

The Pyrolysis of nPropyl Bromide

P. Agius and Allan Maccoll

Citation: *The Journal of Chemical Physics* **18**, 158 (1950); doi: 10.1063/1.1747452

View online: <http://dx.doi.org/10.1063/1.1747452>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/18/1?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[The Pyrolysis of nButylBenzene and the Heat of Formation of nPropyl Radical](#)

J. Chem. Phys. **20**, 407 (1952); 10.1063/1.1700434

[The Pyrolysis of nPropylBenzene and the Heat of Formation of Ethyl Radical](#)

J. Chem. Phys. **20**, 403 (1952); 10.1063/1.1700433

[The Pyrolysis of isoPropyl Bromide](#)

J. Chem. Phys. **19**, 977 (1951); 10.1063/1.1748426

[The Kinetics of the Pyrolysis of Allyl Bromide](#)

J. Chem. Phys. **17**, 1350 (1949); 10.1063/1.1747189

[The Hot Atom Chemistry of the Propyl Bromides](#)

J. Chem. Phys. **17**, 647 (1949); 10.1063/1.1747351



also leads to isomer distributions which closely duplicate the observed distributions. For the particular choice of $a=0.975$ and $b=0.025$ the average deviation of the calculated from the observed isomer concentrations is again 0.7 percent.

The excellent agreement with experiment which is possible in both cases comes about because the same set of fundamental rules for addition of carbon atoms is used. In the absence of further information one has to consider each of the independent assumptions concerning weighting as reasonable; the almost exact comparability of results is, perhaps, encouraging in indicating the correctness of the fundamental procedure.

* Physical chemists, Bureau of Mines, Research and Development Branch, Pittsburgh, Pennsylvania.

¹ S. Weller and R. A. Friedel, *J. Chem. Phys.* **17**, 801 (1949).

² Private communication.

The Pyrolysis of *n*-Propyl Bromide

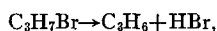
P. AGIUS AND ALLAN MACCOLL

*Sir William Ramsay and Ralph Forster Laboratories,
University College, London, England*

November 29, 1949

THE organic bromides form an interesting series of compounds because of the widely diverse kinetic behavior shown in their pyrolyses. Although all the substances so far investigated have been reported to give first-order kinetics, the evidence suggests that different mechanisms are involved. Thus the work of Daniels and his collaborators¹ on ethyl bromide has led him to postulate a free-radical non-chain mechanism for its pyrolysis. In the case of allyl bromide² a different type of free radical mechanism has been suggested. Again for *t*-butyl bromide, Kistiakowsky and Stauffer³ have been led to the view that the rate controlling step is the elimination of molecular HBr. It is the purpose of the present note to show that a fourth type of mechanism operates in the case of *n*-propyl bromide.

In his preliminary survey of the field of organic halides, Lessig⁴ calculated a number of first-order coefficients for *n*-propyl bromide and observed that they were strongly pressure dependent. He also showed that the reaction was predominantly homogeneous, could be represented by the equation,



and was appreciably catalyzed by oxygen. The present note deals with an investigation of the reaction in the temperature range 300–380°C. In confirmation of Lessig's results, the reaction has been shown to be homogeneous, to follow the same equation, and to be catalyzed by oxygen. However, it soon became apparent that the first-order rate coefficients did not tend to a limiting value as the initial pressure was increased. Further, a plot of the first-order coefficients as a function of the square root of the initial pressure led to a straight line, passing through the origin, as shown in Fig. 1. This suggested the calculation of 1.5-order coefficients, which were found to show no trend with initial pressure. So it was concluded that the reaction was of the 1.5 order. The variation of the rate constants with temperature was represented by the equation

$$k = 7.2 \times 10^{10} \exp(-33,800/RT)$$

k being expressed in $(\text{g/mole})^{-1/2}(\text{cc})^{1/2}(\text{sec})^{-1}$. The energy of activation is thus much lower than that for ethyl bromide (53.0 kcal.).

The 1.5-order constants were only calculated for the early stages of a run, as they were found to fall as the reaction proceeded. As propylene, one of the products of reaction, is a well-known

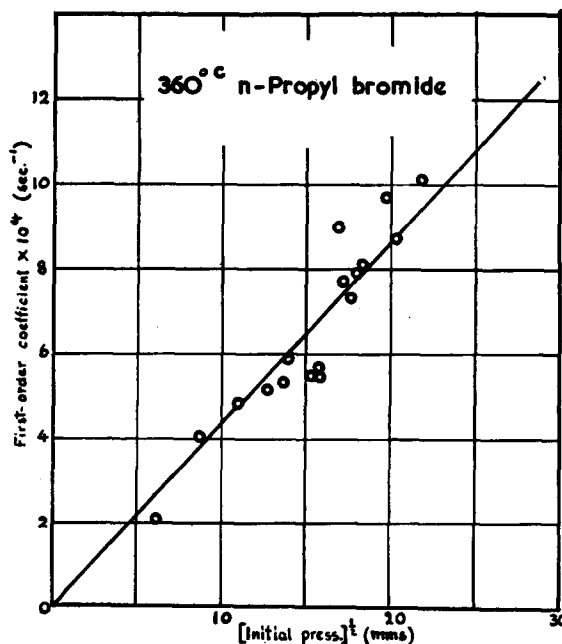
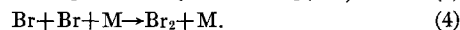
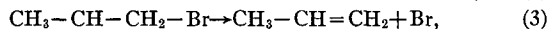
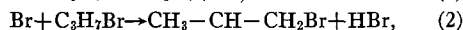
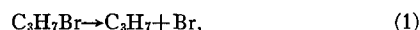


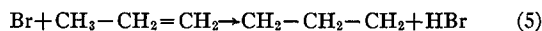
FIG. 1.

inhibitor of chain reactions, the effect of propylene on the rate was investigated. It was found strongly to inhibit the rate, but with increasing propylene pressure, the rate approached a limiting value. The limiting rate is believed to be that of a heterogeneous reaction, as it was found to be dependent on the surface-volume ratio.

The effect of oxygen and propylene, and the 1.5-order character of the reaction are all in favor of a chain mechanism. The following mechanism is put forward for the early stages of the decomposition



The 1.5-order kinetics of the reaction follows from the nature of the chain-ending step, namely the recombination of bromine atoms. Assuming reasonable values for the rates of the elementary reactions, the observed rate can be satisfactorily accounted for. Further, a mechanism for the propylene-inhibited reaction, in which (2) is in competition with



leads to general agreement with the form of the inhibition curve.

The present work raises the question as to whether any higher members of the series also show 1.5-order behavior. For preliminary measurements suggest that *i*-propyl bromide behaves in the same fashion.

A fuller account of this work will be published in due course.

¹ Lessig, *J. Phys. Chem.* **36**, 225 (1932). Vernon and Daniels, *J. Am. Chem. Soc.* **55**, 922 (1933). Fugani and Daniels, *ibid.* **60**, 721 (1938). Daniels and Veltman, *J. Chem. Phys.* **7**, 256 (1939).

² A. Maccoll, *J. Chem. Phys.* **17**, 1350 (1949).

³ Kistiakowsky and Stauffer, *J. Am. Chem. Soc.* **59**, 165 (1937).