Kinetics of the Hydrolysis of Diethyl Acetal Catalyzed by Iron(III) in Aqueous Solution

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The catalytic activity of iron(III) on the hydrolysis of diethyl acetal was investigated in aqueous solutions. The reaction rate was followed dilatometrically. The reaction is of the first order with respect to acetal concentration, the rate constant being expressed by

$$k_{app}=k_0+k_H[H^+]+k_{Fe}[Fe].$$

The respective rate constants are $k_0=1.30\times10^{-4}$ s^{-1}, $k_H=1.28$ M^{-1} s^{-1}, and $k_{Fe}=1.86$ M^{-1} s^{-1} at an ionic strength $\mu=0.2$ M and 25 °C. A tentative reaction scheme for iron(III) catalysis was proposed.

Diethyl acetal is known to be easily hydrolyzed on producing acetaldehyde and ethanol under the acid catalysis *via* an A-1 mechanism.

$$CH_3CH(OC_2H_5)_2 + H_2O \xrightarrow{H^+} CH_3CHO + 2C_2H_5OH \qquad (1)$$

Although investigations on the solvent and substituent effects on the reaction mechanisms were carried out in detail,[1-12] the catalytic activities of various metal ions have not so far been studied. We have measured the rates of the hydrolysis of diethyl acetal in the presence of iron(III) and determined the rate constants of the individual reaction steps.

Experimental

Materials. Diethyl acetal (Schuchardt München, Germany) was used without further purification. Its density at 25 °C was 0.827 g/cm^3 which agreed with that in literature. Iron(III) perchlorate was prepared by dissolving pure iron wire in perchloric acid and oxidizing it with hydrogen peroxide. Pure water obtained by distillation of city water which had been treated with ion-exchange resin was used.

Procedure of Rate Measurement. As the hydrolysis of diethyl acetal proceeds, its aqueous solution increases in volume at constant temperature. Since the hydrolysis proceeds almost irreversibly and the increase in volume of the solution is proportional to the degree of reaction, the reaction rate can be followed by means of dilatometry. The dilatometer consists of a glass tube about 1 cm in diameter, connected with a vertical capillary of 0.03 cm in diameter and of 30 cm in height at one end of the tube. The other end is attached to a glass stop-cock, through which the reaction solution is quickly introduced from the reservoir where two reactant solutions are mixed at the initiation of hydrolysis. The content of the dilatometer is about 70 cm^3. The dilatometer and the other vessels containing the reactant solutions were set in a thermostat at 25 °C in advance. The ionic strength was always kept at $\mu=0.2$ M with sodium perchlorate.

Photometry. A Hitachi UV-VIS spectrophotometer Model 139 and a Hitachi recording spectrophotometer EPS-3T were used for the concentration determination of iron(III) and for the observation of the spectral variation during the course of reaction.

Results and Discussion

If we denote the heights of the reaction solution surface in the capillary of the dilatometer at time t and at the time of completion of the reaction by h and h_∞ respectively, the plots of $\log(h_\infty-h)$ against t always exhibit straight lines, indicating that the reaction is of the first order with respect to acetal concentration [A]. The slopes give apparent rate constants, k_{app}.

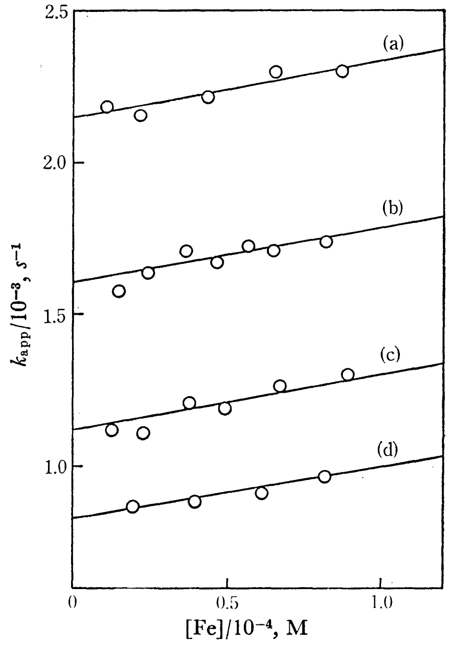

Fig. 1. Relationships between k_{app} and [Fe] at various [HClO$_4$] at [A]$=5.55\times10^{-2}$M.
[HClO$_4$]: (a): 1.44×10^{-3}M, (b); 1.00×10^{-3}M, (c): 7.50×10^{-4}M, (d): 5.00×10^{-4}M.

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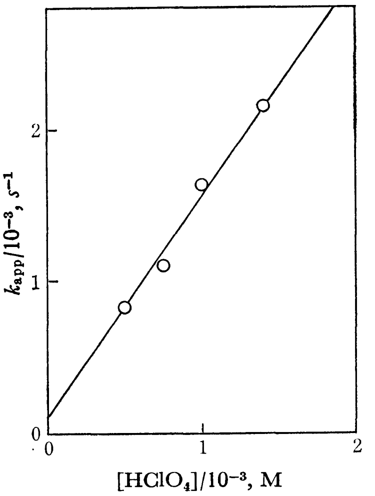


Fig. 2. Relationships between k_{app} and [HClO$_4$] at [Fe]=0 (extrapolated) and [A]=5.55×10^{-2}M.

The relationships between k_{app} and total iron concentration, [Fe], at various acid concentrations, [HClO$_4$], are shown in Fig. 1. It is seen that k_{app} is linear with respect to [Fe] with a common slope irrespective of [HClO$_4$]. The intercepts of the straight lines also show a linear relationship with [HClO$_4$] as is depicted in Fig. 2. The apparent rate constant can therefore be expressed by the sum of three terms, *viz.*

$$k_{app} = k_0 + k_H[H^+] + k_{Fe}[Fe] \qquad (2)$$

The individual rate constants are determined from Figs. 1 and 2 as $k_0=1.30\times10^{-4}\,s^{-1}$, $k_H=1.28\,M^{-1}\,s^{-1}$, and $k_{Fe}=1.86\,M^{-1}\,s^{-1}$ at $\mu=0.2$ M and 25 °C. The value of k_H agrees fairly well with that in the literature.[4]

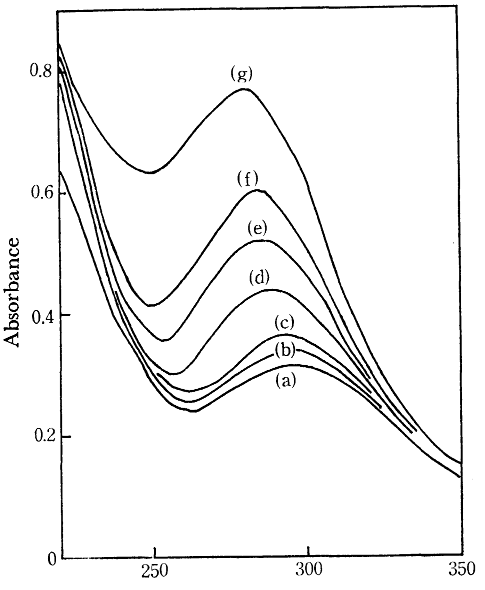
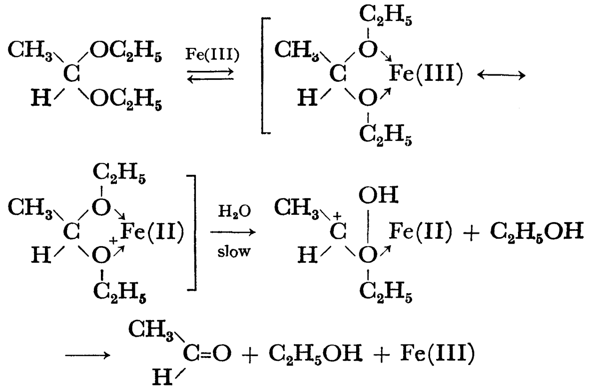


Fig. 3. Spectral changes with time of diethyl acetal hydrolysis at [A]=5.55×10^{-2}M, [Fe]=1.5×10^{-4}M, and [HClO$_4$]=6.14×10^{-5}M.
(a): t=0, (b): 3 min, (c): 15 min, (d): 30 min, (e): 60 min, (f): 90 min, (g): 240 min.

The three terms in the right-hand side of Eq. (2) might correspond to the respective three reaction paths; (i) a spontaneous one without catalyst, (ii) an acid catalysis, and (iii) an iron(III) catalysis. Since k_{Fe} is independent of the acid concentration, the iron catalysis is not wholly attributed to the apparent increment of hydrogen ion concentration due to the hydrolysis of Fe^{3+}_{aq} at the given acid concentration. The expected increment of hydrogen ion concentration under the present conditions is too small to be compared with the observed catalytic effect resulting from iron(III). The chemical forms of iron(III) in the reaction system are predominantly Fe^{3+}_{aq} and $FeOH^{2+}$, and their concentration ratio should change according to the variation in the acid concentration. However, the catalytic activity of iron(III) was not seriously affected by its chemical form. A presumable reaction scheme in analogy with acid catalysis[13,14] might be as follows;



in which Fe(III) behaves as a Lewis-type acid-base catalyst.

Spectral changes during the reaction are shown in Fig. 3, where the absorption in the wavelength range 200—400 nm increases with time and finally reaches a spectrum with a peak at 280 nm. The final absorption spectrum subtracted by the initial one agrees with that in the absence of iron(III) catalyst at infinite reaction time. Thus, the reaction products are found to be the same irrespective of whether the reaction is catalyzed by acid or iron(III), although the absorption spectrum in this wavelength range is mainly due to acetaldehyde and not to acetal or ethanol. The hypothetical intermediate of a complex between iron(III) and acetal was not recognized, probably because of the fact that the formation of the complex was very minute or no distinct absorption band appeared in the wavelength range studied.

Catalytic activities of metal ions other than iron(III) were also qualitatively determined. Silver(I), copper(II), cobalt(II), and zinc(II) were found to be less catalytic than iron(III).

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