Relative Selectivities in Bromination Reactions—A Note of Warning

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Summary Hydrogen bromide is shown to have a pronounced effect on atomic brominations in the gas phase; this is due to two effects, (i) a possible reversible reaction of alkyl radicals with hydrogen bromide, and (ii) the direct reaction between hydrogen bromide and alkyl bromides leading to olefins.

WHILE reinvestigating the gas phase bromination of 1-bromobutane we have found that 1-bromobutane reacts with HBr in the gas phase to produce but-1-ene (Table 1). The distribution of isomeric dibromobutanes in photobromination is therefore affected by the HBr produced in the hydrogen abstraction step, reaction (2), since but-1-ene may add bromine to produce 1,2-dibromobutane. We have extended these studies to bromocyclohexane (Table 2) which behaves similarly; cyclohexene is formed and adds bromine to give *trans*-1,2-dibromocyclohexane. Allylic attack on cyclohexene produces 3-bromocyclohexene.

In all experiments the products of reaction were distilled from the reaction vessel through "Carbosorb" to remove unchanged bromine and HBr, thus preventing a solution phase reaction between products and allowing the detection of olefinic products, which otherwise re-add HBr to give 2-bromobutane and bromocyclohexane, respectively. The suggested mechanism is given by reactions (1)—(5).

$$\operatorname{Br}_{2} \xrightarrow{h_{\mathcal{V}}} \operatorname{Br}^{\bullet} + \operatorname{Br}^{\bullet}$$
 (1)

 $Br + RCH_2CH_2Br \longrightarrow \dot{RCHCH_2Br} + HBr$ (2)

$$Br_2 + RCHCH_2Br \longrightarrow RCHBrCH_2Br + Br$$
 (3)

$$HBr + RCH_2CH_2Br \longrightarrow RCH = CH_2 + 2HBr$$
(4)

The formation of the 1,2-isomer was enhanced by the addition of HBr to the 1-bromobutane-bromine mixture at the start of the reaction. The two shorter timed photolyses shown in Table 1 illustrate this clearly. In the original bromination of 1-bromobutane¹ using a flow reactor, 1,3-dibromobutane was the major product. Presumably this was due to the short contact time (*ca.* 45 s) which

		1,4-Dibromo	ļ	I	I		traces	
TABLE 1	The bromination of 1-bromobutane with and without added HBr, at 100°	BuBr) 1,3-Dibromo	1	$1.64 imes 10^{-2}$	$8.03 imes10^{-2}$	1.94×10^{-2}	$3.00 imes10^{-2}$	
		Products (expressed as moles; relative to moles of BuBr) 2-Bromobutane 1,1-Dibromo 1,2-Dibromo 1,3-I		$11 \cdot 1 \times 10^{-2}$	$2\cdot 27 imes 10^{-2}$	$14.9 imes 10^{-2}$	$6.60 imes10^{-2}$	
		ssed as moles; rel 1,1-Dibromo	!	traces	1.71×10^{-3}	$5.95 imes10^{-3}$	$4\cdot 61 imes10^{-8}$	
		Products (expre 2-Bromobutane	Products (expressed as moles; r But-1-ene 2-Bromobutane 1,1-Dibromo 6.01×10^{-2} 7.01×10^{-3} $$ 6.01×10^{-2} 7.01×10^{-3} $$ 6.01×10^{-2} 5.85×10^{-3} $$ 1.71×10^{-3} 1.71×10^{-3} traces 1.60×10^{-2} 5.95×10^{-3} traces 2.61×10^{-2} 4.61×10^{-3}					
		But-1-ene						
		HBr (mol 1-1)	$7 \cdot 12 imes 10^{-4}$	$7.12 imes 10^{-4}$		$7.12 imes10^{-4}$	1	
	L	tants Br ₂ (mol 1-1)		$6.96 imes10^{-5}$	$6.96 imes 10^{-5}$	6.96×10^{-5}	6.96×10^{-5}	
		Reactants BuBr (mol 1-1) Br ₂ (mol 1-1)	3.33×10^{-4}	$3.33 imes 10^{-4}$	$3.33 imes 10^{-4}$	3.33×10^{-4}	$3.33 imes10^{-4}$	
		Time (min)	120	10	10	120	120	

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	cis-1.4-	Dibromo	$5.5 imes10^{-4}$	traces	
) trans-1.4-	Dibromo	$6.0 imes 10^{-4}$	traces	ļ
	es of C ₆ H ₁₁ Br cis-1.3-	Dibromo	$6.7 imes 10^{-4}$	traces	
。(ative to mole <i>trans</i> -1.3-	Dibromo	$9.9 imes 10^{-4}$	traces	I
HBr, at 10(s moles; rel <i>cis</i> -1.2-	Dibromo	1		I
without added	Products (expressed as moles; relative to moles of $C_6H_{11}Br$) 1.1-Di- trans-1.2- cis-1.2- trans-1.3- cis-1.3-	Dibromo	$2{\cdot}72 imes10^{-3}$	$11.2 imes 10^{-3}$	I
me with and r	Products	bromo	$4{\cdot}1 imes10^{-4}$	$2{\cdot}2 imes 10^{-4}$	•
romocyclohexa		C,HBr	$1{\cdot}08 imes 10^{-3}$	9.11×10^{-4}	ł
The bromination of bromocyclohexane with and without added HBr, at 100°		hexene		$4 \cdot 11 \times 10^{-3}$	•
The bi	HBr	$(mol \ 1^{-1})$	ļ	7.12×10^{-4}	1.78×10^{-4}
		$(mol \ l^{-1})$			
	C.H.R.	$(mol l^{-1})$	$3.02 imes 10^{-4}$	$3\cdot02 imes10^{-4}$	$1{\cdot}67 imes10^{-4}$
		Time (min)	60	60	600

allowed virtually no opportunity for reaction between the 1-bromobutane and HBr.

Olefin can thus be formed by direct interaction of HBr with the bromoalkane which may occur by a surface reaction or by autocatalytic decomposition of the bromoalkane. Alternatively the reverse of step (2) could give a thermally excited bromobutane molecule which eliminates HBr to produce but-1-ene, reaction (5). However, this seems unlikely since [RCH₂CH₂Br]* would not be very excited as the HBr bond has to be broken.

This formation of the 1,2-dibromo-products via the olefin in the gas phase means that arguments about directive effects or about anchimeric assistance by the bromine substituent as suggested by Skell² and Thaler,³ to explain the

³ W. Thaler, J. Amer. Chem. Soc., 1963, 85, 2607.

⁴ D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, J. Amer. Chem. Soc., 1969, 91, 7398.

high yields of 1,2-dibrominated products obtained in their solution phase reactions must be treated with some reservation.

A mechanism which involves the β -(1-bromobutyl) radical (formed initially by hydrogen abstraction) eliminating a bromine atom to give the corresponding olefin, has been suggested by Tedder¹ and by Tanner⁴ for their respective chlorinations and brominations of 1-bromobutane. A direct interaction between HBr and a bromocycloalkane would not be noticed when studied in the solvent phase, since such a reaction would be reversible.

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¹ P. S. Fredericks and J. M. Tedder, J. Chem. Soc., 1960, 144. ² P. S. Skell and P. D. Readio, J. Amer. Chem. Soc., 1964, 86, 3334.