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FORMATION AND REACTIVITY OF SOME AQUEOUS ION-RADICALS CONTAINING METAL-TO-CARBON BONDS *

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Summary

Organometallic ion-radicals are formed during reactions of Cr^{2+}, V^{2+}, Eu^{2+} and Ti^{3+} ions in acid aqueous media with unsaturated carboxylic and α-keto-acids, by direct attack on the carbon of the double bond. Subsequently these ion-radicals may undergo transformation via nucleophilic attack on carbon by a second metal ion, or disproportionation, or olefin elimination, or free radical formation, or dimerization. Examples are given for each type of reaction, and comparisons are made between different metal ions and different ligands.

Introduction

For several years we have been working on the kinetics and the mechanisms of the reactions of Cr_{aq}^{2+}, V_{aq}^{2+}, Eu_{aq}^{2+}, and Ti_{aq}^{3+} in acid aqueous media with compounds of the general formulae shown below (I through IV).

These low-valent metal ions are one-electron reducing agents, whereas the unsaturated free ligands are two-electron oxidants. The reaction will then go through formation of ion-radical intermediates. Spectroscopic and kinetic data led us to the conclusion that the first step is direct attack on the carbon–carbon double bond in I to III, and on the carbon–oxygen double bond in IV [1]. This nucleophilic attack occurs even in the presence of pyridinium and carboxylic groups.

In reaching this conclusion we also used the information on the metal–alkyl bond strength provided by Halpern and co-workers [2]. Since these bonds are weaker than the corresponding metal–oxygen bonds, their detection can be taken as strong evidence for direct attack on carbon, rather than initial attachment on oxygen and then "uphill" transfer to carbon. In fact, this new perspective led to a reinterpretation of our old results, based on ion-radical formation, and also to new comparisons

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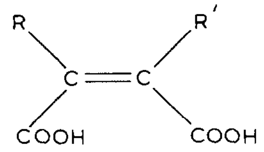
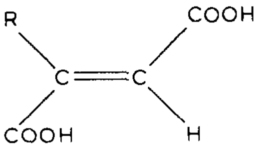
* Dedicated to Prof. J. Halpern on the occasion of his 60th birthday.



($R, R' = H, CH_3, Cl$)

(I)



($R = H, CH_3$)

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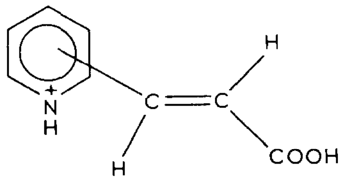

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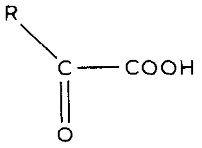


($R = CH_3, C_6H_5$)

(IV)

and correlations. We also found it useful to include in this paper new experimental data in order to support further the new interpretation.

We first focus on the following questions:

(1) Whether or not the intermediates in the reactions between the metal ions and the unsaturated free ligands investigated contain metal-to-carbon bonds.
(2) How these intermediates react further.

Halpern and co-workers presented [3] evidence that the organocobalt chelate complexes, $[RCo(chel)]^+$, where chel represents tetradentate or bis-bidentate equatorial ligands derived from Schiff bases or dioximes, react in acetonitrile and other solvents by the following ways:

-Nucleophilic attack on carbon
-Disproportionation
-Free radical formation (homolytic cleavage) [4]
-Heterolytic cleavage [4]

These reaction categories will be further documented here, using the data for organo-chromium, -titanium, -vanadium, and -europium ion-radicals formed in the reactions of aqueous low-valent metal ions with unsaturated compounds. In addition, the evidence for dimerization will be reviewed. The comparisons and correlations will be made at the end of this review.

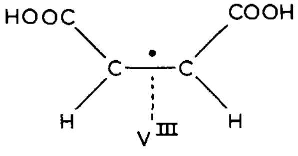
The evidence for metal-to-carbon bonds

With chromium(II) as the reductant the resulting organochromium(III) complexes have characteristic absorptions in the 280–320 nm region [5] with high absorptivities and they are sufficiently inert to be separated and characterized. This was the case in the reactions with maleic, fumaric, chloromaleic, and pyridine-acrylic acids [1b,6,7]. The detection of such complexes is, as stated above, direct evidence that the ion-radical formed during the attack by the first chromium contains metal-to-carbon bonds; owing to the "weakness" of the Cr–C bond [2], migration of chromium from carbon to oxygen is possible, but the reverse can be ruled out as thermodynamically unfavorable. The Cr–C bonds detected in the final products are formed right from the beginning.

The evidence for ion-radical formation between V^{2+}, Ti^{3+} and substituted olefins or carbonyl compounds is indirect but equally convincing [1a,8,9]. It consists of the following:

(i) Initial increase in the absorption of the reaction mixtures, due to formation of complexes with relatively high absorptivities (Table 1), indicating metal-to-ligand charge transfer, that is extensive enough to justify characterization of the corresponding species as ion-radicals. These complexes are formed even at high acidities, where the carboxyl group is effectively protonated.

In the reaction between V_{aq}^{2+} and maleic acid two species are formed immediately upon mixing the reactants, their relative concentrations depending on the acidity [8a]. These species were thought to be complex ion-radicals, $V^{III}–{}^{\cdot}ma$, (ma = maleic) with the protonated and non-protonated forms of maleic acid, in which the ligand is coordinated through oxygen. Now we have to reconsider this early assumption and suggest that the two species correspond to the formulae V and VI:



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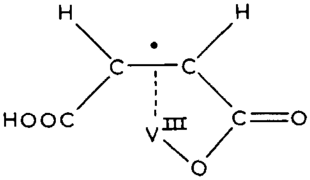


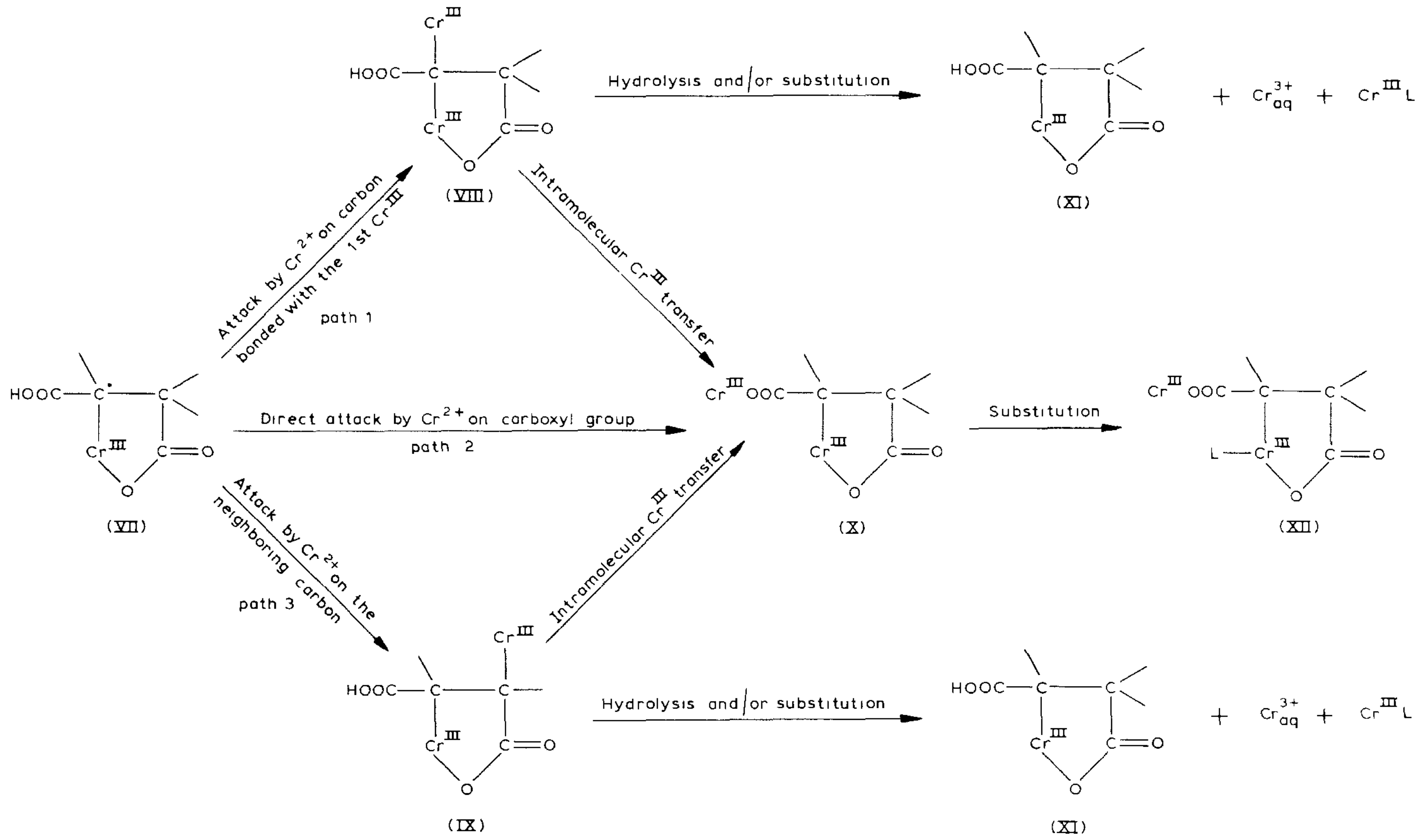
(VI)

TABLE 1

ZERO-TIME ABSORPTIVITIES[a] OF REACTION MIXTURES OF V^{II} AND Ti^{III} WITH UNSATURATED CARBOXYLIC ACIDS

Metal ion concentration (M)		Organic acid concentration (M)		[$HClO_4$] (M)	Wavelength (nm)	Molar absorptivity, ϵ (M^{-1} cm^{-1}) (per metal ion)
V^{II}	(0.01)	maleic	(0.156)	0.042	450 [b]	12.6
V^{II}	(0.01)	maleic	(0.156)	0.83	450 [b]	3.1
V^{II}	(0.05)	pyruvic	(0.500)	1.00	420 [c]	4.3
V^{II}	(0.02)	phenylglyoxylic	(0.100)	1.00	420 [c]	8.2
Ti^{III}	(0.005)	pyruvic	(0.500)	pH 2.00	504 [d]	90.0
Ti^{III}	(0.02)	pyruvic	(1.000)	0.65	504 [d]	23.5

[a] Average of all species present. [b] From ref. 8. The formation constant of the ion-radical, $K_{form} = 0.7$. The absorptivity of V_{aq}^{2+} at this wavelength is $\epsilon \simeq 0.8$ M^{-1} cm^{-1}. [c] From ref. 9. The formation constant of the ion-radical for pyruvic is $K_{form} = 0.2$. For phenylglyoxylic it is $K_{form} = 4$. The absorptivity of V_{aq}^{2+} at this wavelength is $\epsilon \simeq 0.8$ M^{-1} cm^{-1}. [d] From ref. 1a. The absorptivity of Ti_{aq}^{3+} at this wavelength is $\epsilon \simeq 4.0$ M^{-1} cm^{-1}.



L is either the original unsaturated ligand or its reduction product

SCHEME 1

(ii)-Activation by V^{II} of the double bond of maleic acid, as manifested by hydrogen exchange with the solvent, and by *cis-trans* isomerization [10]. These reaction paths occur simultaneously with the redox reaction.

Nucleophilic attack on carbon

Scheme 1 represents the network of all possible reactions originating from Cr^{III} ion-radical intermediate VII formed during the hydrogenation of olefinic compounds, with carboxylic and other substituents, in the presence of an excess of Cr^{2+}_{aq} [1].

The option that path 2 is the only path for reaction is not likely. The network represents the reactions taking place at short (stopped-flow) times. Interconversion of the species XI and XII and further aquation [6] take place, but these processes are slow on this time scale and are not included in the scheme.

For a variety of substituted olefins [1] the rate law in excess Cr^{2+} contains a single term, second order in Cr^{2+} and first order in the free ligand. The observed third-order rate constant is composite, containing the equilibrium constant of the ion-radical formation. The following trend in the rate of the reactions has been observed: chloromaleic (Clma) > maleic (ma) > dichloromaleic (Cl_2ma) > methylmaleic (mema)

The inevitable conclusion seems to be that Cr^{2+} attacks the ion-radical nucleophilically, on one of the carbons (upper and lower branches in the network). Other evidence supporting this idea is that in the reactions of Cr^{2+}_{aq} with chloromaleic and dichloromaleic acids free chloride ion is detected [1b]. The activation of the C–Cl bond and the release of chloride can be regarded as the displacement of one nucleophile by another.

All the final products in this network have been separated by ion exchange and characterized [7,1], and all paths are consistent with the observed rate law, which is second order in Cr^{2+} and first order in substituted olefin.

The carbon and/or the carbon–carbon bridged intermediate binuclear species VIII and IX were identified as the highly charged species staying at the top of the ion exchange column [7], which were shown to contain Cr^{III}–carbon bonds.

Carbon-bridged binuclear chromium, carbene-like intermediates, analogous to VIII, were postulated in the reaction between Cr^{2+} and polyhalomethanes [11]. Also, the reactions of Cr^{2+} with acetylene and derivatives are believed [12] to involve binuclear intermediates, having the characteristic Cr^{III}–C absorptions [12a] (for acetylenedicarboxylic acid, $HOOCC{\equiv}CCOOH$, at 272 nm, ϵ 2720 M^{-1} cm^{-1}. The behavior of propargyl alcohol, $HC{\equiv}CCH_2OH$, with no effective donor group, is analogous, indicating again carbon or carbon–carbon bridging [12b].

Transfer of the $Cr^{III}(OH_2)_5$ moiety from carbon to oxygen has been demonstrated [6,1c] for species of the type Cr^{III}–R^-, obtained from pyridineacrylic or phenylglyoxylic acids ($H\overset{+}{N}C_6H_4CH{=}CHCOOH$, $C_6H_5COCOOH$). This transfer is expected to be more facile for species of the type Cr^{III}–$R^{\cdot}$ (or Cr^{IV}–R^-) especially in excess Cr^{2+}, since intramolecular transfers of this kind are catalyzed by Cr^{2+}, as is in general the corresponding transfer of the $Cr^{III}(OH_2)$ group to the solvent (aquation) [1].

The nucleophilic attack on carbon described resembles nucleophilic attack on

$[CoR]^+$ [3], but it also differs from it in an important aspect: With $[CoR]^+$, attack by nucleophiles like Cl^- leads to detachment of R^+ and reduction of the formal oxidation state of the metal, e.g.

$$[Co^{IV}R]^+ + Cl^- \rightarrow Co^{II} + RCl$$

In our systems, the ligand is being reduced, and transformed into the hydrogenated product.

Kinetic evidence for the nucleophilic attack by a second metal ion is also available for the two V^{III}–˙ma ion-radicals V and VI [8b].

The rate law of the reaction between maleic acid and V_{aq}^{2+} is complex:

$$R = \left[k_a[A] + k_b[H^+][A] + k_c[A]^2 + k_d[H][A]^2\right][V^{2+}]^2 \qquad (1)$$

The first two terms in this rate law correspond to nucleophilic attack on the two ion-radicals V and VI by V_{aq}^{2+}. V^{III}–˙ma is formed upon mixing the solutions and is in equilibrium with the reactants:

$$V_{aq}^{2+} + HM \overset{K_2}{\rightleftarrows} VMH^{2+} \qquad (2)$$

$$V_{aq}^{2+} + M^- \overset{K_3}{\rightleftarrows} VM^+ \qquad (3)$$

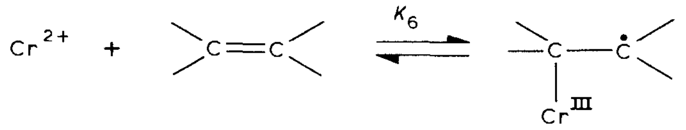
$$V_{aq}^{2+} + VMH^{2+} + H^+ \xrightarrow{k_4} 2\,V_{aq}^{3+} + S^- \qquad (4)$$

$$V_{aq}^{2+} + VM^+ + H^+ \xrightarrow{k_5} 2\,V_{aq}^{2+} + S^- \qquad (5)$$

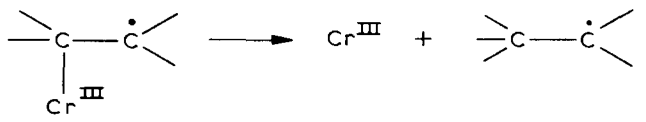
Consequently, $k_a = K_3 k_5$ and $k_b = K_2 k_4$. The other two terms in the rate law correspond to reaction between two radical-ions leading to disproportionation (vide infra).

Free radical formation

In the reactions of Cr_{aq}^{2+} with substituted olefins [1b], when the olefin is in excess, the organochromium ion-radical, which is formed by reaction 6, undergoes a homolytic scission as in reaction 7:



(6)



(7)

Chromium(III) is coordinated also to five water molecules.

The empirical rate law is first order in Cr^{2+} and first order in the ligands. In some cases the rate law also contains a term first order in Cr^{2+} and second order in the ligand. The first of these terms is attributed to the reaction of $Cr(H_2O)_6{}^{2+}$ with the free unsaturated ligand L, the second to the reaction of $Cr(H_2O)_5L$ with a free L.

The trends in the observed rate constants are different than those observed in excess Cr^{2+}. For the third-order term:

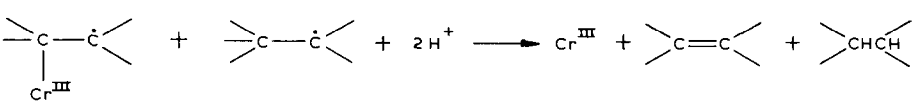
chloromaleic > maleic > methylmaleic > dichloromaleic

For the second-order term:

maleic > dichloromaleic ~ methylmaleic > chloromaleic

The observed rate constants are also composite, including the constant of the preequilibrium (eq. 6).

The free radical formed in eq. 7 reacts fast with an ion-radical, giving the fully hydrogenated product (Reaction 8):



(8)

Reaction of the free radical with Cr^{2+} is not likely, because in excess ligand there is very little free Cr^{2+} left, since the equilibrium (6) lies far to the right. Reaction (8) can be regarded as another kind of nucleophilic attack on the ion-radical, this time not by Cr^{2+}, but by an organic free radical.

Free radical mechanisms were postulated also in the reactions of V^{2+} with pyruvic and phenylglyoxylic acids [9], on the basis of kinetic evidence, stoichiometry, and product analysis. This one-electron reduction of the carbonyl group of these ligands leads to carbon–carbon bond formation. In the case of pyruvic acid, the rate law is:

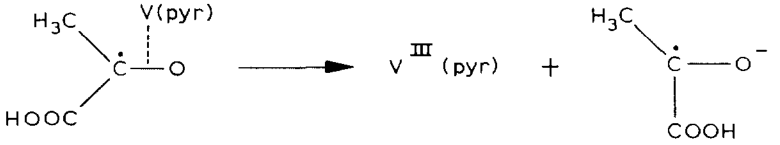
$$R = \left[k_{\rm i}[V^{2+}] + k_{\rm ii}[V^{2+}]^2\right][\mathrm{pyr}]^2$$

The rate constants are again composite, containing the constants of two successive equilibria:

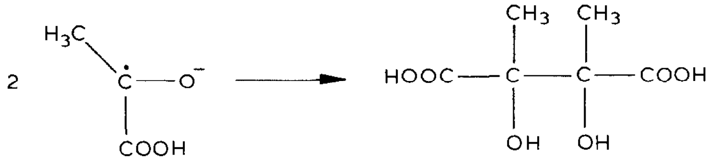
$$V^{2+} + \mathrm{pyr} \quad \overset{K_9}{\rightleftarrows} \underset{\text{(XIII)}}{[\mathrm{V{-}pyr}]^{2+}} \tag{9}$$

$$[\mathrm{V{-}pyr}]^{2+} + \mathrm{pyr} \overset{K_{10}}{\rightleftarrows} \underset{\text{(XIV)}}{[\mathrm{V(pyr)_2}]^{+}} \tag{10}$$

These equilibria lie to the left ($K_9 \simeq 0.20$, K_{10} smaller). In XIV one of the ligands is believed to be coordinated through the C=O bond, the second through the carboxyl group. Complex XIV reacts further via two paths, free radical formation (eq. 10) and dimerization (vide infra). Free radical formation leads to a product of reductive dimerization, dimethyltartaric acid (eq. 12). The second ligand is apparently assisting free radical formation (eq. 11).



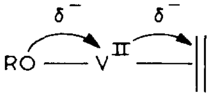
(11)



(12)

In eq. 11 the aquo ligands of vanadium have been omitted.

The effect of a second carboxylic ligand in facilitating free radical release in L–V^{III}–R$^{\cdot}$ is observed also with saturated carboxylic acids (Table 2). The effect seems to be small, but it must be recalled that, at the high acidities used, the formation constants of the reacting complexes, L–V^{III}–R$^{\cdot}$, are small. It should be noted that under these conditions the rate of the reaction was found to be independent of ionic strength. Upon coordination to the double bond, vanadium(II) loses at least some of its donor capacity because of a net transfer of charge to the ligand. Accordingly we speculate that the second ligand coordinates through oxygen, and that its function is to give back some of the electron density lost and to facilitate reduction:



In the reactions of Eu^{2+} with pyruvic [14] and phenylglyoxylic [1c] acids, only free radical paths are observed.

Europium(III) was found to affect the rate of the redox reactions (Table 3). The reaction of V^{2+} with pyruvic acid is accelerated, while those with maleic [15a,8b] or isonicotinic (4-pyridinecarboxylic) acid [15] are unaffected. The reaction between Ti^{3+} and pyruvic acid [1a,15a] is inhibited by Eu^{3+}. The reactions of Eu^{2+} with pyruvic acid [14] and isonicotinic acid [16] are also inhibited.

The effect of Eu^{3+} seems to be closely related to free radical formation, and it is interesting to investigate it further and more systematically. Chromium(III) has a

TABLE 2

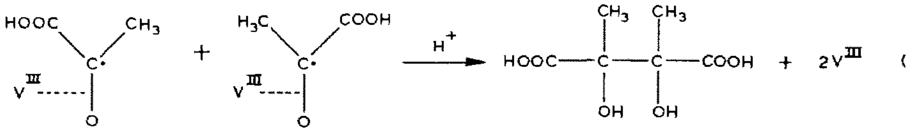
EFFECT OF SATURATED CARBOXYLIC ACIDS ON THE RATE OF REACTION BETWEEN V_{aq}^{2+} AND PYRUVIC ACID ($HClO_4$ concentration 0.5 *M*, room temperature)

$[V^{2+}]_0$ ($M \times 10^3$)	$[pyr]_0$ ($M \times 10^2$)	Carboxylic acid concentration	$k_{obs} \times 10^3$ (s^{-1})
4.2	4.3	-	1.27 ± 0.05
4.2	4.3	tartaric (0.18 *M*)	1.53 ± 0.06
8.0	4.3	acetic (0.32 *M*)	1.58 ± 0.08

similar effect (Table 3) but generally europium(III) is more convenient as a probe, because of its transparency to light, and its lability and solubility characteristics.

Dimerization

In the reaction between V^{2+} and pyruvic acid [9] free radical formation competes with dimerization, which is analogous to pinacolic coupling (eq. 13).


(13)

Thus, carbon–carbon bonds are formed not only via free radical paths, but also by this dimerization of the ion-radical itself.

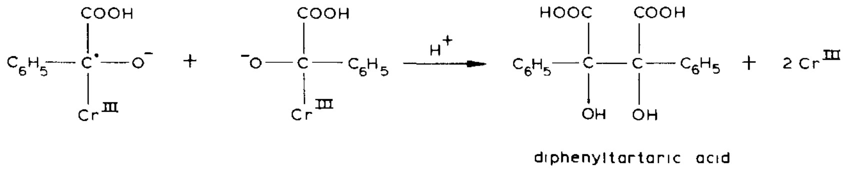
With the Ti^{3+}/pyruvic acid system [1a], dimerization is the only path observed, over a range of hydrogen ion concentrations of two-and-a half orders of magnitude. Also, dimerization is one of the competing paths in the reduction of phenylglyoxylic

TABLE 3

EFFECT OF TRIVALENT IONS ON THE RATE OF REACTION BETWEEN V_{aq}^{2+} AND PYRUVIC ACID (Room temperature)

Reducing ion ($M\times10^2$)	Organic acid ($M\times10^2$)	$[Me^{3+}]$ or $[Me^{2+}]$ ($M\times10^2$)	$[H^+]$ (M)	$k_{obs}\times10^3$ (s^{-1})
V^{2+} (1.14)	pyr (5.71)	–	1.00	1.77 ± 0.04
V^{2+} (1.14)	pyr (5.71)	Cr^{3+} (3.57)	1.00	2.80 ± 0.08
V^{2+} (1.14)	pyr (5.71)	Cr^{3+} (7.14)	1.00	2.90 ± 0.15
V^{2+} (0.57)	pyr (3.57)	–	1.00	1.11 ± 0.10
V^{2+} (0.57)	pyr (3.57)	Eu^{3+} (0.40)	1.00	1.37 ± 0.06
V^{2+} (0.57)	pyr (3.57)	Eu^{3+} (7.00)	1.00	3.30 ± 0.20
V^{2+} (0.57)	pyr (3.57)	Eu^{3+} (10.00)	1.00	6.65 ± 0.10
V^{2+} (0.71)	pyr (5.71)	–	0.90	1.20 ± 0.03
V^{2+} (0.71)	pyr (5.71)	Ca^{2+} (7.14)	0.90	1.70 ± 0.06
V^{2+} (0.71)	pyr (5.71)	Ca^{2+} (17.86)	0.90	1.67 ± 0.05
V^{2+} (0.71)	pyr (5.71)	La^{3+} (7.14)	0.90	1.83 ± 0.14
V^{2+} (0.71)	pyr (5.71)	La^{3+} (17.86)	0.90	1.67 ± 0.08
V^{2+} (0.71)	pyr (5.71)	La^{3+} (42.86)	0.90	1.35 ± 0.09
				($M^{-1}s^{-1}$)
V^{2+} (1.00)	ma (15.60)	–	1.80	27.00 ± 2.40
V^{2+} (1.00)	ma (15.60)	Eu^{3+} (15.00)	1.80	27.45 ± 2.10
V^{2+} (3.30)	iso (17.00)	–	0.30	2.60 ± 0.16
V^{2+} (3.30)	iso (17.00)	Eu^{3+} (17.00)	0.30	2.65 ± 0.20
Ti^{3+} (1.40)	pyr (14.30)	–	1.00	25.02 ± 2.35
Ti^{3+} (1.40)	pyr (14.30)	Eu^{3+} (14.30)	1.00	10.85 ± 0.95
Eu^{2+} (0.58)	pyr (10.00)	Eu^{3+} (3.00)	0.50	(2.75 ± 0.10)$\times10^6$
Eu^{2+} (0.58)	pyr (10.00)	Eu^{3+} (10.00)	0.50	(0.83 ± 0.03)$\times10^6$
Eu^{2+} (0.58)	pyr (10.00)	Eu^{3+} (20.00)	0.50	(0.39 ± 0.01)$\times10^6$
Eu^{2+} (0.14)	iso (7.14)	Eu^{3+} (0.91)	0.90	225 ± 37
Eu^{2+} (0.14)	iso (7.14)	Eu^{3+} (1.43)	0.90	133 ± 6
Eu^{2+} (0.14)	iso (7.14)	Eu^{3+} (2.86)	0.90	55 ± 6

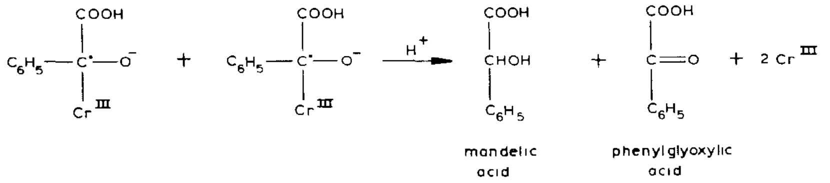
acid by Cr^{2+} represented by the overall eq. 14:



(14)

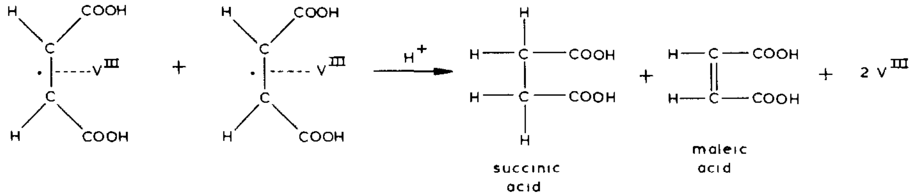
Disproportionation

This process takes place in the reaction between Cr^{2+} and phenylglyoxylic acid [1c], in competition with dimerization, and leads to reduction of the carbonyl double bond represented by the overall eq. 15:



(15)

Disproportionation is also observed in the reaction between V^{2+} and maleic and fumaric acids [8b], and corresponds to terms second-order in V^{2+} and second-order in the organic ligand (eq. 16, see also the rate law (1) for the reaction):

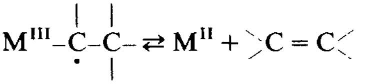


(16)

Reaction 16 is associated with isomerization of maleic to fumaric acid. The dimer is not formed.

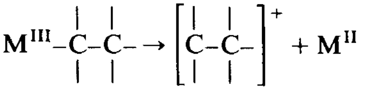
Heterolytic cleavage-olefin elimination

This process is the reverse of the ion-radical formation reaction (eq. 17):

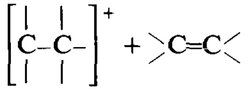


$$M^{III}-\underset{\bullet}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}- \rightleftarrows M^{II} + {>}C=C{<} \qquad (17)$$

Equilibrium 17 is established rapidly, as indicated by an increase in the absorbance at zero time in all the systems which were investigated. The values of the equilibrium constants [8,9] lie between 10^{-1} and 10. Kinetic data for the establishment of these equilibria are not available, but from the equilibrium constants, the rates of the overall reactions, and the products obtained, we are tempted to postulate that at least in some cases the mechanism of the forward reaction involves formation of a carbocation (eq. 18), see also eq. 5, which is transformed quickly into an olefin (eq. 19),

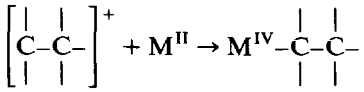


$$M^{III}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}- \rightarrow \left[\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\right]^{+} + M^{II} \qquad (18)$$



$$\left[\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-\right]^{+} + \;{>}\text{C}{=}\text{C}{<} \tag{19}$$

unless intercepted by another reagent present in the solution, e.g. by an oxidative addition to a metal ion (eq. 20):



$$\left[\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-\right]^{+} + \text{M}^{\text{II}} \rightarrow \text{M}^{\text{IV}}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}- \tag{20}$$

From this point of view olefin elimination from the ion-radicals is related to the heterolytic cleavage [3].

Comparisons

The information summarized in Table 4 can be used to compare different metal ions and ligands.

Let us first compare the ion-radicals derived from maleic acid and Cr^{2+} or V^{2+}. Nucleophilic attack by a second metal ion is observed in both cases, but with Cr^{2+} the reaction is faster by several orders of magnitude (Table 5). This striking difference can be attributed, at least partly, to the mode of coordination. Eisenstein

TABLE 4

OBSERVED REACTION PATHWAYS OF VARIOUS ION-RADICALS

Ion-radical	Coordination	Competing paths	Overall reaction
$\text{Cr}^{\text{III}}\text{-}\dot{\text{m}}\text{a}$	η^1	Nucleophilic attack by a second chromium(II) ion and free radical [a]	Hydrogenation of the carbon–carbon double bond
$\text{Cr}^{\text{III}}\text{-}\dot{\text{m}}\text{ema}$	η^1	Same as above	Same as above
$\text{Cr}^{\text{III}}\text{-}\dot{\text{p}}\text{gl}$	η^1	Dimerization and Disproportionation	Hydrogenation of the carbon–oxygen double bond and C–C bond formation
$\text{V}^{\text{III}}\text{-}\dot{\text{m}}\text{a}$	η^2	Nucleophilic attack by a second vanadium(II) ion and dimerization.	Hydrogenation of the carbon–carbon double bond
$\text{V}^{\text{III}}\text{-}\dot{\text{m}}\text{ema}$	η^2	Dimerization only	Same as above
$\text{V}^{\text{III}}\text{-}\dot{\text{p}}\text{yr}$	η^2	Free radical and dimerization [b]	C–C bond formation
$\text{Ti}^{\text{IV}}\text{-}\dot{\text{p}}\text{yr}$	η^2	Dimerization only	C–C bond formation
$\text{Eu}^{\text{III}}\text{-}\dot{\text{p}}\text{yr}$	η^1	Free radical only	Hydrogenation of the carbon–oxygen double bond
$\text{Eu}^{\text{III}}\text{-}\dot{\text{p}}\text{yr}$	η^1	Free radical only	Same as above

[a] Nucleophilic attack in excess Cr^{2+}. Similarly for $\text{Cr}^{\text{III}}\text{-Cl}\dot{\text{m}}\text{a}$, $\text{Cr}^{\text{III}}\text{-Cl}_2\dot{\text{m}}\text{a}$. [b] Assisted by a second pyr.

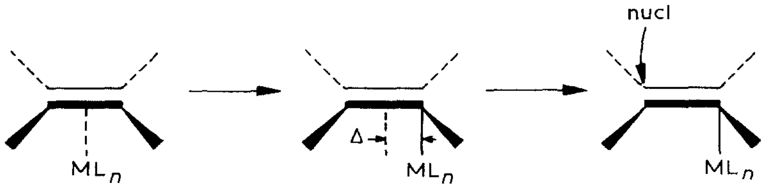
TABLE 5

THIRD-ORDER RATE CONSTANTS [a] IN THE REACTIONS OF $\text{Cr}^{2+}_{\text{aq}}$ AND $\text{V}^{2+}_{\text{aq}}$ WITH MALEIC ACID (Room temperature)

Ion	$k^{(3)}$ (s^{-1} M^{-2})
Cr^{2+}	59.5
V^{2+}	0.018 [b]

[a] Rate term $k^{(3)}$ $[\text{M}^{2+}]^2[\text{L}]$. [b] Acid independent term (see rate law 1).

and Hoffmann [17] have shown theoretically that nucleophilic attack on an η^2-olefin complex like that formed between V^{2+} and maleic acid is preceded by a displacement of the metal towards one of the carbons (eq. 21).



(21)

This displacement is not necessary in the Cr^{III}–˙ma ion-radical, which already has η^1-geometry because of the symmetry of the donor (HOMO) orbital of Cr^{2+}.

Free radical formation is less facile than nucleophilic attack. With Cr^{III}–˙ma (or Cr^{III}–˙mema) it is observed only in the absence of free Cr^{2+} and with V^{III}–˙ma not at all. The difference between chromium and vanadium can be attributed to the difference in oxidation potentials ($E°$ +0.40 V for Cr^{2+}/Cr^{3+}_{aq}, $E°$ +0.255 V for V^{2+}_{aq}/V^{3+}_{aq}). With Cr^{2+} the donor electron is more effectively displaced over the organic ligand. Between the two extremes:

M^{II}–olefin ↔ M^{III}–free radical

V^{III}–˙ma [4] lies more to the left, while Cr^{III}–˙ma to the right.

The fact that Cr^{III} is substitution inert certainly contributes to the slowness of the free radical path. With the labile Eu^{III} this path generally dominates.

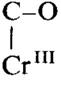
In comparing V^{III}–˙pyr and Ti^{IV}–˙pyr (pyr = pyruvic acid) we first note that in both there is no free radical formation, which is consistent with the explanation given above for V^{III}–˙ma. In the V^{III}–˙pyr system a free radical path is observed, but only if it is assisted by a second pyruvate or by a saturated carboxylic ligand [18], which facilitates electron displacement over the η^2-bonded pyruvic acid. With Ti^{3+}_{aq}, which is a weaker reducing agent (for $Ti^{III}_{aq}/Ti^{IV}_{aq}$ $E°$ 0.04 V), even this assistance does not help. The free radical path predominates in the V^{III}–˙pgl (phenylglyoxylic acid) system, presumably because of the presence of the electron attracting phenyl ring.

In contrast to Cr^{III}–˙ma, with Cr^{III}–˙pgl we have neither nucleophilic attack nor free radical formation. Assuming for simple electrostatic reasons that the nucleophilic attack takes place on the neighboring carbon:

$$\begin{array}{l} C\text{–}\dot{C} \\ | \\ Cr^{III} \end{array}$$

(1)

we may argue that it is less favored if this carbon is replaced by the more electronegative oxygen:



$$\begin{array}{l} C\text{–}\dot{O} \\ | \\ Cr^{III} \end{array}$$

(2)

TABLE 6

RATE LAWS OF THE REACTIONS OF Cr_{aq}^{2+} WITH MALEIC ACID AND ITS CHLORO- AND METHYL DERIVATIVES

Free ligand, L		Rate law $[Cr^{2+}]_0 > [L]_0$	$k^{(3)}$ $(s^{-1}\,M^{-2})$	Rate law $[Cr^{2+}]_0 < [L]_0$	$k'^{(2)}$ $(s^{-1}\,M^{-1})$	$k'^{(3)}$ $(s^{-1}\,M^{-2})$
Name	Formula					
Chloromaleic acid	ClCCOOH ‖ HCCOOH	$k^{(3)}[Cr^{2+}]^2[L]$	75 ±7	$k'^{(3)}[Cr^{2+}][L]^2$	–	16.5 ±1.7
Maleic acid	HCCOOH ‖ HCCOOH	same law	59.5 ± 3	$k'^{(2)}[Cr^{2+}][L] + k'^{(3)}[Cr^{2+}][L]^2$	0.65 ± 0.3	2.5 ±0.05
Dichloromaleic acid	ClCCOOH ‖ ClCCOOH	same law	3.0 ± 0.3	same law	0.13 ± 0.01	0.37 ± 0.01
Methylmaleic acid	H_3CCCOOH ‖ HCCOOH	same law	0.02	same law	0.11	1.78

We may also argue that this electron displacement towards oxygen and the fact that the acceptor $\pi^\star$ orbital of the carbonyl is polarized on carbon making the overlap with the donor orbital better, makes the chromium–carbon bond in **2** stronger than in **1**, and homolysis more difficult.

Similar considerations apply in the comparison of V^{III}– ˙pyr and V^{III}– ˙ma, except that now we also have the preceding displacement of the metal ion from the η^2- towards the η^1-geometry (eq. 21), which requires more activation.

Finally, it is also instructive to compare ligands differing only in substituents. More specifically we compare maleic, chloromaleic, dichloromaleic, and methylmaleic acids. The rate laws and rate constants are summarized in Table 6. The observed rate constants are mainly determined by two factors: the equilibrium constant for the formation of the ion-radical, and the rate constants of the subsequent reactions, i.e. of the nucleophilic attack by Cr^{2+} or of the homolytic cleavage of the Cr^{III}–C bond.

In chloromaleic acid the LUMO ($\pi^\star$) is polarized on the carbon next to that bound to the electronegative chlorine and the overlap in an η^1-coordination is larger. As a result the equilibrium constant for chloromaleic acid is larger than those for maleic and dichloromaleic. Strictly speaking the value of the equilibrium constant is determined by other factors as well (e.g. hydration energies), but within the series examined these factors are not expected to vary much.

For the same reasons, Cr–C bond is stronger in Cr^{III}–Cl˙ma, and homolytic cleavage slower. In fact, for this ligand, only the ligand-assisted homolytic path (second order in L) is observed. With methylmaleic (citraconic) acid $\pi^\star$ is polarized on the carbon bearing the methyl group, and the attachment of the first chromium is sterically hindered. Steric hindrance has opposite effects on the equilibrium constant and on the rate constants for homolytic cleavage. As a result the observed rate constant $k'^{(2)}$ for methylmaleic acid is almost equal to that for dichloromaleic, and $k'^{(2)}$ is larger (Table 6).

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4 If we designate our species as $Cr^{IV}R^-$, $V^{IV}R^-$ etc., the reverse reaction can be characterized as olefin elimination, and the formation of a free radical as homolytic cleavage. In principle, these metal–olefin systems can range all the way from M^{II}–olefin to M^{III}–free radical, and to M^{IV}–anion. For simplicity we use throughout the symbol M^{III}–R˙ (M^{IV}–R˙ for titanium). We also use the abbrevia-

tions: ma = maleic, Clma = chloromaleic, Cl_2ma = dichloromaleic, mema = methylmaleic, pyr = pyruvic, pgl = phenylglyoxylic acids, iso = isonicotinic acid.

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