ORGANIC HYPOHALITES

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Received August 11, 1954

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I. INTRODUCTION

A. HISTORICAL BACKGROUND

Acyl hypohalites were first obtained in 1861 by Schutzenberger (172, 173, 174), who found that acetyl hypochlorite was formed by the action of chlorine monoxide on acetic acid. Although objections have been raised against this work (9), it has been confirmed spectrophotometrically (6). Acetyl hypobromite and hypoiodite were obtained in acetic acid solution through the action of bromine and iodine monochloride, respectively, on acetyl hypochlorite. Similarly,

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Schutzenberger obtained iodine triacetate through the oxidation of iodine in acetic anhydride by means of nitric acid.

Acetyl hypoiodite has been formed *in situ* by the action of iodine on silver acetate, and the silver complexes of acyl hypoiodites have been studied extensively (10, 25, 36, 90, 152, 153, 154, 186, 187, 200). The addition of hypoiodites formed from the silver salts of polyfunctional acids to double bonds has also been studied (26). This material has been reviewed (107) and therefore does not come within the scope of this article.

An exhaustive study of the properties of various acyl hypochlorites and hypobromites in solution has been made (32). More recently, the chemistry of isobutyryl and benzoyl hypobromites was investigated (157). Formyl hypobromite presumably is formed when trinitrobromomethane reacts with cyclohexene in formic acid solution (168, 169). The first acyl hypofluorite to be prepared was trifluoroacetyl hypofluorite (37). Trifluoroacetyl hypohalites have been used preparatively (85, 89).

Various kinetic investigations have been carried out in which acyl hypohalites have been postulated as intermediates: the chlorination of anisole in acetic acid (111; *cf.* 5); the reaction between hypochlorous acid and allyl alcohol in the presence of sodium acetate–acetic acid buffers (97; *cf.* 98); the decomposition of iodine acyls (138); the addition of hypochlorous acid to various olefins in the presence of carboxylic acids (179; *cf.* 176, 178). Although no acyl hypohalite has been isolated from its corresponding solution, except as a complex, these substances are well-defined species in solution. Thus, a recent spectrophotometric study has shown the identity of acetyl hypohalites prepared by different methods (6).

Alkyl hypohalites were first obtained by Sandmeyer in 1885. Ethyl hypochlorite was the first ester of hypochlorous acid to be prepared (162), following Schmidt's suggestion (171) that such an ester would be obtained by the action of hypochlorous acid solution on ethyl alcohol. Sandmeyer's study of the properties of methyl and ethyl hypochlorites (163) was extended by Chattaway and Backeberg (10, 39), who prepared other alkyl esters and studied their decomposition products. Although they did not succeed in preparing benzyl hypochlorite, they postulated its existence in the reaction between benzyl alcohol and hypochlorous acid. Benzyl hypochlorite was subsequently prepared in carbon tetrachloride solution (195). Other workers have postulated the existence of alkyl hypochlorites in oxidation reactions of alcohols (40, 64). Similarly, these compounds were believed to be present in addition reactions of halogens in alcoholic solutions (167, 197). Extensive studies of the reaction of *tert*-butyl hypochlorite with various organic compounds have been carried out (42, 43, 72, 73, 194) and the mechanisms of formation and hydrolysis of this compound have been elucidated (5).

Some workers believe that alkyl hypobromites form *in situ* when bromine is used in methyl alcohol solution (*cf.* 13, 57). Solutions of these substances have been studied spectrophotometrically (6). No alkyl hypoiodite has thus far been isolated, although here, again, these substances have been formed *in situ* (24). The only alkyl hypofluorite known is trifluoromethyl hypofluorite (103).

The third group of esters of hypohalous acids to be mentioned consists of the phenyl hypohalites. These compounds are notable in that each may have a quinoid tautomer in which the halogen is not bound to an oxygen atom. Nitrosophenyl hypochlorite was isolated and its reactions studied (125). A discussion has long been raging in the literature as to the structure of tribromophenyl hypochlorite and hypobromite (47, 48, 49, 182). Phenyl hypochlorite has been postulated as an intermediate in chlorination reactions of phenols (114; *cf.* 173).

B. SCOPE AND LIMITATIONS

This review deals with the reactions of organic hypohalites, used as such or formed *in situ*, with organic compounds. The preparation of these compounds and their physical properties are described. These reagents usually effect halogenation and, in certain cases, oxidation of the compounds involved. Reactions in which organic hypohalites have been postulated as intermediates have been included in the discussion.

The literature has been reviewed through 1952, although some later reports have been included in the tables. The tabular material in tables 1 through 12 is divided according to the classes of compounds being chlorinated, as seen from the table headings.

Since the tabular material in this review is of particular interest to the synthetic chemist, those reactions in which the product appears to result from the action of an organic hypohalite are included, whether or not the mechanism of the reaction has been elucidated.

II. Preparation and Purification of Organic Hypohalites

Alkyl hypochlorites may be prepared by the action of chlorine monoxide on absolute alcohol (162) or on an alcohol in carbon tetrachloride solution (6); by the action of a concentrated solution of hypochlorous acid on alcohols (162); by shaking solutions of hypochlorous acid with carbon tetrachloride solutions of alcohols (3, 6, 195); by the action of chlorine on an alkaline alcoholic solution (39, 44, 96, 163); by the action of chlorine on an aqueous alcoholic suspension of calcium carbonate (84); and by the action of sodium hypochlorite solution on alcohols in the presence of acetic acid (43, 194).

These methods are appropriate for *tert*-butyl, *tert*-amyl, and perhaps ethyl hypochlorite only. The other organic hypohalites are too unstable to be isolated and purified. The above-mentioned hypochlorites may be distilled at atmospheric pressure (2, 39, 162) and at reduced pressure (2, 39); *tert*-butyl hypochlorite may be recrystallized by partial freezing (2).

III. Physical Properties of Organic Hypohalites

Boiling points: The boiling points of some organic hypohalites are given in the table shown at the top of the following page.

Vapor pressure: The vapor pressure of *tert*-butyl hypochlorite is 136 mm. at 31.5°C., 34.5 mm. at 19°C., and 30.5 mm. at 17°C. (2). The vapor pressure curve of this compound in acetic acid solution has been determined (2).

Compound	Boiling Point	Pressure	Reference
	°C.	mm.	
CH_3OCl	12	726	(163)
C_2H_5OCl	36	752	(162)
t-C_4H_9OCl	79.6	750	(39)
t-$C_5H_{11}OCl$	76 (dec.)	752	(39)

Densities: Ethyl hypochlorite, $d_{4°}^{6°} = 1.013$ (59). *tert*-Butyl hypochlorite: $d_{4°}^{18°} = 0.9583$ (39); $d_{4°}^{25°} = 0.9531$ (2). *tert*-Amyl hypochlorite: $d_{4°}^{25°} = 0.8547$ (39). The density curve of the system *tert*-butyl hypochlorite–acetic acid has been determined (2).

Viscosities: The viscosity of *tert*-butyl hypochlorite at 25.2°C. is 0.543 centipoise (2). The change of viscosity in the system *tert*-butyl hypochlorite–acetic acid has been determined (2).

Ultraviolet absorption spectra: The spectra of hypochlorites and hypobromites, including the ethyl, *tert*-butyl, and acetyl esters, have been determined (6; *cf.* 164). The organic hypohalites have a characteristic curve similar to the curves of the corresponding free acids and the halogen monoxides. The absorption coefficients increase in the order ethyl hypochlorite, *tert*-butyl hypochlorite, acetyl hypochlorite, chlorine monoxide. The peaks of the hypobromites are shifted to longer wave lengths.

Solubilities: All organic hypohalites are sparingly soluble in water. The total solubility of *tert*-butyl hypochlorite, including the hydrolyzed ester at equilibrium, does not exceed 20 g./liter (2). Organic hypohalites are freely soluble in carbon tetrachloride, chloroform, and alcohols. The partition coefficient between water and carbon tetrachloride has been determined for ethyl hypochlorite (195).

Molecular weight determination: Ethyl and *tert*-butyl hypochlorites were found to be monomeric in solution by vapor density and cryoscopic methods (39, 195).

IV. ANALYTICAL USES OF ORGANIC HYPOHALITES

The insolubility of hypochlorous acid in carbon tetrachloride and the high partition coefficient of alkyl hypochlorites between carbon tetrachloride and water have been utilized analytically for the determination of small amounts of alcohols in aqueous solution (3, 195). The method is based on equilibration of the aqueous alcoholic solution with excess of hypochlorous acid in the presence of a known amount of carbon tetrachloride. The ester formed is extracted into the non-polar phase and is determined iodometrically. Precautions must be taken that oxidation and photochemical decomposition do not occur. In the case of ethyl alcohol a calibration curve must be obtained (195). With *tert*-butyl alcohol, which is much less liable to oxidative decomposition or autodecomposition, measurements are of higher accuracy. The procedure has been suggested as the best known method for the quantitative determination of tertiary alcohols (3).

TABLE 1

Reactions of organic hypohalites with saturated hydrocarbons

Hydrocarbon	Hypohalite	Solvent	Temperature	Product	Yield	Reference
			°C.		*per cent*	
Hexane..........	*t*-C_4H_9OCl		100	2-Chlorohexane	30	(42)
				1-Chlorohexane	9	
				Dichlorohexanes	14	
Cyclohexane.....	*t*-C_4H_9OCl*			Chlorocyclohexane		(104)
Heptane.........	*t*-C_4H_9OCl	CCl_4	Reflux	*sec*-Chloroheptanes	25	(194)
				1-Chloroheptane	9	

* In the presence of dibenzoyl peroxide.

V. Synthetic Applications of Organic Hypohalites

It will be noted in Section VI that in many reactions in which the product appears to have resulted from the addition to an olefinic bond of a hypohalite in the form of the fragments RO^- and X^+, the mechanism does not involve such addition. Indeed, it is quite clear, for example, that when stilbene is treated with bromine in methanol solution, methyl hypobromite is *not* an intermediate in the reaction, although the product formed is 1-bromo-2-methoxy-1,2-diphenylethane (13, 100). From the point of view of synthetic applications, however, the use of bromine in methanol solution can sometimes accomplish the synthetic aim of adding the elements of methyl hypobromite to a double bond. For this reason the tabular survey of this review includes, for the benefit of the synthetic organic chemist, reagents other than organic hypohalites, which *appear* to involve the latter as intermediates in the respective reactions, even though the mechanism of these reactions may contradict this view categorically.

A. CHLORINATION OF OLEFINS

Organic hypohalites generally add to the double bond of olefinic compounds. The known cases of such reactions are recorded in table 2A; table 2B assembles the data on the chlorination of cyclohexene with a variety of "positive" halogenating agents. An examination of the tables permits one to deduce the following generalizations: the "positive" halogen adds to the negative end of the double bond and the other fragment of the attacking species adds to the other end of the double bond. Thus, propylene gives derivatives of 1-chloropropane, the substituent in the 2-position depending upon the solvent in which the reaction is carried out (96).

With dienes such as butadiene and isoprene, 1,2-addition predominates over 1,4-addition. It appears, however, from the quantitative work carried out with isoprene (139), that when a bulky group is part of the active species, 1,4-addition may predominate. Thus, when isoprene is treated with *tert*-butyl hypochlorite in butyric acid or isobutyric acid solution, only the 1,4-adducts are obtained.

The problem of allylic chlorination of olefins with organic hypohalites must

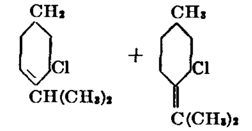
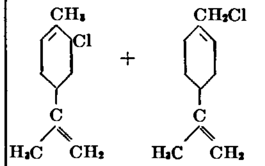
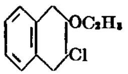
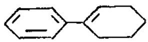
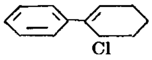
TABLE 2A

Reactions of organic hypohalites with olefins and halogenated olefins

Olefin	Hypohalite	Solvent	Temperature	Product	Yield	Reference
			°C.		*per cent*	
Ethylene	$t\text{-}C_4H_9OCl$	$ClCH_2CH_2OH$		$ClCH_2CH_2OCH_2CH_2Cl$	61	(96)
	$t\text{-}C_4H_9OCl$	CH_3COOH		$ClCH_2CH_2OCOCH_3$	53	(96)
	$t\text{-}C_4H_9OCl$	H_2O	18–22	$ClCH_2CH_2OH$		(14)
	$I_2 + AgNO_3$*	CH_3OH	15–20	$ICH_2CH_2OCH_3$		(196)
Propylene	$t\text{-}C_4H_9OCl$	CH_3OH		$ClCH_2CH(OCH_3)CH_3$	22	(96)
	$t\text{-}C_4H_9OCl$	CH_3OH		$ClCH_2CH(OCH_3)CH_3$	56	(96)
	$t\text{-}C_4H_9OCl$	CH_3COOH		$ClCH_2CH(OCOCH_3)CH_3$	72	(96)
	$t\text{-}C_4H_9OCl$	C_6H_6 + phenol		$ClCH_2CH(OC_6H_5)CH_3$	36	(96)
	$t\text{-}C_4H_9OCl$			$ClCH_2CH(OC_4H_9\text{-}t)CH_3$		
Allyl chloride	$t\text{-}C_4H_9OCl$	CH_3OH		$ClCH_2CH(OCH_3)CH_2Cl$	44	(62)
1-Butene	$C_6H_5SO_2NCl_2$*	CH_3OH		$CH_3CH_2CH(OCH_3)CH_2Cl$		(115)
	$C_6H_5SO_2NCl_2$*	C_2H_5OH		$CH_3CH_2CH(OC_2H_5)CH_2Cl$		(115)
	$C_6H_5SO_2NCl_2$*	$i\text{-}C_4H_9OH$		$CH_3CH_2CH(OC_4H_9\text{-}i)CH_2Cl$		(115)
	$C_6H_5SO_2NCl_2$*	$i\text{-}C_5H_{11}OH$		$CH_3CH_2CH(OC_5H_{11}\text{-}i)CH_2Cl$		(115)
Methallyl chloride	$t\text{-}C_4H_9OCl$	CH_3OH		$ClCH_2C(CH_3)(OCH_3)CH_2Cl$	35	(62)
2-Butene	$C_6H_5SO_2NCl_2$*	CH_3OH		$CH_3CHClCH(OCH_3)CH_3$		(115)
	$C_6H_5SO_2NCl_2$*	C_2H_5OH		$CH_3CHClCH(OC_2H_5)CH_3$		(115)
	$C_6H_5SO_2NCl_2$*	$i\text{-}C_4H_9OH$		$CH_3CHClCH(OC_4H_9\text{-}i)CH_3$		(115)
	$C_6H_5SO_2NCl_2$*	$i\text{-}C_5H_{11}OH$		$CH_3CHClCH(OC_5H_{11}\text{-}i)CH_3$		(115)
Butadiene	$C_6H_5SO_2NCl_2$*	CH_3OH	−15	$ClCH_2CH(OCH_3)CH{=}CH_2$	39	(143)
				$ClCH_2CH{=}CHCH_2OCH_3$	8	
	$C_6H_5SO_2NCl_2$*	C_2H_5OH	−12	$ClCH_2CH(OC_2H_5)CH{=}CH_2$		(143)
	$t\text{-}C_4H_9OCl$		−12	$ClCH_2CH(OC_4H_9\text{-}t)CH{=}CH_2$	28	(143)
				$ClCH_2CH{=}CHCH_2OC_4H_9\text{-}t$	4	(143)
	$C_6H_5SO_2NBr_2$*	CH_3OH		$BrCH_2CH(OCH_3)CH{=}CH_2$	54	(151)
	$C_6H_5SO_2NBr_2$*	C_2H_5OH		$BrCH_2CH(OC_2H_5)CH{=}CH_2$	69	(151)
	$C_6H_5SO_2NBr_2$*	C_3H_7OH		$BrCH_2CH(OC_3H_7)CH{=}CH_2$	54	(151)
	$C_6H_5SO_2NBr_2$*	C_4H_9OH		$BrCH_2CH(OC_4H_9)CH{=}CH_2$	57	(151)
	$C_6H_5SO_2NBr_2$*	$i\text{-}C_4H_9OH$		$BrCH_2CH(OC_4H_9\text{-}i)CH{=}CH_2$	56	(151)
	$C_6H_5SO_2NBr_2$*	$i\text{-}C_5H_{11}OH$		$BrCH_2CH(OC_5H_{11}\text{-}i)CH{=}CH_2$	55	(151)
	$HgO + I_2$*	CH_3OH	−15	$ICH_2CH(OCH_3)CH{=}CH_2$	50	(143)
	$HgO + I_2$*	C_2H_5OH	−12	$ICH_2CH(OC_2H_5)CH{=}CH_2$	66	(143)
	$HgO + I_2$*	C_3H_7OH		$ICH_2CH(OC_3H_7)CH{=}CH_2$	35	(143)
$CHBr{=}CHCH{=}CH_2$	$HgO + I_2$*	CH_3OH		$ICH_2CH(OCH_3)CH{=}CHBr$	72	(147)
	$HgO + I_2$*	C_2H_5OH		$ICH_2CH(OC_2H_5)CH{=}CHBr$	70	(147)
	$HgO + I_2$*	C_3H_7OH		$ICH_2CH(OC_3H_7)CH{=}CHBr$	44	(147)
$CH_2{=}CClCH{=}CH_2$	$HgO + I_2$*	CH_3OH		$ICH_2CH(OCH_3)CCl{=}CH_2$	62	(146)
	$HgO + I_2$*	C_2H_5OH		$ICH_2CH(OC_2H_5)CCl{=}CH_2$	46	(146)

$CH_2{=}CBrCH{=}CH_2$	$HgO + I_2$*	CH_3OH		$ICH_2CH(OCH_3)CBr{=}CH_2$	70	(146)
	$HgO + I_2$*	C_2H_5OH		$ICH_2CH(OC_2H_5)CBr{=}CH_2$	47	(146)
$CH_2{=}CHCCl{=}CHCl$	$HgO + I_2$*	CH_3OH		$ICH_2CH(OCH_3)CCl{=}CHCl$	60	(149)
	$HgO + I_2$*	C_2H_5OH		$ICH_2CH(OC_2H_5)CCl{=}CHCl$		(149)
2-Pentene	$t\text{-}C_4H_9OCl$	CH_3OH†		$CH_3CHClCH(OCH_3)CH_2CH_3$	78	(96)
	$t\text{-}C_4H_9OCl$	C_2H_5OH†		$CH\ CHClCH(OC_2H_5)CH_2CH_3$	57	(96)
	$t\text{-}C_4H_9OCl$	CH_3COOH		$CH_3CHClCH(OCOCH_3)CH_2CH_3$	65	(96)
1, 1, 2-Trimethylethylene	C_2H_5OCl	C_2H_5OH		$CH_3CCl{=}C(CH_3)_2$		
	$t\text{-}C_4H_9OCl$	CH_3OH†		$CH_3CHClC(OCH_3)(CH_3)_2$	38	(96)
	$t\text{-}C_4H_9OCl$	CH_3OH†	5	$CH_3CHClC(OCH_3)(CH_3)_2$	45	(96)
	$t\text{-}C_4H_9OCl$	CH_3COOH		$CH_3CHClC(OCOCH_3)(CH_3)_2$	22	(96)
	CH_3OBr‡	CH_3OH	25	$CH_3CHBrC(OCH_3)(CH_3)_2$	74	(168)
	$HCOOBr$‡	$HCOOH$	25	$CH_3CHBrC(HCOO)(CH_3)_2$	69	(168)
Isoprene	$t\text{-}C_4H_9OCl$	H_2O	10–15	$ClCH_2C(CH_3)(OH){=}CH_2$	17	(139)
				$ClCH_2C(CH_3){=}CHCH_2OH$	3	
	$t\text{-}C_4H_9OCl$	CH_3OH	0–10	$ClCH_2C(CH_3)(OCH_3){=}CH_2$	27	(139)
				$ClCH_2C(CH_3){=}CHCH_2OCH_3$	19	
	$t\text{-}C_4H_9OCl$	C_2H_5OH	0–10	$ClCH_2C(CH_3)(OC_2H_5){=}CH_2$	27	(139)
				$ClCH_2C(CH_3){=}CHCH_2OC_2H_5$	18	
	$t\text{-}C_4H_9OCl$	C_3H_7OH	25–30	$ClCH_2C(CH_3)(OC_3H_7){=}CH_2$	28	(139)
				$ClCH_2C(CH_3){=}CHCH_2OC_3H_7$	16	
	$t\text{-}C_4H_9OCl$	$i\text{-}C_3H_7OH$	25–30	$ClCH_2C(CH_3)(OC_3H_7\text{-}i){=}CH_2$	17	(139)
				$ClCH_2C(CH_3){=}CHCH_2OC_3H_7\text{-}i$	19	
	$t\text{-}C_4H_9OCl$	C_4H_9OH	30	$ClCH_2C(CH_3)(OC_4H_9){=}CH_2$	18	(139)
				$ClCH_2C(CH_3){=}CHCH_2OC_4H_9$	16	
	$t\text{-}C_4H_9OCl$	$HCOOH$	10–15	$ClCH_2C(CH_3)(OCHO){=}CH_2$	28	(139)
				$ClCH_2C(CH_3){=}CHCH_2OCHO$	32	
	$t\text{-}C_4H_9OCl$	CH_3COOH	10–15	$ClCH_2C(CH_3)(OCOCH_3){=}CH_2$	20	(139)
				$ClCH_2C(CH_3){=}CHCH_2OCOCH_3$	32	
	$t\text{-}C_4H_9OCl$	C_2H_5COOH	25–30	$ClCH_2C(CH_3)(OCOC_2H_5){=}CH_2$	15	(139)
				$ClCH_2C(CH_3){=}CHCH_2OCOC_2H_5$	18	
	$t\text{-}C_4H_9OCl$	C_3H_7COOH	25–30	$ClCH_2C(CH_3){=}CHCH_2OCOC_3H_7$	14	(139)
	$t\text{-}C_4H_9OCl$	$i\text{-}C_3H_7COOH$	25–30	$ClCH_2C(CH_3){=}CHCH_2OCOC_3H_7\text{-}i$	7	(139)
	$HgO + I_2$*	CH_3OH		$ICH_2C(CH_3)(OCH_3)CH{=}CH_2$	40–45	(150)
	$HgO + I_2$*	C_2H_5OH		$ICH_2C(CH_3)(OC_2H_5)CH{=}CH_2$	40–45	(150)
3-Hexene	$t\text{-}C_4H_9OCl$	CH_3OH†		3-Chloro-4-methoxyhexane	63	(96)
	$t\text{-}C_4H_9OCl$	CH_3COOH		3-Chloro-4-acetoxyhexane	59	(96)
Cyclohexene	C_2H_5OCl	CCl_4				(104)
	$t\text{-}C_4H_9OCl$			1-Chloro-2-ethoxycyclohexane		(79)
	$t\text{-}C_4H_9OCl$	Dilute CH_3COOH		2-Chlorocyclohexanol	70	(77)

TABLE 2A—*Concluded*

Olefin	Hypohalite	Solvent	Temperature	Product	Yield	Reference
			°C.		*per cent*	
1,3-Cyclohexadiene	Br_2*	CH_3OH		Bromomethoxycyclohexene§	45	(121)
1-Heptene	t-C_4H_9OCl	CH_3OH		1-Chloro-2-methoxyheptane	41	(96)
	t-C_4H_9OCl	C_2H_5OH†		1-Chloro-2-ethoxyheptane	70	(96)
	t-C_4H_9OCl	C_3H_7OH†		1-Chloro-2-propoxyheptane	60	(96)
	t-C_4H_9OCl	C_4H_9OH†		1-Chloro-2-butoxyheptane	60	(96)
	t-C_4H_9OCl	CH_3COOH		1-Chloro-2-acetoxyheptane	56	(96)
	t-C_4H_9OCl	C_6H_6 + phenol		1-Chloro-2-phenoxyheptane	38	(96)
3-Menthene	t-C_4H_9OCl		100			(71)
α-Pinene	t-C_4H_9OCl		100			(159)
	C_2H_5OCl	CCl_4	—20			(79)
	t-C_4H_9OCl		Reflux			(78)

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* The corresponding alkyl hypohalite is presumably formed *in situ*.

† In the presence of p-toluenesulfonic acid.

‡ Formed from trinitrobromomethane.

§ The structure was not unequivocally proved.

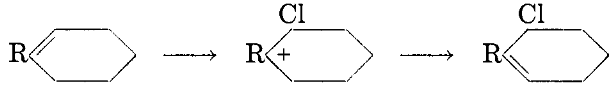
next be taken up. There are several reports in the literature in which allylic halides are obtained. Although cyclohexene treated with *tert*-butyl hypochlorite in aqueous acetic acid affords 2-chlorocyclohexanol (77), in the presence of benzoyl peroxide 3-chlorocyclohexene is obtained (104). Similarly, 1-phenylcyclohexene affords 3-chloro-2-phenylcyclohexene (78). Most reactions have been carried out in the absence of peroxides. In these cases it is difficult to decide unequivocally whether substitutive allylic chlorination is taking place, or whether addition to the double bond is the first step of the reaction.

In principle, when an ionic mechanism is operative, chlorination with *tert*-butyl hypochlorite may take place through either formulation A or formulation B.

$$\text{(A)}\quad RCH_2CH{=}CHR' \xrightarrow{t\text{-}C_4H_9OCl} RCH_2\overset{+}{C}HCHClR' \xrightarrow{-H^+} RCH{=}CHCHClR'$$

$$\text{(B)}\quad RCH_2CH{=}CHR' \xrightarrow{t\text{-}C_4H_9OCl} RCHClCH{=}CHR'$$

In the chlorination of cyclohexane or 1-phenylcyclohexene, formulation A would give:



R = H, C_6H_5.

The final product is the same as that expected by direct allylic chlorination through formulation B, because of the inherent symmetry of these systems.

When unsymmetrical molecules are chosen, however, the products may be plausibly explained only on the basis of the addition and proton ejection scheme illustrated above (76). Although insufficient cases have been studied to permit a broad generalization, it seems that although allylic chlorination appears to have taken place in symmetrical molecules, actually the double bond has shifted from its original position in the molecule. For ionic chlorinations with alkyl hypochlorites, this point may be of great value in synthesis and structural studies.

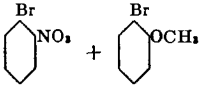
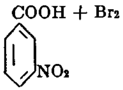
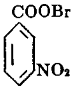
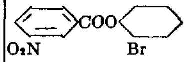
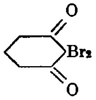
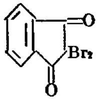
B. CHLORINATION OF AROMATIC HYDROCARBONS

The reactions carried out with aromatic hydrocarbons are summarized in table 4. In compounds bearing a side chain containing a double bond, addition to this bond takes place. Benzene is not attacked in non-polar media. Naphthalene gives a 4 per cent yield of a chlorinated product. However, in compounds having reactive hydrogen atoms, e.g., anthracene, chlorination takes place in high yield in the reactive meso position. Similarly, fluorene is halogenated in the 9-position by means of 2,4,6-trichlorophenyl- or 2,4,6-tribromophenyl hypobromite (204).

Hydrocarbons such as toluene or ethylbenzene are chlorinated in the side chain. Toluene yields primarily benzyl chloride and some benzal chloride (194).

TABLE 2B

The action of various organic hypohalite-generating reagents with cyclohexene

Reagent	Active species	Solvent	Temperature	Product	Yield	References
			°C.		*per cent*	
$C_6H_5COOAg + Cl_2$	C_6H_5COOCl	CCl_4	−10	1-Chloro-2-benzoxycyclohexane		(198)
Br_2	CH_3OBr	CH_3OH		1-Bromo-2-methoxycyclohexene	50–60	(79, 121)
$AgNO_3 + Br_2$	CH_3OBr	Pyridine + CH_3OH	−25 to −30			(198)
$CH_3COOAg + Br_2$	CH_3COOBr	CCl_4	−20	1-Bromo-2-acetoxycyclohexane	32	(198)
$C_3H_7COOAg + Br_2$	C_3H_7COOBr	CCl_4	25	1-Bromo-2-butyroxycyclohexane	55	(32; *cf.* 198)
$C_2H_5COOAg + Br_2$	C_2H_5COOBr	Pyridine + $CHCl_3$	−25 to −30	1-Bromo-2-propionoxycyclohexane	48	(198)
$C_6H_5COOAg + Br_2$	C_6H_5COOBr	CCl_4	−10	1-Bromo-2-benzoxycyclohexane	42	(198)
		$CHCl_3$	−10 to −15		44	(198)
$CBr(NO_2)_3$	HCOOBr	HCOOH	25	1-Bromo-2-formyloxycyclohexane	70	(169)
CH_3CONBr	CH_3COOBr	CH_3COOH	25	1-Bromo-2-acetoxycyclohexane	70	(168)
$CH_3COOAg + I_2$	CH_3COOI	Ether	25	1-Iodo-2-acetoxycyclohexane	80	(25)
$(CH_3COO)_2Ag + I_2$	CH_3COOI	Ether		1-Iodo-2-acetoxycyclohexane		(36)
$C_6H_5COOHg + I_2$	C_6H_5COOI	Ether	25	1-Iodo-2-benzoxycyclohexane	60	(25)
$HgO + I_2$	CH_3OI	CH_3OH	−80	1-Iodo-2-methoxycyclohexane		(24)
$(CH_3OOC)_2CBr_2$	CH_3OBr	CH_3OH	100	1-Bromo-2-methoxycyclohexane	11	(166)
$(C_2H_5OOC)_2CBr$	CH_3OBr	CH_3OH	100	1-Bromo-2-methoxycyclohexane	18	(166)
	CH_3OBr	CH_3OH	Reflux	1-Bromo-2-methoxycyclohexane	58	(166)
	CH_3OBr	CH_3OH	100	1-Bromo-2-methoxycyclohexane	54	(166)

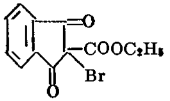
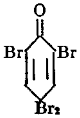
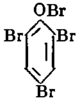
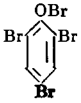
	CH_3OBr	CH_3OH	100	1-Bromo-2-methoxycyclohexane	23	(166)
Dibromobarbituric acid	CH_3OBr	CH_3OH	25	1-Bromo-2-methoxycyclohexane	44	(166)
	CH_3OBr	CH_3OH	0	1-Bromo-2-methoxycyclohexane	86	(166)
		CCl_4	Reflux		24	(204)
CH_3CONBr	CH_3OBr	CH_3OH	25	1-Bromo-2-methoxycyclohexane	81	(168)
$C_2H_5CH(NO_2)Br$	CH_3OBr	CH_3OH	100	1-Bromo-2-methoxycyclohexane	79	(166)
$CBr_2(NO_2)_2$	CH_3OBr	CH_3OH	Reflux	1-Bromo-2-methoxycyclohexane	76	(166)
CBr_3NO_2	CH_3OBr	CH_3OH	100	1-Bromo-2-methoxycyclohexane	49	(166)
$CBr(NO_2)_3$	CH_3OBr	CH_3OH	Reflux	1-Bromo-2-methoxycyclohexane	84	(167)
$CBr(NO_2)_3$	C_2H_5OBr	C_2H_5OH	Reflux	1-Bromo-2-ethoxycyclohexane	58	(167)
$CBr(NO_2)_3$	$CH_2{=}CHCH_2OBr$	$CH_2{=}CHCH_2OH$	0	1-Bromo-2-allyloxycyclohexane	65	(167)
$AgClO_4 + I_2$	CH_3OI	CH_3OH	−80	1-Iodo-2-methoxycyclohexane	90	(25)
$AgNO_3 + I_2$	CH_3OI	CH_3OH	15–20	1-Iodo-2-methoxycyclohexane		(196)

TABLE 3

Reactions of organic hypohalites with acetylenic compounds

Compound	Hypohalite	Solvent	Temperature	Product	Yield	Reference
			°C.		*per cent*	
Divinylacetylene	C_2H_5OCl	CCl_4	5–15	$ClCH_2CH(OC_2H_5)C\equiv CCH=CH_2$*		(106)
Phenylacetylene	Cl_2†	CH_3OH		$C_6H_5C(OCH_3)_2CHCl_2$	70	(101)
	C_2H_5OCl	C_2H_5OH		$C_6H_5COCHCl_2$‡		(79)
Sodium phenylacetylide	C_2H_5OCl			$C_6H_5C\equiv CCl$	Low	(127)

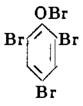
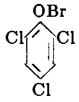
* The structure of the product was not unequivocally proved.

† Methyl hypochlorite is presumably formed *in situ*.

‡ The intermediate is $C_6H_5C(OC_2H_5)=CHCl$.

TABLE 4

Reactions of organic hypohalites with aromatic hydrocarbons and their derivatives

Compound	Hypohalite	Solvent	Temperature	Product	Yield	Reference
			°C.		*per cent*	
Benzene	C_2H_5OCl	C_2H_5OH		No reaction		(127)
	t-C_4H_9OCl		100	No reaction		(42)
	t-$C_4H_9OCl + AlCl_3$			t-Butylbenzene	43	(23)
	t-$C_4H_9OCl + H_2SO_4$	CH_3COOH	25	Chlorobenzene	95	(2)
Chlorobenzene	t-$C_4H_9OCl + H_2SO_4$	CH_3COOH	Reflux	*o*-Dichlorobenzene	80	(2)
Toluene	t-C_4H_9OCl		100	Benzyl chloride	62	(194)
				Benzal chloride	9	
	t-$C_4H_9OCl + H_2SO_4$	CH_3COOH	25	*o*-Chlorotoluene	90	(2)
	t-C_4H_9OCl*			Benzyl chloride		(104)
Benzyl chloride	t-C_4H_9OCl		100	Benzal chloride	49	
Benzal chloride	t-C_4H_9OCl		100	Phenyltrichloromethane	29	(194)
p-Bromotoluene	t-C_4H_9OCl*			*p*-Bromobenzyl chloride		(104)
p-Nitrotoluene	t-C_4H_9OCl*			*p*-Nitrobenzyl chloride		(104)
Ethylbenzene	t-C_4H_9OCl*			β-Phenethyl chloride		(104)
Styrene	t-C_4H_9OCl	Dilute CH_3COOH	25	$C_6H_5CHOHCH_2Cl$	60–70	(84)
Allylbenzene	Br_2†	CH_3OH		$C_6H_5CH_2CH(OCH_3)CH_2Br$‡		(121)
Propenylbenzene	Br_2†	CH_3OH		$C_6H_5CH(OCH_3)CHBrCH_3$	50	(121)
	CH_3OBr§	CH_3OH	0	$C_6H_5CH(OCH_3)CHBrCH_3$	76	(167)
	C_2H_5OBr§	C_2H_5OH	0	$C_6H_5CH(OC_2H_5)CHBrCH_3$	56	(167)
	$HCOOBr$§	$HCOOH$	25	$C_6H_5CH(HCO_2)CHBrCH_3$	69	(169)
Naphthalene	t-C_4H_9OCl			*x*-Chloronaphthalene	4	(194)
Diphenylmethane	t-C_4H_9OCl		100	Diphenylchloroethane	31	(194)
Fluorene		CCl_4	Reflux	9-Bromofluorene	50	(204)
		CCl_4	Reflux	9-Bromofluorene	50	(204)
Stilbene	Br_2	CH_3OH		$C_6H_5CH(OCH_3)CHBrC_6H_5$	64	(100; *cf.* 13)
Anthracene	t-C_4H_9OCl		20	9-Chloroanthracene	91	(43)
				9,10-Dichloroanthracene	9	
	t-C_4H_9OCl	$CHCl_3$	20	9,10-Dichloroanthracene	10	(194)
	t-C_4H_9OCl	CCl_4	20	9,10-Dichloroanthracene	55	(194)
	t-C_4H_9OCl	CH_3COOH	20	9.10-Dichloroanthracene	65	(194)
Triphenylmethane	t-C_4H_9OCl		100	Triphenylmethyl chloride	10	(194)

* In the presence of dibenzoyl peroxide.

† Methyl hypobromite is presumably formed *in situ*.

‡ The structure of the product was not unequivocally proved.

§ Formed from trinitrobromomethane.

TABLE 5

Reactions of organic hypohalites with alcohols

Alcohol	Hypohalite	Solvent	Temperature	Product	Yield	Reference
			°C.		per cent	
Ethyl alcohol	C_2H_5OCl	C_2H_5OH	20	Acetaldehyde		(162)
	C_2H_5OCl	C_2H_5OH		Chloral		(39)
Allyl alcohol	t-C_4H_9OCl			3-Chloro-2-allyloxypropanol	36	(62)
	t-C_4H_9OCl	CH_3OH		3-Chloro-2-methoxypropanol	20	(62)
n-Butyl alcohol	t-C_4H_9OCl			*n*-Butyl butyrate	77	(194)
	t-C_4H_9OCl	Petroleum ether-pyridine	25	*n*-Butyl butyrate	10	(165)
Cyclohexanol	t-C_4H_9OCl	CCl_4-H_2O		Cyclohexanone	58	(194)
	t-C_4H_9OCl	CCl_4-pyridine	−5	Cyclohexanone	90	(165)
Benzyl alcohol	t-C_4H_9OCl		0	Benzaldehyde	99	(194)
	t-C_4H_9OCl	CCl_4-pyridine	20	Benzaldehyde	60	(165)
β-Phenethyl alcohol	t-C_4H_9OCl		10	Phenylacetaldehyde	95	(194)
	t-C_4H_9OCl	$CHCl_3$	10–23	β-Phenethyl phenylacetate	38	(194)
	t-C_4H_9OCl	Dilute CH_3COOH	20	β-(*p*-Chlorophenyl)ethyl alcohol	39	(194)
Cholesterol	t-C_4H_9OCl	CH_3COOH	20 Reflux	6β-Chlorocholest-4-en-3-one		(76)
3β-Cholestan-ol	t-C_4H_9OCl	CCl_4	25	3-Cholestanone	76	(16)
	t-C_4H_9OCl	CH_3COOH	70	2α-Chloro-3-cholestanone	45	(16)
11α-Hydroxyprogesterone	t-C_4H_9OCl			4-Chloro-11α,17α-dihydroxy-3,20-pregnanedione		(112)
3α,17α-Dihydroxy-11,20-pregnanedione	t-C_4H_9OCl			4-Chloro-17α-hydroxy-3,11,20-pregnanetrione		(112)

In the presence of benzoyl peroxide, toluene gives benzyl chloride and ethylbenzene gives β-phenethyl chloride (104). In polar media, however, in the presence of mineral acids, quantitative nuclear chlorination takes place (2).

C. CHLORINATION OF ALCOHOLS

Alkyl hypohalites usually oxidize alcohols to the corresponding carbonyl compounds. Pyridine has been used to catalyze this reaction (38, 165). In certain cases secondary reactions take place. Thus, ethyl alcohol gives chloral, the acetaldehyde formed presumably being further chlorinated. Allyl alcohol, which contains a double bond, adds the active reagent, but it is also possible to oxidize it to acrolein under suitable conditions (77). *tert*-Butyl hypochlorite has recently been used to oxidize a number of steroid alcohols to ketones (16, 76, 112). By employing an excess of the hypochlorite it is possible to obtain the α-chloroketone directly from the alcohol (16). The data on alcohols are summarized in table 5.

D. CHLORINATION OF ALDEHYDES

tert-Butyl hypochlorite is a useful reagent for the chlorination of aromatic aldehydes. Benzaldehyde, *o*- and *m*-chlorobenzaldehydes, *p*-tolualdehyde, and *p*-acetoxybenzaldehyde are all chlorinated to yield the corresponding acid

TABLE 6

Reactions of organic hypohalites with aldehydes

Aldehyde	Hypohalite	Solvent	Temperature	Product	Yield	Reference
			°C.		*per cent*	
Acetaldehyde	C_2H_5OCl	C_2H_5OH		Chloroacetaldehyde		(194)
Crotonaldehyde	*t*-C_4H_9OCl			Methyl 2-methoxy-3-chlorobutanoate	30	(62)
Benzaldehyde	C_2H_5OCl	C_2H_5OH		Benzal chloride		(79)
	t-C_4H_9OCl	CCl_4	5	Benzoyl chloride	98	(194)
	t-C_4H_9OCl	CCl_4	20 to reflux	Benzoyl chloride	58-90	(194, 72)
	t-C_4H_9OCl	90% CH_3COOH	Reflux	Benzoic acid	90	(72)
o-Chlorobenzaldehyde	*t*-C_4H_9OCl	CCl_4; *t*-C_4H_9OH; 90% CH_3COOH	25 to reflux	*o*-Chlorobenzoic acid	90–94	(72)
m-Chlorobenzaldehyde	*t*-C_4H_9OCl	90% CH_3COOH	25 to reflux	*m*-Chlorobenzoic acid	87	(72)
p-Tolualdehyde	*t*-C_4H_9OCl	90% CH_3COOH	25 to reflux	*p*-Toluic acid	83	(72)
o-Hydroxybenzaldehyde	*t*-C_4H_9OCl	90% CH_3COOH	25 to reflux	5-Chloro-2-hydroxybenzaldehyde	79	(72)
o-Methoxybenzaldehyde	*t*-C_4H_9OCl	90% CH_3COOH	25 to reflux	5-Chloro-2-methoxybenzaldehyde	84	(72)
	t-C_4H_9OCl	CCl_4	25 to reflux	2-Methoxybenzoic acid	93	(72)
m-Hydroxybenzaldehyde	*t*-C_4H_9OCl	90% CH_3COOH	25 to reflux	2-Chloro-3-hydroxybenzaldehyde	73	(72)
m-Methoxybenzaldehyde	*t*-C_4H_9OCl	90% CH_3COOH	25 to reflux	6-Chloro-3-methoxybenzaldehyde	68	(72)
p-Hydroxybenzaldehyde	*t*-C_4H_9OCl	90% CH_3COOH	25 to reflux	3-Chloro-4-hydroxybenzaldehyde	82	(72)
p-Methoxybenzaldehyde	*t*-C_4H_9OCl	90% CH_3COOH	25 to reflux	3-Chloro-4-methoxybenzaldehyde	77	(72)
	t-C_4H_9OCl	CCl_4	25 to reflux	*p*-Anisoyl chloride or *p*-anisic acid	94	(72)
p-Acetoxybenzaldehyde	*t*-C_4H_9OCl	90% CH_3COOH; CCl_4	25 to reflux	*p*-Acetoxybenzoic acid	86; 91	(72)
m-Nitrobenzaldehyde	*t*-C_4H_9OCl	90% CH_3COOH; CCl_4; *t*-C_4H_9OH	25 to reflux	No reaction		(72)
p-Nitrobenzaldehyde	*t*-C_4H_9OCl	90% CH_3COOH; CCl_4; *t*-C_4H_9OH	25 to reflux	No reaction		(72)
Vanillin	*t*-C_4H_9OCl	90% CH_3COOH; CCl_4; *t*-C_4H_9OH	25 to reflux	5-Chlorovanillin	81–84	(72)
Veratraldehyde	*t*-C_4H_9OCl	90% CH_3COOH; *t*-C_4H_9OH	25 to reflux	6-Chloroveratraldehyde	84; 77	(72)
	t-C_4H_9OCl	CCl_4	25 to reflux	Veratric acid	85	(72)
Cinnamaldehyde	*t*-C_4H_9OCl			2-Chloro-3-methoxy-3-phenylpropanal	35	(62)
1-Naphthaldehyde	*t*-C_4H_9OCl	90% CH_3COOH	25 to reflux	5-Chloro-1-naphthaldehyde	69	(72)
2-Hydroxy-1-naphthaldehyde	*t*-C_4H_9OCl	90% CH_3COOH	25 to reflux	3(?)-Chloro-2-hydroxy-1-naphthaldehyde	73	(72)
Furfural	Br_2*	CH_3OH		4,5-Dimethoxy-4,5-dihydrofurfural dimethylacetal		(121)

* Methyl hypobromite is presumably formed *in situ*.

TABLE 7

Reactions of organic hypohalites with ketones

Ketone	Hypohalite	Solvent	Temperature	Product	Yield	Reference
			°C.		*per cent*	
Acetone	C_2H_5OCl	C_2H_5OH		Chloroacetone		(79)
	t-C_4H_9OCl		0	Chloroacetone	21	(194)
Cyclohexanone	*t*-C_4H_9OCl		100	2-Chlorocyclohexanone	71	(77)
	C_2H_5OCl			2-Chlorocyclohexanone		(127)
Acetophenone	*t*-C_4H_9OCl		20	ω-Chloroacetophenone	11	(194)
Benzophenone	*t*-C_4H_9OCl		20	No reaction		(194)
Benzalacetophenone	Br_2*	CH_3OH	65	$C_6H_5COCHBrCH(OCH_3)$-C_6H_5	45	(100, 45)
3-Cholestanone	*t*-C_4H_9OCl	CH_3COOH	85–90	2α-Chlorocholestan-3-one	90	(75, 16)
Methyl 3-ketoalloetianate	*t*-C_4H_9OCl	CH_3COOH	85–90	Methyl 2-chloro-3-ketoalloetianate	50	(16)
Androstan-17β-ol-3-one acetate	*t*-C_4H_9OCl	CH_3COOH	85–90	2-Chloroandrostan-17β-ol-3-one acetate		(16)
Allopregnane-3, 20-dione	*t*-C_4H_9OCl	CH_3COOH	85–90	2-Chloroallopregnane-3, 20-dione		(16)
Testan-17β-ol-3-one acetate	*t*-C_4H_9OCl	CH_3COOH	85–90	4-Chlorotestan-17β-ol-3-one acetate	83	(16)
Coprostanone	*t*-C_4H_9OCl	CH_3COOH	85–90	4-Chlorocoprostanone		(16)

* Methyl hypobromite is presumably formed *in situ*.

chloride. Hydroxybenzaldehydes, methoxybenzaldehydes, 1-naphthaldehyde, and 2-hydroxy-1-naphthaldehyde undergo nuclear chlorination. The solvent used exerts some influence on the course of the reaction. Nitro groups deactivate the aromatic nucleus sufficiently so that no chlorination occurs (72).

Cinnamaldehyde and furfural, both containing double bonds, undergo the addition reactions expected in olefinic compounds. The data for aldehydes are summarized in table 6.

E. CHLORINATION OF KETONES

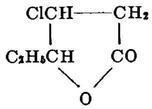
Ketones invariably yield the α-haloketones with organic hypohalites. Although the number of cases in which these reagents have been employed for chlorination is low, it is felt that *tert*-butyl hypochlorite should be the reagent of choice for the preparation of α-chloroketones. The yields are high and the chlorinations are simpler to carry out than with gaseous chlorine. The chlorination data for ketones are assembled in table 7.

F. CHLORINATION OF PHENOLS

The phenolic hydroxyl group activates the aromatic nucleus for chlorination with alkyl hypohalites. It may be seen from table 11 that the chlorine atom prefers to enter ortho to the phenolic group even when, on the basis of steric considerations, another position might be expected to be attacked. *m*-Cresol,

TABLE 8

Reactions of organic hypohalites with acids

Acid	Hypohalite	Solvent	Temperature	Product	Yield	References
			°*C.*		*per cent*	
Acetic acid	*t*-$C_4H_9OCl + H_2SO_4$		25	*t*-Butyl chloroacetate	78	(2)
	t-C_4H_9OCl		100	Chloroacetic acid	Trace	(194)
Acrylic acid	Br_2*†	CH_3OH		α-Bromo-β-methoxypropionic acid		(65)
Crotonic acid	Br_2*†	CH_3OH		α-Bromo-β-methoxybutyric acid		(65)
β,β-Dimethylacrylic acid	Br_2*†	CH_3OH		α-Bromo-β-methoxyisovaleric acid		(65)
$CH_3CH_2CH{=}CHCH_2COOH$	C_2H_5OCl	Ether			93	(31)
Benzoic acid	*t*-C_4H_9OCl		20	No reaction		(194)
Salicylic acid	*t*-C_4H_9OCl	$CHCl_3$	20	5-Chloro-2-hydroxybenzoic acid	69–73	(42, 194)
	t-C_4H_9OCl	CCl_4	20 to reflux	3-Chloro-2-hydroxybenzoic acid	78	(73)
Anthranilic acid	*t*-C_4H_9OCl	$CHCl_3$	−78	2-Amino-5-chlorobenzoic acid	44	(194)
	t-C_4H_9OCl	$CHCl_3$–CCl_4	20	2-Amino-3,5-dichlorobenzoic acid	11	(194)
	t-C_4H_9OCl (2 moles)	$CHCl_3$–CCl_4	20	2-Amino-3,5-dichlorobenzoic acid	49–73	(194)
Cinnamic acid	Cl_2*	CH_3OH	20–30	$C_6H_5CH(OCH_3)CHClCOOCH_3$	55	(100)
	t-C_4H_9OCl	CH_3OH		$C_6H_5CH(OCH_3)CHClCOOCH_3$	24	(62)
	Br_2*	CH_3OH	65	$C_6H_5CH(OCH_3)CHBrCOOCH_3$	34	(100)

---

* The alkyl hypohalite is presumably formed *in situ*.

† In the presence of lead salts.

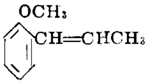
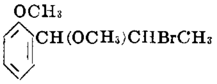
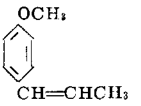
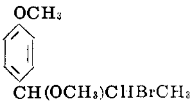
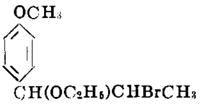
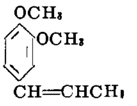
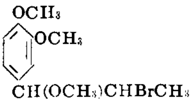
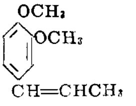
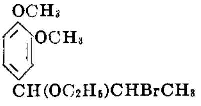
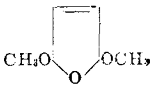
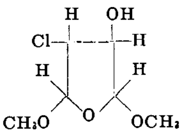
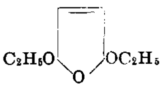
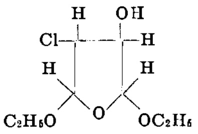
TABLE 9

Reactions of organic hypohalites with esters

Ester	Hypohalite	Solvent	Temperature	Product	Yield	Reference
			°C.		*per cent*	
Ethyl acetate	$t\text{-}C_4H_9OCl$		100	Chloroethyl acetate	46	
Ethyl acrylate	$t\text{-}C_4H_9OCl$	CH_3COOH-acetic anhydride	60–70	$ClCH_2CH(OCOCH_3)COOC_2H_5$ $+ CH_3COOCH_2CHClCOOC_2H_5$		(158)
Diethyl malonate	$t\text{-}C_4H_9OCl + AlCl_3$			Diethyl dichloromalonate		
Diethyl sodiomalonate	C_2H_5OCl			Diethyl chloromalonate		(127)
Methyl salicylate	$t\text{-}C_4H_9OCl$	CCl_4	25 to reflux	Methyl 3,5-dichloro-2-hydroxybenzoate	35	(73)

TABLE 10

Reactions of organic hypohalites with ethers

Ether	Hypohalite	Solvent	Temperature	Product	Yield	References
			°C.		*per cent*	
Diethyl ether	$t\text{-}C_4H_9OCl$		0	α-Chloroethyl ethyl ether α,β-Dichloroethyl ethyl ether α,β,β-Trichloroethyl ethyl ether	9 3 2	(194)
Anisole	C_2H_5OCl	C_2H_5OH		No reaction		(79)
	$t\text{-}C_4H_9OCl + H_2SO_4$	CH_3COOH	25	o-Chloroanisole	87	(2)
	CH_3OBr*	CH_3OH	0		78	(167, 120)
	CH_3OBr*	CH_3OH	0		84	(167)
	C_2H_5OBr*	C_2H_5OH	0		74	(167)
	CH_3OBr*	CH_3OH	0		87	(167)
	C_2H_5OBr*	C_2H_5OH	0		79	(167)
	$t\text{-}C_4H_9OCl$	90% CH_3COOH				(74)
	$t\text{-}C_4H_9OCl$	CH_3COOH				(190)

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* Formed *in situ*.

TABLE 11

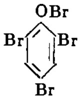
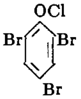
Reactions of organic hypohalites with phenols

Phenol	Hypohalite	Solvent	Temperature	Product	Yield	References
			°*C.*		*per cent*	
Phenol..........	C_2H_5OCl	C_2H_5OH		*o*- and *p*-Chlorophenol		(194)
	t-C_4H_9OCl (1:1)		20	*o*-Chlorophenol	94	(42, 43)
	t-C_4H_9OCl (1:2)		20	2,4-Dichlorophenol*	87	(42, 43)
	t-C_4H_9OCl (1:4)		20	2,4,6-Trichlorophenol	82	(42, 43)
	t-C_4H_9OCl (1:5)		20	Tetrachloroquinone	83	(42, 43)
	t-C_4H_9OCl (1:1)	$CHCl_3$	0–40	*o*-Chlorophenol	46–52	(42, 43)
				p-Chlorophenol	36–42	
	t-C_4H_9OCl (1:1)	CCl_4	20	*o*-Chlorophenol	57	(42, 43)
				p-Chlorophenol	29	
Catechol........	*t*-C_4H_9OCl		20	Chlorocatechol	78	(42, 43)
Resorcinol.......	*t*-C_4H_9OCl		20	Chlororesorcinol	72	(42, 43)
Hydroquinone..	C_2H_5OCl	C_2H_5OH		2,3-Dichlorohydroquinone		(79)
	t-C_4H_9OCl (1:1.5)		20	Quinhydrone	77	(194)
	t-C_4H_9OCl (1:2.1)		20	Quinone	13	(194)
o-Cresol.........	*t*-C_4H_9OCl	CCl_4	25 to reflux	6-Chloro-2-methylphenol	31	(73)
				4,6-Dichloro-2-methylphenol	18	(73)
m-Cresol.......	*t*-C_4H_9OCl	CCl_4	25 to reflux	2-Chloro-3-methylphenol	44	(73)
p-Cresol.........	*t*-C_4H_9OCl	CCl_4	25 to reflux	2-Chloro-4-methylphenol	69	(73)
Pyrogallol.......	*t*-C_4H_9OCl	CCl_4	25 to reflux	4-Chloropyrogallol	79	(73)
Carvacrol.......	*t*-C_4H_9OCl	CCl_4	25 to reflux	2-Methyl-4(?),6-dichloro-5-isopropylphenol	21	(73)
Thymol.........	*t*-C_4H_9OCl	CCl_4	25 to reflux	4-Chloro-3-methyl-6-isopropylphenol	48	(73)
Guaiacol........	*t*-C_4H_9OCl	CCl_4	25 to reflux	5-Chloro-2-methoxyphenol	68	(73)
o-Chlorophenol	*t*-C_4H_9OCl	CCl_4	25 to reflux	2,6-Dichlorophenol	73	(73)
p-Chlorophenol	*t*-C_4H_9OCl	CCl_4	25 to reflux	2,4-Dichlorophenol	80	(73)
o-Nitrophenol...	*t*-C_4H_9OCl	CCl_4	25 to reflux	No reaction		(73)
p-Nitrophenol...	*t*-C_4H_9OCl	CCl_4	25 to reflux	No reaction		(73)
α-Naphthol.....	*t*-C_4H_9OCl	CCl_4	25 to reflux	2-Chloro-1-naphthol	77	(73)
β-Naphthol......	*t*-C_4H_9OCl	CCl_4	25 to reflux	1-Chloro-2-naphthol	67	(73)

* This structure is probably incorrect in view of the result of the chlorination of *o*-chlorophenol.

TABLE 12

Reactions of organic hypohalites with nitrogen-containing compounds

Compoun	Hypohalite	Solvent	Temperature	Product	Yield	References
			°*C.*		*per cent*	
Amides:						
Acetamide..........	*t*-C_4H_9OCl		20	*N*-Chloroacetamide	68	(194)
Benzamide..........	*t*-C_4H_9OCl		20	*N*-Chlorobenzamide	44	(194)
Acetanilide..........	*t*-C_4H_9OCl		20	*p*-Chloroacetanilide	90	(194)
Benzenesulfonamide.	*t*-C_4H_9OCl		20	*N*-Chlorobenzenesulfonamide	3	(194)
Amines:						
Ethylamine.........	C_2H_5OCl	C_2H_5OH		*N*,*N*-Dichloroethylamine		(79)
Diethylamine.......	C_2H_5OCl	C_2H_5OH		*N*-Chlorodiethylamine		(201)
Aniline.............				Tribromoaniline		(193; *cf.* 125 and 162)
				Trichloroaniline		(193)
Diphenylamine.....	*t*-C_4H_9OCl		0	4-Chlorodiphenylamine	63	(43)
Miscellaneous:						
Phenylhydrazine....	*t*-C_4H_9OCl		20	2-Chlorophenylhydrazine	49	(194)
Benzalaniline........	*t*-C_4H_9OCl	CCl_4		$C_6H_5CHClN(OC_5H_{11})C_6H_5$		(68)
Benzonitrile.........	*t*-C_4H_9OCl		20	No reaction		(194)

for example, gives 2-chloro-3-methylphenol. The preference for ortho-chlorination is reminiscent of the attack of phenols by peroxides. This may point to a free-radical chlorination mechanism in the attack of phenols by alkyl hypochlorites.

VI. Ionic Mechanisms Involved in Reactions of Organic Hypohalites

A. FORMATION AND HYDROLYSIS

An ionic mechanism has been established in many cases for the halogenation reactions of organic hypohalites and for those in which they undergo hydrolysis. It must be emphasized, however, that under certain circumstances halogenation undoubtedly proceeds also by a free-radical mechanism.

It was shown recently (5) that alkyl hypohalites in aqueous media undergo rapid hydrolysis. In certain cases involving these media, the actual reagent may be the corresponding hypohalous acid. The reactions of hypohalous acids in aqueous media have been studied extensively by Soper and coworkers (119, 140, 156, 188, 202), by Derbyshire and Waters (51, 52, 53, 54, 55), and by Berliner (20, 21, 22). A full discussion of their work is outside the scope of this review.

In media containing considerable proportions of organic or inorganic acids and their salts (such as buffered solutions) alkyl hypochlorites react to give the hypochlorites of the corresponding acids (or the chlorine salts), which are more effective halogenating agents than the free alkyl hypochlorites. The formation and hydrolytic reactions of alkyl hypochlorites in buffered aqueous media have recently been reported (5). By the use of O^{18} as label, it was established that in both the formation and hydrolytic reactions under alkaline and acid conditions, the bond between the alkyl group and the oxygen atom remains intact. This illustrates the positive polarization of the chlorine atom in hypohalous acids and in the hypohalites. The same authors found that the formation of alkyl hypochlorites from the alcohols and hypochlorous acid and the hydrolysis of these compounds are subject to general acid–base catalysis, the general rate coefficient having the form

$$k = k_0 + \Sigma k_i c_i$$

where k_i is the catalytic coefficient of the catalyst i present at concentration c_i. Some of the catalytic coefficients reported are collected in table 13.

TABLE 13

Catalytic constants for a number of acids and their conjugate bases for the formation and hydrolysis of tert-butyl hypochlorite at 25°C. in aqueous media

Acid	k_{HA}	k_{A^-}	Acid	k_{HA}	k_{A^-}
	l.mole⁻¹min.⁻¹	*l.mole⁻¹min.⁻¹*		*l.mole⁻¹min.⁻¹*	*l.mole⁻¹min.⁻¹*
H_3O^+..........	1.1×10^2	$<10^{-4}$	$H_2PO_4^-$*....	3.6	4.5×10
H_3PO_4.........	8.2×10	1.1×10^{-2}	HOCl......	2.4×10	9.1×10^3
CH_3COOH.....	5.7	3.1×10^{-1}	H_2O........	$<10^{-4}$	2.3×10^7

* A minimum in the rate is observed at about pH 4.5.

The kinetics and isotopic results have been interpreted (5) in terms of the following generalized mechanism:

$$\left.\begin{array}{l} HOCl + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ACl + H_2O \\ ACl + t\text{-}C_4H_9OH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} t\text{-}C_4H_9OCl + HA \end{array}\right\}\text{Acid region}$$

$$\left.\begin{array}{l} HOCl + A^- \rightleftharpoons ACl + OH^- \\ ACl + t\text{-}C_4H_9O^- \rightleftharpoons t\text{-}C_4H_9OCl + A^+ \end{array}\right\}\text{Alkaline region}$$

This mechanism leads to the following expression for the rate coefficients:

$$k_{\text{cat.}} = [HA]\,\frac{k_{-1}k_2[H_2O] + k_1k_2[ROH]}{k_{-1}[H_2O] + k_2[ROH]}$$

It appears that under the experimental conditions used by these authors the observed catalytic coefficients approximate to k_1 and k_2, i.e., to the rate coefficients of the formation of the active intermediates ACl.

From quite general considerations it is possible to deduce the effectiveness of the intermediate ACl as a chlorinating agent. The more electronegative the group A, the more effective will the compound ACl be as a chlorinating agent and the stronger will the acid AH be. The following sequence has been established: $t\text{-}C_4H_9OCl < t\text{-}C_4H_9OHCl^+$; $t\text{-}C_4H_9OCl < HOCl < CH_3COOCl$; $HOCl < H_2OCl^+$; $HOCl < Cl_2O < Cl_2$.

It is clear that any compound AH which gives an intermediate more active than HOCl and $t\text{-}C_4H_9OCl$ will be an effective catalyst for the formation and hydrolysis reactions. Some of the catalysts and the intermediates derived from them are listed in table 14.

The reviewers believe that the reactions of aqueous solutions of alkyl hypochlorites containing any of the above catalysts may be interpreted as occurring through the intermediates listed above. If several catalysts are present, the reaction (such as chlorination) will proceed simultaneously through all the possible intermediates ("halogen carriers"). The percentage occurring through a particular catalyst will be in proportion to the free energy of activation required for the formation of the corresponding intermediate (*cf.* table 13).

De la Mare and coworkers (111) have assumed similar intermediates (acetyl hypochlorite) for the chlorination reaction of hypochlorous acid in the presence of acetic acid.

An interesting result of the work described above (5) is the demonstration of two zero-order reactions with respect to substrate. Thus, for moderately reac-

TABLE 14

Catalysts and intermediates in the formation and hydrolysis of alkyl hypochlorites (5)

Catalyst......	H_2O	H_3O^+	CH_3COOH	H_3PO_4	$H_2PO_4^-$	HPO_4^{--}	HOCl	HCl	H_2SO_4	ROH
Intermediate.	HOCl	H_2OCl^+	CH_3COOCl	H_2PO_4Cl	HPO_4Cl^-	$ClPO_4^{--}$	Cl_2O	Cl_2	HSO_4Cl	ROCl

tive substrate (e.g., anisole) a zero-order rate has been observed (109, 110), which may be interpreted as the rate of formation of the active species Cl^+ by ionization of H_2OCl^+. With many reactive substrates, e.g., alcohols (such that may react even with H_2OCl^+), another zero-order reaction is observed, some 10^4 times faster than the first, which may be taken as representing the rate of formation of H_2OCl^+.

So far, no evidence has been presented for the direct participation of alkyl hypochlorites in ionic chlorination reactions.

B. SUBSTITUTION AND ADDITION REACTIONS

1. *General considerations*

This section deals with reactions involving either positively charged species of the hypohalite type or neutral molecules which undergo polarization induced by nucleophilic reagents.

It has been stated above that a dynamic equilibrium exists between all hypohalite species (cases of irreversible reactions will be considered in Section IX). When hydroxylic species are present in the reaction medium, all possible hypohalites will be formed in concentrations determined by their equilibrium constants. Their influence on the course of the reaction, however, is dependent mainly upon their reactivity as electrophilic reagents rather than upon their relative concentrations.

"Positive" halogenating agents may react, in analogy to alkyl halides, by two principal mechanisms: self-ionization

$$AX \rightarrow A^- + X^+$$

and the bimolecular nucleophilic reaction (94),

$$B^- + AX \rightarrow BX + A^-$$

perhaps with a continuum of stages between both limiting possibilities.

There are cases of catalysis in which an intermediate of the type AX is formed and the rate-determining step is that of formation of the intermediate (108b); the reaction is of zero order with respect to active substrate. These cases appear to be of the first type, although they are really bimolecular. Substrates with nucleophilic tendency are primarily aromatic compounds, olefins, alkynes, and hydroxyl derivatives.

There is, in principle, little difference between aromatic substitution and addition to double bonds or to acetylenic bonds (155). The only difference is that the carbonium ion formed by an electrophilic attack of a positively charged species stabilizes itself through the loss of a proton in the case of substitution, or takes up an ion in a further electrophilic attack resulting in an addition product. Neither the proton transfer to any base in solution (123), nor the taking up of a nucleophilic species (13), was found to be a rate-determining step. This point brings aromatic substitution and olefinic addition into one category with respect to halogenation, as the rate-determining step in these cases is either the formation of the positive halogen carrier (109, 110, 111, 118) or its attack on the substrate (13, 50, 52, 55). A similar state of affairs exists in hydroxylic substitution. Here again, the rate-determining step is the nucleophilic attack on the hypohalite or the formation of an intermediate active halogenating agent. In aliphatic substitution of the ionic type there may be another rate-determining step,—the formation of a carbanion by the action of a nucleophilic reagent on the substrate; the subsequent X^+ attack is a quite rapid reaction (92; *cf.* 18).

The role in ionic halogenation of some of the hypohalite species included in table 13 will now be considered in some detail.

2. HOX, ROX, AcOX

The mechanism of chlorination by hypohalous acids has been studied mainly by Soper and coworkers (97, 98, 119, 140, 156, 188, 202) and by Shilov and coworkers (176, 177, 178, 179, 180; *cf.* 21). They found that hypohalous acids are weaker halogenating agents than the corresponding free halogens (180, 188), and that they become effective only when the halide-ion concentration is fairly low. In practically all interactions between hypohalous acids and organic substrates, the only reactive agent is the free hypohalous acid and not hypohalite ion (21, 188). These results are in agreement with tracer experiments (5), which always show cleavage of the oxygen–chlorine bond. Very few instances are recorded in the literature which indicate that hypohalite ion takes part in the reaction (191), as the reaction proceeds even at high concentrations of sodium hydroxide. No accurate kinetic study has been undertaken in these cases, but it seems conceivable that if the substrate is a much weaker acid than hypohalous acid, an interaction may occur between hypohalous acid and a carbanion, in which disappearance of the former may be compensated for by the formation of the latter, with the apparent result of independence of hydroxide-ion concentration.

The formation and hydrolysis of alkyl hypohalites by the action of hypohalous acids on alcohols has been considered on page 943. It is not possible to compare directly the efficacy of an alkyl hypohalite as a chlorinating agent with that of the corresponding acid, since the media in which these reactions would have to be carried out are quite different. Indeed, no such studies have been carried out. The reviewers suggest that the relative reactivity of alkyl hypohalites as compared to the free acids could, however, be deduced by the addition of small quantities of alcohols to aqueous hypohalite solutions. As the reaction between hypohalous acid and alcohol is much faster than with any other organic substrate, a catalytic effect could be detected if an alkyl hypohalite were more reactive than the hypohalous acid. No such experiment has been carried out to date, and one may predict the reactivity of alkyl hypohalites only indirectly, on the basis of the electrophilic sequence on page 944, from which it is seen that alkyl hypohalites are less reactive than the corresponding free acids. On the other hand, it has been proved that the free hypohalous acids are less reactive than the free halogens (180, 188). Hence, in all reactions in which free halogen is used in alcoholic solution and an apparent addition of alkyl hypohalite to a double bond had occurred (122), the active reagent must be the free halogen. The carbonium ion formed then attacks the alcoholic solvent and an alkoxy group is introduced into the molecule. These assumptions are fully confirmed by the thorough study by Bartlett and Tarbell (13) of the addition of methyl hypobromite to stilbene. Further evidence for this view is beautifully reviewed by Ingold (94a).

Acyl hypohalites might similarly be postulated as intermediates in addition reactions of halogens in solutions of carboxylic acids (84, 168, 169). However, this assumption is untenable, since acyl hypohalites are less reactive halogenating agents than the corresponding free halogens. It has been shown that chlorine monoxide is more reactive than acetyl hypochlorite (176) and free chlorine is more reactive than chlorine monoxide (181), as it has a catalytic effect on a chlorine monoxide reaction. This would imply that in the case of free halogen in carboxylic acid solution, the active species is still the free halogen (*cf.* 94b). Complications may occur if the carboxylic acids are not anhydrous. In the presence of water, the hydronium ion formed may further react with the acyl hypohalite to give $AcOHCl^+$, which is much more reactive than the free halogen. In inert solvents the acyl hypohalites formed from the silver salts of the corresponding carboxylic acids are the active reagents (36, 152, 153, 154), but in this case the ionic character of the reaction is in doubt.

While they are weaker reagents than the free halogens,[2] the acyl hypohalites are stronger halogenating agents than alkyl hypohalites and free hypohalous acids. Hence, they are catalytic intermediates in halogenation reactions by hypohalous acids (20, 21, 33, 97, 119, 140, 179). They are the reactive species in carboxylic acid solutions in the absence of halide ions (2, 111), or are intermediates in the formation of the more reactive $AcOHX^+$.

Phenyl hypohalites, which are apparently of strength similar to that of acyl hypohalites, are assumed as intermediates in the halogenation of phenols (114). The proof for their existence in this case is not valid as long as it is not shown that they are more reactive than free chlorine. Their existence may be proved by looking for a catalytic effect in the halogenation of phenols at increasing phenol concentrations (*cf.* 188), an effect which will *a priori* be smaller than that of free acetic acid under the same conditions. Mention must be made, however, of the catalytic effect of picric acid (99), which points to the existence of picryl hypochlorite.

3. X^+, H_2OX^+, $ROHX^+$, $AcOHX^+$

The general problem of the existence and stability of positively charged halogen ions in the form of X^+ (17, 50, 185, 189) or in complex form (108, 198,

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[2] If a small amount of X^- is added to a solution of acyl hypohalite in acetic acid, all of the active halogen will be in the form of X_2 (32). This does not contradict the contention that the equilibrium

$$ACl + B^- \rightleftharpoons BCl + A^-$$

is always shifted towards the less reactive species. X_2 is liberated in the reaction

$$AcOBr + Br^- \rightleftharpoons Br_2 + AcO^-$$

because the concentration of AcO^- in glacial acetic acid solution is negligible. The equi-

199) is outside the scope of this review. The existing evidence has recently been reviewed by Ingold (94c). Only those kinetic studies are included here which postulate their existence either as intermediates of a definite stationary concentration or as highly reactive species which react with the substrate as soon as they are formed.

It has been observed that halogenation by hypohalous acids in aqueous solutions is catalyzed by rather high concentrations of mineral acids:

$$\text{Rate} = k(\text{HOX})(\text{H}_3\text{O}^+)\,(\text{substrate}) \qquad (52, 55, 180, 202)$$
$$\text{Rate} = k(\text{HOX})(\text{H}_3\text{O}^+) \qquad (109, 110)$$

As a three-body collision is improbable at the high rates measured experimentally and a reaction between the substrate and a proton is very unlikely to occur (13), the following equilibria have been assumed to hold:

$$\text{HOX} + \text{H}_3\text{O}^+ \rightleftharpoons \text{X}^+ + 2\text{H}_2\text{O}$$
$$\text{HOX} + \text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{OX}^+ + \text{H}_2\text{O}$$

The second equilibrium is much more favored considering the thermodynamic instability of X^+ (17). The second rate equation points to the presence of highly reactive substrates and implies that the rate-determining step is either the protonation of hypohalous acid or the splitting off of X^+ from the H_2OX^+ complex.The second possibility is favored by analogy with the nitration reaction (67a) in which the existence of NO_2^+ has been established. Much more convincing is the fact that in two systems, both containing an acid-catalyzed hypochlorous acid reagent with two different substrates (phenol and anisole), a zero-order reaction rate with respect to substrate was found (5, 109, 110). However, these rates differed by a factor of ten thousand, implying that by reaction of a proton with hypochlorous acid two different active species are formed. The less active H_2OCl^+ is capable of attacking hydroxylic hydrogen (5), while aromatic substitution (109, 110) requires the much more reactive Cl^+, the formation of which is rate-determining.

On the other hand, it has been found that in the presence of a large amount of X^- there is a negligible influence of H_3O^+ on the rate of halogenation (202), implying that the free halogen produced by the reaction

$$\text{HOX} + \text{X}^- \rightarrow \text{X}_2 + \text{OH}^-$$

is the main reagent of halogenation. This reagent is completely indifferent towards acid concentration. Solutions containing high concentrations of X^- have very low concentrations of HOX. In the case of bromine, for example, the hydrolysis constant is 5×10^{-9} at room temperature (113) and the equilibrium constant $(H_2OBr^+)/(H_3O^+)(HOBr)$ is of the order of 10^{-6} (13). It can therefore be calculated that even if H_2OBr^+ is more reactive than Br_2 by a factor larger than 10^{10}, its activity could not be detected in the presence of excess bromide ion. The case of iodine is no more favorable. Although the $(H_2OI^+)/(H_3O^+)$

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librium, then, is shifted to the right. For this reason, also, free halogens are liberated by the action of halides on hypohalites in acid solution.

(HOI) equilibrium constant is 3×10^{-2} (17), the corresponding hydrolysis constant is 3×10^{-13} (34). If the hydrolysis equilibrium is shifted to one side by removal of halide ion, then the high efficiency of H_2OX^+ seems reasonably well demonstrated (1, 51, 53, 54).

No direct indication has been obtained regarding the existence of $ROHX^+$, the alkyl analog of H_2OX^+. Its existence has been postulated in the dehydration reaction of alcohols by iodine (56) and bromine (8) and in the oxidation of ethyl alcohol by bromine (64).

The presence of $CH_3COOHCl^+$ must be assumed in order to interpret the kinetic results of halogenation in glacial acetic acid in the presence of sulfuric acid (2, 111). It has been pointed out that $CH_3COOHCl^+$ is the main chlorine carrier in glacial acetic acid solutions containing alkyl hypochlorite or chlorine monoxide and a mineral acid. The reactivity of CH_3COOCl as a halogenating agent was found to be proportional to Hammett's H^0 function for sulfuric acid solutions in glacial acetic acid (2). This may be readily understood by assuming the existence of $CH_3COOHCl^+$. It was found (3) that the reaction

$$t\text{-}C_4H_9OCl + CH_3COOH \rightarrow t\text{-}C_4H_9OH + CH_3COOCl$$

in the presence of sulfuric acid is much faster than the zero-order reaction of CH_3COOCl with anisole in the presence of the corresponding concentration of the catalyst (2, 111). By an argument analogous to the one used with respect to the H_2OCl^+–Cl^+ system, it may be shown that the active intermediate attacking anisole is Cl^+ (3).

4. X_2, XY, X_2O

As has been noted above, the free halogens occur as intermediates in halogenation reactions by hypohalous derivatives in the presence of halide ions. They are more reactive than the corresponding hypohalous acids and their alkyl and acyl derivatives (66), so that their stationary concentration in the presence of active substrates may be extremely small. Shilov (176) attributes results obtained by de la Mare (109, 110) in an acid-catalyzed hypochlorous acid system to the effect of free chlorine and not to that of H_2OCl^+. This criticism seems to the authors unjustified in the light of the results obtained in a zero-order reaction with respect to substrate by the action of free chlorine on phenol (188). Furthermore, it has been pointed out above that convincing evidence exists for the short-lived existence of Cl^+ (5, 109, 110; *cf.* 202).

By the action of chloride ion on hypobromous or hypoiodous compounds an interhalogen compound is formed. Its formation is analogous to that of another compound of the type ACl (5, 99). Its electrophilic power is greater than that of all hypohalous species except those which are positively charged (95, 180). Chloride ion is therefore a catalyst in bromination and iodination reactions in polar media. In contradistinction, the reaction

$$Br^- + HOCl \rightarrow HOBr + Cl^-$$

is irreversible (63).

Another intermediate which may become the primary one in certain hypohalous reactions is chlorine monoxide. In many kinetic studies of halogenation by hypochlorous acid a simultaneous term is present which is dependent upon the square of the hypochlorous acid concentration (5, 97, 176, 178, 179, 181). This term is related to the chlorine monoxide formed by the interaction of two hypochlorous acid molecules, or of a hypochlorite ion with a hypochlorous acid molecule:

$$HOCl + OCl^- \rightarrow Cl_2O + OH^-$$

Chlorine monoxide was found to be more reactive than hypochlorous acid (5) but less reactive than chlorine (181).[3]

The reviewers believe that the great reactivity of chlorine monoxide, considering the strong nucleophilic power of the hypohalite ion, may be explained by the statistical factor, as this molecule may donate either one of its two chlorine atoms. No catalytic effect has been detected in the case of hypobromous acid, perhaps because of the instability of bromine monoxide in aqueous solution (*cf.* 35). Similarly, there is no experimental evidence for the existence of any mixed halogen monoxide which might be formed by the action of hypochlorous acid on hypobromite solution.

5. *Other halogenating agents*

It is not within the scope of this review to discuss all known nucleophilic carriers of halogens. A recent review is of interest in this field (67; *cf.* 184). Mention must be made, however, of certain classes of compounds which are "positive" halogen carriers, examples of which appear in the tabular survey: certain ketones, diketones, and carboxylic compounds bearing α-halogen atoms (67, 136); 1-halogenoalkynes (93, 137, 192); certain aromatic compounds containing activated halogen atoms (70, 120, 130, 131, 132, 134, 135, 203); halogenonitromethanes (28, 81, 117, 118, 166, 167, 169); halogenoacetylmethanes (29); halogenocyanomethanes (27, 28); halogenonitrosomethanes (30); trifluorohalogenomethanes (12); halogenomethanes (87, 91, 129, 141); certain trivalent nitrogen compounds containing halogen (58, 168, 175, 183, 205); nitroxyl chloride (nitryl chloride) (15, 142).

Most of the above compounds contain oxygen. As the hydrolysis product is always a hypohalous acid, it has been assumed (60) that in these compounds the halogen is transferred to an oxygen atom in an enol or aci-tautomeric structure. Evidence exists that in most cases the halogen atom is bound to carbon, e.g., in the bromomalonic derivatives (81), the chloromalonic derivatives and halogenonitromethanes (117), and the halogen-substituted dihydroresorcinols (136). In the case of 2,6-dibromo-4-chlorophenyl hypobromite and 2,4,6-tribromophenyl hypochlorite, the hypohalite structure may be correct (193). Iso-

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[3] *Cf.* however, reference 178, where it is shown that chlorine monoxide is more efficient than free chlorine. The discrepancy in Shilov's work may be explained by the fact that in the second case the rate measured was the rate of formation of chlorine monoxide. See also references 97 and 98.

lation of both halogen-containing tautomers in the latter type of compound has been claimed (182).

It seems reasonable that any halogen-containing compound can donate an electrophilic halogen provided the remaining radical is more nucleophilic than the halogen. Thus, for example, "positive" chlorine is not furnished by diacetylchloromethane, but the corresponding bromo derivative provides electrophilic bromine (117).

The compounds listed above behave like hypohalites. In polar hydroxylic solvents they fit into the general electrophilic halogenation scheme as halogen carriers (41, 80). In non-polar solvents they also behave analogously to hypohalites under the same conditions (82, 165; *cf.* 160). There is evidence that acyl hypohalites undergo heterolytic cleavage more readily than *N*-bromoamides (157). The tendency towards heterolytic cleavage of an electrophilic halogen carrier may be increased by replacement of hydrogen in the nucleophilic radical by the more electronegative fluorine (88). It may be concluded that the greater the acidity of AH, the more probable is the heterolytic fission of the A—X bond. The activation energy of such a fission, given proper solvating conditions, is smaller than that of a homolytic one (88). It should be possible to employ these considerations of acidity and activation energy in the elucidation of reaction mechanisms.

6. Hypohalites of inorganic acids

Halogen derivatives of inorganic acids have been assumed as intermediates in addition reactions of halogens in the presence of silver salts (25). Mineral acids such as sulfuric acid, phosphoric acid, and their anions strongly catalyze halogenation reactions in addition to their effect as mere proton donors. It was shown that phosphoric acid and phosphate ion are more efficient catalysts in the halogenation of various organic compounds than are the carboxylic acids (2, 20, 119, 140, 178, 179). This effect has been attributed to phosphatyl hypochlorite. A specific catalytic effect of sulfuric acid on chlorination by hypochlorous acid (55) points to the existence of sulfatyl hypochlorite, which is presumably a stronger nucleophilic reagent than H_2OCl^+.

VII. FREE-RADICAL MECHANISMS INVOLVED IN REACTIONS OF ORGANIC HYPOHALITES

A free-radical mechanism seems operative in certain reactions of hypohalites, e.g., aliphatic substitution in the presence of peroxides (104, 160), the production of quinones (105), the chlorination of toluene with alkyl hypohalites in sunlight (2), and the reaction of alkyl hypohalites with benzaldehyde to yield benzoyl chloride (42, 72, 194). The oxidation of hydrazine to nitrogen by all "positive" halogen donors may also be a free-radical reaction (69a).

The autodecomposition of alkyl hypohalites is photosensitized (39, 162, 194, 195). Primary hypohalites yield an aldehyde and hydrochloric acid. Secondary hypochlorites give a ketone and hydrochloric acid, while tertiary compounds yield a ketone together with alkyl halide, alkanes, and olefins. The mechanism is similar to the homolytic one. There occurs a homolytic cleavage of the oxygen–chlorine bond followed by fission of a carbon–hydrogen or a carbon–carbon bond at the α-carbon atom (204a).

The formation and decomposition of acyl hypohalites involves both ionic and free-radical features. Acyl hypohalites decompose in a photosensitized chain reaction to yield alkyl halides, carbon dioxide, and esters (32). The stability sequence of various acyl hypohalites was found to be: $C_6H_5COOCl < C_3H_7COOCl < CH_3COOCl$; $C_3H_7COOCl < C_3H_7COOBr$.

VIII. OXIDATION BY MEANS OF ORGANIC HYPOHALITES

The mechanism of the oxidation reactions in which organic hypohalites participate has not been studied to the extent that sufficient kinetic data are available. There seems to be no justification for reviewing the fragmentary data at hand, as any conclusions drawn would necessarily be speculative. For this reason, discussion of the oxidative mechanisms of hypohalites is deferred to a later date.

It has been assumed that in most cases of oxidation of hydroxyl compounds the primary intermediate is the corresponding hypohalite (3, 40, 41, 64, 70, 165). This implies that the oxidation mechanism is equivalent to the mechanism of the further reaction of the hypohalite. Various workers have presented evidence for an ionic oxidation mechanism (60, 64). The formation of olefins from alcohols through the intermediate species $ROHX^+$ has been postulated (8, 56).

Other investigators have shown that the mechanism of decomposition in specific cases is a free-radical one (195; *cf.* 19). It seems clear, however, that both mechanisms may operate; indeed, Schmid (165) has shown this to be the case in the oxidation of various alcohols in the presence of pyridine (*cf.* 38).

Evidence has been obtained (3, 58a) that the oxidation of alkyl hypohalites, which has been found to be base-catalyzed (3, 58a, 165), fits into a general scheme of $\rangle CHOX$ base-catalyzed oxidation, where X is Cl, Br, $HCrO_3$, OH, NO, NO_2, NR_2, $C(C_6H_5)_3$, and others (*cf.* reference 7). It has come to the attention of the authors that similar evidence has been obtained by Kornblum (108a).

IX. REACTIONS OF ORGANIC HYPOHALITES WITH INORGANIC COMPOUNDS

Most of the reported reactions of organic hypohalites with inorganic substances are of the oxidative type. The behavior of organic hypohalites as reductants has not been investigated.

The reactions of organic hypohalites with various halogen species in neutral solution have been represented as in the following equations:[4]

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[4] The above reactions have been formulated in this way by the authors of the respective papers. One of the readers of the review article correctly points out that these reactions are further complicated by the following:

$$\begin{aligned} Cl^- + ICl &\rightleftharpoons ICl_2^- \\ I^- + I_2 &\rightleftharpoons I_3^- \\ Br^- + Br_2 &\rightleftharpoons Br_3^- \\ Cl^- + BrCl &\rightleftharpoons BrCl_2^- \end{aligned}$$

$$ROCl + Cl^- \rightleftharpoons Cl_2 + RO^- \qquad (60)$$

$$ROCl + Br^- \rightarrow ClBr + RO^-;\ ClBr + Br^- \rightarrow Br_2 + Cl^- \qquad (60)$$

$$AcOCl + Br_2 \rightarrow AcOBr + BrCl \qquad (173)$$

$$\begin{aligned} ROCl + I^- \rightarrow ICl + RO^-;\ ICl + I^- &\rightarrow I_2 + Cl^- \\ ICl + RO^- &\rightarrow ROI + Cl^- \qquad (60) \end{aligned}$$

$$ROCl + HBr \rightarrow ROBr + HCl \qquad (57)$$

All of the above reactions are irreversible, with the exception of the first.

No irreversible reaction could be detected between ROCl and fluoride ion. Fluoride ion is, however, a catalyst in the formation and hydrolysis reactions of alkyl hypochlorites (3). In the reaction of free bromine with ROCl the formation of ROBr is postulated, as is that of ROI in the action of iodine monochloride on ROCl (60, 173).

The oxidative character of ethyl hypochlorite was further investigated in its reactions with sodium arsenite (83) and potassium cyanide in aqueous solution (128). Sodium thiosulfate is oxidized by hypochlorites in aqueous solution and hydrogen peroxide yields oxygen quantitatively (2). No oxidative reaction of hypochlorites has been detected with carbon, sulfur, or carbon monoxide (162), but a vigorous reaction occurs with sulfur dioxide, the major product being the alkyl sulfonyl chloride (3, 163).

The decomposition of alkyl hypohalites is initiated by finely divided metals such as copper (162), cobalt, and zinc (3), and a reaction has been detected between *tert*-butyl hypochlorite and mercury (3). It has been claimed (44) that dry hydrogen chloride is the major catalyst in the decomposition of alkyl hypochlorites.

Many of the ideas expressed in this review evolved from discussions with Dr. Israel Dostrovsky. The authors also gratefully acknowledge Dr. Dostrovsky's criticism of the manuscript.

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