THE EFFECT OF PRESSURE ON THE RATE OF FRAGMENTATION ON β-BROMOANGELATE ION[1]

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Among the various reactions encountered in organic chemistry, the heterolytic fragmentation reaction, symbolized by equation 1, constitutes an important type.[2]

$$a\text{-}b\text{-}c\text{-}d\text{-}X \longrightarrow a\text{-}b + c\text{=}d + \ :X \qquad\qquad (\text{Eq. 1})$$

One of the questions that usually arise in mechanistic studies of such reactions is whether the two bonds to be broken cleave simultaneously, or whether the second is broken in a stage following the highest energy transition state (a pre-equilibrium with the first bond breaking prior to the transition state can usually be affirmed or ruled out on other grounds).

Activation volumes have been measured for many types of reactions, and satisfactory correlations obtain in virtually every case between known mechanisms and semi-empirical estimates of $\Delta V^{*}$ for such mechanisms.[3]  Among reactions not previously studied under high pressure is the fragmentation reaction.[4]  Since bond cleavage makes a positive contribution to $\Delta V^{*}$ and since two bonds are presumably broken, a relatively large $\Delta V^{*}$ would be indicative of concerted fragmentation.

β-Bromoangelic acid rapidly decomposes under conditions to which the isomeric β-bromotiglic acid is stable,[5] and it has been considered a good example of the single step fragmentation process by Grob[2] for that reason:



$$\longrightarrow \quad CH_3C \equiv CCH_3 + \bar{Br} + CO_2$$
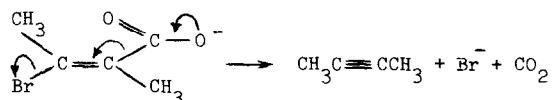
If loss of carbon dioxide alone were rate determining, $\Delta V^{*}$ would resemble that of other typical decarboxylations[6] such as tribromoacetate (+8 cm$^3$ at 66°), trichloroacetate (+10 cm$^3$ at 80°), α,α-dimethylacetoacetate (+5 cm$^3$ at 66°), benzoylacetate (+5 cm$^3$ at 54°) and phenylpropriolate (+10 cm$^3$ at 102°); if bromide ion is released at the same time, $\Delta V^{*}$ should be substantially larger than that.

β-Bromoangelic acid was prepared from commercially available tiglic acid by the method of Buckles and Mock;[7] m.p. 92.5 - 93.0°, pKa = 3.40, n.m.r. (CCl4) τ7.9 (3), 7.2 (3) and -2.7 (1).  Aqueous solutions containing the acid and a threefold excess of sodium hydroxide

were heated to $65.0\pm0.2°$; periodically a sample was quenched with dilute nitric acid and assayed for bromide by means of a silver nitrate titration to the usual electrometric end point. Excellent first order plots were obtained; three or four points sufficed at every pressure used. The apparatus has been described earlier;[8] the results are shown in the Table.

Rate Constants at 65.0° and at Several Pressures

| Pressure, kbar | $10^6 k_1$, sec$^{-1}$ | # Observations |
|---|---|---|
| 0.001 | 2.58 | 4 |
| 1.034 | 1.36 | 3 |
| 2.068 | 0.94 | 3 |
| 3.103 | 0.68 | 3 |
| 4.137 | 0.57 | 4 |

$\Delta V^*$ can be evaluated by means of the equation, $\Delta V^* = -RT\,(\partial \ln k/\partial p)$, and the slope in turn can be obtained[9] by means of $\ln k = a + bp + cp^2$; our data fit this expression with a correlation coefficient of 0.999 to give: $\Delta V^* = +17.7$ cm$^3$/mole at zero pressure. This large pressure induced deceleration is strong evidence for Grob's mechanism, particularly if it is realized that the charge, dispersed over two oxygen atoms in the initial molecule, is transferred to a single bromine atom. We conclude that it seems reasonable to hope that the activation volume may be a useful criterion for reactions of this type.

## References

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