

THE GAS-PHASE REACTION OF HYDROGEN BROMIDE WITH VINYL CHLORIDE

By K. D. KING*† and E. S. SWINBOURNE*‡

[Manuscript received May 25, 1970]

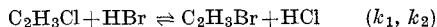
A recent investigation¹ has shown that the pyrolysis of 1-bromo-2-chloroethane yields essentially vinyl chloride and HBr. Minor products are vinyl bromide and HCl which arise mainly from a secondary reaction between vinyl chloride and HBr. This was supported by evidence for the formation of vinyl bromide in the HBr-catalysed decomposition of 1,2-dichloroethane.² We now wish to report some quantitative kinetic information on the gas-phase reaction of HBr with vinyl chloride.

Experimental

Anhydrous HBr (Matheson) was used. Vinyl chloride (Imperial Chemical Industries) and vinyl bromide (Aldrich) were fractionated under vacuum until gas-chromatographically pure.

The apparatus, which was a conventional static system, has been described previously.² Known pressures of HBr and vinyl chloride were mixed in an unpacked reactor (c. 400 ml) coated with the pyrolysis products of allyl bromide³ and after suitable reaction times, the mixtures were analysed for vinyl halides by gas chromatography.

Attempts to measure the equilibrium



by leaving mixtures in the reaction vessel for prolonged periods before analysis were thwarted by discrepancies in the vinyl chloride mass balance which may have been due to polymerization.⁴

Results and Discussion

Rate measurements were made at points far removed from equilibrium. An independent check on reaction (2) showed it to be extremely slow and no rate data were obtained from this direction.

Table 1 contains values for the second-order rate constant k_1 , calculated by standard methods⁵ at temperatures around 305 and 348°C. The values are constant

* School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033.

† Present address: Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, Cal. 94025, U.S.A.

‡ Present address: New South Wales Institute of Technology, Broadway, N.S.W. 2007.

¹ King, K. D., and Swinbourne, E. S., *J. chem. Soc.*, 1970, 687.

² King, K. D., and Swinbourne, E. S., *Trans. Faraday Soc.*, 1970, **66**, 1145.

³ Maccoll, A., *J. chem. Soc.*, 1955, 965.

⁴ Jones, T. T., and Melville, H. W., *Proc. R. Soc. (A)*, 1946, **187**, 39; Hogg, A. M., and Kebarle, P., *J. Am. chem. Soc.*, 1964, **86**, 4558.

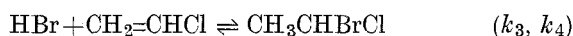
⁵ Frost, A. A., and Pearson, R. G., "Kinetics and Mechanism." (John Wiley: New York 1953.)

at each temperature. There are insufficient data to warrant an Arrhenius plot but we estimate that $\log(k_1/\text{l. mol}^{-1} \text{ s}^{-1}) \simeq 9.34/\theta$, where $\theta = 2.303RT$ in kcal mol⁻¹.

TABLE 1
KINETIC DATA FOR THE GAS-PHASE REACTION OF HBr WITH VINYL CHLORIDE
(All concentrations in mol l.⁻¹)

Temp. (°C)	Reaction Time (min)	10 ⁴ [C ₂ H ₃ Cl] (initial)	10 ⁴ [HBr] (initial)	10 ⁴ [C ₂ H ₃ Br]	10 ⁴ k ₁ (l. mol ⁻¹ s ⁻¹)
305.0	20	7.20	29.9	0.040	1.75
305.0	30	7.75	29.7	0.058	1.47
304.9	45	6.56	30.1	0.073	1.20
305.1	90	8.88	31.5	0.283	1.99
348.5	30	14.3	26.6	0.082	12.4
348.4	45	14.0	13.9	0.063	12.0
348.5	60	14.4	13.4	0.088	11.0
348.5	90	14.2	13.6	0.114	11.0

For reaction (1), a multi-step molecular mechanism seems appropriate. The formation of vinyl bromide could occur by the addition of HBr to vinyl chloride followed by subsequent decomposition of the bromochloroethane:



Product analyses failed to reveal the presence of any bromochloroethane but the steady-state concentration is likely to be quite small. Under conditions far removed from equilibrium, the rate of reaction (6) will be negligible in comparison with the other reactions and, assuming that the intermediate bromochloroethane is present in steady-state concentration, the rate of formation of vinyl bromide is given by

$$\begin{aligned} d[\text{C}_2\text{H}_3\text{Br}]/dt &= k_5[\text{CH}_3\text{CHBrCl}] \\ &= \{k_3k_5/(k_4+k_5)\}[\text{C}_2\text{H}_3\text{Cl}][\text{HBr}] \end{aligned}$$

Comparison of this expression with the rate law for reaction (1) gives

$$k_1 = k_3k_5/(k_4+k_5)$$

It is possible to calculate k_1 from the above equation by estimating k_3 , k_4 , and k_5 from the rate of addition of HBr to ethylene⁶ and the rates of decomposition of ethyl bromide⁷ and ethyl chloride⁷ respectively. Thus $k_1 = 10^{8.3-36.6/\theta} = 3 \times 10^{-6} \text{ l. mol}^{-1} \text{ s}^{-1}$ at 305°C compared to the experimental value (Table 1) of $1.6 \times 10^{-4} \text{ l. mol}^{-1} \text{ s}^{-1}$. The actual rate is therefore considerably faster than is predicted by the above scheme but the decomposition of 1,1-bromochloroethane⁸ has been shown

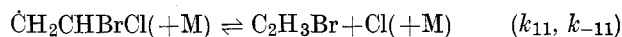
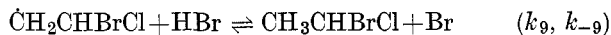
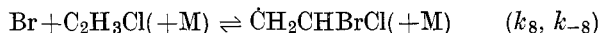
⁶ Benson, S. W., and Bose, A. N., *J. chem. Phys.*, 1963, **39**, 3463.

⁷ Maccoll, A., *Chem. Rev.*, 1969, **69**, 33.

⁸ Wellington, C. A., Symp. on Gas Kinetics, University College of Swansea, July, 1967.

to have a large heterogeneous component and this could account for the above discrepancy. The effect of changes in surface area was not investigated in this study.

A radical-chain scheme may also be considered and feasible reaction steps are listed below:



plus various chain termination steps. However, a kinetic analysis by the usual methods⁹ leads to the conclusion that this type of mechanism is unsatisfactory.

The kinetics of formation of vinyl bromide from HBr and vinyl chloride are difficult to explain on the basis of the proposed molecular and radical mechanisms. However, there are insufficient data to resolve the question of surface participation or the possibility of reaction (1) being a direct molecular process.

⁹ Benson, S. W., "Thermochemical Kinetics." (John Wiley: New York 1968.)

