Mechanism of the Photo-initiated Addition of HBr to C_2H_4

By K. T. WONG and D. A. ARMSTRONG

(*Department of Chemistry, University of Alberta, Calgary, Alberta, Canada*)

THE photo-sensitised addition of HBr to ethylene has been studied by using an optical system of conventional design and a mercury-free vacuum line. A small carefully measured quantity (~0·1 torr.) of acetone vapour was incorporated in the reaction mixture to serve as a photosensitiser. Methyl and acetyl radicals formed by the 3000 to 3250 Å photolysis of this compound subsequently produced bromine atoms by hydrogen atom abstraction from HBr. In the presence of 300 torr. of added propane and with $[HBr] > [C_2H_4] \sim 60$ torr. the ethylene exponent was unity and the intensity exponent 0·5, indicating mutual termination by bromine atom conbination, *viz.*:

$$Br + Br + M \xrightarrow{k_M} Br_2 + M \qquad (20)$$

There was no evidence of radical attack on propane.

The simple mechanism originally postulated[1] for hydrogen halide additions:

$$Br + C_2H_4 \rightarrow BrC_2H_4 \qquad (2)$$

$$BrC_2H_4 \rightarrow Br + C_2H_4 \qquad (-2)$$

$$BrC_2H_4 + HBr \rightarrow C_2H_5Br + Br \qquad (3)$$

assumes that all radicals are in thermal equilibrium with the surrounding gas molecules. It leads to a rate expression which may be written in the form:

$$\frac{[C_2H_4][HBr]}{\left(\frac{d[C_2H_5Br]}{dt}\right)} = \frac{1}{k_2[Br]}\left\{[HBr] + \frac{k_{-2}}{k_3}\right\} \qquad (i)$$

In this expression [Br] represents the stationary concentration of halogen atoms and is determined by the rates of the initiation and termination reactions. In the present system it can be shown that $k_{M=HBr} \leqslant k_{M=C_3H_8}$, and thus the rate of termination is independent of HBr concentration, as is the rate of initiation. Under these conditions plots of the left hand side of expression (i) against HBr concentration are straight lines (see Figure). The values of k_{-2}/k_3 found from the ratios of the intercepts to the slopes of these plots at four different temperatures are given in the Table. They require a value of 4·5 ± 0·5 kcal. for $E_{-2} - E_3$, which is to be compared with a value of 6·1 kcal. obtained by Schmitz, Schumacher, and Jäger[2] for $E_{-2} - E_{3'}$ in the chain addition of bromine to ethylene in the presence of a large excess of CF_2Cl_2. In this system reaction (3) is replaced by the analogous reaction

$$BrC_2H_4 + Br_2 \rightarrow C_2H_4Br_2 + Br \qquad (3')$$

Vibrational relaxation studies[3] have demonstrated that propane is a comparatively good agent for the transfer of vibrational quanta (in fact several orders of magnitude better than either ethylene or HBr). It is therefore reasonable to expect that the bromoethyl radicals involved under our conditions are close to thermal equilibrium with the surrounding gas molecules as is required by the simple mechanism. The observation of a positive temperature dependence of k_{-2}/k_3 bears this out.

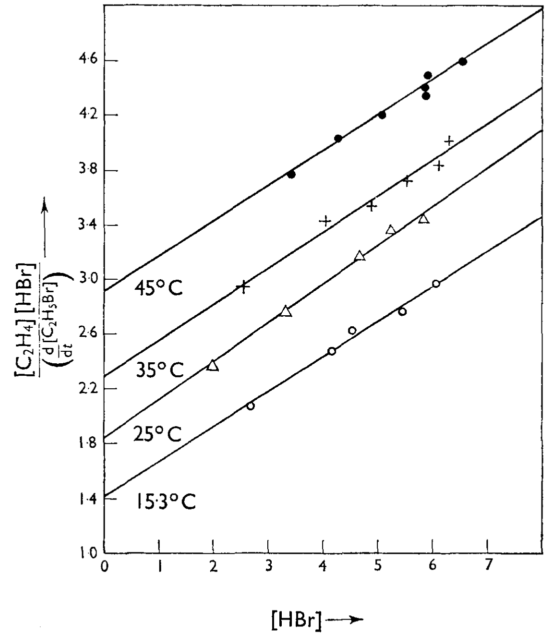

FIGURE I. $\frac{I^{0\cdot5}_{abs.}[C_2H_4][HBr]}{d[C_2H_5Br]/dt}$ *versus* HBr concentration

Ordinate: $\frac{I^{0\cdot5}_{abs.}[C_2H_4][HBr]}{d[C_2H_5Br]/dt} \times 10^{-26}\left(\frac{\text{molecules}}{\text{ml.}}\right)^{3/2}(\text{sec.})^{1/2}$

Abscissa: $[HBr] \times 10^{-18}\left(\frac{\text{molecules}}{\text{ml.}}\right)$

TABLE

Dependence of rate-constant ratios on temperature

Temp. (°c)	(a) $\frac{k_{-2}^*}{k_4 + k_5} \times 10^{-18}$ (molecules/ml.)	(b) $\frac{k_{-2}}{k_3} \times 10^{-18}$
15·3	5·5	5·6
25·0	5·7	6·5
35·0	5·6	8·7
45·0	5·5	11·4

(*a*) propane absent
(*b*) propane present

In the absence of propane the apparent values of k_{-2}/k_3 obtained from an analogous treatment are within experimental error independent of temperature over the range 15—45°c (See Table).

This observation implies that a different mechanism is operative in the absence of propane.

It should be realized that the initial product of reaction (2) is a vibrationally excited radical[4]. Oldershaw and Cvetanovic[5] have presented evidence that the following reactions may occur if this excited radical is not deenergised to thermal energies by collisional energy transfer to non-reactive molecules.

$$BrC_2H_4^* \xrightarrow{k^*_{-2}} Br + C_2H_4 \quad (-2^*)$$

$$BrC_2H_4^* + HBr \xrightarrow{k_4} Br + C_2H_4 + HBr \quad (4)$$

$$BrC_2H_4^* + HBr \xrightarrow{k_5} BrC_2H_4 + HBr^* \quad (5)$$

If reaction (−2) is unimportant in the absence of propane then it can be shown[5] that the apparent values of k_{-2}/k_3 in fact are to be associated with the ratio $k_{-2}^*/(k_4 + k_5)$, for which a temperature-independence would have been expected. The present results in the absence of propane are in accord with this interpretation. They do not agree with the results of the earlier study of the radiation-induced addition,[6] and it appears that the latter addition must involve ion–molecule reactions or other processes which influence its temperature and HBr dependence in a more complex manner.

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[1] W. E. Vaughan, F. F. Rust, and T. W. Evans, *J. Org. Chem.*, 1942, **7**, 477; and F. R. Mayo and C. Walling, *Chem. Rev.*, 1940, **7**, 351.

[2] H. Schmitz, H. J. Schumacher, and A. Jäger, *Z. phys. Chem.*, 1942, *B*, **51**, 281.

[3] T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworths, London, 1961.

[4] P. B. Ayscough, A. J. Cocker, F. S. Dainton, and S. Hirst, *Trans. Faraday Soc.*, 1962, **58**, 318 and preceeding papers.

[5] G. A. Oldershaw and R. J. Cvetanovic, *J. Chem. Phys.*, 1964, **41**, 3639.

[6] D. A. Armstrong and J. W. T. Spinks, *Canad. J. Chem.*, 1959, **37**, 1210.