

the same reagent is analogous to the situation prevailing in alkali<sup>9</sup> and sulphate<sup>10,11</sup> cooking, where phenolic  $\alpha$ -arylether structures of the phenylcoumaran type also gave *o,p'*-dihydroxy-stilbene structures, whereas non-phenolic units of the same structural type proved stable.

During sulphate cooking, the cleavage of the  $\alpha$ -arylether bond in phenolic phenylcoumaran structures carrying a hydroxymethyl group on the hydrofuran ring (instead of a methyl group as in compound I) is accompanied by a loss of the hydroxymethyl group (presumably as formaldehyde)<sup>11</sup>. It appears that an analogous elimination of formaldehyde also takes place during neutral sulphite cooking<sup>8</sup> (cf. also Ref. 1).

The formation of methane sulphonic acid during neutral sulphite treatment of methoxyl-containing model compounds of the  $\alpha$ - and  $\beta$ <sup>1</sup>-arylether types and of isolated lignins<sup>8</sup> further parallels the results of sulphate cooking. Subjected to the conditions of the latter process, methoxyl-containing model compounds<sup>12</sup> and lignins<sup>13</sup> are partially demethylated with formation of methyl mercaptan and dimethyl sulphide.

The splitting of the  $\alpha$ -arylether bond in phenolic phenylcoumaran units and the cleavage of methylether linkages increase the content of phenolic hydroxyl groups and, thus, together with the sulphonation in  $\alpha$ -position, facilitate the dissolution of lignin without contributing to its degradation. Apparently, the findings that *o,p'*-dihydroxy-stilbene structures are formed from phenolic phenylcoumaran units and that they are photochemically and thermally converted into potential chromophoric systems<sup>14</sup> provide a possible explanation for some of the colour characteristic of neutral sulphite pulps.

The mechanisms of the cleavage of arylether linkages by neutral sulphite are currently being studied.

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1. Gellerstedt, G. and Gierer, J. *Acta Chem. Scand.* **22** (1968). *In press.*
2. Aulin-Erdtman, G. *Svensk Kem. Tidskr.* **54** (1942) 168.
3. Erdtman, H. *Ann.* **503** (1933) 283.
4. Rottendorf, H., Sternhell, S. and Wilmhurst, J. R. *Australian. J. Chem.* **18** (1965) 1759.

5. Aulin-Erdtman, G., Tomita, Y. and Forsén, S. *Acta Chem. Scand.* **17** (1963) 535.
6. Emmons, W. D. and Ferris, A. F. *J. Am. Chem. Soc.* **75** (1953) 2257.
7. Karplus, M. *J. Chem. Phys.* **30** (1959) 11; *J. Am. Chem. Soc.* **85** (1963) 2870. (1964) 51.
8. Gellerstedt, G. and Gierer, J. *Unpublished results.*
9. Gierer, J. and Norén, I. *Acta Chem. Scand.* **16** (1962) 1713.
10. Gierer, J., Lenz, B. and Wallin, N.-H. *Acta Chem. Scand.* **18** (1964) 1469.
11. Adler, E., Marton, J. and Falkehaug, I. *Acta Chem. Scand.* **18** (1964) 1311.
12. Turunen, J. Doctoral thesis, Helsinki Univ., *Soc. Sci. Fennica Commen. Phys. Math.* **28** (1963) 9.
13. McKean, W. T., Hrutford, B. F. and Sarkanen, K. V. National AIChE meeting San Francisco, May 1965.
14. Gierer, J. and Lenić, J. *Unpublished results.*

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## Enolization of Ketones

### VII.<sup>1</sup> The Effect of Solvent on the Orientation of Acid-Catalyzed Deuterium Exchange in 2-Butanone

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The application of NMR technique to the measurements of deuterium exchange in ketones allows the direct observation of the rate of deuterium uptake at the two positions  $\alpha$ - to the carbonyl function, and in the special case of unsymmetric ketones in which both sets of  $\alpha$ -protons are distinguishable and exchangeable, permits the calculation of the thermodynamic param-

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eter  $K_D$  ( $k_{CH_2}/k_{CH_3}$ ). The method has been widely applied in varying forms and has been the subject of a number of recent papers.<sup>3-8</sup> Most studies treating the orientation,  $K_D$ , however, have been carried out in a simple solvent or solvent mixture. The effect of solvent variation has generally not received much attention.

Any rate expression for a reaction in the liquid phase contains a solvent-term which would ordinarily be included in the kinetic expression, but because its order is unknown and because solvent is present in excess, is generally assumed constant and is thus included in the rate constant.<sup>9</sup> Thus, *a priori*, a change of solvent is expected to affect in some way the rate constant, and there are many treatments designed to predict and explain these effects.<sup>10</sup> The effect of solvent variation on a rate ratio is somewhat more complex because of the introduction of an extra unknown; *i.e.* a given solvent may affect the two given rate constants in a different manner. In the simplest case where a reactant has two paths of reaction available of the same or similar mechanism, the solvent term will largely cancel (provided the mechanisms are unaltered by a change in solvent). This is, however, an unreasonable restriction. In deuterium exchange in unsymmetric ketones, one has a reactant with two paths of reaction of similar mechanism available. The effect of solvent variation on the orientation of exchange will of necessity be due to changes in the differential solvation of the two transition states, or equivalently, due to alteration in the structures of the transition states (by definition a change of mechanism).

Warkentin and Tee<sup>3</sup> have considered a dioxane- $D_2O$  system of varying dioxane content, and a small effect on the orientation of base-catalyzed exchange in 2-

butanone was observed. A comparison of two other studies<sup>2,5</sup> indicates a similar effect in acid-catalyzed exchange, but the effect is again small.

The present paper considers the effects of some solvents of different properties on the orientation of acid-catalyzed deuterium exchange in 2-butanone. The results (Table 1) are compared with a recent study of the effect of solvent on the orientation of the acid-catalyzed bromination of 2-butanone.<sup>11</sup>

An NMR study of deuterium exchange is limited by the availability of solvents with readily exchangeable deuterium and with spectra which do not overlap with the resonances of the exchanging groups of the ketone in question, or by the availability of solvents which are miscible with a deuterium pool such as  $D_2O$ . In these cases one is forced to consider the effect of the mixture, solvent- $D_2O$ .

With these rather severe restrictions it has been impossible to consistently vary solvents with respect to a limited number of solvent properties. Unfortunately, the solvents we have studied differ in hydrogen-bonding ability, dipole moment and polarizability, dielectric constant, steric bulk, and acidity and basicity; all of which vary from solvent to solvent and may be expected to have some effect on the variation of  $K_D$ . In addition, the nature of the catalyzing species and of the conjugate base cannot be postulated with any certainty and these may affect the transition states for exchange.<sup>12</sup>

It is clear from the data that the orientation of deuterium exchange is affected by the solvent and that the effect is small. The orientation of exchange varies from 1.5 for methanol- $d_1$  to 5.6 for acetic acid- $d_4$ . For dioxane- $D_2O$  (1:2.7), DMSO- $D_2O$  (1:2.4) and pure  $D_2O$ , the values range

Table 1. Orientation of exchange in 2-butanone.

Solvent mixture	Solvent: $D_2O$ ratio (molar)	Temperature °C	$K_D$ ( $k_{CH_2}/k_{CH_3}$ )
$CH_3OD/D_2O$	8:1	45	$1.5 \pm 0.3$
Dioxane/ $D_2O$	1:2.7	42.7	$2.3 \pm 0.3$
DMSO- $d_6$ / $D_2O$	1:2.4	45	$2.3 \pm 0.3$
$D_2O$		30	$2.5^3$
$CF_3COOD/D_2O$	8:1	45	$3.2 \pm 0.3$
$CD_3COOD/D_2O$	8:1	45	$5.6 \pm 0.5$

between 2.3 and 2.5 indicating that the perturbing effect of the added solvent is small at these concentration ratios. In these cases, the ketone may be preferentially solvated by  $D_2O$ , thus accounting for the negligible effect. The overall variation in orientation with solvent is small, and small changes in  $K_D$  are not detectable within the error-limitations imposed by the method.

The changes are not readily correlated to the variation of any single solvent property on which data are available and are undoubtedly due to a complex combination of the factors already mentioned.

It is remarkable to note the parallel between these results and the effect of solvent on the orientation of the bromination of the same ketone.<sup>11</sup> Thus  $K_{Br}$  in pure  $D_2O$  is 1.8–2.1, while  $K_D$  is ca. 2.5.<sup>2</sup> Similarly  $K_{Br}$  in pure acetic acid is 6.8–7.0, while  $K_D$  in an 8:1 mixture (molar ratio) of acetic acid and  $D_2O$  is 5.1–6.1.  $K_{Br}$  (5.1:1 methanol-acetic acid) is 1.7 and  $K_D$  (8:1 methanol- $D_2O$ ) is 1.2–1.8. The remarkable coincidence of these results is independent evidence in support of the postulate that acid-catalyzed deuterium exchange and bromination of simple ketones occur *via* similar transition states.<sup>13</sup> The absence of common solvents and ketones prevents a direct comparison with the bromination results of Gaudry *et al.*<sup>14</sup> and of Garbisch.<sup>15</sup> The variations observed by Gaudry *et al.* are more striking, which may well be due to the fact that the orientation of bromination was studied in pure solvent, whereas we have been limited to solvent- $D_2O$  mixtures.

*Experimental.* Spectra were recorded on a Varian A-60 NMR spectrometer.

*Solvents:*  $D_2O$  (>99.7%), acetic acid- $d_4$ , trifluoroacetic acid- $d_1$ , methanol- $d_1$ , and DMSO- $d_6$  were obtained commercially and used without further treatment. Commercial dioxane was treated according to Wiberg<sup>16</sup> and distilled from sodium prior to use. Commercial 2-butanone (Merck *pro analysi*) was used as supplied.

*Kinetic runs.* The general procedure and the treatment of primary data has been described in detail elsewhere.<sup>2,3,5,6</sup> Deviations from this procedure occur in setting up the runs (*vide infra*).

In treating different solvent systems it is desirable to fix as many variables as possible. Accordingly, all runs are solvent- $D_2O$  mixtures in which DCl is present as a formal catalyst.

For all solvents, the ratio of available deuterium to exchangeable protium is ca. 4.5 and the total volume is 1.5 ml (volume additivity assumed). Thus conditions for strict first-order kinetics are only fulfilled in early stages of exchange. For solvents with available deuterium, the ratio of solvent available deuterium to  $D_2O$  available deuterium is ca. 4.5, and for solvents with no or difficultly exchangeable deuterium (dioxane and DMSO- $d_6$ ), the volume ratio solvent to  $D_2O$  to ketone is 0.8:0.5:0.2. Data were treated by the method of linear least-squares and the error limits assigned  $K_D$  are derived from the roots of the variances of the rate constants.

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1. Part VI: Rappe, C. and Sachs, W. H. *Tetrahedron* **24** (1968) 6287.
2. Rappe, C. *Acta Chem. Scand.* **20** (1966) 2236.
3. Warkentin, J. and Tee, O. S. *J. Am. Chem. Soc.* **88** (1966) 5540.
4. Bothner-By, A. A. and Sun, C. *J. Org. Chem.* **32** (1967) 492.
5. Rappe, C. and Sachs, W. H. *J. Org. Chem.* **32** (1967) 3700.
6. Rappe, C. and Sachs, W. H. *J. Org. Chem.* **32** (1967) 4127.
7. Hine, J., Hampton, K. G. and Menon, B. C. *J. Am. Chem. Soc.* **89** (1967) 2664.
8. Warkentin, J. and Cox, R. A. *J. Org. Chem.* **33** (1968) 1301.
9. Frost, A. A. and Pearson, R. G. *Kinetics and Mechanism*, 2nd Ed., Wiley, New York 1961.
10. Amis, E. S. *Solvent Effects on Reaction Rates and Mechanisms*, Academic, London 1966.
11. Rappe, C. *Acta Chem. Scand.* **22** (1968) 1359.
12. Swain, C. G. and Rosenberg, A. S. *J. Am. Chem. Soc.* **83** (1961) 2154.
13. Ingold, C. K. *Structure and Mechanism in Organic Chemistry* Cornell, Ithaca, N. Y. 1953, p. 569.
14. Gaudry, M. and Marquet, A. *Bull. Soc. Chim. France* **1967** 1849.
15. Garbisch, E. W., Jr. *J. Org. Chem.* **30** (1965) 2109.
16. Wiberg, K. B. *Laboratory Technique in Organic Chemistry*, McGraw, New York 1960, p. 245.

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