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# A SOLVENT ISOTOPE EFFECT UPON THE ACETOLYSIS OF AN EPOXIDE

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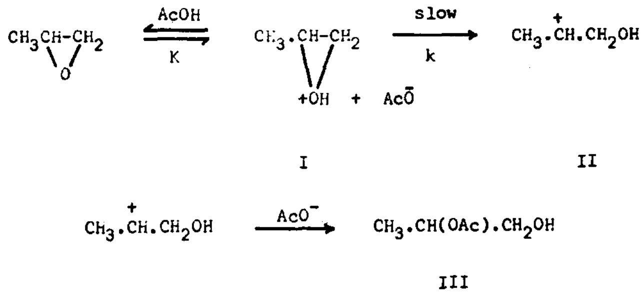
Of compounds which undergo acid-catalysed acetolysis, propylene oxide has recently been examined (1). In glacial acetic acid ring-opening occurs yielding principally propylene glycol β-monoacetate, III, ('abnormal ring fission' (2)) presumably by way of the more stable carbonium ion II.



This system offers an opportunity to test the prediction (3) that a solvent isotope effect should be observed in acetic acid-d and that its magnitude, measured by the value of $k_H/k_D$ should be approximately 1.1 (4).

The rates of acetolysis of propylene oxide in pure acetic acid and acetic acid-d have now been measured, employing a gas-chromatographic analytical technique to be described (1). Reproducible pseudo first-order kinetics were observed (Fig. 1) and specific rate constants evaluated (Table 1).

TABLE 1

Pseudo First-Order Rate Constants for the Acetolysis of Propylene Oxide at 70.2 C.

| solvent | $10^4 k$ (sec$^{-1}$) |
|---|---|
| acetic acid ($k_H$) | 1.52 ± 0.01 |
| acetic acid-d ($k_D$) | 0.993 " |
| Isotope effect, $k_H/k_D$ = 1.53 | |

The results thus bear out the prediction although the magnitude of the effect is unexpectedly high. One of several considerations may account for this discrepancy. Firstly, the predicted value of $k_H/k_D$ was made on the basis of the protonation of tertiary amines in acetic acid and acetic acid-d and may not be strictly applicable to oxygen bases owing, for instance to differences in hydrogen-bonding to the solvent.

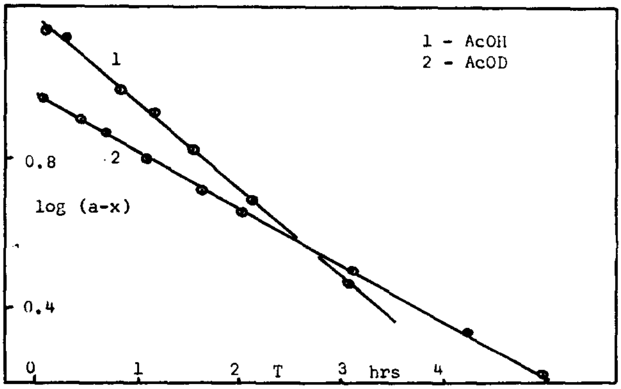
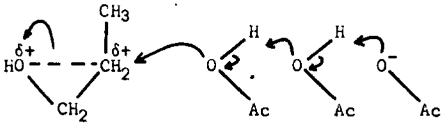


Fig. 1

Also, the absolute values for the dissociations of these amines may be somewhat in error due to uncertainty in the values of the extinction coefficients for the free bases. A third possibility is that ring-opening of I is brought about by attack of acetate ion rather than a molecule of acetic acid, either directly or by applying its influence as a base through solvent molecules (IV).



IV

The concentration of acetate ion (IV) must be higher in acetic acid than in acetic acid-d thus bringing about an amplification of the isotope effect. The carbonium ion produced may then be incipient rather than free.

## REFERENCES

(1) N. S. Isaacs, to be published.

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(3) N. S. Isaacs, preceding paper.

(4) K. B. Wiberg, Chem. Revs. **55**, 713 (1955).

## ACKNOWLEDGMENT

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