

Study of Mn(II) acetate oxidation in acetic acid by air in the presence of Co(II) acetate

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Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation

The influence of Co(II) acetate on the Mn(II) acetate oxidation by air in acetic acid has been studied. It was found out that the presence of Co(Ac)₂ has a profound catalytic effect on the reaction which is of the first order with respect to the concentration of Mn(II) as well as Co(II) acetate.

Изучалось влияние уксуснокислого Co(II) на окисление уксуснокислого Mn(II) воздухом в присутствии уксусной кислоты. Было найдено, что Co(Ac)₂ оказывает значительное каталитическое действие, причем изучаемая реакция окисления по отношению к концентрации уксуснокислых Mn(II) и Co(II) является реакцией первого порядка.

It is well known that cobalt and manganese salts are effective catalyst of hydrocarbon oxidation [1—4] and their mixtures obey a synergistic effect. In spite of the practical importance of this effect, mechanism of synergism is still obscure.

In the present paper, the effect of Co(Ac)₂ concentration on the oxidation of Mn(Ac)₂ in acetic acid is described.

Experimental

Chemicals

Co(Ac)₂ · 4H₂O and Mn(Ac)₂ · 4H₂O of anal. grade were used without purification. Acetic acid was purified by the method described [5].

The mixed solutions of Co(Ac)₂ and Mn(Ac)₂ were prepared by mixing their equimolar solutions so that the overall volume of the solution as well as the sum of concentrations of the components was always constant.

Spectroscopic measurements

The spectra of solutions of metal acetates were recorded on a Specord UV VIS (Zeiss, Jena) instrument using thermostatted cells of 0.5—5 cm thickness.

Oxidation

The oxidation of $\text{Co}(\text{Ac})_2$ and $\text{Mn}(\text{Ac})_2$ solutions in acetic acid was carried out in a 100 cm³ glass flask equipped with a stirrer, reflux condenser, and air supply. The flask was thermostatted at 25.0 ± 0.1 °C.

Results and discussion

While the solution of Co(II) or Mn(II) acetates in acetic acid are stable several days or weeks, their mixtures are very sensitive to the presence of oxygen. Mixed Co—Mn solutions in the presence of oxygen turn brown and at the same time the increase of absorption intensity in ultraviolet and visible range is dependent upon the ratio of Co(II) to Mn(II). The increase of absorption intensity for an isomolar series of $\text{Co}(\text{Ac})_2$ and $\text{Mn}(\text{Ac})_2$ solutions is depicted in Fig. 1.

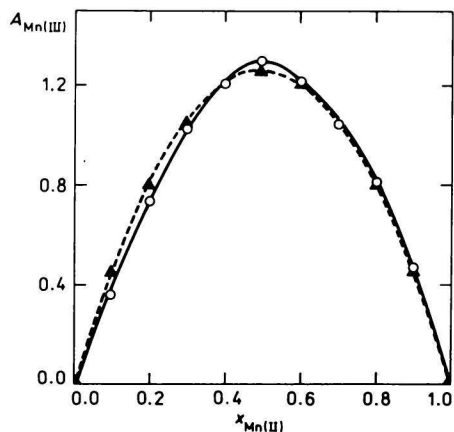


Fig. 1. Dependence of absorbance increase of Co(II)—Mn(II) solutions on the mole fraction of $\text{Mn}(\text{Ac})_2$ in the initial mixture. Oxidation by air at 25 °C for 20 h.

— Experimentally measured;
 - - - - calculated from eqn (8).

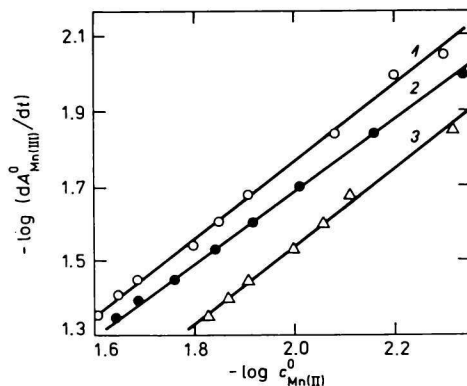


Fig. 2. Dependence of $\log(dA_{\text{Mn(III)}}^0/dt) = f(\log c_{\text{Mn(II)}}^0)$ at 1. 2.1×10^4 cm⁻¹; 2. 2.0×10^4 cm⁻¹; 3. 1.8×10^4 cm⁻¹.

The electronic spectra of the above-mentioned solutions were analyzed for the number of absorbing components having linearly independent spectra by the method of the matrix rank analysis. The rows of the matrix consisting of spectra of an isomolar series of $\text{Co}(\text{Ac})_2$ and $\text{Mn}(\text{Ac})_2$ solutions represent the absorbance of the mentioned solutions at various wavenumber over the interval 3.0×10^4 — $1.3 \times 10^4 \text{ cm}^{-1}$, while the column represents absorbances of various solutions at given wavenumber. The rank of the matrix written in this way agrees with the number of absorbing components in the solution in the case when the spectra of these components are linearly independent and the differences among them are at least for one wavenumber greater than the accuracy of the spectral instrument used.

For the determination of the rank of the absorbance matrix the following methods were employed:

- i) graphical method of *Colleman et al.* [6],
- ii) elimination method of *Wallace et al.* [7] with testing the statistical significance of the elements of the resulting Gaussian matrix,
- iii) iterative method of determining the eigenvectors of the analyzed matrix with testing their statistical significance in the modification according to *Maeder et al.* [8].

All three methods equivocally pointed out that in a freshly prepared isomolar series of solutions, $\text{Co}(\text{Ac})_2$ is the only significantly absorbing component. The changes of spectrum induced by the presence of $\text{Mn}(\text{Ac})_2$ are in the range of errors of the spectral measurements. In solutions exposed to oxidation by molecular oxygen, only one new absorbing component appears. From the comparison of redox potentials of the studied components follows that $\text{Mn}(\text{Ac})_2$ will be oxidized to $\text{Mn}(\text{Ac})_3$. The following experiments prove this proposal. Thus, by adding $\text{Mn}(\text{III})$ acetate to the brown-coloured mixed solution of $\text{Co}(\text{Ac})_2$ and $\text{Mn}(\text{Ac})_2$, the absorption is increased but the number of absorbing components remains unchanged. Solutions prepared from suitable amounts of $\text{Co}(\text{Ac})_2$, $\text{Mn}(\text{Ac})_2$, and $\text{Mn}(\text{Ac})_3$ have the same spectra as the brown-coloured mixed solutions of $\text{Co}(\text{Ac})_2$ and $\text{Mn}(\text{Ac})_2$ with an equal overall concentration of cobalt and manganese. By subtracting the spectrum of $\text{Co}(\text{Ac})_2$ from the spectrum of the brown-coloured mixed solutions, a typical spectrum of $\text{Mn}(\text{Ac})_3$ is always obtained. Adding a suitable colourless reducing agent, e.g. Na_2SO_3 , the spectrum of the freshly prepared solution is restored.

From the symmetry of the absorbance increase due to an increase of $\text{Mn}(\text{Ac})_3$ concentration in an isomolar series of solutions (Fig. 1) it follows that the concentration of $\text{Co}(\text{II})$ has the same influence on the rate of $\text{Mn}(\text{Ac})_2$ oxidation as $\text{Mn}(\text{II})$. This suggestion was confirmed also by kinetic measurements showing the dependence of the logarithm of the initial rate of the absorbance change for $\text{Mn}(\text{Ac})_3$ on the logarithm of the initial $\text{Mn}(\text{Ac})_2$ concentration at constant $\text{Co}(\text{Ac})_2$ concentration (Fig. 2) as well as on the logarithm of the initial $\text{Co}(\text{Ac})_2$ concentra-

tion at constant $\text{Mn}(\text{Ac})_2$ concentration (Fig. 3). From the dependences plotted at ten wavenumbers the estimated reaction order with respect to the concentration of $\text{Mn}(\text{II})$ acetate is 1.0 ± 0.1 and for $\text{Co}(\text{II})$ acetate 1.1 ± 0.4 . The apparent rate constant at 25°C has the value $1.5 \pm 0.7 \text{ dm}^3 \text{ mol}^{-1} \text{ h}^{-1}$.

Thus, for the rate of $\text{Mn}(\text{Ac})_3$ concentration change ($c_{\text{Mn}(\text{III})}$), the following equation holds

$$\frac{dc_{\text{Mn}(\text{III})}}{dt} = k_{\text{ef}} \cdot c_{\text{Mn}(\text{II})} \cdot c_{\text{Co}(\text{II})} \quad (1)$$

where k_{ef} is the apparent rate constant; $c_{\text{Mn}(\text{II})}$ and $c_{\text{Co}(\text{II})}$ are analytical concentrations of the appropriate components. The rate of change of $\text{Mn}(\text{Ac})_3$ absorbance ($A_{\text{Mn}(\text{III})}$) is expressed by

$$\frac{dA_{\text{Mn}(\text{III})}}{dt} = \varepsilon_{\text{Mn}(\text{III})} \cdot d \cdot k_{\text{ef}} \cdot c_{\text{Mn}(\text{II})} \cdot c_{\text{Co}(\text{II})} \quad (2)$$

where $\varepsilon_{\text{Mn}(\text{III})}$ is the molar extinction coefficient of $\text{Mn}(\text{Ac})_3$ and d is the cell thickness.

If $c_{\text{Co}(\text{II})}$ does not change in the course of oxidation, after treatment and integration of eqn (2), the following equation is obtained

$$A_{\text{Mn}(\text{III})} = \varepsilon_{\text{Mn}(\text{III})} \cdot d \cdot c_{\text{Mn}(\text{II})}^0 [1 - \exp(-k_{\text{ef}} \cdot c_{\text{Co}(\text{II})} \cdot t)] \quad (3)$$

where $c_{\text{Mn}(\text{II})}^0$ is the initial concentration of $\text{Mn}(\text{Ac})_2$. For other reaction orders, the following equations can be written

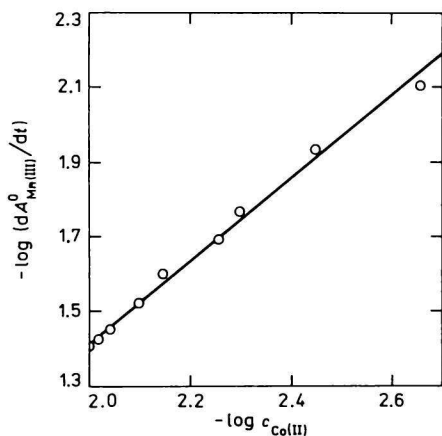


Fig. 3. Dependence of $\log(dA_{\text{Mn}(\text{III})}^0/dt) = f(\log c_{\text{Co}(\text{II})})$ at $2.1 \times 10^4 \text{ cm}^{-1}$.

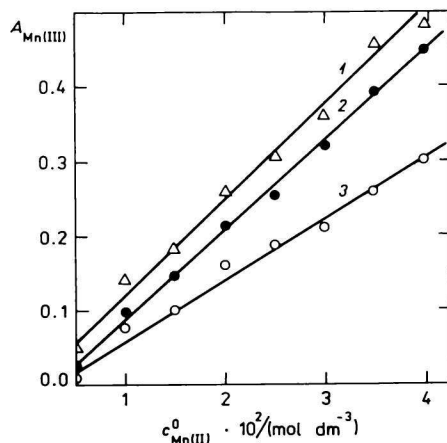


Fig. 4. Dependence of $A_{\text{Mn}(\text{III})}$ on $c_{\text{Mn}(\text{II})}$ at
1. $2.1 \times 10^4 \text{ cm}^{-1}$; 2. $2.0 \times 10^4 \text{ cm}^{-1}$;
3. $1.8 \times 10^4 \text{ cm}^{-1}$.

Reaction time 20 h at 25°C ; $c_{\text{Co}(\text{II})} = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $d = 1 \text{ cm}$.

$$\frac{dc_{\text{Mn(III)}}}{dt} = k_{\text{ef}} \cdot c_{\text{Mn(II)}}^n \cdot c_{\text{Co(II)}}^m \quad (4)$$

$$A_{\text{Mn(III)}} = \varepsilon_{\text{Mn(III)}} \cdot d \cdot c_{\text{Mn(II)}}^0 [1 - (1 + (n-1) \cdot k_{\text{ef}} \cdot c_{\text{Co(II)}}^m \cdot c_{\text{Mn(II)}}^{0n-1} \cdot t)^{1/1-n}] \quad (5)$$

As seen from Fig. 4, the dependence of $A_{\text{Mn(III)}}$ on the concentration $c_{\text{Mn(II)}}^0$ for constant $c_{\text{Co(II)}}$ and equal reaction times is linear, which confirms the first order of oxidation with respect to the concentration of Mn(II) acetate. Good agreement of the theoretically computed and measured dependence of $A_{\text{Mn(II)}}$ vs. $c_{\text{Co(II)}}$ (Fig. 5)

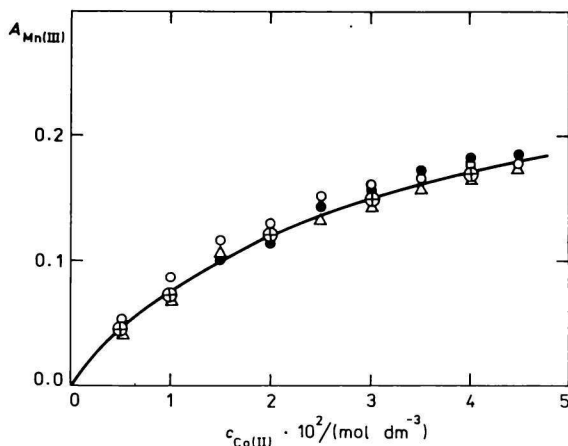


Fig. 5. Dependence of $A_{\text{Mn(III)}}$ on $c_{\text{Co(II)}}$ at $\Delta 2.1 \times 10^4 \text{ cm}^{-1}$; $\bullet 2.0 \times 10^4 \text{ cm}^{-1}$; $\circ 1.9 \times 10^4 \text{ cm}^{-1}$. Reaction time 20 h at 25°C ; $c_{\text{Mn(II)}}^0 = 5 \times 10^{-3} \text{ mol dm}^{-3}$; \oplus values calculated from eqn (3), $d = 1 \text{ cm}$.

for constant $c_{\text{Mn(II)}}^0$ and equal reaction times confirms the first order of reaction with respect to $\text{Co}(\text{Ac})_2$ concentration. In addition to it, eqn (3) can be transformed to a form enabling estimation of the absorbance increase in the studied isomolar series of solutions. If the sum of $\text{Co}(\text{Ac})_2$ and $\text{Mn}(\text{Ac})_2$ concentrations is denoted as c_{tot} and the mole fraction of $\text{Mn}(\text{Ac})_2$ as $X_{\text{Mn(II)}}$, then

$$c_{\text{Mn(II)}}^0 = X_{\text{Mn(II)}} \cdot c_{\text{tot}} \quad (6)$$

$$c_{\text{Co(II)}} = (1 - X_{\text{Mn(II)}}) \cdot c_{\text{tot}} \quad (7)$$

$$A_{\text{Mn(III)}} = \varepsilon_{\text{Mn(III)}} \cdot d \cdot X_{\text{Mn(II)}} \cdot c_{\text{tot}} \cdot [1 - \exp(-k_{\text{ef}} \cdot (1 - X_{\text{Mn(II)}}) \cdot c_{\text{tot}} \cdot t)] \quad (8)$$

The values of $A_{\text{Mn(III)}}$ calculated from this equation are compared in Fig. 1 with the measured ones.

The above-mentioned results and kinetic analysis point to the existence of Mn(II) oxidation to Mn(III) in mixed solutions of Mn(II)—Co(II) acetates in acetic acid with molecular oxygen.

References

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