The Reduction of Multiple Bonds by Low-Valent Transition Metal Ions. The Homogeneous Reduction of Olefins by Chromous Sulfate

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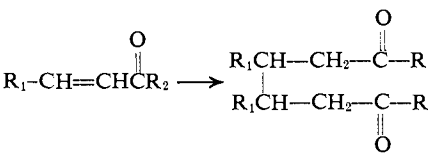
Abstract: Appropriately substituted olefins can be cleanly reduced to alkanes by solutions of chromous sulfate in aqueous dimethylformamide at room temperature. The stoichiometry, stereochemistry, and kinetics are consistent with a mechanism in which Cr^{II} attacks an olefin–Cr^{II} complex to yield product.

The reduction of carbon–carbon double bonds by low-valent transition metal species received sporadic attention in the early half of this century. Thus, aqueous solutions of chromous chloride and hydrochloric acid at 100° were reported to reduce maleic and fumaric acids to succinic acid. These conversions were also effected with aqueous suspensions of chromous hydroxide at 100° as was the reduction of cinnamic acid to phenylpropionic acid.[1] In contrast the reductive coupling



$$R_1\text{-}CH{=}CH\overset{O}{\overset{\|}{C}}R_2 \longrightarrow \begin{array}{l} R_1CH{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}R \\ \;| \\ R_1CH{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}R \end{array} \qquad (1)$$

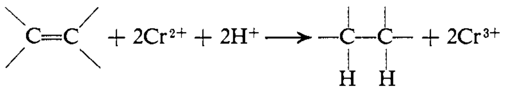
of benzalacetone and benzalacetophenone was noted to occur[2] by the action of chromous chloride–hydrochloric acid in aqueous ethanol or acetone or by similar treatment with vanadous salts. The reduction of the olefinic linkage of cinnamic acid, cinnamic acid amide, and benzalacetone with aqueous enthanolic solutions of ammoniacal titanous chloride at 100° has been noted,[3] and recently similar reductions of cinnamic acid and mesityl oxide with chromium(II) in concentrated aqueous ammonia have been reported.[4] The cinnamic acid derivatives[1–4] and mesityl oxide[2] were found to be inert to the acidic reagents. In most of these cases the yields of reduced products were either poor or not reported.

Quite recently a qualitative study of the kinetics of the reduction of maleic acid with aqueous acidic chromous perchlorate was made by utilizing a matrix analysis of spectrophotometric data.[5] The technique was also briefly applied to fumaric acid and the isomeric diethyl esters.

As a parallel to studies of the homogeneous reduction of acetylenes by chromous sulfate,[6] we wish to portray the scope and mechanism of the reduction of olefins by this reagent. In addition to sketching the synthetic utility of the reaction the results are of interest in relation to the role of conjugated bridging ligands in electron-transfer processes.

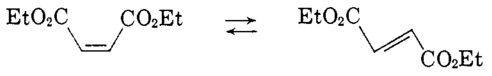
Results

Stoichiometry and Stereochemistry. The results of the reaction of a series of olefins (0.02–0.1 *M*) with chromous sulfate (0.07–1 *M*) in water or aqueous dimethylformamide at room temperature are given in Table I. The over-all stoichiometry for the process is



$$\rangle C{=}C\langle + 2Cr^{2+} + 2H^+ \longrightarrow -\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{H}{\underset{|}{\overset{|}{C}}}- + 2Cr^{3+} \qquad (2)$$

The stereochemical consequence of the reduction of three of the four tetrasubstituted olefins is, within experimental error, an even distribution of *meso* and *dl* alkanes. In contrast, dimethyl 2,3-dimethylmaleate reduces entirely in a cisoid fashion to yield only *meso*-dimethyl 2,3-dimethylsuccinate. The olefins were not isomerized under reaction conditions. A study of the possible isomerizations (eq 3 and 4) demonstrated that excess unreacted diethyl maleate or diethyl fumarate had not isomerized. Moreover, kinetic plots of the respective rate expressions for these olefins are nicely linear through 90% completion. The isomerization (3) could not be induced with chromous sulfate, chromic sulfate, or cobaltous sulfate or nitrate. Similarly the interconversion (4) was not brought about by either chromous or chromic sulfate.



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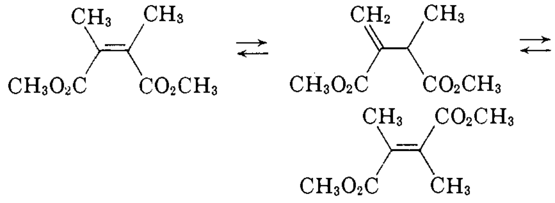

(4)

Reactivity. The substrates are grouped roughly in a decreasing order of reactivity toward the metal ion. In addition to the substances listed in Table I, the following olefins were found to be inert or extremely slow to react under scanning conditions (0.1 *M* olefin, 0.2 *M* Cr^{II}, room temperature): ethyl acrylate, ethyl

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[1] W. Traube and W. Passarge, *Ber.*, 49, 1692 (1916).

[2] J. B. Conant and H. B. Cutter, *J. Am. Chem. Soc.*, 48, 1016 (1926).

[3] P. Karrer, Y. Yen, and I. Reichstein, *Helv. Chem. Acta*, 13, 1308 (1930).

[4] K. D. Kopple, *J. Am. Chem. Soc.*, 84, 1586 (1962).

[5] A. Malliaris and D. Katakis, *ibid.*, 87, 3077 (1965).

[6] C. E. Castro and R. D. Stephens, *ibid.*, 86, 4358 (1964).

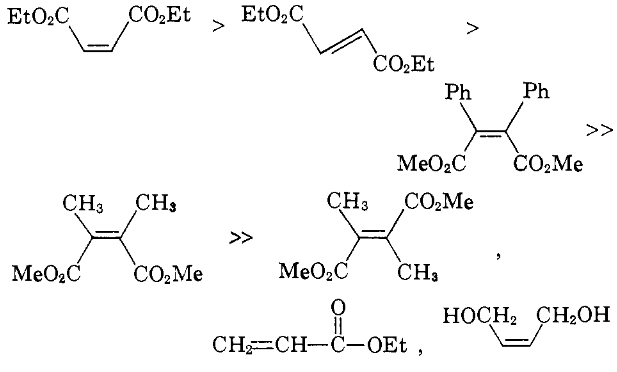
(7) For a recent summary, *cf.* H. Taube in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 114, and references therein.

Table I. Products of the Reduction of Olefins with Chromous Sulfate at Room Temperature

Olefin	Solvent (DMF:H_2O)	Product distribution[a]	$[O]_0$, M	$[Cr^{II}]_0$, M	Yield,[b] %
Dimethylmaleic anhydride	1:2.6	Dimethylsuccinic[c] anhydride: *meso* 48%, *dl* 52%	0.1	0.5	85
Maleic acid	H_2O	Succinic acid	0.08	0.25	86
Fumaric acid	H_2O	Succinic acid	0.08	0.25	91
Diethyl maleate	1:1	Diethyl succinate	0.05	0.15	95
Diethyl fumarate	1:1	Diethyl succinate	0.05	0.15	88
trans-2,3-Diphenylfumaronitrile	1:2	2,3-Diphenylsuccinonitrile: *meso* 48%, *dl* 48%	0.02	0.7	84
cis-Dimethyl 2,3-diphenylmaleate	1:2	Dimethyl 2,3-diphenylsuccinate: *meso* 53%, *dl* 48%	0.5	0.2	97
Cinnamic acid[d]	1:1	3-Phenylpropionic acid	0.1	0.2	89
Dimethyl 2,3-dimethylmaleate	H_2O	Dimethyl 2,3-dimethylsuccinate: *meso* 100%	0.04	0.14	92
Acrylonitrile	H_2O	Propionitrile	0.1	1	100

[a] Fraction of total yield. [b] Based on Cr^{II} consumed. [c] This product was not isolated but was hydrolyzed to the diacid. Isomer distribution is based on the distribution of the acids, *cf.* Experimental Section. [d] This reduction was accomplished at 100°; $[O]_0$ and $[Cr^{II}]_0$ represent initial concentrations.

cinnamate, crotonitrile, cinnamonitrile, vinyl acetate, methyl vinyl ether, *cis*- and *trans*-1,4-dihydroxybutene-2, allyl alcohol, dimethyl 2,3-dimethylfumarate, isoprene, styrene, 1,1-diphenylethylene, 1,2-dibromoethene, and the stilbenes. In general *cis* olefins oxidize chromous sulfate more rapidly than the *trans* isomers. The sequence



illustrates this theme and points up the fact that both conjugated coordination sites and electron-withdrawing substituents enhance the rate of reaction. Thus, diethyl maleate and diethyl fumarate are completely reduced in 3.5 and 30 min with a 0.02 M initial concentration of reactants, whereas the 2,3-diphenyl- and 2,3-dimethylmaleate esters at the much higher concentrations of reactants noted in Table I are consumed to the extent 100% in 10 hr and 36% in 3 days, respectively. The lessened reactivity of the 2,3-disubstituted esters is in keeping with the diminished capacity of substituted olefins to coordinate with metal ions.[8,9]

Kinetics. The rates of reduction of diethyl maleate and diethyl fumarate were monitored spectrophotometrically at 580 mμ. Typical optical density *vs.* time curves taken from the recorder chart are portrayed in Figure 1.

With diethyl fumarate, absorption at 580 mμ approached a maximum corresponding to that of chromic sulfate and remained constant. Infinity readings were taken at 12–24 hr. The product spectrum at these times, pictured in Figure 2, though similar is not identical with the spectrum of chromic sulfate. After 5 days the 420-mμ peak decreases to that of chromic sulfate.

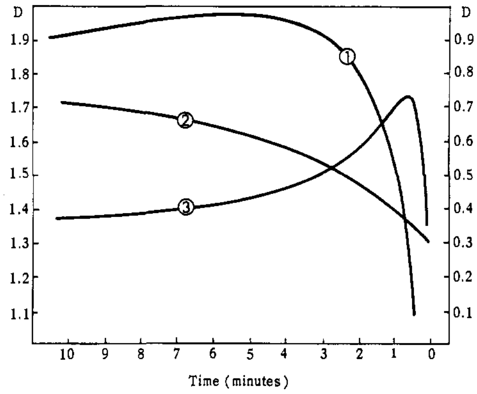


Figure 1. Optical density *vs.* time plots: curve 1, $[Cr^{II}]_0 = 0.014$ M, [diethyl maleate]$_0$ = 0.0206 M, λ 420 mμ; curve 2, $[Cr^{II}]_0 =$ 0.0131 M, [diethyl fumarate]$_0$ = 0.0204 M, λ 580 mμ; curve 3, $[Cr^{II}]_0$ = 0.0335 M, [diethyl maleate]$_0$ = 0.0103 M, λ 580 mμ. For curves 1 and 3, left ordinate; for curve 2, right ordinate.

With diethyl maleate absorption rapidly approached a maximum and slowly decayed. Separate titrimetric determinations[10a] at the time of maximum indicated that the stoichiometric amount of Cr^{II} had been consumed at this point. The maximum was taken as the infinity reading. The product spectrum of the green intermediate taken at this time, Figure 2, show it to be a more strongly absorbing species than $CrSO_4^+$. In runs containing a large excess of Cr^{II}, the 580-mμ peak rapidly assumed the calculated maximum (Figure 2), but its rate of decay was vastly increased.

Contrary to the implication of recent reports[5] diethyl fumarate reacted cleanly in an over-all third-

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(8) G. K. Helmkamp, F. L. Carter, and H. J. Lucas, *J. Am. Chem. Soc.*, **79**, 1308 (1957) have demonstrated this trend with Ag^+–olefin complexes.

(9) M. A. Bennet, *Chem. Rev.*, **62**, 611 (1962).

(10) (a) The mixture was quenched with excess iodine; unreacted iodine was determined with standard thiosulfate. Our ordinary titrimetric procedure employing ferric chloride as a quench and titrating Fe^{II} with Ce^{IV} could not be employed because the ferrous phenanthroline end point could not be discerned. (b) Calculated from $(D_\infty - D_0)/\epsilon$.

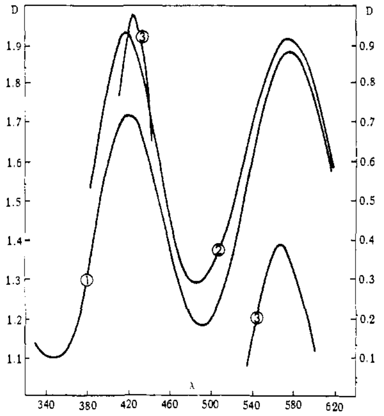


Figure 2. Product spectra: curve 1, 0.019 *M* chromic sulfate in 1:1 dimethylformamide-water, 0.5 *M* in $HClO_4$; curve 2, typical product spectrum with diethyl maleate or diethyl formate 22 hr after mixing; curve 3, typical product spectrum with diethyl maleate 6 min after mixing. For curves 1 and 2, right-hand ordinate. For curve 3, left-hand ordinate.

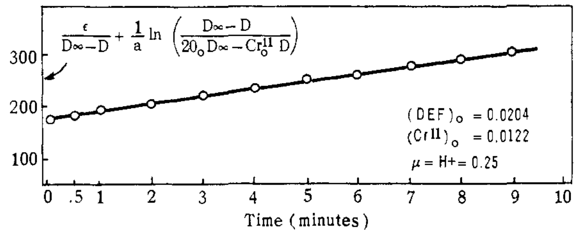


Figure 3. Third-order plot of the reduction of diethyl fumarate (DEF).

order process (5) past 90% completion. The rate

$$\frac{d[Cr^{III}]}{dt} = k_3[Cr^{II}]^2[\text{diethyl fumarate}] \quad (5)$$

expression is analogous to that found to be valid for the reduction of acetylenes.[6] Rate constants were evaluated from the general third-order expression

$$\frac{\epsilon}{D_\infty - D} + \frac{1}{a}\ln\left(\frac{(D_\infty - D)}{2[O]_0D_\infty - [Cr^{II}]_0D}\right) = \frac{ak_3t}{2} + \frac{1}{[Cr^{II}]_0}$$

in which ϵ is the extinction coefficient of Cr^{III}; the *D* values refer to optical densities; $[O]_0$ and $[Cr^{II}]_0$[10b] are the initial concentrations of reactants; and $a = 2[O]_0 - [Cr^{II}]_0$. A typical plot is presented in Figure 3. It should be noted that lower order plots of the data are highly curved. The third-order rate constants are given in Table II. The values represent an average of four separate determinations and the noted limits reflect the reproducibility.

Table II. Rates of Reduction of Diethyl Fumarate by Chromous Sulfate in 1:1 Dimethylformamide-Water[a] at 25°

H^+	μ[b]	k_3 (l.^{2}/mole^2 sec)
~10^{-4}[c]	0.5	116 ± 15
0.50	0.5	25 ± 3
0.10	0.5	23 ± 5
0.25	0.25	15.5 ± 1.5
0.125	0.25	15.5 ± 1.6

[a] Concentration range: $[Cr^{II}]$, 0.01–0.02 *M*; $[O]_0$, 0.01–0.02 *M*.
[b] Perchloric acid and ammonium perchlorate used as electrolytes.
[c] No added perchloric acid.

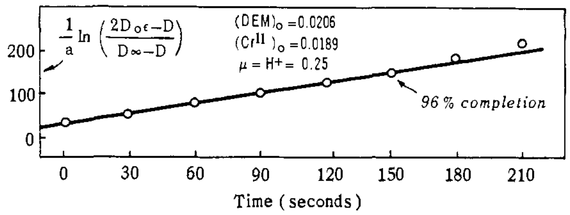


Figure 4. Second-order plot of the reduction of diethyl maleate (DEM).

On the contrary diethyl maleate reduces in an over-all second-order process. That is, the rate of production of the green intermediate is given by eq 6. More-

$$\frac{d[Cr^{III}]}{dt} = k_2[Cr^{II}][\text{diethyl maleate}] \quad (6)$$

over, although the rate law for the process does not change, the second-order rate constants depend upon the ratio $[Cr^{II}]_0/[\text{diethyl maleate}]_0$ and are given in Table III. For conditions A, Table III ($[Cr^{II}]_0 \simeq$ or $< [O]_0$), k_2 was evaluated from the expression

$$\frac{1}{a}\ln\left(\frac{2[O]_0\epsilon - D}{D_\infty - D}\right) = k_2t + \text{constant}$$

A typical plot is presented in Figure 4. Other order plots were greatly curved. For conditions B, Table III ($[Cr^{II}]_0 >> [O]_0$), the expression

$$\frac{1}{a}\ln\left(\frac{D_\infty - D - a\epsilon}{D_\infty - D}\right) = k_2t + \text{constant}$$

was employed. The values presented in Table III are an average of three determinations. The actual rates under condition B are extremely rapid (D_∞ at 36 sec) and are at the upper limits of measurability by our techniques.

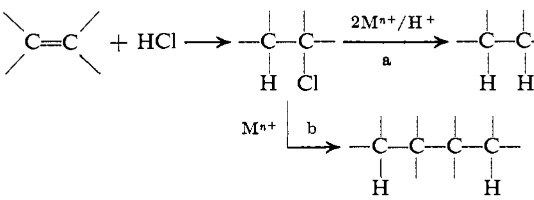
Table III. Rates for the Reduction of Diethyl Maleate at 25°, $\mu = H^+ = 0.25$

	M			
	$[Cr^{II}]$	$[O]_0$	$[Cr^{II}]_0/[O]_0$	k_2 (l./mole sec)
A	0.011–0.019	0.01–0.02	1.3–0.92	1.67 ± 0.08
B	0.034–0.035	0.004–0.01	8.3–3.3	12 ± 1.6

Discussion

The homogeneous reaction of olefins with chromous sulfate in aqueous dimethylformamide is a convenient procedure for saturating selected olefinic bonds. Indeed the scope of this reduction, as well as the conversion of acetylenes to olefins[6] by this reagent, might well be increased by operating at higher temperatures.

It should be emphasized, however, that the nature of the reagent employed can alter the mechanism and products of the reaction. Thus, the more complex pattern of the reaction of olefins with acidic vanadous,[2] chromous,[1,2] and titanous[3] chlorides and hydrochloric acid may best be formulated as a process involving HCl addition followed by reaction of the metal ion with an intermediate organic chloride (7a,b).[11] The



(7)

reaction of halides by both paths with Cr^{II} has been described.[12] The reductive coupling of 1,1-diphenylethylene by acidic Cr^{II} in the presence of chloride but not in its absence[13] is an example of (7b). Moreover, although ammoniacal solutions of low valent salts[3,4] appear to be more reactive[4] than the highly acidic reagents noted above, the greater stability of the product complex in this milieu renders isolation difficult.

The reactivity sequence, kinetics, and stereochemistry observed in the present work suggest a mechanism analogous to that advocated for the reduction of acetylenes[6] under these conditions

$$\text{olefin} + Cr^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (\text{olefin–}Cr^{II}) \tag{8}$$

$$(\text{olefin–}Cr^{II}) + Cr^{II} \xrightarrow{k_2} \text{alkane} + 2Cr^{III} \tag{9}$$

Thus, for diethyl fumarate, the equilibrium (8) is rapid and reversible with $k_{-1} > k_1$. The attack of metal ion on the 1:1 complex is rate determining, whence

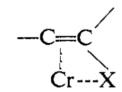
$$\text{rate} = k_2[Cr^{II}][\text{olefin–}Cr^{II}] = k_2K_1[Cr^{II}]^2[\text{olefin}]$$

where $K_1 = k_1/k_{-1}$. For the chelating ligand diethyl maleate K_1, the equilibrium constant for complex formation, is large. Moreover, the number of diethyl maleates coordinated to chromous should be a function of the $[Cr^{II}]_0/[O]_0$ ratio. Thus, the predominant form of the reactants at high metal ion/maleate ratios is most plausibly the 1:1 complex and uncomplexed Cr^{II}. Under these conditions (B in Table III) $[\text{olefin–}Cr^{II}] = [\text{olefin}]$ and

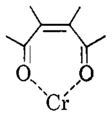
$$\text{rate} = k_2[Cr^{II}][\text{olefin–}Cr^{II}] = k_2[Cr^{II}][\text{olefin}]$$

For conditions in which the olefin is in stoichiometric excess (A in Table III), the same kinetic argument obtains except that the number of olefins in the rapidly formed complex is greater than one. That is, the different second order constants can be interpreted to reflect the rate of step 9 for two different Cr^{II} complexes of diethyl maleate.[14]

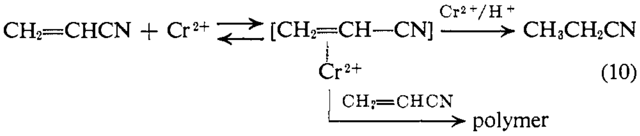
The 1:1 Complex. The Cr–olefin complex can be formulated in many ways; however, the data at hand suggest the substrates function as bidentate ligands. Thus, structures like



with X = CO_2R, CN, would seem appropriate for the fumarates and olefins bearing one coordinating substituent. The greater reactivity of the maleates suggests a seven-membered chelate.

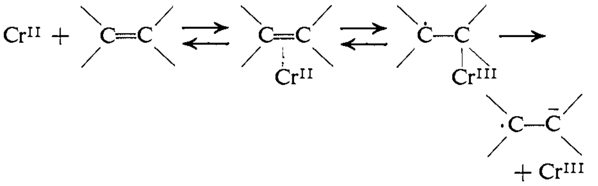


The gross reactivity and kinetic evidence for complex formation is supported by the diversion of the intermediate to a path other than reaction with Cr^{II}. Thus, with an excess of chromous ion the reduction of acrylonitrile proceeds slowly but quantitatively to propionitrile. However, if the metal ion is presented with an excess of this olefin the yield of propionitrile is decreased to 0–40%, polymerization ensues (10),



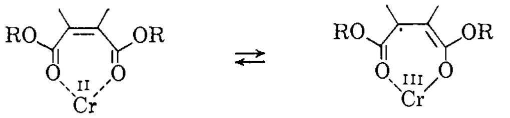
$$CH_2{=}CHCN + Cr^{2+} \rightleftarrows \underset{Cr^{2+}\ \xrightarrow{CH_2=CHCN}\ \text{polymer}}{[CH_2{=}CH{-}CN]} \xrightarrow{Cr^{2+}/H^+} CH_3CH_2CN \tag{10}$$

and chromous ion consumption is low. This observation could be taken as evidence for a radical anion intermediate (11) in the reduction path.



(11)

However, if process 11 were operative, that is, if "electron transfer" did occur spontaneously within the 1:1 complex, excess unreacted olefins should isomerize. They do not. If, however, the electron were transferred through a conjugated carbonyl moiety, possibly maleates might not isomerize to fumarates because of a retained chelation.



On the other hand, by the same argument, fumarates ought to isomerize to maleates because of an increased stability of the chelated radical in that form. Furthermore the rapidity with which Cr^{II} should scavenge free radicals of this type militates against (11) for the maleate esters.[15] Thus, certainly for the *trans* olefins, and also most plausibly for the *cis* compounds, "electron transfer" occurs upon approach of the second Cr^{II} to the olefin–Cr^{II} complex or subsequent to it.[16]

The Reduction Step. Although our results allow no precise formulation of this process, collapse of a 2:1 metal ion–olefin aggregate[17a] in the manner depicted

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[11] Alternatively an intermediate cation possessing a halide ligand may function as the intermediate in metal halide–HCl reductions.

[12] C. E. Castro and W. C. Kray, Jr., *J. Am. Chem. Soc.*, **85**, 2768 (1963).

[13] C. E. Castro, *ibid.*, **83**, 3262 (1961).

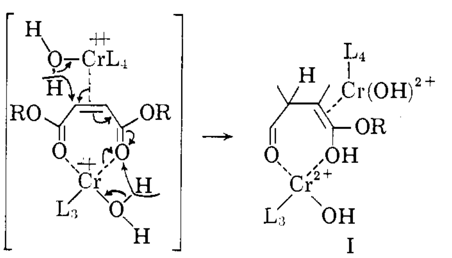
[14] This rationale is in accord with the suggestion of Malliaris and Katakis (ref 5) that more than one colored species is present in the reduction of maleic acid by chromous perchlorate. Our interpretation differs from these authors in that we attribute the slow second-order step to the attack of the metal ion on a maleate complex of Cr^{II}. In keeping with the kinetics for the fumarate ester, it seems unlikely that complex formation with the better ligand diethyl maleate should be rate determining.

[15] That is, k_2 (eq 9) ought to be much larger if this were to occur.

[16] This sentiment is not in contradiction with the contention that "electron transfer" proceeds through a conjugated bridging ligand. Rather, it implies that this process does not begin to happen unless two ions are in the vicinity of the olefin (without regard to their oxidizing or reducing capacities). Our system is quite analogous to the reduction of pentaamminocobalt(III) complexes of the maleates by Cr^{II} except that in our study both ions are oxidized.

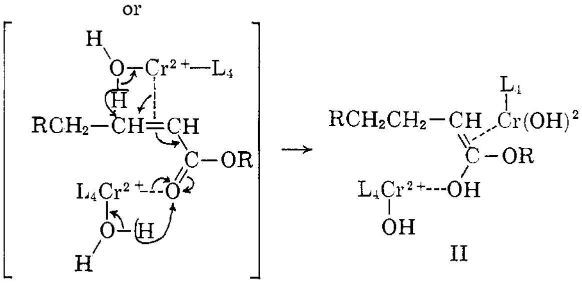
[17] (a) Which may or may not be a discrete intermediate. (b) The spectral data for diethyl maleate suggest all the Cr^{III} produced is in the complex.

(eq 12, 13, and 14) accounts for the bulk of the data[17b]



(12)

or

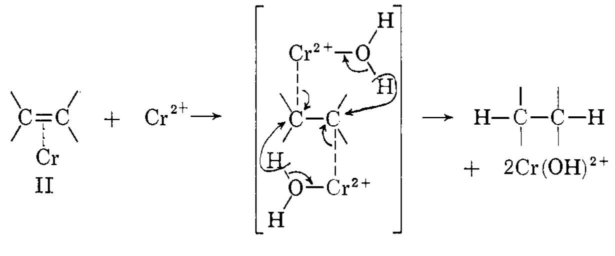


(13)

followed by

$$\text{I or II} \longrightarrow 2\text{Cr}^{\text{III}} + \text{reduced enol ester} \longrightarrow \text{reduced ester} \quad (14)$$

The pictures (12 and 13) are meant to convey that proton and electron transfer occur concomitantly from both metal ions to yield a $\text{Cr}^{\text{III}}(\text{OH})$ complex of the reduced enol ester. Random stereochemistry would than be expected for ketonization of the ester within or without of a complex. The process not involving conjugated ligands would be



In keeping with our formulation the green intermediate observed in the reduction of diethyl maleate would reasonably be a chelated complex of the reduced enol ester like I. The more rapid decay of the green intermediate in the presence of Cr^{II} (Figure 1) would be explained by the more ready dissociation of a Cr^{II} ester complex. That is, process 14 would be hastened *via* (15) in which I′ and II′ would be the corresponding Cr^{II} complexes. If this is assumed, a

$$\text{I or II} + \text{Cr}^{\text{II}} \xrightarrow{k_{15}} \text{Cr}^{\text{III}} + \text{I}' \text{ or II}' \longrightarrow \text{Cr}^{\text{II}} + \text{ester} \quad (15)$$

pseudo-first-order rate plot[18] would set k_{15} at 0.84 l./mole sec[19] in the diethyl maleate system.

The exclusively *cis* reduction of dimethyl 2,3-dimethylmaleate is not easily explained with the data at hand[20] and this finding warrants additional study.

Experimental Section

Materials. Chromous sulfate solutions were prepared by reducing solutions of $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ (Mallinckrodt) with amalgamated mossy zinc. Transfers, storage of the solution, and analyses were accomplished in the manner previously described[12,13] as was the preparation of solid $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$ employed in the kinetic studies.

The following purchased substances were recrystallized or distilled before use and their physical properties checked those of the literature: maleic acid, fumaric acid, acrylonitrile, *trans*-cinnamic acid, dimethylmaleic anhydride, ethyl acrylate, ethyl cinnamate, crotonitrile, cinnamonitrile, vinyl acetate, methyl vinyl ether, *trans*-1,4-dihydroxybutene-2, allyl alcohol, styrene, 1,1-diphenylethylene, 1,2-dibromoethene, *cis*- and *trans*-stilbene, dimethylformamide. Dimethyl 2,3-dimethylfumarate was prepared *via* the route dimethylmaleic anhydride, dimethylfumaric acid,[21] diacid chloride,[22] diester.[22] *cis*-1,4-Dihydroxybutene-2 was obtained in 96% yield from the Raney nickel catalyzed hydrogenation of 2-butyne-1,4-diol in methanol.[23] Diphenylfumaronitrile was prepared from phenylacetonitrile by bromination[24] and base coupling.[25] Dimethyl 2,3-dimethylmaleate was prepared from the anhydride by treatment with methanol–sulfuric acid.[26] Dimethyl 2,3-diphenylmaleate was synthesized from phenylacetic acid *via* bromination[27] and coupling.[28]

Kinetics. Stock solutions of Cr^{II} were prepared from $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$ and the requisite amounts of reagents. Nitrogen-preflushed glass syringes were employed to transfer the solution to cells preflushed and swept with N_2 and fitted with a serum cap. Neat olefins were injected directly into the cell. It was given a fast shake and placed in the sample cavity of the spectrophotometer; the absorption at 580 mμ was plotted with a recorder. The cylindrical cells had a path length slightly greater than 1.0 cm, and this length is embodied in the extinction coefficients used in the calculations. For $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, using the formula weight 542 determined from the repeated preparation[29] of large batches of stock Cr^{II} solutions (*vide infra*), ϵ (Cr^{III}) was 48.4 at 580 mμ. The green intermediate produced in the diethyl maleate runs had ϵ (Cr^{III}) 58. Absorption in runs with an excess of Cr^{II} rose to the calculated value assuming a stoichiometry of 2Cr^{III} produced per mole of olefin added.

The Cr^{2+} Reductions. Reaction solutions were magnetically stirred under nitrogen and were carried out in the manner previously described for acetylenes.[6]

Maleic Acid. The acid (2.0 g, 0.0173 mole) dissolved in 25 ml of water was added to 100 ml of 0.473 *m* CrSO_4 solution. The reaction mixture immediately became red.[30] Titration of a 2-ml aliquot after 30 min indicated 0.0312 mole (95%) of Cr^{II} had been oxidized (based on olefin charged). After an additional 30 min, the solution was saturated with ammonium sulfate and evaporated to dryness in a rotary evaporator. The residue was extracted repeatedly with acetone. The acetone solution was dried over sodium sulfate and stripped to dryness to afford 1.75 g (0.0148 mole, 86%) of succinic acid having mp 186–188°. A mixture melting point with an authentic sample was 187–188°.

Fumaric Acid. Similarly 100 ml of 0.473 *m* CrSO_4 solution treated with 2.0 g (0.0173 mole) of fumaric acid also turned a deep red and after 1 hr yielded, upon work-up, 1.85 g (0.1057 mole) of succinic acid in 91% yield.

Dimethylmaleic Anhydride. The anhydride (2.0 g, 0.0158 mole) was dissolved in 100 ml of warm 1:1 dimethylformamide–water. After cooling, the solution was added to 80 ml of 0.680 *M* CrSO_4 solution (0.0545 mole). The reaction turned green immediately. At 20 min the Cr^{II} consumption was quantitative. The reaction solution was evaporated to dryness and the residue treated with 100 ml of 50% H_2SO_4. After dilution, this solution was extracted continuously with ether in a liquid–liquid extraction apparatus for 3 days. The dried concentrated extracts yielded 1.9 g of white crystals having mp 130–165°. The solid was dissolved in a minimum of warm ether–chloroform. Upon cooling, 0.84 g (0.058

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[18] The plot is linear through 79% completion.

[19] A value in the range of rates for related processes, ref 7.

[20] Thus for diethyl maleate if Cr^{IV} were an intermediate the rate should not be a function of the Cr^{II}/olefin ratio. Furthermore, even if a metal ion mediated ketonization were to occur, there is no reason why the second hydrogen should be placed on the same side of the bond as the first one in this ester and not in the 2,3-diphenyl compound.

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[29] The values are within 1% agreement.

[30] In accordance with recent results; ref 5.

mole) of *meso*-dimethylsuccinic acid, mp 199–200° (lit.[31a] 199–200°), was obtained. The ether was boiled from the mother liquid, and petroleum ether was added. Upon cooling 0.81 g (0.056 mole) of *dl*-dimethylsuccinic acid, mp 127–128° (lit.[31b] 127–128°), was obtained. The total yield of product was 85% and the yield of isomer separated materials was 73% with a distribution of 51% *meso* and 49% *dl*.

Cinnamic Acid. The *trans* acid (4.0 g, 0.027 mole) dissolved in 50 ml of dimethylformamide was added to 200 ml of 0.327 *M* $CrSO_4$ solution and 50 ml of DMF. A yellow-green precipitate was formed immediately upon addition of the cinnamic acid solution. The reaction flask was warmed on the steam bath and most of the precipitate redissolved. After 6 hr, 0.027 mole (50%) of the Cr^{II} had been consumed. After 40 hr the consumption (0.054 mole) was quantitative. The solution was diluted with 200 ml of water, saturated with ammonium sulfate, and extracted 3 days with ether in a liquid–liquid extractor. The concentrated extract, a DMF solution of product, was diluted with 200 ml of water and extracted thrice with ether; the ether extracts were washed with water and dried over sodium sulfate. Evaporation of the solvent afforded 3.6 g (0.024 mole, 89%) of hydrocinnamic acid, mp 47–48° (lit.[32] mp 48°). An infrared spectrum was identical with that of hydrocinnamic acid.

In another experiment in which the mixture was not warmed, the precipitate did not dissolve and no chromous consumption occurred in 5 days. Both the salt and the starting acid are easily soluble under these conditions.

Diethyl Maleate. The ester (2.0 g, 0.0116 mole) dissolved in 100 ml of DMF was added to 100 ml of 0.272 *M* chromous sulfate. The reaction solution immediately became a deep green. Titration of an aliquot indicated 96% of the Cr^{II} had reacted. The solution was diluted with 300 ml of water and repeatedly extracted with ether. Ether extracts were washed with water and dried over magnesium sulfate. Concentration yielded 1.85 g (0.0108 mole) of diethyl succinate; bp 216° (734 mm), $n^{20}\text{D}$ 1.4185 (lit. bp 217.7° (760 mm)[33a], $n^{18.5}\text{D}$ 1.4176[33d]). An infrared spectrum was identical with that of diethyl succinate.

Diethyl Fumarate. Under the same conditions 2.0 g of the ester yielded 1.75 g of diethyl succinate.

Diphenylfumaronitrile. The nitrile (2.0 g, 0.0087 mole) dissolved in 200 ml of DMF was treated with 200 ml of 0.136 *M* chromous sulfate. The solution became green immediately. After 3 hr, 0.0157 mole of Cr^{II} (90%) had been consumed. After another 2 hr the solution was diluted with 600 ml of water and extracted three times with ether. During the extraction a solid, 0.85 g, separated having mp 235–238°. The ether extracts were washed with water and dried over magnesium sulfate. Concentration afforded 1.15 g of a solid with mp 145–165°. The solids were combined and digested in warm benzene. Filtration of the benzene-insoluble material gave 0.75 g of pure *meso*-diphenylsuccinonitrile, mp 240° (lit.[34] 239–240°) (infrared: CN at 4.28, 4.53 μ); concentration of the benzene filtrate and dilution with petroleum ether gave, upon cooling, 0.83 g of white needles of *dl*-diphenylsuccinonitrile, mp 162–163° (lit.[34] 164°). Nitrile absorption in the infrared was strong at 4.23, 4.50 μ. The mother liquor upon further concentration yielded 0.12 g of starting olefin, mp 159–160°; total yield of recovered material was 84% of which 7% was starting olefin and 93% reduced product.

Acrylonitrile. The nitrile (5.0 g, 0.0945 mole) was added to 200 ml of 1.09 *M* chromous sulfate (0.218 mole). The solution slowly became a dark green. After 2 hr 69% of the Cr^{II} (0.131 mole) had been consumed. No additional Cr^{II} reacted after 1 day. The reaction solution was saturated with ammonium sulfate and continuously extracted with ether for 3 days in a liquid–liquid extractor. This procedure yielded only 0.4 g of a gelatinous polymer. The infrared spectrum of the material showed strong CN absorption.

In another run, 1.16 g of the nitrile (0.022 mole) was added slowly to 200 ml of 1.11 *M* chromous sulfate (0.22 mole). Titration after 8 hr indicated 0.044 mole of Cr^{II} (100%) had been consumed. The solution was saturated with ammonium sulfate and extracted four times with ether. The ether solution was dried over magnesium sulfate and concentrated. The propionitrile content of the concentrate was quantitated by gas chromatography employing a 6-ft triethylene glycol column at 110° with acetone as a marker. The yield was 100%. The peak corresponding to propionitrile was trapped and its infrared spectrum was identical with an authentic sample.

Dimethyl 2,3-Diphenylmaleate. The ester (1.5 g, 0.0051 mole), in 10 ml of DMF, was added to a solution composed of 20 ml of 1.11 *M* chromous sulfate (0.0222 mole), 80 ml of water, and 90 ml of DMF. The solution very slowly became green. After 10 hr the required amount of Cr^{II} (0.0102 mole) had been oxidized. The solution was diluted with 300 ml of water and extracted three times with chloroform. The chloroform solution was dried over magnesium sulfate and concentrated, and the residue crystallized to yield 1.46 g of material with mp 158–205°. The white solid was digested three times in boiling ether. The ether-insoluble *meso*-dimethyl 2,3-diphenylsuccinate, mp 220–221° (lit.[35] 219–220°), 0.75 g, was isolated as white crystals. Concentrations of the ether filtrate afforded 0.70 g of white crystals of *dl*-dimethyl 2,3-diphenylsuccinate having mp 169–171° (lit.[35] 173–174°). The latter substance was sublimed at 115° (0.1 mm) to give 0.65 g of material with mp 171–172°; total purified and separated product isolated 97%.

Dimethyl 2,3-Dimethylmaleate. The ester, 4.87 g (0.0284 mole) in 25 ml of DMF, was added to a solution of 225 ml of DMF and 100 ml of 0.8884 *M* chromous sulfate (0.0884 mole) and 130 ml of water. After 3 days 36% of the required Cr^{II} had been oxidized. The solution was diluted with 400 ml of water and extracted thrice with ether. Ether extracts were dried over magnesium sulfate and concentrated. The residual oil was treated with 3.0 g of sodium hydroxide dissolved in 30 ml of water and refluxed for 24 hr. After ether extraction, the mixture was acidified with HCl to pH 1 and extracted repeatedly with ether. The ether extracts were dried over sodium sulfate and concentrated. The solids obtained were dissolved in boiling chloroform; upon cooling 1.32 g of *meso*-2,3-dimethylsuccinic acid (75%) was obtained, mp 197–198° dec (lit.[31a] 199° dec). Further concentration afforded dimethylmaleic anhydride but no *dl* acid.

In another experiment the original reaction mixture was analyzed directly by flame ionization gas chromatography employing a 10% Carbowax column containing 5% silver nitrate on Chromosorb W. Analysis showed a quantitative yield of *meso* ester[36] and unreacted olefin; no *dl* ester could be detected.

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