Halogen exchange Between Methylene Halides and Ionic Halides in Water–Methylene Halide Two-phase Systems

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Phase transfer catalysts have been used to perform a variety of exchange reactions between ionic species in the aqueous phase and covalently bonded groups in the organic phase. Methylene halide halogens have been exchanged in this way with aqueous inorganic halides. In the latter case the phase transfer catalyst can be dispensed with if higher temperatures are used.

HALOGEN exchange reactions between inorganic halides and alkyl halides have usually been carried out in polar organic solvents under anhydrous conditions.[1-3] The development of the phase transfer catalysis technique[4] has made it possible to perform such exchanges under two-phase conditions, with the inorganic halide in aqueous solution. Landini and Rolla[5] have applied this technique to the preparation of di-iodo- and chloroiodo-methane from methylene chloride and aqueous sodium iodide. A 20 h contact at 100 °C gave a product containing 67% di-iodo- and 13.6% chloroiodomethane.

We report here halogen exchanges between methylene halides and aqueous ionic halides performed under two-phase conditions at elevated temperatures in the absence of phase transfer catalysts.

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[1] J. B. Conant and W. R. Kirner, *J. Amer. Chem. Soc.*, 1924, **46**, 232.

[2] L. C. Swallen and C. E. Boord, *J. Amer. Chem. Soc.*, 1930, **52**, 651.

[3] N. Altabev, R. D. Smith, and N. S. I. Suratwala, *Chem. and Ind.*, 1973, 331.

[4] C. M. Starks, *J. Amer. Chem. Soc.*, 1971, **93**, 195.

[5] D. Landini and F. Rolla, *Chem. and Ind.*, 1974, 533.

EXPERIMENTAL

All reactions were run at 150 °C in a Carius tube reactor.[6] At this temperature all salts were in solution and two liquid phases existed. At 100 °C reaction was very slow; at 200 °C marked decomposition occurred.

The organic phase was analysed by g.l.c. on a 4 m × 0.125 in column packed with Chromosorb G AW DMCS (80—100 mesh) coated with 3% of its weight of silicone oil OV 101, programmed from 40 to 100 °C at 16° min^{-1}.

The extent of hydrolysis of the methylene halides[7] [reaction (1)] was determined by titrating the free acid in the aqueous phase.

$$CH_2X_2 + H_2O \longrightarrow CH_2O + 2HX \qquad (1)$$

The mixing speed did not appear to have a marked effect on the reaction rate as long as the suspension was kept well dispersed.

TABLE 1

The $CH_2Cl_2 \rightleftharpoons CH_2ClI \rightleftharpoons CH_2I_2$ system

	Conditions [a]			Results						
	Initial aqueous phase [halide] (mequiv. g^{-1}) [b]			Organic phase composition (mole %)				% of CH_2X_2 halogens [c] exchanged		
Expt. no.	NaI	KCl	Period (h)	CH_2Cl_2	CH_2ClI	CH_2I_2	$\frac{[CH_2ClI]^2}{[CH_2Cl_2][CH_2I_2]}$	Cl	I	% of CH_2X_2 hydrolysed
1	3.8		0	100						
			4	15	32	53	1.3	69		3
2		5.4	0			100				
			2	13	22	65	0.6		24	
			4	13	37	54	1.6		30	3

[a] At 150 °C. [b] Molar ratio NaI : CH_2Cl_2 = KCl : CH_2Br_2 = 2.4 : 1. [c] Calculated from organic phase composition.

TABLE 2

The $CH_2Br_2 \rightleftharpoons CH_2BrI \rightleftharpoons CH_2I_2$ system

	Conditions [a]			Results						
	Initial aqueous phase [halide] (mequiv. g^{-1}) [b]			Organic phase composition (mole %)				% of CH_2X_2 halogens [c] exchanged		
Expt. no.	NaI	KBr	Period (h)	CH_2Br_2	CH_2BrI	CH_2I_2	$\frac{[CH_2BrI]^2}{[CH_2Br_2][CH_2I_2]}$	Br	I	% of CH_2X_2 hydrolysed
3	3.8		0	100						
			1	3	26	71	3.2	84		
			4	3	30	67	4.5	82		1
4		4.3	0			100				
			1	7	9	84	0.1		12	
			2	3	29	68	4.1		18	

[a] At 150 °C. [b] Molar ratio NaI : CH_2Br_2 = KBr : CH_2I_2 = 2.3 : 1. [c] Calculated from organic phase composition.

Concentrations of the acid solutions are given in the usual form (mol l^{-1}). However, since in some cases the amount of salt taken produced homogeneous solutions only above ambient temperature, it was more convenient to express salt concentrations on a weight basis (mequiv. g^{-1}). On a volume basis their concentrations were similar to those of the equivalent acid solutions.

RESULTS AND DISCUSSION

Three systems [(2)—(4)] were examined, the first two only cursorily (Tables 1 and 2). Both methylene chloride and methylene bromide were readily and fairly rapidly iodinated by sodium iodide at 150 °C. With a 20% excess of sodium iodide, 60% halogen exchange was achieved with methylene chloride and 82% with methylene bromide. The extent of hydrolysis was very small. Since the reverse reactions gave the same

$$CH_2Cl_2 \underset{Cl^-}{\overset{I^-}{\rightleftharpoons}} CH_2ClI \underset{Cl^-}{\overset{I^-}{\rightleftharpoons}} CH_2I_2 \qquad (2)$$

$$CH_2Br_2 \underset{Br^-}{\overset{I^-}{\rightleftharpoons}} CH_2BrI \underset{Br^-}{\overset{I^-}{\rightleftharpoons}} CH_2I_2 \qquad (3)$$

$$CH_2Cl_2 \underset{Cl^-}{\overset{Br^-}{\rightleftharpoons}} CH_2ClBr \underset{Cl^-}{\overset{Br^-}{\rightleftharpoons}} CH_2Br_2 \qquad (4)$$

product distribution, these appear to be equilibrium systems. As depicted by equations (2)—(4), these systems involve consecutive reactions between ionic and non-ionic species. However, redistribution of the halogens amongst the three methylene halides also appears to take place, probably according to equation (5), where X′ and X″ represent different halogens.

$$CH_2X'_2 + CH_2X''_2 \rightleftharpoons 2CH_2X'X'' \qquad (5)$$

If methylene halide disproportionations are equilibrium systems as shown in equation (5), the equilibrium constant K will be $[CH_2X'X'']^2/[CH_2X'_2][CH_2X''_2]$. Most of the values for this reaction in Tables 3 and 4 fall in the region 2.5—3.5. This includes not only reactions with methylene chloride but also those where methylene bromide and chlorobromide served as starting materials. The values for the equilibrium constants of

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[6] L. M. Shorr, M. Rogozinski, and U. Hashman, *Chem. and Ind.*, 1964, 52.

[7] ‘Encyclopedia of Chemical Technology,’ ed. K. Othmer, Interscience, New York, 2nd edn., 1964, vol. 5, p. 112.

TABLE 3

The $CH_2Cl_2 \rightleftharpoons CH_2ClBr \rightleftharpoons CH_2Br_2$ system

Cations Na^+, K^+

	Conditions [a]					Results						
	Initial aqueous phase [halide] (mequiv. g^{-1})			X^- : CH_2X_2 ratio (equiv. mol^{-1})	Period (h)	Organic phase composition (mole %)			$\frac{[CH_2ClBr]^2}{[CH_2Cl_2][CH_2Br_2]}$	% CH_2X_2 halogens exchanged [b]		% CH_2X_2 hydrolysed
Expt. no.	NaBr	KBr	KCl			CH_2Cl_2	CH_2ClBr	CH_2Br_2		Cl	Br	
5	4.7			2.4	0	100						
					1	73	26	1	9.3	14		
					2	62	35	3	6.6	21		
					4	63	33	4	4.3	21		6
6		4.3		2.3	0	100						
					1	62	35	2	10.5	20		
					2	52	38	6	4.3	25		
					4	54	38	8	3.3	27		7
7		4.3		4.6	0	100						
					2	49	40	11	3.0	31		
					4	37	46	17	3.4	40		24
8		2.9		2.3	0	100						
					1	55	39	6	4.6	26		
					2	64	31	5	3.0	21		
					4	71	26	3	3.2	16		35
9		4.3		1.15	0		100					
					1	15	74	11	33	5	7	
					2	22	63	15	12	7	11	5
10		4.3		2.3	0		100					
					1	17	67	16	16	8	8	
					2	27	50	23	4.0	11	13	
					3	30	46	24	2.9	12	15	11
11			5.3	2.3	0		100					
					1	77	21	2	2.9	1	38	
					2	82	17	1	3.5	0.5	40	
12			5.4	2.4	0			100				
					1	70	19	11	0.5		80	
					2	69	25	6	1.5		82	
					4	68	28	4	2.9		82	13

[a] At 150 °C. [b] Calculated from organic phase composition.

TABLE 4

The $CH_2Cl_2 \rightleftharpoons CH_2ClBr \rightleftharpoons CH_2Br_2$ system

Cation Mg^{2+}

	Conditions [a]				Results						
	Initial aqueous phase [halide] (mequiv. g^{-1})		X^- : CH_2X_2 ratio (equiv. mol^{-1})	Period (h)	Organic phase composition (mole %)			$\frac{[CH_2ClBr]^2}{[CH_2Cl_2][CH_2Br_2]}$	% CH_2X_2 halogens exchanged [b]		% CH_2X_2 hydrolysed
Expt. no.	$MgBr_2$	$MgCl_2$			CH_2Cl_2	CH_2ClBr	CH_2Br_2		Cl	Br	
13	4.8		2.3	0	100						
				1	61	35	4	5.0	22		
				2	56	37	7	3.5	26		
				4	51	38	11	2.6	30		4
14	4.8		4.6	0	100						
				1	44	45	11	4.2	34		
				2	42	40	18	2.1	38		
				4	36	43	21	2.4	43		9
15	3.0		2.3	0	100						
				1	70	28	2	5.6	16		
				2	65	30	5	2.8	20		
				4	65	29	6	2.2	21		18
16		6.0	2.3	0			100				
				1	39	22	39	0.3		50	
				2	41	29	30	0.7		56	
				4	54	32	14	1.4		70	4

[a] At 150 °C. [b] Calculated from organic phase composition.

reactions with hydrogen bromide (Table 5) are also in this range where methylene bromide was the starting material. With methylene chlorobromide as starting material the values are higher, and with methylene bromide, lower. The reactions listed in Table 5 were run for shorter periods, which appear to have been insufficient to reach equilibrium.

TABLE 5

The $CH_2Cl_2 \rightleftharpoons CH_2ClBr \rightleftharpoons CH_2Br$ system

Cation H+

	Conditions [a]				Results						
	Initial aqueous phase [halide] (mol l⁻¹)		$X^- : CH_2X_2$ ratio (equiv. mol⁻¹)	Period (h)	Organic phase composition (mole %)			$\frac{[CH_2ClBr]^2}{[CH_2Cl_2][CH_2Br_2]}$	% CH_2X_2 halogens exchanged [b]		% CH_2X_2 hydrolysed
Expt. no.	HBr	HCl			CH_2Cl_2	CH_2ClBr	CH_2Br_2		Cl	Br	
17	6.3		2.3	0	100						
				1	65	31	4	3.7	20		
				1.5	59	33	8	2.3	25		
				2	54	38	8	3.3	27		2
18	6.3		4.6	0	100						
				1	30	47	23	3.2	47		
				1.5	38	40	22	1.9	42		11
19	3.15		2.3	0	100						
				1	61	33	6	3.0	23		
				1.5	65	28	7	1.7	21		
				2	63	30	7	2.0	22		13
20	5.9		1.15	0		100					
				0.7	8	84	8	110	4	4	
				1.5	15	72	13	26	7	8	
21	5.9		2.3	0		100					
				0.7	8	79	13	60	7	4	
				1.5	20	57	23	7	12	10	
22		6.5	2.3	0			100				
				1	40	27	33	0.6		54	
23			0 [c]	0		100					
				1	12	85	3	200			11
				2	24	69	7	28			18
				4	43	46	11	4.5			30
24			0 [c]	0	50	0	50				
				2	49	12	39	0.08			
				4	47	26	27	0.5			16
25			0 [d]	0		100					
				1	3	96	1				
				2	5	94	1				

[a] At 150 °C. [b] Calculated from organic phase composition. [c] Reactions run without halide salts, the initial aqueous phase being distilled water. [d] Reaction run without aqueous phase, *i.e.* methylene chlorobromide heated without additives.

TABLE 6

Summary of methylene chloride–bromide ion reactions for various cations [a]

	Cation [b]								
	H+	Na+	K+	Mg^{2+}	$Br^- : CH_2Cl_2$ ratio (equiv. mol⁻¹)	Period (h)	$\frac{[CH_2ClBr]^2}{[CH_2Cl_2][CH_2Br_2]}$	% CH_2Cl_2 chlorine exchanged	% CH_2Cl_2 hydrolysed
Expt. no.	(mol l⁻¹)	(mequiv. g⁻¹)							
17	6.3				2.3	2	3.3	27	2
5		4.7			2.4	4	4.3	21	6
6			4.3		2.3	4	3.3	27	7
13				4.8	2.3	4	2.6	30	4
18	6.3				4.6	1.5	1.9	42	11
7			4.3		4.6	4	3.4	40	24
14				4.8	4.6	4	2.4	43	9
19	3.15				2.3	2	2.0	22	13
8			2.9		2.3	4	3.2	16	35
15				3.0	2.3	4	2.2	21	18

[a] At 150 °C. [b] Anion Br⁻.

The Tables also indicate that, in all cases where halide ions were present, equilibrium was reached much more rapidly than when added ions were not present initially, such as reactions **23** and **24** in Table 5. Heating the methylene chlorobromide to 150 °C alone, that is in the absence of both water and salts, resulted in only a very slow disproportionation (experiment **25**, Table 5). In contact with water (reactions **23** and **24**) reaction is faster probably because hydrolysis supplies ions. Their concentration however would be lower than in the exchange reactions with ionic halides, which would explain the lower rate in the absence of added salts. This suggests that the ions in the aqueous phase mediate the halogen redistribution among the three methylene halides (reaction 5), and that this is slower than halogen exchange between ionic halogen and the methylene halides (reaction 4). Differences in *K* values for the various cations under the same reaction conditions, *e.g.* 4.3 for Na^+ (experiment 5 in Table 3) and 2.6 for Mg^{2+} (experiment 13 in Table 4) probably reflect differences in reaction rates, the former being further from equilibrium than the latter.

The reactions between methylene chloride and bromide ions listed in Tables 3—5 for the various cations are summarized in Table 6. For stoicheiometric amounts of bromide ions (plus 20% excess), 20—30% of the chloride in methylene chloride is exchanged for bromide, the rates being similar for H^+, K^+, and Mg^{2+}, but somewhat less for Na^+. Doubling the bromide ion to methylene chloride ratio approximately doubles the proportion of chloride exchanged. Halving the bromide ion concentration in the aqueous phase appears to have only a minor effect on the conversion. Both halving the bromide ion aqueous phase concentration and doubling the ionic bromide to methylene chloride ratio increases the extent of hydrolysis. This can be explained if it is assumed that the hydrolysis takes place in the aqueous phase, as in both cases the relative amount of the aqueous phase is increased and therefore also the absolute amount of methylene halide in solution in the aqueous phase. Differences in halide salt concentration in the aqueous phase can be expected to affect the solubility of the methylene halide in this phase, and this would also affect the extent of hydrolysis. The various cations differ in their effects on the hydrolysis, highest rates being exhibited by K^+ and lowest by H^+. The sensitivities of the various methylene halides to hydrolysis by water (no added salts) at 150 °C are given in Table 7.

TABLE 7

Rates of hydrolysis of methylene halides at 150 °C

Expt. no.	Halide	Period (h)	Hydrolysis %
24	CH_2Cl_2	1	2
		2	5
		4	8
27	CH_2ClBr	1	12
		2	19
		4	31
28	CH_2Br_2	1	5
		2	9
		4	15
29	CH_2I_2	1	3
		2	3
		4	5

These reactions were run at phase volume ratios similar to those used in the exchange reactions. Both methylene chloride and bromide have some solubility in water (2 and 1.2%, respectively, at 20 °C [8]), which can be expected to increase with temperature.

It seems probable that these reactions occur in the aqueous phase between halide ions and the dissolved methylene halide.

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[8] 'Handbook of Chemistry,' ed. N. A. Lange, McGraw-Hill, London, 10th edn., 1967.