_2$  as a function of temperature are given there. Using the Dewar calorimeter described by Frankvoort and Dammers<sup>15</sup>, the reaction enthalpy was found to be  $\Delta H_{298\text{K}} = -20.9 \pm 0.5 \text{ kJ mol}^{-1}$ .



The equilibrium reaction in eqn. (12) is motivated on one side by the reaction between acetone and hydrogen peroxide as described by Sauer and Edwards<sup>3</sup> and on the other side by preliminary reaction-rate experiments carried out in the spectrophotometer as explained in Sect. 2.1.

We recorded the absorption-time behaviour of initial reaction mixtures with different diacetyl hydrogen peroxide ratios. Directly after mixing the components, a sharp drop in the diacetyl concentration was found which became slower after some time. This can be explained by an equilibrium reaction with a forward rate constant ( $k_3$ ) somewhat greater than the reverse rate constant ( $k_4$ ) followed by a slower irreversible reaction ( $k_5$  or  $k_6$ ).

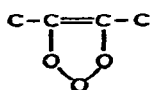
Comparing the rate of these reactions with the equilibrium reaction between diacetyl and water, the value of  $k_3$  (300 K) appears to be about  $0.09 \text{ kg mol}^{-1} \text{ s}^{-1}$  compared with  $k_1$  (300 K) =  $0.07 \text{ s}^{-1}$  and  $k_2$  (300 K) =  $0.03 \text{ s}^{-1}$ .

Our preliminary reaction-rate experiments indicated that the reaction in eqn. (12) is not coupled with a measurable evolution of heat.

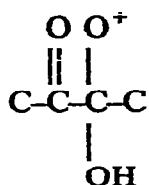
When  $k_5 \ll k_3$ , the concentration of diacetyl is mainly determined by the position of the equilibrium reaction (12). In that case, the ratio between  $k_3$  and  $k_4$  at 300 K can be calculated.

$$\frac{k_3}{k_4} \approx 15 \quad (17)$$

Our suggestion for the intermediate  $m_5$  in eqn. (13) is not proved by any experiment. Both alternatives, those of Weitz and Scheffer<sup>2</sup> and Leffler<sup>5</sup>, are possible. The proposition of Weitz and Scheffer<sup>2</sup>, i.e.



appears to be artificial. Leffler's<sup>5</sup> intermediate, i.e.



and the one given in eqn. (13) could appear after each other. However, which of these alternatives is the correct one is not important for the kinetic calculations as will be shown in Sect. 4.

In eqn. (14), acetic anhydride, detected by NMR experiments, is found. The enthalpy of formation of  $m_4$  can be calculated from  $m_1$  and  $m_3$  combined with the enthalpy of reaction of eqn. (12):  $\Delta H_{298\text{K}} = 0.0 \text{ kJ mol}^{-1}$ . Accepting the fact that the enthalpies of formation of  $m_4$  and  $m_5$  are identical, the enthalpy of the reaction given in eqn. (13) is therefore  $\Delta H_{298\text{K}} = 0 \text{ kJ mol}^{-1}$ . The enthalpy of the reaction<sup>10, 11</sup> given in eqn. (14) is now calculated as  $\Delta H_{298\text{K}} = -356.8 \pm 1.5 \text{ kJ mol}^{-1}$ .

The hydrolysis of acetic anhydride has been extensively investigated<sup>12-14</sup>. Bunton et al.<sup>12</sup> proposed the mechanism given in eqns. (15) and (16). Hoffman<sup>13</sup> and Maelicke<sup>14</sup> gave a detailed discussion about the values of the kinetic constants. They showed that  $k_9 \gg k_7$  and that for this reason the concentration of  $m_7$  is very small. This means the backward reaction via  $k_8$  will be very small and can be neglected. The rate-determining step is the forward reaction. The value for  $k_7$  given by Maelicke<sup>14</sup>, and in good agreement with those of Hoffman<sup>13</sup> and Bunton et al.<sup>12</sup> is

$$k_7 = 7.883 \times 10^5 \exp\left(-\frac{4.835 \times 10^4}{RT}\right) \quad (18)$$

The enthalpy of the reactions given in eqns. (15) and (16) together, based on the enthalpies of formation<sup>10, 11</sup> is  $\Delta H_{298\text{K}} = -58.36 \pm 1.0 \text{ kJ mol}^{-1}$ .

The numerical methods described by Frankvoort<sup>17</sup> with the experimental method explained in Sect. 2.4 can be used in the determination of the unknown kinetic constants.

These methods are based on the determination of temperature as a function of time and setting up a usable descriptive function, fittable as easily as possible.

The rate of temperature change of the complete mechanism is given by

$$\frac{dT}{dt} = \frac{Q_1}{c_p} (k_1 m_1 - k_2 m_2) + \frac{Q_2}{c_p} k_6 m_5 + \frac{Q_3}{c_p} k_9 m_7 \quad (19)$$

This equation cannot be changed into a similar kinetic equation as discussed by Frankvoort and Dammers<sup>16</sup>. In fact, the impossibility to fit the data by means of the modified Arrhenius equation has forced us to use the method explained by Frankvoort<sup>17</sup>. The following section deals with the details in solving this problem.

#### 4. RESULTS AND DISCUSSION

As explained in Sect. 3.2, the modified Arrhenius method is not applicable to the determination of the kinetic constants in eqn. (19). The only alternative is to integrate all the equations describing the course of the reaction, simultaneously. These equations read

$$\frac{dm_1}{dt} = -k_1 m_1 + k_2 m_2 - k_3 m_1 m_3 + k_4 m_4 \quad (20)$$

$$\frac{dm_2}{dt} = -k_2 m_2 + k_1 m_1 \quad (21)$$

$$\frac{dm_3}{dt} = -k_3 m_1 m_3 + k_4 m_4 \quad (22)$$

$$\frac{dm_4}{dt} = +k_3 m_1 m_3 - k_4 m_4 - k_5 m_4 \quad (23)$$

$$\frac{dm_5}{dt} = +k_5 m_4 - k_6 m_5 \quad (24)$$

$$\frac{dm_6}{dt} = +k_6 m_5 - k_7 m_6 + k_8 m_7 \quad (25)$$

$$\frac{dm_7}{dt} = +k_7 m_6 - k_8 m_7 - k_9 m_7 \quad (26)$$

$$\frac{dT}{dt} = \frac{Q_1}{c_p} (k_1 m_1 - k_2 m_2) + \frac{Q_2}{c_p} k_6 m_5 + \frac{Q_3}{c_p} k_9 m_7 \quad (27)$$

Remembering the conditions mentioned in Sect. 3, the following assumptions will be made.

We do not expect that the concentrations in eqns. (11) and (12) fulfil the equilibrium condition. For the numerical integration it is not essential, but convenient

to accept  $k_6 \gg k_5$ . This implies  $m_5$  is very small and constant,  $dm_5/dt = 0$  and  $k_5m_4 = k_6m_5$ .

From the investigations of Maelicke<sup>14</sup>, it is clear that  $k_9 \gg k_7$  which results in  $dm_7/dt = 0$ ,  $k_8m_7 \approx 0$  and  $k_7m_6 = k_9m_7$ .

These considerations reduce the differential equations to the following.

$$\frac{dm_1}{dt} = -k_1m_1 + k_2m_2 - k_3m_1m_3 + k_4m_4 \quad (28)$$

$$\frac{dm_2}{dt} = -k_2m_2 + k_1m_1 \quad (29)$$

$$\frac{dm_3}{dt} = -k_3m_1m_3 + k_4m_4 \quad (30)$$

$$\frac{dm_4}{dt} = +k_3m_1m_3 - k_4m_4 - k_5m_4 \quad (31)$$

$$\frac{dm_6}{dt} = +k_5m_4 - k_7m_6 \quad (32)$$

$$\frac{dT}{dt} = \frac{Q_1}{c_p}(k_1m_1 - k_2m_2) + \frac{Q_2}{c_p}k_5m_4 + \frac{Q_3}{c_p}k_7m_6 \quad (33)$$

From our own experiments and from literature data, the values of  $k_1$ ,  $k_2$  and  $k_7$  are known as functions of temperature in the range from 285 to 315 K. The values of  $Q_1$ ,  $Q_2$  and  $Q_3$  are known from calorimetric experiments and from thermodynamic calculations. For  $c_p$ , a value can be estimated from calorimetric experiments with the final reaction mixture.

The preliminary reaction-rate experiments yield an estimate for  $k_3$  and  $k_3/k_4$ . Only for  $k_5$  are estimates based on physical or chemical grounds unavailable.

To determine the kinetic constants in the Arrhenius equation of  $k_3$ ,  $k_4$  and  $k_5$ , the techniques explained by Frankvoort<sup>17</sup> are used. Equations (28)–(33) are integrated simultaneously. The calculated temperatures are compared with the experimental ones. This is done, meanwhile adjusting the parameters, as long as the calculated temperatures do not fit the observed temperatures.

In fact, six differential equations have been integrated simultaneously, and eight parameters estimated, namely  $Z_3$ ,  $Z_4$ ,  $Z_5$ ,  $E_3$ ,  $E_4$ ,  $E_5$ ,  $Q_2$  and  $Q_3$ .

Another reason for adjusting the values for  $Q_2$  and  $Q_3$  is found in the possible changes in the value of  $Q$  and  $c_p$  due to the experimental conditions, resulting in unnecessarily worse adaptation of the fitted curve.

A second, and unexpected point was the poorer adaptation of the calculated temperature at the last part of the curve. This indicates a possibly less acceptable value for  $k_7$ .

TABLE 2

RESULTS OF THE PARAMETER ESTIMATION

$i$	$Z_i$ ( $s^{-1}$ )	$E_i$ ( $kJ\ mol^{-1}$ )	$Q_i$ ( $kJ\ mol^{-1}$ )
1	$(7.60 \pm 0.90) \times 10^2$	$(2.31 \pm 0.07) \times 10^4$	$-20.0 \pm 0.9$
2	$(1.69 \pm 0.85) \times 10^3$	$(3.88 \pm 0.13) \times 10^4$	$-61.0 \pm 2.1$
3	$(2.510 \pm 0.008) \times 10^{6.2}$	$(3.78 \pm 0.02) \times 10^4$	$-354 \pm 10$
4	$(1.664 \pm 0.004) \times 10^3$	$(4.28 \pm 0.14) \times 10^4$	—
5	$(9.16 \pm 0.16) \times 10^{10}$	$(7.03 \pm 0.02) \times 10^4$	—
7	$(3.30 \pm 0.14) \times 10^6$	$(4.77 \pm 0.04) \times 10^4$	—

$\ast\ \text{kg mol}^{-1}\ \text{s}^{-1}$ .

To avoid this, we introduced two extra parameters,  $Z_7$  and  $E_7$ . This has resulted in a much better adaptation of the calculated temperatures to the observed ones. We thus integrated at least six differential equations simultaneously and have determined ten parameters.

The concentration range of diacetyl to hydrogen peroxide was from 10:1 to 1:10. The temperature range was from about 285 to 315 K.

The calculations result in the values for the kinetic constants, including the enthalpy of reaction, given in Table 2.

In Fig. 7, a typical example of the course of the concentrations of  $m_1$ – $m_6$  is given. As we can see, a rapid change of the concentrations  $m_1$ ,  $m_2$  and  $m_3$  occurs. This indicates a set of stiff differential equations. The numerical calculations showed the same behaviour by very small steps in the beginning of the integration, followed by an increasing time step ranging to the experimental time step.

The importance of the combination of an adiabatic calorimeter and an advanced numerical method lies in the very satisfying tackling of complex reaction systems. In

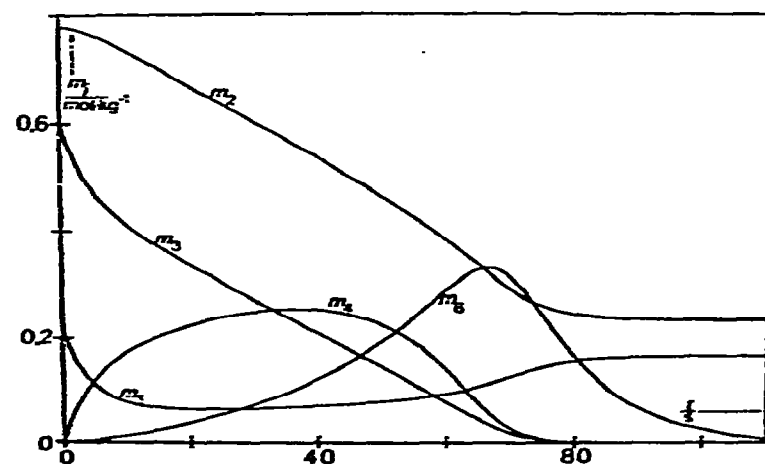


Fig. 7. Concentration–time curves for the reaction of diacetyl and  $\text{H}_2\text{O}_2$ .

one single reaction experiment all the kinetic data describing the complete course of reaction is determined. Compared with isothermal methods using spectrophotometrically detected diacetyl concentration, the simplicity of our experiments and the free choice of the concentration are remarkable for the method explained in this paper. Particularly in reaction systems with a great enthalpy of reaction, isothermal experiments with high concentrations are very difficult to carry out at sufficiently constant temperature.

## 6. NOTATION

$A$	spectrophotometrically determined transmission.
$c_p$	specific heat capacity.
$E_i$	activation energy of reaction number $i$ .
$\Delta H$	thermodynamically calculated enthalpy of reaction.
$k_i$	reaction rate constant of reaction number $i$ .
$K$	equilibrium constant.
$l$	length of light path.
$m_i$	molality of solute of component $i$ .
$m_{i,0}$	initial molality of component $i$ .
$m_{i,c}$	equilibrium molality of component $i$ .
$Q_i$	experimentally determined reaction enthalpy.
$R$	molar gas constant ( $R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$ ).
$T$	absolute temperature of reaction mixture.
$t$	time.
$Z_i$	frequency factor of reaction number $i$ .
$\epsilon$	molar absorption coefficient.

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