

Relative Selectivities in Bromination Reactions—A Note of Warning

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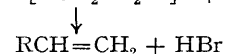
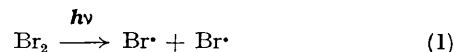
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Summary Hydrogen bromide is shown to have a pronounced effect on atomic brominations in the gas phase; this is due to two effects, (i) a possible reversible reaction of alkyl radicals with hydrogen bromide, and (ii) the direct reaction between hydrogen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



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

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 $[RCH_2CH_2Br]^*$ 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

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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² P. S. Skell and P. D. Readio, *J. Amer. Chem. Soc.*, 1964, **86**, 3334.

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.