KINETIC ANALYSIS OF OXALIC AND CITRIC ACIDS MIXTURES WITH MANGANESE(III) SULPHATE*

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Model mixtures of oxalic and citric acids were used to verify the applicability of the logarithmic extrapolation method for 2nd order reactions to the analysis of mixtures of pairs of substances reacting with the oxidant employed with the exchange of different numbers of electrons.

As part of our systematic study of the oxidation of organic substances by compounds of trivalent manganese, the applicability is tested of the logarithmic extrapolation method for 2nd order reactions[1] to the kinetic analysis of mixtures of two substances which react with the oxidizing reagent with different stoichiometry. Mixtures of citric and oxalic acids, which are formed, *e.g.*,in the fermentation production of the former acid[2] and for which a titrimetric method of analysis has been suggested by us previously[3], served as model systems. The oxidant used was manganese(III) sulphate, reacting quantitatively with oxalic acid by reaction[4-6]

$$(COOH)_2 + 2\,Mn^{3+} \rightarrow 2\,CO_2 + 2\,Mn^{2+} + 2\,H^+ \qquad (A)$$

and with citric acid by reaction[7]

$$(HOOCCH_2)_2COHCOOH + 14\,Mn^{3+} + 5\,H_2O \rightarrow$$
$$\rightarrow 2\,HCOOH + 4\,CO_2 + 14\,Mn^{2+} + 14\,H^+ \qquad (B)$$

In agreement with the routine[8] recommended for working out new kinetic methods, the fact that both reactions are 2nd order in the conditions of the experiment was first verified, and the dependences of the rate constants of these reactions on the sulphuric acid and manganese(II) sulphate concentrations and on temperature were then measured. Since the rate of the reactions in question satisfied the condition for the applicability of the logarithmic extrapolation method for 2nd order reactions[1,9],

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the possibility of utilizing the reactions for the indirect titrimetric determination of the total concentration of the two acids by the equilibrium method and for the determination of the two components by the differential kinetic method was further investigated.

EXPERIMENTAL

Reagents and Apparatus

The solutions of oxalic and citric acids in the concentration of choice were prepared by dissolving precisely weighed amounts of the substances of reagent grade purity in sulphuric acid and diluting to volume. The manganese(III) sulphate solutions in systems of sulphuric acid with magnanese(II) sulphate were prepared as reported previously[10]. Iron(II) sulphate solution in a concentration of 50 mmol l^{-1} was prepared conventionally and standardized daily using potassium dichromate[11]. All the chemicals employed were of reagent grade purity.

The spectrometric measurements were carried out on a Specord UV VIS spectrophotometer (Zeiss, Jena) in 2 cm cells; the temperature was held constant with a precision of $\pm 0{\cdot}2°C$ by means of a U 10 ultrathermostat (Mechanik-Prüfgeräte, Medingen, GDR). The potentiometric titrations were performed by using an ABU 1b autoburette and a TTT 1c titrator (both Radiometer, Copenhagen) fitted with a platinum indicator electrode and a calomel reference electrode.

Procedures

Verification of the reaction order. To 10·00 ml of manganese(III) sulphate solution in an approximate concentration of 10 mmol l^{-1} in 0·1M manganese(II) sulphate and 8M sulphuric acid was added 10·00 ml of a solution containing a precisely equivalent amount of oxalic or citric acid, also in 8M sulphuric acid to prevent temperature (20°C) changes during the mixing. The solution was shaken shortly and the time dependence of the absorbance at the wavelength corresponding to the absorption peak of manganese(III) sulphate in the system used was measured. The molar absorptivity of manganese(III) sulphate in 8M sulphuric acid was determined from the slope of the calibration curve plotted for the region of $c_{\mathrm{Mn(III)}} = 1-6$ mmol l^{-1}.

Dependence of the reaction rate on the concentrations of sulphuric acid and divalent manganese and on temperature. The procedure was as above, only the values were measured in dependence on the concentrations of sulphuric acid and divalent manganese and on temperature.

Determination of the total concentration of oxalic and citric acids by the equilibrium method. The time course of the oxidation was monitored as follows: To 10·00 ml of manganese(III) sulphate (50 mmol l^{-1}) in 8M sulphuric acid and 0·1M manganese(II) sulphate was added 10·00 ml of oxalic acid (10 mmol l^{-1}) or citric acid (1·5 mmol l^{-1}) in 8M sulphuric acid. Regarding the effect of oxygen on the course of the reactions[7], the solutions of the reactants had been freed from dissolved oxygen by a 10 min purging with nitrogen, and an inert atmosphere was maintained also during the stirring and reaction course monitoring. After a time t, the unreacted manganese(III) sulphate was determined by potentiometric titration with iron(II) sulphate (50 mmol l^{-1}).

The recommended procedure for the determination of both acids in mixture is similar, only 10·00 ml of a solution containing 3—20 mg of oxalic acid and 0·5—4 mg of citric acid is added, and the retitration is accomplished in 60 min.

Kinetic analysis of oxalic and citric acids in mixtures. 10·00 ml of the solution to be analyzed, containing 3—20 mg of oxalic acid and 0·5—4 mg of citric acid in 8M sulphuric acid (the total concentration of the two acids is known from the equilibrium method measurement), is diluted to 50 ml with 8M sulphuric acid, and to a 15·00 ml aliquot of this solution is added 10·00 ml of approximately 0·01M manganese(III) sulphate in 8M sulphuric acid and 0·1M manganese(II) sulphate of a precisely known titre. The system is mixed rapidly and placed in a thermostated cell, and the time dependence of the absorbance is measured at a wavelength of 19 600 cm^{-1}, corresponding to the absorption peak of trivalent manganese. The solutions of the reactants as well as the vessels and the cell have to be thermostated in advance to the temperature of measurement, namely, 30°C.

RESULTS AND DISCUSSION

Verification of the Reaction Order

Assume that trivalent manganese and oxalic (HA) or citric (HB) acids are present in equivalent concentrations. Then the relations

$$[\mathrm{Mn(III)}] = 2[\mathrm{HA}] \qquad (1)$$

or

$$[\mathrm{Mn(III)}] = 14[\mathrm{HB}]\,, \qquad (2)$$

where the bracketed symbols denote the corresponding molar concentrations, are satisfied throughout the reaction. The 2nd order reactions obey Eqs (*3*) and (*4*),

$$-\mathrm{d}[\mathrm{HA}]/\mathrm{d}t = -(1/2)\,\mathrm{d}[\mathrm{Mn(III)}]/\mathrm{d}t = k[\mathrm{Mn(III)}]\,[\mathrm{HA}] \qquad (3)$$

and

$$-\mathrm{d}[\mathrm{HB}]/\mathrm{d}t = -(1/14)\,\mathrm{d}[\mathrm{Mn(III)}]/\mathrm{d}t = k'[\mathrm{Mn(III)}]\,[\mathrm{HB}]\,, \qquad (4)$$

where k and k' are the 2nd order rate constants. Taking into account the equalities (*1*) and (*2*) we obtain

$$1/[\mathrm{Mn(III)}]_t = 1/[\mathrm{Mn(III)}]_0 + kt\,, \qquad (5)$$

where the subscripts indicate the time elapsed since the mixing of the reactants. Relating the trivalent manganese concentration to the absorbance by the Lambert-Beer law we have

$$1/A_t = 1/A_0 + kt/\varepsilon l\,, \qquad (6)$$

where A is the absorbance at the wavelength of the absorption maximum of trivalent manganese, ε is the molar absorptivity of trivalent manganese at this wavelength, and l is the optical path length; the meaning of the subscripts is as above.

Thus, for a 2nd order reaction a linear plot is obtained in $1/A_t$ *vs* time coordinates, and its slope can be used for the determination of the rate constant of the reaction involved. The procedure described in Experimental furnished linear dependences of $1/A_t$ *vs* t for both acids, thus confirming the 2nd order kinetics for them. The 2nd order rate constants derived from the plots are 1·5 $\text{mol}^{-1}\,\text{l}\,\text{s}^{-1}$ for oxalic acid and 0·26 $\text{mol}^{-1}\,\text{l}\,\text{s}^{-1}$ for citric acid.

Dependence of the Reaction Rate on the Concentrations of Sulphuric Acid and Divalent Manganese and on Temperature

The 2nd order rate constants were determined as above for different concentrations of sulphuric acid. Depending on the medium, the molar absorptivity had also to be determined for each system (Table I). From the point of view of the absolute as well as the relative value of the rate constants, the concentration of sulphuric acid of 8 $\text{mol}\,\text{l}^{-1}$ appeared as optimum.

The dependence of the 2nd order rate constants for oxalic acid (k_{HA}) and for citric acid (k_{HB}) (both in $\text{l}\,\text{mol}^{-1}\,\text{s}^{-1}$) on the concentration of divalent manganese (in $\text{mmol}\,\text{l}^{-1}$) was as follows:

c_{MnSO_4}	25	50	100	250
k_{HA}	25·5	25·6	25·0	25·5
k_{HB}	0·35	0·14	0·08	0·05

From the point of view of the kinetic analysis, with regard to the effect of the concentration of divalent manganese on the stability of the reagent[10], the concentration of MnSO_4 of 50 $\text{mmol}\,\text{l}^{-1}$ was chosen as optimum.

TABLE I

Values of the molar absorptivity of manganese(III) sulphate ($\text{l}\,\text{mol}^{-1}\,\text{cm}^{-1}$) and of the 2nd order rate constants ($\text{l}\,\text{mol}^{-1}\,\text{s}^{-1}$) for the oxidation of oxalic acid (k_{HA}) and citric acid (k_{HB}), for various concentrations of sulphuric acid ($\text{mol}\,\text{l}^{-1}$). $[\text{Mn(III)}]_0 = 2\,[\text{HA}]_0 = 14\,[\text{HB}]_0 = 5\,\text{mmol}\,\text{l}^{-1}$, $[\text{Mn(II)}]_0 = 50\,\text{mmol}\,\text{l}^{-1}$, temperature 20°C

$c_{\text{H}_2\text{SO}_4}$	ε	k_{HA}	k_{HB}
4	88·8	25·6	0·14
6	107·2	3·8	0·18
8	121·7	1·5	0·26
10	131·5	0·7	0·30

The dependence of the reaction rate on temperature was examined over the region of 20–40°C in the system of 8M sulphuric acid and 0·05M manganese(II) sulphate. The following values were obtained by the conventional procedure[12]: for the oxidation of oxalic acid, the activation energy and the frequency factors were $E_A = 0{\cdot}117$ J . . mol^{-1}, $A = 10^{21}\,\text{l mol}^{-1}\,\text{s}^{-1}$, respectively; for citric acid, $E_A = 0{\cdot}0638$ J mol^{-1}, $A = 10^{11}\,\text{l mol}^{-1}\,\text{s}^{-1}$. With regard to these data, an elevated temperature of 30°C, requiring a shorter reaction time, was chosen for the kinetic analysis.

Determination of the Total Concentration of Oxalic and Citric Acids by the Equilibrium Method

The following dependence of the oxidant consumption on the time t (in min) was observed:

t	0	5	10	20	30	60
$n(\text{Mn(III)})/n(\text{HA})$	0·98	1·99	2·00	2·00	2·00	2·01
$n(\text{Mn(III)})/n(\text{HB})$	11·12	11·91	13·55	13·93	14·05	14·10

(the n's denote the corresponding amounts of substance). It was therefore decided to allow an at least twofold excess of reagent to act on the acid mixture for 60 minutes.

Some of the results of analysis carried out in this manner are given in Table II; clearly, the method is applicable to the determination of the total concentration of the two acids.

Kinetic Analysis of Oxalic and Citric Acids in Mixture

In the logarithmic extrapolation method for 2nd order reactions, $\log \{([\text{R}]_0 - X_\text{R})/([\text{M}]_0 - X_\text{R})\}$ is plotted[1,9] against t; here $[\text{R}]_0$ is the initial concentration of reagent, $[\text{M}]_0$ is the sum of the initial concentrations of the substances to be determined, and X_R is the concentration of the reagent that had reacted in time t. The graph displays two linear segments (Fig. 1*A*), the second of which coresponds to the reaction of the slower-reacting component. This linear part is extrapolated to give the intercept O, and a straight line parallel to the horizontal axis is drawn through this point *O*. This straight line interesects the curve in point *P*, to which time t_1 corresponds. The initial concentration of the faster-reacting substance then is found *via* the amount of reagent consumed up in time t_1. For determining this concentration it is convenient to draw a plot of X_R *vs* t (Fig. 1*B*). The initial concentration of the slower-reacting substance then is calculated by subtracting the established initial concentration of the faster-reacting substance from the total initial concentration of the two substances as determined by the equilibrium method.

TABLE II

Determination of the total concentration of oxalic and citric acids by the equilibrium method

Taken, µmol		Consumption of manganese(III) sulphate	
citric acid	oxalic acid	calculated, µmol	found[a], % theory
14·29	0	200	101·0
11·43	120	400	100·5
11·43	160	480	101·3
5·71	60	200	101·0
5·71	180	440	101·3
2·86	60	160	100·8
2·86	140	320	99·7
0·57	11	30	98·2
0·57	18	44	100·8
0	100	200	100·4

[a] Average from triplicate determinations, which agreed mutually to within ±1%.

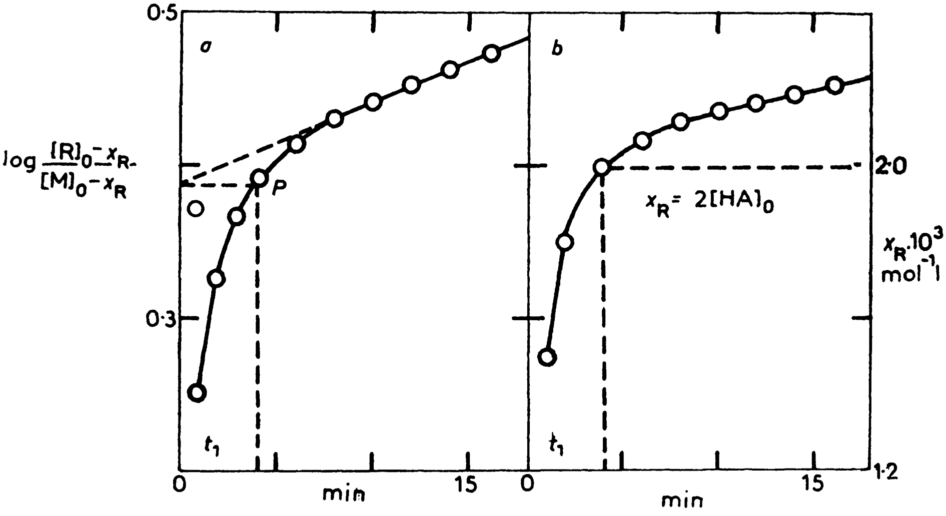

FIG. 1

Kinetic analysis of a mixture of oxalic and citric acids by the logarithmic extrapolation method for 2nd order reactions. *a* determination of t_1, *b* determination of $[HA]_0$. $[R]_0 = 3{\cdot}98$ mmol l^{-1}, $[M]_0 = 2{\cdot}80$ mmol l^{-1}, $c_{H_2SO_4} = 8$ mol l^{-1}, $c_{MnSO_4} = 50$ mmol l^{-1}, temperature 30°C

The method has been derived for systems in which one molecule of either substance reacts with one molecule of reagent. In our case, however, a molecule of oxalic or citric acid reacts with two or fourteen molecules of trivalent manganese, respectively. So for making the method readily usable, the concentrations are to be expressed in units of chemical equivalents to trivalent manganese; otherwise the kinetic equations would include the stoichiometric coefficients and their integral form would become substantially more complex, precluding the use of the graphical method in its simplest form as described above.

The symbols will be therefore understood in the following sense: while [R], [HA], and [HB] are, as above, the concentrations of trivalent manganese, oxalic acid, and citric acid, respectively, in mol l^{-1}, and $X_R = [\mathrm{Mn(III)}]_0 - [\mathrm{Mn(III)}]_t$ is the concentration of trivalent manganese, in mol l^{-1}, consumed up in time t after the mixing of the reactants, the total initial concentration of the two acids $[M]_0$ will be expressed *via* the equivalent concentration of trivalent manganese (in mol l^{-1}) as $[M]_0 = 2[\mathrm{HA}]_0 + 14[\mathrm{HB}]_0$. With respect to the stoichiometry of the reactions of trivalent manganese with oxalic and citric acids we have

$$X_R = 2([\mathrm{HA}]_0 - [\mathrm{HA}]_t) + 14([\mathrm{HB}]_0 - [\mathrm{HB}]_t)\,. \quad (7)$$

TABLE III

Kinetic analysis of mixtures of oxalic and citric acids

Taken, mg		Found, % theory	
oxalic acid	citric acid	oxalic acid	citric acid
1·89	0·15	108	77
2·52	0·15	108	84
3·15	0·15	102	88
3·78	0·15	95	120
1·89	0·30	107	90
2·52	0·30	107	85
3·15	0·30	100	100
3·78	0·30	94	120
4·41	0·30	106	80
5·04	0·30	97	110
3·78	0·60	103	95
4·41	0·60	97	104
5·04	0·60	97	106
2·52	1·20	117	92
3·15	1·20	112	92

In the analysis, $[M]_0$ is first determined by the method as described above. Then the kinetic measurement is carried out as reported in Experimental. $[R]_0$ is calculated from the known concentration of trivalent manganese in the reagent solution by multiplying it by a factor of 10/25, and $[M]_0$ is calculated from the total concentration of the two acids in analyte, as determined by the equilibrium method, by multiplying it by a factor of 15/25. X_R is calculated as

$$X_R = [R]_0 - A_t/\varepsilon l \,, \qquad (8)$$

where A_t is the absorbance of the reaction mixture in time t, ε is the experimental molar absorptivity of trivalent manganese in the system used ($\varepsilon = 121{\cdot}7 \text{ mol}^{-1} \text{ l s}^{-1}$), and l is the optical path length. Time t_1 is determined by the procedure illustrated by Fig. 1*A* and $[HA]_0$ is calculated by Eq. (*9*) from the X_R value for time t_1 determined as apparent from Fig. 1*B*:

$$[HA]_0 = (X_R)_{t_1}/2 \qquad (9)$$

$[HB]_0$ is calculated as

$$[HB]_0 = ([M]_0 - 2[HA]_0)/14 \,, \qquad (10)$$

which follows from the definition equation for $[M]_0$.

The results of the kinetic analysis of a mixture of oxalic and citric acids are given in Table III, demonstrating the possibilities and limitations of the method. Clearly, the accuracy depends on the absolute as well as relative amounts of the two acids in sample, and is different for either of them. Oxalic acid can be determined with a relative error not exceeding 10% in mixtures containing 85–95% (*m*/*m*) of this compound; in this case the relative error of determination of citric acid is higher, 5–20%, owing to its lower content in the system. For mixtures containing 60–80% (*m*/*m*) citric acid, on the other hand, the relative error of determination of this acid is lower than 10%, whereas that of determination of oxalic acid can be as high as 20%.

Thus, it can be claimed that despite the above limitations the method can complement well the previously developed titrimetric method of analysis of the mixtures in question based on the oxidation with permanganate and manganese(III) sulphate, applicable to mixtures containing 20–50% (*m*/*m*) oxalic acid.[3]

In conclusion, the logarithmic extrapolation method for 2nd order reactions has been found applicable to the analysis of mixtures of substances which react with the oxidant with the exchange of different number of electrons, although if the difference between the numbers of exchanged electrons is high, an appreciable error of determination can be expected to arise for the substance exchanging the higher number of electrons.

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