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The effect of additives on the practical electrolytic separation of hydrogen and deuterium. II. Separation factor at Hg in aqueous and non-aqueous media

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Studies of the effects of additives on the electrolytic H/D separation factor, $S_{H/D}$, previously reported in Part I [2] for Pt and Fe electrodes, are extended to the case of Hg for which the mechanism of cathodic H_2 evolution is well established. The behaviour of urea and guanidine was investigated. In the case of urea, the separation factor at Hg is enhanced but decreases with increasing current density or cathodic potential. The dependence of $S_{H/D}$ on current density can be correlated with the diminishing surface excess of urea with increasing negative potential. Experiments with proton sources other than H_2O in liquid water were investigated by making measurements of $S_{H/D}$ from solutions of H_2O/HOD, CH_3COOH/CH_3COOD and CF_3COOH/CF_3COOD in CH_3CN with $NaClO_4$ as electrolyte. An interesting inverse H/D isotope effect arises with trifluoroacetic acid (TFA) as proton source; the effect is interpreted in terms of competitive reactions of H and D with TFA rather than unusual bonding and vibrational characteristics of the TFA activated complex. The results suggest that useful isotopic separations can be made by use of selective competitive reactions. A kinetic analysis of the inverse isotope effect is given.

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1. Introduction

The study and interpretation of the electrolytic H/D separation factor S has played an important role in understanding the mechanisms of the cathodic H_2 evolution reaction (HER) at various metals, and the role and extent of coverage, $_H$, of adsorbed H in the cathodic process. A fuller understanding of the factors that determine S, that could lead to enhanced values up to the theoretical maximum [1, 2] of about 12–13, are also of great importance for developments in nuclear reactor technology of the CANDU type where reliance is made on heavy water heat exchange and moderation using uranium with the natural 235/238 isotopic abundance ratio. Large volumes of 99·8% D_2O are required for this operation so that optimization of S values for the electrolytic up-grading process is of great importance for the economics of the operation.

The mechanism of the HER at Hg electrodes has been considered as understood, where the proton discharge step

$$M + H_3O^+ + e \rightarrow MH_{ads} + H_2O\ (\theta_H \ll 1) \quad (1)$$

is rate-determining, followed by fast desorption in the step

$$MH_{ads} + H_3O^+ + e \rightarrow H_2 + M \quad (2)$$

since θ_H is very low so that the H recombination pathway is not competitive with Reaction 2. However, on the question of the interpretation of S for Hg, conflicting views have been presented by Horiuti [3] and by Keii and Kodera [4] who regard the rate-determining step as discharge of the H_2^+ ion in the mechanism

$$M + H_3O^+ + e \rightarrow MH_{ads} \xrightarrow{H^+} H_2^+ \quad (3)$$

$$H_2^+ + e \rightarrow H_2. \quad (4)$$

In fact, Keii and Kodera [4] have argued that the simple discharge step, Equation 1, would give $S \simeq 12$–13 and not the observed value of about 3 at Hg which they attribute to the mechanism in Equations 3 and 4. Criticisms of this conclusion have, however, already been published [5, 6, 7] on the basis of; (a) lack of observation of an appreciable adsorption pseudo-capacitance at Hg due to potential-dependent coverage by H or H_2^+, and (b) neglect of the contribution of the asymmetric stretch mode in the H_3O^+–Hg transition state complex in the calculation of S.

There are other very good reasons which have been widely treated in the literature for accepting the view that the mechanism of the HER at Hg in acid solutions is in fact Equations 1 and 2 and not Equations 3 and 4. Hence Hg can be regarded as a kind of reference-standard case for investigating effects of changing conditions on S for a metal having a 'known mechanism' with negligible coverage of its surface by H.

In a previous paper [2], we have discussed the effect of additives which have been used in practical deuterium separation on the values of S obtained at Fe and Pt electrodes. Significant enhancement of S towards the theoretical maximum value was demonstrated using urea and guanidine and these effects were shown to arise, in part, on account of changes in adsorption of the H intermediate. In the present paper we examine; (a) the behaviour of such additives at the Hg electrode where effects associated with coverage by adsorbed H are likely to be absent or less important, and the HER mechanism is known; and (b) the behaviour of Hg in a non-aqueous, aprotic solvent CH_3CN with water, acetic and trifluoroacetic (TFA) acids as three proton-donor solutes of different acidities. In the case of TFA as the proton source, interesting *inverse* isotope effects are observed, favouring preferential generation of D over H in the product gas mixture ($S < 1$).

2. Experimental

2.1. *Separation factor measurements*

The measurements of S were performed as previously described [2], using a special cell connected to a vacuum system with a Toepler pump gas-sampling arrangement. Gas samples were analysed by means of a gas chromatograph [2] using a 15 ft chromium-activated Al_2O_3 column at liquid N_2 temperature. This method has been described previously [2]. Determinations of S were made at various controlled constant current densities and the corresponding electrode potentials were recorded as in previous work.

2.2. *Current–potential relations*

The dependence of log (current density) on potential (Tafel relations) was recorded for the Hg electrode under the same conditions as those for the S measurements.

2.3. *Solutions*

Water was prepared by alkaline permanganate distillation, followed by pyrodistillation. H_2O/D_2O mixtures were prepared from this water and 99·8% D_2O which, as shown previously [2], is already of high purity (with respect to organic and metal impurities) on account of the repetitive electrolytic and gas-combustion steps involved in its preparation.

Acetonitrile used for the non-aqueous solvent study was exhaustively purified by the technique of O'Donnell [8], followed by a slow distillation through a tall fractionating column. TFA was distilled twice and the fraction boiling at 72–73° C was collected.

Glacial acetic acid (reagent grade) was purified by refluxing for 10 h with an excess of chromium trioxide to remove any easily oxidizable materials. The acid was then distilled from the solid residue. The distillate was redistilled and the fraction boiling at 118° C was collected.

Deuteroacetic acid, d-1 was prepared from acetic anhydride and 99·8% D_2O; AR grade acetic anhydride was added carefully to an appropriate quantity of D_2O, shaken well and distilled. The distillate was distilled again and the fraction boiling around 118° C was collected and stored in a sealed flask.

Trifluoroacetic acid-d was prepared by adding the appropriate amount of D_2O to trifluoroacetic anhydride (Eastman grade) followed by distillation. The distillate was redistilled and the fraction boiling at 71–73° C was collected.

In the non-aqueous solution work, sodium perchlorate was used as the supporting electrolyte. The Anachemia anhydrous material, dried in a vacuum oven for 12 h, was made up in the CH_3CN to a concentration of 0·2 M.

Table 1. Effect of guanidine on $S_{H/D}$ at Hg in 1 N aqueous H_2SO_4, 50% D

Current density ($A\,cm^{-2}$)	*Guanidine concentration* *0·00 M*	*0·17 M*
0·001	4·20 + 0·15*	3·70 + 0·11*
0·005	4·88 + 0·78	4·22 + 0·15
0·010	4·26 + 0·24	4·03 + 0·20
0·020	4·15 + 0·05	4·63 + 0·41
0·050	3·88 + 0·20	4·12 + 0·36
0·10	3·74 + 0·02	4·44 + 0·31

* The data shown are the means of 3 or 4 separate runs.

2.4. *Hg electrodes*

The mercury electrodes were prepared by amalgamating gold wires. A 'new' Hg surface was generated for each run by dipping the initially amalgamated surface in a pool of purified Hg. Amalgamated gold electrodes are known to give the same electrode kinetic behaviour as liquid Hg provided they have not become aged or exposed to the atmosphere for extended periods of time.

2.5. *Electrical measurements*

Conventional electronic equipment was used, as referred to in previous papers. A.c. modulated cyclic voltammetry with a lock-in phase-sensitive amplifier was used for some capacity measurements at the Hg electrode based on procedures previously discussed by Barker [9] and by Sevčik [10].

2.6. *Solutes*

Guanidine and urea, used as additives, were prepared as described previously [2]. H_2SO_4 as electrolyte (1 M) was the BDH Aristar material.

3. Results

3.1. *Values of S in aqueous urea and guanidine solutions*

The mean values of S for Hg in 1 N aqueous H_2SO_4 with and without guanidine are shown in Table 1 for six current densities. Corresponding data were also tabulated for urea solutions (Table 2). Addition of guanidine (Table 1) can hardly be said to have any significant effect on S at Hg although the trend of S with increasing current density seems to be in the opposite direction to that with urea. Urea, on the other hand, especially at high concentrations (5·0 M, 10·0 M),

Table 2. Values of $S_{H/D}$ for Hg electrodes in 1 N aqueous H_2SO_4 (25° C) with urea

Current density ($A\,cm^{-2}$)	*Urea concentration* *0·0 M*	*1·0 M*	*5·0 M*	*10·0 M*
0·001	4·20 + 0·15*	5·39 + 0·47*	5·70 + 0·38*	6·08 + 0·43*
0·005	4·88 + 0·78	4·77 + 0·31	5·39 + 0·29	5·56 + 0·28
0·01	4·26 + 0·24	4·81 + 0·31	5·30 + 0·35	5·36 + 0·29
0·02	4·15 + 0·05	4·72 + 0·10	5·07 + 0·15	5·23 + 0·23
0·05	3·88 + 0·20	5·26 + 0·08	4·73 + 0·08	4·89 + 0·13
0·10	3·74 + 0·07	4·50 + 0·16	4·70 + 0·11	4·89 + 0·33
0·20	3·72 + 0·10	3·97 + 0·10	4·39 + 0·27	4·74 + 0·10

* The data shown are the means of 3 or 4 separate experimental results.

has an appreciable effect on S, increasing it by about 25% especially at low current densities (Table 2). These effects are similar in direction to those reported for Fe in the previous paper [2].

Comparison with the effects of urea on the Tafel lines for the HER at Hg shows that in strong urea solutions there is a tendency for the increase in S (Fig. 1) to become less significant as current densities, where a small inflection is observed in the log (current density)–potential relation, are approached. The kink (wave) in the log (current density)–potential plots is substantially dependent on urea concentration above about 0·1 M and so is not a reduction wave for urea itself. Despite the high dipole moment of urea, the inflection in the log i versus V profiles may be due to desorption of urea at sufficiently negative potentials, as indicated by the work of Parsons, Peat and Reeves [11] on urea adsorption.

The effect of urea on S for Hg, shown in Fig. 1, is to increase the value of S, but to a smaller extent with diminishing current density. While there is some substantial spread in the data for the effect of guanidine on S, the trend seems to be in the opposite (Fig. 1) direction from that with urea with increasing current density. Since in the acid solutions employed, guanidine will be present as the guanidinium ion which will tend to be more strongly adsorbed with increasing potential, while urea will remain uncharged, the contrasting directions of the effects of urea and guanidine with increasing current density are consistent with expected adsorption behaviour.

3.2. *Values of S from discharge of proton donors in a non-aqueous, aprotic supporting solution*

In the water solvent itself, the strong structural H-bond interactions impose special constraints on a water molecule or H_3O^+ undergoing discharge to produce H and H_2. In this part of the work, it was thought to be of interest to evaluate S for the HER under conditions where the H is not discharged from bulk solvent or from H_3O^+ in bulk water. Three systems were studied, H_2O, CH_3COOH and CF_3COOH and their D-analogues at 5·0 M concentration in excess anhydrous CH_3CN. In these solutions, H_2O, CH_3COOH and CF_3COOH are proton donors of varying acidity and will not be H-bonded in the same way as in the respective pure liquids.

The data for S are recorded in Table 3 for 50% D in the proton sources. In the case of TFA, both 10% and 50% D-enriched acid was used. S remains almost constant with current density for evolution of H_2 and HD from CH_3COOH/D in CH_3CN (Fig. 2) but from H_2O/HOD there is a

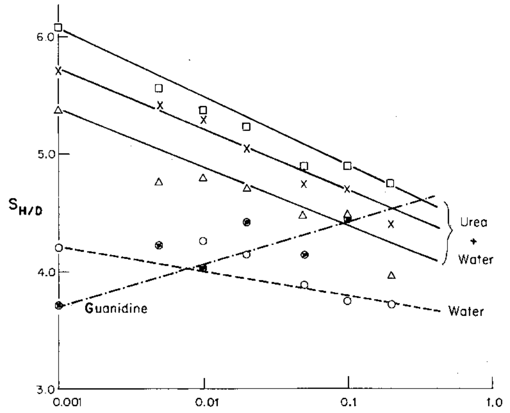


Fig. 1. Values of $S_{H/D}$ at Hg for various current densities for H_2/HD evolution at Hg, 298 K, from aqueous 0·5 M H_2SO_4 and from this solution with additions of urea or guanidine: ○, water solutions; ⊗, guanidine (0·17 M) solution; △, urea 1 M solution; X, urea 5 M solution; □, urea 10 M solution.

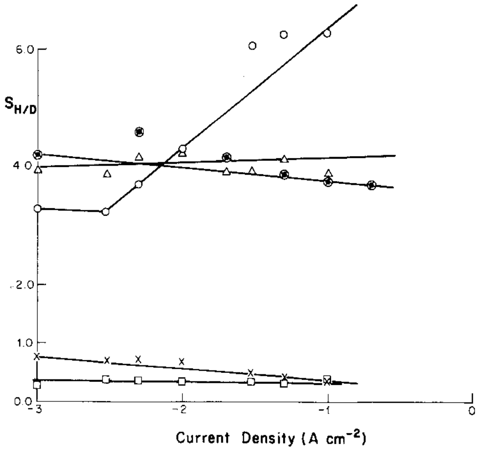


Fig. 2. Dependence of $S_{H/D}$ on current density of H and D production at Hg from water and other proton donors in water and acetonitrile: ⊙, 0·5 M aqueous H_2SO_4; ○, 5 M H_2O/D_2O (50%) in CH_3CN, 0·2 M $NaClO_4$; △, 5 M CH_3COOH/CH_3COOD (50%) in CH_3CN, 0·2 M $NaClO_4$; X, 5 M CF_3COOH/CF_3COOD (10% D) in CH_3CN, 0·2 M $NaClO_4$; □, 5 M CF_3COOH/CF_3COOD (50% D) in CH_3CN, 0·2 M $NaClO_4$.

Table 3. $S_{H/D}$ *for* $H_2/HD/D_2$ *evolution from proton donors in acetonitrile medium at Hg electrode*

Current density ($A\,cm^{-2}$)	5 M CH_3COOH/CH_3COOD	*Mean* $S_{H/D}$	5 M H_2O/D_2O	*Mean* $S_{H/D}$
0·001	4·00, 3·93, 4·20	4·03 + 0·17	3·45, 3·10, 3·38	3·31 + 0·21
0·003	4·14, 3·83, 3·76	3·91 + 0·23	3·29, 3·33, 3·17	3·26 + 0·09
0·005	3·92, 4·38, 4·28	4·19 + 0·27	3·93, 3·62, 3·60	3·72 + 0·21
0·010	4·43, 3·94, 4·41	4·26 + 0·32	4·08, 4·64, 4·19	4·30 + 0·34
0·030	3·71, 3·84, 4·19, 4·06	3·95 + 0·24	6·17, 6·09, 5·99	6·08 + 0·09
0·050	3·81, 4·22, 4·39	4·14 + 0·33	6·31, 6·33, 6·12	6·25 + 0·13
0·100	3·77, 3·78, 4·21	3·92 + 0·29	6·87, 6·66, 6·77	6·27 + 0·11
Current density ($A\,cm^{-2}$)	5 M CF_3COOH/CF_3COOD (*10% D*)	*Mean* $S_{H/D}$	5 M CF_3COOH/CF_3COOD (*50% D*)	*Mean* $S_{H/D}$
0·001	0·74, 0·75, 0·77	0·75 + 0·02	0·28, 0·23, 0·29	0·27 + 0·04
0·003	0·78, 0·72, 0·70	0·73 + 0·05	0·39, 0·38, 0·37	0·38 + 0·01
0·005	0·75, 0·75, 0·72	0·74 + 0·02	0·36, 0·37, 0·37	0·37 + 0·01
0·01	0·71, 0·77, 0·63	0·70 + 0·07	0·35, 0·37, 0·34	0·35 + 0·02
0·03	0·52, 0·51, 0·50	0·51 + 0·01	0·34, 0·35, 0·36	0·35 + 0·01
0·05	0·39, 0·40, 0·40	0·40 + 0·01	0·34, 0·31, 0·28	0·39 + 0·02
0·10	0·38, 0·37, 0·36	0·37 + 0·01	0·39, 0·41, 0·37	0·39 + 0·02

marked decrease with increasing current density (Fig. 2), more so than in 'pure water' itself (Figs. 1 and 2).

The most interesting result is that for TFA as proton source. In this case, a large *negative* isotope effect is observed and D is preferentially evolved in the $H_2/HD/D_2$ product gas mixture. Because of the possible importance of this unusual result, gas mixture standards of known composition were re-run in the chromatograph throughout this series of experiments to verify that the chromatograph was performing normally. Separation experiments both from TFA enriched 10% and 50% in D on the carboxyl group confirmed the fractional separation factor and the continuing satisfactory performance of the chromatographic separation. The 10% D-solution gave H_2 and HD while the 50% D-solution gave only HD and D_2 (Fig. 3). Normally from H_2O solutions of similar composition (see [2]) involving 50% D, where the water is mainly HOD, very little D_2 is detectable and a normal isotope effect gives $H_2 > HD$ in the product mixture.

Inverse isotope effects are of general theoretical interest in proton transfer kinetics since they arise from a larger H/D zero-point energy difference in the transition state than in the initial state and associated different partition functions from which the isotopic differences of $\Delta G^\ddagger$ or $\Delta S^\ddagger$ can be evaluated.

In the case of electrolysis from CH_3CN with H_2O/HOD as the proton source, it appears that Na metal (Na/Hg) is first deposited and then reacts with the water. A visible deposit can be seen after some minutes following commencement of electrolysis at 100 mA cm^{-2}. Upon interrupting the current visible H_2/HD evolution continues, reproducibly from experiment to experiment, for some time until the deposit disappears. This is consistent with deposition of Na-metal at the electrode. In this connection, it is to be noted that the mechanism of the HER at Hg in ordinary aqueous alkaline solutions proceeds [12] by the initial formation of alkali metal amalgam rather than direct discharge from water. The subsequent reaction of the Na-amalgam with H_2O in the CH_3CN then gives H_2 (cf. [10]) presumably through the normal reaction steps in the H_2-evolution reaction at Hg with the deposition of H as a weakly adsorbed intermediate. When acetic acid is the proton source neither a deposit is seen nor does gas evolution continue after termination of the current. Hence, H_2/HD evolution in this case probably proceeds directly from $CH_3COOH/$

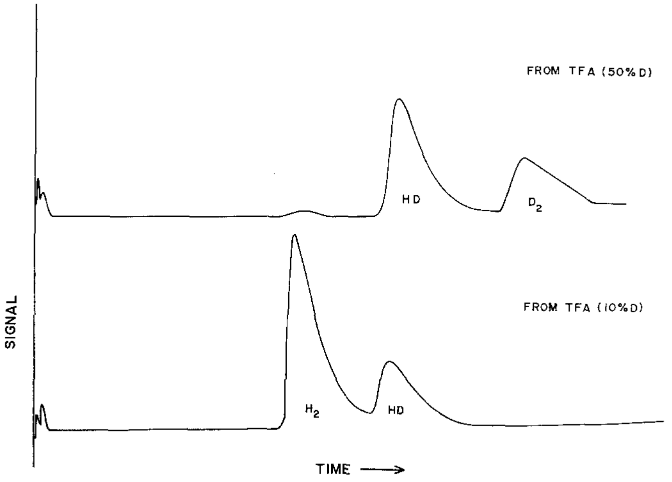


Fig. 3. Typical $H_2/HD/D_2$ chromatograms for cathodic gas evolution from 5 M solutions of TFA (10 and 50% D) as proton donor in CH_3CN, 0·2 M $NaClO_4$.

CH_3COOD rather than via the amalgam. This is consistent with the stronger acidity of acetic acid compared with that of water.

These different conditions may account for the different extents of dependence of S on current density for H_2O/HOD and CH_3COOH/CH_3COOD shown in Fig. 2.

4. Discussion

4.1. *Effects of urea and guanidine*

Recognizing the uncertainties of quantitative theoretical interpretations of electrochemical S values in relation to mechanisms of the HER, we shall restrict ourselves here to only a qualitative discussion of the effects of urea and guanidine as additives.

Two types of effect of urea on S could arise:
(i) An influence of the local concentrations of the H/D proton sources (H_3O^+, H_2DO^+, HD_2O^+ in acid solution) by the presence of urea in the double layer by participation in the H/D exchange process leading to the distribution of H and D amongst the various hydronium ion species in the double layer;
(ii) Participation of urea and its D-exchanged analogues in the discharge process itself, leading to H_2/HD evolution.

While we were able to show that urea in the molten state (135° C) containing 0·01 M KOH could indeed by electrolyzed to give H_2 at a cathode, it seems unlikely that in excess water containing H_3O^+ at 1·0 N concentration, H_2/HD will originate by discharge from urea which is a very weak acid (and base).

The effect of urea on S must hence originate by an indirect mechanism. Drop-time studies of adsorption at the Hg electrode indicate that urea is significantly adsorbed and its surface excess tends to decrease with increasing negative charge, $-q_M$, on the Hg surface (Fig. 4). Presumably, due to its large dipole moment, it will also be preferentially oriented at Hg with the carbonyl group away from the Hg surface at appreciable negative q_M.

It is known that urea interferes with the H-bonded structure of water [13]. It may also participate in the solvation [14] of H_3O^+ in the double layer, changing the state of H_3O^+ prior to discharge. It is unlikely, however, to become

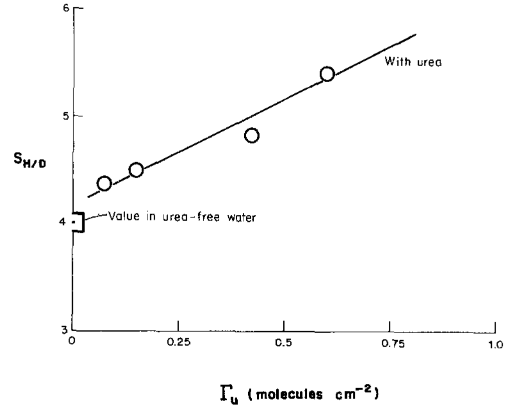


Fig. 4. Dependence of $S_{H/D}$ at 0·02 A cm^{-2} at Hg in urea–water solutions (0·5 M H_2SO_4) on surface excess of urea Γ_u from [11].

itself protonated under the experimental conditions employed due to the excess of water and the relatively low concentration of H^+ (mole fraction $< 0{\cdot}02$).

A recent interpretation of S values for the HER by Krishtalik [15, 16] gives the conclusion that the observed S behaviour, compared at different metals but at the same surface charge, must be consistent with a mechanism of the electron-transfer activation step in which hydration shell reorganization is preferred to stretching of a particular OH bond in H_3O^+ (Butler representation [17]). It seems quite possible for urea to have an effect on the hydration shell reorganization process since the equilibrium solvation of ions in water and urea solutions has been compared by a number of workers (e.g. [14]) and appreciable values for the thermodynamic transfer functions for ions from water to urea–water mixtures are found.

The decreasing effect of urea at a given concentration on S as current density (and hence negative potential and q_M) is increased finds an explanation in terms of the observed [11] decrease of surface excess of urea, Γ_u, at a given concentration, with increasing $-q_M$. The dependence of S on Γ_u is shown in Fig. 4, based on interpolations and some extrapolation of the data of Parsons, Peat and Reeves [11]. As Γ_u decreases with increasing negative potential at higher current density, it becomes less effective in modifying the reorganization process necessary for H_3O^+ activation and discharge.

In general, urea seems to enhance the trend of decreasing S with increasing current density already observed in the pure aqueous acid itself (Fig. 1) and previously by Salomon and Conway [18] for Hg in aqueous $HClO_4$ and H_2SO_4 solutions. Both a surface excess effect due to changing Γ_u and an orientation effect seem plausible since there will always be competition between orientating effects of the field due to excess charge, q_M, and of the field due to ions (H_3O^+, H_2DO^+) in the double layer. At Pt, a similar direction of change of S with increasing current density is observed [2] at high urea concentrations but in that case a different mechanism for the HER is involved and effects on H coverage are significant, as indicated experimentally [2]; of course, at Pt, $\theta_H \geqslant 1$ over the potential range for cathodic H_2 evolution.

4.2. *Inverse isotope effect in proton discharge from TFA in CH_3CN*

The possibility of the effects of additives on S, originating from their acting as alternative proton sources to the solvent or H_3O^+, was considered in Part I [2] and earlier in this paper. It therefore seemed of interest to investigate the behaviour of a series of proton sources, other than liquid water itself or H_3O^+, with regard to the resulting S values. In work on homogeneous proton-transfer processes, Bell and Goodall [19] had investigated the magnitude of kinetic H/D isotope effects and predicted that a maximum in the H/D isotope effect in proton transfer from an acid XH to a base Y would be expected when

$$\Delta pK = pK(XH) - pK(YH) \simeq 0 \qquad (5)$$

i.e. when a symmetrical transition state in proton-transfer would arise. Such a relation was observed experimentally [19] in a series of 20 acid/base pairs. In aqueous media at electrodes there is very little range over which the pK of the system can be varied since water itself, or H_3O^+, from which discharge may occur is always present. The base character of the electrode may be varied a small amount in proportion to the potential-dependent surface charge density, q_M, as we have discussed previously [20]. By using an aprotic solvent with various proton sources as solutes, a wider range of acidic properties of the proton source can be investigated. H_2O/D_2O, CH_3COOH/CH_3COOD and CF_3COOH/CF_3COOD systems in acetonitrile were employed (cf. Fig. 2).

The original purpose of carrying out determinations of S in a non-aqueous solvent was to establish if there was a relation between acid strength of a series of proton donors and the values of S following the predictions of Bell and Goodall [19] for homogeneous reactions.

At appreciable current densities it is found that the order of increasing S from these systems is $H_2O/D_2O > CH_3COOH/CH_3COOD > CF_3COOH/CF_3COOD$, with the latter system giving the interesting inverse isotope effect. An inverse kinetic isotope effect can only be explained in terms of; (a) the transition state having a zero-point energy sum [21, 22] that gives a larger difference of zero-point energies for H and D species in the transition state than in the initial state, so that D transfer is preferred, and/or (b) a transition state which is 'looser' for D than H, giving a larger entropy for the D-state, so that its formation is favoured over that of the H-complex.

The pK difference between CH_3COOH and CF_3COOH, while appreciable, would not seem to be sufficient to lead to a complete inversion of the electrochemical kinetic isotope effect associated with the observed fractional S values. In Bell and Goodall's work [19], for example, kinetic isotope effects (k_H/k_D values) range from about 1·5–12 but a very wide ΔpK range was involved, − 8–+ 14, and no inverse isotope effects were observed.

The rarity of inverse kinetic H/D isotope effects and the difficulty of explaining the present result with TFA in CH_3CN in terms of bonding in the transition state in comparison with that in the initial state led us to consider the following alternative, and we believe plausible, explanation of the effect.

An inverse apparent isotope effect in S for electrolytic generation of H_2, HD and D_2 could arise from normal isotope effects in a parallel competing reaction. It is known [24] that TFA can be electrolytically reduced to less fluorinated acetic acids and eventually to acetic acid itself. Hence, if pathways

$$CF_3COOH + H^+ + 2e \rightarrow CF_2HCOOH + F^-$$

or

$$H^+ + e + Hg \rightarrow HgH \ (\text{low } \theta_H)$$

coupled with

$$CF_3COOH + 2HgH \rightarrow CF_2HCOOH + HF$$

existed which are competitive with the electrolytic processes

$$H^+ + e(Hg) \rightarrow HgH$$

$$HgH + H^+ + e \rightarrow H_2$$

which lead to H_2 evolution and normal values of S, then a normal H/D isotope effect in the reduction of TFA (reduction by H faster than by D) could lead to preferential evolution of the D-containing gaseous species, HD and D_2. Then the alternative pathways

$$\begin{tikzcd} & H_2 \quad (6) \\ HgH_{ads} \arrow[ur, "H^+ + e"] \arrow[dr, "TFA"'] & \\ & CF_2HCOOH \quad (7) \end{tikzcd}$$

will give an inverse isotope effect in the yield pattern of $H_2/HD/D_2$ in Route 6 if a normal kinetic isotope effect arises in Equation 7 by preferential reduction of TFA by H rather than by D, assuming TFA reduction is not diffusion-controlled (the TFA concentration was 5 M). The observed inverse isotope effect in $H_2/HD/D_2$ evolution need not then be explained in terms of unusual bonding in the transition state for proton discharge.

An experiment was performed to see if Pathway 7 was chemically significant. Electrolysis of a 5 M TFA solution in CH_3CN (0·2 M $NaClO_4$) at a mean current of 75 mA at an Hg electrode for 10 h gave a progressively increasing yield of CF_2HCOOH in solution as indicated by periodic n.m.r. spectral measurements on samples from the solution. After 10 h, the concentration of CF_2HCOOH decreased again presumably due to the successive formation of fluoroacetic acid and acetic acid itself. The CF_2HCOOH was identified by appearance of an n.m.r. line pattern characteristic of H–^{19}F coupling effects.

The fact that electrolysis of CH_3COOH/CH_3COOD in CH_3CN gives a normal isotope effect (Fig. 3), and acetic acid cannot undergo a reduction reaction such as Equation 7, confirms indirectly the likely origin of the (apparent) inverse isotope effect in the case of electrolysis of TFA.

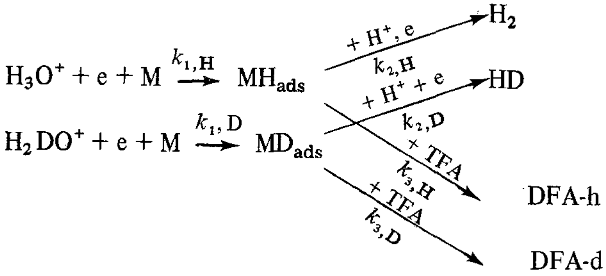
It is necessary that the current efficiency for TFA reduction be comparable with that for $H_2/HD/D_2$ evolution, i.e. 50% or so, if an apparent inverse isotope effect of the magnitude observed (0·75–0·3) is to be explained by the competitive reduction mechanism. In the absence of diffusion control in Equation 7, the current efficiency and hence the apparent kinetic isotope effect corresponding to the measured S will depend on the relative values of the rate constants for Steps 6 and 7 and the H/D kinetic isotope effects in these steps. This can be shown by a kinetic analysis given below.

Various attempts have been made recently to selectively photo-activate a bond in a molecule that carries an isotopically distinguished atom, e.g. H or D in HCHO. The activation is usually carried out at an appropriately tuned frequency using an infra-red laser. The D- or the H-containing molecule, depending on the frequency used, is then promoted to react in a highly selective way with resulting isotopic separation in the photo-reaction products.

The present results with TFA suggest another way for selective production of isotopically related product molecules, by providing a competitive isotopic reduction pathway leaving a favoured relative rate of production of the desired isotopically characterized product.

4.3. *Kinetic analysis of competitive reactions leading to an inverse isotope effect in $H_2/HD/D_2$ evolution*

We consider the following pathways, first as a general example, assuming the HER proceeds by the mechanism of Equations since recombination of H_{ads} is not the favoured desorption pathway at Hg because $\theta_H \ll 1$:



(1, 2, 6)

(1, 2, 6)

(8)

(7)

After discharge of the proton source, written in the above scheme as H_3O^+, H_2DO^+, the adsorbed intermediate H can form H_2 or HD (or D_2 depending on D-content of the original 'proton' source) by Equation 2. When a competitive reactant, TFA in this case, is present, removal of adsorbed H and D can occur competitively by the lower branch pathways in scheme 8 to form difluoracetic acid-h or -d, or more reduced acids down to CH_3COOH. While the above scheme is written for simplicity as involving H_3O^+ as the proton source, equivalent schemes for the discharge step can be written for H_2O and HOD as the proton source, or for CF_3COOH/CF_3COOD or CH_3COOH/CH_3COOD without changing the kinetic scheme of the competitive processes written above (Scheme 8). Of course, in the case of H_3O^+, H_2DO^+ etc., or with H_2O and D_2O, the appropriate statistical factors [25], related to the numbers of H and D atoms in the molecules, must be included in the kinetic equations. For simplicity, we shall consider conditions of low D content so that the principal source of H is H_3O^+ and of D, H_2DO^+.

The steady-state condition for the H and D coverages in the pathways shown above may be written*, for a given appreciable constant overpotential, as

$$\begin{aligned}\frac{d\theta_H}{dt} &= 3k_{1,H}C_{H^+} - 3k_{2,H}\theta_H C_{H^+} \\ &\quad - 3k_{3,H}\theta_H C_{TFA} \\ &= 0\end{aligned} \tag{9}$$

and

$$\begin{aligned}\frac{d\theta_D}{dt} &= k_{1,D}C_{D^+} - 3k_{2,D}C_{H^+} \\ &\quad - 3k_{3,D}\theta_D C_{TFA} \\ &= 0\end{aligned} \tag{10}$$

where C is concentration, and it is assumed that for Hg; θ_H, $\theta_D \ll 1$, so that $1-\theta_H$ or $1-\theta_D$ in the discharge-step rate terms are very close to unity. Also it is assumed that recombination between adsorbed H and D to form HD is a negligible pathway. The rate expressions are also written for $C_{H^+} \gg C_{D^+}$, so that the principal desorption pathways to form H_2 and HD proceed mainly with the further discharge of H^+ (or of H from the H-proton source); the rate expressions thus become a little simplified. Then, from Equations 9 and 10

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*For clarity, statistical factors [25] have been separated in the rate-constant terms.

$$\theta_{\mathrm{H}} = 3k_{1,\mathrm{H}}C_{\mathrm{H}^+}/(3k_{2,\mathrm{H}}C_{\mathrm{H}^+} + 3k_{3,\mathrm{H}}C_{\mathrm{TFA}}) \quad (11)$$

and

$$\theta_{\mathrm{D}} = k_{1,\mathrm{D}}C_{\mathrm{D}^+}/(3k_{2,\mathrm{D}}C_{\mathrm{H}^+} + 3k_{3,\mathrm{D}}C_{\mathrm{TFA}}). \quad (12)$$

Also, for the velocities of the desorption steps (Reaction 2) forming H_2 and HD from H and D

$$v_{\mathrm{H}_2} = 3k_{2,\mathrm{H}}\theta_{\mathrm{H}}C_{\mathrm{H}^+} \quad (13)$$

and

$$v_{\mathrm{HD}} = 3k_{2,\mathrm{H}}\theta_{\mathrm{D}}C_{\mathrm{H}^+} \quad (14)$$

i.e. the ratio $v_{\mathrm{H}_2}/v_{\mathrm{HD}}$ which characterizes the isotopic separation of H and D in the evolved gases is

$$v_{\mathrm{H}_2}/v_{\mathrm{HD}} = (k_{2,\mathrm{H}}/k_{2,\mathrm{D}})(\theta_{\mathrm{H}}/\theta_{\mathrm{D}}). \quad (15)$$

This ratio is related to S through the ratio of concentrations of isotopic proton-source molecules in the initial state, and to the appropriate statistical factors [21, 22, 25].

Then, introducing the ratio $\theta_{\mathrm{H}}/\theta_{\mathrm{D}}$ from Equations 11 and 12, gives for the condition when competition by TFA is important

$$(v_{\mathrm{H}_2}/v_{\mathrm{HD}})_{\mathrm{TFA}} = \frac{k_{2,\mathrm{H}}}{k_{2,\mathrm{D}}}\,\frac{3k_{1,\mathrm{H}}C_{\mathrm{H}^+}}{k_{1,\mathrm{D}}C_{\mathrm{D}^+}}\left(\frac{k_{2,\mathrm{D}}C_{\mathrm{H}^+} + k_{3,\mathrm{D}}C_{\mathrm{TFA}}}{k_{2,\mathrm{H}}C_{\mathrm{H}^+} + k_{3,\mathrm{H}}C_{\mathrm{TFA}}}\right) \quad (16)$$

which determines the competitive effect of TFA on the relative rates of H_2 and HD production.

In the absence of a competitive reactant for adsorbed H or D, the ratio $v_{\mathrm{H}_2}/v_{\mathrm{HD}}$ is simply given by

$$v_{\mathrm{H}_2}/v_{\mathrm{HD}} = \frac{3k_{1,\mathrm{H}}}{k_{1,\mathrm{D}}}(C_{\mathrm{H}^+}/C_{\mathrm{D}^+}) \quad (17)$$

since $\theta_{\mathrm{H}}/\theta_{\mathrm{D}}$ is then determined only by

$$\theta_{\mathrm{H}}/\theta_{\mathrm{D}} = \frac{k_{1,\mathrm{H}}C_{\mathrm{H}^+}k_{2,\mathrm{D}}}{k_{1,\mathrm{D}}C_{\mathrm{D}^+}k_{2,\mathrm{H}}} \quad (18)$$

as follows from the steady-state conditions for θ_{H} and θ_{D} when the pathway is Equations 1, 2 and 6 for production of H_2 and HD only, and Equation 1 is rate-determining for both isotopes.

It is then of interest to show the relation between the relative velocities of production of H_2 and HD in the presence and absence of the competing agent, TFA. Thus, we have

$$\frac{(v_{\mathrm{H}_2}/v_{\mathrm{HD}})_{\mathrm{TFA}}}{(v_{\mathrm{H}_2}/v_{\mathrm{HD}})} = \frac{k_{2,\mathrm{H}}}{k_{2,\mathrm{D}}}\left(\frac{k_{2,\mathrm{D}}C_{\mathrm{H}^+} + k_{3,\mathrm{D}}C_{\mathrm{TFA}}}{k_{2,\mathrm{H}}C_{\mathrm{H}^+} + k_{3,\mathrm{H}}C_{\mathrm{TFA}}}\right) (=R) \quad (19)$$

This ratio R may also be written as

$$R = \frac{1 + k_{3,\mathrm{D}}C_{\mathrm{TFA}}/k_{2,\mathrm{D}}C_{\mathrm{H}^+}}{1 + k_{3,\mathrm{H}}C_{\mathrm{TFA}}/k_{2,\mathrm{H}}C_{\mathrm{H}^+}} \quad (20)$$

From this result it is seen that:

(a) When the ratio of $C_{\mathrm{TFA}}/C_{\mathrm{H}^+}$, i.e., the ratio of concentrations of the competitor to that of the proton source is sufficiently large, R is determined simply by the ratio of rate constants $k_{3,\mathrm{D}}k_{2,\mathrm{H}}/k_{3,\mathrm{H}}k_{2,\mathrm{D}}$. If there is a substantial normal H/D isotope effect in the competitive pathway involving TFA, $k_{3,\mathrm{H}}$ will be greater than $k_{3,\mathrm{D}}$ and thus diminish the value of the ratio $v_{\mathrm{H}_2}/v_{\mathrm{HD}}$ from the value that would otherwise arise in the absence of a competing agent. It is seen that apparent inverse isotope effects will arise when the ratio $k_{3,\mathrm{H}}/k_{3,\mathrm{D}} > k_{2,\mathrm{H}}/k_{2,\mathrm{D}}$, i.e. there is a larger H/D isotope effect in the competing reaction than in the normal desorption in Equations 2 and 6.

(b) That when the concentration ratio TFA/H_3O^+ is small and/or the rate constant ratios are small, the the relative velocities of H_2 and HD evolution become the normal value given by Equation 17.

Under the conditions of the present work, TFA is the competitor for reaction with H or D, as well as the proton source at the COOH/D group. Hence the concentration ratio of competitor to proton source in the reaction paths in Equations 2, 6 and 7 is unity in this case. For TFA, the statistical factor is also 1 with respect to H in the molecule. Then Equation 20 becomes simply

$$R = \frac{1 + k_{3,\mathrm{D}}/k_{2,\mathrm{D}}}{1 + k_{3,\mathrm{H}}/k_{2,\mathrm{H}}} \quad (21)$$

which is determined only by rate constant ratios.

In the present case, with TFA as the proton donor, the reactions to form H_2 and HD are primarily

$$CF_3COOH + Hg + e \rightarrow CF_3COO^- + HgH_{ads} \quad (22)$$

and

$$HgH_{ads} + CF_3COOH + e \rightarrow H_2 + CF_3COO^- \quad (23)$$

with the corresponding reactions for D-species, while the competing reactions originate presumably first from a reduction pathway involving nucleophilic displacement [24] of F as F^- with formation of a radical

$$CF_3COOH + e \rightarrow CF_2COOH + F^- \qquad (24)$$

followed by the competing steps

$$CF_2COOH + \begin{array}{c} HgH_{ads} \\ \text{or} \\ HgD_{ads} \end{array} \longrightarrow \begin{array}{c} CF_2HCOOH \\ \text{or} \\ CF_2DCOOH \end{array} + \begin{array}{c} H_2 \\ \text{or} \\ HD \end{array} \qquad (25)$$

Reduction of the carboxyl group, known at Pt [23], is also a possible but less likely step. Direct abstraction of F by H to form HF, followed by uptake of H or D by the resulting free radical seems less likely on bond-energy grounds.

Bearing in mind that the value of $S_{H/D}$ for CH_3COOH/CH_3COOD in CH_3CN is about 3 while $S_{H/D}$ in the TFA solution is reduced to about 0·7, it is necessary that the ratio of rate constants in Equation 20 be about 4·3/3 since the concentration ratio of competitor to proton source (the H on − COOH) is unity but the statistical factor with respect to F atoms for reduction is 3.

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