

The Mechanism of Hydrogenation by Aqueous Chromium(II) Ion of the Carbon-Carbon Double Bond of Olefinic Compounds with Polar Substituents

Dimitris Katakis, Ersi Vrachnou-Astra, and John Konstantatos*

Inorganic Chemistry Laboratory, University of Athens, Navarinou 13A, Athens, Greece and Greek Atomic Energy Commission, Nuclear Research Centre 'Demokritos', Chemistry Department, Aghia Paraskevi Attikis, Athens 153-10, Greece

The kinetics of the reaction of Cr^{2+} with maleic acid, fumaric acid, methylmaleic acid, chloromaleic acid, dichloromaleic acid, and methylfumaric acid have been investigated over a wide range of chloromaleic > maleic \approx methylmaleic > dichloromaleic > fumaric and maleic > dichloromaleic \approx ligand is in excess. In excess of Cr^{2+} the rate law is as shown below and k_3 follows the trend:

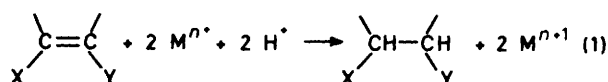
$$\text{Rate} = k_3[\text{Cr}^{2+}]^2[\text{L}]$$

chloromaleic > maleic > dichloromaleic > methylmaleic > methylfumaric. With excess ligand, L, the rate law has two terms (below) and the two rate constants, k'_3 and k'_2 follow the order:

$$\text{Rate} = k'_2[\text{Cr}^{2+}][\text{L}] + k'_3[\text{Cr}^{2+}][\text{L}]^2$$

chloromaleic > maleic \approx methylmaleic > dichloromaleic > fumaric and maleic > dichloromaleic \approx methylmaleic > chloromaleic respectively. The kinetic data are supplemented by stoichiometric data, by determinations of product distribution, and by spectroscopic data, and they are discussed in terms of a model involving at least partial attack by Cr^{2+} directly on the C=C double bonds.

The question of determining the site of attack in electron-transfer reactions was first taken up by Taube and co-workers,¹ who were led to the distinction between adjacent and remote attack. In this work we use free ligands because they offer better 'resolution,' in the sense that different sites of attack lead to different products, different stoichiometries, and different rate laws. The general overall reaction considered can be represented by equation (1) where X and Y are groups containing polar sites,

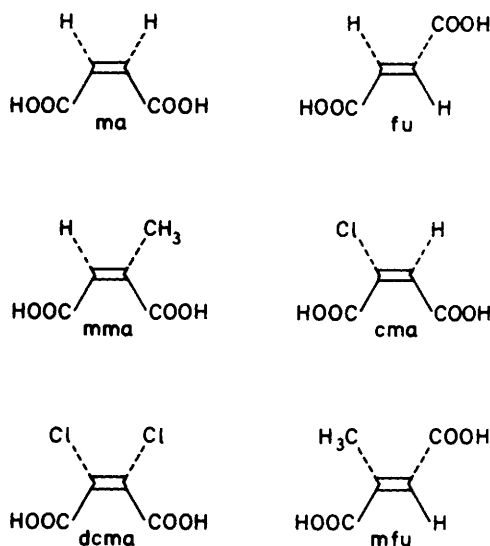


$\text{M} = \text{Cr}$, and $n = 2$. Two M^{n+} ions are consumed for each double bond reduced. Chromium(III) is eventually recovered as $\text{Cr}^{3+}_{\text{aq}}$, but several intermediate inert Cr^{III} complexes containing $\text{Cr}^{\text{III}}-\text{C}$ and $\text{Cr}^{\text{III}}-\text{O}$ bonds have also been isolated and characterized.²

Experimental

Materials.—Maleic, fumaric, and methylmaleic (citraconic) acids were Fluka reagents and were used without further purification. Methylfumaric (mesaconic) acid was purified by recrystallization from ethanol. Chloromaleic and dichloromaleic acids were purified by sublimation of their anhydrides under vacuum. Solutions of hexa-aquachromium(II) were prepared electrolytically with a mercury pool cathode. Water was triply distilled. All experiments were performed under an inert atmosphere.

Products and Stoichiometry.—Stoichiometric measurements were made by determining the excess of the reagent left after the reaction was over. Excess Cr^{2+} was determined by adding Fe^{III} and titrating the amount of Fe^{II} produced potentiometrically with Ce^{IV} . The excess of the organic reagent was determined polarographically with a Metrohm A.G. Herisau



Polarograph. Free chloride was detected as AgCl . Separations of the complexes in solution were done on Dowex 50W and Sephadex SP25 columns. As a diagnostic tool for the formation of organochromium(II) compounds we used³ the characteristic charge-transfer absorption at 280–320 nm; the organochromium species are usually red or pink.

Kinetics.—Fast kinetics were followed with an Applied Photophysics stopped-flow instrument, slow kinetics with a Cary 14 spectrophotometer. The reactions were monitored at the following wavelengths (nm): maleic acid (420), chloromaleic acid (400), dichloromaleic acid (405), methylmaleic acid (410), and methylfumaric acid (410, 550).

Table 1. Kinetic data for the reaction between Cr^{2+} and maleic acid at 23 °C

$[\text{Cr}^{2+}]_0/$ mmol dm^{-3}	$[\text{ma}]_0/$ mol dm^{-3}	$[\text{HClO}_4]/$ mol dm^{-3}	$k_{\text{obs.}}/$ s^{-1}	$k_3^a/$ $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$	$k^b/$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
112	0.001	1.0	0.78	62.2	
56	0.001	1.0	0.19	60.2	
28	0.001	1.0	0.047	60.6	
80	0.001	0.3	0.37	57.4	
32	0.001	0.1	0.06	59.6	
5.3	1.000	1.0	3.08		3.08
7.0	1.000	1.0	3.26		3.26
7.0	0.780	1.0	2.09		2.68
7.0	0.550	1.0	1.01		2.00
7.0	0.440	1.0	0.81		1.85
7.0	0.320	1.0	0.45		1.41
7.0	0.210	1.0	0.25		1.22
5.3	0.500	1.0	0.90		1.80
5.3	0.250	1.0	0.32		1.28
5.3	0.100	1.0	0.055		0.55
7.0	0.155	1.0	0.17		1.08
7.0	0.100	1.0	0.087		0.87
7.0	0.500	0.6	0.87		1.74
7.0	0.500	0.12	1.08		2.17

^a $k_3 = k_{\text{obs.}}/[\text{Cr}^{2+}]_0^2$; average third-order rate constant in excess of Cr^{2+} , $k_3 = 59.5 \pm 3.0 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. ^b $k = k_{\text{obs.}}/[\text{ma}]_0$ vs. $[\text{ma}]_0$ gives a straight line with an intercept, meaning that there is a term in the rate law first order in $[\text{ma}]$ and a term second order in $[\text{ma}]$. The values of the corresponding second- and third-order rate constants are: $k'_2 = 0.65 \pm 0.3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k'_3 = 2.55 \pm 0.5 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. The primed rate constants refer to conditions of excess of ligand, the unprimed to excess of Cr^{2+} .

Results

Maleic Acid.—Previously rate laws first order in $[\text{Cr}^{2+}]$ for maleic acid (ma)^{4,5} and its diethyl ester,⁶ but second order in $[\text{Cr}^{2+}]$ for fumaric acid (fu)⁶ have been reported. On repeating experiments with maleic acid, Table 1, we have confirmed that in excess of the organic acid the reaction is indeed first order in $[\text{Cr}^{2+}]$ but in excess of the reductant it becomes second order in this ion.

Within experimental error the rate constants do not change when the hydrogen ion concentration changes from 0.1 to 1.0 mol dm^{-3} . With excess of Cr^{2+} the reaction is first order in maleic acid, but if the organic acid is in excess two terms appear: one first order and the other second order in maleic acid.

The overall stoichiometry⁴ is two Cr^{2+} for each double bond hydrogenated and the only organic product is succinic acid, but the reaction proceeds through formation of intermediate Cr^{III} complexes in amounts depending on conditions and time² (Table 2). About half of the Cr^{III} product appears in the form of organochromium species, the rest appears as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (with excess of $\text{Cr}^{2+}_{\text{aq}}$), or as Cr^{III} complexes with maleic acid (with excess of maleic acid). In both cases a highly charged species is observed at the top of the ion-exchange column. The latter are usually brown, not green like the di- μ -hydroxochromium(III) dimer which is formed when Cr^{2+} reacts with two equivalents of reagent (and O_2). Comparison of the first and second entry in Table 2 shows that at longer times the highly charged species are partially transformed into organochromium species of lower charge, which means that they also contain Cr–C bonds. Thus the lower limit for the fraction of all kinds of organochromium species formed is about 60%.

Fumaric Acid.—For solubility reasons the reaction between Cr^{2+} and fumaric acid (fu) was studied in an ethanol–water

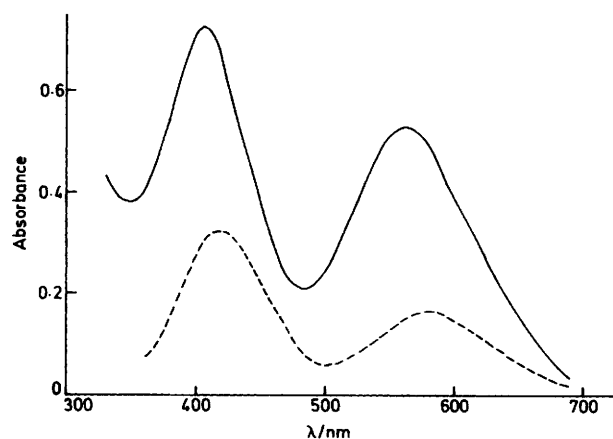
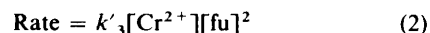


Figure 1. Reaction between $\text{Cr}^{2+}_{\text{aq}}$ and fumaric acid. Comparison of the spectra at zero time (---) and after completion of the redox step (—). $[\text{Cr}^{2+}]_0 = 4.3 \times 10^{-3}$, $[\text{fu}]_0 = 8.6 \times 10^{-2}$, $[\text{H}^+] = 0.05 \text{ mol dm}^{-3}$, 5 cm optical cell, and 24 °C. The former spectrum was obtained by extrapolating kinetic data at different wavelengths to zero time

(1:1) solvent. The kinetic data were obtained under pseudo-first-order conditions and are summarized in Table 3. The reaction is overall third order, equation (2). Table 3 also



includes the zero-time absorbance (A_0) at 560 and 405 nm, obtained by extrapolation. The spectrum of the species at zero time is compared in Figure 1 with the spectrum of the 'final' mixture of Cr^{III} species, after the completion of the redox step. The species at zero time is also 'Cr^{III}-like' but more labile, as indicated by the prompt effect of the concentration of fumaric acid on A_0 .

For fu: Cr^{2+} ratios of 1:1, the logarithm of the absorbance vs. time curve has no intercept.

Methylmaleic Acid.—Methylmaleic acid (mma) reacts with $\text{Cr}^{2+}_{\text{aq}}$ at a much slower rate compared to maleic acid. The stoichiometry was determined with excess Cr^{2+} . In a mixture containing 0.096 mol dm^{-3} Cr^{2+} , 0.014 mol dm^{-3} mma, and 1.0 mol dm^{-3} HClO_4 , the amount of Cr^{2+} oxidized after 8 h (ca. eight half-lives) was 1.85 times the initial amount of mma. The reaction was not yet completed.

The kinetic data are summarized in Table 4. It is seen that again there is no acid dependence in the range investigated (0.3–1.75 mol dm^{-3} HClO_4). Also, in excess of Cr^{2+} , the rate is dominated by a term second order in $[\text{Cr}^{2+}]$ but with a rate constant more than 1 000 times smaller than that for ma. In excess of ligand there are again two terms in the rate law, first- and second-order in the ligand, but both first order in $[\text{Cr}^{2+}]$. The data, however, are very scattered.

Organochromium species were not detected, and various reaction mixtures at different times showed no absorbance in the u.v. region that could be attributed to Cr–C.^{2a}

Chloromaleic Acid.—Chloromaleic acid (cma) reacts with more than two equivalents of Cr^{2+} . Typical stoichiometric data (in 1.0 mol dm^{-3} HClO_4) are as follows. (a) $[\text{Cr}^{2+}] = 0.056$, $[\text{cma}] = 0.017 \text{ mol dm}^{-3}$, reaction time 20 h, stoichiometry 3.2:1. In this experiment chloromaleic acid consumes all available Cr^{2+} . (b) $[\text{Cr}^{2+}] = 0.096$, $[\text{cma}] = 0.014 \text{ mol dm}^{-3}$, reaction time 2 h, stoichiometry 3.5:1. The ratio of the initial concentrations exceeds the observed stoichiometry and the reaction is not yet completed.

Table 2. Product distribution in the reaction of chromium(II) ion with maleic acid

[Cr ²⁺] ₀ /mol dm ⁻³	[ma] ₀ /mol dm ⁻³	[HClO ₄]/mol dm ⁻³	Reaction time (min)	Non organo- chromium(III) (%)	Organo- chromium(III) ^a (%)	High-charge Cr species ^b (%)
0.16	0.500	0.5	3	23	45	32
0.16	0.500	0.5	75	29	50	21
0.50	0.0033	2.0	3		46	54
0.019	0.017	1.2	30	24	50	26
0.05	0.025	0.75	60	21	56	23
0.036	0.20	0.8	45	28	45	27

^a For [Cr²⁺]₀/[ma]₀ ≤ 2 the percentages are estimated over total chromium, for larger excess of Cr²⁺ over maleic acid. ^b Remaining at the top of the resin.

Table 3. Kinetic data for the reaction between Cr²⁺ and fumaric acid in ethanol-water (50:50), at 24 °C, [H⁺] = 0.05 mol dm⁻³

[Cr ²⁺] ₀ / mmol dm ⁻³	[fu] ₀ / mmol dm ⁻³	10 ⁴ k _{obs.} ^a / s ⁻¹	A ₀ ^b	
			at 405 nm	at 560 nm
4.3	43	4.5	0.185	0.080
4.3	86	16	0.328	0.167
2.1	94	27	0.100	
2.1	187	88	0.168	

^a Pseudo-first-order rate constant. The reaction is overall third order with a rate constant: k'₃ = 0.25 ± 0.04 dm⁶ mol⁻² s⁻¹. ^b Light path 5 cm.

Table 4. Kinetic data for the reaction between Cr²⁺ and methylmaleic acid at 23 °C

[Cr ²⁺] ₀ / mmol dm ⁻³	[mma] ₀ / mmol dm ⁻³	[HClO ₄]/ mol dm ⁻³	10 ⁴ k _{obs.} /s ⁻¹	k ₃ ^a /dm ⁶ mol ⁻² s ⁻¹	k ^b /dm ³ mol ⁻¹ s ⁻¹
90	4	0.78	1.8	0.022	
135	4	0.78	3.1	0.017	
180	4	0.78	5.6	0.017	
2	29	0.32	61		0.21
2	29	0.43	57		0.20
2	29	0.64	57		0.20
2	29	1.00	48		0.17
2	29	1.36	41		0.14
2	29	1.71	67		0.23
2	14	1.00	20		0.14
2	18	1.00	26		0.15
2	20	1.00	29		0.15
2	21	1.00	33		0.16
2	25	1.00	40		0.16
2	26	1.00	41		0.15
2	32	1.00	55		0.17
2	36	1.00	62		0.18
2	39	1.00	73		0.19
2	43	1.00	82		0.19
2	46	1.00	92		0.20
2	50	1.00	100		0.20
2	54	1.00	111		0.21
2	57	1.00	122		0.21

^a k₃ = k_{obs.}/[Cr²⁺]₀²; average third-order rate constant in excess Cr²⁺; k₃ = 0.02 dm⁶ mol⁻² s⁻¹. ^b k = k_{obs.}/[mma]₀ vs. [mma]₀ gives straight line with an intercept, which means that there is a term in the rate law first order in [mma]₀ and a term second order in [mma]₀. The values of the corresponding second- and third-order rate constants are: k'₂ = 0.11 dm³ mol⁻¹ s⁻¹ and k'₃ = 1.78 dm⁶ mol⁻² s⁻¹. The primed rate constants refer to conditions with excess ligand, the unprimed to excess of Cr²⁺.

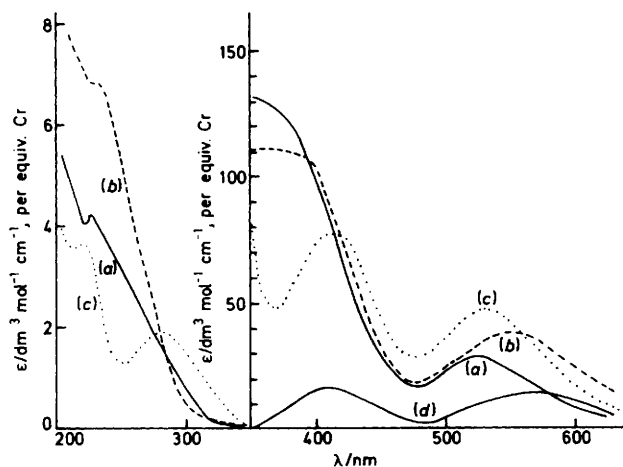
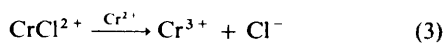


Figure 2. U.v.-visible spectra of organochromium complexes formed in the reaction of Cr²⁺ with chloromaleic acid. (a) Red complex of charge +2. (b) Red complex of charge ≥ +3. The spectra of the high-charge organometallic complex from the reaction of Cr²⁺_{aq} with maleic acid (c) and of Cr³⁺_{aq} (d) are also given for comparison

The results of the separation experiments are summarized in Table 5. The spectra of the two isolated organochromium species are given in Figure 2. Their absorption at 280–300 nm is several orders of magnitude larger than the absorption of the other components present. It is interesting that Cl⁻ is detected right from the beginning of the reaction, even under conditions where CrCl²⁺ is not formed. It should also be noted that CrCl²⁺ was isolated only when an excess of Cr²⁺ was used. Cr²⁺_{aq} catalyses the release of chloride from CrCl²⁺, equation (3). This



$$\text{Rate} = k[\text{CrCl}^{2+}][\text{Cr}^{2+}]/[\text{H}^+] \quad (4)$$

reaction proceeds with a rate law (4) and a rate constant, k = 8.4 × 10⁻⁶ s⁻¹ (at 0 °C and 2.0 mol dm⁻³ ionic strength).⁷ The concentrations in our experiments were in the range 10⁻¹ to 10⁻³ mol dm⁻³, which means half-lives for this reaction of the order of many days or even months. Hence, the chloride detected at shorter times (Table 5) in excess Cr²⁺ must come from another source, directly from the activation of the C–Cl bond. Stopped-flow kinetic data for the redox reaction are summarized in Table 6. In excess Cr²⁺ only one term is observed, second order in Cr²⁺ and first order in the free ligand, as in the previous cases. In excess of ligand there is again only one term (whereas in the previous cases there were two) first order in Cr²⁺ and second order in cma. In excess Cr²⁺, after the stopped-flow stage, the oxidation of Cr²⁺ continues at a slower rate, and it is this slow reaction that makes the stoichiometry (Cr²⁺:cma) exceed the

Table 5. Results of the separation (Dowex 50W) experiments in the reaction between Cr^{2+} and cma

Excess reagent	Reaction time	Non organochromium(III) complexes	Organochromium(III) complexes	Remarks
cma	ca. 5 min	Three blue Cr^{III} complexes, one eluted with $0.5 \text{ mol dm}^{-3} \text{ HClO}_4$ (possible charge +2), the other two with $2 \text{ mol dm}^{-3} \text{ HClO}_4$ (possible charge +3)	Two organochromium(III) complexes (red) eluted with 0.5 and $2 \text{ mol dm}^{-3} \text{ HClO}_4$, respectively (possible charges +2 and +3)	No CrCl^{2+} ; test for Cl^- positive; yield of organochromium species (over total Cr) ca. 20%
Cr^{2+}	1 min and 19 h	Two blue Cr^{III} complexes with possible charge +3 and one green (CrCl^{2+} , spectroscopically verified, see text)	Only one organochromium(III) species, possible charge +3	Test for Cl^- positive (all blanks negative)

Table 6. Kinetic data for the fast stage^a of the reaction between Cr^{2+} and chloromaleic acid, 23°C , $1 \text{ mol dm}^{-3} \text{ HClO}_4$

$[\text{Cr}^{2+}]_0 / \text{mmol dm}^{-3}$	$[\text{cma}]_0 / \text{mmol dm}^{-3}$	$k_{\text{obs.}} / \text{s}^{-1}$	$k_3^b / \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	$k'_3{}^c / \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$
170	2.3	1.74	60.2	
113	2.3	0.82	64.4	
85	2.3	0.39	54.3	
56	2.3	0.20	64.8	
56	2.3	0.20	63.5	
43	2.3	0.09	50.3	
37.5	2.3	0.075	53.3	
37.5	2.3	0.08	57.6	
25	2.3	0.033	52.0	
22	2.3	0.025	50.6	
5	216	0.79		16.9
5	185	0.63		18.6
5	162	0.47		18.1
5	155	0.44		18.4
5	108	0.20		17.0
5	54	0.06		21.3

^a Stopped-flow. ^b Average third-order rate constant in excess of Cr^{2+} : $k_3 = k_{\text{obs.}} / [\text{Cr}^{2+}]_0^2 = 75 \pm 7 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. ^c Average third-order rate constant in excess of cma: $k'_3 = k_{\text{obs.}} / [\text{cma}]_0^2 = 16.5 \pm 1.7 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

Table 7. Reactions at dcma with Cr^{2+} *

$[\text{Cr}^{2+}]_0 / \text{mmol dm}^{-3}$	$[\text{cma}]_0 / \text{mmol dm}^{-3}$	$[\text{HClO}_4] / \text{mol dm}^{-3}$	Reaction time (h)	$[\text{Cr}^{2+}]_{\text{ox}} / [\text{cma}]_0$
56	17	1.0	0.5	1.8/1
96	14	1.0	2.0	2.6/1

* $[\text{Cr}^{2+}]_{\text{ox}}$ = concentration of oxidised Cr^{2+} .

2:1 limit of the double-bond hydrogenation. The slower redox step lasts for days and it is accompanied by an increase in the absorbance at 570 nm, while the absorbance at 400 nm remains constant, within experimental error.

Dichloromaleic Acid.—Dichloromaleic acid (dcma) also gives a reaction that exceeds the stoichiometry of the double-bond reaction limit. The results of the stoichiometry experiments are given in Table 7. Ion exchange separations of the reaction products were performed within a few minutes of reaction initiation. Free Cl^- is also formed at the beginning, by a path several orders of magnitude faster compared to the CrCl^{2+} hydrolysis path. Chloride is detected both in excess cma and in excess of Cr^{2+} , within the time required to separate the mixture (ca. 5 min). It must also be noted that the coloured bands, coming out of the column, with exception of that of CrCl^{2+} , do not give free chloride, even after boiling the solutions.

The separation showed formation of three non organo blue complexes and in excess of Cr^{2+} , one of the green CrCl^{2+}

Table 8. Kinetic data for the fast stage^a of the reaction between Cr^{2+} and dichloromaleic acid, 24°C , $1 \text{ mol dm}^{-3} \text{ HClO}_4$

$[\text{Cr}^{2+}]_0 / \text{mmol dm}^{-3}$	$[\text{dcma}]_0 / \text{mmol dm}^{-3}$	$k_{\text{obs.}} / \text{s}^{-1}$	$k_3^b / \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	$k'_3 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
51	10	0.0105	4.04	
62	10	0.018	4.69	
102	10	0.038	3.65	
106	10	0.039	3.47	
178	10	0.105	3.31	
305	10	0.340	3.66	
15	490	0.147		0.30
15	344	0.085		0.25
15	275	0.065		0.24
15	191	0.038		0.20
15	137	0.024		0.18
15	96	0.016		0.17
15	77	0.011		0.14

^a Stopped-flow. ^b Average third-order rate constant in excess Cr^{2+} : $k_3 = k_{\text{obs.}} / [\text{Cr}^{2+}]_0^2 = 3.00 \pm 0.30 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. ^c $k = k_{\text{obs.}} / [\text{dcma}]_0$ vs. $[\text{dcma}]_0$ gives a straight line with an intercept which means that there is a term in the rate law first order in $[\text{dcma}]$ and a term second order in $[\text{dcma}]$. The values of the corresponding second- and third-order rate constants are: $k'_2 = 0.13 \pm 0.01 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k'_3 = 0.37 \pm 0.04 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

Table 9. Kinetic data for the reaction between Cr^{2+} and methylfumaric acid: $[\text{mfu}]_0 = 8.33 \times 10^{-2}$, $[\text{H}^+] = 0.3 \text{ mol dm}^{-3}$; $[\text{Cr}^{2+}]_0 > [\text{mfu}]_0$, 25°C , in ethanol-water (17:83)

$[\text{Cr}^{2+}]_0 / \text{mmol dm}^{-3}$	$10^5 k_{\text{obs.}} / \text{s}^{-1}$
103	5.7
188	21
188	22
207	33
258	51

species, but no indication of organochromium complexes. The stopped-flow kinetic data are summarized in Table 8. The reaction is much slower compared to the reaction of chloromaleic acid. Again, there is no acid dependence (from 0.2 to 1.0 mol dm^{-3}).

The slower redox stage responsible for the greater than 2:1 stoichiometry lasts several days, as with chloromaleic acid. During this time there is an increase in absorbance, not only at 580 nm, but also at 400 nm and in the u.v.

Methylfumaric Acid.—Methylfumaric acid (mfu) reacts with Cr^{2+} at a slower rate, which is first order in Cr^{2+} when methylfumaric acid is in excess, and second order in Cr^{2+} when the metal ion is in excess. The kinetics were followed in water-ethanol mixtures, for solubility reasons. A second-order term was not found, perhaps because the concentrations were not high enough. Typical results are as follows. (a) In excess of

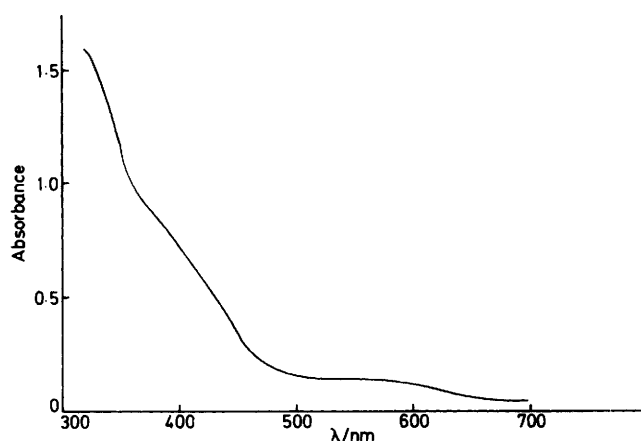


Figure 3. Initial ($t = 0$) absorption of a Cr^{2+} -methylfumaric acid mixture with $[\text{Cr}^{2+}]_0 = 0.046$, $[\text{mfu}]_0 = 0.2$, $[\text{HClO}_4] = 2.5 \text{ mol dm}^{-3}$, in ethanol-water (2:1) solvent. The absorptions of $\text{Cr}^{2+}_{\text{aq}}$ and of mfu (blanks) have been subtracted

methylfumaric acid, and for initial concentrations of Cr^{2+} and mfu of 4.6×10^{-2} and 0.2 mol dm^{-3} respectively [in ethanol-water (2:1)], and in two acidities ($[\text{HClO}_4] = 0.61$ and 0.19 mol dm^{-3}) the values of the first-order rate constants (25°C) are $(2.35 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$ and $(1.85 \pm 0.06) \times 10^{-5} \text{ s}^{-1}$, respectively. The linearity coefficient of the corresponding straight lines in the first-order kinetic plots is better than 0.99. (b) The data obtained in excess of Cr^{2+} are given in Table 9. A plot of the observed pseudo-first-order rate constants of Table 9 *vs.* initial $[\text{Cr}^{2+}]$ gives $k_3 = (6.6 \pm 1.0) \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ for the constant in the rate equation (5). The slow rate of this

$$\text{Rate} = k_3[\text{Cr}^{2+}]^2[\text{mfu}] \quad (5)$$

reaction allows observations of an initial complex with a strong absorption in the u.v. (Figure 3). In the course of the reaction this absorption disappears.

A red complex with an absorption at *ca.* 300 nm and of charge +3 was separated in small yield, after the redox reaction had been completed. This complex was not completely separated from the non organochromium(III) complexes present, but it resembles closely those obtained from maleic acid. The overall stoichiometry is again two $\text{Cr}^{2+}_{\text{aq}}$ for each organic molecule reduced.

Summary of Spectroscopic and Kinetic Data.—In order to facilitate the discussion we collect the available kinetic and spectral data of the investigated and related systems in Tables 10 and 11. The data in Table 10 cover a wide range of concentrations. The ratio $[\text{Cr}^{2+}]_0/[\text{L}]_0$ was changed by a factor of 1 000. The rate laws for all these systems are equations (6) (excess Cr^{2+}) and (7) (excess ligand, L). The two terms of

$$\text{Rate} = k_3[\text{Cr}^{2+}]^2[\text{L}] \quad (6)$$

$$\text{Rate} = k'_2[\text{Cr}^{2+}][\text{L}] + k'_3[\text{Cr}^{2+}][\text{L}]^2 \quad (7)$$

equation (7) were observed with maleic, methylmaleic, and dichloromaleic acids.

With the values of the rate constants given it is estimated that even with a 20-fold excess of maleic acid the contribution of the k_3 term to the overall rate should have been as high as 50%. This would in turn mean a large deviation from linearity. Yet, linearity is better than 0.99. The contribution of the second-order term seems to stop abruptly, as soon as the ratio $[\text{Cr}^{2+}]_0/$

Table 10. Rate laws and rate constants^a (room temperature)

L	Rate law		Rate law	
	$[\text{Cr}^{2+}]_0 > [\text{L}]_0$	$k_3/\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	$[\text{L}]_0 > [\text{Cr}^{2+}]_0$	$k'_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ $k'_3/\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$
ma	<i>b</i>	59.5	<i>c</i>	0.65 2.55
mma	<i>b</i>	0.02	<i>c</i>	0.11 1.78
dcma	<i>b</i>	3.0	<i>c</i>	0.13 0.37
cma	<i>b</i>	75	<i>d</i>	16.5
mfu	<i>b</i>	0.007		(<i>ca.</i> $2.3 \times 10^{-5} \text{ s}^{-1}$) ^e
	<i>b, g</i>	15.5 ^h		
				($1.67 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) ⁱ
				($0.25 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$) ^d
	<i>b</i>	14		
	<i>b</i>	0.5		

^a The values of the rate constants were calculated on the basis of the rate terms stated for each concentration region. For example, the rate constants for the $k[\text{L}][\text{Cr}^{2+}]$ terms were not corrected for possible contribution of the term which dominates in $[\text{L}] < [\text{Cr}^{2+}]$. ^b $k_3[\text{Cr}^{2+}]^2[\text{L}]$. ^c $k'_2[\text{Cr}^{2+}][\text{L}] + k'_3[\text{Cr}^{2+}][\text{L}]^2$. ^d $k'_3[\text{Cr}^{2+}][\text{L}]^2$. ^e Pseudo-first-order rate constant: $[\text{Cr}^{2+}]_0 = 0.046$, $[\text{mfu}]_0 = 0.2$, $[\text{HClO}_4] = 0.61 \text{ mol dm}^{-3}$. ^f From ref. 6. ^g $[\text{Cr}^{2+}]_0 = 0.01$ – 0.02 , $[\text{ester}]_0 = 0.01$ – 0.02 mol dm^{-3} . ^h $I = [\text{H}^+] = 0.25 \text{ mol dm}^{-3}$, 25°C . ⁱ $[\text{Cr}^{2+}]_0/[\text{ester}]_0 = 1.3$ – 0.92 . ^j A. Petrou, Ph.D. Thesis, University of Athens, 1979.

Table 11. Characteristic absorption of Cr^{III} complexes due to the Cr-C bond

Ligand	Charge	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
ma	+3	278	2 040
ma	+2	278	3 071
cma	+3	320*	400
cma	+2	320*	500

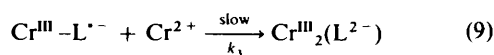
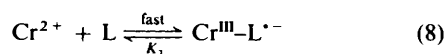
* These absorption peaks appear as shoulders. At lower wavelengths the absorption is very high, but no peaks could be observed, due to the high absorptivity of the ligand itself.

$[\text{L}]_0$ becomes smaller than one. It is as if titrating the ligand kinetically. Similar remarks can be made for chloro- and dichloro-maleic acids. A vertical comparison shows that in excess of Cr^{2+} the third-order rate constants follow the trend: $\text{cma} > \text{ma} > \text{dcma} > \text{mfu}$. In excess of ligand, for the third-order term, $\text{cma} > \text{ma} \approx \text{mma} > \text{dcma} > \text{fu}$, and for the second-order term, $\text{ma} > \text{dcma} \approx \text{mma} > \text{cma}$. For the other ligands in Table 10 the data are not detailed enough to give the complete rate law, but for comparison their inclusion is still instructive.

Discussion

The fact that the rate laws with excess Cr^{2+} and with excess free ligand are different indicates that different mechanisms

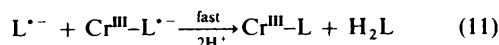
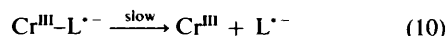
predominate in the two concentration ranges. The second-order dependence on Cr^{2+} concentration in the case of excess Cr^{2+} is consistent with the following mechanism in equations (8) and (9).



The transfer of the electron from Cr^{2+} to the undissociated olefin L [equation (8)] results in the formation of the ion-radical $\text{Cr}^{\text{III}}-\text{L}^{\cdot-}$. The transfer of the second electron leads to the formation of the binuclear chromium(III) species $\text{Cr}^{\text{III}}_2(\text{L}^{2-})$ [equation (9)]. In L^{2-} the carbon-carbon bond is single and there are no unpaired electrons. $\text{Cr}^{\text{III}}_2(\text{L}^{2-})$ itself is transient, eventually breaking in the presence of protons into $\text{Cr}^{3+}_{\text{aq}}$ and the free saturated organic product H_2L .

In the case of the difficult to reduce methylfumaric acid, the absorbance at zero time indicates that the displacement of the electron towards the ligand is not sufficient to allow designation of the product [equation (8)] as a chromium(III) ion-radical. In this case it is preferable to talk about a complex in which chromium retains its +II character and the ligand its olefin character.

In excess free ligand equilibrium (8) is again established rapidly, but there is not enough Cr^{2+} for second attack. Instead, it is suggested that the ion-radical ($\text{Cr}^{\text{III}}-\text{L}^{\cdot-}$) decomposes unimolecularly forming an organic free radical, which reacts further to give the hydrogenated product [equations (10) and (11)].



The appearance of terms second order in the free ligand indicates that not only $\text{Cr}^{2+}_{\text{aq}}$ but also $\text{Cr}^{\text{II}}-\text{L}$ reacts.

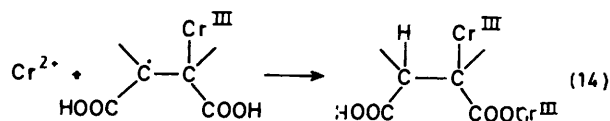
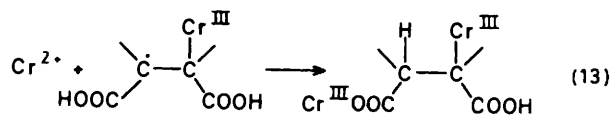
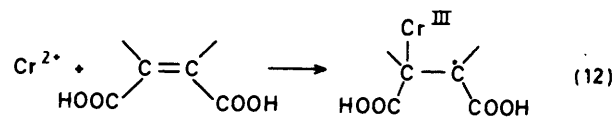
The coincidence of the third-order rate constants for maleic and fumaric acids (Table 10) should not be taken literally, because the corresponding experiments were performed in different solvents, yet it is clearly consistent with a pre-equilibrium involving formation of the same radical-like species, in which the double bond has been activated and the *cis-trans* distinction is not relevant any more. The spectrum at zero time in the Cr^{2+} -fumaric acid system (Figure 1) is also consistent with the postulated labile Cr^{III} -free radical precursor complex.

It is remarkable that in several instances (Table 10) the change of the substituents on L has no effect on the form of the rate law, which indicates that this form is determined by events occurring at the double bond rather than the polar groups. In fact, with ethyl fumarate and excess Cr^{2+} the form of the rate law has been reported to be the same,⁶ as with the systems investigated here, in spite of the fact that in the ester the polar groups are effectively blocked. Accordingly, we suggest that in the course of the reaction, at least one of the Cr^{2+} ions attacks directly the carbon of the double bond.

Further support for this hypothesis is provided by the detection and/or isolation of organochromium intermediates. Metal-carbon bonds (including Cr-C) are considerably weaker^{8a,*} than $\text{Cr}^{\text{III}}-\text{O}$ bonds. Consequently, intra- or intermolecular migration of Cr^{III} from carbon to the carboxyl group is expected to be facile, whereas the reverse is thermodynamic-

ally unfavourable. Bond energies have been determined for $\text{Cr}^{\text{III}}-\text{R}^{\cdot-}$, having paired electrons, whereas our discussion refers to ion-radical species with one electron less. However, there is no reason for the latter bond to be stronger. In fact, the opposite seems more likely because of the increased ionic character of $\text{Cr}^{\text{III}}-\text{R}^{\cdot-}$. An intermediate organochromium species is unlikely to originate from a species in which the oxidized metal ion is bound to oxygen (more generally to a polar group). Actually, it can be stated that the yield of organochromium species is a lower limit for the percentage of the reaction going *via* direct attack on carbon. If an organochromium species is not detected, the possibility of direct attack on carbon still cannot be excluded, but in that case the evidence must necessarily be indirect.

It is conceivable that initially both chromium ions are attached to carbon(s). However, if a choice between the first and the second chromium atoms is made, the first is preferred; it is usually assumed or implied that the reductant is invariably first attached to an electronegative part of the molecule, obviously because of the acidic character of the metal ion. Yet, a reductant like Cr^{2+} can act as a two-electron acceptor, but also as an one-electron donor. We must, therefore, consider not only the occupied orbitals of the ligand, but the empty ones as well, *i.e.* the acceptor part of the acceptor. In an olefinic compound we must consider the empty π^* orbitals. Direct attack by the first Cr^{2+} on carbon will then mean interaction between these orbitals and the partially occupied e_g^* on Cr^{2+} , which leads to the formation of the ion-radical precursor, equation (12),



followed by equations (13) or (14). We then argue that the sequence of reactions (12) and (13) or (14) is favoured over the 'opposite' sequence, namely attack on the carboxylic group by the first Cr^{2+} and then on the carbon by the second.

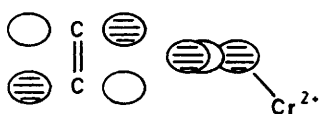
The conclusion that the Cr^{2+} attacks, at least partly, the carbon is further supported by a number of other observations, including the observed release of Cl^- from cma and dcma, by a path other than the dissociation of CrCl^{2+} . If Cr^{2+} attacked chlorine directly, one should expect CrCl^{2+} formation, as in the reactions with alkyl halides.⁹ The analogue of these reactions is indeed observed with cma and dcma also, and they are responsible for the higher than 2:1 stoichiometries, but they are much slower than the initial Cl^- release.

It should also be noted that the free unsaturated dicarboxylic acids and their esters⁶ are reduced by Cr^{2+} with comparable facility (assuming of course that the esters were not hydrolysed) in spite of the fact that the latter have no effective polar groups. Also, the observation that the ketonic form of the α -ketoacid is readily reduced, but not the hydrated form¹⁰ provides further

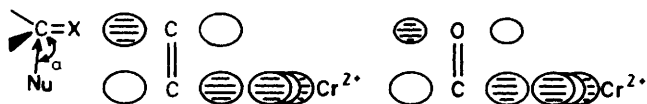
* For a review of the methods of determination of transition metal-alkyl bond dissociation energies and their applications see ref. 8b.

support for attack on carbon. The two forms have comparable thermodynamic stability, yet only the carbonyl form is active. The carbonyl double bond is expected to behave like the olefinic double bond. More generally, direct attack on the double bond provides a common basis for explaining and correlating a lot of diverse observations,¹¹ such as double bond hydrogenation, carbon-carbon bond formation, *cis-trans* isomerization around the double bond, exchange with the solvent of the HC=CH hydrogen, and charge-transfer complex formation. It is also interesting that the reduction by Cr^{2+} of acetylene and derivatives¹² also follows a rate law second order in Cr^{2+} . In fact, in the case of acetylene itself there is no polar group, and the attack by both chromium ions must necessarily be on the carbon (or carbons).

If then attack on the double bond carbons is accepted, the question remains how Cr^{2+} approaches, since there is a mismatch in the donor and the acceptor orbital symmetries. In a symmetric η^2 approach the overlap between the d_{z^2} of Cr^{2+} and the unoccupied antibonding π^* of the double bond vanishes (below). Therefore, for this stage a Dewar-Chat-Duncanson

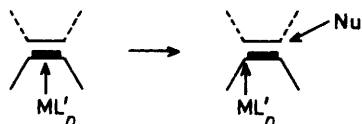


type of intermediate complex¹³ must be ruled out. The approach should rather be non-symmetric (σ), like that proposed^{14,15} for the attack by H^- [below: nucleophile (Nu) = H^- , X = O or CH_2 ; a = angle of attack]. In the hydride ion the



electrons are paired and occupy an s orbital, but these differences from Cr^{2+} do not affect our argument.

In cases of non-symmetric attack, even if the overlap is poor, a σ -donor can still react effectively with a π -acceptor. A non-symmetric complex like those represented above can react further with another Cr^{2+} to yield a two-electron reduction product. For a nucleophilic attack on a co-ordinated olefin, Eisenstein and Hoffmann¹⁴ have postulated a preceding displacement of the metal (below). In our case chromium is already 'displaced'; it is σ -bonded to one carbon only.



Dimethylmaleic anhydride, 2,3-diphenylfumaronitrile, and dimethyl 2,3-diphenylmaleate with excess of chromium(II) give⁶ a nearly even distribution of the corresponding *meso*- and *DL*-alkanes. This indicates that the two chromium(II) ions attack randomly from both sides of the olefinic plane. In contrast, in the case of the dimethyl ester of 2,3-dimethylmaleic acid both chromium ions seem to attack from the same side, giving dimethyl 2,3-dimethylsuccinate as the only product.

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References

- 1 D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, 1961, **83**, 1785; G. Svatos and H. Taube, *ibid.*, p. 4172; E. S. Gould and H. Taube, *ibid.*, 1964, **86**, 1318.
- 2 (a) A. Petrou, E. Vrachnou-Astra, and D. Katakis, *Inorg. Chim. Acta*, 1980, **39**, 161; (b) A. Petrou, E. Vrachnou-Astra, J. Konstantatos, N. Katsaros, and D. Katakis, *Inorg. Chem.*, 1981, **20**, 109.
- 3 W. Schmidt, J. H. Swinehart, and H. Taube, *J. Am. Chem. Soc.*, 1971, **93**, 1117; J. K. Kochi and P. E. Mocaldo, *J. Org. Chem.*, 1965, **30**, 1134; R. G. Coombes, M. D. Johnson, and N. Winterton, *J. Chem. Soc. A.*, 1965, 7029; F. L. Anet and E. Lablanc, *J. Am. Chem. Soc.*, 1957, **79**, 2649.
- 4 A. Malliaris and D. Katakis, *J. Am. Chem. Soc.*, 1965, **87**, 3077.
- 5 P. Sevcik and L. Treindl, *Coll. Czech. Chem. Commun.*, 1972, **37**, 2725.
- 6 C. E. Castro, R. D. Stephens, and S. Mojé, *J. Am. Chem. Soc.*, 1966, **88**, 4964.
- 7 D. E. Pennington and A. Haim, *J. Am. Chem. Soc.*, 1966, **88**, 3450; (b) A. Adin and A. G. Sykes, *J. Chem. Soc. A*, 1966, 1518.
- 8 (a) J. Halpern, *Pure Appl. Chem.*, 1979, **51**, 2171; (b) J. Halpern, *Acc. Chem. Res.*, 1982 **15**, 238; C. W. Kirker, A. Bakač, and J. Espenson, *J. Am. Chem. Soc.*, 1982, **104**, 1249.
- 9 J. K. Kochi, 'Organometallic Mechanisms and Catalysis,' Academic Press, New York, 1978; J. Espenson, *Adv. Inorg. Bioinorg. Mech.*, 1982, **1**, 1.
- 10 J. Konstantatos, N. Katsaros, E. Vrachnou-Astra, and D. Katakis, *J. Am. Chem. Soc.*, 1978, **100**, 3128; 1980, **102**, 3035; *Inorg. Chem.*, 1982, **21**, 122.
- 11 E. Vrachnou-Astra and D. Katakis, *J. Am. Chem. Soc.*, 1967, **89**, 6772; E. Vrachnou-Astra, P. Sakellaridis, and D. Katakis, *ibid.*, 1970, **92**, 811.
- 12 A. E. Shilov, *Kinet. Katal.*, 1970, **11**, 305.
- 13 M. Dewar, *Bull. Soc. Chim. Fr.*, 1951, **48**, 112; J. Chatt and L. Duncanson, *J. Chem. Soc.*, 1953, 2939.
- 14 O. Eisenstein and R. Hoffmann, *J. Am. Chem. Soc.*, 1981, **103**, 4308.
- 15 H. B. Bürgi, J. D. Dunitz, and E. Shefter, *J. Am. Chem. Soc.*, 1973, **95**, 5065; H. B. Bürgi, J. M. Lehn, and G. Wipff, *ibid.*, 1974, **96**, 1956.

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