# Isotopic Fractionation Factor of the Hydrogen-Bonded Complex AcO⁻ ··· (HOAc)$_n$ and Kinetic and Equilibrium Solvent Isotope Effects on Reactions of Acetate Ion in Acetic Acid

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A value of $\varphi$ 0.58 $\pm$ 0.05 has been obtained for the deuterium fractionation factor of the hydrogen-bonded complex AcO⁻ ··· (HOAc)$_n$ from ¹H n.m.r. studies of solutions of potassium acetate in AcOH and 97% AcOD–3% AcOH. The result is used to account for the kinetic solvent isotope effect $k_{AcO⁻}^{AcOH}/k_{AcO⁻}^{AcOD}$ 0.66 $\pm$ 0.10 measured for formation of acetic anhydride from 2,4,6-trinitrophenyl acetate in AcOH and AcOD in the presence of potassium acetate. The equilibrium solvent isotope effect on complex formation between 2,4,6-trinitrophenol and acetate ion in AcOH and 97% AcOD–3% AcOH, $K^{AcOH}/K^{AcOD}$ 0.83 $\pm$ 0.1, leads to a value $\varphi$ *ca.* 0.7 for the complex [2,4,6-$(NO_2)_3C_6H_2O$ ··· H ··· OAc]⁻.

The magnitude of the deuterium fractionation factor ($\varphi$) of the proton in inter- and intra-molecular hydrogen bonds is thought to be related to the shape of the potential function and strength of the hydrogen bond.[1-3] For the complexes $(CF_3CO_2)_2H⁻$ and $(4-NO_2C_6H_4O)_2H⁻$ in acetonitrile, values of $\varphi$ of 0.31 and 0.42 respectively have been observed.[1] For intramolecularly hydrogen-bonded protons, the values of $\varphi$ are usually closer to unity and $\varphi$ 0.6 has been measured for the enol of 1,1,1,5,5,5-hexafluoropentane-2,4-dione in acetonitrile.[2] For maleic acid $\varphi$ 0.84 has been calculated[1] from the ratio of acid dissociation constants in $H_2O$ and $D_2O$ and the results $\varphi$ 0.90 in aqueous solution[4] and $\varphi$ 0.87 in 70% (v/v) $Me_2SO–H_2O$[5] have been obtained for protonated 1,8-bis(dimethylamino)naphthalene and the 2,7-dimethoxy derivative respectively.

There have been extensive studies[3,6] of the species formed when fluoride salts are dissolved in acetic acid. The complex F⁻ ··· (HOAc)$_n$ is strongly hydrogen-bonded and gives $\varphi$ 0.55 compared with $\varphi$ 1.26 observed for solutions of weakly solvated chloride salts in acetic acid.[3] In view of the low values of $\varphi$ observed for hydrogen bis(carboxylate) complexes in acetonitrile,[1] we have now determined a value of $\varphi$ for the solvated acetate ion in acetic acid. In addition, the kinetics of reactions (1) and (2) involving acetate ion have been studied in AcOH and AcOD to investigate whether the strong solvation of acetate is reflected in the value of the kinetic solvent isotope effects. Qualitative results for the acylation of 2-naphthol by acetic anhydride in acetic acid have suggested that the reaction occurs more rapidly in the presence of sodium acetate.[7] We have found that the kinetic rate law for the reaction in equation (2)

occurring in acetic acid contains a term first-order in acetate ion. The reaction has been studied previously in methanol.[8] In studying reaction (2), it was observed that the u.v. spectrum of the product of reaction was dependent on the concentration of acetate ion. The changes in the spectrum are compatible with the formation of a complex as in equation (3) and the equilibrium solvent isotope effect on this reaction in AcOH and 97% AcOD–3% AcOH has been measured.

## Experimental

*Materials.*—Acetic acid and [1-²H₁]acetic acid (97 atom % D) were distilled and dried over molecular sieves. Water content was measured by Karl Fischer titration (Mitsubishi Moisturemeter CA-02) and samples with $[H_2O] > 0.005$ mol dm⁻³ were rejected. Solutions in acetic acid were made up in a dry box under nitrogen. Acetic anhydride was distilled and sodium and potassium acetate were recrystallised from acetic acid and dried at 120 °C under vacuum. Samples of 2,4,6-trinitrophenyl acetate, 2,4,6-trinitrophenol, and 1-naphthol were recrystallised from carbon tetrachloride, toluene, and water respectively and dried at room temperature under vacuum.

*N.m.r. Measurements.*—Spectra (¹H) were run at 250 MHz using a Bruker WM 250 spectrometer. A concentric sealed capillary containing $CD_2Cl_2$ provided the deuterium lock and chemical shifts of the hydroxy protons in AcOH were measured relative to the methyl protons at $\delta$ 0. The shift of the methyl signal is unchanged by the presence of salts in the solution or by
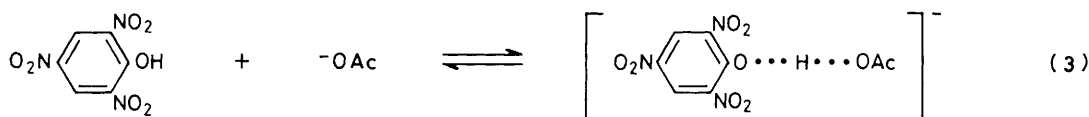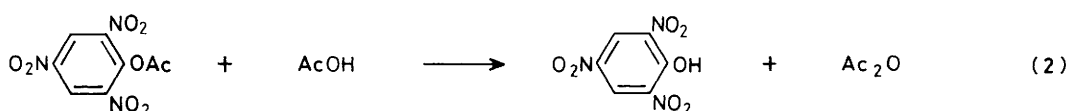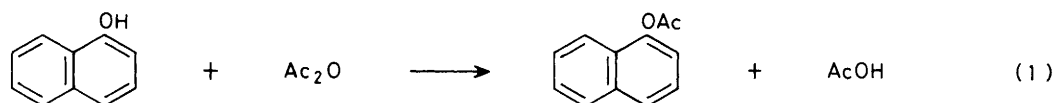
**Table 1.** Chemical shifts of the hydroxy proton in AcOH and 97% AcOD containing potassium acetate at 298 K

| | $\delta$/p.p.m. | |
| --- | --- | --- |
| [KOAc]/mol dm$^{-3}$ | AcOH | 97% AcOD–3% AcOH |
| 0 | $9.746 \pm 0.02$ | $9.649 \pm 0.03$ |
| 0.25 | $9.838 \pm 0.02$ | — |
| 0.50 | $9.893 \pm 0.04$ | $9.924 \pm 0.03$ |
| 1.00 | $10.053 \pm 0.03$ | $10.171 \pm 0.04$ |
| 1.50 | $10.254 \pm 0.04$ | $10.471 \pm 0.05$ |
| 2.00 | $10.392 \pm 0.07$ | $10.747 \pm 0.06$ |

**Table 2.** First-order rate coefficients ($k$) for reaction of 1-naphthol with acetic anhydride at 320 K in various solvents

| | $10^3 \ k$/min$^{-1}$ | | |
| --- | --- | --- | --- |
| [KOAc]/mol dm$^{-3}$ | Solvent* A | B | C |
| 0 | 6.32 | 5.14 | 5.43 |
| 0.5 | 9.45 | 6.79 | 8.58 |
| 1.0 | 13.06 | 11.07 | 11.98 |
| 1.5 | 18.03 | 15.96 | 18.86 |
| 2.0 | 26.83 | 22.20 | 26.15 |

* Solvent A: Ac$_2$O (1 cm$^3$), AcOH (4 cm$^3$); B: Ac$_2$O (1 cm$^3$), 97% AcOD–3% AcOH (4 cm$^3$); C: Ac$_2$O (1 cm$^3$), AcOH (2 cm$^3$), AcOD (2 cm$^3$).

**Table 3.** First-order rate coefficients for reaction of 2,4,6-trinitrophenyl acetate with acetate in AcOH and 97% AcOD at 298 K

| [KOAc]/mol dm$^3$ | 0.0 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.75 |
| --- | --- | --- | --- | --- | --- | --- | --- |
| $10^3 \ k$/min$^{-1}$ (AcOH) | 0.0 | 2.06 | 4.58 | 5.60 | 7.49 | 8.87 | 15.49 |
| $10^3 \ k$/min$^{-1}$ (97% AcOD) | 0.0 | 1.87 | 4.50 | 8.70 | 10.89 | 11.69 | 19.76 |

| [KOAc]/mol dm$^3$ | 1.00 | 1.25 | 1.40 | 1.50 | 1.75 | 2.00 |
| --- | --- | --- | --- | --- | --- | --- |
| $10^3 \ k$/min$^{-1}$ (AcOH) | 15.49 | 30.37 | 31.67 | 33.70 | 49.24 | 59.77 |
| $10^3 \ k$/min$^{-1}$ (97% AcOD) | 19.76 | 41.46 | — | 55.89 | 74.12 | 99.68 |

**Table 4.** Complex formation between 2,4,6-trinitrophenol and acetate ion in AcOH and 97% AcOD at 298 K. [2,4,6-Trinitrophenol] *ca.* $3.4 \times 10^{-5}$ mol dm$^{-3}$; absorbance ($A$) at 330 nm

(i) AcOH

| [KOAc]/mol dm$^{-3}$ | 0.0 | 0.005 | 0.010 | 0.050 | 0.100 |
| --- | --- | --- | --- | --- | --- |
| $A$ | 0.185 | 0.245 | 0.290 | 0.430 | 0.490 |
| [KOAc] | 0.0 | 0.0064 | 0.016 | 0.040 | 0.100 |
| $A$ | 0.180 | 0.245 | 0.310 | 0.410 | 0.465 |

(ii) 97% AcOD

| [KOAc] | 0.0 | 0.0064 | 0.016 | 0.040 | 0.100 |
| --- | --- | --- | --- | --- | --- |
| $A$ | 0.185 | 0.280 | 0.375 | 0.470 | 0.565 |
| [KOAc] | 0.0 | 0.0064 | 0.016 | 0.040 | 0.100 |
| $A$ | 0.205 | 0.300 | 0.400 | 0.480 | 0.550 |

partial replacement of AcOH by AcOD. The chemical shift of the hydroxy proton in AcOH and in 97% AcOD at 298 K was determined at various concentrations of potassium acetate in the range 0—2 mol dm$^{-3}$. The solutions were made up to an appropriate volume by adding solvent to a weighed amount of potassium acetate. In some cases solutions were prepared by mixing weighed amounts of potassium acetate and solvent, so that concentrations could be expressed as mole fractions. Within the limits of our experimental errors, the use of mole fractions instead of molarities made no appreciable difference to our results. Measurements of the chemical shift were repeated 4—7 times with fresh solutions at each concentration and the average values with standard deviation are given in Table 1. Solutions containing 0.25 and 0.50 mol dm$^{-3}$ sodium acetate in place of potassium acetate gave similar results within experimental error.

*Kinetics.—Reaction of acetic anhydride with 1-naphthol.* Kinetic studies of reaction (1) were carried out at 320 K in a solvent consisting of acetic anhydride (1 cm$^3$) together with either AcOH (4 cm$^3$), AcOD (4 cm$^3$), or AcOH (2 cm$^3$) and AcOD (2 cm$^3$). The reaction was studied in the presence of potassium acetate (0—2.0 mol dm$^{-3}$) and was followed by observing the decrease in absorbance due to 1-naphthol at 322 nm. Initial concentrations of 1-naphthol of 1.0 and 3.0 $\times 10^{-4}$ mol dm$^{-3}$ were used. The reaction was accurately first-order under these conditions and the average values of the first-order rate coefficients from at least two determinations at each acetate concentration are given in Table 2. Rate coefficients were also determined in a solvent of Ac$_2$O (0.5 cm$^3$) with AcOH (4.5 cm$^3$). At potassium acetate concentrations of 0 and 1.0 mol dm$^{-3}$ the values were $3.35 \times 10^{-3}$ and $6.92 \times 10^{-3}$ min$^{-1}$ which are approximately two-fold lower than the results (Table 2) in a solvent of Ac$_2$O (1.0 cm$^3$) and AcOH (4.0 cm$^3$) as expected if the reaction is first-order in Ac$_2$O.

The product of reaction (1), 1-naphthyl acetate, was isolated in 98% yield from an initial reaction mixture consisting of potassium acetate (1.5 mol dm$^{-3}$) and 1-naphthol (0.58 g, 0.1 mol dm$^{-3}$) in Ac$_2$O (8 cm$^3$) and AcOH (32 cm$^3$).

*Reaction of 2,4,6-trinitrophenyl acetate in acetic acid.* The kinetics of reaction (2) were studied at 298 K in AcOH and 97% AcOD in the presence of potassium acetate (0—2.0 mol dm$^{-3}$) with initial concentrations of the ester of 5.0 $\times 10^{-5}$ mol dm$^{-3}$. The reaction was followed by observing the increase in absorbance at 340 nm due to the formation of 2,4,6-trinitrophenol. The values of the first-order rate coefficients are given in Table 3 and the results have an uncertainty of *ca.* $\pm 7\%$. The products of reaction (2) under these conditions were established by following changes in the $^1$H n.m.r. spectrum. Spectra were run at *ca.* 30 min intervals over a period of five hours for a solution of 2,4,6-trinitrophenyl acetate (0.05 mol dm$^{-3}$) and sodium [2-$^2$H$_3$]acetate (0.25 mol dm$^{-3}$) in [1,2-$^2$H$_4$]acetic acid. The spectrum was referenced to the residual methyl protons in acetic acid at $\delta$ 0. As the reaction proceeded, peaks at $\delta$ 0.44 and 7.13 corresponding to the methyl and aromatic protons respectively of the ester were observed to disappear and peaks at $\delta$ 0.025 due to the methyl protons in acetic anhydride and at $\delta$ 6.82 for the aromatic protons in 2,4,6-trinitrophenol increased in intensity. The changes in spectrum occurred at a rate which was similar to that observed spectrophotometrically and after 18 hours the peaks at $\delta$ 0.44 and 7.13 were undetectable whereas those at $\delta$ 0.025 and 6.82 did not increase further.

*Equilibrium studies of complex formation between acetate ion and 2,4,6-trinitrophenol.* The peak at 332 nm (molar absorptivity $\varepsilon$ *ca.* $5.5 \times 10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$) in the spectrum of a solution of 2,4,6-trinitrophenol (*ca.* $3.4 \times 10^{-5}$ mol dm$^{-3}$) in AcOH changes on addition of potassium acetate. With increasing concentrations of potassium acetate up to 0.1 mol dm$^{-3}$, the spectrum changes successively giving a good isosbestic point at 295 nm and the final spectrum consists of a peak at 338 nm ($\varepsilon$ *ca.* $1.5 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$) and a shoulder at *ca.* 390 nm ($\varepsilon$ *ca.* $8 \times 10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$). The absorbance data (see Table 4) were plotted in the form of equation (4) in which $A$ is the absorbance of a solution of 2,4,6-trinitrophenol (concentration $a$ mol dm$^{-3}$) at a fixed wavelength in the presence of a particular concentration of potassium acetate, $A_0$ is the absorbance in the

absence of potassium acetate, $\varepsilon_c$ is the molar absorptivity of the complex, and $K$ is the equilibrium constant for complex formation in equation (3). Plots of $A$ against $(A - A_0)/[OAc^-]$ for data at different wavelengths were linear and the value $K^{AcOH}$ $34.8 \pm 1$ dm$^3$ mol$^{-1}$ was calculated for the reaction in AcOH and $K^{AcOD}$ $41.7 \pm 4$ dm$^3$ mol$^{-1}$ was calculated for 97% AcOD.

$$A = (A - A_0)/K[OAc^-] + a\varepsilon_c \qquad (4)$$

For solutions of 2,4,6-trinitrophenol in acetic acid containing concentrations of potassium acetate above 0.1 mol dm$^{-3}$, further small changes in the spectrum occurred. However, the isosbestic point at 295 nm was no longer observed and the data were not analysed in detail. On addition of potassium acetate to solutions of 4-nitrophenol and 2,4-dinitrophenol in acetic acid the spectra were almost unchanged and it was concluded that complex formation between these more weakly acidic phenols and acetate ion is unfavourable.

## Results and Discussion

In the $^1$H n.m.r. spectrum of solutions of potassium acetate in acetic acid, the signal due to the acidic proton is shifted downfield by increasing concentrations of potassium acetate. The dependence of chemical shift ($\delta$) on concentration is given by equation (5) in which $\delta_0$ and $b$ have values of 9.743 p.p.m. and 0.327 p.p.m. dm$^3$ mol$^{-1}$, respectively in AcOH and in 97% AcOD the values are $\delta_0$ 9.644 p.p.m. and $b$ 0.550 p.p.m. dm$^3$ mol$^{-1}$. The effect of potassium acetate on the chemical shift of the acetic acid proton is similar to the effect of fluoride salts, and in contrast to the upfield shifts produced by the addition of chloride salts.[3] The explanation of the behaviour of acetates and fluorides is that these species are strongly solvated in complexes of the type $AcO^- \cdots (HOAc)_n$ and that the observed chemical shift of the solution is a weighted average of the chemical shifts of the protons in the hydrogen-bonded complex and in the bulk solvent ($\delta_0$). The gradients of the plots of chemical shift against acetate concentration can be used[9] to calculate a value $\varphi$ $0.58 \pm 0.05$ for the fractionation factor of the exchangeable protons in the complex $AcO^- \cdots (HOAc)_n$. The result means that this proton site has a reduced atom fraction of deuterium compared with the bulk solvent which in turn implies that the acidic proton is involved in a strong hydrogen bond with acetate. The values of $\delta_0$ in AcOH and in 97% AcOD are slightly higher than the results obtained previously[3] and this may reflect slight differences in the water content of the solvent.

$$\delta = \delta_0 + b[OAc^-] \qquad (5)$$

The first-order rate coefficient for the reaction of acetic anhydride with 1-naphthol in AcOH [equation (1)] is increased 4.2-fold in the presence of 2.0 mol dm$^{-3}$ potassium acetate, but a strongly curved dependence of rate coefficient on acetate concentration was observed. At each concentration of potassium acetate the reaction was found to occur ca. 1.2 times more slowly in 97% AcOD than in AcOH (Table 2). In view of these observations it seems likely that the increase in rate in the presence of acetate is due to an electrolyte effect and that acetate is not involved in the reaction as a catalyst.

The solvolysis of 2,4,6-trinitrophenyl acetate in acetic acid at 298 K occurs negligibly slowly except in the presence of potassium acetate. The first-order rate coefficient for the

formation of 2,4,6-trinitrophenol [equation (2)] is directly proportional to the concentration of potassium acetate up to 0.5 mol dm$^{-3}$, but at higher concentrations the plot of rate coefficient against $[AcO^-]$ is curved and the gradient decreases as the concentration of acetate increases. The linear dependence at low concentration is compatible with a mechanism for the reaction involving nucleophilic attack of the solvated acetate ion on the ester, as in (1). The curvature at high $[^-OAc]$ may be due to an electrolyte effect similar to that for the reaction of acetic anhydride with 1-naphthol. The second-order rate



( 1 )
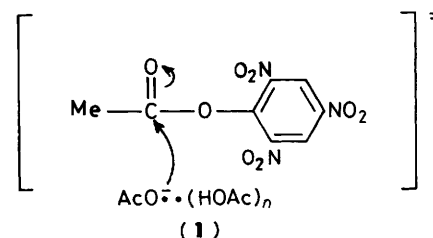
coefficient for reaction of 2,4,6-trinitrophenyl acetate at low $[AcO^-]$ has a value $k_{AcO^-}^{AcOH}$ $1.68 \pm 0.13 \times 10^{-2}$ dm$^3$ mol$^{-1}$ min$^{-1}$ in AcOH and the result $k_{AcO^-}^{AcOD}$ $2.56 \pm 0.22 \times 10^{-2}$ dm$^3$ mol$^{-1}$ min$^{-1}$ was obtained in 97% AcOD. The reaction has been studied previously in methanol[9] and the value of the second-order rate coefficient is ca. 110-fold higher than in AcOH. If reaction in acetic acid involves the complex $AcO^- \cdots (HOAc)_n$ as in (1), the kinetic solvent isotope effect $k_{AcO^-}^{AcOH}/k_{AcO^-}^{AcOD}$ $0.66 \pm 0.1$ is given by equation (6) in which $\varphi$ is the fractionation factor of the proton in the complex and $\varphi^{\neq}$ is the fractionation factor of the corresponding proton in the transition state.

$$k_{AcO^-}^{AcOH}/k_{AcO^-}^{AcOD} = \varphi/\varphi^{\neq} \qquad (6)$$

Use of equation (6) assumes that the fractionation factors of other solvent species are unchanged between the reactant and transition state. Substitution of $\varphi$ $0.58 \pm 0.05$ into equation (6) gives $\varphi^{\neq}$ $0.88 \pm 0.2$. Since this result is intermediate in value between $\varphi$ 0.58 for the reactant complex $AcO^- \cdots (HOAc)_n$ and $\varphi$ 1.0 for the acetic acid which is liberated, the magnitude of the kinetic solvent isotope effect is compatible with reaction through (1) involving partial bond formation between the solvated acetate ion and the ester carbonyl.

The u.v. spectrum of a solution of acetate ion and 2,4,6-trinitrophenol in acetic acid is very similar to the spectrum of the complexes of 4-nitrophenolate with benzoic acid in sulpholane[1] and of 2,4,6-trinitrophenol with amines in acetonitrile.[10] In these latter cases, complex formation occurs with large equilibrium constants whereas in the present case the equilibrium constant is quite low ($K^{AcOH}$ 34.8 dm$^3$ mol$^{-1}$) and a shift in the position of the equilibrium with acetate concentration can be observed. If complex formation is represented by equation (7), the ratio of equilibrium constants in AcOH and 97% AcOD is given by (8) in which $\varphi_R$, $\varphi$, and $\varphi_c$ are the fractionation factors of 2,4,6-trinitrophenol, the acetate solvate, and the 2,4,6-trinitrophenol–acetate complex respectively. On the assumption that $\varphi_R$ has a value of unity, the experimental values $K^{AcOH}/K^{AcOD}$ $0.83 \pm 0.1$ and $\varphi$ $0.58 \pm 0.05$ lead to $\varphi_c$ $0.70 \pm 0.15$. Although the uncertainty on this value is high, the



( 7 )
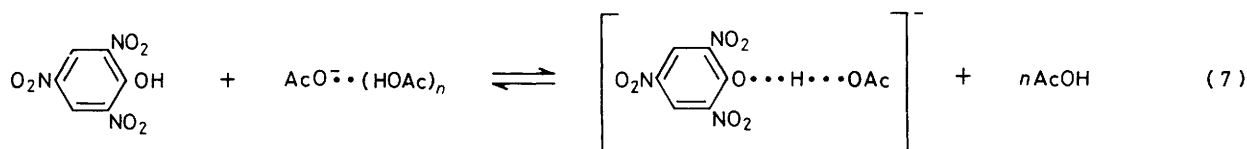
$$K^{\text{AcOH}}/K^{\text{AcOD}} = \varphi_{\text{R}}\varphi/\varphi_{\text{c}} \qquad (8)$$

observation that the ratio $K^{\text{AcOH}}/K^{\text{AcOD}}$ is less than unity implies that the fractionation factor of the trinitrophenol–acetate complex is greater than $\varphi$ for the acetate–acetic acid complex. It follows that the acetate–acetic acid complex involves a stronger hydrogen bond.

## Acknowledgements

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