

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

Complex Ions of Chromium. V. Reactions of Malonate Ion with Chromium(III)<sup>1,2</sup>

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Evidence has been presented for the existence of malonate complexes of chromium(III) containing one, two and three malonate groups per chromium. The *trans* and *cis* isomers of dimalonatodiaquochromate(III) have been prepared and identified. The rates, heats of activation and entropies of activation, of the reactions to form the successive complexes have been reported. The values have been compared with those for the reaction of oxalate with chromium(III), the third step of which is reported in this paper. The comparison between malonate and oxalate for the first and second chelation steps indicated that the slow steps were nearly identical. A possible explanation is that the slow step may have been a dissociation process.

There have been a few<sup>3</sup> references to the trimalonate complexes of chromium(III), but the only work on complexes containing fewer than three molecules of malonate per chromium that could be found was that of Howe,<sup>4</sup> who prepared the hydrogen and potassium salts of dimalonatodiaquochromate(III). Because of our previous work<sup>2b</sup> on the kinetics of the reactions between oxalate and chromium(III) and the knowledge that normally the five-membered chelates of metal ions are the more stable, it was decided to investigate the kinetics of the formation of the six-membered malonate chelates of chromium(III).

## Experimental

**Apparatus.**—The apparatus used was the same as has been described in previous papers from this Laboratory.<sup>2</sup>

**Procedures.**—Examination of polarograms of chromium(III) in malonate solution showed waves similar to those found for chromium(III) in oxalate solution, so the rate of reaction of hexaquo chromium(III) ion with malonate, and the rate of reaction of monomalonatotetraquo chromium(III) ion with malonate were determined by polarographic techniques which were identical with those used for oxalate.<sup>2b</sup> The rates of the reaction of dimalonatochromate(III) with malonate and dioxalatochromate(III) with oxalate were determined by observing the change in absorbancy with time when the chelating agent was added to a thoroughly aged solution of the dichelated chromium ion.

In an attempt to determine what complexes of chromium(III) and malonate existed in solution, a continuous variation experiment was carried out following the method of Job<sup>5</sup> as modified by Vosburgh and Cooper.<sup>6</sup> Since the reaction between malonate and chromium(III) was slow, measured quantities of the two reagents (0.2 *M* chromium(III) nitrate and 0.2 *M* disodium malonate) were mixed and heated just below the boiling point for about one hour. The solution was diluted in a volumetric flask after cooling and the absorbancy was measured against a chromium(III) nitrate solution of identical chromium concentration and *pH* as a reference solution. The absorbancy of these solutions was found to be constant for a period of several hours and was therefore assumed to have reached equilibrium.

**Reagents.**—Malonic acid and disodium malonate of Eastman Kodak Co. white label grade were used as purchased. Chromium nitrate and chromium perchlorate were used without recrystallization.

**Potassium Dimalonatodiaquochromate(III).**—The two isomers of this salt were prepared by taking 0.1 mole of

chromium nitrate in water solution and adding just sufficient sodium hydroxide to precipitate all of the chromic hydroxide. The precipitate was separated and washed by centrifugation. The freshly prepared chromic hydroxide was treated with 0.2 mole of malonic acid and 0.1 mole of potassium hydroxide in 100 ml. of water and maintained at about 80° for 12 hours. When the solution was allowed to evaporate slowly to crystallization, a reddish-violet salt was obtained. When the solution was crystallized rapidly by adding alcohol, a violet salt was obtained. It is believed that the reddish-violet salt was the *trans* form and the violet salt was the *cis* form. This conclusion was arrived at primarily from the analogy to the known *trans* and *cis* isomers of dioxalatochromate(III) where the *trans* isomer has the smaller solubility and the lower spectral absorbancy and the *cis* isomer is the one stable in solution. It is very unlikely that the dimalonatochromate(III) would be chemically very much different. The relationship of the isomeric forms was verified by the fact that solutions of the two gave different absorption spectra which became identical as the spectra of the *trans* form shifted with time due to isomerization. Each salt was analyzed after drying at 110° for 3 hours.

**Anal.** Calcd. for  $K[Cr(C_3H_3O_2)_2(H_2O)_2]$ : Cr, 15.70;  $CH_2(COO)_2$ , 61.7. Found reddish-violet (*trans*): Cr, 15.72;  $CH_2(COO)_2$ , 60.8. Violet (*cis*): Cr, 15.58;  $CH_2(COO)_2$ , 59.7.

The method of analysis for chromium was the classical method of oxidation with excess ammonium persulfate in the presence of silver ion and final titration of the dichromate formed with a standard ferrous solution. The analysis for malonate was performed by titration with standard ferrous solution after reaction of the malonate with excess ceric perchlorate in perchloric acid as outlined by Smith.<sup>7</sup>

## Results and Discussion

The results of the measurements made by the method of continuous variations are shown in Fig. 1, where relative absorbancy is plotted against  $[malonate]/[chromium] + [malonate]$  concentrations at two different wave lengths. In each of these curves there was a sharp break at 0.75 establishing the formation 1:3 chromium to malonate complex. In each of the curves there were indications of breaks at 0.50 and 0.67 which show the possibility of complexes containing 1:1 and 1:2 chromium to malonate. The indication at 0.50 when coupled with the fact that an aged 1:1 mixture gave a polarographic reduction wave of half-wave potential  $-1.18$  volts *vs.* S.C.E., which had a wave height equivalent to the total chromium concentration, was evidence for the existence of the 1:1 complex. The hexaquo chromium(III) ion gave a polarographic reduction wave at  $-0.90$  volt *vs.* S.C.E. The 1:2 mixture of chromium and malonate after aging and the solution of dimalonatochromate(III) prepared in this investigation were not reducible to chromium(II) at the dropping mercury electrode.

(7) G. F. Smith, "Cerate Oxidimetry," G. F. Smith Chemical Co., Columbus, Ohio, 1942.

(1) This investigation was supported by National Science Foundation Research Grants NSF G-62 and G-756.

(2) Previous papers in this series (a) R. E. Hamm, *THIS JOURNAL*, **75**, 609, 5670 (1953); (b) R. E. Hamm and R. E. Davis, *ibid.*, **75**, 3085 (1953).

(3) F. M. Jaeger and J. J. Woldendorp, *Vers. Akad. Wetenschappen Amsterdam*, **27**, 1212 (1919); F. M. Jaeger, *Rec. trav. chim.*, **38**, 171 (1919); H. Brintzinger and F. Jahn, *Z. anorg. allgem. Chem.*, **235**, 115 (1937).

(4) J. L. Howe, *THIS JOURNAL*, **25**, 444 (1903).

(5) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

(6) W. C. Vosburgh and G. R. Cooper, *THIS JOURNAL*, **63**, 437 (1941).

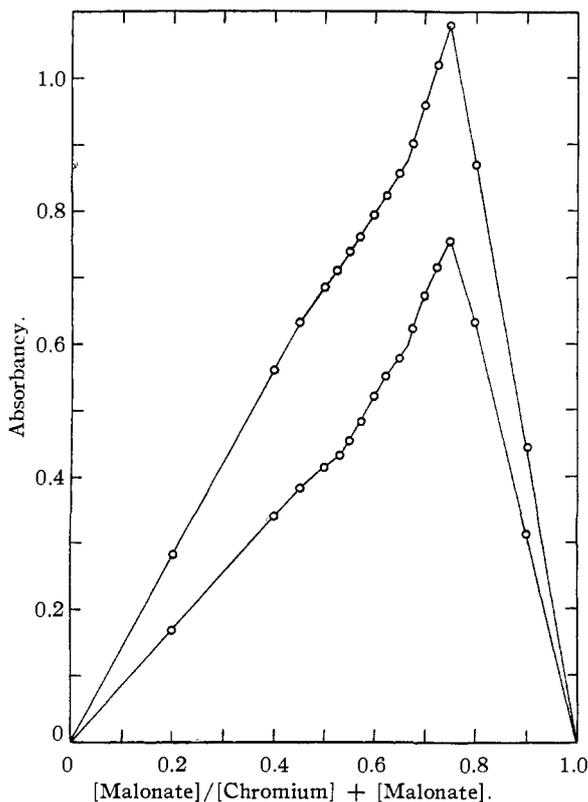


Fig. 1.—Continuous variation measurements on chromium(III) nitrate and disodium malonate: upper curve, at 560  $m\mu$ ; lower curve, at 420  $m\mu$ .

The apparent break at 0.67 when considered along with the fact that the dimalonate was recovered from an aged 1:2 mixture was sufficient evidence of the existence of the 1:2 complex. A similar experiment with chromium and oxalate gave a similar set of curves.

The rate of reaction of malonate with chromium(III) in the chelation of the first malonate with chromium(III) is extremely similar to the reaction of oxalate with chromium(III). The reaction is first order in chromium, inverse first order in hydrogen ion, and independent of the malonate ion concentration. This indicated a mechanism which is identical to that in the case of the oxalate reaction. The mechanism proposed is that the malonate reacts by a fairly rapid reaction with the chromium to form a loosely bound complex which undergoes an acid ionization, and the hydroxy compound formed in this step reacts by a slow step to result in the malonate chelate. Table I shows the rate data obtained as a function of  $pH$ .

TABLE I

$pH$	$k_1' \times 10^4, \text{sec.}^{-1}$	$pK_1$
4.83	1.33	2.68
5.07	2.03	2.71
5.22	2.90	2.69
5.39	4.32	2.66
5.51	6.12	2.60
5.62	6.55	2.65
5.77	9.66	2.58

Av.  $pK_1 = 2.65$ , std. dev. = 0.045

The previously derived<sup>2b</sup> relation existing between the apparent rate constant  $k_1'$ , and the real rate constant,  $k_1$ ,  $k_1 = k_1'(K + [H^+])/K$  was used with a value of  $1.0 \times 10^{-6}$  as the constant for the acid ionization step. This is identical to the value used in the case of the oxalate reaction. The results indicate a reaction almost identical to that for oxalate at the same temperatures and  $pH$  values.

The rate of the second chelation step when malonate reacted with chromium was inverse first order in hydrogen ion, first order in chromium and independent of malonate ion concentration. This indicated a mechanism similar to that of the first chelation step. The data for this reaction when calculated in the same manner as the first step is shown in Table II.

TABLE II

$pH$	$k_2' \times 10^4, \text{sec.}^{-1}$	$pK_2$
4.81	0.50	3.08
4.88	0.76	2.98
5.09	1.29	2.93
5.14	1.17	3.02
5.23	1.45	3.00
5.44	1.45	3.18
5.63	2.24	3.13
5.71	2.63	3.11
6.02	3.10	3.22
6.15	3.99	3.10

Av.  $pK_2 = 3.07$ , std. dev. = 0.09

This result was different from the result previously obtained with oxalate, where the reaction was found to be independent of hydrogen ion concentration. This difference was further shown by the effect of ionic strength on the reaction rates. The rates of both the first and second chelation steps of malonate ion increased with increasing ionic strength, whereas only the first chelation step speeded up with increasing ionic strength when oxalate reacted with chromium(III). The second chelation step was independent of ionic strength in the case of oxalate.

The reaction  $[\text{Cr}(\text{CH}_2)(\text{H}_2\text{O})_2]^- + \text{Ch} \rightarrow [\text{Cr}(\text{Ch})_3]^{-3}$  was studied where Ch represents either oxalate or malonate. The rates were determined by observing the increase in absorbance at 570  $m\mu$  for oxalate and at 580  $m\mu$  for malonate when oxalate or malonate was added to the thoroughly aged corresponding dichelated chromium ion. In both cases the rates were found to be first order in the chromium species and independent of the added anion concentration. The rates were also independent of hydrogen ion concentration over the range 4.0 to 9.3 for oxalate, and 5.5 to 8.0 for malonate. The shorter range for this independence in the case of malonate seemed to be related to the fact that the trimalonate complex is more unstable and can be more easily decomposed by adding acid or base than can the trioxalate complex. The average rate constants obtained over these ranges were  $1.05 \times 10^{-4} \text{sec.}^{-1}$  for oxalate and  $4.0 \times 10^{-5} \text{sec.}^{-1}$  for malonate at 39.9°. Where the rates of formation of the mono- and dichelates of oxalate and malonate were very similar, the third chelation step is much slower in the case of malonate.

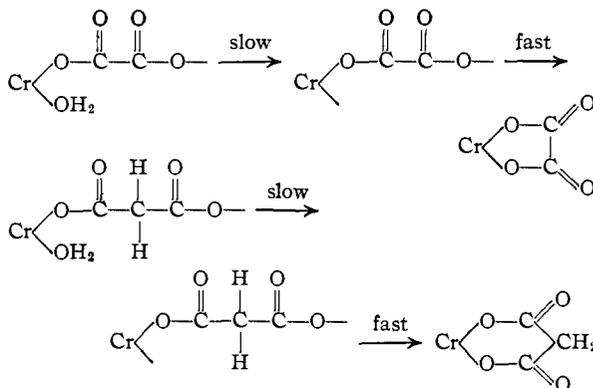
The various reactions reported in this investigation were studied over a range of temperatures from 10 to 40°. The values of  $K$  used for calculation ranged from  $0.6 \times 10^{-6}$  at 10° to  $3.0 \times 10^{-6}$  at 40°, as a result of determinations of the pH dependence at these temperatures. The results were plotted according to the theory of absolute reaction rates, and the heats of activation and entropies of activation shown in Table III were calculated.

TABLE III

	$\Delta H^\ddagger$ , kcal./mole	$\Delta S^\ddagger$ , cal./deg. mole
$\text{Cr}(\text{H}_2\text{O})_6^{+++} + \text{Mal}^-$	22.4	3.3
$\text{Cr}(\text{Mal})(\text{H}_2\text{O})_4^+ + \text{Mal}^-$	23.1	4.4
$\text{Cr}(\text{Mal})_2(\text{H}_2\text{O})_2^- + \text{Mal}^-$	26.0	-5.1
$\text{Cr}(\text{Ox})_2(\text{H}_2\text{O})_2^- + \text{Ox}^-$	22.6	4.2

The heats of activation and entropies of activation for the first two chelation steps shown in Table III are not experimentally different from those previously obtained on similar reactions using oxalate. This may indicate that the actual slow step is identical and independent of the chelating agent. This would be the situation if the slow step being measured with the dissociation of a water molecule followed by a relatively rapid step which would be the formation of the ring.

By this mechanism the slow step would be nearly identical since the number of atoms in the final chelate ring would have little or no effect on the



slow step. Plane and Taube<sup>8</sup> obtained  $24 \pm 2$  kcal./mole for the heat of activation for water exchange. Our measurements are in agreement, and indicate dissociation as a possible mechanism of water exchange.

The values obtained for the third step of chelation were sufficiently different that considerable difference in the nature of the third step was indicated when malonate was reacting. This may have been caused by the steric difficulty in forming the third six-membered ring around the central chromium.

(8) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

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## Studies of Iron(III) Thiocyanate in Dioxane<sup>1</sup>

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The electric and magnetic dipole moments of iron(III) thiocyanate determined in dioxane solutions are  $8.2 \pm 1 D$  and  $5.6 \pm 0.2 \text{ B.M.}$ , respectively. In order to account for the high electric moment, the formation of a dioxane complex is suggested. The absorption spectra of iron(III) thiocyanate in various solvents give support to this view.

It is well established that the red color of iron(III) thiocyanate in aqueous solution is due to the existence of a complex cation  $\text{Fe}(\text{SCN})^{++}$ , the stability constants of which and other Fe(III)-thiocyanate complexes have been determined at various ionic strengths by a number of investigators.<sup>2</sup> Iron(III) thiocyanate is soluble in a variety of organic solvents such as acetone, alcohol, dioxane, ether, etc., yielding violet solutions. Uri<sup>3</sup> concluded from conductometric measurements that only one compound between iron(III) ion and thiocyanate with a ratio of 1 to 3 exists in alcohol solution and that the cationic complexes  $\text{Fe}(\text{SCN})^{++}$  and  $\text{Fe}(\text{SCN})_2^+$  do not occur in this medium. Schlesinger and Van Valkenburgh<sup>4</sup> showed by cryoscopic and ebulliometric methods that iron(III) thiocyanate is dimeric both in

benzene and in ether and that the absorption spectra in these solvents are the same as in aqueous solutions. A bridge structure, analogous to the generally accepted structure of iron(III) chloride  $\text{Fe}_2\text{Cl}_6$ , was proposed for the dimer by Schlesinger.<sup>5</sup> However, Mitchell and Macdonald<sup>6</sup> redetermined the molecular weight of iron(III) thiocyanate in organic solvents and found, in contradiction to the results of Schlesinger and Van Valkenburgh, that only the monomer is present in ether and alcohol solutions. They also observed that iron(III) thiocyanate cannot be extracted from aqueous solution by benzene and concluded that it is insoluble in benzene. In view of the uncertainty of the nature of this compound in solvents of low dielectric constant, we have determined the electric and magnetic dipole moments of iron(III) thiocyanate in dioxane solution, and its absorption spectra in benzene, dioxane, ether, ethylene chloride and tetrahydrofuran solutions in the hope of obtaining a probable structure for this compound.

(1) Taken in part from the M.S. thesis of C. T. Fujii, Duquesne University, 1954.

(2) See, for instance, R. H. Betts and F. S. Dainton, *THIS JOURNAL*, **75**, 5721 (1953), where a thorough literature review is given.

(3) N. Uri, *J. Chem. Soc.*, 336 (1947).

(4) H. I. Schlesinger and H. B. Van Valkenburgh, *THIS JOURNAL*, **53**, 1212 (1931).

(5) H. I. Schlesinger, *ibid.*, **63**, 1765 (1941).

(6) K. M. Mitchell and J. Y. Macdonald, *J. Chem. Soc.*, 1310 (1951).