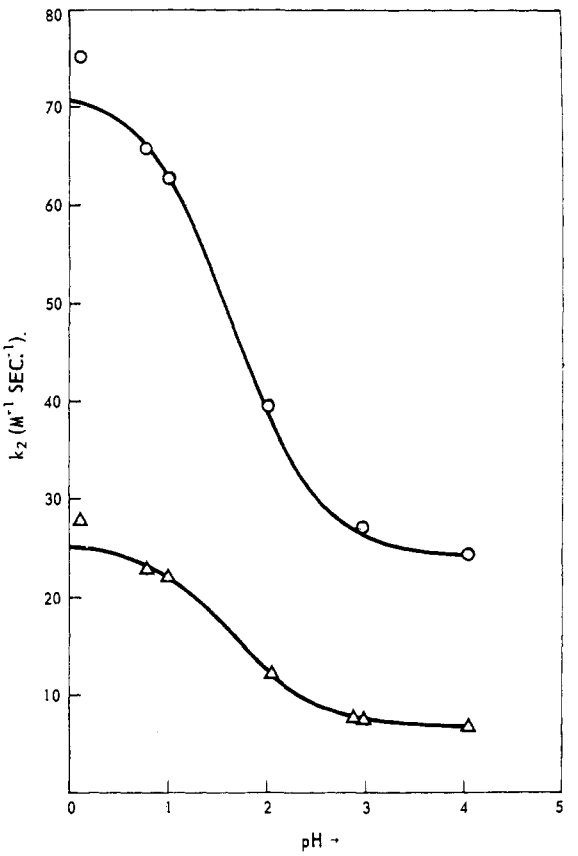


Fig. 6.—Dependence of second-order rate constant on pH at 25.0: O, experimental points for hydroquinone; Δ, experimental points for *p*-methoxyphenol.

the agreement between calculated and observed values is good. Our results are depicted graphically in Fig. 6, and they lead to the conclusion that both the un-ionized and monoionized forms of periodate are active in oxidizing hydroquinone and *p*-methoxyphenol.

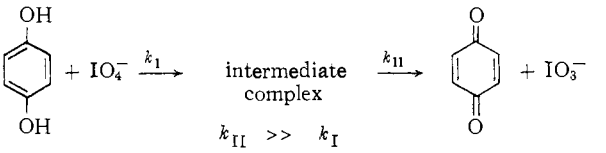
TABLE V

VARIATION OF THE SECOND-ORDER RATE CONSTANT FOR THE OXIDATION OF *p*-METHOXYPHENOL WITH pH AT 25.0°

pH	Obsd. k_2,[a] M^{-1} sec.$^{-1}$	Calcd. k_2,[b] M^{-1} sec.$^{-1}$
0.105	27.9	25.0
0.78	22.9	23.2
1.00	21.9	22.0
2.04	12.9	12.0
2.89	7.83	7.67
2.97	7.65	7.48
4.05	6.76	6.72

[a] Except for the pH 1 data, all observed k_2 values are the result of 3 runs at each pH. [b] k_2 is calculated from eq. 9 with k_a = 25.5 M^{-1} sec.$^{-1}$ and k_b = 6.65 M^{-1} sec.$^{-1}$ for *p*-methoxyphenol.

The kinetic results obtained for the oxidation of hydroquinone and *p*-methoxyphenol contrast markedly with those previously reported for aliphatic glycols. We have found no evidence for the formation of a kinetically detectable intermediate in the oxidation of hydroquinone and its monomethyl ether at pH 1 even with stopped-flow methods. Our results are best interpreted in terms of second-order kinetics. However, this does not rule out the possibility that substrate–periodate complexes are intermediates in oxidation at pH 1 if their formation rather than their decomposition to products is rate controlling.



Further evidence concerning the mechanism of the periodate oxidation of aromatic diols and their mono ethers is being actively sought in our laboratory.

[CONTRIBUTION FROM THE DEPARTMENTS OF NEMATOLOGY AND CHEMISTRY, UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIF.]

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

BY C. E. CASTRO AND R. D. STEPHENS

RECEIVED MAY 1, 1964

The homogeneous reduction of acetylenes by chromous sulfate in water or aqueous dimethylformamide at room temperature yields *trans*-olefins in high yields. The stoichiometry, stereospecificity, kinetics, and reactivities of the acetylenes toward Cr^{+2} are in accord with a mechanism which involves a rate-determining attack of Cr^{+2} upon a 1:1 acetylene–Cr^{+2} complex.

Introduction

Low-valent transition metal species are present in Ziegler–Natta polymerization catalysts[1] and active sites in these systems have been located at a transition metal center.[2] Moreover, transition metal complexes are well known to play a key role in many enzymatic transformations in which a valence change of the metal species occurs.[3] Yet, much is to be learned about the nature of the interaction of low valent ions with organic structures in less complicated environments.

As part of a study of the homogeneous reduction of organic molecules by transition metal ions we have found the acetylenic bond to be one of the most effective multiply bonded structures to accomplish the oxidation of Cr(II) to Cr(III).[4]

The reduction of acetylene to ethylene by an am-

(1) M. L. Cooper and J. B. Rose, *J. Chem. Soc.*, 795 (1959); C. Beerman and H. Bestian, *Angew. Chem.*, **71**, 618 (1959).

(2) W. L. Carrick, F. J. Karol, G. J. Karapinka, and J. J. Smith, *J. Am. Chem. Soc.*, **82**, 1502 (1960); W. L. Carrick, *et al.*, *ibid.*, **82**, 5319 (1960), *et seq.*

(3) J. S. Fruton and S. Simonds, "General Biochemistry," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 11, 12, and 13.

(4) This work has been reported in part: C. E. Castro and R. D. Stephens, 143nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, Abstracts, p. 23Q.

moniacal solution of chromous sulfate was first reported[5a] early in this century. Subsequently, the acetylene to ethylene conversion has been accomplished in acidic media with chromous chloride.[5b-d] Similarly, propiolic acid[5e] and monosodium acetylenedicarboxylate[5f] are reported to oxidize chromous chloride solutions. The heterogeneous reduction of phenylpropiolic acid by chromous hydroxide to *cis*- and *trans*-cinnamic acid[6] and phenylpropionic acid[5c] has been noted, as has the reduction of enynes[7] to dienes of the vitamin A series with this reagent.

Results

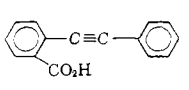
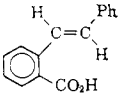
Stoichiometry and Stereochemistry.—The homogeneous reduction of acetylenes (0.1–0.3 *M*) by chromous sulfate (0.4–0.7 *M* Cr^{+2}) proceeds readily at room temperature in water (pH ~ 4) or aqueous dimethylformamide under a nitrogen atmosphere. Internal acetylenes are converted in a stereospecific manner to *trans*-olefins (1).

$$2H^+ + 2Cr^{+2} + RC{\equiv}CR' \longrightarrow 2Cr^{+3} + \begin{matrix} R & & H \\ & C{=}C & \\ H & & R' \end{matrix} \quad (1)$$

The results of the reduction of a variety of acetylenes are reported in Table I. No other organic products

TABLE I

PRODUCTS OF THE REDUCTION OF ACETYLENES BY CHROMOUS SULFATE IN WATER

Reactant	Product	Yield, %
$HC{\equiv}CCH_2OH$	$CH_2{=}CHCH_2OH$	89
$HC{\equiv}CPh$[a]	$CH_2{=}CHPh$	94
$HO_2CC{\equiv}CCO_2H$	$\begin{matrix} HO_2C & & H \\ & C{=}C & \\ H & & CO_2H \end{matrix}$	94
$PhC{\equiv}CCO_2H$	$\begin{matrix} Ph & & H \\ & C{=}C & \\ H & & CO_2H \end{matrix}$	91
$CH_3C{\equiv}CCH_2OH$	$\begin{matrix} CH_3 & & H \\ & C{=}C & \\ H & & CH_2OH \end{matrix}$	84
$HO{-}CH_2C{\equiv}CCH_2{-}OH$	$\begin{matrix} HO{-}CH_2 & & H \\ & C{=}C & \\ H & & CH_2{-}OH \end{matrix}$	92
		85

[a] Run in 2:1 DMF–H_2O.

were detected, and the yields reflect the efficiency of the work-up procedure. Isomerization of *cis*- or *trans*-olefins did not occur under reaction conditions.[8] The

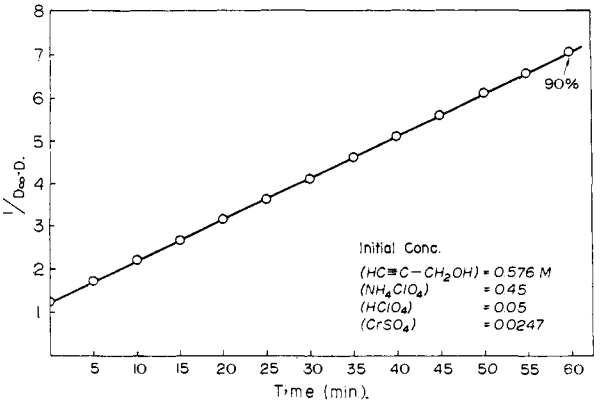


Figure 1.

trans stereochemistry of these reductions accords with that reported for the reduction of dideuterioacetylene[5d] and, by analogy with this case, for propyne-1-*d*[9] by aqueous acidic chromous chloride.[10]

It is noteworthy that in water the spectrum of the Cr(III) product (λ_{max} 409, 575 mμ) corresponds to that of the aquo ion $Cr(H_2O)_6^{+3}$. However, when the reaction is run in dimethylformamide–water the product spectrum corresponds to that of the inner sulfate complex[11] $Cr(SO_4)^+$ (λ_{max} 585 mμ) in this solvent. The spectra and extinction coefficients are given in the Experimental section (Table IV).

Reactivity.—Qualitatively the reactivity of acetylenes (~0.2 *M*) toward chromous sulfate (~0.5 *M*) can be grouped as (a) very reactive (instantaneous reaction essentially complete in 5–15 min. at room temperature) (propargyl alcohol, 1-butyn-3-ol, acetylenedicarboxylic acid, phenylpropiolic acid, and 1,4-dihydroxybutyne-2); (b) moderately reactive (reaction complete in 2–3 hr.) (2-butyne-1-ol, phenylacetylene, hexyne-1); (c) slow (1 day for completion) (2-carboxydiphenylacetylene); (d) inert (no appreciable reaction in 1 day) (diphenylacetylene, 2-amino-, 4-amino-, 2-methoxy-, 4-methoxy-, 4-hydroxy-, 4-carboxydiphenlacetylene, pentyne-2, and 2,5,5-trimethyl-3-hexyn-2-ol).

Thus, in the absence of hydroxylic substituents terminal acetylenes are more reactive than internal ones. On the contrary, the sequence illustrates the importance

$$HOCH_2C{\equiv}CCH_2OH \sim HC{\equiv}CCH_2OH > CH_3C{\equiv}CCH_2OH > HC{\equiv}C\textit{n}Bu \gg CH_3C{\equiv}CCH_2CH_3, \begin{matrix} CH_3 & & CH_3 \\ | & & | \\ CH_3C{-}C{\equiv}C{-}CCH_3 & & \\ | & & | \\ OH & & CH_3 \end{matrix}$$

of accessible coordination sites on the acetylene.

Kinetics.—The kinetics were studied by employing varying high (20-fold excess) initial concentrations of substrates. A typical pseudo-second-order plot of $1/(Cr^{+2})$ *vs.* time is depicted in Fig. 1. In all cases good linearity was obtained through 90% completion. With stoichiometric ratios of reactants, third-order

(5) (a) M. Berthelot, *Ann. chim. phys.*, [4] **9**, 401 (1909); (b) W. Traube and W. Passarge, *Ber.*, **49**, 1692 (1916); (c) W. I. Patterson and V. du Vigneaud, *J. Biol. Chem.*, **123**, 127 (1938); (d) J. E. Douglas and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **74**, 2486 (1952); (e) R. S. Bottei, *Anal. Chem. Acta*, **30**, 6 (1964); (f) R. S. Bottei and N. H. Furman, *Anal. Chem.*, **27**, 1183 (1955).

(6) E. Ott and V. Barth, *Ber.*, **67**, 1672 (1934).

(7) Ortho Pharmaceutical Corp., British Patent 740,851 (1955).

(8) The reduction of acetylenes by Cr^{+2} can be cleanly controlled to stop at the olefin. However, contrary to recent reports [K. D. Kopple, *J. Am. Chem. Soc.*, **84**, 1586 (1962)], olefins bearing electron-withdrawing substituents can be reduced at room temperature under the same (acidic) reaction conditions to the alkane. Our studies of the slower reduction of olefins will be reported separately.

(9) B. S. Rabinovitch and F. S. Looney, *ibid.*, **75**, 2652 (1953).

(10) In the case of reactive carbonyl conjugated acetylenes, acidic solutions of this reagent allow the possibility of reduction by a nonstereospecific path involving HCl addition followed by Cr(II) cleavage of the carbon–halogen bond. The reductive dimerization of 1,1-diphenylethylene is such a case: C. E. Castro, *ibid.*, **83**, 3262 (1961).

(11) Detailed spectra of these solutions were recently published: N. B. Fogel, J. M. J. Tai, and J. Yarborough, *ibid.*, **84**, 1145 (1962).

plots of $1/(Cr^{+2})^2$ *vs.* time were nicely linear. The disappearance of Cr(II) was followed by a titrimetric procedure.[12] In separate runs the appearance of Cr(III) was determined spectrophotometrically at 590 mμ. The third-order rate expression (2) was cleanly obeyed.

$$\text{rate} = k_3(Cr^{+2})^2(\text{acetylene}) \qquad (2)$$

A summary of the kinetic data appears in Table II. The very mild temperature dependence of k_3 for the reduction of propargyl alcohol in water is portrayed in Table III.

TABLE II
RATES OF REDUCTION OF ACETYLENES BY CHROMOUS SULFATE AT 22°

Acetylene	Solvent[a]	H^+,[b] mole/l.	μ[c]	k_3[d] × 10², l.²/mole²/sec.	Method[e]
$HC{\equiv}CCH_2OH$	H_2O	0.50	0.5	1.2	T
$HC{\equiv}CCH_2OH$	H_2O	.50	.5	1.32	S
$HC{\equiv}CCH_2OH$	D_2O	.50	.5	0.37	S
$HC{\equiv}CCH_2OH$	1:1 DMF–H_2O	.50	.5	13.0	S
$HC{\equiv}CCH_2OH$	1:1 DMF–H_2O	.05	.5	12.6	S
$HC{\equiv}CCH_2OH$	1:1 DMF–H_2O	10^{-4}	.5	13.7	S
$HC{\equiv}CCH_2OH$	1:1 DMF–H_2O	1.10	1.10	23.7	S
$CH_3C{\equiv}CCH_2OH$	2:1 DMF–H_2O	0.55	0.55	1.7	S
$PhC{\equiv}CH$	2:1 DMF–H_2O	0.55	0.55	0.028	S

[a] Volume ratios. [b] Perchloric acid added. [c] Ionic strength adjusted with NH_4ClO_4. [d] Rate constants are the average of at least 3 runs; precision was within 5%. [e] T = titrimetric, S = spectrophotometric.

TABLE III
TEMPERATURE DEPENDENCE OF k_3 FOR THE REDUCTION OF PROPARGYL ALCOHOL BY CHROMOUS SULFATE IN WATER WITH (H^+) = 0.53 *M* = IONIC STRENGTH

Temp., °C.	k_3 × 10², l.²/mole²/sec.	Method
0.3	0.88	T
18.3	1.4	S
18.3	1.4	T
21.4	1.3	T
41.6	1.2	T

Reduction with Cr(II) EDTA.—The reduction of 2-butyn-1-ol with chromous ethylenediaminetetraacetate in aqueous media at pH 9–10 was examined to ascertain the influence of a highly coordinated Cr(II) upon the course of the reaction.[13] Moreover, the large reductive capacity of this entity (Cr(II) EDTA → Cr(III) EDTA, $E_{1/2} = -1.4$ v. *vs.* s.c.e.[14]) was desirable. The reaction proceeded only to 6% completion in 2 days. The product distribution indicated by gas chromatography was *trans*-crotyl alcohol 1–2%, *cis*-crotyl alcohol ~60%, 3-buten-1-ol ~40%. This reaction was too slow for rate studies and consequently the more rapid reduction of propargyl alcohol by Cr(II) EDTA was examined. This latter reduction proceeded with a rate independent of acetylene. The expression

$$\text{rate} = k_3(Cr^{(II)})^3_{\text{total}} \qquad (3)$$

(3) was valid through 85% completion.

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

(13) Recent studies [R. L. Pecsok, *Anal. Chem.*, **35**, 1995 (1963)] suggest a quinquedentate coordination of Cr^{+2} with EDTA; W. C. E. Higginson, *J. Chem. Soc.*, 2761 (1962), proposes such a binding for a variety of divalent cations.

(14) R. L. Pecsok, L. D. Shields, and W. P. Schaefer, *J. Inorg. Chem.*, **3**, 114 (1964), and references therein.

Discussion

A mechanism that is most consistent with our observations is: the rapid and reversible formation of a 1:1 acetylene–chromous complex (4) followed by the rate-determining attack of chromous on the chromous–acetylene complex (5).

$$Cr^{+2} + RC{\equiv}CR \underset{}{\overset{K_1}{\rightleftharpoons}} \left[\begin{matrix} RC{\equiv}CR \\ \vdots \\ Cr^{++} \end{matrix}\right]_I \qquad (4)$$

$$Cr^{+2} + \left[\begin{matrix} RC{\equiv}CR \\ \vdots \\ Cr^{++} \end{matrix}\right]_I \xrightarrow[\text{slow}]{k_2} 2Cr^{+3} + \begin{matrix} R & & H \\ & C{=}C & \\ H & & R' \end{matrix} \qquad (5)$$

The 1:1 Complex.—The reactivity sequence noted above is not what would be expected for the reaction of acetylenes with nascent hydrogen,[5b,15] but, rather, it parallels the facilities with which the acetylenes might be expected to function as ligands for metal ions.[16,17]

That coordination is essential to reaction is emphasized by the fact that *o*-carboxytolane is reduced by chromous whereas the *para* isomer is not. Furthermore, upon the reduction of the former bidentate ligand a transient red color is observed initially which might be attributed to the 1:1 complex.[18] A similar red color is observed during the initial phase of the reduction of acetylenedicarboxylic acid. The rapid equilibrium (4) is in keeping with the rapid exchange rates of Cr (II) complexes.[19]

By similar considerations the Cr(II) EDTA reduction of 2-butyne-1-ol would not be expected to proceed by the same mechanism. Indeed, the facts that the reaction is quite slow in spite of the very favorable thermodynamics[12] and that the *trans* stereochemistry is lost points up the necessity for "proper" coordination with the acetylene. Similarly, the markedly different kinetics of the reduction of propargyl alcohol by Cr(II) EDTA and Cr^{+2} further emphasize the different course of these reductions.[20]

It would seem reasonable that a quinquedentate Cr(II) EDTA complex should be capable of binding an acetylene but not a water molecule simultaneously. Consequently, a transition state corresponding to II depicted below should be precluded in this milieu.[21,21a]

The Rate-Determining Step.—Certainly the second chromous ion should approach a chromous–acetylene complex (I) from the side opposite to that of the metal ion already there and at a position most remote from it. Thus, electrostatic considerations and the stereospeci-

(15) The chromous titer of stock solutions is stable for months.

(16) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

(17) Though not strictly a fair comparison, because of different coordination properties, the stabilities of Ag^+–acetylene complexes decrease with substitution of methyl groups on the α-carbon: G. K. Helmkamp, F. L. Carter, and H. J. Lucas, *J. Am. Chem. Soc.*, **79**, 1308 (1957).

(18) If a Cr(III)–acetylene complex should be present, it must rapidly be reduced by Cr^{+2} since even with stoichiometric ratios of reactants good third-order kinetic plots were obtained. Hence the Cr(III) product is not inhibiting the reaction as might be expected if significant concentrations of a slow reacting Cr(III)–acetylene complex were present.

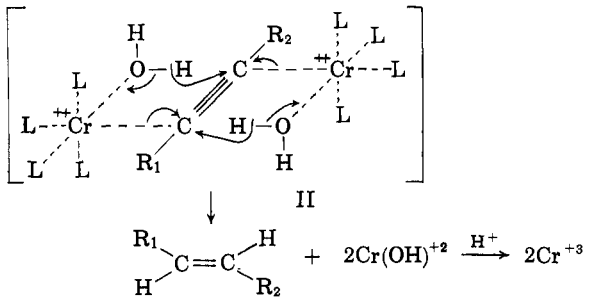
(19) D. R. Stranks and R. G. Wilkins, *Chem. Rev.*, **57**, 743 (1957).

(20) It is possible that with propargyl alcohol the Cr(II) EDTA reduction proceeds *via* an acetylide bond to metal.

(21) The nature of the Cr(II) EDTA reduction as well as the influence of other ligands upon the course of these and related transformations bear a much more detailed study.

(21a) NOTE ADDED IN PROOF.—Evidence for a 2:1 complex of Cr(II) with acetylenedicarboxylic acid has recentley been obtained; private communication from Dr. R. S. Bottei and Mr. W. A. Joeru, Department of Chemistry, University of Notre Dame.

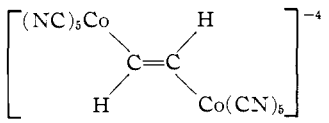
ficity of the reaction suggest a transition state (II) that resembles the structure advanced for the *trans*-



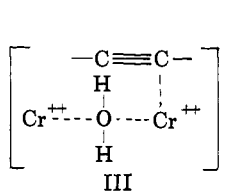
II

$$\frac{R_1}{H}C{=}C\frac{H}{R_2} + 2Cr(OH)^{+2} \xrightarrow{H^+} 2Cr^{+3}$$

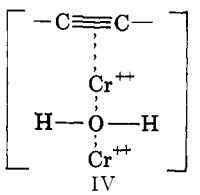
σ-bonded acetylenedicobalticyanide.[22] The *trans* stereo-



chemistry would be imparted by a concomitant departure of chromium and back-sided proton transfer from the solvation spheres of the metal ions. Such a process is analogous to that advocated to explain the reduction of alkyl halides by chromous ions.[12] In support of II, an Arrhenius plot of the exceedingly small temperature dependence of k_3 for propargyl alcohol places $\Delta H^* < 1$ kcal. and $\Delta S^* \sim -60$ e.u. This large entropy loss is what would be expected for a charged, highly ordered transition state that should be strongly solvated.[23] Additional support for proton transfer in the transition state is adduced from the observation that the reduction of propargyl alcohol proceeds 3.5 times more rapidly in water than in D_2O. However, since the rate of reduction of $(H_3N)_5Co(H_2O)^{+3}$ by Cr^{+2}, which does not involve hydrogen transfer, decreases by a factor of 3.8 in D_2O,[24] our argument, though compelling, is not without ambiguity. On the other hand, it is difficult to conceive of an alternate transition state that would account for the stereochemistry. Thus, III and IV which more



III



IV

nearly parallel the movements thought to occur in the reduction of $(H_3N)Co(OH)_2^{+3}$ by Cr^{+2}, should collapse to *cis* or a mixture of *cis* and *trans*-olefin, respectively.

The increased rate in DMF–H_2O and the fact that sulfate is in the Cr(III) product indicate that sulfate is present in the transition state as a ligand on Cr(II). Thus, even though the media is of lower dielectric constant than water, the reaction is more rapid because of a lessened repulsive interaction between the chromium species. The spectrum of $CrSO_4$ in DMF–H_2O and H_2O is presented in Fig. 2 and might be taken to indicate some degree of ion pairing.

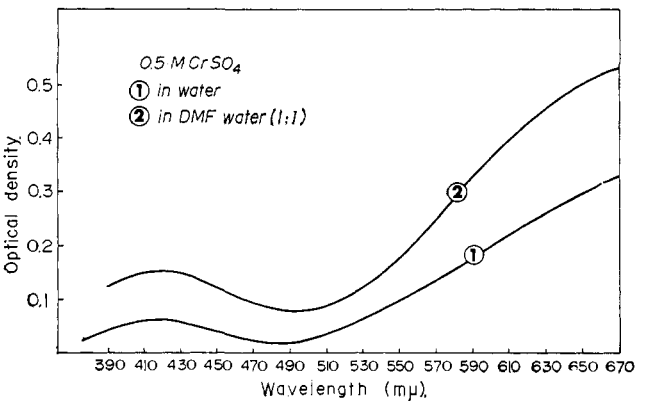


Figure 2.

The mechanism proposed for these reductions is similar to that recently suggested for the reduction of carbonyl conjugated olefins by cobalt hydrocarbonyl,[25] although in this case hydride is transferred from metal to carbon within a complex. Furthermore, the Ru(II) catalyzed hydrogenation of fumaric acid, in which the hydrogen that adds to the olefin is derived from the solvent,[26] would seem to be related.

Finally it should be noted that a transition state similar to II could explain the *trans* stereospecificity of the Birch reduction of acetylenes[27] as cogently as a "solvated electron" addition–protonation pathway.[28] In this system collapse of a 2:1 sodium ammonia–acetylene complex should result directly in *trans*-olefin and sodium amide.

Experimental

Materials.—Solutions of chromous sulfate and solid $CrSO_4 \cdot 5H_2O$ were prepared and stored as previously described.[12] Commercial samples of acetylenes were either freshly distilled or recrystallized before use and their physical properties checked those of the literature. The preparation of most of the unsymmetrical tolanes used in this work has been described.[29]

2-Aminodiphenylacetylene was obtained by the stannous chloride reduction of 2-nitrodiphenylacetylene.[30] The purified material had m.p. 88–89°.

2-Carboxydiphenylacetylene.—Methyl *o*-iodobenzoate (6.05 g., 0.023 mole), obtained from treatment of the acid with diazomethane, was allowed to react with 3.8 g. (0.023 mole) of cuprous phenylacetylide in 100 ml. of refluxing pyridine under nitrogen. After 6 hr. the reaction mixture was diluted with 200 ml. of water and extracted thrice with ether. The ether extracts were washed with dilute HCl and water and dried over $MgSO_4$. The dried extracts were concentrated to yield 5.2 g. (0.022 mole, 95%) of crude 2-carboxymethyldiphenylacetylene. The infrared spectrum of this material showed C=O at 5.86, C≡C at 4.58, and C—O—C at 9.5 μ. The ester was saponified with 1.5 *N* KOH at reflux for 1 hr. The basic solution was extracted with ether. The aqueous phase was acidified with 6 *N* H_2SO_4, extracted with ether, and dried over magnesium sulfate. The dried concentrated extracts afforded a viscous glass. The substance was crystallized from 4:1 DMF–H_2O to yield 4.2 g. (76%) of 2-carboxydiphenylacetylene hemihydrate, m.p. 116–118°. The infrared spectrum showed C≡C at 4.6, C=O at 5.8, and broad acid OH at 2.9–3.4 μ.

Anal. Calcd. for $C_{15}H_{11}O_{2.5}$: C, 78.18; H, 4.78. Found: C, 78.53; H, 4.68.

Kinetics.—The titrimetric procedure has been described.[12] For the present studies initial concentrations of Cr^{+2} generally

(22) G. Wilkinson and W. P. Griffith, *J. Chem. Soc.*, 1629 (1959). Indeed, a finite existence for a reversibly formed II cannot be discounted.

(23) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 132–133.

(24) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **81**, 1288 (1959); the activation parameters ($\Delta H^* \sim 3$ kcal., $\Delta S^* \sim -52$ e.u.) are not vastly different from the present case.

(25) R. W. Goetz and M. Orchin, *ibid.*, **85**, 2782 (1963).

(26) J. Halpern and B. R. James, Abstracts, 143nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, p. 23N.

(27) K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, **63**, 216, 2683 (1941).

(28) K. W. Greenlee and W. C. Fernelius, *ibid.*, **64**, 2505 (1942).

(29) R. D. Stephens and C. E. Castro, *J. Org. Chem.*, **28**, 3313 (1963).

(30) K. Shofield and T. Swain, *J. Chem. Soc.*, 2397 (1949).

ranged from 0.025 to 0.03 M and that of the acetylene from 0.5 to 0.7 M. Rate constants were evaluated from slopes of plots of $1/(Cr^{+2})$ *vs.* time by using the expression

$$k_3 = (\text{slope})/(\text{acetylene})_0$$

The best reproducibility in the spectrophotometric procedure was obtained when solid $CrSO_4 \cdot 5H_2O$ was dissolved in water in the ultraviolet cell under nitrogen and requisite amounts of $HClO_4$ and NH_4ClO_4 in DMF–water solutions were added under a nitrogen sweep. A 1-cm., 2-neck Cary cell fitted with a stopcock and a serum cap was employed. After recording the initial absorbance, the acetylene was injected, usually neat, into the cell with a hypodermic syringe. The change in absorbance at 590 mμ was recorded at 20°. The concentration range was that employed with the titrimetric procedure except that for runs at stoichiometric ratios of reactants $(Cr)^{+2}$ was 0.04–0.05 M and $(\text{acetylene})_0$ was 0.02–0.025 M. The expression 6 was plotted

$$1/D_\infty - D = kt/\epsilon_{Cr^{+3}} + 1/D_\infty - D_0 \qquad (6)$$

for runs in which an excess of acetylene was used. In eq. 6, D_0 = initial optical density, D_∞ = final optical density, D = optical density at time t, and $\epsilon_{Cr^{+3}}$ is the extinction coefficient at 590 mμ of either Cr^{+3} or $CrSO_4^+$ depending upon the solvent employed. The extinction coefficients are portrayed in Table IV. Rate constants were evaluated from the expression

$$k_3 = (\text{slope})\epsilon_{Cr^{+3}}/(\text{acetylene})_0$$

In water the product spectrum matched that of chromic perchlorate in water. The product spectrum in DMF–H_2O corresponded to that for chromic sulfate in DMF–H_2O. Third-order rate constants were evaluated from the slopes of the plots of eq. 7.

$$1/(D_\infty - D)^2 = k_3t/\epsilon_{Cr^{III}} + 1/(D_\infty - D_0)^2 \qquad (7)$$

Third-order rate constants were calculated from

$$k_3 = \text{slope}\ (\epsilon_{Cr^{+3}})$$

For propargyl alcohol rate constants calculated from either (6) or (7) were within 5% agreement.

TABLE IV

SPECTRA OF CHROMIC SULFATE AND PERCHLORATE IN DMF–WATER AND WATER

Chromic perchlorate (Cr^{+3})				Chromic sulfate ($CrSO_4^+$)			
1:1 DMF–H_2O		H_2O		1:1 DMF–H_2O		H_2O	
λ_{max}, mμ	ϵ[c]	λ_{max}, mμ	ϵ	λ_{max}, mμ	ϵ	λ_{max}, mμ	ϵ
409	12.9	409	14.0	425	35.5[a]	420	16.5
575	10.5	575	10.9	585	41.4	580	19.0
ϵ_{590}	10.1	ϵ_{590}	10.8	ϵ_{590}	40.8[b]	ϵ_{590}	18.4

[a] Absorption masked by DMF. [b] ϵ_{590} in 2:1 DMF is 34.7. [c] Molar absorbance.

With Cr(II) EDTA.—Solutions of EDTA disodium salt were adjusted to pH 11.5 with NaOH, made up to volume in the titrimetric reactor,[12] and thoroughly flushed with nitrogen while being vigorously stirred. The requisite amount of solid $CrSO_4 \cdot 5H_2O$ was added under a nitrogen sweep and the solution was stirred for 12 hr.[31] before the substrate was added in water. Initial concentrations were in the range $(Cr(II)) \sim 8.4 \times 10^{-3}$ M, Na_4EDTA 15×10^{-3} M, propargyl alcohol $6.3–12.6 \times 10^{-2}$ M. The pH was 10. Pseudo-third-order plots of $1/(Cr(II))_{total}^2$ *vs.* t were linear and the slopes were not influenced by changes in the total initial acetylene concentration. The expression

$$\text{rate} = k_3(Cr(II))_{total}^3$$

was obeyed through 85% completion.[32]

Reductions with $CrSO_4$.—The reduction of propargyl alcohol is presented as a typical case.

Propargyl Alcohol.—Into a 500-ml. 3-neck Morton flask containing 400 ml. of 0.71 N $CrSO_4$ reagent and equipped with a magnetic stirring bar, nitrogen inlet, and a serum cap, was injected 7.28 g. (0.13 mole) of propargyl alcohol. The blue to green color change of the stirred, nitrogen-blanketed, reaction solution was instantaneous. Within 5 min. after injecting the substrate, analysis of a 2-ml. aliquot demonstrated that 0.25 mole of Cr(II) had been consumed. The solution was allowed to stir overnight with no additional consumption of Cr(II). The dark green product solution was saturated with ammonium sulfate and extracted four times with ether. The ether extracts were dried over sodium sulfate and concentrated. The residue was distilled at atmospheric pressure; a fraction weighing 4.0 g. and having b.p. 95–97° and $n^{20}D$ 1.4138 was obtained. The infrared spectrum of this material was identical in every respect with that of authentic allyl alcohol.

In another run like the one above the dried ethereal extracts were analyzed by v.p.c. employing a 10-ft. diisodecyl phthalate–β,β-oxydipropionitrile column at 110°. Acetone was used as a marker. The gas chromatogram showed only ether, allyl alcohol, and acetone and no unreacted propargyl alcohol (which was readily resolved on this column). The saturated aqueous solution was stripped to dryness *in vacuo* and the distillate was analyzed for allyl alcohol by bromine titration. The combined yield of allyl alcohol was 89%.

The Reduction of Acetylenedicarboxylic Acid.—In the fashion described above for propargyl alcohol, 1.14 g. (0.010 mole) of acetylenedicarboxylic acid dissolved in 10 ml. of water was added to 50 ml. of 0.48 M $CrSO_4$. The reaction solution immediately became red. An aliquot withdrawn *ca.* 20 min. after mixing indicated that 0.021 mole of Cr^{+2} had been consumed. The green reaction solution was then basified with KOH and vacuum filtered from chromic hydroxide. The filtrate was acidified with concentrated H_2SO_4 to pH 1 and extracted three times with ethyl acetate. The organic extracts were dried over sodium sulfate, filtered, and concentrated *in vacuo*. The resulting light tan residue crystallized; 1.05 g., m.p. 290–294° (with sublimation). The acid was recrystallized once from ether–petroleum ether to yield 1.01 g. of white needles having a m.p. and mixture m.p. with authentic fumaric acid of 294° (with sublimation). The infrared spectrum of the product acid was identical with that of authentic fumaric acid.

A 1-g. sample of maleic acid was exposed to 50 ml. of 0.48 M chromic sulfate, obtained by preoxidizing the above chromous sulfate reagent, for 24 hr. The reaction was worked up in a manner entirely analogous to that described above. Unreacted maleic acid was recovered in 92% yield.

Phenylacetylene.—The acetylene (0.93 g., 0.0091 mole) was treated with a solution composed of 40 ml. of 0.495 N $CrSO_4$ (0.0183 mole), 20 ml. of water, and 50 ml. of dimethylformamide. Duplicate aliquots (2 ml.) were withdrawn after 12 hr. One analyzed for Cr^{+2}, the other, after injecting into water, extracting with ether, and drying, was analyzed for styrene and phenylacetylene by v.p.c. A 6 ft. Carbowax 20M column was used. The results showed 2 moles of Cr^{+2} consumed (at this time 0.0049 mole) for every mole of styrene produced and phenylacetylene consumed. After 72 hr. the reaction yielded 0.85 g. (0.0082 mole) of styrene (89%). The infrared spectrum, refractive index, and gas chromatogram were identical with authentic styrene.

Phenylpropiolic Acid.—The acetylene (2.50 g., 0.017 mole) in 200 ml. of 1:1 DMF–water was treated with 100 ml. of 0.47 M $CrSO_4$ (0.047 mole). The solution immediately turned green. After 15 min., 0.0135 mole of Cr^{+2} (40% reaction) was consumed. After 3 hr., work-up like that for propargyl alcohol yielded 2.28 g. (0.031 mole, 91%) of *trans*-cinnamic acid. The infrared spectrum, m.p. and mixture m.p. 131–132° were identical with authentic *trans*-cinnamic acid.

2-Butyn-1-ol.—The acetylene (0.40 g., 0.0057 mole) in 25 ml. of water was treated with 25 ml. of 0.482 N $CrSO_4$ (0.012 mole). After 2 days, 0.0115 mole of $CrSO_4$ was consumed, and 0.336 g. (0.0047 mole, 83%) of *trans*-crotyl alcohol was obtained. The crude product was purified by gas chromatography using a 10-ft. Carbowax 1540 column that was saturated with silver nitrate. Infrared spectrum, $n^{25}D$ 1.4265, and emergence time were identical with authentic *trans*-crotyl alcohol. The *cis*-alcohol, obtained from the Raney nickel catalyzed hydrogenation of the olefin, was resolved on this column. No trace of the *cis* isomer was present in the product.

Reduction by Cr(II) EDTA.—EDTA (0.10 mole) was dissolved in 200 ml. of water and adjusted to pH 11.5. The volume was

(31) The Cr^{+2} titer did not change during this period. If kinetics were started immediately a rapid initial consumption of Cr(II) occurred which slowed markedly after 25 min. Presumably this was the result of a rapid oxidation of a Cr(II) species other than the one that is predominant after 12 hr.

(32) As in all cases reported herein graphs of the kinetic data for other orders of reaction than the one reported were clearly curved.

adjusted to 250 ml., and to the thoroughly nitrogen purged solution was added 12.0 g. (0.05 mole) of $CrSO_4 \cdot 5H_2O$ under nitrogen. The deep blue solution was allowed to stir overnight. The acetylene (1.0 g., 0.014 mole) was added. An aliquot after 2 days indicated ~6% of the Cr(II) had been consumed. The reaction solution was saturated with K_2CO_3 and extracted with ether. The extracts were dried over K_2CO_3, filtered, concentrated, and subjected to gas chromatographic analysis on a Carbowax–$AgNO_3$ column. The oil contained ~90% of unreacted acetylene. Of the small amount of products, the distribution was *trans*-crotyl alcohol ~1–2%, *cis*-crotyl alcohol ~60%, and 3-buten-1-ol ~40%.

2-Butyne-1,4-diol.—The acetylene (9.0 g., 0.105 mole) in 25 ml. of water was treated with 450 ml. of 0.483 *N* $CrSO_4$ (0.218 mole). The reaction was 90% complete in 30 min. After 2 hr. the green solution was basified with sodium hydroxide, filtered from $Cr(OH)_3$, and the filtrate stripped of water on a rotary evaporator at room temperature. The pasty residue was extracted with ether, dried over Na_2SO_4, and treated with 17 g. (0.106 mole) of bromine. The resulting solution was washed with dilute Na_2SO_4 and concentrated, thereby yielding 22.2 g. (0.0925 mole) of *meso*-1,4-dihydroxy-2,3-dibromobutane, m.p. 131° (lit.[33] m.p. 131°).

A sample of *cis*-2-butene-1,4-diol, prepared by the Raney nickel catalyzed hydrogenation of 2-butyne-1,4-diol, when brominated under these conditions gave *dl*-1,4-dihydroxy-2,3-dibromobutane, m.p. 86–87° (lit.[34] 87°).

2-Carboxydiphenylacetylene.—The acetylene (0.15 g., 6.8×10^{-4} mole) in 10 ml. of DMF was treated with a solution of 0.43 g. (18×10^{-4} mole) of $CrSO_4 \cdot 5H_2O$ in 30 ml. of water and 50 ml. of DMF. Upon mixing, the reaction solution became red. The red color gradually dissipated. At 2 days the reaction solution was green. After 3 days the solution was diluted with 200 ml. of water and extracted thrice with ether. The ether extracts were extracted with $NaHCO_3$. The basic aqueous extracts were washed with ether and acidified with 6 *N* H_2SO_4. The acidic aqueous solution was extracted with ether and dried over Na_2SO_4. Concentration of the ether solution afforded 0.138 g. (85%) of white crystals of *trans*-2-carboxydiphenylethylene, m.p. 158–160° (lit.[35] 158–160°). The infrared and ultraviolet spectra were identical with that reported.[35]

Attempted Reduction of 4-Carboxydiphenylacetylene.—The acetylene, 0.15 g., was exposed to $CrSO_4$ under conditions identical with those for the *ortho* isomer. After 1 week, 0.14 g. of starting material was isolated.

Acknowledgment.—The authors are indebted to the National Science Foundation for support (G19145, GP2698) of this work.

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Concerning the Structure of the Grignard Reagent. II.[1] In Diethyl Ether. Relevance of Grignard Composition to the Mechanism of Addition to Ketones

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Grignard compounds in diethyl ether solution have been assumed for many years to consist of the dimeric species $R_2Mg \cdot MgX_2$. Molecular weight measurements are reported which indicate that many Grignard compounds in diethyl ether contain essentially monomeric species at low concentrations (0.05 *M*) and essentially dimeric species at higher concentrations (0.5–1.0 *M*).[4] Of the compounds studied, the alkyl- and arylmagnesium bromides and iodides follow this pattern, whereas the alkylmagnesium chlorides are essentially dimeric, even at low concentrations. E dence is presented to support the conclusion that the composition of Grignard compounds in diethyl ether best represented by equilibria containing both monomeric and dimeric species: $(RMgX)_2 \rightleftarrows 2RMgX \rightleftarrows R_2Mg + MgX_2 \rightleftarrows R_2Mg \cdot MgX_2$, with the position of the equilibria being a function of the nature of the R group, the halogen, and the solvent as well as the concentration. Re-evaluation of data from several publications, with respect to the newly accumulated association–concentration data, leads to the conclusion that the RMgX species definitely exists in solution to a considerable degree and that the dimeric species in solution can be described as the symmetrical species $(RMgX)_2$, as well as the unsymmetrical species $R_2Mg \cdot MgX_2$. It is also shown that an equimolar mixture of $(C_2H_5)_2Mg$ and $MgBr_2$ in diethyl ether solution need not necessarily be equivalent to the corresponding Grignard solution. Mechanisms for the reaction of R_2Mg and MgX_2 to form 2RMgX are discussed. The mechanism describing Grignard compound addition to ketones in terms of an attacking unsymmetrical dimer, $R_2Mg \cdot MgX_2$, is questioned. It would appear in the light of the discussion presented herein that this mechanism is more accurately described in terms of RMgX species, either monomeric or dimeric. A possible pathway involving ionic species is also presented.

Introduction

The composition of Grignard compounds has been the subject of much study and controversy since Grignard's[5] first report in 1900 that alkyl halides react with magnesium in ether solution to produce this highly versatile reagent. Although many suggestions have been made concerning the composition of Grignard compounds, only two of these have received much attention. The first suggestion made by Grignard,[6] and later supported by Meisenheimer,[7] was that Grignard compounds are best represented by the formula RMgX. The second suggestion which received acceptance was made by Jolibois[8] and involved the representation of Grignard compounds by the formula $R_2Mg \cdot MgX_2$. Since this time, there has been much discussion and speculation as to which of these two formulations best describes the composition. The first convincing evidence permitting a clear-cut choice between these formulations was presented, in 1957, by Dessy and coworkers.[9] They found no exchange between $Mg^{28}Br_2$ and $(C_2H_5)_2Mg$ and presented evidence that an equimolar mixture of $MgBr_2$ and $(C_2H_5)_2Mg$ has the same characteristics as the Grignard reagent prepared from

(1) Part I: *J. Am. Chem. Soc.*, **85**, 118 (1963).

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(4) Monomeric species are referred to as those species containing one magnesium atom per molecule, such as, R_2Mg, MgX_2, and RMgX. Dimeric species are referred to as those species containing two magnesium atoms per molecule, such as $R_2Mg \cdot MgX_2$ and $(RMgX)_2$.

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