[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF UTAH]

Complex Ions of Chromium. VIII. Mechanism of Reaction of Organic Acid Anions with Chromium(III)[1,2]

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RECEIVED JULY 23, 1958

The reaction rates of a series of organic acid anions (acetate, glycolate, lactate, phthalate, citrate and tartrate) with chromium(III) ion have been determined by polarographic methods. From similarities in these rates and those previously reported for oxalate and malonate, a general reaction mechanism has been proposed, which involves the dissociation of a water molecule as the slow step. The determination of the rate of completion of the chelate ring by using a spectrophotometric method on the citrate ion resulted in a rate which indicated there was only a single slow step. The reactions have been studied as a function of variation in temperature and electrolyte concentration.

Previous papers from this Laboratory have reported on the kinetics of the reactions of chromium(III) ion with oxalate[3] and malonate.[2] The rates of reaction with malonate were found to be practically identical to those with oxalate. The similarity of these results and the discovery that the reaction of chromium(III) ion with monobasic organic anions, such as acetate, could be followed polarographically, led to the study of kinetics of several other organic acid anions with chromium(III) ion in the hope of more fully understanding the mechanism of the reactions.

It has long been known that the ions of many organic acids form complexes by slow reactions with chromium(III) solutions. Serfass, *et al.*,[4,5] have established a penetration order for several organic acid anion complexing agents. Shuttleworth[6] has shown that five- and six-membered rings are formed with organic acid anions but that seven-membered rings form only when a double carbon–carbon bond is in the ring (without the double bond, polymers are formed). Küntzel and co-workers[7] have studied reactions with acetate and formate and have made some suggestions about the mechanism of the reactions.

Experimental

Apparatus.—A Sargent Model XXI Polarograph was used for making the polarographic measurements described in this paper. A Beckman DK-2 Recording Spectrophotometer was used for the determination of the absorption spectra of the various complexes and a Beckman DU Spectrophotometer was used for the spectro-determination of rates of reaction.

A Beckman Model GS *p*H meter was used for the measurement of *p*H during the course of reactions by standardizing against a quantity of 0.05 *M* potassium acid phthalate buffer which was maintained at the same temperature as the test solution. In most experiments an excess of the reacting anion was used. This had the effect of buffering the solutions to such an extent that the change in *p*H during the reaction was found to be negligible.

Reagents.—Reagent grade sodium acetate, sodium citrate, sodium tartrate and potassium acid phthalate were used as sources of the acid anions. Crystalline glycolic acid (Matheson, Coleman and Bell) and technical lactic acid were neutralized with carbonate-free sodium hydroxide before use. Reagent grade chromium nitrate was the source of the chromium(III) ion.

Methods.—For the polarographic determination of a reaction rate, a solution was prepared which was 0.10 molar in the organic anion 0.002 molar in chromium(III) nitrate, with sufficient added nitric acid to give the desired *p*H and sufficient added potassium nitrate to give the desired electrolyte concentration. Some of this solution was added to an H-type polarographic cell which was placed in a constant temperature bath set at the desired temperature and held to about 0.1°. The dissolved oxygen was removed by passing a stream of hydrogen through the solution, and a recording was made of the polarographic current at a potential which was on the plateau of the disappearing wave. The current was recorded for at least one half-time of the reaction, but usually for several half-times.

The techniques used in determination of reaction rates by spectrophotometric methods were essentially the same as those described in previous papers in this series.[3,8]

A freshly mixed solution of 0.002 *M* chromium(III) nitrate in 0.10 *M* sodium acetate was found to give a polarographic wave at a half-wave potential of −0.90 volt against the saturated calomel electrode, but this wave disappeared just as was the case with oxalate[6] and malonate.[2] Determination of the current at a potential of about −1.0 volt against the saturated calomel electrode enabled the calculation of the rate of the reaction. Similar measurements have been possible for all organic acid anions investigated.

In the case of all anions investigated, a plot of the logarithm of the wave height against time gave straight line plots which indicates a reaction first order in chromium(III) ion concentration.

For all anions investigated the reaction was independent of anion concentration. The data for glycolate and citrate at a constant ionic strength of 2.0 with added potassium nitrate to give the ionic strength are shown in Table I.

These results show a rate independent of the acid anion concentration. In the case of the citrate anion, two runs were made spectrophotometrically where an excess of chromium was in the presence of a small amount of citrate at a *p*H of about 3.0 and attempts were made to determine the rate by following the change in absorbancy with a chromium solution of the same concentration as the reference solution. The accuracy obtainable under these conditions was very poor but the order of magnitude of the rate determined was the same as those reported in Table I.

TABLE I

REACTION RATES FOR GLYCOLATE AND CITRATE WITH CHROMIUM(III) ION AT 25° AND IONIC STRENGTH = 2.0, AT *p*H 4.00

Glycolate concn., moles/l.	$-\log k$	Citrate concn., moles/l.	$-\log k$
1.00	4.12	1.00	3.91
0.80	4.13	0.80	4.09
.60	4.13	.60	3.90
.40	3.94	.40	3.91
.20	3.88	.20	3.90
.10	3.75	.10	3.75

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[1] The work reported in this paper has been supported by research grants NSF G-62 and G-756 from the National Science Foundation.

[2] Previous papers in this series, THIS JOURNAL, **77**, 2083 (1955); **78**, 3006 (1956).

[3] R. E. Hamm and R. E. Davis, *ibid.*, **75**, 3085 (1953).

[4] E. J. Serfass, E. R. Theis, T. C. Thorstensen and R. E. Agarwal, *J. Am. Leather Chemists Assoc.*, **43**, 132 (1948).

[5] E. J. Serfass, C. D. Wilson and E. R. Theis, *ibid.*, **44**, 647 (1949).

[6] S. G. Shuttleworth, *ibid.*, **45**, 169, 296, 302, 447, 799 (1950); **46**, 409 (1951).

[7] A. Küntzel, H. Erdman and H. Spahrkas, *Das Leder*, **3**, 30, 73, 148 (1952); (b) **14**, 73 (1953).

[8] R. E. Hamm, THIS JOURNAL, **75**, 609, 5670 (1953).

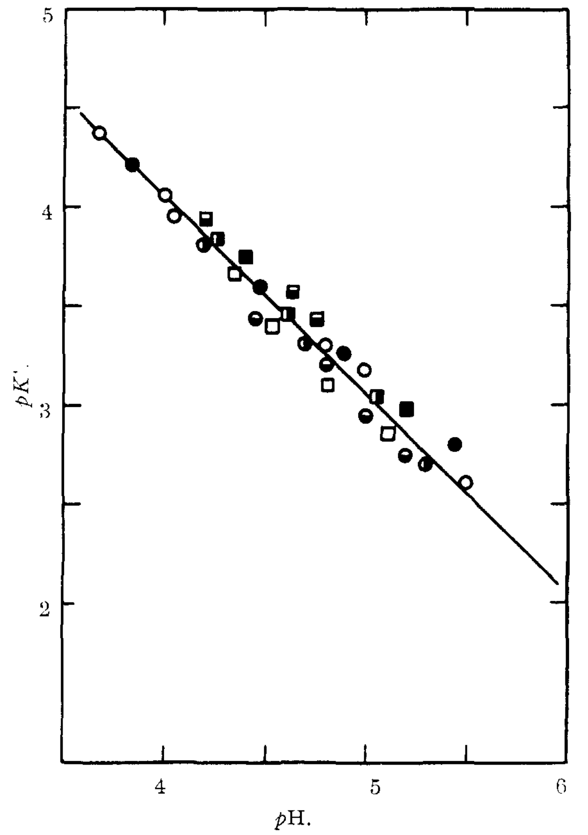


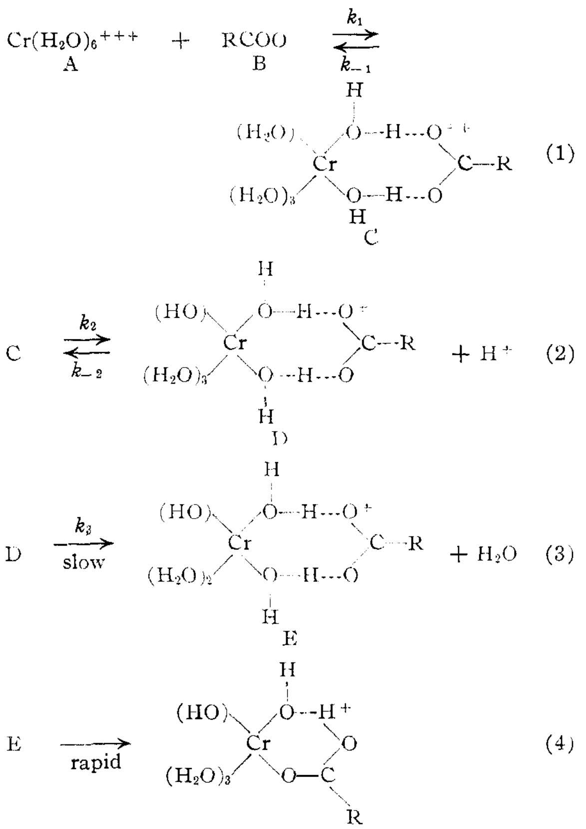
Fig. 1.—○, malonate; ●, citrate; ⊖, lactate; ◑, tartrate; □, glycolate; ■, phthalate; ⊟, acetate; ◨, oxalate.

Of the ions investigated only oxalate and malonate have given a second disappearing wave to allow the determination of the rate of the second ligand ion reacting.

In Fig. 1 the negative logarithm of the apparent rate constant is shown plotted against *p*H for reactions of acetate, glycolate, lactate, phthalate, citrate and tartrate, with chromium(III) ions. The points plotted also include some points for oxalate[6] and malonate.[2] All of these rates were determined at 25°, polarographically, using solutions that were 0.10 molar in organic acid anion and 0.002 molar in chromium(III) nitrate, with no potassium nitrate present. The line included has a slope of -1, indicating that the reaction rates were inversely proportional to the first power of the hydrogen ion concentration. The fact that all of the points for the various acid anions are near the line may be taken as an indication that the actual slow step was nearly independent of the anion being investigated and that the minor differences were due to structural differences and differences in charge. If this is true, a general mechanism may be proposed for the reaction.

Discussion

The observation that the rate of reaction of the acetate ion with chromium(III) was nearly the same as the rate when oxalate ion reacted with chromium(III) resulted in the conclusion that the slow step could not be the completion of the chelate ring, as was originally proposed,[8] but must be concerned with the primary step to produce the first covalent bond to the chromium.[9] The following reactions are consistent with the presently known facts.[10]



The charges indicated are correct for a reacting single negative anion. If the charge on the reacting anion is different, appropriate changes should be made in the charges on the products.

Reactions 1 and 2 represent the reaction with the acid anion and the acid ionization of the aquated chromium ion. The reacting form is probably one which has a hydroxyl group in a position to give a *trans* effect consistent with the known favoring of reaction paths involving chromium(III) containing a hydroxyl group.[11] Reactions 1 and 2 must be relatively rapid with respect to the slow step, reaction 3.[12] The rate equation for the slow step will be

$$\frac{d[\mathrm{Cr_t}]}{dt} = -k_3[\mathrm{D}] \qquad (5)$$

where $[\mathrm{Cr_t}]$ represents the concentration of the total polarographically measurable chromium.

$$[\mathrm{Cr_t}] = [\mathrm{A}] + [\mathrm{C}] + [\mathrm{D}] \qquad (6)$$

The equilibrium constants of the reactions indi-

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[9] The authors recognize that the present data alone do not permit making a decision as to whether the exact mechanism is the SN2 mechanism through an activated complex of coördination number seven or a SN1 mechanism through a penta-coördinate complex, but have chosen to call this mechanism dissociation because of the agreement of the activation energies with those obtained for water exchange, (a) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952), and those obtained for dimerization of dioxalatochromium, (b) D. M. Grant and R. E. Hamm, THIS JOURNAL, **78**, 3006 (1956), where there is evidence that the mechanism is the dissociation step.

[10] The chromium(III) 6-coördinate structure will be represented by showing three of the water molecules as located at one position in order to represent readily the structure on the plane of the paper.

[11] (a) N. Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907); (b) R. E. Hamm and C. M. Shull, THIS JOURNAL, **73**, 1240 (1951); (c) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).

[12] The bond to the acid anion is represented by "ion-pair" or "outer-sphere" complexes which have been indicated by some recent studies; (a) A. W. Adamson and R. G. Wilkins, THIS JOURNAL, **76**, 3379 (1954); (b) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

cated in (1) and (2) are

$$\frac{[C]}{[A][B]} = \frac{k_1}{k_{-1}} = K_1, \qquad \frac{[D][H^+]}{[C]} = \frac{k_2}{k_{-2}} = K_2 \quad (7)$$

Substituting equations 7 and 6 in equation 5 gives the rate equation

$$\frac{d[Cr_t]}{dt} = -\frac{k_3K_2K_1[B][Cr_t]}{[H^+] + ([H^+] + K_2)K_1[B]} \quad (8)$$

which under the condition that $K_1[B] >> 1$, reduces to

$$\frac{d[Cr_t]}{dt} = -\frac{k_3K_2[Cr_t]}{([H^+] + K_2)} \quad (9)$$

This will be true for anion concentrations such that $k_{-1} << k_1[RCOO^-]$, a condition apparently satisfied over the anion concentration range studies. Equation 9 further reduces to demonstrate the inverse dependence of rate upon hydrogen ion concentration when $[H^+] >> K_2$, a condition which has been satisfied for the points plotted in Fig. 1. The derivation can be carried out including the additional equilibrium for the direct acid ionization of $Cr(H_2O)_6^{+++}$, however the additional term from this equilibrium is negligible and the result is identical to equation 8; and reaction 4 is the relatively rapid step following the dissociation of a water molecule.

The species shown as the product in equation 4 would be the end of the reaction for the acetate ion and chromium(III), but for a single oxalate ion the chelate ring would not yet be complete. Chelation of chromium(III) always gives a much higher spectral absorption than was found for non-chelated species, as is shown by the molar absorbancy indices given in Table II. From these values it may be seen that the anions forming chelated structures give much more absorption that the non-chelating anions do. Because of this, an attempt was made to differentiate the rate of formation of the chelate ring and the rate of dissociation of the first water molecule, by determining the rate of reaction of an acid anion which formed a 1:1 chelated structure with chromium(III) by two methods: the polarographic method as a possible method of determining the rate of the preliminary reaction as has been shown above; the spectrophotometric method as a possible method of determining the rate of formation of the chelated compound.

TABLE II

MOLAR ABSORBANCY INDICES OF CHROMIUM(III) SOLUTIONS IN 1:1 MIXTURE WITH VARIOUS ORGANIC ACID ANIONS AFTER HEATING 24 HOURS AT 90° IN 0.25 *M* PERCHLORIC ACID[a]

Anion	Wave length, mμ	a_M	Wave length, mμ	a_M	% comp.[b]
Acetate	406	19.2(20.7)	568	18.1(21.6)	44
Glycolate	409	19.7(23.6)	569	17.3(21.8)	33
Lactate	409	22.6(31.2)	563	18.9(25.7)	35
Oxalate	417	42.0	557	35.6	>99
Malonate	416	27.2	559	32.4	>99
Citrate	418	33.8	562	30.8	>99
Tartrate	416	36.6	555	33.4	>99

[a] The molar absorbancy indices for chromium(III) nitrate solution in 0.25 *M* perchloric acid were 18.0 at 406 mμ and 15.2 at 571 mμ. [b] The percentages of completion were determined polarographically. The figures in parentheses are the calculated values for complete reaction.

Citrate was chosen as the reacting anion for this attempt, as the result of a continuous variation experiment which showed that the 1:1 complex was the only important product formed when chromium(III) and citrate ions reacted. The results at 25° gave apparent rate constants of 2.2×10^{-5} sec.$^{-1}$ spectrophotometrically and 2.4×10^{-5} sec.$^{-1}$ polarographically at *p*H 4.07. The conclusion drawn from this experiment was that there is a single slow step as indicated in equation 3 for both the chelating and non-chelating anions, and that the subsequent steps leading to the chelated structure are relatively rapid. Another but less tenable explanation would be that in case of the chelating ions, the two bonds are formed in a concerted manner.

Investigation of the rate of reaction of these organic acid anions with chromium(III) as a function of electrolyte concentration showed that increasing ionic strength caused an increase in the speed of reaction which was approximately parallel for all of the anions investigated. The range of the electrolyte concentration was from ionic strength 0.25 to 2.0. The mean range of the reaction rate of the slow step at 25° and *p*H 4.85 for all species was from 5.0×10^{-3} at 0.25 to 2.5×10^{-2} at 2.0.

An investigation of the effect of electrolyte concentration on the activation energy of the reaction was undertaken, where the speed of the reaction was determined for acetate, citrate and oxalate over an electrolyte concentration range of 0.1 to 1.1 moles per liter and a temperature range of 25 to 46°. The value of K for reaction 2 was determined by curve fitting as previously indicated[3] to be 1.0×10^{-6} at 25° and the values at other temperatures were determined by using the 25° value and the value of ΔH_7 given by Postmus and King.[11b] The values determined by curve fitting at temperatures other than 25° were in remarkable agreement with those calculated. The slope and intercept of the plot of $-\log k_r h/hT$ against $1/T$ were determined by means of the method of least squares, where k_r was the rate constant determined from the previously derived equation,[5] $k_r = k(K + [H])/K$ where k' is the apparent first-order rate constant determined by plotting the logarithm of the polarographic current against time. The results of these calculations are shown in Table III.

TABLE III

ACTIVATION ENERGIES OF REACTIONS OF ACID ANIONS WITH CHROMIUM(III) (ΔH^* IN KCAL./MOLE)

	Ionic strength					
	0.1	0.3	0.5	0.7	0.9	1.1
Citrate	22.2	22.6	22.4	22.3	21.8	21.9
Oxalate	23.2				22.8	
Malonate	22.4				22.6	
Acetate	21.0				20.9	
o-Phthalate	22.4					

These results are of such agreement that the assumption that the slow step is the same for all the processes involving reactions of acid anions with chromium(III) ion is further verified.

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