example of the infrared spectra. The infrared data are summarized in Tables II and III.

A study of the effect of added water on the infrared spectra was carried out in the case of the cyclopentyl and cyclobutyl complexes. Smears of the neat complexes were prepared between two Irtran plates in a drybox. The smears were then taken out of the drybox and the two Irtran plates separated. The films were exposed to air for periods of 30 sec, 1 min, 3 min, and 5 min, then the plates were pressed together and the spectra obtained.

Nmr Investigations. The spectra were obtained on Varian Associates Model A60, A56-60, and HA60 spectrometers in sulfur dioxide solution at −20 to −70°. The spectra were found temperature independent. The spectra are shown in Figures 2 to 8 and the data are summarized in Table III. The chloride complexes decompose when dissolved in SO_2 and no meaningful spectra could be obtained.

Reaction of Oxocarbonium Salts with Aromatic Compounds. (A) **Without Solvent.** The cycloalkyloxocarbonium salt (0.2 mole) was added to 0.5 mole of well-stirred aromatic hydrocarbon (benzene, toluene). The complex salts are generally not soluble in the aromatics. In most cases gentle heating was necessary to start the reaction. The formed ketones give complexes with the byproduct Lewis acids and separate from the excess aromatic as a separate lower layer. After washing the reaction mixtures with water, they were dried over Na_2SO_4 and the products isolated in the usual manner.

(B) **In Solution.** In these experiments, the reaction was carried out in nitromethane solutions in which the aromatics and the oxocarbonium salts are both soluble. The reactions are much slower in solvent, and owing to the partial decomposition of the oxocarbonium salts in nitromethane the yields are lower.

Reaction of Oxocarbonium Salts with Alcohols. Oxocarbonium salt (0.1 mole) was added as nitromethane solution or in small portions as a solid into excess of the appropriate stirred and cooled alcohol. A fast reaction takes place. The resulting mixture was washed with water, dried over Na_2SO_4, and fractionated.

Reaction of Oxocarbonium Salts with Mercaptans. The oxocarbonium salt (0.1 mole) was added in nitromethane solution or in small fractions as a solid to an excess of well-stirred and cooled mercaptan. The reaction is very fast. After completion of the reaction, the mixture was washed with water, dried over Na_2SO_4, and fractionated.

Reaction of Oxocarbonium Salts with Amines. The solution of 0.1 mole of oxocarbonium salt in nitromethane solution was added to excess of the sitrred and cooled primary or secondary amine. The products, after water washings, were isolated.

Acknowledgment. This work was supported by grants from the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society.

Carbenoid Intermediates from Polyhalomethanes and Chromium(II). The Homogeneous Reduction of Geminal Halides by Chromous Sulfate

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Contribution from the Departments of Nematology and Chemistry, University of California, Riverside, California 92502. *Received May 31, 1966*

Abstract: The rapid homogeneous reduction of a wide array of geminal halides and polyhalomethanes by chromous sulfate in aqueous dimethylformamide has been examined at room temperature. The products, reactivities, and kinetics suggest a mechanism involving metal ion complexes of α-halomethyl radicals and carbenes. A dimethylmethyl fragment could be transferred to olefins to result in *gem*-dimethylcyclopropanes.

Earlier studies[1] of the homogeneous oxidation of chromous sulfate by alkyl halides have pointed up the unusual rapidity of the reaction of methylene bromide with this salt in aqueous dimethylformamide. The present work portrays the general scope and mechanism of the interaction of geminal halides and polyhalomethanes with this reagent.

Based upon ion exchange and elemental analysis of the resulting solution, a red ion noted to result from the addition of chloroform[2] to aqueous chromous perchlorate was assigned the formula $(CrCHCl_2)^{2+}$. Warming the solution of the ion resulted in the production of a green solution of Cr(III) that contained

$$HCCl_3 + Cr^{2+} \longrightarrow CrCl^{2+} + (CrCHCl_2)^{2+} \longrightarrow Cr(III) + Cl^- \quad (1)$$

chloride ion (eq 1). No organic products were detected. The existence of such an ion was in keeping with reports of the production of benzylchromium,[3] $(PhCH_2Cr)^{2+}$, by a process similar to eq 1. Subsequently, the rates of production of a series of substituted benzylchromium ions[4a] and their decomposition[4b] to bibenzyl and toluene have been examined. Quite recently solutions of air-stable ions derived from haloethyl- and halomethylpyridinium salts and Cr(II) have been observed.[5]

Several isolated cases of the oxidation of transition metal species by polyhalomethanes have been reported. Thus, carbon tetrachloride has been noted to oxidize cobaltocene,[6] bis(ethylbenzene)chromium,[7] and chromous chloride.[2,8a,b] Benzal chloride has been converted to a mixture of stilbenes and ethers, and diphenyldichloromethane to *sym*-tetraphenylethylene,

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

(2) F. A. L. Anet, *Can. J. Chem.*, 37, 58 (1959).

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

(4) (a) J. K. Kochi and D. D. Davis, *ibid.*, 86, 5264 (1964); (b) J. K. Kochi and D. Buchanan, *ibid.*, **87**, 853 (1965).

(5) R. G. Coombes, M. D. Johnson, M. L. Tobe, N. Winterton, and L.-Y. Wong, *Chem. Commun.*, 251 (1965); R. G. Coombes, *et al.*, *J. Chem. Soc.*, 7029 (1966).

(6) S. Katz, J. F. Weher, and A. E. Voigt, *J. Am. Chem. Soc.*, **80**, 6459 (1958).

(7) G. A. Razuvaev and G. A. Domrachev, *Tetrahedron*, **19**, 341 (1963).

(8) (a) H. Lux, D. Sarre, and I. Schaffelhofer, *Ber.*, **97**, 2301 (1964); (b) T. Kiba and K. Terada, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **75**, 196 (1954).

Table I. Products of Reaction of Polyhalides with Chromous Sulfate in 1:1 Dimethylformamide–Water at Room Temperature

Substrate	Cr^{2+} stoichiometry[a]	Products	Conversion,[b] %	Yield (calcd),[c] %	Reactivity
Methylene iodide	(4)	Methane	98		Rapid, less than 1 hr to completion
1,1-Diiodoethane	(4)	96% ethane	86		
	(2)	4% ethanol			
1,1-Diiodopropane	(4)	96% propane	82		
	(2)	4% propylene			
	(2)	Trace (<1%) 1-propanol			
Iodoform	(6)	Methane	96		
Bromoform	6	Methane	101	99	
p-Bromophenyl dibromomethyl ketone	4	86% *p*-bromoacetophenone	93	99	
	6	14% 1,2-bis(*p*-bromobenzoyl)-ethane			
Carbon tetrachloride	(8)	25% methane	103	69	
	(2)	75% carbon monoxide			
Carbon tetrabromide	8	52% methane	102	86	
	2	39% carbon monoxide			
	12	5% ethylene			
		4% carbon dioxide			
Benzotrichloride	6	68% toluene	82	96	
	4	32% benzyl alcohol (benzaldehyde)[d]			
Methylene bromide	4	Methane	97	101	Moderate, 1 hr to 1 day to conversion indicated
1,1-Dibromoethane	4	73% ethane	93	96	
	2	27% ethanol			
2,2-Dibromopropane	4	3% propane	103	97	
	2	21% propylene			
	2	76% 2-propanol			
Benzal chloride	4	74% toluene	94	98	
	2	26% benzyl alcohol			
Chloroform	6	Methane	96	96	
1,1,1-Trichloroethane	4	66% ethanol (acetaldehyde)[d]	74	102	
	6	26% ethane			
	4	8% ethylene			
	2	Trace (<1%) vinyl chloride			
Methylene chloride	4	Methane	30	100	Slow, 1 to 5 days to conversion indicated
1,1-Dichloroethane	4	70% ethane	99	97	
	2	30% ethanol			
1,1-Dichloropropane	4	62% propane	78	95	
	2	23% propylene			
	2	15% 1-propanol			
2,2-Dichloropropane	4	2% propane	94	92	Slow, 1 to 5 days to conversion indicated
	2	23% propylene			
	2	75% 2-propanol			
1,1-Dibromopropene	4	50% propylene	68	98	
	2	Trace propyne			
	2	50% 1-bromopropene			

[a] Values in parentheses denote inferred stoichiometry. [b] Conversion to indicated products. [c] Yields bases on Cr^{2+} stoichiometry. [d] Aldehyde was shown to be a product but was further reduced under the reaction conditions.

by the action of chromous chloride in aqueous ethanol.[9]

A recent study[8a] of dehalogenations with chromous chloride in 80% aqueous ethanol has shown chloroform, bromoform, iodoform, methylene iodide, trichloroacetic acid, and trichloroacetaldehyde to oxidize this reagent. Although the reactions were not quantitated, chloroform was observed to produce methane. Trichloroacetic acid and trichloroacetaldehyde yielded acetic acid and acetaldehyde, respectively, and most significantly carbon tetrachloride when treated with chromous sulfate and sulfuric acid was found to yield methane, carbon monoxide, and hydrogen sulfide.

In a model system for biological dehalogenations, iron(II) deuteroporphyrin was found to convert 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane (DDT) to the corresponding dichloromethyl derivative[10] (DDD).

Results

Stoichiometry. The results of the homogeneous reaction of a series of polyhalomethanes with chromous sulfate in 1:1 dimethylformamide–water at room temperature are presented in Table I. The substrates are listed in decreasing order of reactivity. The initial concentrations of chromous sulfate and organic halide were in the range 0.1–0.35 and 0.012–0.05 *M*, respectively.

In keeping with the general lethargy of vinylic halides,[11] tetrabromoethylene reacted very slowly but products were not determined. For the haloforms, methyl halides and the ethylidene and isopropylidene chlorides and bromides, the product distribution is independent of the nature of the halide substituents. Both ethylidene and propylidene iodides, however, afford a larger amount of alkane than the chloride or bromide derivatives. The effect of increasing the initial

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(9) J. F. Neumer and S. Aktipis, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, p 90.

(10) C. E. Castro, *J. Am. Chem. Soc.*, 86, 2310 (1964), and references therein.

(11) W. C. Kray, Jr., and C. E. Castro, *ibid.*, **86**, 4603 (1964).

Table II. Product Distribution as a Function of Initial Concentrations

Substrate	Ratio of concn $(Cr^{2+})_0/(RBr_2)_0$	Product distribution	Conversion,[a] %	Yield (calcd), %[b]
1,1-Dibromoethane	5.45	27% ethanol 73% ethane	93	96
	7.26	14% ethanol 80% ethane	88	88
2,2-Dibromopropane	5.45	76% 2-propanol 21% propylene 3% propane	103	97
	10.9	75% 2-propanol 21% propylene 4% propane	90	

[a] Conversion to indicated products. [b] Yields based on Cr^{2+} stoichiometry.

Cr(II):substrate ratio upon the distribution of products is given in Table II for ethylidene and isopropylidene bromides.

The general chemistry and material balance given in Table I is exemplified by the following sets of equations. For tetrahalides

$$\mathrm{CBr_4}\begin{cases} \xrightarrow{52\%}\ 8Cr^{2+} + 4H^+ \longrightarrow CH_4 + 8Cr^{3+} + 4Br^- \\ \xrightarrow{39\%}\ 2Cr^{2+} + H_2O \longrightarrow CO + 2H^+ + 2C^{3+} + 4Br^- \\ \xrightarrow{5\%}\ 6Cr^{2+} + 2H^+ \longrightarrow \tfrac{1}{2}CH_2{=}CH_2 + 6Cr^{3+} + 4Br^- \\ \xrightarrow{4\%}\ 2H_2O \longrightarrow CO_2 + 4H^+ + 4Br^- \end{cases} \qquad (2)$$

For trihalides

$$\mathrm{CH_3CCl_3}\begin{cases} \xrightarrow{26\%}\ 6Cr^{2+} + 3H^+ \longrightarrow CH_3CH_3 + 6Cr^{3+} + 3Cl^- \\ \xrightarrow{66\%}\begin{cases} 2Cr^{2+} + H_2O \longrightarrow CH_3CHO + 2Cr^{3+} + 3Cl^- + H^+ \\ 4Cr^{2+} + 2H^+ + H_2O \longrightarrow CH_3CH_2OH + 4Cr^{3+} + 3Cl^- + H^+ \end{cases} \\ \xrightarrow{8\%}\ 4Cr^{2+} + H^+ \longrightarrow CH_2{=}CH_2 + 4Cr^{3+} + 3Cl^- \\ \xrightarrow{<1\%}\ 2Cr^{2+} \longrightarrow CH_2{=}CHCl + 2Cr^{3+} + 2Cl^- \end{cases} \qquad (3)$$

For dihalides

$$\mathrm{(CH_3)_2CBr_2}\begin{cases} \xrightarrow{3\%}\ 4Cr^{2+} + 2H^+ \longrightarrow CH_3CH_2CH_3 + 4Cr^{3+} + 2Br^- \\ \xrightarrow{21\%}\ 2Cr^{2+} \longrightarrow CH{=}CHCH_3 + 2Cr^{3+} + 2Br^- \\ \xrightarrow{76\%}\ 2Cr^{2+} + H_2O \longrightarrow CH_3CH(OH)CH_3 + 2Cr^{3+} + 2Br^- \end{cases} \qquad (4)$$

It should be noted that for the trihalides benzotrichloride and 1,1,1-trichloroethane the alcoholic products also arise by a secondary path

$$RCHO + 2H^+ + 2Cr^{2+} \longrightarrow RCH_2OH + 2Cr^{3+} \qquad (5)$$

where $R = CH_3$ or phenyl. Thus in separate experiments under reaction conditions, acetaldehyde and benzaldehyde were reduced to the alcohols. When the halide reductions were run with an excess of Cr(II), no aldehydes could be detected. However, with less than stoichiometric amounts of reagent, both aldehyde and alcohol could be found. Runs with 1,1,1-trichloroethane were quenched with ferric chloride and monitored gas chromatographically. Although ethanol was always present in the product mixture, the rise and fall of acetaldehyde could be observed.

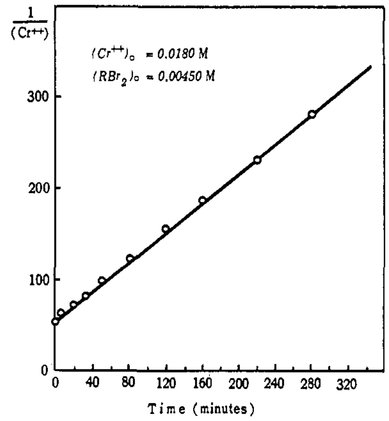

Figure 1. Second-order plot for methylene bromide with stoichiometric ratios of reactants.

Reactivities. In agreement with other studies,[1,8a,11] the rates of reaction of the halides for a given substitution type are in the order $I > Br > Cl$, and the speed of reaction is enhanced by increasing the number of halogen substituents. The sequence $CCl_4 > CHCl_3 > CH_2Cl_2 \gg CH_3Cl$ is illustrative, methyl chloride being inert. The favorable influence of phenyl and methyl substituents upon the reactivities of the halides is evident in the tri- and dihalide series: $PhCCl_3 > CH_3CCl_3 > HCCl_3$ and $PhCHCl_2 > (CH_3)_2CCl_2 > CH_3CHCl_2 > CH_2Cl_2$.

Kinetics. Reaction rates were followed by monitoring Cr(II) titrimetrically in the fashion previously described.[1] Reactions were carried out in 1:1 (v/v) aqueous dimethylformamide 1.0 *F* in perchloric acid at 29.8°. The calculated order by the fractional life method[12] for methylene bromide was 2.06. With the exception of chloroform, both stoichiometric and nonstoichiometric runs provided good second-order plots through 90% completion. A typical plot for methylene bromide is presented in Figure 1. With chloroform, however, the rate of consumption of Cr(II) decreased markedly after about 50% reaction. The reaction was found to obey the second-order rate expression valid for the other halides

$$\text{rate} = k_2(Cr^{2+})(\text{polyhalide})$$

by assessing initial slopes at various concentrations of the reactants. The constants are given in Table III, and the values represent an average of three separate determinations. In general, reproducibility was within 10%. Initial concentrations were in the range 0.012–0.03 *M* Cr(II) and 0.002–0.009 *M* organic halide.

The reduction of methylene bromide (eq 6) and chloroform (eq 7) was also examined under the higher

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(12) A. Frost and R. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p 40.

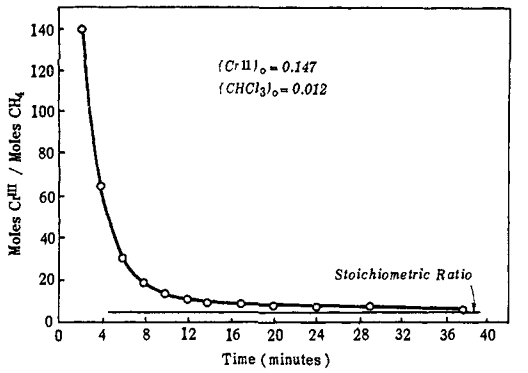


Figure 2. Relative rates of production of Cr(III) and methane from chloroform.

concentrations employed for general reaction conditions (without added acid to control ionic strength).

$$CH_2Br_2 + 4Cr^{2+} + 2H^+ \longrightarrow CH_4 + 4Cr^{3+} + 2Br^- \quad (6)$$

$$CHCl_3 + 6Cr^{2+} + 3H^+ \longrightarrow CH_4 + 6Cr^{3+} + 3Cl^- \quad (7)$$

In separate identical runs for each halide, Cr(II) was monitored in one flask and CH_4 production in another. The second-order rate constant for CH_2Br_2 checked[13] well with the value in Table III. For *neither* of these halides, however, did the rate of methane production parallel that of Cr(II) consumption. Indeed methane is produced at a much slower rate, and the stoichiometric balance for Cr(III) and methane is only attained near the end of the reaction. The plot in Figure 2 illustrates this trend for chloroform. The high 2-min point may reflect a lag in escape time of methane to the gas phase.[14a] Moreover, for both halides, after a brief initial lag, methane is produced in a first-order process, and the rate constant for this event *is the same* for either chloroform or methylene bromide. Thus, with $[CHCl_3]_0 = 0.012\ M$ and $[Cr(II)]_0 = 0.147\ M$, the reaction is 91% complete in 1 hr,[14b] and k_1 for methane production is 0.080 min^{-1}. Similarly with $[CH_2Br_2]_0 = 0.025$ and $[Cr(II)]_0 = 0.155$, k_1 was calculated to be 0.074 min^{-1}. That is, the rate of methane production is independent of the nature and concentrations of the starting halide!

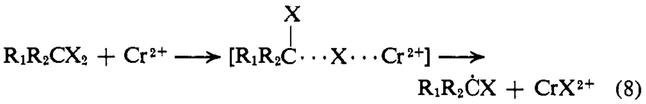
Table III. Second-Order Rate Constants for the Polyhalomethanes at 29.8°[a]

Halide	k_2, l./mole min
$(CH_3)_2CCl_2$	0.49
CH_2Br_2	0.76
$HCCl_3$	15[b]
$(CH_3)_2CBr_2$	138[c]

[a] μ = H$^+$ = 1.0; 1:1 dimethylformamide–H_2O. [b] Valid though only 50% completion and estimated from initial slopes. [c] An estimate, plots are nicely linear and extrapolate to correct zero time reading, but first point, at 2 min, represents 80% completion.

Discussion

The First Step. In harmony with the results of studies of the oxidation of chromous sulfate by monohalides[1] and vicinal dihalides,[11] the data in the foregoing section bespeak a rate-determining initial scission to an α-halo radical.



$$R_1R_2CX_2 + Cr^{2+} \longrightarrow [R_1R_2\overset{X}{\overset{|}{C}}\cdots X\cdots Cr^{2+}] \longrightarrow R_1R_2\dot{C}X + CrX^{2+} \quad (8)$$

The transfer of a halogen atom from carbon to chromium should be facilitated by the capacity for delocalization of the incipient radical inherent in the remaining carbon–halogen bond(s). That is, the more rapid reactions of the polyhalomethanes with Cr(II) as compared to monohalides can be rationalized by the same arguments that explain the easy initiation and long-chain radical halogenations with trichlorobromomethane.[15] In addition to the general reactivity sequence

$$Cl_3CBr + R\cdot \longrightarrow RBr + \cdot CCl_3 \quad (9)$$

and kinetics, a rate-determining initial scission to radicals[16] in the present study is supported by the observation that the addition of a chromous sulfate solution to a solution of isopropylidene bromide in water, dimethylformamide, and acrylic acid immediately polymerized the olefin. Visually no polymer was observed in the absence of organic halide.[17] Furthermore, the dichloromethyl and trichloromethyl radicals, generated by the action of ferrous and cuprous chloride upon chloroform,[18a] and carbon tetrachloride[18b] at 100–145°, have been scavenged by styrene and other olefins.

It is the lability of α-halomethyl radicals toward further reactions with the metal ion that impart a uniqueness to the intermediates and the ultimate course of the reactions with these polyhalides.

Subsequent Steps. The reactivity sequence noted above precludes a stepwise reduction

$$CCl_4 \longrightarrow CHCl_3 \longrightarrow CH_2Cl_2 \longrightarrow CH_3Cl \longrightarrow CH_4 \quad (10)$$

of the polyhalides to alkanes. Rather, the results imply a process in which highly reactive intermeidates encounter the metal ion. We believe these intermediates to be the α-halomethyl radicals and the corresponding carbene species resulting from them in a manner analogous to the initial scission. Thus, the reduction of the methyl polyhalides to methane can be rationalized in simplest form by the following equations.

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(13) With (Cr^2) at 0.155 M and (CH_2Br_2) at 0.025 M, k_2 was 0.763 l. mole^{-1} min^{-1}.

(14) (a) Although the reaction was begun at 300 mm. (b) For comparative purposes it is significant that the reduction of chloroform with chromous perchlorate under the same conditions is much slower. After 19 hr the reaction was only 82% complete. We attribute the more rapid reactions with the sulfate salt to indicate that in our system sulfate is a ligand on Cr(II), hence any repulsive interactions between positively charged reactants is lessened. This result is consistent with solvent influences observed in studies of the reduction of acetylenes; *cf.* C. E. Castro and R. D. Stephens, *J. Am. Chem. Soc.*, **86**, 4358 (1964). The yield of methane for either reductant at the times indicated was theoretical.

(15) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 247 ff.

(16) They are likely metal ion affiliates; *cf.* ref 1.

(17) Acrylic acid could be more slowly polymerized to low molecular weight materials since acylonitrile is polymerized slowly to a tacky oil under similar conditions; *cf.* C. E. Castro, R. D. Stephens, and S. Mojé, *J. Am. Chem. Soc.*, **88**, in press.

(18) (a) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 3921 (1963); (b) *ibid.*, 1887 (1963).

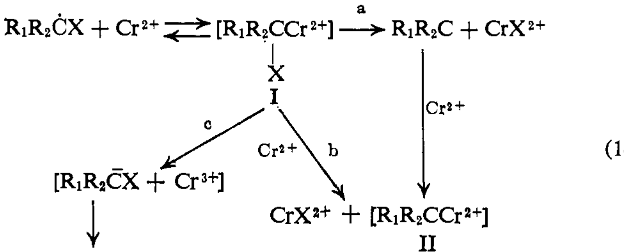
$$\begin{gathered}
CCl_4 + Cr^{2+} \longrightarrow \dot{C}Cl_3 + CrCl^{2+} \\
\dot{C}Cl_3 + Cr^{2+} \longrightarrow :CCl_2 + CrCl^{2+} \\
:CCl_2 + Cr^{2+} + H^+ \longrightarrow H\dot{C}Cl_2 + Cr^{3+} \\
H\dot{C}Cl_2 + Cr^{2+} \longrightarrow :CHCl + CrCl^{2+} \qquad (11) \\
:CHCl + Cr^{2+} + H^+ \longrightarrow H_2\dot{C}Cl + Cr^{3+} \\
H_2\dot{C}Cl + Cr^{2+} \longrightarrow :CH_2 + CrCl^{2+} \\
:CH_2 + Cr^{2+} + H^+ \longrightarrow \dot{C}H_3 + Cr^{3+} \\
\dot{C}H_3 + Cr^{2+} + H^+ \longrightarrow CH_4
\end{gathered}$$

The recurring theme in this set of electron transfers would be simply formulated as eq 12 and 13, in which interaction of an α-halomethyl radical with Cr(II)

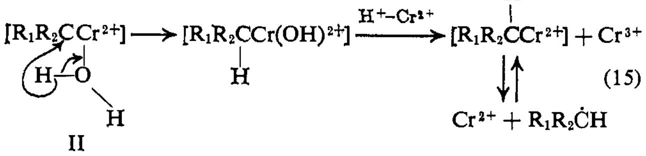
$$R_1R_2CX + Cr^{2+} \longrightarrow R_1R_2C + CrX^{2+} \qquad (12)$$

$$R_1R_2C + Cr^{2+} + H^+ \longrightarrow R_1R_2\dot{C}H + Cr^{3+} \qquad (13)$$

results in the carbene (eq 12), and the carbene is reduced by the metal ion to the methyl radical bearing one less halogen (eq 13). In accord with this an earlier works noted above,[1-4] an amplified version of these processes which more clearly conveys the complexities and ambiguities of the mechanism is sketched in reactions 14and 15.



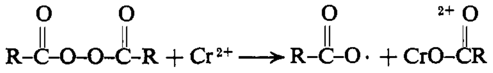
(14)



(15)

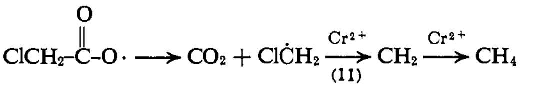
The intermediacy of an ion like I accords with the red ion obtained from chloroform in water[2] and aqueous ethanol[8a] (*vide infra*) and is consistent with results of the present study. Thus the decreasing rate of chromous consumption by chloroform would be expected if subsequent steps in the path to methane were slower than the rate of the initial scission, and subsequent steps like reactions 14 and 15 in sequence 11 could be such transformations. Although paths 14b and c cannot be eliminated[19] as routes to free or complexed carbenes we prefer path 14a. If a halomethide ion were the carbene precursor some of the less than completely dehalogenated products should result from protonation of the anion for they are inert to Cr(II). In a process resembling 14c and a, the ion I could dissociate to Cr^{3+} and X^- simultaneously. In view of the proximity of halogen to chromium in I this would seem to be a path of maximum energy requirement. Also because of electrostatic considerations path 14a should be more facile than 14b for a species like I at low concentrations. Equation 15 portrays a proton transfer from the solvation sphere of a carbene–Cr(II) complex as one of the modes of dissipation of ions like II.

In support of sequence 11, Cr(II) was exposed to monochloro- and trichloromethyl radicals under conditions similar to the reduction of the polyhalides. This was accomplished by decomposing bischloroacetyl peroxide and bistrichloroacetyl peroxide[20] with chromous sulfate at 0°. The facile cleavage of the O–O bond of peroxides by low-valent metal ions including Cr^{2+} is well documented.[21] With bischloroacetyl peroxide, additions of chromous sulfate resulted in the instantaneous (almost explosive) liberation of equal amounts of carbon dioxide and methane as the only products.[22]

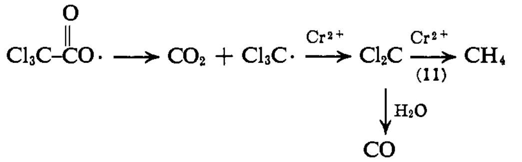


$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}R + Cr^{2+} \longrightarrow R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\cdot + CrO\text{-}\overset{\overset{2+\,O}{\|}}{C}R \qquad (16)$$

R = CH₂Cl, CCl₃



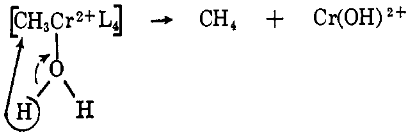
$$ClCH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\cdot \longrightarrow CO_2 + Cl\dot{C}H_2 \xrightarrow[(11)]{Cr^{2+}} CH_2 \xrightarrow{Cr^{2+}} CH_4 \qquad (17)$$



$$Cl_3C\text{-}\overset{\overset{O}{\|}}{C}O\cdot \longrightarrow CO_2 + Cl_3C\cdot \xrightarrow{Cr^{2+}} Cl_2C \xrightarrow[(11)]{Cr^{2+}} CH_4 \qquad (18)$$

$$Cl_2C \xrightarrow{H_2O} CO$$

Similarly bistrichloroacetyl peroxide afforded largely carbon dioxide and carbon monoxide (eq 18) in about equal ratio along with trace amounts of methane. Moreover, the fact that methane is produced by a first-order process and with the same rate from either CH_2Br_2 or $CHCl_3$ would be expected as a result of common intermediates emanating from these substances in a sequence like (11). Indeed, we ascribe this fact to the last step of (11) which in more detailed form is the hydrolysis of methylchromium.



$$[CH_3Cr^{2+}L_4] \rightarrow CH_4 + Cr(OH)^{2+} \qquad (19)$$

The products listed in Table I suggest a carbenoid intermediate of greater versatility than that obtained from the photolysis of diazo compounds,[23a] the action

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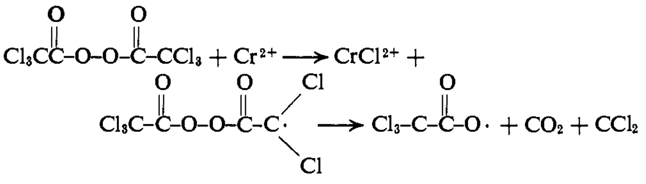
[19] Ion exchange of the chloroform product solutions is consistent with an even distribution of $CrClSO_4$ and $CrSO_4^+$, supporting path 14a or b, but, regrettably, blank runs with $Cr_2(SO_4)_3$ at product concentrations in our solvent system also afforded two Cr(III) fractions not different enough in spectra and distribution from the reaction mixture to warrant any conclusions.

[20] Because of the explosions sustained in attempting to isolate the pure peroxides, these compounds were generated *in situ* (*cf.* Experimental Section). Hence, a material balance was not obtained. The ratio of CO_2 to other products is indicative of the ability of the metal ion to decimate these substances cleanly.

[21] J. K. Kochi and P. M. Macaldo, *J. Org. Chem.*, **30**, 1134 (1965), and references therein.

[22] By contrast chloroacetic acid is inert to Cr^{2+} under these conditions, and, although ethyl trichloroacetate does react, the speed of this process is quite slow compared to the violent reaction of the corresponding peroxide. Based on these findings, but with some ambiguity, an alternate route to products entailing initial C–Cl scission

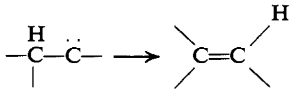


$$Cl_3C\overset{\overset{O}{\|}}{C}\text{-}O\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}CCl_3 + Cr^{2+} \longrightarrow CrCl^{2+} +$$

$$Cl_3C\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\dot{C}Cl_2 \longrightarrow Cl_3\text{-}C\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\cdot + CO_2 + CCl_2$$

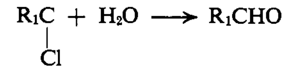
is probably not operating.

of base[23b] and metal alkyls[24] upon alkyl halides, or the entity obtained from the Cu–Zn couple and alkylidene iodides.[25] Thus, considering the results of Table I, in addition to the olefinic products typical of hydrogen rearrangements in carbenes (eq 20) formed by various processes,[26] substantial yields of hydrolysis products are


(20)

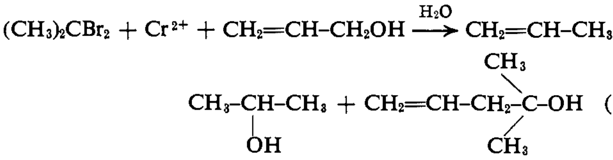
obtained (eq 21 and 22). For benzotrichloride and 1,1,1-trichloroethane the product aldehyde and alcohol

$$R_1R_2C + H_2O \longrightarrow R_1R_2CHOH \qquad (21)$$



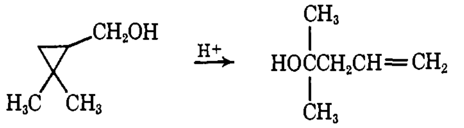
$$R_1C(Cl) + H_2O \longrightarrow R_1CHO \qquad (22)$$

represent the hydrolytic trapping of the first- and second-produced carbenoid species intermediate on the route to toluene and ethane by a path analogous to (11).[27] The most compelling evidence for a unique kind of carbenoid intermediate in these reactions can be adduced from the result that a dimethylmethyl fragment can be transferred to olefins. That is, treatment of isopropylidene bromide with chromous sulfate in aqueous allyl alcohol afforded propylene, isopropyl alcohol, and a minimum yield (6%)[28] of allyldimethylcarbinol.

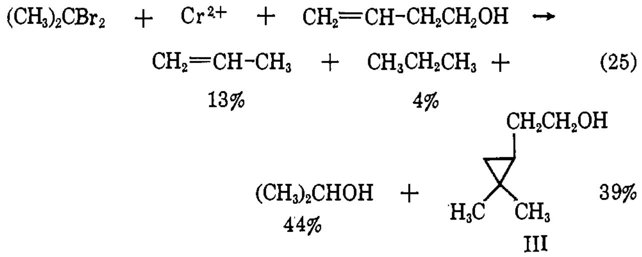


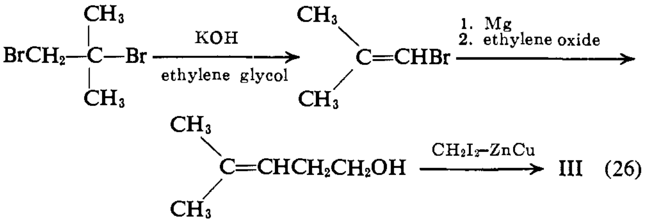
$$(CH_3)_2CBr_2 + Cr^{2+} + CH_2{=}CH\text{-}CH_2OH \xrightarrow{H_2O} CH_2{=}CH\text{-}CH_3 + CH_3\text{-}CH(OH)\text{-}CH_3 + CH_2{=}CH\text{-}CH_2\text{-}C(CH_3)_2\text{-}OH \qquad (23)$$

The latter carbinol obtained in this fashion was identical with an authentic sample prepared from the reaction of allylmagnesium bromide with acetone. We attribute its formation to the rearrangement of the labile cyclopropylcarbinol.[29]

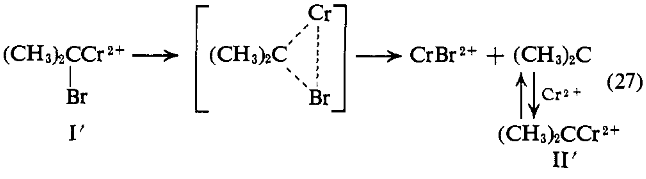

(24)

More convincingly, when 3-butenol was employed as the trapping olefin, in a solvent system, 2:1:1 dimethylformamide–water–3-butenol, the novel 1,1-dimethyl-2-hydroxyethylcyclopropane (III) was isolated (eq 25). The structure of III was substantiated by its elemental analysis and infrared and characteristic nmr spectra which were identical with III obtained from the sequence

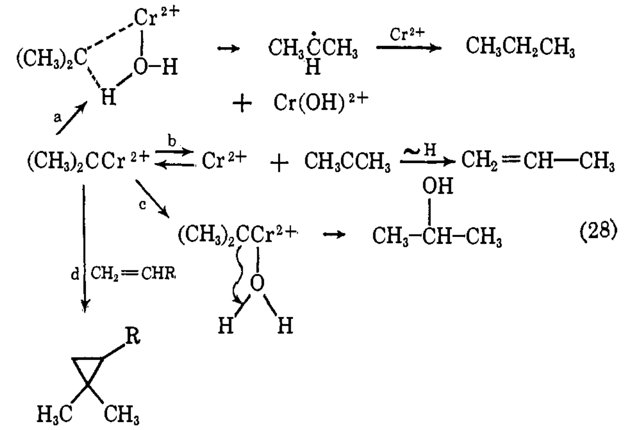




Taken together our results point to a carbenoid entity of attenuated reactivity which we are inclined to formulate as a Cr(II) complex[30] (eq 27). Beginning with an ion like I (eq 14), the following transformations of isopropylidene bromide are illustrative.



The carbene complex II′ might then dissipate in a variety of ways



Reduction to a radical (eq 28, path a) and water insertion (path c) would be convenient regroupings of atoms for a complex that contains essentially reactant ligands. Indeed the insertion into the olefinic alcohol may occur within a chromium complex. It should be emphasized the ions I and II (eq 14) and I′ and II′ (eq 27), in a sense, represent different versions of a "complexed carbenoid." In our system, ions like I may in fact be the carbenoid entity, with type II ions perhaps a part of the transition state for some of their dissipation processes. Simply put, the "alkylidene transfer reagent"

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(23) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964: (a) Chapter 7, p 108; (b) Chapter 3, p 36, and references therein.

(24) For a recent discussion in addition to ref 21, *cf.* G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **87**, 4270 (1965). The difference in reactivities of free carbenes and carbenoids are discussed in this paper on p 4274.

(25) E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964), and references therein.

(26) R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, **19**, 1394 (1951); W. Kirmse, *Angew. Chem.*, **74**, 183 (1962); L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961).

(27) The trace of vinyl chloride from 1,1,1-trichloroethane can be rationalized by

$$CH_3\text{-}CCl \longrightarrow CH_2{=}CHCl \qquad (22a)$$

(28) The yield of this substance was higher but reflects a poor workup.

(29) M. Julia, S. Julia, and J. A. Du Chaffant, *Bull. Soc. Chim. France*, 1736 (1960).

(30) Evidence for a tungsten pentacarbonyl complex of methoxymethylcarbene has been presented: E. O. Fischer and A. Maasböl, *Angew. Chem.*, **76**, 645 (1964). Quite recently an iridium complex of methylene has been described: F. D. Mango and I. Dvoretzky, *J. Am. Chem. Soc.*, **88**, 1654 (1966).

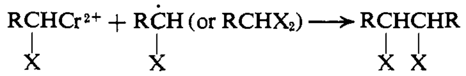
produced in these systems cannot adequately be described as a free methylene by virtue of its relative facility to be scavenged by water and olefins as compared to the speed of internal rearrangement.

The higher yield of alkanes resulting from the iodides as compared to the same distribution patterns noted with the corresponding dibromo and chloro derivatives is accountable if it is assumed that relatively high concentrations[31] of a "chromium-complexed carbene" would favor attack by yet another Cr(II) to directly yield the alkylchromium *via* (29) rather than by (28a).

$$[R_1R_2CCr^{2+}] + Cr^{2+} + H^+ \longrightarrow R_1R_2CHCr^{2+} + Cr^{3+} \qquad (29)$$

Similar arguments would explain the mild increase in ethane from ethylidene bromide upon increasing the initial concentration of Cr^{2+} (Table II).

Finally, the small amount of ethylene obtained from carbon tetrabromide, the 1,2-bis(*p*-bromobenzoyl)-ethane from *p*-bromophenyl dibromomethyl ketone (*cf.* Table I), and the tetraphenylethylene reported to result from diphenyldibromomethane[9] suggest "dimerization" as another path for the dissipation of free or complexed α-halomethyl radicals.[32] The general chemistry and synthetic utility of alkylidene transfer reagents of chromium and other metal salts are under examination.



$$\underset{X}{RCHCr^{2+}} + \underset{X}{R\dot{C}H}\ (\text{or } RCHX_2) \longrightarrow R\underset{X}{CH}\underset{X}{CHR}$$

Experimental Section

Materials. The chromous sulfate reagent and the solid chromous sulfate pentahydrate used in the kinetic studies were prepared in the manner described previously.[11]

The physical properties of the following compounds checked with those of the litereature and were used without further purification: J. T. Baker Chemical Co. chloroform, Columbia Organic Chemicals *p*-bromophenyl dibromomethyl ketone; Eastman Kodak White Label methylene bromide, carbon tetrabromide, and benzal chloride, Matheson Coleman and Bell methylene chloride, methylene iodide, iodoform, bromoform, carbon tetrachloride, 1,1-dichloroethane, 1,1,1-trichloroethane, and benzotrichloride. The following were freshly distilled before use and their physical constants were those of the literature: allyl alcohol, 3-butenol, dimethylformamide, 1,1-dibromoethane, 2,2-dichloropropane, 2,2-dibromopropane, and 1,1-dibromopropene. Samples of 1,1-dichloropropane (bp 88°, n^{22}D 1.4281), 1,1-diiodopropane (bp 78–80° (10 mm), $n^{22.5}$D 1.6383), and 1,1-diiodoethane (bp 79° (20 mm), n^{23}D 1.6667) were kindly supplied by Dr. R. C. Neuman. The latter two diiodides were prepared by titrating a benzene solution of the corresponding diazoalkane with iodine.[33] Chloroacetyl peroxide was prepared from chloroacetyl chloride and sodium peroxide in water at 0° by the method of Price, Kell, and Krebs.[34] Since the compound decomposes quite readily on standing it was used immediately after filtration while still damp. Trichloroacetyl peroxide was made similarly.[35] The damp peroxide decomposed rapidly upon dissolving in dimethylformamide or aqueous dimethylformamide even at −15°. An attempt to further dry the compound resulted in a violent explosion. It was therefore necessary to prepare the compound in the solvent system to be used, namely 50% aqueous dimethylformamide (v/v). Under these conditions very poor yields of peroxide (5–10%) were obtained.

The Cr^{2+} Reductions. Reactions were run in the manner described for the vicinal polyhalides.[11] Gas evolution was measured manometrically and when several gases were produced, the relative amounts were determined by gas chromatography. The gases were identified by their infrared spectra and emergence times. The following gas chromatographic columns were employed: 10-ft SF-96 column at 0° (for methane, ethylene, propane, and propylene), 6-ft molecular sieve 30X column at room temperature (for methane and carbon monoxide), 10-ft silica gel column at room temperature (for ethane), 7-ft silica gel column at room temperature (for ethylene and vinyl chloride), and 30-ft dimethyl sulfolane column at room temperature (for propane, propylene, and carbon dioxide). All liquid products were identified qualitatively and quantitatively by gas chromatography on 5-ft Carbowax 20M, 5-ft Hall-comid M 18, and 5-ft diethylene glycol succinate columns at temperature ranging from room temperature to 110° depending upon the substrate. The products were then isolated by saturation of the reaction mixture with ammonium sulfate and extraction with ether for several days using a continuous liquid–liquid extractor. The extract was then dried with anhydrous calcium chloride or sodium sulfate and the ether was evaporated. The remaining solution of product and DMF was separated by preparative gas chromatography on a DC-710 column. Final identification was made by comparison with a known sample. With trace amounts of products which could not be isolated, identification was made by gas chromatographic retention times on three different columns. Solid products were isolated by ether extraction and identified by comparison with known samples.

Methylene bromide (1.189 g, 0.00683 mole) in 50 ml of DMF was treated with 100 ml of 0.518 *M* Cr^{2+}. After 10 hr, 0.0261 mole of Cr^{2+} had been consumed and 0.00660 mole of methane had been produced.

Methylene chloride (0.8493 g, 0.0100 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). After 2 days, 0.0111 mole of Cr^{2+} had been consumed and 0.00302 mole of methane had been produced.

Methylene iodide (2.6810 g, 0.0100 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). After 30 min 0.00981 mole of methane had been produced. Cr^{2+} could not be analyzed by the usual technique because of the presence of iodine

Bromoform (1.263 g, 0.00500 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). After 30 min, 0.0308 mole of Cr^{2+} had been consumed and 0.00506 mole of methane had been produced.

Chloroform (0.598 g, 0.00500 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). After several hours, 0.0303 mole of Cr^{2+} had been consumed and 0.00481 mole of methane had been produced.

Iodoform (1.968 g, 0.00500 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). After 30 min, 0.00481 mole of methane had been produced.

Carbon tetrabromide (1.657 g, 0.00500 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). Within 1 hr, 0.0322 mole of Cr^{2+} had been consumed and 0.00509 mole of gas had been produced. The gas composition determined by gas chromatography was found to be 52% methane, 39% carbon monoxide, 5% ethylene, and 4% carbon dioxide. Carbon dioxide also resulted from a similar solution of the halide where Cr^{3+} was used instead of Cr^{2+}.

Carbon tetrachloride (0.772 g, 0.00501 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.11 *M* Cr^{2+} (0.0555 mole). After 30 min, 0.0291 mole of Cr^{2+} had been consumed and 0.00515 mole of gas had been produced. The gas composition was 75% carbon monoxide and 25% methane.

1,1-Dibromoethane (1.878 g, 0.0100 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). After several hours, 0.0337 mole of Cr^{2+} had been consumed and 0.00682 mole of ethane had been produced. Gas chromatographic analysis of the reaction mixutre showed that 0.00251 mole of ethanol had also been produced.

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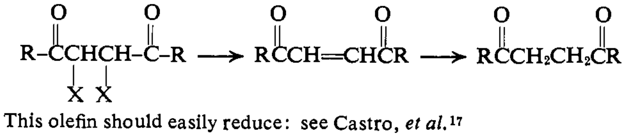
[31] Halogen stripping from the iodides must be quite rapid.

[32] For a discussion, *cf.* ref 1. Ethylene is easily obtained from ethylene dibromide[11] and the saturated diketone most likely arises, *via*



$$R\text{-}\overset{O}{\overset{\|}{C}}\underset{X}{CH}\underset{X}{CH}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \longrightarrow R\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}R \longrightarrow R\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}R$$

This olefin should easily reduce: see Castro, *et al.*[17]

[33] R. C. Neuman, *Tetrahedron Letters*, 37, 2541 (1964).

[34] C. C. Price, R. W. Kell, and E. Krebs, *J. Am. Chem. Soc.*, **64**, 1104 (1942).

[35] W. T. Miller, A. L. Dittman, and S. K. Reed, U. S. Patent 2,580,358 (Dec 25, 1951).

Similarly another reaction was run using 1.411 g (0.00751 mole) of the halide. After several hours, 0.0280 mole of Cr^{2+} had been consumed and 0.00569 mole of ethane and 0.000939 mole of ethanol had been produced.

1,1-Dichloroethane (0.989 g, 0.0100 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). After 2 days, 0.0345 mole of Cr^{2+} had been consumed and 0.00692 mole of ethane and 0.00294 mole of ethanol had been produced.

1,1-Diiodoethane (2.113 g, 0.00750 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). After 30 min, 0.00623 mole of ethane and 0.000239 mole of ethanol had been produced. Cr^{2+} could not be analyzed by the usual technique owing to the presence of iodine.

1,1-Dichloropropane (1.133 g 0.0100 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). After 2 days, 0.0265 mole of Cr^{2+} had been consumed and 0.00663 mole of gas (73% propane and 27% propylene) and 0.00114 mole of 1-propanol had been produced.

1,1-Diiodopropane (1.6923 g, 0.00572 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). After 30 min, 0.00468 mole of gas (96% propane and 4% propylene) and 0.0000331 mole of 1-propanol had been produced.

2,2-Dibromopropane (2.017 g, 0.0100 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). Within several hours, 0.0219 mole of Cr^{2+} had been consumed and 0.00248 mole of gas (88% propylene and 12% propane) and 0.00787 mole of 2-propanol had been produced. Similarly another reaction was run using 1.0108 g (0.00501 mole) of the halide. After several hours 0.00113 mole of gas (85% propylene and 15% propane) and 0.00335 mole of 2-propanol had been produced.

2,2-Dichloropropane (1.1306 g, 0.0100 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole). After 2 days, 0.0198 mole of Cr^{2+} had been consumed and 0.00230 mole of gas (92% propylene, 8% propane) and 0.00706 mole of 2-propanol had been produced.

1,1,1-Trichloroethane (0.6672 g, 0.00500 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.12 *M* Cr^{2+} (0.0560 mole). After several hours, 0.0165 mole of Cr^{2+} had been consumed and 0.00245 mole of ethanol and 0.00126 mole of gas (78% ethane, 22% ethylene, and a trace of vinyl chloride) had been produced. Similarly, using 1.334 g (0.0100 mole) of 1,1,1-trichloroethane, acetaldehyde was detected gas chromatographically in aliquots quenched in $FeCl_3$ at time intervals ranging from 6 min to 43 hr. During this time acetaldehyde concentration increased for several hours and then decreased with concomitant increase in ethanol concentration. Under similar conditions using acetaldehyde instead of the halide, the Cr^{2+} solution was slowly oxidized and ethanol was produced.

1,1-Dibromopropene (2.006 g, 0.0100 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.12 *M* Cr^{2+} (0.0560 mole). After 5 days 0.0209 mole of Cr^{2+} had been consumed and 0.00345 mole of gas (98% propylene and 2% propyne) and 0.00337 mole of 1-bromopropene had been produced.

Benzyl chloride (1.6114 g, 0.0100 mole) in 100 ml of DMF was added to a solution of 50 ml of H_2O and 50 ml of 1.12 *M* Cr^{2+} (0.0560 mole). After several hours, 0.0332 mole of Cr^{2+} had been consumed and 0.00694 mole of toluene and 0.00242 mole of benzyl alcohol had been produced.

Benzotrichloride (0.979 g, 0.00501 mole) in 100 ml of DMF was added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.12 *M* Cr^{2+} (0.0560 mole). After several hours, 0.00228 mole of Cr^{2+} had been consumed and 0.00276 mole of toluene and 0.00133 mole of benzyl alcohol had been produced. An aliquot of the reaction mixture was quenched in $FeCl_3$ after the reaction had proceeded for 5 min and was found to contain benzaldehyde along with benzyl alcohol and toluene. Under similar conditions using benzaldehyde instead of the halide, the Cr^{2+} solution was rapidly oxidized and benzyl alcohol was produced.

***p*-Bromophenyl dibromoethyl ketone** (3.567 g, 0.0100 mole) in 100 ml of DMF was added to a solution of 50 ml of H_2O and 50 ml of 1.12 *M* Cr^{2+} (0.0560 mole). After 15 min, 0.0350 mole of Cr^{2+} had been consumed. Filtration of the reaction mixture provided 0.4388 g (0.0011 mole) of 1,2-bis(*p*-bromobenzoyl)ethane, mp 183.5° (from benzene), mmp 183.5° (lit. 182°). The infrared spectrum was identical with a known sample. Saturation of the reaction mixture with ammonium sulfate followed by ether extraction provided 1.273 g (0.00640 mole) of *p*-bromoacetophenone, mp 51–52°. The infrared spectrum of the sample was identical with that of known sample. In kinetic studies, Cr(II) was monitored titrimetrically using the apparatus previously described.[1]

The Cr^{2+} Reduction in the Presence of Olefins. 1,1-Dibromopropane (5.5010 g, 0.02726 mole) was dissolved in a solution of 50 ml of H_2O and 50 ml of allyl alcohol. To this solution, 50 ml of 1.09 *M* Cr^{2+} (0.0545 mole) was slowly added. After allowing the reaction mixture to stand for 24 hr, 0.0412 mole of Cr^{2+} had been consumed and 0.00216 mole of propylene and trace amounts of 2-propanol had been produced. Saturation of the reaction mixture with ammonium sulfate caused it to separate into two phases, H_2O and allyl alcohol. The allyl alcohol phase was then dried over anhydrous calcium chloride and distilled from calcium chloride. The allyl alcohol phase was then fractionally distilled on a 3-ft spinning-band column and the residue (~0.5 ml) which contained the other product was further purified by preparative gas chromatography on a 10-ft DC-710 column at 70°. In this way 0.175 g (0.00175 mole) of 1,1-dimethyl-3-butenol was isolated. This product was identified by comparison with a known sample prepared by the addition of allylmagnesium bromide to acetone.[36]

1,1-Dibromopropane (4.881 g, 0.0242 mole) was dissolved in a solution of 25 ml of DMF and 25 ml of 3-butenol. To this solution was slowly added 50 ml of 0.968 *M* Cr^{2+} (0.0484 mole). After allowing the reaction mixture to stand for 22 hr, 0.0426 mole of Cr^{2+} had been consumed and 0.00387 mole of gas (82% propylene and 18% propane) had been produced. Quantitative gas chromatographic analysis of the reaction mixture on a 3-ft Carbowax 20M column at 90° showed 0.0101 mole of 2-propanol and 0.00896 mole of 2-(2,2-dimethylcyclopropyl)ethanol. The latter compound was isolated by the following procedure. The reaction mixture was saturated with ammonium sulfate and extracted with ether. The ether extract was washed with water to remove DMF, dried over anhydrous sodium sulfate, and fractionally distilled on a 2-ft spinning-band column. The residue, which contained the desired compound, was further fractionated by preparative gas chromatography using a 3-ft Carbowax 20M column at 90°. In this way, 0.540 g (0.00474 mole) of product was isolated. Rechromatography provided a very pure sample for analysis. This product was shown to be identical with a sample of 2-(2,2-dimethylcyclopropyl)ethanol prepared in the following manner. 1-Bromo-2-methylpropene was prepared by treating 1,2-dibromo-2-methylpropane with potassium hydroxide in ethylene glycol at 125° according to the method of Braude and Evans.[37] 4-Methyl-3-pentenol was then prepared by converting the 1-bromo-2-methylpropene to the Grignard reagent with magnesium in tetrahydrofuran followed by addition of ethylene oxide to the Grignard reagent and subsequent hydrolysis.[38] The 4-methyl-3-pentenol was then converted to 2-(2,2-dimethylcyclopropyl)ethanol by the method of Simmons and Smith;[39] however, the zinc–copper couple was prepared by an improved method described by LeGoff.[40] The 2-(2,2-dimethylcyclopropyl)ethanol prepared in this manner had bp 66° (13mm), n^{25}D 1.4349. *Anal.* Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.76; H, 12.14. The infrared spectrum contained bands characteristic of the cyclopropane ring.[41] A sharp band appeared at 3060 cm^{-1} and a wide band appeared with maxima at 1045, 1026, and 994 cm^{-1}. The latter band is probably a composite of contributions from both the cyclopropyl and alcohol groups. The structure was confirmed by the nuclear magnetic resonance spectrum: τ 6.15 (singlet, 1.16 H), 6.42 (triplet, 2.11 H), 8.43 (multiplet, 2.19 H), 8.95 (singlet, 6.00 H), 9.48 (multiplet, 1.91 H), 10.10 (multiplet, 0.88 H).

The Cr^{2+} Reductions of Haloacetyl Peroxides. A stirred solution of 1.6 g of Na_2O_2 (0.020 mole) in 100 ml of DMF and 100 ml of H_2O was chilled to −15° and to this was added 6.0 g (0.033 mole) of trichloroacetyl chloride which had been previously chilled to −15°. The solution was stirred for 0.5 hr at −15° and transferred to a dropping funnel from which it was added to a solution of 100 ml of

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DMF, 50 ml of H_2O, and 50 ml of 1.12 *M* Cr^{2+} (0.0560 mole). Within an hour, gas evolution had ceased after producing 0.00170 mole with the following composition: 50% carbon dioxide, 50% carbon monoxide, and a trace of methane.

Chloroacetyl chloride (2.4 g, 0.021 mole) was added to a solution of 1.0 g (0.013 mole) of Na_2O_2 in 15 ml of H_2O at 0° and stirred for 0.5 hr. Solid chloroacetyl peroxide was filtered off, washed with ice water, and dissolved immediately in 100 ml of chilled DMF. This solution was placed in a dropping funnel and added to a solution of 100 ml of DMF, 150 ml of H_2O, and 50 ml of 1.12 *M* Cr^{2+} (0.0560 mole). A gas was rapidly evolved which contained only carbon dioxide and methane.

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Reactions in Frozen Solutions. VI.[1] The Reaction of Ethylene Chlorohydrin with Hydroxyl Ion in Ice

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Abstract: The reaction of ethylene chlorohydrin with sodium hydroxide in frozen aqueous solutions follows second-order kinetics, with rates up to 1000 times faster than in supercooled liquid solutions at the same temperatures. The effects of variation in concentration of reactants, of added solutes, and of temperature are consistent with a "concentration effect." The observed second-order rate constants are quantitatively correlated by the relationship $k_{obsd} = k_2C_h/C_s$, where k_2 is the normal second-order rate constant for reaction in liquid solution, C_h is the total concentration of the liquid "reaction regions" in a frozen solution, and C_s is the total concentration of all solutes in the initial unfrozen solution.

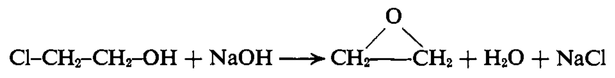
It has recently been shown that, for a number of different reactions in dilute solutions, rate accelerations occur when the solutions are frozen. In aqueous solutions, examples of rate increases in ice include anhydride, amide, and ester hydrolysis,[2,3] aminolysis of amides, esters and lactones,[4-6] as well as some oxidation and dehydration reactions.[7,8] For the case of acid- and base-catalyzed hydrolysis of acetic anhydride, Butler and Bruice[2] have presented evidence that the greater rate of reaction in ice is due to a concentration effect. The anhydride and the catalyst are brought together at high concentrations in regions of the frozen system which remain liquid. Since the reaction follows second-order kinetics, the rate is increased by the concentration change which accompanies the freezing out of water.

The "concentration effect" should be a general phenomenon. However, some experimental features of "frozen reactions" have seemed inconsistent with expectations for this effect. For most of the reported reactions in frozen aqueous solutions, other possibilities have been put forward. These suggestions include the possible involvement of ice itself in imposing some favorable substrate–catalyst orientation or by facilitating required proton transfers to or from substrate.[3-8]

Kinetic studies of two types of reaction in frozen organic solutions (the E2 base-catalyzed elimination reaction of *t*-butylperoxy formate in *p*-xylene[9a,b] and the SN2 reaction of methyl iodide and triethylamine in benzene[9c]) show that the observed results are completely consistent with the concentration effect. It has also been shown in general that the observation of changes in kinetic order, rate–temperature maxima, sensitivity to low concentrations of ordinarily inert solutes, and some other unusual features of reactions in frozen solutions are necessary consequences of the concentration effect.[9] Even when there is no change in mechanism and no *direct* involvement of the solid part of the frozen system, the concentration effect may give rise to observations greatly different from those for the same reaction under normal (*i.e.*, nonfrozen) conditions.[10]

As noted above, reactions in ice might involve interesting features not yet found in frozen organic solvents. An investigation of a simple, well-known bimolecular reaction in ice would best allow separation of factors due to concentration from those due to other effects. To further simplify the interpretation of results, the reactants (as well as products) should behave as more or less ideal solutes in the ice–aqueous solution phase equilibria.

The reaction of ethylene chlorohydrin with sodium hydroxide[11] is convenient for such an investigation of a reaction in ice. This reaction strictly follows second-order kinetics and rate constants are well established



$$Cl\text{-}CH_2\text{-}CH_2\text{-}OH + NaOH \longrightarrow \overset{O}{CH_2\text{—}CH_2} + H_2O + NaCl$$

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