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 Со(Ac)$_2$ оказывает значительное катализическое 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)$_2$·4H$_2$O and Mn(Ac)$_2$·4H$_2$O 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 Co(Ac)$_2$ and Mn(Ac)$_2$ solutions in acetic acid was carried out in a 100 cm$^3$ 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 Co(Ac)$_2$ and Mn(Ac)$_2$ solutions is depicted in Fig. 1.

![Graph showing the dependence of absorbance increase of Co(II)—Mn(II) solutions on the mole fraction of Mn(Ac)$_2$ in the initial mixture. Oxidation by air at 25 °C for 20 h.

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

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

![Graph showing the dependence of log (dA$_{MnIII}$/dt) = f(log c$_{Mn(II)}$) at 1. 2.1 × 10$^4$ cm$^{-1}$; 2. 2.0 × 10$^4$ cm$^{-1}$; 3. 1.8 × 10$^4$ cm$^{-1}$.

Fig. 2. Dependence of log (dA$_{MnIII}$/dt) = f(log c$_{Mn(II)}$) 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 Co(Ac)$_2$ and Mn(Ac)$_2$ solutions represent the absorbance of the mentioned solutions at various wavenumber over the interval $3.0 \times 10^4$—$1.3 \times 10^4$ 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, Co(Ac)$_2$ is the only significantly absorbing component. The changes of spectrum induced by the presence of Mn(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 Mn(Ac)$_2$ will be oxidized to Mn(Ac)$_3$. The following experiments prove this proposal. Thus, by adding Mn(III) acetate to the brown-coloured mixed solution of Co(Ac)$_2$ and Mn(Ac)$_2$, the absorption is increased but the number of absorbing components remains unchanged. Solutions prepared from suitable amounts of Co(Ac)$_2$, Mn(Ac)$_2$, and Mn(Ac)$_3$ have the same spectra as the brown-coloured mixed solutions of Co(Ac)$_2$ and Mn(Ac)$_2$ with an equal overall concentration of cobalt and manganese. By subtracting the spectrum of Co(Ac)$_2$ from the spectrum of the brown-coloured mixed solutions, a typical spectrum of Mn(Ac)$_3$ is always obtained. Adding a suitable colourless reducing agent, e.g. Na$_2$SO$_3$, the spectrum of the freshly prepared solution is restored.

From the symmetry of the absorbance increase due to an increase of Mn(Ac)$_3$ concentration in an isomolar series of solutions (Fig. 1) it follows that the concentration of Co(II) has the same influence on the rate of Mn(Ac)$_2$ oxidation as Mn(II). This suggestion was confirmed also by kinetic measurements showing the dependence of the logarithm of the initial rate of the absorbance change for Mn(Ac)$_3$ on the logarithm of the initial Mn(Ac)$_2$ concentration at constant Co(Ac)$_2$ concentration (Fig. 2) as well as on the logarithm of the initial Co(Ac)$_2$ concentra-
tion at constant Mn(Ac)$_2$ concentration (Fig. 3). From the dependences plotted at ten wavenumbers the estimated reaction order with respect to the concentration of Mn(II) acetate is 1.0 ± 0.1 and for Co(II) acetate 1.1 ± 0.4. The apparent rate constant at 25 °C has the value 1.5 ± 0.7 dm$^3$ mol$^{-1}$ h$^{-1}$.

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

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

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

$$\frac{dA_{Mn(III)}}{dt} = \varepsilon_{Mn(III)} \cdot d \cdot k_{ef} \cdot c_{Mn(II)} \cdot c_{Co(II)}$$  \hspace{1cm} (2)

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

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

$$A_{Mn(III)} = \varepsilon_{Mn(III)} \cdot d \cdot c^0_{Mn(II)} \left[1 - \exp \left(-k_{ef} \cdot c_{Co(II)} \cdot t\right)\right]$$  \hspace{1cm} (3)

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

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

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

Reaction time 20 h at 25 °C; $c_{Co(II)} = 5 \times 10^{-3}$ mol dm$^{-3}$, $d = 1$ cm.
As seen from Fig. 4, the dependence of $A_{\text{Mn(III)}}$ on the concentration $c_{\text{Mn(II)}}$ 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) for constant $c_{\text{Mn(II)}}$ and equal reaction times confirms the first order of reaction with respect to Co(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 Co(Ac)$_2$ and Mn(Ac)$_2$ concentrations is denoted as $c_{\text{tot}}$ and the mole fraction of Mn(Ac)$_2$ as $X_{\text{Mn(II)}}$, then

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

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

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

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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