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amount of sorption in the experiments described was not sufficient to cause marked swelling of the polystyrene. The highest benzene volume fraction encountered here was 0.05, at the lower end of the range investigated by Baughan (2).

It is appreciated that the molecular weights of the samples were quite different. However, from the point of view adopted here, the effect of molecular weight on the amount of heat evolved or the shape of the "fast" isotherm should be of little consequence.

An alternative explanation which has been kindly suggested by the Referee does not involve capillary condensation but instead the transition from physical (surface) adsorption to solution near the surface of the substrate. In a theoretical treatment of this transition, Hill (14) has indicated that an intermediate region of sorption at an essentially constant pressure should be observed. It is possible that the nearly vertical portions in Fig. 1 may correspond to an equilibrium between benzene vapor and a saturated solution of polystyrene in benzene on the surface of the polymer. Since Type A polymer, being of lower molecular weight than Type B, is the more soluble of the two it may be expected that solution would occur at a lower relative vapor pressure for Type A. It is, however, difficult to account for the observed energies on this basis, since the (exothermic) heat of solution may be expected to increase with increasing molecular weight (15).

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RECEIVED MARCH 21, 1958. DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY. MONTREAL, QUEBEC.

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## THE MECHANISM OF THE PYROLYSIS OF PRIMARY ALKYL BROMIDES\*

## ARTHUR T. BLADES

Considerable literature has appeared in the last few years on the pyrolysis of alkyl bromides to form the corresponding olefin and hydrogen bromide (1, 2, 3, 4, 5, 6, 7, 8). With secondary and tertiary bromides this reaction appears to involve primarily a unimolecular split and the kinetics of these reactions can be studied reasonably well without inhibitors. With primary bromides the reaction involves free radicals and it is necessary to use an inhibitor to reduce the rates to a limiting value; this residual reaction is believed to be similar to that for the secondary and tertiary compounds. This communication refers to the uninhibited pyrolysis of ethyl and *n*-propyl bromides.

\*Contribution No. 67 from the Research Council of Alberta, Edmonton, Alberta.

Can. J. Chem. Vol. 36 (1958)

#### CANADIAN JOURNAL OF CHEMISTRY. VOL. 36, 1958

Agius and Maccoll (10) consider that the uninhibited pyrolysis of *n*-propyl bromide is a chain reaction initiated by a break into propyl radicals and bromine atoms. A plot of the "first order" data vs.  $P_0^{\frac{1}{2}}$  indicated that a 3/2 order described the data much more adequately, and an appropriate chain mechanism was devised. These observations have been confirmed by Semenov, Sergeev, and Kapralova (7), who also note the catalytic effect of bromine and hydrogen bromide. More recently, Goldberg and Daniels (8) reported similar studies on ethyl bromide, and also indicated that a chain decomposition occurs. They stated that the rate became "first order" after an induction period but that the rate constants were pressure dependent. They also found that the reaction was greatly accelerated by the addition of one of the products (hydrogen bromide), and inhibited by the other product (ethylene). It is of interest to examine the data of Goldberg and Daniels to see whether it can be reconciled with the kinetics for *n*-propyl bromide proposed by Agius and Maccoll.

The order of decomposition of ethyl bromide was inferred by Goldberg and Daniels from a plot of the logarithm of the fraction of bromide remaining, against time. However, this is not a particularly good indicator of order, especially when an induction period is observed. The fact that the rate decreased with decreasing pressure suggests that some other order might fit the data more adequately. A replot of the k vs.  $P_0$  data in Goldberg and Daniels' Fig. 2 as k vs.  $P_0^{\frac{1}{2}}$  gives a reasonably straight line with an intercept at k = 0.6sec.<sup>-1</sup>. Since a first-order decomposition corresponding to a simple molecular split is proceeding simultaneously with the chain reaction, the intercept should correspond to this rate, and it is possible to predict a value of k = 0.5 sec.<sup>-1</sup> from the data on this uncatalyzed reaction (9). Therefore, a more realistic rate expression for ethyl bromide would be:

$$r = k[C_2H_5Br] + k_1[C_2H_5Br]^{3/2}.$$

This does not imply that the mechanism proposed by Goldberg and Daniels is incorrect but it appears that some alteration must be made in their mathematical treatment of it. Their steady-state approximations are that the bromine, bromine atom, and  $C_2H_4Br$ radical concentrations become stable. As pointed out by Hirschfelder (10), the stationarystate approximation can be applied only if the rate of destruction of intermediates is many order of magnitude greater than that of the over-all reaction. For bromine, with a bond energy of 45.5 kcal./mole, this condition is not fulfilled. Insofar as this argument vitiates the steady-state treatment, their suggestion that at high bromide pressures the concentration on the wall is independent of the pressure can no longer be accepted.

Since the bromine atoms are in quasi-equilibrium with the bromine, it seems equally unlikely that this concentration would be constant but it might vary roughly according to the  $\frac{1}{2}$  power of the ethyl bromide pressure as suggested by the kinetics equation of Goldberg and Daniels:

$$r = k_{a}[C_{2}H_{5}Br] + k_{d}[C_{2}H_{5}Br] [Br] + k_{b}[C_{2}H_{5}Br_{wall}] [HBr_{wall}].$$

In the absence of analytical data on the bromine concentration, it is impossible to properly apply the stationary-state approximation. It is possible that the molecular reaction between bromine and ethylene might alter the concentration of the former substantially.

Since Agius and Maccoll have not investigated the effect of hydrogen bromide on the *n*-propyl bromide decomposition, examination must be confined to their kinetics data. A plot of first order "k" vs.  $P_0^{\frac{1}{2}}$  in their Fig. 3 and plots of  $p^{-\frac{1}{2}}$  vs. time in Fig. 5 indicate a purely 3/2 order for *n*-propyl bromide. Extrapolation of data on the purely

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intramolecular decomposition of this compounds to 360° C. gives a value of  $k = 0.3 \times 10^{-4}$ sec.<sup>-1</sup> (11). This small value has been lost in their rather large experimental error, but it is sufficiently large to be included in the rate expression:

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$$r = k[C_{3}H_{7}Br] + k_{1}[C_{3}H_{7}Br]^{3/2}.$$

Their kinetics data are then not inconsistent with the same mechanism as has been proposed for ethyl bromide.

The observation of the catalytic effect of hydrogen bromide on this decomposition (7) completes the evidence that the decompositions of ethyl and n-propyl bromides are mechanistically identical. The mechanism proposed by Goldberg and Daniels is the more plausible for both compounds since it explains all of the experimental facts.

If this mechanism is correct, the theories advanced by Semenov (12) and by Maccoll and Thomas (1) to explain the difference in mechanisms of decomposition of n-propyl and isopropyl bromides must be modified to include the possibility of the rate of reaction between hydrogen bromide and the alkyl bromide being the mechanism-controlling factor.

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## GASEOUS AND LIOUID STATES OF AGGREGATION IN THE SUPERCRITICAL REGION

# F. G. Smith

A considerable amount of geological theory of formation of mineral deposits is dependent on the properties of water at supercritical temperatures and/or pressures. Consequently, geochemists and economic geologists are interested in physical theories of supercritical fluids, and in experimental studies of heterogeneous systems containing one or more such fluids. For example, if the volume of a liquid phase is kept constant as the temperature and pressure are increased to values above the critical temperature, and it can be shown that thermodynamic functions are continuous and uninflected, then we can extrapolate chemical properties of the liquid state into the supercritical region. There is a controversy in the geochemical literature regarding the appropriate term for designating a supercritical fluid, but it seems to be preferable to call it a liquid if it has the thermodynamic properties of a liquid, and a gas, if it has those of a gas.

In a review of data on the state of supercritical fluids of geological interest (1), it was emphasized that the liquid state is not limited by the critical temperature, but is limited Can. J. Chem. Vol. 36 (1958)

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