OXIDATION OF GLYCOLALDEHYDE BY MANGANESE(III) SULPHATE*

Jiří Barek, Antonín Berka and Alena Pokorná-Hladíková

Department of Analytical Chemistry,
Charles University, 128 40 Prague 2

Glycolaldehyde was found to be oxidized by manganese(III) sulphate with exchange of two electrons to give formaldehyde and formic acid. The kinetics of the reaction was studied and the reaction mechanism deduced. A convenient procedure is suggested for an indirect determination of glycolaldehyde based on its oxidation with excess manganese(III) sulphate and subsequent retitration of the unreacted reagent with ferrous sulphate.

As part of a systematic study of oxidation of organic substances by trivalent manganese compounds, the present work is concerned with the reaction of glycolaldehyde with manganese(III) sulphate. So far, oxidation of the substance by periodic acid[1] and by vanadium pentoxide[2] has been studied and of the oxidimetric methods, only the periodatometric method could be recommended for the determination[3]. The results of the present work indicate the possibility of indirect determination of glycolaldehyde, and contribute to the elucidation of the reaction mechanism of oxidation of organic substances of the more complex structure by the action of various trivalent manganese species.

EXPERIMENTAL

Reagents and Apparatus

Solutions of manganese(III) sulphate in systems containing a quantity of sulphuric acid and manganese(II) sulphate were prepared as described previously[4]. 0·1M and 0·01M ferrous sulphate solutions in 0·25M sulphuric acid were prepared in the common fashion, their titre was checked daily dichromatometrically. Solutions of glycolaldehyde of various concentrations (val = mol/2) were prepared by dissolving precisely weighed quantity of the *p.a.* substance in distilled water and diluting to 1 litre. Their titre was checked by oxidation with sodium periodate[3] whose excess was retitrated with hydrazine sulphate[5]. 2,4-Dinitrophenylhydrazine was used in the form of its saturated solution in 2M hydrochloric acid. Solution of chromotropic acid was prepared by dissolving 10 g of the *p.a.* chemical in 100 ml of distilled water. Solution of formaldehyde with 100 µg of the chemical in 1 ml and containing in addition sulphuric acid and manganese(II) sulphate in concentrations 1·6 and 0·04 mol l^{-1}, respectively, was prepared by diluting stock

---

* Part XIX in the series Oxidation of Organic Substances by Trivalent Manganese Compounds; Part XVIII: Microchem. J., in press.

solution of formaldehyde with distilled water, adding the corresponding quantities of sulphuric acid and manganese(II) sulphate, and making up to the mark. The titre of this solution was determined by the sulphite method[6]. The chemicals used were of *p.a.* purity.

Potentiometric titrations were carried out by means of a TTT 1c valve millivoltmeter and an ABU 1b autoburette (both Radiometer, Copenhagen), using platinum and saturated calomel electrodes.

Polarographic measurements were performed on an OH-102 polarograph (Radelkis, Budapest) in a whole-glass thermostatted vessel using a mercury dropping indication electrode and a saturated calomel reference electrode. The solutions were purged with nitrogen to free them from oxygen gas.

Spectrophotometric measurements were carried out on a Specord UV VIS instrument (Zeiss, Jena) in 1 cm quartz cells.

Working Procedure

Study of the stoichiometry and time course of the reaction. 20 ml of 0·05M manganese(III) sulphate solution in 6M sulphuric acid and 0·1M manganese(II) sulphate was placed in a beaker, 5 ml of 0·05M glycolaldehyde was added, and the mixture was stirred and allowed to stand at room temperature. After a time t the unreacted reagent was determined by potentiometric titration with 0·1M ferrous sulphate. By comparison with a blank the consumption of trivalent manganese was calculated in val per 1 mol of glycolaldehyde.

Detection of formaldehyde. 15 ml of 0·05M glycolaldehyde was added to 60 ml of 0·05M manganese(III) sulphate, and after 5 min, excess of the latter was removed by adding 2 g of solid oxalic acid. To the solution was then added 80 ml of saturated solution of 2,4-dinitrophenylhydrazine in 2M hydrochloric acid. The yellow precipitate formed was collected and dried, and its melting point was determined.

Determination of formaldehyde. The formaldehyde formed was determined by a modification of the chromotropic acid method[7]. For obtaining the calibration curve, 1·00, 1·20, 1·40, 1·60, 1·80, and 2·00 ml volumes of solution containing 100 μg of formaldehyde in 1 ml and sulphuric acid and manganese(II) sulphate in concentrations 1·6 and 0·04 mol l^{-1}, respectively, were placed in ground-in test tubes, 1 ml portions of 10% solution of chromotropic acid in distilled water were added, the contents were shaken, and 10 ml of concentrated sulphuric acid was cautiously added. The test tubes were closed and after thorough shaking, placed in boiling water bath for 30 min; then they were cooled down to room temperature, the contents transferred quantitatively into 100 ml volumetric flasks and after dilution to volume, immediately measured spectrophotometrically at 570 nm; the absorbances were plotted against the concentrations.

For the determination of the formaldehyde formed by oxidation of glycolaldehyde, 5·00 ml of 0·05M glycolaldehyde was added to 20·00 ml of 0·05M manganese(III) sulphate solution in 6M sulphuric acid and 0·1M manganese(II) sulphate, and after 5 min, the unreacted reagent was removed by adding 1 g of solid oxalic acid. The solution was transferred quantitatively into a 50 ml volumetric flask and brought to volume with distilled water. After shaking, 1 ml of the solution was pipetted into a ground-in test tube, and further proceeded as in the case of the calibration curve plotting; the amount of the formaldehyde formed was read from the calibration curve based on its absorbance at 570 nm.

Free radicals as the reaction intermediates were identified analogously as in the work[8].

Study of the Reaction Kinetics

10·00 ml of freshly prepared solution of glycolaldehyde of a suitable concentration, containing also sulphuric acid, manganese(II) sulphate, and occasionally also perchloric acid or sodium sulphate, was thermostatted in a polarographic vessel and freed from oxygen by nitrogen purging for 10 min. To the solution was rapidly injected 1·00 ml of 0·01M manganese(III) sulphate solution also containing sulphuric acid and manganese(II) sulphate and prior thermostatted and freed from oxygen. Simultaneously the chart recorder drive was switched on, and the solution was purged with nitrogen for additional 30 s for its thorough mixing; then the bubbling was discontinued and nitrogen was fed above the solution level. The trivalent manganese concentration was monitored polarographically at the applied voltage of 0 V, where the current is directly proportional to the manganese(III) sulphate concentration. The initial concentrations of the solution components were calculated from the concentrations of the substances in the solution of the oxidized substance and the oxidant.

Analytical Application of the Reaction

The following procedure can be recommended for the indirect determination of glycolaldehyde based on its oxidation with excess manganese(III) sulphate and titration of the unreacted reagent with ferrous sulphate: 20·00 ml of 0·05M manganese(III) sulphate solution in 6M sulphuric acid and 0·1M manganese(II) sulphate is placed in a beaker, and 5·00 ml of aqueous solution of glycolaldehyde containing 7 to 22 mg of the substance is added. The solution is stirred, and after 5 min standing at room temperature, the unreacted fraction of manganese(III) sulphate is determined by potentiometric titration with 0·1M ferrous sulphate. A parallel reference experiment is run with a blank solution. The amount of glycolaldehyde in the solution is calculated from the difference in the consumption of ferrous sulphate in the two experiments. 1 ml of 0·1M ferrous sulphate solution corresponds to 3·003 mg of glycolaldehyde.

RESULTS

Stoichiometry of the Reaction

The take-up of the oxidant was found to depend on time as follows:

Time, min	1	2	5	15	30	60	120	240
Degree of oxidation val/mol	1·97	2·03	2·01	2·03	2·00	2·02	2·03	2·02

The determined melting point of the isolated 2,4-dinitrophenylhydrazine of the product of oxidation of glycolaldehyde by manganese(III) sulphate is 165°C, which is in a good agreement with the value of 166°C reported[9] for formaldehyde.

Based on the measured absorbance at 570 nm, it was found from the calibration curve for the spectrophotometric determination of formaldehyde with chromotropic acid that after oxidation of 300 µg of glycolaldehyde with manganese(III) sulphate the sample contained approximately 150 µg of formaldehyde; this indicates that 1 mol glycolaldehyde affords 1 mol formaldehyde.

The above facts show that glycolaldehyde is oxidized by manganese(III) sulphate according to the scheme

$$OCH-CH_2-OH + 2 Mn^{3+} + H_2O \rightarrow HCOOH + CH_2{=}O + 2 Mn^{2+} + 2 H^+ . \quad (A)$$
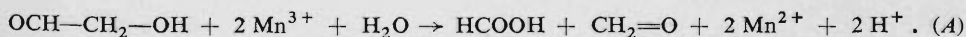
Reaction Kinetics

Dependence of the reaction rate on the concentration of manganese(III) *sulphate.*
The dependence of the limiting diffusion current of trivalent manganese on time
was measured for the following initial concetrations of the components: $c_{Mn(III)}$
$= 0.455 \text{ mmol l}^{-1}$, $c_{CH_2OHCHO} = 4.55 \text{ mmol l}^{-1}$, $[H^+] = 5.9 \text{ mol l}^{-1}$, $[HSO_4^-] =$
$= 6.1 \text{ mol l}^{-1}$, $c_{Mn(II)} = 0.1 \text{ mol l}^{-1}$ (the $[H^+]$ and $[HSO_4^-]$ concentrations were
calculated from the known total concentrations of sulphuric acid and manganese(II)
sulphate assuming that sulphuric acid was completely dissociated to the 1st degree).

In the conditions applied the concentrations of the components in the solution
except that of trivalent manganese can be looked upon as virtually constant during
the reaction. The plot of $\ln I_t$ *vs* t, where I_t is the limiting diffusion current of trivalent
manganese in time t, is a straight line. Hence, the reaction under study is first order
with respect to the concentration of trivalent manganese. The slope of the straight
line $(\text{tg } \alpha)$ afforded the pseudo-first order rate constant, $k' = -\text{tg } \alpha = 0.145 \text{ min}^{-1}$.

Dependence of the reaction rate on the concentration of glycolaldehyde. In the
same manner and in the same conditions as in the preceding case, the pseudo-first
order rate constant was determined for 10 to 30 fold molar excess of glycolaldehyde
with respect to manganese(III) sulphate. The following values were obtained:

c_{CH_2OHCHO} mmol l^{-1}	4.545	6.835	9.091	11.364	13.774
k' min^{-1}	0.145	0.25	0.329	0.416	0.477

In view of the nature of the dependence in question, the inverse value of the pseudo-
-first order rate constant was plotted against the inverse value of the concentration
of glycolaldehyde. A straight line was obtained with the slope of $0.031 \text{ min l mol}^{-1}$
and the $1/k'$ intercept of -0.25 min.

*Dependence of the reaction rate on the concentration of the hydrogen sulphate
ions.* In the same manner and in the same conditions as in the preceding cases, the
pseudo-first order rate constant was measured for various concentrations of sulphuric
acid; the concentration of hydrogen ions was held constant, 5.9 mol l^{-1}, by adding
perchloric acid. The dependence obtained was as follows:

$[HSO_4^-]$ mol l^{-1}	2.1	3.1	4.1	5.1	6.1
k' min^{-1}	0.238	0.189	0.175	0.156	0.145

Regarding the nature of this dependence, the inverse value of the pseudo-first
order rate constant was plotted aginst the concentration of hydrogen sulphate ions.
The plot is a straight line whose slope is $0.529 \text{ min l mol}^{-1}$ and the $1/k'$ intercept
is 3.2 min.

Dependence of the reaction rate on the concentration of the hydrogen ions. In the same fashion and in the same conditions as above, the pseudo-first order rate constant was related to the concentration of hydrogen ions. The concentration of hydrogen sulphate ions was held constant, $6 \cdot 1 \, \text{mol} \, l^{-1}$, by additions of sodium sulphate. The following values were found:

$[H^+] \, \text{mol} \, l^{-1}$	0·9	1·9	2·9	3·9	4·9	5·9
$k' \, \text{min}^{-1}$	0·090	0·104	0·112	0·118	0·130	0·145

The plot of this dependence is a straight line with the slope of $0 \cdot 11 \, l \, \text{min}^{-1} \, \text{mol}^{-1}$ and the k' intercept $0 \cdot 08 \, \text{min}^{-1}$.

Dependence of the reaction rate on the concentration of the manganese(II) ions. In the same manner and in the same conditions as in the previous cases the reaction rate was measured for various concentrations of divalent manganese, added to the solution in the form of manganese(II) sulphate. The decrease in the concentration of the hydrogen sulphate ions resulting from the decreasing content of manganese(II) sulphate in the solution was made up for by adding zinc sulphate, which has been verified not to affect the reaction rate. The values found were as follows:

$c_{Mn(II)} \, (\text{mol} \, l^{-1})$	0·02	0·04	0·06	0·08	0·10
$k' \, (\text{min}^{-1})$	7·0	6·9	6·9	7·1	6·9

It can be thus claimed that within the concentration region of $0 \cdot 02 - 0 \cdot 10 \, \text{mol} \, l^{-1}$, the rate of the reaction under study is independent of the concentration of manganese(II) ions.

Dependence of the reaction rate on temperature. In the same manner and in the same conditions as in the previous cases, the pseudo-first order rate constant values were determined at various temperatures in the region of $20 - 40°C$. The values obtained are summarized in Table I; for the calculation of the thermodynamic data, the log k', T log k', and $1/T$ transforms are also given (T is the absolute temperature).

The plot of log k' vs $1/T$ is a straight line with the slope of $-4 \cdot 6 \cdot 10^3$ deg, which multiplied by the $-2 \cdot 30R$ value affords the activation energy of the reaction, $E = = 88 \cdot 1 \, \text{kJ} \, \text{mol}^{-1}$.

The plot of T log k' vs T is a straight line whose slope is $14 \cdot 76$ (for k' in min^{-1}), and as this value represents the logarithm of the frequency factor, the frequency factor is $A = 5 \cdot 75 \cdot 10^{14} \, \text{min}^{-1}$.

Analytical Application of the Reaction

Considering the established effect of the various parameters on the rate of the reaction and taking into account the factors affecting the stability of the reagent[10], a procedure as given in the Experimental is suggested for analytical application of the reagent

under study. The accuracy and reproducibility of the determination are demonstrated by Table II.

DISCUSSION

Based on the determined stoichiometry and kinetics of the reaction and with regard to the analogous oxidation of monosaccharides by periodic acid[1] or vanadium pentoxide[2], and also taking into account data concerning oxidation of related substances by various trivalent manganese compound[10], a mechanism is suggested involving a reversible formation of a complex of the oxidized substance with the oxidant. In the rate-determining step of the reaction, this complex breaks down

TABLE I

Dependence of the reaction rate on temperature. Initial concentrations: $c_{Mn(III)} = 0.455$ mmol . $. 1^{-1}$, $c_{CH_2OHCHO} = 45.5$ mmol 1^{-1}, $[H^+] = 5.9$ mol 1^{-1}, $[HSO_4^-] = 6.1$ mol 1^{-1}, $c_{Mn(II)} = 0.1$ mol 1^{-1}

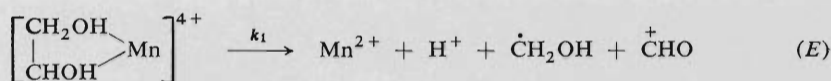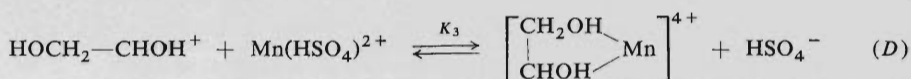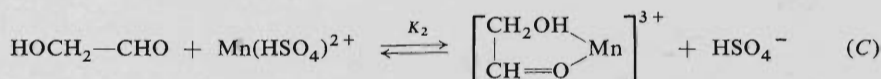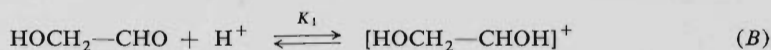| T K	k' min^{-1}	$10^3/T$ K^{-1}	log k'	T log k' K
293.16	0.145	3.41	−0.839	−245.7
298.16	0.250	3.35	−0.602	−179.4
303.16	0.430	3.30	−0.367	−111.3
308.16	0.900	3.25	−0.046	− 14.2
313.16	1.600	3.19	+0.204	+ 63.9

TABLE II

Accuracy and reproducibility of indirect determination of glycolaldehyde with manganese(III) sulphate

Taken mg	Found^a. mg	Standard deviation mg
7.505	7.906	0.03
15.015	15.692	0.05
22.520	22.928	0.09

^{a} Average from 10 determinations, from which the standard deviation was calculated.

to give a free radical of the type of $\overset{\cdot}{C}H_2OH$ and an ion of the type of $\overset{+}{C}HO$. The former is then oxidized rapidly to formaldehyde, while the latter reacts with water to give formic acid. The positive effect of hydrogen ions on the reaction rate can be explained in terms of a reversible formation of the protonized form of glycolaldehyde attacked preferably by the trivalent manganese. The mechanism suggested can be represented by the following equations:

$$HOCH_2{-}CHO + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} [HOCH_2{-}CHOH]^+ \qquad (B)$$

$$HOCH_2{-}CHO + Mn(HSO_4)^{2+} \underset{}{\overset{K_2}{\rightleftharpoons}} \left[\begin{matrix} CH_2OH \\ | \\ CH{=}O \end{matrix}\!\!\diagdown\!\!Mn\right]^{3+} + HSO_4^{-} \qquad (C)$$

$$HOCH_2{-}CHOH^+ + Mn(HSO_4)^{2+} \underset{}{\overset{K_3}{\rightleftharpoons}} \left[\begin{matrix} CH_2OH \\ | \\ CHOH \end{matrix}\!\!\diagdown\!\!Mn\right]^{4+} + HSO_4^{-} \qquad (D)$$

$$\left[\begin{matrix} CH_2OH \\ | \\ CHOH \end{matrix}\!\!\diagdown\!\!Mn\right]^{4+} \overset{k_1}{\longrightarrow} Mn^{2+} + H^+ + \overset{\cdot}{C}H_2OH + \overset{+}{C}HO \qquad (E)$$

$$\left[\begin{matrix} CH_2OH \\ | \\ CH{=}O \end{matrix}\!\!\diagdown\!\!Mn\right]^{3+} \overset{k_2}{\longrightarrow} Mn^{2+} + \overset{\cdot}{C}H_2OH + \overset{+}{C}HO \qquad (F)$$

$$\overset{+}{C}HO + H_2O \rightarrow H^+ + HCOOH \qquad (G)$$

$$\overset{\cdot}{C}H_2OH + Mn(HSO_4)^{2+} \rightarrow CH_2O + Mn^{2+} + HSO_4^{-} + H^+ . \qquad (H)$$
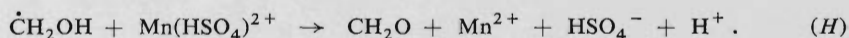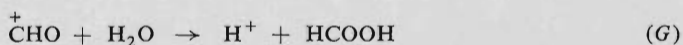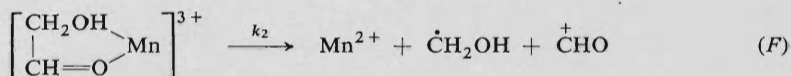
Assuming that the rate-determining step is the decomposition of the complex of the oxidized substance or its protonized form with the oxidant, the reaction rate can be written as

$$v = -d[Mn(III)]/dt = nk_1[MnG^{3+}]_{eq} + nk_2[MnGH^{4+}]_{eq} , \qquad (1)$$

where $n = 2$ is the number of the electrons exchanged, G stands for glycolaldehyde and GH$^+$ for its protonized form. The subscript eq is used to indicate that the concentrations refer to the equilibrium state.

The total concentrations of glycolaldehyde (c_G), trivalent manganese ($c_{Mn(III)}$), and hydrogen sulphate ions ($c_{HSO_4^-}$) obey the relations

$$c_G \quad = [G] + [GH^+] + [MnG^{3+}] + [MnGH^{4+}] \qquad (2)$$

$$c_{Mn(III)} = [Mn(HSO_4)^{2+}] + [MnG^{3+}] + [MnGH^{4+}] \qquad (3)$$

$$c_{HSO_4^-} = [HSO_4^-] + [Mn(HSO_4)^{2+}] . \qquad (4)$$

Henceforth, the concentrations denoted as c will be the total analytical concentrations, whereas the expressions in brackets will denote the equilibrium concentrations.

In the conditions applied, with the concentration of sulphuric acid highly exceeding that of trivalent manganese, the last term in Eq. (4) can be neglected. Analogously, the two last terms in Eq. (2) can be neglected as well, since glycolaldehyde is present in an excess of an order of magnitude with respect to trivalent manganese.

The equilibrium constants of the reactions $(B)-(D)$ are

$$K_1 = [GH^+]/\{[G][H^+]\} \tag{5}$$

$$K_2 = [MnG^{3+}][HSO_4^-]/\{[G][Mn(HSO_4)^{2+}]\} \tag{6}$$

$$K_3 = [MnGH^{4+}][HSO_4^-]/\{[GH^+][Mn(HSO_4)^{2+}]\} . \tag{7}$$

Dividing Eq. (6) by Eq. (7), rearranging, and substituting for $[G]/[GH^+]$ from Eq. (5) we obtain

$$(K_2[G])/(K_3[GH^+]) = [MnG^{3+}]/[MnGH^{4+}] = K_2/(K_1K_3[H^+]) \tag{8}$$

or on further rearrangement,

$$[MnG^{3+}] = \{K_2/(K_1K_3[H^+])\} [MnGH^{4+}] . \tag{9}$$

This relation can be inserted in the equation for the reaction rate, Eq. (1), to obtain

$$v = [MnGH^{4+}] \{(K_2k_1)/(K_1K_3[H^+]) + k_2\} . \tag{10}$$

Substituting for $[MnGH^{4+}]$ from Eq. (7), the relation transforms to

$$v = \{k_2 + (k_1K_2)/(K_1K_3[H^+])\} \{(K_3[GH^+][Mn(HSO_4)^{2+}])/[HSO_4^-]\} . \tag{11}$$

The $[Mn(HSO_4)^{2+}]$ concentration can be expressed from Eq. (3), substituting for $[MnG^{3+}]$ and $[MnGH^{4+}]$ from Eqs (6) and (7), respectively, as

$$[Mn(HSO_4)^{2+}] = c_{Mn(III)} - \frac{K_2[G][Mn(HSO_4)^{2+}]}{[HSO_4^-]} - \frac{K_3[GH^+][Mn(HSO_4)^{2+}]}{[HSO_4^-]} \tag{12}$$

or

$$[Mn(HSO_4)^{2+}] = \frac{c_{Mn(III)}c_{HSO_4}-(K_1[H^+] + 1)}{(K_1[H^+] + 1) c_{HSO_4-} + K_2c_G + K_1K_3[H^+] c_G} . \tag{13}$$

Now, this can be inserted in Eq. (11), substituting $c_G K_1[\text{H}^+]/(K_1[\text{H}^+] + 1)$ for $[\text{GH}^+]$ (Eqs (2) and (5)), to obtain the final relation for the rate of the reaction under study:

$$v = n\left(k_2 + \frac{k_1 K_2}{K_1 K_3 c_{\text{H}^+}}\right) \frac{K_1 K_3 c_G c_{\text{H}^+}}{K_1 K_3 c_G c_{\text{H}^+} + K_2 c_G + c_{\text{HSO}_4^-} \cdot (K_1 c_{\text{H}^+} + 1)} c_{\text{Mn(III)}} \qquad (14)$$

or

$$v = \frac{n(k_2 K_1 K_3 c_{\text{H}^+} + k_1 K_2)\, c_G}{K_1 K_3 c_G c_{\text{H}^+} + K_2 c_G + c_{\text{HSO}_4^-} \cdot (K_1 c_{\text{H}^+} + 1)} c_{\text{Mn(III)}} . \qquad (15)$$

Assuming that the concentration of glycolaldehyde and of hydrogen, hydrogen sulphate, and manganese(II) ions exceed by orders of magnitude the concentration of trivalent manganese, Eq. (15) can be looked upon as a proportionality relation, $v = k' c_{\text{Mn(III)}}$, with the proportionality factor

$$k' = \{(n k_2 K_1 K_3 c_{\text{H}^+} + n k_1 K_2)\, c_G\}/\{K_1 K_3 c_{\text{H}^+} + K_2)\, c_G +$$
$$+ (K_1 c_{\text{H}^+} + 1)\, c_{\text{HSO}_4^-}\} , \qquad (16)$$

which is consistent with the observed fact that the reaction in question is first order with respect to the concentration of trivalent manganese.

If the concentrations of hydrogen and hydrogen sulphate ions are constant, Eq. (16) reduces to $k' = a_1 c_G/(b_1 + c_1 c_G)$, which can be rearranged to the form $1/k' = c_1/a_1 + (b_1/a_1)/c_G$, consistent with the experimentally established linear dependence of $1/k'$ on $1/c_G$ (a_1, b_1, c_1 are constants). If the concentrations of glycolaldehyde and hydrogen ions are held constant, Eq. (16) reduces to the form $k' = = a_2/(b_2 + c_2 c_{\text{HSO}_4^-})$, from which $1/k' = b_2/a_2 + (c_2/a_2)\, c_{\text{HSO}_4^-}$; this is in accordance with the experimentally found linear dependence of $1/k'$ on $c_{\text{HSO}_4^-}$ (a_2, b_2, c_2 are constants). If the constant concentrations are those of glycolaldehyde and hydrogen sulphate ions, Eq. (16) takes on the form $k' = n c_G(k_2 K_1 K_3 c_{\text{H}^+} + k_1 K_2)/ /\{K_1 K_3 c_G c_{\text{H}^+} + K_2 c_G + c_{\text{HSO}_4^-} \cdot (K_1 c_{\text{H}^+} + 1)\}$. In case that $K_1 \ll 1$ (low degree of protonation), the $K_1 c_{\text{H}^+}$ term can be neglected with respect to 1 and the $K_1 K_3 c_{\text{H}^+} c_G$ term with respect to $c_{\text{HSO}_4^-}$, whereupon $k' = a_3 c_{\text{H}^+} + b_3$, which agrees with the observed linear dependence of k' on c_{H^+}.

The mechanism suggested is also consistent with the observed fact that the reaction rate is independent of the concentration of divalent manganese.

The assumed formation of the free radical, $\overset{\bullet}{\text{C}}\text{H}_2\text{OH}$, as a reaction intermediate can account for the observed initiation of polymerization of acrylonitrile as well as for the fact that the infrared spectrum of the polymer formed exhibits bands due to the —OH group stretching vibration.

REFERENCES

1, Fleury P. F., Lange J.: C. R. Acad. Sci., *195*, 1395 (1932).
2. Heldorsen K. M.: Carbohyd. Res. *63*, 61 (1978).
3. Fleury P. F., Lange J.: J. Pharm. Chim. *8*, 404 (1933).
4. Barek J., Berka A., Korečková J.: Chem. Anal. (Warsaw) *20*, 749 (1975).
5. Berka A., Zýka J.: Česk. Farm. *8*, 136 (1959).
6. Siggia S., Maxcy W.: Ind. Eng. Chem., Anal. Ed. *19*, 1023 (1947).
7. Bricker C. E., Johnson H. R.: Ind. Eng. Chem., Anal. Ed. *17*, 400 (1945).
8. Barek J., Beneš P., Berka A.: This Journal *43*, 2555 (1978).
9. Večeřa M., Gasparič J., Churáček J., Borecký J.: *Chemické tabulky organických sloučenin.* Published by SNTL, Prague 1975.
10. Barek J., Berka A.: CRC Crit. Rev. Anal. Chem. *9*, 55 (1980).

Translated by P. Adámek