each other in τ, unless one term is much larger than the other and solely determines τ. Thus τ_1 in the piperidine and pyrrolidine systems does not reveal any significant medium effect outside the limit of error, but τ_1 in the butylamine reaction does, because here $\tau_1^{-1} = k_{-1}[H^+]/(K_{XH} + [H^+])$, without contribution of k_1.

Interestingly, the medium effect is much more pronounced with tetramethylammonium chloride than with sodium chloride as compensating electrolyte (Figures 2 and 3). It is not clear whether the medium effect is inherently large but greatly compensated by sodium chloride in a certain concentration range, or if tetramethylammonium chloride introduces an effect of its own. Intuitively, the first hypothesis seems more reasonable because tetramethylammonium chloride is a better model for the amine hydrochloride and should be a more suitable compensating electrolyte. This is also consistent with data obtained by Bunton and Robinson[42] on the effect of a series of electrolytes on the reaction of aniline with 2,4-dinitrochlorobenzene.

Analysis of the data at different pH values, with $(CH_3)_4NCl$ compensating electrolyte, demonstrates that both the amine and the amine hydrochloride contribute about equally to a decrease in τ_1^{-1}, *i.e.*, both tend to stabilize the MC with respect to reactants.

Several nucleophilic aromatic substitution reactions by amines, in a variety of solvents, have been found to proceed faster in the presence of high amine concentrations,[3d,43] implying a stabilization of the intermediate relative to reactants.[44] The problem is very complex and there has been no agreement as to the precise nature of this stabilization.

The stabilization of the MC by the amine hydrochloride on the other hand might be due to hydrogen bonding to the rather strongly negatively charged nitro groups;[20] that *intra*molecular hydrogen bonding plays a role has been shown previously.

Acknowledgment. I wish to thank Professor J. F. Bunnett for criticism and discussion.

(43) See, *e.g.* (a) J. F. Bunnett and R. H. Garst, *J. Amer. Chem. Soc.*, 87, 3875 (1965); (b) H. Suhr, *Ber. Bunsenges.*, 67, 893 (1963); (c) C. F. Bernasconi and H. Zollinger, *Helv. Chim. Acta*, 49, 2570 (1966).

(44) This is to be differentiated from the occasional finding that the amine acts as a general base catalyst.[6b-h]

The Mechanism of Reduction of Alkyl Halides by Chromium(II) Complexes. Alkylchromium Species as Intermediates

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Abstract: Alkyl halides are reduced quantitatively to alkanes by an ethylenediaminechromium(II) reagent prepared *in situ* from chromous salts and ethylenediamine in aqueous dimethylformamide solutions. The reduction proceeds *via* an alkylethylenediaminechromium(III) intermediate, which is hydrolytically unstable. The kinetics of the formation of the alkylchromium species is first order each in the alkyl halide and the chromium(II) reagent. The mechanism is postulated to proceed in two steps: a rate-limiting transfer of a halogen atom from the alkyl halide to ethylenediaminechromium(II) followed by a rapid association of the resultant alkyl radical with a second chromium(II) species. The second-order rate constant for the latter reaction is estimated as 4×10^7 M^{-1} sec^{-1} based on competition studies of the cyclization of the ω-hexenyl radical to the cyclopentylmethyl radical. The absorption spectra of various alkylchromium complexes are also examined, and the rates of acetolysis to afford alkane are measured in DMF solutions.

A reagent useful for the facile reduction of alkyl halides to alkanes was presented in a preliminary report.[1] Chromium(II) perchlorate and ethylenediamine react rapidly in aqueous dimethylformamide (DMF) solutions to form ethylenediamine–chromium(II) complexes, which reduced even primary alkyl chlorides to alkanes and aryl bromides and iodides to arenes at room temperature. Indirect evidence suggested the formation of a metastable alkylchromium intermediate.[1] In this paper, we wish to delineate the scope of the reduction of alkyl halides by the ethylenediaminechromium(II) reagent, to establish the kinetics, to demonstrate the role of alkylchromium complexes[2] as intermediates, and to elaborate on the mechanism of the reduction.

Results

Reduction of Alkyl Halides to Alkanes by Cr^{II}(en). The chromous reagent was prepared *in situ* by simply treating a solution of chromous perchlorate with stoichiometric amounts of ethylenediamine(en) in aqueous DMF solutions in the absence of air. The organic halide was then added and the reduction allowed to proceed at room temperature.[3]

(1) J. K. Kochi and P. E. Mocadlo, *J. Am. Chem. Soc.*, 88, 4094 (1966).

(2) Other aralkylchromium complexes have been isolated: (a) R. G. Coombs, M. D. Johnson, and N. Winterton, *J. Chem. Soc.*, 7029 (1965); 177 (1966); *Chem. Commun.*, 251 (1965); (b) R. P. A. Sneeden and H. P. Throndsen, *ibid.*, 509 (1965). (c) Alkylchromium(III) complexes have also been obtained by metathesis: H. H. Zeiss and R. P. A. Sneeden, *Angew. Chem. Intern. Ed., Engl.*, 6, 435 (1967).

(3) Cr^{II} is used to denote chromous ion in aqueous solutions of DMF and other solvents. Hexacoordination with solvent is indicated but no attempt will be made to specify coordination unless pertinent to the discussion.

Table I. Reduction of Alkyl Halides by $Cr^{II}(en)$ Reagent[a]

Alkyl halide	Alkane[b]	Alkyl halide	Alkane[b]
n-Propyl chloride	Propane		
Isopropyl bromide	Propane		
Isopropyl iodide	Propane	*t*-Butyl chloride	Isobutane
Cyclopropyl bromide	Cyclopropane	*t*-Butyl bromide	Isobutane[c]
n-Butyl bromide	Butane	Cyclobutyl chloride	Cyclobutane
n-Butyl iodide	Butane	Cyclopropylmethyl chloride	Butene-1
Isobutyl chloride	Isobutane	Neopentyl chloride	Neopentane
		Cyclopentylmethyl bromide	Methylcyclopentane
Isobutyl iodide	Isobutane	5-Hexenyl bromide	1-Hexene[d]

[a] In 83 vol % DMF–H_2O at 25°. [b] Yields determined by gas chromatography were greater than 95%, unless stated otherwise. [c] Isobutylene also formed; approximately 5% from chloride, 30% from bromide, and 60% from iodide. [d] Variable amounts of methylcyclopentane also found; see Table VI.

$$Cr^{II}(ClO_4)_2 + n(en) \longrightarrow Cr^{II}(en)_n(ClO_4)_2 \quad (1)$$

The rate of reduction increased with increasing en concentration, and a stoichiometric ratio of (en)/(Cr^{II}) = 3 was generally optimum (*vide infra*).[4] The purple $Cr^{II}(en)$ species was completely soluble in aqueous DMF under these conditions. Alkyl iodides reacted instantaneously. The reaction with alkyl bromides required less than 5 min, and the reduction of alkyl chlorides was complete within 1 hr at room temperature. If the reaction was quenched with aqueous acetic acid at this point, alkane could be isolated immediately. Alternatively, the orange alkylchromium intermediate (*vide infra*) itself underwent hydrolysis in the aqueous DMF medium, and after several hours the reaction mixture slowly turned red and yielded alkane directly.

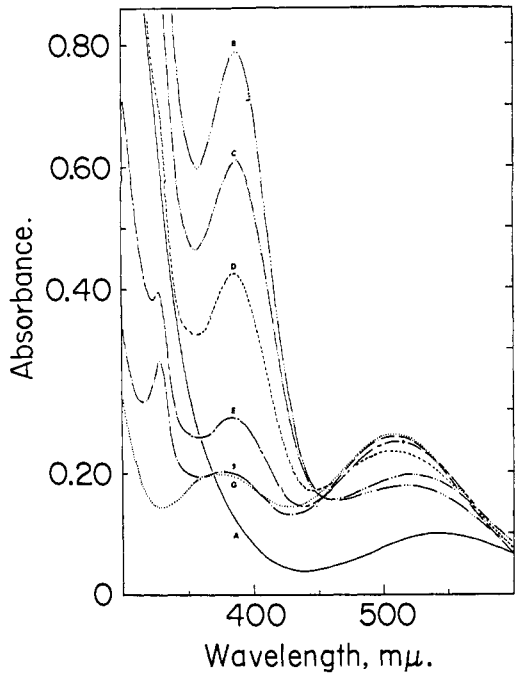


Figure 1. Visible absorption spectra for the formation and disappearance of the *n*-butyl(en)chromium(III) intermediate in the reduction of *n*-butyl bromide by the $Cr^{II}(en)_2$ reagent in 85% DMF–H_2O: A = $Cr^{II}(en)_2^{2+}$; B = 5 min after addition of *n*-butyl bromide; C = 8 min; D = 32 min; F = 89 min; G = 24 hr.

Some representative alkyl chlorides, bromides, and iodides listed in Table I were reduced in this manner. Reductions were carried out either with excess alkyl halide or excess $Cr^{II}(en)$ reagent. In the former instance, the yield was based on $Cr^{II}(en)$ reagent and in the latter, on the alkyl halides. In either case, the unreacted excess alkyl halide or chromous reagent was analyzed by gas chromatography or dichromate titrimetry, respectively. The stoichiometry of the reduction is given by eq 2. Alkanes were produced quantitatively

$$RX + 2Cr^{II}(en)_2^{2+} + H_2O \xrightarrow[DMF]{} RH + Cr^{III}(en)_2(OH)^{2+} + Cr^{II}(en)_2X^{2+} \quad (2)$$

from the reduction of most of the alkyl halides listed in Table I. The exceptions were *t*-butyl bromide and iodide which underwent partial elimination in aqueous DMF solutions to afford isobutylene.

Alkyl(ethylenediamine)chromium Species as Intermediates. A series of dramatic and interesting color changes accompany the reduction of alkyl halides by the $Cr^{II}(en)$ reagent in aqueous dimethylformamide solutions. Initially, a solution of the pale blue (λ_{max} 710 mμ (ϵ 5 M^{-1} cm^{-1})) Cr^{II} species instantaneously turned dark purple to form the ethylenediaminechromium(II) complex (λ_{max} 550 mμ (ϵ 25 M^{-1} cm^{-1})) on the addition of en. The treatment of this $Cr^{II}(en)$ reagent with *n*-butyl iodide was accompanied by an immediate color change to orange. Butane was evolved slowly as the reaction mixture gradually changed to the final red solution of the Cr^{III} products (*vide infra*). When *n*-butyl bromide was employed, the complete change to orange required approximately 5 min, and with *n*-butyl chloride, the solution never fully attained the orange color, but proceeded from the initial purple to the final red color *via* an orange-red stage.

These color changes could be followed readily by examining the visible absorption spectrum. This is shown in Figure 1 for the reduction of *n*-butyl bromide by $Cr^{II}(en)$ reagent. The concentration of the transient species with an absorption at 380 mμ reached a maximum after 5 min at 25°. A similar species absorbing at 390 mμ was formed from isopropyl bromide and $Cr^{II}(en)^{2+}$. It disappeared at a rate equal to the rate of liberation of propane, which was followed independently by gas chromatography. The 1:1 correspondence between the decrease in absorbance at 390 mμ and the evolution of propane is shown in Figure 2. The transient species which disappeared by hydrolysis was identified as an *n*-butyl(ethylenediamine)chromium(II) intermediate.[5]

(4) This composition is hereafter referred to as the $Cr^{II}(en)$ reagent.

(5) The oxidation state of III assigned to chromium in these complexes is a formality. They are substitution inert, yet readily oxidized.[6]

(6) (a) F. A. L. Anet and E. Le Blanc, *J. Am. Chem. Soc.*, 79, 2649

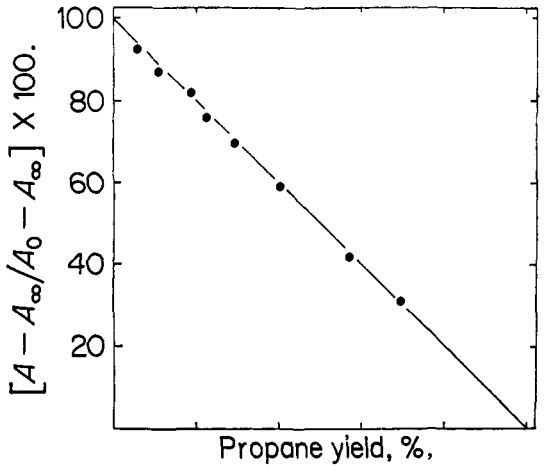


Figure 2. Relationship between the decrease in the visible absorption band at 309 mμ and the yield of propane from the hydrolysis of isopropyl(en)chromium(III) intermediate in 83 vol % DMF–H_2O. The line drawn represents the theoretical correlation for a 1:1 correspondence between absorbance and yield.

$$CH_3CH_2CH_2CH_2Cr^{III}en_2^{2+} + H_2O \longrightarrow CH_3CH_2CH_2CH_3 + Cr^{III}en_2OH^{2+} \quad (3)$$

The same *n*-butyl(en)chromium complex absorbing at 380 mμ was formed instantaneously on mixing *n*-butyl iodide or *n*-valeryl peroxide with Cr^{II}(en) reagent. The stoichiometry of the latter reaction is similar to that studied earlier with chromous ion.[6d] The extinction coefficient of the band at 380 mμ for the *n*-butylchromium complex could also be determined using various *n*-butyl precursors. The values found were independent of the concentration of Cr^{II}(en) reagent when used in excess. The latter indicated that the alkyl(en)chromium species were formed quantitatively from the alkyl halides before hydrolysis had proceeded to any appreciable extent. Primary alkyl chlorides, such as *n*-propyl, *n*-butyl, and isobutyl chlorides, were the exceptions since the rates of formation of the alkyl(en)chromium complexes competed with their hydrolysis.

$$(CH_3CH_2CH_2CH_2CO_2)_2 + 2Cr^{II}en_2^{2+} \longrightarrow CH_3CH_2CH_2CH_2Cr^{III}en_2^{2+} + Cr^{III}en_2O_2CC_4H_9^{2+} + CO_2 \quad (4)$$

Solutions of the alkyl(en)chromium species could be examined spectrally for prolonged periods if the water content in the medium was reduced. Thus, *n*-butyl-, *sec*-butyl-, and *t*-butyl(en)chromium(III) complexes were generated quantitatively from the corresponding alkyl bromides and iodides or diacyl peroxides with Cr(II)en reagent in DMF solutions containing less than 0.4% water. Under these conditions their half-lives at room temperature exceeded several hours.

All of the alkyl(en)chromium complexes showed three prominent bands at approximately 550, 400, and 300 mμ. The band at 550 mμ ($\epsilon \approx 60\ M^{-1}\ cm^{-1}$) was also associated with the accompanying Cr(III)en products and was not examined extensively. Protonolysis studies showed that the bands at 400 and 300 mμ were associated exclusively with the alkyl(en)chromium species. Both absorption bands were relatively intense ($\epsilon_{400} \approx 500\ M^{-1}\ cm^{-1}$ and $\epsilon_{300} \approx 2500\ M^{-1}\ cm^{-1}$) and varied little with the structure of the alkyl moiety. The band at approximately 300 mμ showed hypsochromic shifts in protic solvents (Table II).

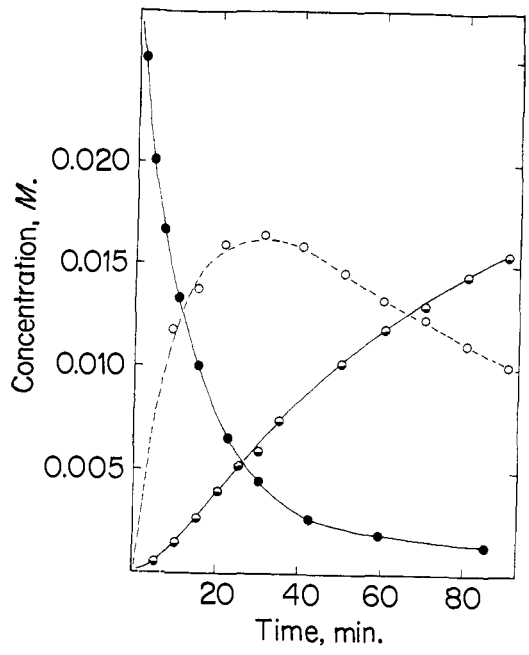


Figure 3. The isopropyl(en)chromium(III) intermediate in the reduction of isopropyl chloride by $Cr^{II}(en)_2$ reagent in 83 vol % DMF–H_2O by the liberation of propane: ●, *i*-PrCl; ◒, propane before protonolysis with HOAc; ○, propane after protonolysis minus propane before; – – –, isopropyl chloride initial minus propane before protonolysis.

The role of alkyl(en)chromium species as direct intermediates in the conversion of alkyl halides to alkanes could be demonstrated quantitatively. Since the rate of formation of the isopropyl(en)chromium complex from isopropyl chloride and Cr^{II}(en) reagent proceeded in aqueous DMF solution at a rate comparable to its hydrolysis, its concentration never attained 100%, as it did for *n*-propyl iodide. This is shown in Figure 3, in which the rates of disappearance of isopropyl chloride and appearance of propane were followed independently by gas chromatography. The dotted line in the figure represents the calculated difference between the isopropyl chloride originally charged and the sum of butane liberated and isopropyl chloride remaining at various times. A separate series of identical reactions were also run and quenched with acetic acid at various times. The protonolysis of the isopropyl(en)chromium complex was rapid and complete under these conditions (*vide infra*). The open circles represent the *extra propane* liberated by the acetic acid quench. The same dotted curve was obtained when the reaction was followed spectrophotometrically at 390 mμ. These studies show unequivocally that the transient intermediate is a monoalkyl(ethylenediamine)chromium(III) complex.[7]

The absorption spectra of the final reaction mixtures showed two bands at 510 (ϵ 75 $M^{-1}\ cm^{-1}$) and 380 mμ (ϵ 59 $M^{-1}\ cm^{-1}$) characteristic of Cr(III) complexes. Slight variations occurred in the position and absor-

(1957); (b) J. K. Kochi and D. D. Davis, *ibid.*, **86**, 5264 (1966); (c) J. K. Kochi and D. B. Buchanan, *ibid.*, **87**, 859 (1965); (d) J. K. Kochi and P. E. Mocadlo, *J. Org. Chem.*, **30**, 1134 (1965).

(7) (a) Studies are in progress to isolate these alkylchromium complexes. (b) In the discussion hereafter we will refer to these as alkylbis-ethylenediaminechromium(II) complexes, although this must be established.

Table II. Absorption Spectra of Alkylchromium Complexes[a]

Alkyl halide	Solvent	Alkylchromium(III)[b]	Band II λ, mμ	Band II ε,[c] M^{-1} cm^{-1}	Band III λ, mμ	Band III ε,[c] M^{-1} cm^{-1}
n-Propyl chloride	DMF	*n*-PrCr(en)$_2^{2+}$	380		328	
n-Propyl bromide	DMF	*n*-PrCr(en)$_2^{2+}$	381	5.2×10^2	329	2.5×10^3
n-Propyl iodide	DMF	*n*-PrCr(en)$_2^{2+}$	380		327	
Isopropyl chloride	DMF	*i*-PrCr(en)$_2^{2+}$	387		330	
Isopropyl bromide	DMF	*i*-PrCr(en)$_2^{2+}$	389	4.9×10^2	329	2.4×10^3
Isopropyl bromide	EtOH	*i*-PrCr(en)$_2^{2+}$	385		290	
Isopropyl bromide	CH_3CN	*i*-PrCr(en)$_2^{2+}$	381		285	
Isopropyl iodide	DMF	*i*-PrCr(en)$_2^{2+}$	388	5.2×10^2	328	2.7×10^3
Isopropyl bromide[d]	DMF	*i*-PrCr^{2+}	416			
t-Butyl chloride	DMF	*t*-BuCr(en)$_2^{2+}$	398		329	
t-Butyl chloride	EtOH	*t*-BuCr(en)$_2^{2+}$	400		293	
t-Butyl bromide	DMF	*t*-BuCr(en)$_2^{2+}$	400	5.1×10^2	331	2.5×10^3
t-Butyl bromide	EtOH	*t*-BuCr(en)$_2^{2+}$	400	5.1×10^2	300	
t-Butyl chloride	CH_3CN	*t*-BuCr(en)$_2^{2+}$	391			
t-Butyl iodide	DMF	*t*-BuCr(en)$_2^{2+}$	399		329	
n-Butyl bromide	DMF	*n*-BuCr(en)$_2^{2+}$	380	5.25×10^2	329	2.6×10^3
n-Butyl iodide	DMF	*n*-BuCr(en)$_2^{2+}$	380	5.35×10^2	330	2.6×10^3
Valeryl peroxide	DMF	*n*-BuCr(en)$_2^{2+}$	380	4.9×10^2	324	2.5×10^3
Valeryl peroxide	EtOH	*n*-BuCr(en)$_2^{2+}$	390	5.0×10^2	300	2.4×10^3
Valeryl peroxide[d]	EtOH	*n*-BuCr^{2+}	400	5.1×10^2	278	4×10^3
Valeryl peroxide[d]	CH_3CN	*n*-BuCr^{2+}	360		300	
Ethyl bromide	DMF	EtCr(en)$_2^{2+}$	380			
sec-Butyl bromide	DMF	*sec*-BuCr(en)$_2^{2+}$	380			
Isobutyl bromide	DMF	*i*-BuCr(en)$_2^{2+}$	384	5.1×10^2		
Isoamyl bromide	DMF	*i*-AmCr(en)$_2^{2+}$	382			
3-Bromopentane	DMF	3-AmCr(en)$_2^{2+}$	391			
t-Amyl chloride	DMF	*t*-AmCr(en)$_2^{2+}$	401		327	
t-Amyl chloride	EtOH	*t*-AmCr(en)$_2^{2+}$	402		300	
Cyclohexyl bromide	DMF	*c*-C_6H_{11}Cr(en)$_2^{2+}$	389	5.3×10^2	329	2.9×10^3

[a] In DMF solutions containing 0.01–5.0 × 10^{-3} *M* Cr^{II}, 0.03–15 *M* en, and 10^{-4}–1 *M* alkyl halide at 25°. [b] Bisethylenediamine complex assumed; see text. [c] Calculated on the assumption that the alkylchromium complex was formed quantitatively when either alkyl halide or Cr^{II}(en) reagent was used in excess. [d] No ethylenediamine.

bance of these bands depending on the halide and the concentration of the ethylenediamine employed relative to Cr(II). Similar spectra were obtained when Cr^{II}(en) reagent was treated with a solution of either iodine or bromine in DMF. The latter are due to bromo(iodo)-

$$2Cr^{II}en_2^{2+} + Br_2 \xrightarrow[DMF]{} 2Cr^{III}en_2Br^{2+} \quad (5)$$

bis(ethylenediamine)chromium(II) complexes containing DMF as solvate.[8,9] Even at relatively high ratios of ethylenediamine, we could find no evidence for the trisethylenediaminechromium(III) cation, which has absorption bands at 460 (ε 75 M^{-1} cm^{-1}) and 351 mμ (ε 63 M^{-1} cm^{-1}).[10] We attribute the spectrum of the products to a mixture of $Cr^{III}en_2X(DMF)^{2+}$ where X = Cl, Br, or I and $Cr^{III}en_2(H_2O)(DMF)^{3+}$.[11]

Alkyl(ethylenediamine)chromium(III) species can be classified as substitution inert, in common with other chromium(III) complexes. Thus, *n*-butyl(ethylenediamine)chromium(III) was prepared independently from *n*-butyl bromide or iodide and Cr^{II}(en) reagent under conditions in which an excess of the latter was absent. Excess isopropyl iodide was then added and the reaction mixture allowed to stand until hydrolysis was complete. Butane was formed quantitatively and no propane (<0.1%) was detected.

$$n\text{-}BuCr^{III}(en)_2^{2+} + i\text{-}PrI \rightleftharpoons n\text{-}PrCr^{III}(en)_2^{2+} + n\text{-}BuI \quad (6)$$

n-Butyl(en)chromium complex was also prepared in the absence of halide from *n*-valeryl peroxide and Cr^{II}(en) reagent. Excess lithium bromide or chromium(II) bromide was added. Butane was formed quantitatively on standing until hydrolysis was complete and no *n*-butyl bromide (<0.1%) was found.

$$n\text{-}BuCr^{II}(en)_2^{2+} + Cr^{III}Br^{2+} \rightleftharpoons n\text{-}BuBr + Cr^{II}(en)_2^{2+} + Cr^{II} \quad (7)$$

Finally, a mixture of benzyl bromide and isopropyl(en)chromium complex prepared from isopropyl bromide and Cr^{II}(en) reagent was allowed to react. Propane was liberated quantitatively and no isobutylbenzene (<0.1%) was found. The latter observation is in

$$(CH_3)_2CHCr^{III}(en)_2^{2+} + PhCH_2Br \rightleftharpoons PhCH_2CH(CH_3)_2 + Cr^{III}(en)_2Br^{2+} \quad (8)$$

strong contrast to the facile coupling of benzyl bromide and benzylchromium ion observed earlier.[6]

Protonolysis of Alkyl(en)chromium Complexes. The hydrolysis of the alkyl(en)chromium intermediate under reaction conditions (*i.e.*, unbuffered solutions of 83 vol % DMF–H_2O) followed pseudo-first-order kinetics. The rate could be measured by monitoring the appearance of alkane by gas chromatography. Al-

(8) *Cf.* (a) H. Taube and H. Myers, *J. Am. Chem. Soc.*, 76, 2103 (1954); (b) R. C. Thompson and G. Gordon, *Inorg. Chem.*, 5, 557, 562 (1966).

(9) The absorption spectra of a series of halobisethylenediaminechromium(III) complexes in DMF have been reported. Preliminary indications are that the stereochemistry of these complexes is *trans*, but their relationship to the alkylchromium species must be established: (a) C. S. Garner, *Transition Metal Chem.*, in press; (b) D. J. McDonald and C. S. Garner, *Inorg. Chem.*, 1, 20 (1962); (c) L. P. Quinn and C. S. Garner, *ibid.*, 3, 1348 (1964)

(10) (a) R. D. Gillard, *J. Chem. Soc., A*, 2129 (1968); (b) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *ibid.*, 2883 (1965).

(11) Separation by ion exchange and complete characterization of these Cr(III) complexes are in progress.

Table III. Rates of Acetolysis of Alkyl(en)chromium Complexes in DMF[a]

Alkyl halide	$10^2 M$	10^3 Cr^{II}, M	10^2 en, M	10^2 HOAc, M	λ_{max},[b] mμ	$10^4 k_1$, sec^{-1}
n-Propyl bromide	4.5	5.4	1.2	7.3	380	5.1
n-Propyl bromide	4.0	5.4	1.2	7.3	380	5.2
Isopropyl bromide	4.4	5.4	1.2	7.3	389	6.3
Isopropyl iodide	4.6	5.4	1.2	7.3	389	6.8
Valeryl peroxide[c]	0.22	0.074	0	0	278	7.3
Valeryl peroxide	0.22	0.074	0	0	300	7.7
n-Butyl bromide	4.5	5.4	1.2	7.3	380	5.0
sec-Butyl bromide	4.0	5.4	1.2	7.3	390	8.9
Cyclohexyl bromide	3.8	5.4	1.2	7.3	390	4.0
t-Butyl chloride	0.25	5.4	1.2	7.3	398	2.7
t-Butyl bromide	0.19	5.4	1.2	7.3	398	2.3
t-Butyl bromide	0.19	5.4	1.2	3.6	398	1.1
t-Butyl iodide	0.19	5.4	1.2	7.3	398	2.2

[a] At 25°. [b] Absorption band followed. [c] In 92% ethanol-H_2O, no en and no HOAc.

ternatively, the absorption bands of the alkyl(en)chromium species at 300 and 400 mμ (Table II) were followed spectrally at either the maxima or on the shoulders.[12] In every case, the rates of change of the absorbancies were the same for both bands. Acetolysis could also be effected quantitatively under essentially anhydrous conditions (less than 0.4 vol % H_2O) by the addition of

$$RCr^{III}en_2^{2+} + H_2O \longrightarrow RH + Cr^{III}en_2(OH)^{2+} \quad (9)$$

a solution of glacial acetic acid in DMF. The rates of protonolysis of each alkyl(en)chromium species were not dependent on their mode of formation (*i.e.*, from the

$$RCr^{III}en_2^{2+} + HOAc \longrightarrow RH + Cr^{III}en_2(OAc)^{2+} \quad (10)$$

various halides or diacyl peroxide). Some typical first-order rate constants for acetolysis are given in Table III.

The *protic* origin of the hydrogen in the alkane product was determined by deuterium labeling. The product from the reduction of *t*-butyl chloride in 83 vol % DMF-D_2O was examined by gas chromatography. The nmr spectrum of the isobutane thus obtained was examined in deuteriochloroform solution. The doublet splitting (J_{AB} = 6.1 Hz) of the methyl groups in isobutane was replaced by a broad singlet centered at the

$$(CH_3)_3CCr(en)_2^{2+} + D_2O \longrightarrow (CH_3)_3CD + Cr^{III}en_2(OD)^{2+} \quad (11)$$

average chemical shift (τ 9.13) in the isobutane isolated from the reaction mixture. *n*-Butane was similarly isolated from the reduction of *n*-butyl bromide by $Cr^{II}(en)$ in 83 vol % DMF-D_2O. Mass spectral analysis indicated 95.6% C_4H_9D, labeled exclusively in the methyl group. The small amount of C_4H_{10} was undoubtedly derived from the protiated en employed. We conclude, therefore, that alkane does not arise from the alkyl radical by hydrogen abstraction from DMF, but rather from the water.

The hydrolysis of *n*-butyl(en)chromium species in aqueous DMF solutions could be accelerated by the addition of various acids. The rate of protonolysis was not related to the strength of the acid, since acetic acid was much more effective than hydrochloric, sulfuric, or perchloric acid at the same acid concentrations (Figure 4). In each case, *n*-butane was liberated quantitatively from the *n*-butyl(en)chromium species. A similar effect of anions on rates of protonolysis was noted earlier in the study of benzylchromium ions.[6]

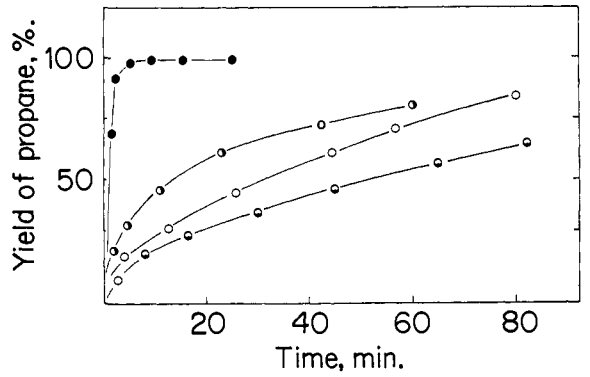


Figure 4. Propane formation by the protonolysis of 0.03 *M* isopropyl(en)chromium(III) in 83 vol % DMF-H_2O by various acids (1 *M*): ●, acetic acid; ◑, sulfuric acid; ○, perchloric acid; ◒, hydrochloric acid.

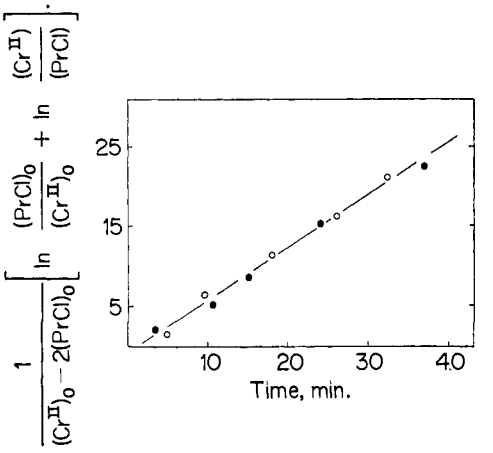


Figure 5. Second-order kinetics for the reduction of isopropyl chloride by $Cr^{II}(en)_2$ reagent in 83 vol % DMF-H_2O at 25°. Disappearance of $Cr^{II}(en)_2^{2+}$ followed by potentiometric titration. Disappearance of isopropyl chloride followed by gas chromatography.

The Kinetics of Reduction of Alkyl Halides by $Cr^{II}(en)$. The reduction of isopropyl chloride by $Cr^{II}(en)$ in aqueous DMF at 25° proceeded at a rate which could be conveniently followed by conventional techniques. The concentration of isopropyl chloride was determined by periodically removing an aliquot, quenching with a large excess of water, extracting with chlorobenzene, and analyzing by quantitative gas chromatography.

(12) This was necessary to obviate difficulties with overlapping absorption bands.

The Cr^{II}(en) species could be analyzed quantitatively in the presence of the alkyl(en)chromium complex by first hydrolyzing the latter with aqueous acetic acid. The Cr^{II}(en) complex was then oxidized with a ferric chloride solution, and the resultant ferrous ion titrated with dichromate. Without the acetic acid quench, reproducibility was limited due to oxidation of the alkyl(en)chromium species by ferric ions.[6] By this technique, it was possible to follow the disappearance of alkyl halide and Cr^{II}(en) simultaneously. A typical kinetic run is illustrated in Figure 5 showing the Cr^{II}(en) reagent being consumed at exactly twice the rate at which isopropyl chloride was reduced.

The initial concentrations of alkyl halide and Cr^{II}(en) were each varied over a 20-fold range. The reduction followed over-all second-order kinetics for greater than 70% reaction, being first order in alkyl halide and Cr^{II}(en). The second-order rate constants are listed in Table IV.

Table IV. Second-Order Rate Constants for Reduction of Alkyl Halides by Cr^{II}(en)

Alkyl halide (M)	Cr^{II}, M	en, M	(en)/(Cr^{II})	10^2k, M^{-1} sec^{-1}
2-PrCl (0.025)	0.106	0.133	1	0.21
2-PrCl (0.025)	0.106	0.266	2	0.62
2-PrCl (0.025)	0.106	0.400	3	1.07
2-PrCl (0.025)	0.106	0.534	4	1.40
2-PrCl (0.025)	0.106	0.667	5	1.59
2-PrCl (0.025)	0.106	1.06	8	1.65
1-BuCl (0.026)	0.108	0.400	3	0.166

It was observed earlier[1] that the rate at which *butane* was liberated from the reduction of *n*-butyl bromide increased as the stoichiometric ratio of en to Cr^{II} was increased. The rate reached a maximum at a ratio between 2 and 2.5. The optimum ratio of (en)/(Cr^{II}) was different for the reduction of *n*-butyl chloride, lying between 3 and 4. Owing to the ambiguity lent from the presence of the *n*-butyl(en)chromium intermediate, we reexamined the rate dependence on en by following the disappearance of *alkyl halide directly* by gas chromatography. Under these conditions we find that the second-order rate constant did not attain a maximum but assumed a limiting value. The discrepancy is readily accounted for by the inverse dependence of the rate of hydrolysis of the alkyl(en)chromium intermediate on pH. In aqueous DMF solutions, en not only is a ligand for Cr^{II}, but also is a sufficiently strong base to enhance the pH of the solution. Thus, for synthetic purposes, there is an optimum concentration of en. We suggest that a ratio of (en)/(Cr^{II}) equal to 3 represents a reasonable compromise.

The apparent second-order rate constant for a given ratio of (en)/(Cr^{II}) did not remain invariant as the Cr^{II} (or en) concentration was varied. The variation is attributed to the different formation constants K_i of the various $Cr^{II}(en)_n$ complexes (eq 12–14).[13,14]

$$Cr^{II}(DMF)_6^{2+} + en \overset{K_1}{\rightleftharpoons} Cr^{II}en(DMF)_4^{2+} + 2DMF \quad (12)$$

$$Cr^{II}en(DMF)_4^{2+} + en \overset{K_2}{\rightleftharpoons} Cr^{II}en_2(DMF)_2^{2+} + 2DMF \quad (13)$$

$$Cr^{III}en_2(DMF)_2^{2+} + en \overset{K_3}{\rightleftharpoons} Cr^{II}en_3^{2+} + 2DMF \quad (14)$$

Reactivities of Alkyl Halides toward Cr^{II}(en). The absolute second-order rate constants for the reduction of *n*-butyl and isopropyl chlorides were measured separately by the technique described above. The relative rates of reduction were obtained by subjecting various mixtures of *n*-butyl chloride and isopropyl chlorides (each in at least a tenfold molar excess) to the Cr^{II}(en) reagent. Propane and butane were measured quantitatively by gas chromatography. The relative reactivities (given by the ratio of second-order rate constants) were obtained from the pseudo-first-order rate

$$\frac{k_{Pr}}{k_{Bu}} = \frac{(PrH)}{(BuH)}\frac{(BuCl)_0}{(PrCl)_0} \quad (15)$$

expression 15 where Pr and Bu represent isopropyl and *n*-butyl moieties. The reactivity of isopropyl chloride relative to *n*-butyl chloride obtained by the competitive method (k_{Pr}/k_{Bu} = 6.26) compared favorably with a value (6.44) obtained from the ratio of second-order rate constants.

The applicability of the competition method for the determination of relative rates of reduction of pairs of alkyl halides depended on the integrity of the alkyl(en)chromium intermediate to yield only alkane. It was shown above (eq 6–8) that alkyl(en)chromium species were not formed reversibly and did not exchange or react with alkyl halides. The reduction of alkyl chlorides, bromides, and iodides listed in Table V was examined by the competition method. Various pairs of alkyl halides were chosen and the relative reactivities compared directly. The rate of reduction of *n*-butyl chloride was arbitrarily chosen as 1.0. For consistency, relative reactivities were also measured between a pair of alkyl halides relative to a third.

Table V. Relative Rates of Reduction of Alkyl Halides by Cr^{II}(en) Reagent at 25°

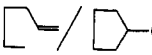
Alkyl halide	Relative rate	Alkyl halide	Relative rate
Isobutyl chloride	0.7	Isopropyl bromide	1,100
n-Propyl chloride	0.9	*sec*-Butyl bromide	1,400
n-Butyl chloride	1.00	*t*-Butyl bromide	5,800
Isopropyl chloride	3.6		
t-Butyl chloride	29	Isobutyl iodide	7,700
		n-Butyl iodide	10,000
Isobutyl bromide	100	*n*-Propyl iodide	11,000
n-Propyl bromide	130	Isopropyl iodide	63,000
n-Butyl bromide	140	*sec*-Butyl iodide	110,000

Reduction of Cyclopropylcarbinyl, ω-Hexenyl, and Cyclopentylcarbinyl Derivatives. The possibility that alkyl radicals were intermediates in the formation of alkyl(en)chromium species was investigated. The reduction of cyclopropylcarbinyl chloride by Cr^{II}(en) in 83 vol % DMF–H_2O afforded only butene-1 in quantitative yields. Even in the presence of a 20-fold excess (0.4 M) of Cr^{II}(en) or at reduced temperatures (−50°), we could find no evidence of methylcyclopropane.

(13) (a) C. K. Jorgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, p 61 ff.

(14) (a) In aqueous solutions $K_1 = 1.4 \times 10^6$, $K_2 = 1 \times 10^4$, $K_3 \simeq 0.1$ [R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, II, 1418 (1957)]. (b) Planar complexes with coordination number of four from amine nitrogens have been suggested and are supported with studies with diethylenetriamine and triethylenetetramine complexes with Cr(II) which are still high spin [R. L. Pecsok, R. A. Garber, and L. D. Shields, *Inorg. Chem.*, 4, 447 (1965)]. (c) See also A. Earnshaw, L. F. Larkworthy, and K. C. Patel, *J. Chem. Soc.*, *A*, 1339 (1969).

Table VI. Reduction of 6-Bromohexene-1 and ω-Heptenoyl Peroxide by Cr^{II}(en) Reagent[a]

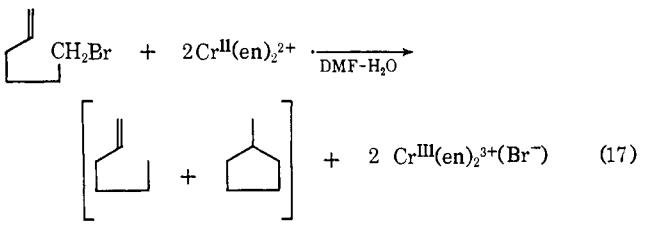
Alkyl halide	Concn, *M*	Cr^{II}, *M*	en, *M*	 , mmole/mmole × 10^{-2}
6-Bromohexene-1	0.0020	0.026	0.078	0.501
6-Bromohexene-1	0.0020	0.052	0.156	0.932
6-Bromohexene-1	0.0020	0.078	0.234	1.428
6-Bromohexene-1	0.0020	0.104	0.312	1.880
6-Bromohexene-1	0.0020	0.039	0.117	0.797
6-Bromohexene-1	0.0020	0.065	0.195	1.156
6-Bromohexene-1	0.0020	0.091	0.273	1.640
6-Bromohexene-1	0.078	0.022	0.065	0.0266
6-Bromohexene-1	0.262	0.013	0.039	0.0152
Cyclopentylcarbinyl bromide	0.055	0.023	0.069	0[c]
ω-Heptenoyl peroxide	0.0020	0.052	0.156	0.92
ω-Heptenoyl peroxide	0.0020	0.104	0.312	1.90
Cyclopentylacetyl peroxide	0.040	0.023	0.069	0[c]

[a] In 30 ml of 83% DMF–H_2O at 25°. [b] Total yields of alkanes greater than 95%. [c] Less than 0.01% hexene-1.

$$c\text{-}C_3H_5CH_2Cl + 2Cr^{II}(en)_2^{2+} \xrightarrow[DMF\text{-}H_2O]{} CH_2{=}CHCH_2CH_3 + 2Cr^{III}(en)_2^{3+}(Cl^-) \quad (16)$$

Similarly, cyclopropylacetyl peroxide produced only butene-1, in addition to carbon dioxide and cyclopropylacetic acid.

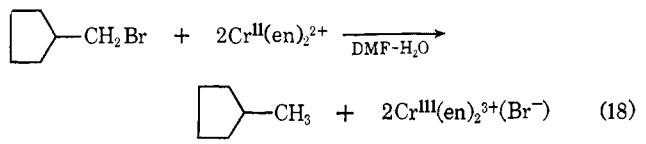
The reduction of 6-bromohexene-1 by Cr^{II}(en) gave quantitatively a mixture of hexene-1 and methylcyclopentane. The relative amounts of methylcyclopentane



(17)

decreased with increasing concentrations of Cr^{II}(en) reagent. When excess 6-bromohexene-1 was employed relative to Cr^{II}(en) reagent, a hydrocarbon mixture was produced which consisted of 28% methylcyclopentane and 72% hexene-1. The extent of rearrangement of the ω-hexenyl moiety to cyclopentylcarbinyl during reduction of 6-bromohexene-1 was determined by carrying out the reduction in the presence of varying amounts of Cr^{II}(en) reagent. The latter was employed in large excess (Table VI) in order to approximate kinetically zero-order conditions. Analogously, the reduction of ω-heptenoyl peroxide also produced a mixture of hydrocarbons, the composition of which varied predictably with the Cr^{II}(en) concentration.

Cyclopentylcarbinyl bromide and cyclopentylacetyl peroxide were both reduced by Cr^{II}(en) to afford only methylcyclopentane in excellent yields. Even in the



(18)

presence of excess halide or peroxide, no evidence for hexene-1 could be found.

Discussion

The reduction of a variety of alkyl halides of the Cr^{II}(en) reagent affords alkanes in quantitative yields. The rates of these reductions are at least a hundred times faster than Cr(II) alone,[15] and proceed rapidly at room temperature even for the least reactive alkyl chlorides. Furthermore, the mild conditions and convenience with which these reactions can be carried out enable the Cr^{II}(en) reagent to be attractive for synthetic applications. In the following discussion we are principally concerned with the mechanistic aspects of these facile reductions.

A variety of ethylenediaminechromium(II) complexes are extant in dynamic equilibrium (*cf.* eq 12–14) in solutions of Cr(II) and ethylenediamine in aqueous DMF. Cr(II) complexes are substitution labile;[16] and the formation constants for the mono- and bisethylenediamine complexes are much larger than the constant for the trisethylenediaminechromium(II) species.[14] Product studies on the inert Cr(III) complexes also indicate that the bisethylenediaminechromium(II) species are mainly responsible for the reduction. Quantitative evaluation of the formation constants of various $Cr^{II}(en)_n$ complexes in DMF solutions and their correlation with the rates of reduction of alkyl halides are in progress.[17] The contrary notwithstanding, we will assume in further discussions that reductions of alkyl halides occur primarily *via* these $Cr^{II}en_2^{2+}$ complexes, although we realize that other $Cr^{II}(en)_n^{2+}$ complexes may also be involved.

$$Cr^{II}(DMF)_6^{2+} + 2en \rightleftharpoons Cr^{II}en_2(DMF)_2^{2+} + 4DMF \quad (19)$$

In discussing the mechanism of these reactions, it is convenient to separate the reaction into two parts. Since alkyl(en)chromium(III) complexes are the principal intermediates we will first discuss their formation and, second, their subsequent hydrolysis to alkane.

Mechanism of the Formation of Alkyl(en)chromium(III) Intermediates. The stoichiometry of the formation of alkyl(en)chromium(III) complexes is given by eq 20. The reaction follows over-all second-order

$$RX + 2Cr^{II}en_2^{2+} \longrightarrow RCr^{III}en_2^{2+} + Cr^{III}en_2X^{2+} \quad (20)$$

kinetics, being first order each in alkyl halide and Cr^{II}(en) reagent. Since the stoichiometry of the reac-

(15) (a) J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968); (b) D. M. Singleton and J. K. Kochi, *J. Am. Chem. Soc.*, **89**, 6547 (1967); (c) J. K. Kochi and D. M. Singleton, *ibid.*, **90**, 1582 (1968); (d) J. K. Kochi and D. M. Singleton, *J. Org. Chem.*, **33**, 1027 (1968).

(16) H. Taube, *Chem. Rev.*, 50, 69 (1952).

(17) (a) W. Joern, unpublished results; (b) see also ref 14.

tion differs from that of the activation step, a multistep sequence of reactions must be involved.

Two mechanisms are consistent with these data.

mechanism I

$$RX + Cr^{II}en_2^{2+} \longrightarrow R\cdot + Cr^{III}en_2X^{2+} \quad (21)$$

$$R\cdot + Cr^{II}en_2^{2+} \xrightarrow{\text{fast}} RCr^{III}en_2^{2+} \quad (22)$$

mechanism II

$$RX + Cr^{II}en_2^{2+} \longrightarrow RCr^{IV}en_2X^{2+} \quad (23)$$

$$RCr^{IV}en_2X^{2+} + Cr^{II}en_2^{2+} \xrightarrow{\text{fast}} RCr^{III}en_2^{2+} + Cr^{III}en_2X^{2+} \quad (24)$$

The first mechanism involves a rate-limiting transfer of a halogen atom from the alkyl halide to $Cr^{II}en_2^{2+}$ (eq 21). This step is followed by a rapid reaction of the resulting alkyl radical with a second $Cr^{II}en_2^{2+}$ (eq 22).

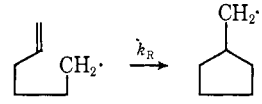
Alternatively, an insertion reaction[18] represented by eq 23 involves the formation of a metastable chromium(IV) derivative.[19] The latter is expected to react rapidly with $Cr^{II}en_2^{2+}$ to generate the alkyl(en)chromium(III) intermediate (eq 24). In both mechanisms 1 equiv of $Cr^{II}en_2^{2+}$ is used to produce $Cr^{III}en_2X^{2+}$ and the other is involved in the formation of the alkyl(en)chromium(III) intermediate.[20]

The relative rates of reduction of various alkyl halides determined by the competition method are tabulated in Table V. For a given halide, the rates of reduction of the alkyl group are generally tertiary > secondary > primary, roughly in the order 10^2:10:1. For a particular alkyl group, iodides are reduced approximately 3×10^3 faster than chlorides, and bromides have intermediate ($\sim 4 \times 10^2$) reactivity. The reactivity of various alkyl halides parallels the inner-sphere reduction of various pentaamminechromium(III) and pentaamminecobalt(III) halides by Cr(II).[21] Analogous mechanisms have been postulated for the reduction of alkyl halides by pentacyanocobaltate(II) complexes[22] and tributyltin hydride.[23] Similar transformations also pertain to the reduction of halides by cobalt(I) complexes.[24] We postulate that the activation step in the reduction of alkyl halides also involves halogen atom transfer directly to the various Cr(II) species according to mechanism I.[25] In such a process, iodine is more readily transferred than bromine or chlorine, and tertiary alkyl radicals are more readily generated than their secondary or primary counterparts.[27]

The reductions of diacyl peroxides and tertiary alkyl hydroperoxides also afford alkyl(en)chromium(III) complexes as intermediates, which are identical with those derived from alkyl halides. We formulate a mechanism in common with alkyl halides in which a peroxidic oxygen is directly transferred *via* an inner-sphere activated complex to the chromium(II) species in the rate-limiting step.[26] Mechanism II offers no reasonable counterpart for the reduction of peroxides.[28]

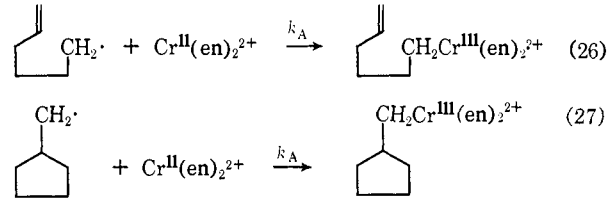
Alkyl Radicals as Intermediates. The applicability of mechanism I to the reduction of alkyl halides (and peroxides) demands that alkyl radicals are intermediates. Furthermore, the quantitative formation of alkyl(en)chromium intermediates requires that the subsequent association step (eq 22) of the alkyl radical with Cr(II) must be rapid in order to compete effectively with other reactions, such as attack on solvent.

We chose to examine the radical nature of the intermediate and its rate of association with $Cr^{II}en_2^{2+}$ in competition with a facile unimolecular rearrangement. Thus, other studies have established that the ω-hexenyl radical undergoes rapid and irreversible isomerization to the cyclopentylmethyl radical.[29] During reduction of 6-bromohexene-1 or 6-heptenoyl peroxide, such a unimolecular rearrangement of the ω-hexenyl radical



(25)

must compete with its association with $Cr^{II}en_2^{2+}$. Two isomeric alkyl(en)chromium complexes are formed from these radicals (eq 26 and 27). Since the stability of the carbon–chromium bond has been demonstrated in a



number of alkyl(en)chromium(III) complexes, we assume that under reaction conditions the ω-hexenyl(en)chromium(III) intermediate only undergoes protonolysis and does not rearrange to the cyclopentylcarbinyl(en)chromium(III) isomer.[30] Alkanes are formed quantitatively from alkyl(en)chromium complexes. We further assume that the yields of hexene-1 and methylcyclopentane are quantitative representations of the alkyl(en)chromium complexes formed in eq 26 and 27, respectively. In the presence of a measured excess of Cr^{II}(en) reagent, the rate constants for unimolecular rearrangement, k_R, and association with $Cr^{II}en_2^{2+}$, k_A, are related to the $Cr^{II}en_2^{2+}$ concentration according to eq 28.[31] From the data in Table VI, we obtained an

(18) *Cf.* J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

(19) *Cf.* A. E. Ogard and H. Taube, *J. Phys. Chem.*, **62**, 357 (1958); A. E. Cahill and H. Taube, *J. Am. Chem. Soc.*, **74**, 2312 (1952).

(20) (a) A third possibility of an outer-sphere electron transfer from Cr(II) to the alkyl halide does not lead to the correct Cr(III) products and is energetically unfeasible; (b) *cf.* J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Am. Chem. Soc.*, **88**, 4260 (1966); (c) G. D. Sargent and G. A. Lux, *ibid.*, **90**, 7160 (1968); (d) E. Warhurst and R. Whittaker, *Trans. Faraday Soc.*, **62**, 707 (1966).

(21) For a recent review, see A. G. Sykes, *Advan. Inorg. Radiochem.*, **10**, 153 (1967); H. Taube, *ibid.*, **1**, 1 (1959).

(22) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **91**, 582 (1969).

(23) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964); *Accounts Chem. Res.*, **1**, 299 (1968).

(24) (a) G. N. Schrauzer and R. J Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966); **90**, 6631 (1968); (b) E. Ochiai, K. M. Long, C. R. Sperati, and D. H. Busch, *ibid.*, **91**, 3201 (1969); (c) G. N. Schrauzer and E. Deutsch, *ibid.*, **91**, 3341 (1969).

(25) The relevance of the halochromium(III) species to the mechanism of inner-sphere electron transfer has been discussed.[26]

(26) (a) J. K. Kochi and P. E. Mocadlo, *J. Org. Chem.*, **30**, 1134 (1965); (b) for related reductions see J. K. Kochi, *Rec. Chem. Progr.*, **27**, 207 (1966); (c) D. E. Pennington and A. Haim, *J. Am. Chem. Soc.*, **90**, 3700 (1968); (d) J. K. Kochi and A. Bemis, *Tetrahedron*, **24**, 5099 (1968).

(27) According to arguments based on bond energies.

(28) Such a mechanism would require, unreasonably, an insertion of Cr(II) between *carbon* atoms in peroxides.

(29) (a) R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963); (b) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *ibid.*, **88**, 5363 (1966); (c) M. Julia, *Rec. Chem. Progr.*, **26**, 108 (1965).

(30) Neither ω-hexenylsodium[32b] nor ω-hexenylmagnesium bromide (representative of *carbonionic systems*) rearranges under these conditions, although at evaluated temperatures the rearrangement of related compounds has been reported [H. G. Richey, Jr., and T. C. Rees, *Tetrahedron Lett.*, 4297 (1966)].

$$\frac{k_R}{k_A} = \frac{\text{CH}_3\text{-CH=CH}_2}{(\text{Cr}^{II}(\text{en})_2^{2+})} \quad (28)$$

excellent linear relationship (Figure 6) between the concentration of $Cr^{II}en_2^{2+}$ and the relative yields of hexene-1 and methylcyclopentane. The ratio of rate constants, k_R/k_A, is evaluated as 2×10^{-3} M at 25° in 83 vol % DMF–H_2O. If we assume that the unimolecular rate of rearrangement of the ω-hexenyl radical is unchanged in this medium from the value ($k_R = 1 \times 10^5$ sec^{-1}) in benzene,[32] the association of ω-hexenyl radical with $Cr^{II}en_2^{2+}$ proceeds with a rate constant of 4×10^7 M^{-1} sec^{-1}.[33] The rate constant for association obtained in this manner is certainly large enough to account for the complete trapping of alkyl radicals by $Cr^{II}en_2^{2+}$.[34] Furthermore, the rate of association which we have evaluated is consistent with the inability of $Cr^{II}en_2^{2+}$ to trap cyclopropylmethyl radical prior to isomerization, since the rate constant for reaction 29 is estimated to be greater than 10^8 sec^{-1}.[35]

$$c\text{-}C_3H_5CH_2\cdot \longrightarrow CH_2{=}CHCH_2CH_2\cdot \quad (29)$$

Protonolysis of Alkyl(en)chromium(III) Complexes. The hydrolysis of alkyl(en)chromium(III) complexes afford alkanes quantitatively and is catalyzed by acids, although not necessarily according to their strengths. The rates of hydrolysis or acetolysis of these complexes follow pseudo-first-order kinetics. These rates do not vary by more than a factor of 2 on proceeding from *n*-alkyl, secondary alkyl, to tertiary alkyl(en)chromium(III) derivatives. We tentatively postulate that heterolysis of the alkylchromium bond is not an important factor in the rate-limiting step. We suggest that ligand exchange (eq 30) proceeds *via* intramolecular protonolysis of the alkyl moiety (eq 31). According to

$$RCr^{III}en_2(DMF)^{2+} + HS \rightleftharpoons RCr^{III}en_2(SH)^{2+} + DMF \quad (30)$$

$$RCr^{III}en_2(SH)^{2+} \longrightarrow RH + Cr^{III}en_2S^{2+} \quad (31)$$

this hypothesis, acid catalysis involves prior protonation of the ligand. A similar multiplicity of reaction rates and mechanisms for the protic acid cleavage of

$$RCr^{III}en_2(DMF)^{2+} + H^+ \rightleftharpoons RCr^{III}en_2(DMFH)^{3+} \text{ etc.}$$

the related carbon–mercury bond in organomercurials has been discussed.[36]

(31) Competition studies show that ω-hexenyl bromide and *n*-hexyl bromide are reduced at the same rate of Cr^{II}(en). Double bond participation, therefore, does not appear to be relevant in the rate-limiting step.

(32) (a) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, 90, 7047 (1968); (b) G. F. Garst and F. E. Barton, *Tetrahedron Lett.*, 587 (1969); (c) J. Eastham *Chem. Commun.*, 139 (1969).

(33) The large magnitude of this rate constant is expected, since the association of the radical with the substitution labile Cr(II) species would require very little activation energy owing to the quintet character of high-spin Cr(II) in solution. It is only several orders of magnitude removed from the diffusion-controlled limit of 1.2×10^{10} M^{-1} sec^{-1} estimated by Garst and Barton[32b] for the reaction between alkyl radicals and sodium naphthalenide.

(34) We estimate that the hydrogen transfer rate constant between alkyl radical and DMF in the competing reaction is less than 10^2 M^{-1} sec^{-1} at 25°. For rates of some related hydrogen transfer reactions in the gas phase, see J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, 1, 107 (1961).

(35) (a) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Am. Chem. Soc.*, 91, 1877 (1969). (b) This represents a lower limit and is based on the analogous cholesteryl-isocholesteryl rearrangement.[32a] (c) *Cf.* also L. K. Montgomery and J. W. Matt, *J. Am. Chem. Soc.* 89, 6556 (1967).

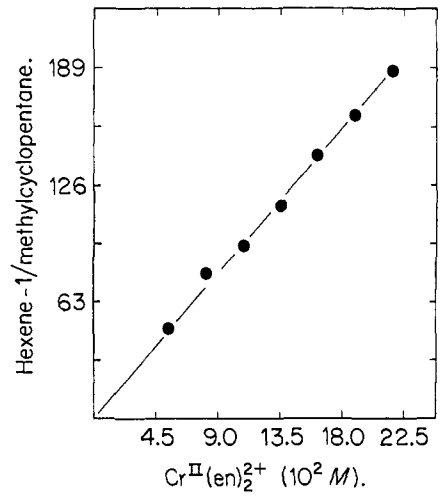


Figure 6. Variation in the relative amounts of hexene-1 and methylcyclopentane formed in the reduction of 6-bromohexene-1 with a measured excess of $Cr^{II}(en)_2$ reagent.

Summary. Alkyl(en)chromium(III) species are intermediates in the facile reduction of alkyl halides by Cr^{II}(en) reagent. These unique organochromium complexes can be classified as substitution inert, but undergo hydrolysis and protonolysis quantitatively to alkanes. The formation of the alkyl(en)chromium intermediate occurs by two successive one-equivalent steps: a halogen atom transfer from the alkyl halide to the Cr^{II}(en) reagent followed by a rapid association ($k_A = 4 \times 10^7$ M^{-1} sec^{-1}) of the resultant alkyl radical with a second Cr^{II}(en) species. Further studies on the properties, reactions, and mechanism of electrophilic substitutions of alkylchromium complexes are in progress.

Experimental Section

Materials. Most of the **alkyl halides** were readily available commercial materials which were redistilled and analyzed by gas chromatography for isomeric impurities. 6-Bromohexene-1 and cyclopentylcarbinyl bromide were from Columbia Organic Chemical Co.

Valeryl, ω-heptenoyl, and cyclopentylacetyl peroxides were kindly donated by Mr. C. L. Jenkins. **Ethylenediamine** was anhydrous material from Matheson Coleman and Bell and was used directly. The **chromous perchlorate** was prepared in aqueous solution (1.5 M) from the pure metal and perchloric acid as described previously. DMF was kindly donated by the E. I. du Pont de Nemours and Co. and used without further purification. It contained small amounts of water and dimethylamine.

General Procedures for Reduction. The general technique for carrying out the reaction and the analysis of the products has been described previously.

Kinetic Procedure. A typical kinetic run was carried out as follows. DMF (16.8 ml), 1.49 M en in DMF (8 ml), and water (2 ml) were placed in a 125-ml erlenmeyer flask. The flask was sealed with a gas-tight septum and the contents were thoroughly degassed with a stream of helium. An aqueous solution of 1.33 M $Cr(ClO_4)_2$ was added (3 ml) by syringe. A small sample (0.8 ml) was extracted for a zero point titer, and the flask placed in a thermostated bath (25°). The reaction was initiated by adding a solution of 0.8 M alkyl halide in DMF (1 ml). Care must always be exercised to wash the hypodermic needle immediately after use when in contact with Cr(II) solutions.

The alkyl halide was monitored by periodically extracting samples (1 ml). The aliquot was quenched in a mixture of 0.8 ml of chlorobenzene and 10 ml of 1 M $HClO_4$. A solution of an isomeric alkyl halide dissolved in DMF was added (1 ml) as an internal standard, and the chlorobenzene solution was analyzed by gas chroma-

(36) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill Book Co., Inc., New York, N. Y., 1968. *Cf.* also J. M. Williams and M. M. Kreevoy, *Advan. Phys. Org. Chem.*, 6, 63 (1968).

tography. Calibration curves were constructed using the same extraction procedure but omitting the Cr(II) solution.

Analytical Methods. All titrations were carried out potentiometrically with a constant drive buret (E. H. Sargent Co.). The magnetically stirred cell could be thoroughly deaerated by bubbling a stream of nitrogen through the solution. HOAc (10 ml of 4 *M*) was purged of air, and 1 ml of reaction solution added *via* a hypodermic syringe under nitrogen. After 5 min, a thoroughly degassed solution of 0.2 *M* ferric chloride in 2 *M* sulfuric acid (1 ml) was added (the ferric content represented a 100% excess). The solution was then diluted with 50 ml of 2 *M* H_2SO_4 and titrated with standard 0.01 *M* dichromate solution. In the absence of any alkylchromium species, the acetic acid solution was omitted from the procedure.

Gas chromatographic analysis was carried out by the internal standard method. Alkanes containing fewer than four carbon atoms were readily analyzed by sampling the gas phase. All calibrations were performed using standards which matched the reaction conditions as closely as possible. Analyses of liquids were also carried out by the internal standard method on at least two columns loaded with stationary phases of different polarity.

The absorption spectra were measured in 1 cm (~3 ml) cells equipped with standard taper joints using a Beckman DBG spectrometer. The cell was capped with a gas-tight rubber septum and could be thoroughly degassed prior to introduction of various solutions with hypodermic syringes. Inhibitors and dyes were removed by repeatedly boiling the septa in the solvent employed. Small amounts of standard solution were introduced with microliter syringes, and reproducibility was limited to approximately 5%.

Competition Reactions. In all competition experiments, a pair of alkyl halides was used which afforded alkanes separable by gas chromatography. In a typical procedure, 4.5 ml of DMF, 1.75 ml of H_2O, and 2 ml of 1.49 *M* ethylenediamine in DMF were placed in a 50-ml erlenmeyer flask. Solutions (0.8 *M*) of the alkyl halides were added in the proper ratio to maintain a total volume of 6 ml. The flask was sealed with a septum and deaerated with a stream of nitrogen. The reaction was initiated by introduction of 0.75 ml of 1.3 *M* aqueous $Cr(ClO_4)_2$.

Acknowledgment. We wish to thank the National Science Foundation for a generous financial support of this work.

Halogenated Ketenes. X. Further Studies on the Dehydrohalogenation of 2-Halopropanoyl Halides in the Presence of Cyclopentadiene[1]

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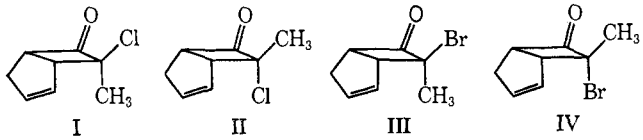
Contribution from the Department of Chemistry, North Texas State University, Denton, Texas. *Received June 5, 1969*

Abstract: The dehydrohalogenation of 2-chloro- and 2-bromopropanoyl halides with triethylamine in the presence of cyclopentene in hexane produced the same distribution of *endo*-methyl and *exo*-methyl 1,2-cycloadducts as cyclopentadiene. Thus, the isomer distribution is not influenced by the residual double bond. However, the isomer distribution of the cycloadducts is strongly dependent upon the polarity of the solvent used in the preparations. The dehydrochlorination of 2-chloropropanoyl chloride in the presence of cyclopentadiene in hexane yielded an *endo*-:*exo*-methyl ratio of 1,2-cycloadducts of 4.3. This became 0.59 when acetonitrile was employed as the solvent. The dehydrochlorination of 2-bromopropanoyl chloride in the presence of cyclopentadiene in hexane produced an *endo*-:*exo*-methyl ratio of 1,2-cycloadducts of 0.71 which became 0.14 in acetonitrile. The dehydrobromination of 2-bromopropanoyl bromide in hexane in the absence or cyclopentadiene produced a solution of methylbromoketene as evidenced by infrared.

In preceding papers, we reported that *endo*- and *exo*-methyl 1,2-cycloaddition isomers are produced from the dehydrohalogenations of 2-haloalkanoyl halides with triethylamine in the presence of cyclopentadiene.[3,4] It was reported that there is a reversal in the *endo*- and *exo*-methyl cycloadduct isomers which appear to be derived from *in situ* reactions of methylchloro- and methylbromoketenes with cyclopentadiene. There was a predominance of the *endo*-methyl isomer I for the 2-chloropropanoyl chloride–triethylamine–cyclopentadiene system and a predominance of the *exo*-methyl IV isomer for the 2-bromopropanoyl bromide–triethylamine–cyclopentadiene system. An examination of molecular models of the ketenes and cyclopentadiene does not reveal an explanation for the observed isomer distributions. We suggested earlier that this could possibly be due to an interaction between the bromine atom and the residual unsaturated system in the adduct. Since the bromine atom is right over this π-electron system, possibly this atom has an orbital far enough out to interact appreciably with this unsaturated system whereas chlorine does not. Also, it was mentioned earlier that two steps may be involved with the isomer distribution being determined by a final ring closing step. However, this seemed unlikely in view of recent reports on the "near-concerted" nature of ketene–olefin cycloadditions.[5-7]



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The purpose of this report is to relate some information which indicates that in the dehydrohalogenation of

(1) Paper IX: W. T. Brady, E. D. Dorsey, and F. H. Parry, III, *J. Org. Chem.*, 34, 2846 (1969).
(2) NDEA Title IV Fellow.
(3) W. T. Brady and B. M. Holifield, *Tetrahedron Lett.*, 5511 (1966).
(4) W. T. Brady and B. M. Holifield, *Tetrahedron*, 23, 4251 (1967).
(5) G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Lett.*, 4497 (1968).
(6) W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, 32, 612 (1967).
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