

White.⁴ They considered the rate-determining step of the reaction to be the nucleophilic displacement of chloride ion on the peroxidic oxygen (reaction 2). The kinetic results, the evidence for hypochlorite intermediates just adduced, and the reaction with styrene to form a mixture of chloroacetate and benzoate adducts (see Experimental) are in accord with this formulation.

Displacements on peroxides by a variety of nucleophiles have been considered.¹ A linear free-energy correlation of the logarithms of the rates of reaction of halide ions with monosubstituted peroxides in aqueous solution and the base strength (pK_B) of the leaving group has been observed. However, hypohalites as actual intermediates³⁶ in these reactions is more difficult to determine in aqueous solution, since subsequent attack by halide to form molecular halogen is the usual course.³⁷

The use of chloride as a nucleophile in displacements on peroxides is facilitated in nonaqueous solution. Bamford and White's studies in dimethylformamide and our studies in acetic acid and acetonitrile show that chloride can act effectively as a nucleophile. The usual nucleophilic reactivity sequence, $I^- > Br^- > Cl^-$, has been attributed largely to polarizability or related factors.¹ Recently Weaver and Hutchison³⁸ have presented evidence that the differences in nucleophilic reactivity of lithium halides in nonaqueous solution is largely attributed to ion-pair formation, and in some cases chloride is a more effective nucleophile than iodide.

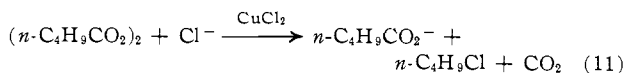
The addition of small amounts of cupric chloride to the reaction system consisting of benzoyl peroxide and lithium chloride is not characteristic of its effect on peroxides generally. With benzoyl peroxide cupric chlo-

(36) For example, it can be postulated that attack of halide ion on peroxide leads directly to a halogen atom as in the reaction: $ROOR' + X^- \rightarrow RO^- + X \cdot + R'O$ [cf. W. K. Wilmarth and A. Haim, ref. 1, p. 192].

(37) Cf. M. C. R. Symons, *J. Chem. Soc.*, 273 (1955); D. H. Fortnum, C. J. Battaglia, S. R. Cohen, and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 778 (1960).

(38) W. M. Weaver and J. D. Hutchison, *ibid.*, **86**, 261 (1964).

ride has little effect (*vide supra*) other than to inhibit extraneous radical chain processes. With aliphatic diacyl peroxides, on the other hand, cupric chloride has a catalytic effect, especially in the presence of excess halide salts in nonaqueous solutions.³⁹ The stoichi-



ometry of such reactions (11) is different. For example, *n*-valeryl peroxide yields a mole of *n*-butyl chloride, carbon dioxide, and lithium valerate. There is a marked similarity of these reactions to other decompositions of peroxides catalyzed by copper salts,⁵ which all proceed *via* cuprous salt intermediates. In the absence of cupric salts, *n*-valeryl peroxide reacts only very slowly with lithium chloride at temperatures (65°) where the unimolecular thermolysis of the peroxide is a significantly complicating factor. The reaction of valeryl peroxide with lithium bromide is exceedingly rapid and in the presence of cupric salts the two processes^{2,11} occur concomitantly.³⁹

In summary, we have presented evidence that both molecular chlorine and benzoyl (acetyl) hypochlorite formed by reactions 2 and 5 are the principal species responsible for chlorinations in a system comprised of benzoyl peroxide and lithium chloride in acetic acid. With toluene as substrate, the radical chain chlorination (reaction 6, 7) to form benzyl chloride is the preferred reaction in the absence of air or with cupric chloride. The slower electrophilic chlorination of toluene to form nuclear substituted chlorotoluenes⁴⁰ in the presence of inhibitors is attributed to molecular chlorine.²⁷

Acknowledgment.—We wish to thank the National Science Foundation and the Petroleum Research Fund of the American Chemical Society for generous grants which supported this work.

(39) Unpublished results, R. V. Subramanian.

(40) Electrophilic side chain halogenation (cf. E. Baciocchi and G. Illuminati, *Tetrahedron Letters*, **15**, 637 (1962)) is not obtained with toluene.

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Reduction of Organic Halides by Chromium(II). Mechanism of the Formation of Benzylchromium Ion¹

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Benzylchromium ion, $C_6H_5CH_2Cr(H_2O)_5^{+2}$, has been prepared by several independent routes and found to be the same as that formed⁷ during the reaction of benzyl chloride and chromium(II). The kinetics of the formation of this complex ion have been studied and a mechanism proposed which includes the generation of benzyl radicals as intermediates in the reaction. Trapping experiments with acrylonitrile and butadiene are described. The similarity of the slow step of the reaction with atom-transfer reactions involving a bridge-activated complex and the ligand-transfer oxidation of free radicals is discussed. Related aralkylchromium ions have been prepared and their electronic absorption spectra and kinetics of formation studied.

Introduction

It has been known for some time² that chromous ion is a potent and versatile reducing agent for organic

(1) Presented in part at the 1st International Conference on Organometallic Chemistry, Cincinnati, Ohio, June, 1963.

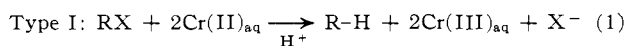
(2) M. Berthelot, *Ann.*, [4] **9**, 401 (1866); W. Traube, *et al.*, *Ber.*, **49**, 1692 (1916); **58**, 2773 (1925); J. B. Conant, *et al.*, *J. Am. Chem. Soc.*, **45**, 2466 (1923); **47**, 1959 (1925); **48**, 1016 (1926); **53**, 676 (1931).

compounds. The reduction of unsaturated functional groups, nitriles, carbonyl-containing compounds, carbonium ions, and organic halides has been summarized recently.³ We have been engaged in the study⁴ of

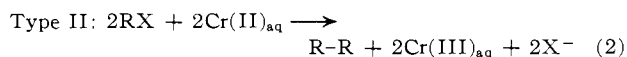
(3) (a) V. Schwarz, A. Kasal, *Pokroky v organicke synthese*, **4**, 877 (1957); (b) L. H. Slauch and J. H. Raley, *Tetrahedron*, **20**, 1005 (1964); (c) C. E. Castro and W. C. Kray, *J. Am. Chem. Soc.*, **85**, 2768 (1963); (d) K. D. Kopple, *ibid.*, **84**, 1586 (1962).

the mechanism of the reduction of organic compounds by metal species. Among transition metal reductants, chromous salts are of particular interest since they are oxidized by an over-all one-electron change to the chromic state by organic compounds which generally undergo a concomitant two-electron reduction.

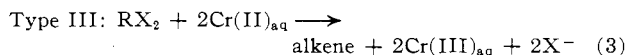
The ease of reduction of an alkyl halide depends on its structural type as well as the halide moiety.³ In general, the rates of reduction parallel their solvolytic reactivity. Alkyl are usually reduced to alkanes by a type I reduction (eq. 1)⁵



Allylic, benzylic, and α -halocarbonyl compounds yield bimolecular reduction products (eq. 2) of type II.



In some cases, competition between products of type I and type II occur. A third type of reduction is that of *vic*-dihalides³ or halohydrins and related compounds^{3c,6} to olefins. *gem*-Polyhalides^{3c} are also reducible, but the stoichiometry is not completely clear.



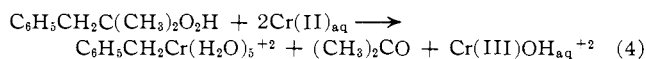
Anet and LeBlanc⁷ showed that benzyl chloride is reduced by chromous ion to a mixture of toluene and bibenzyl. The formation of a metastable intermediate, which was identified in solution as a benzylchromium ion $\text{C}_6\text{H}_5\text{CH}_2\text{-Cr(H}_2\text{O)}_5^{+2}$, was adduced. Neumer and Aktipis⁸ reported that a similar reaction between benzal chloride and chromous ion in ethanol yielded stilbene and stilbenediol ethers *via* an α -chlorobenzylchromium ion, $\text{C}_6\text{H}_5\text{CHClCr(H}_2\text{O)}_5^{+2}$, postulated by analogy with the ion reported by Anet and LeBlanc.

We assumed that reductions of organic halides generally by chromous ion proceed by a common path. The reaction between benzyl halides and chromous ion was chosen for study because the formation of an observable intermediate would facilitate the investigation of the mechanism of these reactions. In this and the following paper we wish to demonstrate that the benzylchromium ion is, in fact, the actual intermediate in these reactions. The kinetics of the formation of benzylchromium from benzyl chloride and bromide are presented here, and a mechanism for the formation of the complex ion is proposed. The formation and spectral properties of related aralkylchromium complex ions will also be presented.

Results

Benzylchromium Ion, $\text{C}_6\text{H}_5\text{CH}_2\text{Cr(H}_2\text{O)}_5^{+2}$.—Benzylchromium ion (I) was prepared by several independent routes. It is a metastable compound and attempts to isolate it as a crystalline salt were unsuccessful. However, it could be determined quantitatively in solution by examining its absorption spectrum. The band at 360 $\text{m}\mu$ was used for all quantitative work. In order

to determine the molar extinction coefficient of this band, benzylchromium ion was made by quantitatively converting α,α -dimethyl- β -phenethyl hydroperoxide with chromous ion.⁹ The reduction of this hydro-



peroxide by chromous ion was instantaneous at 0°. One mole of acetone was produced and no evidence for α,α -dimethyl- β -phenethyl alcohol was found by gas chromatography. Dilute standard hydroperoxide solution was added incrementally to excess chromous solution in various stoichiometric ratios varying from 10 to 1 to 1000 to 1. Constant and quantitative yields of benzylchromium ion were obtained and were independent of the order of addition provided chromous ion was added quickly and maintained in stoichiometric excess. Since I itself is a reducing agent, it will react further with the hydroperoxide; at low chromium(II) to hydroperoxide ratios, the formation of benzylchromium ion was not quantitative. However, even at stoichiometric concentrations of 2:1, the yield (based on hydroperoxide) of I was greater than 88%.

Benzylchromium ion was separated from other chromium salts by ion-exchange chromatography on a Dowex 50 sulfonic acid resin at 0° under oxygen-free conditions. The absorption spectrum of these solutions showed no characteristic chromous¹⁰ or chromic¹¹ absorption in the region 800 $\text{m}\mu$. The ultraviolet and visible spectra are shown in Fig. 1. The band at 540 $\text{m}\mu$ reported by Anet and LeBlanc⁷ was not found. However, the oxidation of $\text{Cr(II)}_{\text{aq}}$ with oxygen does yield a chromic species which has an absorption at 580 $\text{m}\mu$.¹²

In order to ensure that the spectrum of I given in Fig. 1 was homogeneous, the decomposition of the benzylchromium ion was followed by observing the rate of decay of the three maxima at 360, 297, and 274 $\text{m}\mu$. The half-time for disappearance of all three bands taken at various initial concentrations was the same within 2%. The absorption spectrum was the same in aqueous solution as it was in ethanol-water mixtures and unaffected by perchloric acid.

The spectrum of I shows a single maximum at 360 $\text{m}\mu$ (ϵ 2470 l./mole-cm.) in the visible region and the ultraviolet spectrum shows three additional strong peaks at 297 (ϵ 7920 l./mole-cm.), 274 (ϵ 8380 l./mole-cm.), and 243 $\text{m}\mu$. The last absorption band is a composite peak mainly associated with the aromatic ring since it is the main band of toluene in the ultraviolet absorption spectrum. After benzylchromium ion was completely decomposed, there was a remnant of a very weak band at 412 $\text{m}\mu$ attributed to chromic species and a band centered at 250 $\text{m}\mu$ attributed to toluene. The origin of the bands in benzylchromium ion is probably not caused by d-d transitions of the chromium species by virtue of their high intensity, ϵ 2500–8000. Most chromic species have low extinction absorptions in this region owing to spin-forbidden transitions.¹³ The shift in the maxima of the

(4) J. K. Kochi, *J. Org. Chem.*, **28**, 1960, 1969 (1963).

(5) In these equations only the oxidation state of the chromium species is specified. The nature of the chromium complexes formed is discussed later (*vide infra*).

(6) (a) F. A. L. Anet and E. Isabelle, *Can. J. Chem.*, **33**, 849 (1955); **36**, 589 (1958); (b) F. A. L. Anet, *ibid.*, **37**, 58 (1959).

(7) F. A. L. Anet and E. LeBlanc, *J. Am. Chem. Soc.*, **79**, 2649 (1957).

(8) J. F. Neumer and J. Aktipis, Abstracts, 139th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961, p. 9Q.

(9) J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **83**, 2007 (1961).

(10) R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1419 (1957); H. L. Schäfer and H. Skoludek, *Z. physik. Chem.*, **11**, 277 (1957).

(11) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955); C. K. Jorgensen, *Acta Chem. Scand.*, **8**, 1495 (1954); H. S. Gates and E. L. King, *J. Am. Chem. Soc.*, **80**, 5011 (1958).

(12) M. Ardon and G. Stein, *J. Chem. Soc.*, 2095 (1956).

(13) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Reading, Mass., 1962.

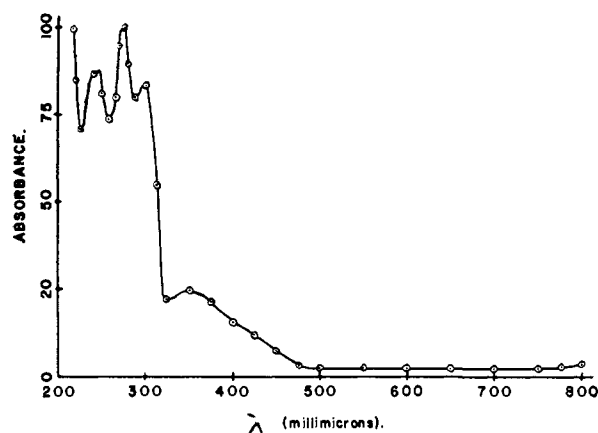


Fig. 1.—Absorption spectrum of benzylchromium ion.

absorption bands of I with substitution in the aromatic ring is small as shown in Table I. Substitution for the

TABLE I
SPECTRAL CHARACTERISTICS OF SUBSTITUTED
BENZYLCHROMIUM IONS^a

Benzylchromium ion	Prepared from	$\lambda_1, m\mu^b$	$\lambda_2, m\mu$	$\lambda_3, m\mu$	$\lambda_4, m\mu$
Unsub.	Hydroperoxide	360	297	274	243
<i>o</i> -Methyl	Chloride	370	306	280	240 (sh)
<i>m</i> -Methyl	Bromide	357	300	277	240
<i>p</i> -Methyl	Bromide	364	302	278	240
<i>m</i> -Fluoro	Chloride	354	296	274	240 (sh)
<i>p</i> -Fluoro	Chloride	358	290	274	...
<i>m</i> -Chloro	Bromide	360	298	278	240 (sh)
<i>p</i> -Chloro	Chloride	364	303	281	...
<i>m</i> -Bromo	Bromide	362	302	283	240 (sh)
<i>p</i> -Bromo	Bromide	360	300	280	255
<i>m</i> -Methoxy	Chloride	360	300 (sh)	284	245 (sh)
<i>p</i> -Methoxy	Chloride	368
2,5-Dimethyl	Chloride	368	304	284	240 (sh)
3,4-Dimethyl	Chloride	364	303	278	241 (sh)
2,4-Dimethyl	Chloride	370	308	283	240 (sh)
α -Chloro	Chloride	356	298 (sh)	275	238 (sh)
2,3-Benz (α -Naphthylcarbinylchromium ion)	Chloride	322, 345 (sh)	292 (sh)	282	...
				274	

^a In aqueous solution at 25° in 83% v. ethanol-water. ^b sh = shoulder.

most part does not affect the general characteristics of the spectrum of I, but results in shifting the maxima. The majority of substituents shift the maxima toward lower energies. The most pronounced (though limited) effect was observed with the electron-releasing *p*-methoxy and *p*-methyl and the *o*-substituted methyl compounds. Electron-attracting substituents exert a hypsochromic effect, particularly with fluoro and the α -chloro substituents. In some respects the absorption spectrum of I and related compounds resembles that of the benzyl radical observed in rigid glass¹⁴ and alkali salts of benzylic carbanions.¹⁵ We attribute the bands at 360–270 $m\mu$ to charge transfer between chromium and the benzylic ligand.

Reaction of Chromous Perchlorate with Benzyl Bromide and Iodide.—Benzylchromium ion was also formed rapidly and quantitatively from benzyl bromide and iodide in the presence of excess chromous ion as shown in Fig. 2. The molar extinction coefficient of the band at 360 $m\mu$ for I obtained from benzyl bromide and iodide was the same (2470 l./mole-cm.) as that ob-

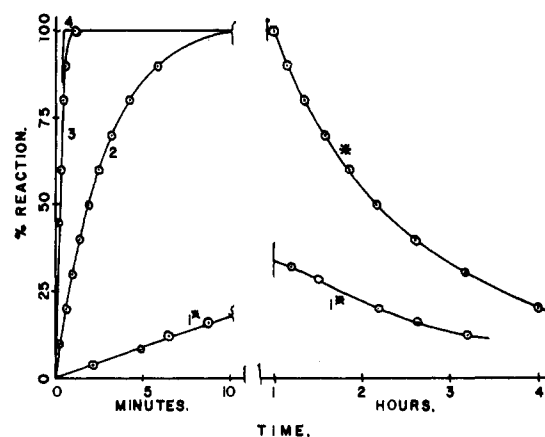


Fig. 2.—Rates of appearance and disappearance of benzylchromium from benzyl chloride (1), benzyl bromide (2), benzyl iodide (3), and phenyl-*t*-butyl hydroperoxide (4) at 28°; 1* at 41°.

tained from dimethylphenethyl hydroperoxide. The complete spectra of the species obtained by these various methods were identical. The rate of appearance of the complex ion I was much faster with benzyl bromide and iodide than it was with the chloride, and the rate constant was determined by a pseudo-first-order method. If benzyl bromide reacted with an excess of chromous ion in the cell of a spectrophotometer the absorbance quickly reached a plateau and stayed at that value for a period several times longer than the reaction time. The decay of I was negligible under these conditions. Neither toluene nor bibenzyl was formed, and the pseudo-first-order rate constant k_1 was calculated from the half-life. The second-order rate constant k_2 was then obtained: $k_2 = k_1/\text{Cr(II)}_{\text{aq}}$. The second-order rate constant at an ionic strength of 0.1 at $27.5 \pm 0.5^\circ$ for benzyl bromide was 4.1×10^{-1} l./mole-sec. and for benzyl iodide 1.8 l./mole-sec. The relative rates are: iodide > bromide > chloride in the order 555:124:1. Benzyl thiocyanate and *p*-toluenesulfonate do not react under these conditions.

The formation of benzylchromium ion quantitatively from the reaction of chromium(II) and benzyl bromide or iodide in our studies differs from the results obtained by Slauch and Raley^{3b} who observed that the yield of bibenzyl *increased* in the order benzyl chloride, bromide, and iodide. However, their studies were conducted by adding the halides to refluxing ($\sim 65^\circ$) solutions of 70% v. tetrahydrofuran-water under conditions where the benzylchromium ion has an extremely short lifetime and the coupling reaction is very rapid. Under these circumstances it is difficult to make statements about the relative rates of formation of the benzylchromium intermediate.

Kinetics of the Formation of Benzylchromium from Benzyl Chloride.—The rate of the reaction between benzyl chloride and chromous perchlorate was determined by following the rate of appearance of benzylchromium ion spectrophotometrically and the rate of disappearance of benzyl chloride by gas chromatography. Spectroscopic rate determinations were carried out during the first 25% or less of the reaction since benzylchromium ion decays at a rate comparable to its formation from benzyl chloride at higher conversions. Under ordinary conditions, I attains a

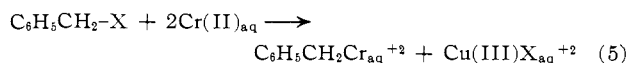
(14) G. Porter and R. Strachan, *Spectrochim. Acta*, **12**, 299 (1958); A. F. Gaines and F. M. Page, *Trans. Faraday Soc.*, **59**, 1266 (1963).

(15) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963); K. Kuwata, *Bull. Chem. Soc. Japan*, **33**, 1091 (1960); A. Streitwieser, Jr. and J. I. Bauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963).

maximum concentration which varies from 30–50% of the theoretical limit as shown in Fig. 3.

The rate of formation of I in the initial stages of the reaction is first order in chromous ion and benzyl chloride, which was determined by varying the initial concentration of the reactants and, alternatively, by using a large excess of each reactant. The ionic strength was maintained constant with lithium perchlorate. The second-order rate constant in 71.5% ethanol–water at 27.5° was 4.0×10^{-3} l./mole-sec. Since this rate was largely unaffected by pH changes in the acid region no attempt was made to buffer the system. The rate of disappearance of benzyl chloride followed by gas chromatography was found to have the same rate constant (3.9×10^{-3} l./mole-sec.) as the appearance of I.

The metastable benzylchromium ion at approximately 30–50% reaction decomposes as fast as it is being formed to yield a mixture of toluene and bibenzyl. The stoichiometry of the combination of type I and type II reactions under these conditions was complex. However, the stoichiometry for the formation of I from benzyl bromide and iodide are readily obtainable, since its formation from these halides was much more rapid than its decay. An analogous reaction is undoubtedly obtained with benzyl chloride, and the stoichiometry is as written in eq. 5.



The nature of the chromic species was also obtained by ion-exchange studies. In the case of the bromide and iodide it was not possible to determine the chromic species $\text{CrBr}_{\text{aq}}^{+2}$ and $\text{CrI}_{\text{aq}}^{+2}$ because of their hydrolytic instability.¹⁶ The chlorochromic species $\text{CrCl}_{\text{aq}}^{+2}$ can be separated from the reaction mixture by ion-exchange chromatography and it preceded the elution of benzylchromium ion in 1 *M* perchloric acid. It can be identified by its visible absorption at 425 and 602 $\mu\mu$.¹⁷ The aquochromic ion $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ was eluted with 6 *N* perchloric acid.¹⁸ Only a small amount of free chloride ion was detected.⁷ Although precise separation and quantitative determination of the chromic species was difficult, it was found that roughly (80–90%) 1 mole of $\text{CrCl}_{\text{aq}}^{+2}$ was formed for each benzylchromium ion, and only traces of aquochromic ion were detected.

Relative Rates of Substituted Benzyl Halides.—The pseudo-first-order rate constants for the reaction of substituted benzyl bromides were studied in a manner analogous to the one used for benzyl bromide and iodide. The extinction coefficients for several of the substituted benzylchromium ions was determined by assuming that the bromide was quantitatively converted to the aralkylchromium ion. This assumption appears valid since all these bromides reacted rapidly with chromous ion. The relative rates of reduction and the extinction coefficients are given in Table II. The values of the extinction coefficient do not differ greatly from that of the unsubstituted compound.

(16) F. A. Guthrie and E. L. King, *J. Inorg. Chem.*, **3**, 916 (1964); J. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960).

(17) P. J. Elving and B. Zemel, *J. Am. Chem. Soc.*, **79**, 1281 (1957); E. L. King, J. W. Woods, and H. S. Gates, *ibid.*, **80**, 5015 (1958).

(18) E. L. King and E. B. Dismukes, *ibid.*, **74**, 1674 (1952).

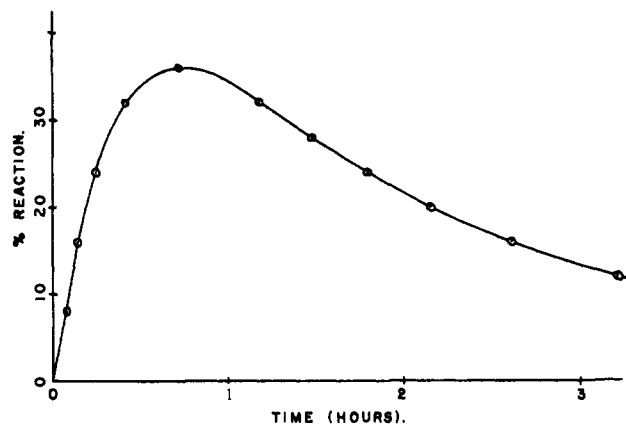


Fig. 3.—Complete reaction with benzyl chloride at 41°. Formation and disappearance of benzylchromium ion.

The reductions of substituted benzyl chlorides suffer from the same problem as the parent chloride does—from the competing decomposition of the aralkyl-

TABLE II
RATES OF SUBSTITUTED BENZYL BROMIDES WITH CHROMOUS ION^a

Benzyl bromide	(ArCH ₂ X), M × 10 ⁴	(Cr _{aq} ⁺²), l./mole-min.	k ₂ , l./mole-min.	k ^b /k	λ _{max} , l./mole-cm.
Unsub.	3.6	0.016	24.5	1	2440
<i>p</i> -Me	4.06	.016	32.5	1.33	2360
<i>m</i> -Me	4.26	.016	25.5	1.04	2320
<i>p</i> -Br	1.54	.016	34.9	1.43 (1.3)	2480
<i>m</i> -Br	..	.016	28.8	1.17 (1.2)	..
<i>m</i> -Cl	2.96	.016	26.3	1.07	2245
<i>m</i> -MeO	..	.016	25.7	1.04	..

^a In 71.5% ethanol–water at 27.5°. ^b Rates relative to benzyl bromide. Values in parentheses determined by gas chromatography, intermolecular competition method.

TABLE III
RATES OF SUBSTITUTED BENZYL CHLORIDES WITH CHROMOUS PERCHLORATE^a

Benzyl chloride	(ArCH ₂ Cl), M	(Cr _{aq} ⁺²), M	k ₂ , l./mole-min.	k/k ₀ ^b
Unsub.	0.0050	0.033	0.190	1
<i>p</i> -Me	9.43×10^{-4}	.033	.305	1.60 (1.57)
<i>m</i> -Me	8.67×10^{-4}	.033	.195	1.02 (0.98)
<i>p</i> -Cl	7.12×10^{-4}	.033	.240	1.26 (1.34)
<i>m</i> -MeO	9.44×10^{-4}	.033	.18	0.95

^a At 27.5° in 71.5% ethanol–water for the first 25% of the reaction. ^b Rate relative to benzyl chloride. Values in parentheses determined by gas chromatography.

chromium intermediate. The kinetics were treated for the first 25% of the reaction as a pseudo-first-order reaction, since the chromous ion was used in excess to facilitate the formation of the complex.

Reaction with Acrylonitrile and Butadiene.—Attempts to trap a benzyl intermediate in the reaction was investigated by using acrylonitrile and butadiene in 80–90% ethanol as traps. If a 10-fold excess of acrylonitrile was present during the reaction of benzyl chloride and chromous perchlorate a 30–40% yield of γ -phenylbutyronitrile and 50–70% toluene was found. A similar reaction with benzyl bromide yielded 40–50% and 40–45% of phenylbutyronitrile and toluene, respectively. The yields of phenylbutyronitrile were slightly but not significantly greater if acrylonitrile was added before the chromous salt (*i.e.*, during the formation of benzylchromium ion) than if it was added to the preformed benzylchromium ion. In neither

case was polyacrylonitrile or bibenzyl significant products.

A similar reaction of butadiene and benzylchromium gave a 60–80% yield of toluene and only 4–6% 4-phenylbutene-1. The latter was the only isomeric phenylbutene formed in detectable amounts.

Experimental

Materials.—Chromous perchlorate was prepared by the reaction of electrolytic chromium metal chips (99.996% Cr, Var-lacoid Corp.) with perchloric acid (Mallinckrodt, AR grade) under a nitrogen atmosphere by the method of Lux and Illman.¹⁹

Chromous chloride was made by the reduction of chromic chloride with powdered zinc under a nitrogen atmosphere, or by dissolution of electrolytic chromium in hydrochloric acid.

Chromous titer was determined by quenching an aliquot of chromous solution in excess ferric chloride and titration of the resultant ferrous ion with standard ceric sulfate to the ferrous-phenanthroline end point (emerald green).

Benzyl chloride (Baker, AR grade) was redistilled before use; b.p. 83.5° at 27 mm.; **benzyl bromide** (Eastman Chemical) redistilled; b.p. 106–107° at 25 mm.; *m*-methylbenzyl chloride (Benzol Products Corporation) redistilled, b.p. 62.5–63° at 3 mm.; *p*-methylbenzyl chloride (Matheson Coleman and Bell) redistilled, b.p. 45–46° at 0.5 mm.; *p*-chlorobenzyl chloride (Matheson Coleman and Bell) redistilled, b.p. 80° at 2 mm.; *m*- and *p*-fluorobenzyl chloride (Peninsular Chemresearch); *m*-cyanobenzyl chloride was prepared by the photolytic chlorination of *m*-cyanotoluene in carbon tetrachloride; m.p. 69–70° (uncor.). *m*-Bromobenzyl bromide was made by bromination of *m*-bromotoluene in carbon tetrachloride; m.p. 40°. *p*-Bromobenzyl bromide (Matheson Coleman and Bell) was recrystallized from ethanol; needles, m.p. 61–62°. *m*-Methylbenzyl bromide (Benzol Products Corp.) was used as supplied. *p*-Methylbenzyl bromide (Matheson Coleman and Bell) was recrystallized from ethanol; needles, m.p. 31–32°. *m*-Chlorobenzyl bromide (K & K Laboratories) was redistilled; b.p. 85° at 2 mm. *p*-Cyanobenzyl bromide (K & K Laboratories) was used as supplied; m.p. 115° (lit. 115–116°); α -chloronaphthalene (Benzol Products Corp.); **benzal chloride** (Hooker Chemical Co.).

Acrylonitrile and butadiene (Matheson Co.) were redistilled prior to use; chromic sulfate and chromic chloride (Mallinckrodt AR grade); chromic perchlorate and lithium perchlorate (G. F. Smith Chem. Co.).

α, α -Dimethyl- β -phenethyl Hydroperoxide.—A 69% solution of sulfuric acid (33 g. of sulfuric acid and 15 g. of water) was chilled to 0°. α, α -Dimethyl- β -phenethyl alcohol (39 g.) was added dropwise, followed by a solution of 23.8 g. of 90% hydrogen peroxide in 19.2 g. of water at 0°. The reaction was stirred at room temperature for 6 hr. Water and 50 ml. of ether were added and the ethereal extract was washed with water, saturated sodium carbonate, dried over sodium sulfate, and distilled *in vacuo*. The forerun consisted of 0.5 g. of a phenylbutene mixture, and the residue of a mixture of α, α -dimethyl- β -phenethyl alcohol and hydroperoxide (48% by hydroperoxide titration). The hydroperoxide was isolated *via* the sodium salt (extraction with 40% sodium hydroxide) as a colorless oil which crystallized on standing. It was recrystallized several times from isopentane; m.p. 45–46°.

Determination of Rate Constants. A. General Spectroscopic Methods.—Solvent (95 or 71% ethanol) was placed in a specially constructed Pyrex cell. The cell was sealed by means of serum caps and flushed with nitrogen, using hypodermic needles as inlet and outlet. Chromous solution was added by hypodermic syringe. The cell was placed in the thermostated cell compartment of a Beckman Model DB spectrophotometer and allowed to come to thermal equilibrium and the absorbance meter balanced to read 0 absorbance at the wave length maximum of the benzylchromium complex to be studied. The cell was then charged with benzyl halide, shaken, and replaced. The rate of appearance of complex was recorded on a Sargent Model SRL recorder at a chart speed of 1 in. per min.

The extinction coefficient of unsubstituted benzylchromium ion was determined by treating incremental amounts of α, α -dimethyl- β -phenethyl hydroperoxide with excess chromous perchlorate in the absorption cell.

For example, 1.6005 g. (9.64 mequiv.) of phenyl-*t*-butyl hydro-

peroxide was dissolved in 25 ml. of 95% ethanol; 49 ml. of 95% ethanol was placed in the spectrophotometric cell and the cell flushed with nitrogen; 1 ml. of 1.18 *N* chromous perchlorate was added with a syringe and the cell balanced at 360 $m\mu$ against a reference cell containing ethanol. Incremental amounts of the hydroperoxide were added, the cell was shaken, replaced, and the absorbance noted. The formation of benzylchromium is linear with added chromous ion as shown in Table IV.

TABLE IV
DETERMINATION OF EXTINCTION COEFFICIENT OF
BENZYLCHROMIUM AT 360 $m\mu$

Concn. of BzCr ²⁺ (m./l.) (assum. 100% concn.) $\times 10^4$	1.00-cm. cell absorbance
7.71	0.185
10.0	.247
15.4	.380
18.5	.456
20.8	.508

The slope of a plot of these data yielded an extinction coefficient of 2470 l./mole-cm.

The formation of benzylchromium was followed by examining the absorption band at 360 $m\mu$. Some typical results are shown in Table V. The complete visible and ultraviolet spectra were taken in degassed 1-cm. quartz cells fitted with rubber serum caps.

TABLE V
SPECTROSCOPIC RATES OF FORMATION OF BENZYLCHROMIUM^a

Solvent	[Cr _{aq} ²⁺], M	[Benzyl Cl], M	Cr ²⁺ /BzCl ratio	k_2 , l./mole-min.
92% EtOH	0.010	0.010	1	0.146 ^b
92% EtOH	.010	.0050	2	.144 ^c
92% EtOH	.020	.0050	4	.146 ^d
92% EtOH	.030	.0050	6	.138
92% EtOH	.0007	.0073	0.1	.162
92% EtOH	.0021	.0220	0.1	.172
92% EtOH	.010	.0014	14	.152
92% EtOH	.020	.0028	14	.155
71.5% EtOH	.025	.00707	3.5	.154

^a Determined for first 15% of the reaction at 25.5°. ^b Calculated from $k_2 = 1/(x/a(a-x))$. ^c Calculated from slope of plot $\log [(a-x)/(b-x)]$, $k_2 = 2.303/\text{slope}(a-b)$. ^d Calculated from slope of plot $\log [(b-2x)/(a-x)]$, $k_2 = 2.303/\text{slope}(b-2a)$.

The effect of added salts on the formation of benzylchromium ion is shown in Table VI.

TABLE VI
EFFECT OF ADDED SALTS ON THE FORMATION OF
BENZYLCHROMIUM ION^a

[Cr _{aq} ²⁺]	[BzCl]	Added salt	Concn. added salt, M	μ	k_2 , l./mole-min.	k/k_0
0.033	0.0050	None	...	0.099	0.197	1.0
.033	.0050	None099	.197	1.0
.33	.0025	None99	.277	1.4
.033	.0050	LiClO ₄	0.9	.999	.25	1.27
.033	.0050	LiClO ₄	.45	.549	.223	1.13
.033	.0050	HClO ₄	.919	1.02	.258	1.31
.033	.0050	LiCl	.9	0.999	.150	0.76

^a In 71.5% ethanol-water at 27.5°.

Gas-Liquid Chromatographic Method. The area ratios, $A_{\text{marker}}/A_{\text{benzylchloride}}$, of solutions of benzyl chloride and marker (naphthalene) in ethanol were determined. A known amount of the benzyl halide-marker solution was pipetted into a 125-ml. erlenmeyer flask and solvent (95% ethanol) added. The flask was sealed by means of a serum cap and flushed with nitrogen. The chromous perchlorate was added *via* syringe. The solution was allowed to react for a period of time and then an aliquot removed and immediately injected into the gas chromatograph. The rate was followed by monitoring the disappearance of benzyl chloride with respect to the marker ($A_{\text{Cl}}/A_{\text{m}}$). The product ($A_{\text{m}}/A^\circ \times A/A_{\text{m}}$) is equal to A/A° , the fraction of benzyl chloride remaining. The

(19) H. Lux and G. Illman, *Ber.*, **91**, 2143 (1958).

parameters of the second-order rate law were calculated from this ratio and the initial concentrations.

An Aerograph Hy-Fi, Model 600 with a 6 ft. \times $1/8$ in. stainless steel column packed with SE-30 on Chromosorb W (80–100 mesh) was used. This column worked well with most chlorides, except the polar cyanobenzyl chlorides, but most of the bromides decomposed on the column. That benzyl chloride did not decompose on the column was shown by the reproducibility of the $A_{\text{chloride}}/A_{\text{marker}}$ ratio at various levels.

Intramolecular competition between two chlorides was also determined by gas chromatography. The areas of the competing reactants relative to a marker (naphthalene) were determined initially. An excess of the chlorides (100%) was used. After allowing the reaction with chromous to proceed to completion, the relative areas of the remaining chlorides to the marker were redetermined. The product of the initial ratio, $A_m/A^{\circ}\text{Cl}_1$, and the final ratio, A/A_m , is the fraction of chloride remaining. The relative rates are then $k_1/k_2 = (\ln f_1/\ln f_2)$, where k_1/k_2 is the relative rate, f_1 = fraction of reactant chloride 1 remaining, and f_2 = fraction of reactant chloride 2 remaining.

Of the two methods (spectroscopic and chromatographic) the spectroscopic method proved to be the more reliable and reproducible.

The rate of disappearance of benzyl chlorides at several temperatures is given in Table VII.

TABLE VII

VARIATION IN THE RATE CONSTANT WITH TEMPERATURE^a

Temp., °C.	[Cr _{aq} ⁺²], M	[C ₆ H ₅ CH ₂ Cl], M	Ratio	k_2 , l./mole-min.
0	0.345	0.097	3.5	0.024
26	.320	.097	3.5	.26
14.7	.345	.097	3.5	.10

^a In 71.5% ethanol-water.

Trapping with Acrylonitrile.—In a large-scale reaction, a mixture of 95% ethanol (50 ml.), water (25 ml.), and 105 mequiv. of acrylonitrile (5.6 g.) was placed in a 250-ml. 3-necked flask fitted with a nitrogen inlet, serum cap, and pressure equalizing addition funnel; 70 mequiv. (8.86 g.) of benzyl chloride in 100 ml. of ethanol was placed in the funnel and the top of the funnel connected to a mercury bubbler. The flask was flushed with nitrogen for 30 min. and then 50 ml. of 2.8 N chromous perchlorate added *via* syringe. The benzyl chloride solution was allowed to drop in slowly forming a yellow-green solution. The yellow color faded within 24 hr. leaving an emerald green solution. The ethanol and excess acrylonitrile were stripped off and the resultant paste of chlorochromic perchlorate extracted with ether. The ether extract yielded 2 g. (20%) of a colorless liquid boiling at 99–100° at 0.5 mm. The liquid had the odor of cinnamon.



The spicy smelling liquid was identified as 4-phenylbutyronitrile by hydrolysis to 4-phenylbutyric acid, m.p. 50–50.5° (lit.²⁰ 47–51°) and by formation of the 4-phenylbutyramide by reaction with alkaline hydrogen peroxide²¹; m.p. 84° (lit.²⁰ 84°). The infrared spectrum was identical with a known sample (Eastman). If a solution of benzylchromium (*ex* hydroperoxide) is treated with acrylonitrile, 4-phenylbutyronitrile is also formed.

Discussion

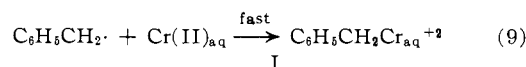
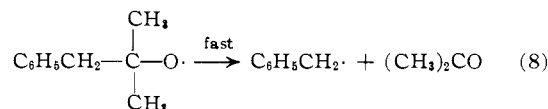
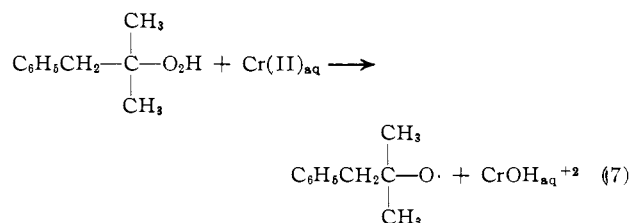
The reaction of benzyl chloride and chromous ion to form toluene and bibenzyl can be considered to proceed in two discrete stages: first, the formation of the benzylchromium complex ion as an intermediate and, second, the decomposition of the benzylchromium ion to the products of the reaction. Though benzylchromium ion is a metastable intermediate and attains less than 50% of its maximum concentration, the formation of the complex is aided by the reactivity of the benzyl halide and in the case of bromide and iodide the competition with its destruction is sufficiently slow at 25°

(20) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 277.

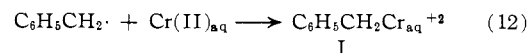
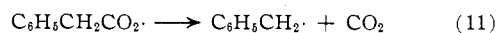
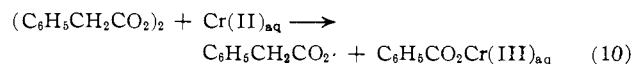
(21) J. W. Murray and W. B. Cloke, *J. Am. Chem. Soc.*, **56**, 2741 (1934).

that a quantitative yield of benzylchromium ion is attained. In the subsequent discussion, the reaction will be treated in terms of the formation and decomposition of the complex ion I. Among various substituted benzyl halides the formation of an aralkylchromium species as an intermediate is a general phenomenon. However, in certain cases like trityl chloride, α -phenethyl chloride, 1-bromotrypticene, and most aliphatic halides where no organochromium ion was detected, it cannot be stated with certainty that these complex ions, labile as they are, are intermediates.

Benzylchromium Ion.—The properties of benzylchromium ion generated from benzyl chloride, bromide, or iodide are the same as that derived from dimethylphenethyl hydroperoxide. In the latter case the formation of benzylchromium ion must proceed *via* the general route²² for the metal ion-catalyzed decomposition of alkyl hydroperoxides given in eq. 7–9. The fragmentation of α,α -dimethoxy- β -phenethoxy radical is known to be rapid.²³ However, the forma-



tion of a benzyl radical as a discrete entity could not be fully established.²⁴ Similarly, bisphenylacetyl peroxide²⁵ is readily reduced by chromous perchlorate at 0° to yield the same benzylchromium ion I.²⁶ The reduction of diacyl peroxides by cuprous salts has been studied,²⁷ and a mechanism proposed which can be readily applied to the stoichiometric reduction of bisphenylacetyl peroxide by chromium(II) (eq. 10–12) to yield benzylchromium ion.



There is no doubt that the reductions of diacyl peroxides by cuprous salts do produce alkyl radicals.^{27,28}

Trapping experiments with acrylonitrile and butadiene were not conclusive since benzylchromium ion

(22) E. G. E. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Inc., New York, N. Y., 1961, p. 104 ff; J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 774 (1962).

(23) R. Hiatt and W. M. J. Strachan, *J. Org. Chem.*, **28**, 1893 (1963).

(24) Though Hiatt has shown that the dimethylphenethoxy radical is an intermediate in the thermolysis of the hydroperoxide, the possibility of a concerted one-step formation of benzyl radical directly from the hydroperoxide (eq. 10 and 11 combined) cannot be eliminated, although it is deemed unlikely.

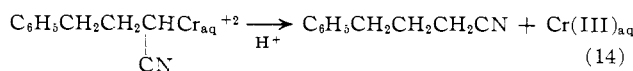
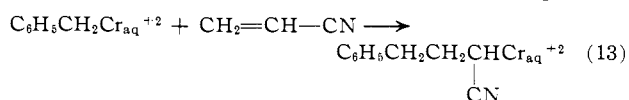
(25) P. D. Bartlett and J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 3030 (1950).

(26) Unpublished results, J. K. Kochi.

(27) J. K. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963); *Tetrahedron*, **18**, 483 (1962).

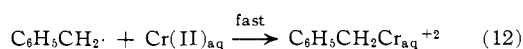
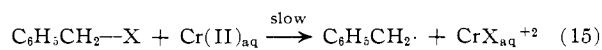
(28) To be published; R. V. Subramanian and H. E. Mains.

itself reacts with these unsaturated compounds.²⁹

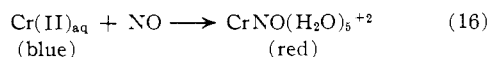


The formation of 4-phenylbutene-1 as the sole isomer from benzylchromium ion and butadiene is consistent with earlier results obtained from the reduction of allylic halides^{3c} and the protonation of the phenylbutenyl carbanion.³⁰ Though definitive evidence for benzyl radical has not been forthcoming, it is unlikely that conventional techniques^{3b} can be applied for its detection since its lifetime would be short, owing to its rapid interaction (eq. 12)³¹ with the paramagnetic chromous ion.⁹

The formation of benzylchromium ion from benzyl halide and chromous ion proceeds according to the stoichiometry given in eq. 5 and utilizes one benzyl halide and two chromous ions. Since the rate of formation of I is first order each in the halide and chromous ion, it requires a multi-step sequence. The rate of disappearance of benzyl chloride being equal to the rate of formation of benzylchromium ion, we propose that the following sequence³² is operable

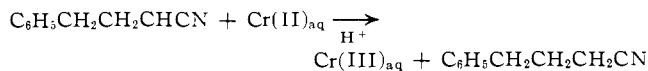
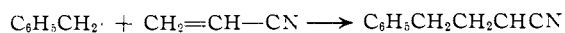
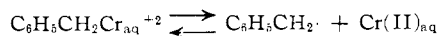


The rapidity of the free radical coupling with chromous ion in the second step (12) is in harmony with the results of the hydroperoxide experiments and the facile formation of an analogous nitrosochromic ion³³ with nitric oxide.



The formation of the chlorochromic ion, $\text{CrCl}_{\text{aq}}^{+2}$, indicates³⁴ that chlorine is being transferred directly from benzyl chloride to the chromous ion in the rate-determining step (15), since such a chlorochromic complex is not formed from the aquochromic ion and chloride ion under the conditions of these reactions. The rate of formation of benzylchromium ion is retarded at moderately high chloride concentrations in a

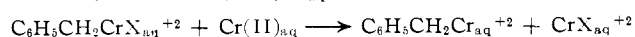
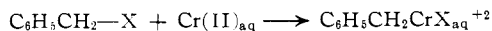
(29) Rather than a concerted addition to the double bond, the reaction may proceed via benzyl radicals (*vide infra*).



(30) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 1145 ff.

(31) It is likely that eq. 12 is reversible²⁹; *vide infra*.

(32) We disfavor an alternative scheme involving a direct insertion. Such a mechanism would require that an entirely different course be formulated



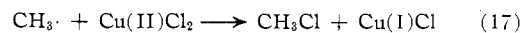
for the reaction of dimethylphenethyl hydroperoxide and bisphenylacetyl peroxide with chromous ion.

(33) M. Ardon and J. Herman, *J. Chem. Soc.*, 507 (1962).

(34) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954); H. Taube, H. Meyers, and R. C. Rich, *ibid.*, **75**, 4118 (1953); N. Bjerrum, *Z. physik. Chem.*, **59**, 581 (1907).

direction opposite to a general salt effect. It is attributed to the regeneration of benzyl chloride from I by reaction with chloride ion.³⁵

Formally, the slow step (15) in these reactions is analogous to the atom-transfer reactions of chromous with transition metal halide complexes,³⁶ and it is the microscopic reverse process for the oxidation of free radicals by the ligand-transfer mechanism³⁷; *e.g.*



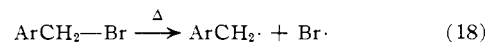
As such, the electronic requirements for both processes should be the same. Thus a measure of these electronic effects in atom-transfer reactions can be determined by comparing the relative rates of reaction of various substituted benzyl halides. These relative rates of reduction are compared with the Hammett σ -parameter in Table VIII. Also included are rates of

TABLE VIII
RELATIVE RATES OF REDUCTION AND PYROLYSIS OF
BENZYL HALIDES

Rel. rates of benzyl bromide reduction, 27.5 ± 0.5°, aq. ethanol	Rel. rates of benzyl bromide pyrolysis, 800°K., toluene carrier method	Hammett σ	Substituent
1.00	1.00	0.00	H
1.04 (1.02) ^a	1.02	- .069	<i>m</i> -Me
1.33 (1.6) ^a	..	- .170	<i>p</i> -Me
1.07	1.13	+ .373	<i>m</i> -Cl
.. (1.26) ^a	1.3	+ .227	<i>p</i> -Cl
1.17	1.24	+ .391	<i>m</i> -Br
1.43	1.24	+ .232	<i>p</i> -Br
1.04 (0.95) ^a	..	+ .115	<i>m</i> -MeO

^a Benzyl chlorides.

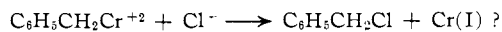
pyrolysis of benzyl bromides in the gas phase obtained by Szwarc, *et al.*,³⁸ using the toluene carrier method. It is apparent that there is no correlation between



the relative rates of reduction and the Hammett linear free-energy relationship. All substituents increase the rate of reduction relative to the unsubstituted compound, albeit in relatively small degree, and the effect is much the same as those obtained by Szwarc from pyrolysis studies. The latter correlation provides further support for the homolytic dissociation of the benzyl-halogen bond in the rate-controlling step.

Recently Menapace and Kuivila³⁹ described the reduction of alkyl halides by organotin hydrides as a free-radical chain process. For discussion here, the relevant chain-transfer step which they postulated as

(35) This can be observed directly by treating benzylchromium ion with lithium chloride or hydrochloric acid in the absence of transition metal ions. Though toluene is the main product, discrete amounts of benzyl chloride are formed. The reaction with iodide is faster, but the stoichiometry of these reactions is not completely clear.

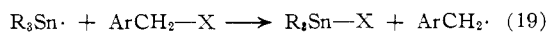


(36) (a) H. Taube, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 1, Academic Press, Inc., New York, N. Y., 1959, p. 1 ff.; *Can. J. Chem.*, **37**, 129 (1959); (b) J. Halpern, *Quart. Rev. (London)*, **15**, 207 (1961).

(37) C. H. Bamford, A. Jenkins, and R. Johnson, *Proc. Royal Soc. (London)*, **A239**, 214 (1957); J. Kumamoto, H. DeLaMare, and F. F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960); J. Kochi, *ibid.*, **78**, 4815 (1956); **79**, 2942 (1957); **84**, 2124 (1962).

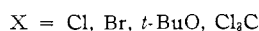
(38) M. Szwarc, C. H. Leigh, and A. H. Sehon, *Proc. Roy. Soc. (London)*, **A209**, 97 (1951).

(39) L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).



is akin to reaction 15 in the reductions by chromous ions. Though only a limited number of aralkyl halides were examined, their results parallel ours. Thus, *m*-trifluoromethylbenzyl chloride is reduced only 1.6 times faster than benzyl chloride, *m*-bromobenzyl bromide 1.1 times faster than benzyl bromide, and benzyl bromide is reduced 67 times faster than benzyl chloride.

The relatively small polar effect in the chlorine atom-transfer reaction and the pyrolysis of the bromides is in marked contrast to the strong Hammett correlation and the pronounced polar effect in hydrogen atom-transfer reactions from substituted toluenes by atoms and free radicals. The implications of this in considering electron transference in free radical-chain-

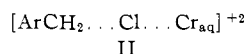


transfer reactions has been discussed.⁴⁰

The slow halogen atom-transfer step is fastest with iodide and slowest with chloride, the relative rates for the iodide, bromide, and chloride being 555, 124, and 1, respectively. This order also follows the bond dissociation energies of the benzyl derivatives, benzyl iodide, benzyl bromide, and benzyl chloride, of 39, 51, and 60 kcal./mole, respectively,⁴¹ and chain-transfer reactivities of alkyl halides toward carbon radicals.⁴²

There is a similarity of reaction type between the reduction of benzyl halides by chromous ion and the reduction of halopentamminechromic complexes in aqueous perchloric acid studied by Taube and Ogard.⁴³ Some results are summarized in Table IX.

It is generally accepted³⁶ that these reactions proceed *via* a halogen-bridged activated complex. Applied to the reduction of benzyl halides, a transition state such as II is proposed.



The only slightly increased rate of the reaction with

(40) (a) J. K. Kochi and D. D. Davis, *Nature*, **202**, 690 (1964); (b) see also G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2361 (1964).

(41) M. Szwarc, *Chem. Rev.*, **47**, 75 (1950); M. Ladaeki and M. Szwarc, *Proc. Roy. Soc. (London)*, **A219**, 341 (1953); F. P. Lossing, K. U. Ingold, and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 1489 (1954).

(42) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 239 ff.

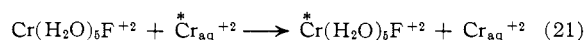
(43) H. Taube and A. Ogard, *J. Am. Chem. Soc.*, **80**, 1084 (1958).

TABLE IX

Oxidant	REDUCTION BY Cr(II)				Ref.
	k_2 , l./mole-sec.	T , °C.	ΔH^* , kcal./mole	ΔS^* , e.u.	
(NH ₃) ₅ CrF ⁺²	2.7×10^{-4}	25	13.4	-30	43
(NH ₃) ₅ CrCl ⁺²	5.1×10^{-2}	25	11.1	-23	43
(NH ₃) ₅ CrBr ⁺²	3.2×10^{-1}	25	8.5	-33	43
(NH ₃) ₅ CrI ⁺²	5.5	25	43
(H ₂ O) ₅ CrF ⁺²	2.6×10^{-2}	27	13.7	-20	44
(H ₂ O) ₅ CrCl ⁺²	5×10^{-2}	0	45
PhCH ₂ Cl	3.2×10^{-3}	27	14.0	-14.3	This work
PhCH ₂ Br	4.1×10^{-1}	27	This work
PhCH ₂ I	1.8	This work

increasing ionic strength is also consonant with this postulate.

The values for the activation enthalpies for the reactions of the pentamminechromic complexes are similar to those for the benzyl halide reactions. The entropies of activation, however, are slightly higher, presumably because the former reaction involves rearrangement in the coordination sphere of the oxidizing agent, leading to the loss of the ammonia ligands. The reaction



in which a ligand is exchanged between isotopes has been studied⁴⁴ and the activation parameters determined as $\Delta H^* = 13.7$ kcal./mole and $\Delta S^* = -20$ e.u. at $\mu = 1.0$. Although still higher, the change in ΔS^* might be accounted for by the fact that the oxidant, benzyl chloride, has a lower requirement of bond stretching and ligand rearrangement compared to an inorganic aquo-ion. Although a study of entropies of activation is by no means conclusive evidence in the elucidation of a mechanism, it is instructive to note that the entropies of activation for the halogen abstraction reaction decrease in the order (NH₃)₅CrX⁺² > (H₂O)₅CrX⁺² > C₆H₅CH₂X, in accordance with decreasing requirements of ligand (NH₃, H₂O, solvent) participation in the transition state.

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(44) D. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

(45) H. Taube and E. L. King, *ibid.*, **76**, 4053 (1954).