Kinetics of the Hydroxide Ion Catalyzed Dealdolization of Diacetone Alcohol at Normal and High Pressure

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The rate constant of the reaction $(CH_3)_2C(OH)$-$CH_2COCH_3 \rightarrow 2(CH_3)_2CO$ in alkaline aqueous solution at 25.00 °C has been measured as a function of pressure in the range 1 to 4000 bar (1 bar = 100 kPa). The reaction was followed by measuring the absorption of chopped UV light at 298 nm in a high pressure cell with sapphire windows.

The pseudo-first-order rate constant k_1 was found to vary in proportion with the concentration of sodium hydroxide in the pressure range examined. At 0.1003 mol dm^{-3}, its variation with pressure is given by

$$\ln (k_1/\text{min}) = \ln 0.04414 - 2.78 \times 10^{-4} \, P/\text{bar}$$

From this the activation volume of the reaction is found to be $\Delta V^{\ddagger} = (+6.90 \pm 0.15)$ cm^3 mol^{-1}; the result is discussed in relation to the mechanism.

The value of the second-order rate constant at 1 bar and 25.00 °C, $k_2 = 0.440$ min^{-1} mol^{-1} dm^3, is about 10 % lower than previously reported values.

In the 80 years that have passed since Koelichen's careful and extensive investigation[1] of the dealdolization of diacetone alcohol, this reaction has repeatedly been chosen as an object of study. Though reversible, it proceeds nearly to completion at dilution; it has always been found to be first-order in the reactant; it is catalyzed by hydroxide ions and some other bases; and it is accompanied by a volume increase sufficient to make dilatometric measurements attractive to workers in the past.

At 25 °C, the equilibrium mixture of diacetone alcohol (A_2) and acetone (A) contains 11.13 wt %[1,2] of the former (at 45 °C, 5.50 wt %[2]); in dilute aqueous solution, Koelichen's figures correspond to an equilibrium constant of about 100 mol dm^{-3}

(see also Ref. 3). At the same temperature, different values have been reported by various authors for the second-order rate constant $k_2 = v/(c_{A_2}c_{OH}-)$ for the NaOH catalyzed reaction in water: k_2/min^{-1} mol^{-1} dm$^3 = 0.53$;[1] 0.47;[4,5] 0.48;[6] 0.51;[7] 0.49;[8] 0.50;[9] with KOH, k_2 is about 3.5 % lower.[4] The activation energy for the reaction is 71[7] (75[6]) kJ mol^{-1}. Other aspects of the reaction kinetics which have been described in the literature are: catalysis by ammonia, amines and amino acids,[10–13] isotope effects,[14,15] salt effect[4–6,16,17] and solvent effect.[18–22]

The effect of pressure on the first-order rate constant $k_1 = v/c_{A_2}$ has been measured twice, but with results that are quite conflicting. In one case activation volumes were found ranging from -6.6 (30 °C) to $+3.8$ cm^3 mol^{-1} (40 °C),[20] while in the other a somewhat uncertain value $(+6.0 \pm 1.5)$ cm^3 mol^{-1} was reported at 15 and 25 °C.[23]

In view of this, a careful redetermination of the activation volume would be desirable, as emphasized by Le Noble in his recent review.[24] In planning the work we rejected the dilatometric procedure, used by most workers, since it tacitly assumes that the partial molar volumes of all constituents remain constant, a condition not always fulfilled (See Koelichen, Ref. 1, p. 157). The calorimetric method of Sturtevant[8] has many advantages but is not suited to high pressure work, and chemical analysis does not seem to be sufficiently precise. Instead, we chose light absorption which may be readily measured in a high pressure cell with windows, and permits continuous recording of the reaction mixture composition. Another innovation is in the calculation where k_1 and the other parameters were fitted according to the least squares principle.

EXPERIMENTAL

The high pressure cell, with a light path of about 12.6 mm between sapphire windows supported by steel blocks with an aperture of 3 mm, and capable of withstanding 10 kbar, has been described elsewhere.[25] It was clamped in a metal block through which water was circulated from a thermostat held at 25.00 ± 0.05 °C (traceable to NBS). Comparison of the temperature inside the cell with that of the thermostat gave a difference of less than 0.05 °C. A floating piston in the top branch of the cell separated the high pressure liquid from the reaction solution. The pressure generator used is capable of producing and maintaining a preset pressure up to 10 kbar; its manometer was calibrated against a $0-4000$ bar NOVA manometer, guaranteed to 1 $^0/_0$.

Chopped UV light from a deuterium lamp was focussed in the cell. A reference signal was also generated from the chopper, so that the main and reference signals had the same frequency and a constant phase difference. The UV light beam, after passing through the cell, was focussed on the entrance slit of a Heath monochromator, in front of which was placed a narrow band-pass interference filter with a maximum at 298 nm. The monochromator was set at this wavelength, and the slit width was typically about 1 mm. A series of experiments showed that the reaction rate was independent of the light intensity in the cell. Light from the monochromator exit slit was collected on an EMI 6256A photomultiplier tube fed from a stable ($\pm 1:1000$) HV supply. The anode current was passed through a 4.7 kΩ resistor, and the resulting voltage drop, in the range 5 to 50 mV, was measured in a PAR HR-8 lock-in amplifier in conjunction with the above-mentioned reference signal. The amplifier output voltage was recorded with paper speed 5 min/cm. As it was necessary to change amplifier range during experiments, the ranges were calibrated relative to each other, and corrections were made in the calculations. With a maximum of electrical stability and mechanical stiffness, variations in the output could be held below $1-2$ $^0/_0$ over a period of at least 5 h.

To prepare the reaction mixture 100 mm^3 of distilled FLUKA diacetone alcohol (b.p. $164-166$ °C at 1 atm) was transferred into a 10 cm^3 volumetric flask immersed in a 25.0 °C thermostat, after which the flask was filled to the mark with thermostated 0.1017 mol dm^{-3} (25 °C, 1 bar) sodium hydroxide solution. The strenth of the latter was verified repeatedly using 0.1 mol dm^{-3} hydrochloric acid, which was in turn controlled with KHCO$_3$. Recording was started at the time of mixing, the solution transferred to the high pressure cell, the apparatus assembled, and high pressure established, all within 5 min. Recording was continued for at least 10 half-lives, during which the light intensity typically increased by a factor of 5. After the run, readings were taken from the recording at 5 min intervals (for slow reactions, 10 min intervals).

CALCULATION

Because of the linear relationship between the concentration of diacetone alcohol in solution and the absorbance A of the latter, a first-order reaction entails

$$A(t) - A(\infty) = \{A(0) - A(\infty)\} \exp(-k_1 t)$$

For the recorded voltage e one therefore has

$$\ln e(t) = \ln e(\infty) + \{\ln e(0) - \ln e(\infty)\} \exp(-k_1 t)$$

from which e may be obtained by exponentiation. In practice, however, e further showed a small constant drift with time, so that the complete expression would be of the form

$$e(t) = \exp\{a_1 + a_2 \exp(a_3 t)\} + a_4 t$$

If e_j' designates the voltage measured at t_j and e_j the value of the above expression for $t = t_j$, the principle of the method consists in minimizing the sum of squares $\sum_j (e_j' - e_j)^2$. A ready-to-use program NLIN of the Statistical Analysis System,[26] available on many IBM 360/370 computers, was used.

When the first-order rate constant $k_1 = -a_3$ has been found, the second-order constant $k_2 = k_1/c_{OH^-}$ may be evaluated as follows: At 1 bar and 25 °C, assuming additivity of volume, the 10 cm^3 sample contained 9.9 cm^3 of base. As pointed out by La Mer,[7] however, the diacetone alcohol may contain acid impurities which neutralize part of the base. By titrating the diacetone alcohol we found in fact a consumption of 0.040 cm^3 0.1017 mol dm^{-3} base per 100 mm^3 diacetone alcohol. Therefore, a sample of volume 10 cm^3 contains $(9.90-0.04) \times 0.1017$ mmol free OH$^-$, and the effective volume concentration of OH$^-$ is $c_{OH^-} = 0.1003$ mol dm^{-3} (at 25 °C, 1 bar).

RESULTS

The results from a typical single experiment at 1 bar are shown in Fig. 1, where e' and e are plotted
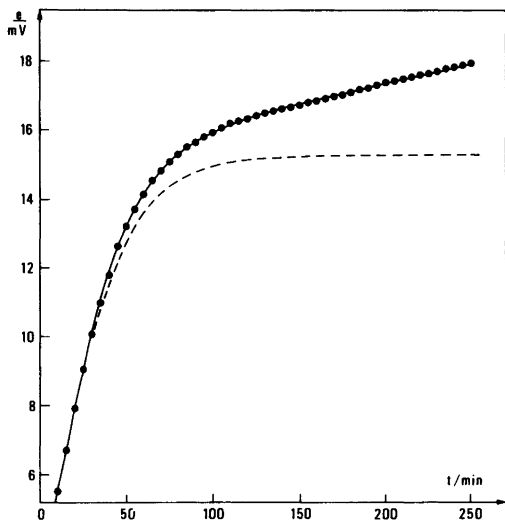

Fig. 1. Plot of measured output voltage e' (●) as a function of time t for a typical kinetic experiment at 25 °C, 1 bar. Curves $e(t)$ based on calculated parameters are also shown, both including all terms (—) and after subtraction of the linear term $a_4 t$ (--).

against t, both with and without correction for the linear variation of e with time. The SAS procedure with input e'/mV and t/min gave for this particular

run the following values of the parameters and their estimated standard deviations (in parenthesis):

$a_1 = 2.717$ (0.00108)
$a_2 = 1.610$ (0.0055)
$a_3 = -k_1 = -0.04422$ (0.00016) min^{-1}
$a_4 = 0.01148$ (0.0009) mV min^{-1}.

If the difference between measured and calculated e values is plotted against time ($(e'-e)$ *vs.* t, not shown), the points are scattered uniformly about zero. The same applies to all runs, demonstrating that the proposed expression $e(t)$ accounts for all essential features.

In a preliminary series of experiments (not cited here), the base concentration was varied from half to twice the standard value (0.1003 mol dm^{-3}) in the range 1 to 4000 bar. In all cases k_1 was found to be proportional to c_{OH^-}.

The experimental values of k_1 at 25.00 °C are listed in Table 1, and a plot of $\ln k_1$ against P is given in Fig. 2. The relationship is apparently linear in the range examined, and a straight line is drawn passing through the average value at 1 bar, corresponding to $k_1 = 0.04414$ min^{-1}, and fitted by least squares to the remaining data. The resulting equation is

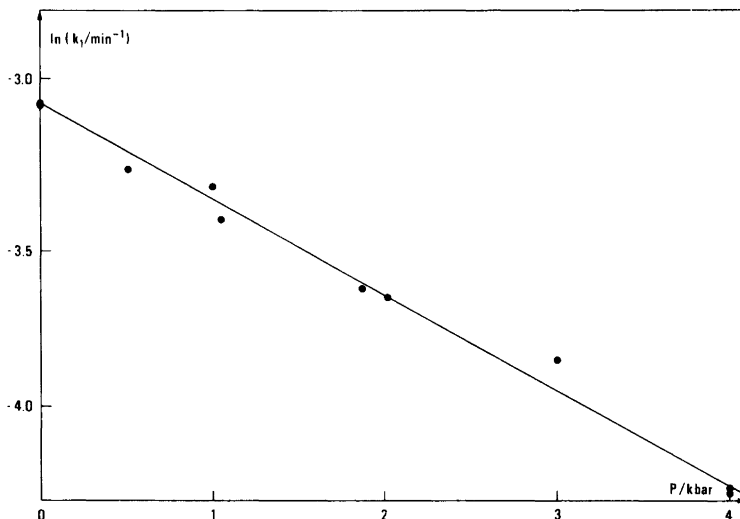$$\ln(k_1/min^{-1}) = \ln 0.0441 - 2.783 \times 10^{-4} \ P/bar$$

Fig. 2. Plot of experimental values of $\ln(k_1/min^{-1})$ *vs.* P/kbar and linear relation based on least squares. The line is forced to pass through the average value at 1 bar.

Table 1. First-order rate constant k_1 of the dealdolization reaction at 25.00 °C with $c_{OH^-} = 0.1003$ mol dm^{-3}.

P/bar	k_1/min^{-1}
1	.04414
1	.04422
1	.04406
510	.03644
1000	.03464
1050	.03148
1870	.02574
2020	.02510
3000	.02092
4000	.01441
4000	.01418

From this it is seen that the second-order rate constant at 25 °C, 1 bar is

$$k_2 = k_1/c_{OH^-} = 0.04414/0.1003 = 0.440 \text{ min}^{-1} \text{ mol}^{-1} \text{ dm}^3$$

and that the activation volume is

$$\Delta V^{\neq} = -RT\left(\frac{\partial \ln k_1}{\partial P}\right)_T = 6.90 \text{ cm}^3 \text{ mol}^{-1}$$

The standard deviation of the latter is 0.15 cm^3 mol^{-1}.

The change of e with time corresponding to the linear term $a_4 t$ is always positive and numerically ten times larger than the negative long term drift of the apparatus. A few experiments of long duration (one week) showed an exponential decay of absorbance with a time constant about a hundred times smaller than k_1, so that the linear approximation is legitimate.*

DISCUSSION

The value found for the second-order rate constant k_2 at 1 bar and 25 °C, 0.440 min^{-1}, with a standard deviation of about 0.001 min^{-1} differs

* After the paper had been written, experiments have shown this to be due to the presence of small amounts of mesityl oxide which absorbs strongly in the UV region ($\lambda_{max} = 242$ nm). When base is added to a solution of diacetone alcohol, mesityl oxide is first formed and subsequently degraded into methanol as the dealdolization proceeds.

significantly from the previously published figures which are centered around 0.48 – 0.49 min^{-1} (see the introduction). One reason for this discrepancy may be that all former determinations of k_2 were based on dilatometry or, in one case, on calorimetry, assuming the relevant partial molar quantity (volume or enthalpy) to be constant. While this is at best an approximation[27] only, we found the absorbance to be a strictly linear function of volume concentration both for acetone and diacetone alcohol. Another reason may be the temperature rise caused by the reaction heat ($\Delta H^{\ominus} = -23$ kJ/mol A$_2$).[8] This tends to increase dilatometer readings and reaction rate, and more so in a large glass vessel than in a 6 mm ID cylindrical metal cell.

If the reaction is summarized in

$$A_2 + OH^- \overset{K}{\rightleftharpoons} (A_2^-)^{\neq} + H_2O \overset{k}{\rightarrow} P$$
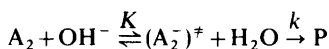
where the reactants are in pseudo-equilibrium with the activated complex present in small concentration, and the complex is subsequently transformed into product in a rate-determining step, the activation volume is

$$\Delta V^{\neq} = V_{(A_2^-)^{\neq}} + V_{H_2O} - (V_{A_2} + V_{OH^-})$$

and the observed rate is

$$v = kc_{(A_2^-)^{\neq}} = kKc_{A_2}c_{OH^-}/X_{H_2O}$$
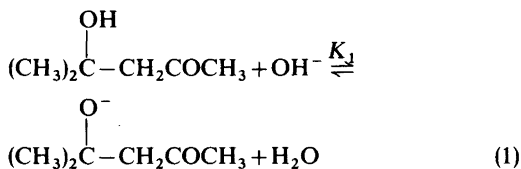
where the product kK may be identified with our k_2. $\Delta V^{\neq}$ may be calculated from the experimental relationship between the rate constant and the pressure. The use of volume concentrations, imposed by spectrophotometric measurements may lead to pitfalls as pointed out by Haman,[28] but an analysis of the problem shows that $\Delta V^{\neq}$ may be found from

$$\Delta V^{\neq} = -RT\left(\frac{\partial \ln k_1}{\partial P}\right)_T$$

Therefore, a plot of $\ln k_1$ (rather than $\ln k_2$ as might perhaps be imagined) against P should be used. The resulting value, $\Delta V^{\neq} = (+6.90 \pm 0.15)$ cm^3 mol^{-1}, is within the rather large margin of uncertainty of Brower's figure[23] (6.0 ± 1.5 cm^3 mol^{-1}) whereas the results given by Moriyoshi[20] (-6.6 cm^3 mol^{-1} at 30 °C, $+3.8$ at 40 °C) should perhaps be considered with some reservation.

The activation volume found should be seen in conjunction with the generally adopted scheme, exposed, *e.g.*, by Frost and Pearson[29] who present a detailed analysis of all relevant data:

$$(CH_3)_2\overset{\overset{\displaystyle OH}{|}}{C}-CH_2COCH_3+OH^- \overset{K_1}{\rightleftharpoons}$$

$$(CH_3)_2\overset{\overset{\displaystyle O^-}{|}}{C}-CH_2COCH_3+H_2O \tag{1}$$

$$(CH_3)_2\overset{\overset{\displaystyle O^-}{|}}{C}-CH_2COCH_3+H_2O \overset{K_2}{\rightleftharpoons}$$

$$(CH_3)_2\overset{\overset{\displaystyle O}{|:}}{C}^-\cdots CH_2COCH_3+H_2O \tag{2}$$

$$(CH_3)_2\overset{\overset{\displaystyle O}{|:}}{C}^-\cdots CH_2COCH_3+H_2O \overset{k}{\rightarrow}$$

$$(CH_3)_2\overset{\overset{\displaystyle O}{||}}{C}+{}^-CH_2COCH_3+H_2O \tag{3}$$

$${}^-CH_2COCH_3+H_2O \rightarrow CH_3COCH_3+OH^- \tag{4}$$
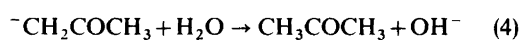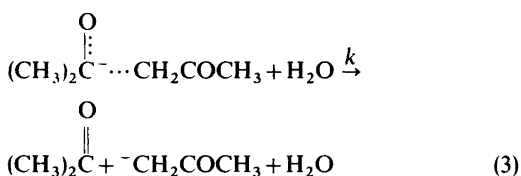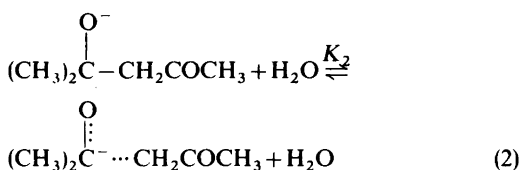
The steps (1) and (2), relatively fast, result in a pseudo-equilibrium between the reactants and an activated diacetone alcohol complex $(A_2^-)^{\ddagger}$ with stretched bond and displaced charge. In the rate-determining step (3) the bond is broken, and step (4) quickly neutralizes the base conjugate to acetone.

In this model, the activation volume represents the volume of the product molecules of (2) minus the volume of the reactant molecules of (1). By comparing the two, one may note the following changes (see, *e.g.*, Refs. 24 and 30):

(a) Transfer of a proton from the hydroxide group of diacetone alcohol to a hydroxide ion; apart from electrostriction (treated in (d)), small effect, ± 1 cm^3 mol^{-1}.

(b) Bond cleavage; effect $+8$ to $+12$ cm^3 mol^{-1}.

(c) Shrinkage of the carbon-oxygen bond during its transition from hydroxide towards carbonyl state with tighter bonding; effect about -5 cm^3 mol^{-1}. This feature seems to have been passed unnoticed by Brower.[23]

(d) Electrical effect of (a), equivalent to the transfer of a negative charge from the hydroxide ion where it is strongly localized to a region near the bond about to break where it is delocalized and may act on the solvent molecules over less than a solid angle of 4π. This results in weaker electrostriction of the solvent with a corresponding expansion of perhaps $+5$ cm^3 mol^{-1}, although the figure is rather uncertain.[30]

The sum of these contributions $+7$ to $+12$ cm^3 mol^{-1} is admittedly uncertain, but at the present stage of our knowledge, it is hardly possible to make more precise estimates. A little more information may be gained by comparing the overall volume change from reactants of (1) to products of (4). Unfortunately, the partial molar volume of diacetone alcohol in dilute aqueous solution remains to be determined, but the volume difference of the pure compounds is $2V_A - V_{A_2} = 23.3$ cm^3 mol^{-1} with no contribution from electrostriction. If one assumes that one third of this total volume increase is associated with the reactions (1) and (2) (which would not appear unreasonable) then the combined changes (b) and (c) would amount to about $+7$ cm^3 mol^{-1}. This leaves no room for the effect of change in electrostriction, however, and though explicitly neglected by Brower, it almost certainly must give a positive contribution.

It will be recognized that the activation volume which has now been firmly established experimentally, may be interpreted in terms of the reaction mechanism generally accepted. On the other hand, the character of the agreement is such as to leave room for considering other reaction models.

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