# Hydrogen Exchange Reactions of 4-(Isotopic Hydrogen Substituted)-Anisoles and -Phenols in Aqueous Sulphuric Acid and Perchloric Acid

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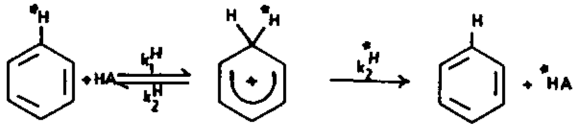
**Summary:** Rates of deuterium and tritium displacement at 25° from the 4-position of anisole and phenol in aqueous perchloric acid, together with the data for the detritiation of anisole in aqueous sulphuric acid are reported. Deuterium is displaced more readily than tritium throughout and isotopic rate ratios for the exchange reactions are substantital; $k^H/k^D$ is 3.93 ± 0.85 for anisole in perchloric acid, 6.50 ± 0.65 for anisole in sulphuric acid and 4.18 ± 1.00 for phenol in perchloric acid. The isotopic effects calculated appear to be constant over a wide range of acidity of both acids. The plots of the observed rates for dedeuteration and detritiation against $-[H_o]$ are linear and thus consistent with an A-$S_E$2 mechanism for the aromatic hydrogen exchange recations. The slopes of these plots are also consistent with the earlier findings.

## Introduction

The electrophilic nature of acid-catalyzed aromatic hydrogen exchange reaction was established by Ingold and his co-workers [1,2]. The mechanism of the reaction remained a subject of discussion [3-7] till Kresge and co-workers [8] established that the exchange reaction was subjected to general acid catalysis via an A-$S_E$2 mechanism (Scheme 1) in strong acids.



Scheme 1

For the deuterium exchange of 4-substituted (2-$^2$H)phenols in concentrated aqueous sulphuric acid, Gold and Satchell [3a] established a relationship between the exchange rate (k) and the Hammett's acidity function ($-H_o$) as in Equation 1 where has value unity and $k_o$ is constant.

$$\log k = \log k_o - \rho H_o \qquad (1)$$

The magnitude of the primary hydrogen isotope effect with respect to symmetry of transition state has often been discussed in the literature [9-11]. For a linear three-centred transition state model Westheimer [9] suggested maximum primary isotope effect for a symmetrical transition state symmetry that was later supported by Melander [12] and Bigeleisen [10]. However, there have been some serious objections [10-11] as to the validity of Westheimer's suggestions. On the other hand, calculations of More O' Ferral and Kouba [15] based on four-centered and five-centered transition state models and those of Albery [16] for a three-centered transition state model are in full agreement with the maximum magnitude of primary isotope effect for a symmetrical transition state. In this respect, aromatic hydrogen exchange reactions have not studies which have been studied to a large extent. However, the undertaken for the exchange of substituted benzenes [17] and substituted azulenes [18] provide a good evidence for a maximum $k^H/k^D$ ratio when the transition state is symmetrical. We, in this paper, report the results of the hydrogen exchange reactions of (4-$^*$H)anisole and (4-$^*$H)phenol in strong acids ($^*$H refers to either $^2$H or $^3$H).

## Experimental

*Substrates:-*

4-Bromonaisole and 4-bromophenol were B.D.H. reagent grade chemicals. (4-$^2$H)Anisole was prepared by the standard Grignard procedure. An ethereal solution of the Grignard reagent prepared from 4-bromoanisole was decomposed with 99.7% deuterium oxide supplied by Koch-Light. The white solid product was exctracted with diethyl ether. Fractional distillation of the dried extract furnished (4-$^2$H) anisole in 80% yield. The amount of 4-deuterated species in the product was estimated to be 95 mole % by mass spectrometry and NMR. Found $n_D^{19}$ for (4-$^2$H) anisole 1.5179, lit. $n_D^{20}$ for anisole [19] 1.5180. (4-$^2$H)Phenol was prepared by an adaptation of the method of Gilman [20]. 4-Bromophenol was dissolved in hexane and a solution of butyllithium in dry diethyl ether added. The mixture was allowed to stand at room temperature for about

Table-1: Experimental condition for Protodetritiation.

| Experimental Conditions | (4-$^3$H)Anisole | (4-$^3$H)Phenol |
|---|---|---|
| Reaction scale (cm$^3$) | 250 | 60 |
| Approximate weight of substrate per experiment (mg) | 2 | 10 |
| Aliquot size (cm$^3$) | 10 | 5 |
| Volume of xylene used for extraction (cm$^3$) | 15 | 10 |
| Volume of xylene layer subjected to conuting. (cm$^3$) | 10 | 5 |
| Volume of scintillator solution (cm$^3$) | 5 | 5 |

two hours. Deuterium oxide was then added dropwise to the ethereal solution of lithium complex formed. After extraction with diethyl ether and purification, the product was fractionally distilled under reduced pressure: mp 39-40°, lit. mp for phenol [21] 41°. The amount of 4-deuterated species in the product was estimated to be 70% by NMR. (4-$^3$H)Anisole and (4-$^3$H)phenol were prepared by similar methods to those used for the preparation of the corresponding deuteriated compound. The experimental conditions differed only in the use of tritiated water instead of deuterium oxide. Found $n_D^{16}$ for (4-$^3$H)anisole 1.5189, lit $n_D^{20}$ for anisole [19] 1.5180, found mp for (4-$^3$H)phenol 39-40°, lit mp [21] for phenol 41°.

*Kinetics:*

Protodetritiation rates were measured from the decrease in radio activity of the substrate with respect to time by use of a liquid scintillation counting procedure. In Table 1 are listed the experimental conditions for protodetritiation of (4-$^3$H)anisole and (4-$^3$H) phenol in concentrated acids. A small amount of tritiated substrate was dissolved in the acid solution by rapid stirring. This solution was then filtered and thermally adjusted to 25°. At various time intervals aliquots were withdrawn and run into 60 cm$^3$ reagent bottle containing fixed amount of xylene and sufficient amount of aqueous sodium hydroxide to quench the reaction. The bottles were shaken manually for about three minutes and the two phases allowed to separate. A fixed amount of xylene layer was then transferred to a low-potassium glass vial containing 5 cm$^3$ of scintillator solution. The scintillator solution consisted of 2,5-diphenyloxazole (10 g) and 1,4-bis (4-methyl-5-phenyl-2-oxazolyl) benzene (0.25 g) in xylene (1 dm$^3$). The radioactive assay was made by a Beckman liquid scintillation counter (Model LS-100).

Protodedeuteriation rates were obtained from quantitative measurements of IR absorption corresponding to the C-H deformation in case of (4-$^2$H)anisole and C-D deformation in case of (4-$^2$H) phenol. The experimental details for the protodeduteriation of the two substrates are given in Table 2. The substrate was dissolved in the acidic solution by rapid stirring. After filtration, these solutions were equilibrated at 25°. At suitable time intervals, aliquots of the reaction mixture were withdrawn and poured into seperating funnels containing a few cm$^3$ of organic solvent and a sufficient amount of dilute sodium hydroxide solution to quench the exchange reaction. After shaking for three minutes, the organic phase was allowed to separate and removed for infrared analysis. In each case matched AgCl-withdow cells were used to measure the absorbances.

A check on the efficiency of the extraction was made by measuring the total amount of the substrate present in the sample either by UV or through an IR absorption common to all isotopic species. Values of $k_o^D$ (Equation 2) were derived by the usual integrated first-order rate equation by the determination of the slope of log [anisole] against time in case of (4-$^2$H)anisole and by log [(4-$^2$H)phenol] against time in case of (4-$^2$H)phenol. The results of a typical experiment with (4-$^2$H) anisole in 7.91M $HClO_4$ are given in Table 3.

Table-2: Experimental conditions for protodedeuteration

| Experimental Conditions | (4-$^2$H)Anisole | (4-$^2$H)Phenol |
|---|---|---|
| Reaction scale (cm$^3$) | 250 | 20 |
| Weight of substrate per experiment (mg) | 60 | 200 |
| Aliquot portion size (cm$^3$) | 15 | 2 |
| Extraction solvent | 2,2,4-Trimethylpentane | Chloroform |
| Cell path-length (mm) | 3.0 | 0.7 |
| Absorption maximum used in kinetics (cm$^{-1}$) | 694 | 850 |
| Type of peak followed | Appearance of C-H | Disappearance of C-D |
| Independent extraction check by | UV absorbance at 36,900 cm$^{-1}$ | IR absorbance at 1613 cm$^{-1}$ |

Table-3: Protodedeuteration of (4-$^2$H)Anisole in 7.91 M $HClO_4$

| Time min. | $10^2$[Anisole] M | $10^2$[4-$^2$H)Anisole] M | Reaction (%) | $10^5 \times k_o^D$ s$^{-1}$ |
|---|---|---|---|---|
| 0 | 0.50 | 1.45 | - | - |
| 10 | 0.70 | 1.25 | 14.0 | 24.5 |
| 25 | 0.95 | 1.00 | 31.0 | 24.6 |
| 40 | 1.18 | 0.77 | 47.1 | 26.4 |
| 60 | 1.38 | 0.57 | 60.6 | 26.0 |
| 80 | 1.53 | 0.42 | 71.0 | 24.7 |
| 100 | 1.65 | 0.30 | 79.3 | 25.0 |
| 150 | 1.79 | 0.16 | 89.3 | 24.0 |
| 900 | 1.95 (estimated from UV absorbance at 36,900 cm$^{-1}$) | | | |

## Results and Discussion

All the kinetic experiments reported were carried out at 25° and the rates followed Equation 2, where v is the reaction rate, $k^H_o$ is the rate constant for the exchange of $^*$H and [substrate] refers to the concentration of the isotopically substituted compounds.

$$v = k_o^{*H} \text{ [substrate]} \qquad (2)$$

The exchange reaction proceeds Via an A-$S_E2$ mechanism illustrated by Scheme 1. The rate constant $k_o^H$, for this sequence may be related to the individual steps using equation 3 by assuming that a steady state condition prevails for the intermediate (I) in Scheme 1.

$$k_o^H = \frac{k_1^H}{1 + (k_2^H/k_2^{*H})} \qquad (3)$$

Following Kresge and Chiang [22] equations (4) and (5) may be written to relate the rate constant of dedeuteration ($k_o^D$) and detriatiation ($k_o^T$) in terms of kinetic leaving atom isotope effect $k_2^H/k_2^D$.

$$k_o^D = \frac{k_1^H}{1 + (k_2^H/k_2^D)} \qquad (4)$$

$$k_o^T = \frac{k_1^H}{1 + (k_2^H/k_2^D)\,1.442} \qquad (5)$$

### *(4-$^*$H)Anisole:*

Hydrogen exchange reactions of (4-$^2$H) anisole and (4-$^3$H) anisole were studied in aqueous perchloric acid solution from 4.05 M to 8.40 M. Values of $k_o^D$ for these reactions are shown in Table 4. Also listed in Table 4 are $k^D_o/k^T_o$ ratios and the corresponding $k_2^H/K_2^D$ ratios calculated from Equations (4) and (5). The kinetic isotope effect appears to be constant within experimental errors. The calculated average value of $k_2^H/k_2^D$ turns out to be 3.93 ± 0.85. In Fig.1 the logarithms of $k_o^D$ and $k_o^T$, are plotted against - $[H_o]$ for perchloric acid [23]. It is evident that both plots are reasonably linear with the same lsope, 1.12 ± 0.02.

In Table 5 are reported the first-order rate coefficients for the protodetritiation of (4-$^3$H)anisole in aqueous sulphuric aicd. In this Table the values measured earlier by Satchell [9] have been used for comparison after correction for more recent $H_o$ data [24]. In Fig. 2 are plotted log $k_o^T$ and log $k_o^D$ against $-[H_o]$ for sulphuric acid. Both plots turned out to be linear and parallel with the slope of 1.20 ± 0.02. Since both $k_o^D$ and $k_o^T$ depend similarly upon acidity it implies that the $k^D_o/k^T_o$ ratio remains constant over the acidity range studied. This ratio is 2.12 ± 0.15. The kinetic isotope effect, $k_2^H/k_2^D$, calculated from $k_2^D/k_o^T$ turns out to be 6.50 ± 0.65 for the hydrogen exchange reactions of (4- $^*$H)anisole in sulphuric acid.

### *(4-$^*$H)Phenol:*

The rates of protodedeuteration and protodetritiation were also measured at 25° in aqueous perchloric acid

Table-4: Hydrogen Exchange of $(4-{}^{*}H)$Anisole in aqueous perchloric acid

| $HClO_4$ M | $-[H_o]$ $s^{-1}$ | $10 \times k_o^D$ $s^{-1}$ | $10^6 \times k_o^T$ (± 0.20) | $k_o^D/k_o^T$ (± 0.85) | $k_2^H/k_2^D$ |
|---|---|---|---|---|---|
| 4.05 | 1.81 | 0.457 | 0.281 | 1.63 | 3.78 |
| 4.41 | 1.85 | 0.616 | 0.387 | 1.59 | 3.60 |
| 4.50 | 2.03 | 0.830 | 0.503 | 1.65 | 3.88 |
| 5.50 | 2.58 | 3.71 | 2.28 | 1.63 | 3.78 |
| 5.97 | 2.87 | 4.62 | 1.63 | 1.63 | 3.78 |
| 7.13 | 3.61 | 62.0 | 35.2 | 1.76 | 4.44 |
| 7.91 | 4.21 | 242 | 143 | 1.69 | 4.08 |
| 8.40 | 4.69 | 618 | 375 | 1.64 | 3.85 |

Table-5: Protodeteritiation of $(4-{}^{3}H)$Anisole in aqueous sulfuric acid

| $H_2SO_4$ M | $-[H_o]$ | $10 \times k_o^T$ $s^{-1}$ |
|---|---|---|
| 3.46 | 1.60 | 1.5 |
| 5.09 | 2.32 | 13.9 |
| 5.33 | 2.41 | 18.3 |
| 6.08 | 2.80 | 57.5 |
| 6.72 | 3.15 | 125 |
| 7.35 | 3.51 | 292 |
| 7.88 | 3.91 | 578 |

ranging from 5.08M to 8.88M in concentration. In Table 6 are listed the first-order rate coefficients $k_o^D/k_o^T$ for these reactions. Calculated $k_2^H/k_2^D$ ratio are also shown in Table 6. The kinetic isotope effect in this case, too, appears to be constant within experimental error. An average value of $k^H{}_2/k_2^D$ is 4.20 ± 0.85. Both log $k_2^D$ and $k_o^T$ are plotted against $-[H_o]$ for perchloric acid [23] in Fig. 3. Again both the plots are linear and parallel to each other with a slope of 0.92 ± 0.02.

The results described in the previous section and summarized in Table 7 show that $k_o^H$ varies linearly with $-[H_o]$ for the exchange reactions of $(4-{}^{*}H)$

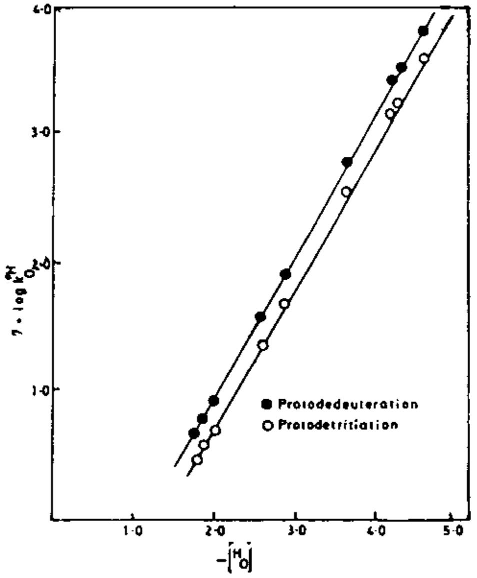


Fig.1: Dependence of exchange rate of (4-$^*$H) anisole on acidity of $HClO_4$

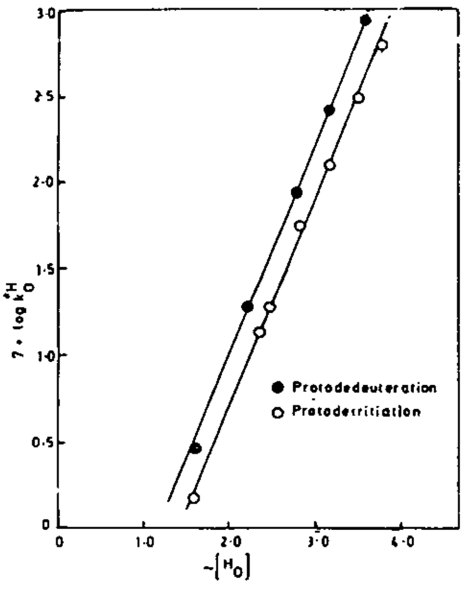


Fig.2: Dependence of exchange rate of (4-$^*$H) anisole on acidity of $H_2SO_4$

anisole and (4-$^*$H)phenol in concentrated aqueous acid. Such a dependence has earlier been observed [25,26] for hydrogen exchange reactions of aromatic compounds and is considered to be consistent with general acid catalysis by an A-$S_E2$ mechanism (Scheme 1). The values of the slopes appear to be in agreement with the earlier finding that these slopes are generally higher for exchange reactions in sulphuric acid than those in perchloric acid, for example, using Hammett's [27] -[$H_o$] values, Satchell [25] reported a slope of 1.18 for the exchange reaction of both (4-$^2$H) anisole and (2-$^2$H)anisole in sulphuric acid as against 0.98 for (3-$^2$H)anisole in the exchange reaction in perhcloric acid. Similarly a slope of 1.12 was reported [25] for the exchange reaction of ($^2$H) benzene in perchloric acid as compared to the previously reported [3b] value of 1.36 for the same reaction in sulphuric acid. Since the slopes of log $k_o{}^*H$ against -[$H_o$] are consistent with an A-$S_E2$ mechanism for isotopic hydrogen exchange, it is of interest to see how for the small differences in these slope can be interpreted mechanistically. The data in Table 7 show that the slopes for the exchange reactions of phenol are lower than those for the exchange reactions of anisole. This implies that a lower slope is obtained for a less reactive compound. This may not be generalized due to the small range of substrates studied. However, a comparison of the values of these slope with those reported in the literature [3a, 25] reveals that lower slopes are usually found for phenol substrates, since equilibrium protonation of phenols usually shows a lower acidity dependence than that of aromatic ethers. It may be pointed out that the protonation of 1,3,5-trimethoxybenzene does not follow [6b] the $H_o$ function; instead it follows a different acidity function $H_R$ [28]. We have no reason to dis-

Table-6: Hydrogen-exchange of $(4-{}^{*}H)$Phenol in aqueous perchloric acid

| $HClO_4$<br>M | $-[H_o]$ | $10^5 \times k_o^D$<br>$s^{-1}$ | $10^5 \times k_o^T$<br>$s^{-1}$ | $k_o^D/k_o^T$<br>(± 0.20) | $k_2^H/k_2^D$<br>(± 0.85) |
|---|---|---|---|---|---|
| 5.08 | 2.33 | 0.583 | 0.352 | 1.65 | 3.85 |
| 6.17 | 2.98 | 1.88 | 1.14 | 1.65 | 3.85 |
| 7.04 | 3.51 | 7.73 | 4.12 | 1.87 | 5.05 |
| 8.00 | 4.28 | 29.4 | 19.5 | 1.51 | 3.20 |
| 8.88 | 5.04 | 166 | 91.2 | 1.82 | 4.78 |

Table-7: Correlation of exchange rates with Hammett's acidity function

| Aromatic substrate | Catalyzing acid | Acidity range<br>$-[H_o]$ | slope |
|---|---|---|---|
| $(4-{}^{3}H)$Anisole | $HClO_4$ | 1.81-4.61 | 1.12 |
| $(4-{}^{2}H)$ Anisole | $HClO_4$ | 1.18-4.61 | 1.12 |
| $(4-{}^{3}H)$Anisole | $H_2SO_4$ | 1.60-3.81 | 1.20 |
| $(4-{}^{2}H)$Anisole | $H_2SO_4$ | 1.63-3.65 | 1.20* |
| $(4-{}^{3}H)$Phenol | $HClO_4$ | 2.33-5.04 | 0.92 |
| $(4-{}^{2}H)$Phenol | $HClO_4$ | 2.33-5.04 | 0.92 |

*A value of 1.81 was reported using a different set of $-[H_o]$ values [25].

regard that the protonation of anisole also follows the latter which would imnply a linear plot of log $k_o^H$ against $-[H_o]$ of slope higher than unity. It appears as if solvation of the phenolic hydrogen is responsible for the lower acidity dependence exchange of phenols. The marked differences in the slopes of log $k_o^H$ against $-[H_o]$ plots of different aromatic substrates are consistent with a single mechanism but different acidity dependencies for the protonation of these substrates.

### *Kinetic hydrogen isotope effects:*

The average kinetic hydrogen isotope effects, $k_2^H/k_2^D$ for the exchange reactions of the two substrates along with the acidity ranges of the catalyzing acids are tabulated in Table 8. Although these values differ from each

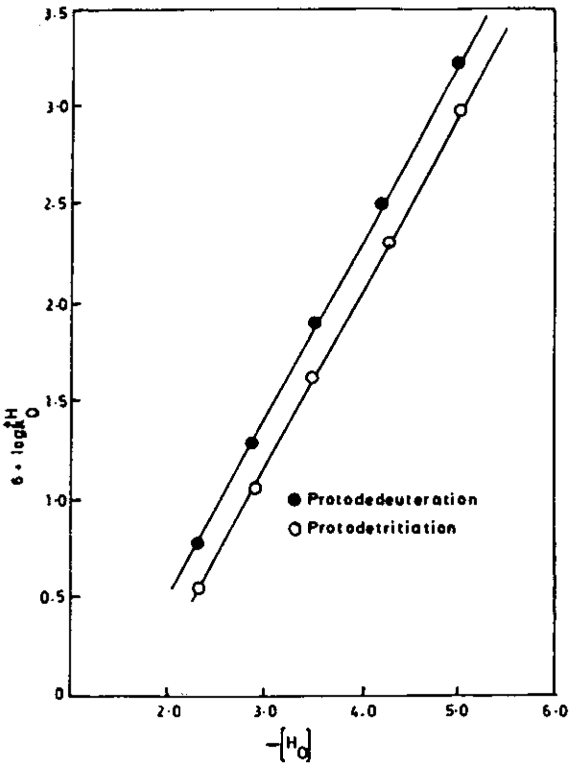


Fig. 3: Dependence of exchange rate of (4-$^*$H) phenol on acidity of $HClO_4$.

other to a considerable extent yet for given substrate-catalyst series, the $k_2^H/k_2^D$ ratios appears to be fairly constant over the acidity range in which these reactions were studied. It may be pointed out that these ratios are a combination of both the primary and secondary isotope effects. For the following discussion, relative rather than absolute, primary isotope effects are important since it is improbable that any secondary effects arising as a result of change of hybridization (from the intermediate to the product) at the 4-position will be dependent upon the hydroxyl or the methoxy group in the two substrates.

The average $k_2^H/k_2^D$ ratios for the exchange reactions of (4-$^*$H)phenol and (4-$^*$H)anisole in aqueous perchloric acid are 4.18 ± 1.00 and 3.93 ± 0.85 respectively. However the ratio turns out to be 6.50 ± 0.65 for the exchange reactions of (4-$^*$H)anisole in aqueous sulfuric acid. The higher magnitude of the ratio for the latter reaction may be attributed to the difference in the nature of the bases present in aqueous sulphuric acid and in aqueous perchloric acid media; in aqueous perchloric acid the only effective base species is the $H_2O$ molecule whereas in aqeuous sulphuric acid, in the concentrations of the present investigation appreciable quantities of $HSO_4^-$ are also present. In this way it is also possible to account for the faster rates of hydrogen exchange observed for the reactions in aqueous sulphuric acid relative to aqueous perchloric acid.

The observation of relatively constant hydrogen isotope effect of these exchange reactions is in line with the suggestion of Challis and

Table-8 Kinetic Hydrogen Isotope Effects

| Substrate | Catalyzing acid | -[$H_o$]range | $K_2^H/k_2^D$ |
|---|---|---|---|
| (4-$^*$H)Phenol | $HClO_4$ | 2.33-5.04 | 4.18 ± 1.00 |
| (4-$^*$H)Anisole | $HClO_4$ | 1.81-4.61 | 3.93 ± 0.85 |
| (4-$^*$H)Anisole | $H_2SO_4$ | 1.60-3.81 | 6.50 ± 0.65 |

Millar [29] to regard this kind of behaviour as normal for all proton transfer reactions. However, since there is enough reason to believe that the primary isotope effects depend upon pK even in aromatic substitution reactions [30] as implication of the constancy of the $k_2^H/k_2^D$ ratios over the wide ranges of acidity of the catalyzing acids may be deduced in terms of the base strength of water. In dilute aqueous solution a value accepted for pK $H_3O^+ = -1.75$. However, other estimates based on acidity function data suggest [31] that pK $H_3O^+$ is -6.66 in concentrated sulphuric acid. Clearly, if the primary isotope effects are to depend upon $\Delta$ pK of the substrate and the catalyst, our results imply that the base strength of water remains almost constant over the wide acidity range studied both in sulphuric acid as well as in perchloric acid.

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