THE REACTIVITY OF HYDROXYL RADICALS IN AQUEOUS SOLUTION

PART 2.—RELATIVE REACTIVITIES WITH HYDROGEN, DEUTERIUM AND HYDROGEN DEUTERIDE

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The yields have been measured of ferric ion obtained from aqueous solutions of ferrous perchlorate and hydrogen peroxide acidified with perchloric acid and containing either hydrogen, hydrogen deuteride or deuterium, and oxygen. The following reactivity ratios are obtained :

$$k_{\rm OH + H_2}/k_{\rm OH + Fe^{2+}} = (14 \pm 6) \exp(-2.7 \pm 0.3 \text{ kcal}/RT),$$

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$$OH + D_2/k_{OH} + Fe^{2+} = (16 \pm 6) \exp(-3.4 \pm 0.2 \text{ kcal}/RT)$$

It is concluded that the OH radical reacts with hydrogen by bond-breakage rather than by electron transfer.

In part 1 of this series, it was shown that at 25°C the rate constant k_1 for the reaction of hydroxyl radicals with hydrogen molecules is about one-sixth of the value of the rate constant k_2 for the reaction of these radicals with ferrous ion :

$$OH + H_2 \xrightarrow{k_1} H_2O + H, \tag{1}$$

$$OH + Fe^{2+} \rightarrow Fe^{3+} + OH^{-}.$$
 (2)

If, as is usually considered to be the case, reaction (2) is an extremely rapid electrontransfer process then the question arises as to whether reaction (1) is also an electrontransfer process and should be more correctly written as

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$$OH + H_2 \to OH^- + H_2^+,$$
 (1')

$$\mathbf{H}_{2}^{+} \rightleftharpoons \mathbf{H}^{+} + \mathbf{H}.$$
 (3)

The existance of the entity H_2^+ and the equilibrium (3) has been postulated by Weiss ² and has received considerable experimental support. The most direct way of discrimination between reactions (1) and (1') is to study the effect of isotopic substitution on the frequency factor and energy of activation, and in this paper we describe experiments carried out to measure the values of the ratio k_1/k_2 for hydrogen, deuterium and hydrogen deuteride as precisely as possible at different temperatures.

The principle of the method of measurement of k_1/k_2 is that already described,¹ namely that, when ferrous ion and hydrogen peroxide react in aqueous solution at pH < 2 in the presence of hydrogen and oxygen, the relation

$$F.E._{Fe^{3+}} = \frac{\Delta[Fe^{3+}]^{H_2} - \Delta[Fe^{3+}]^{\circ}}{\Delta[Fe^{3+}]^{\circ}} = \frac{k_1[H_2]}{k_2[Fe^{2+}]},$$
(4)

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holds if the initial hydrogen peroxide concentration, $[H_2O_2]_0$, is an order of magnitude smaller than the mean ferrous ion concentration during the reaction. F.E._{Fe³⁺} is called the *fractional excess of ferric ion formed*, Δ [Fe³⁺]^{H₂} is the concentration of ferric ion formed in the presence of hydrogen and Δ [Fe³⁺]^o is the concentration of ferric ion formed in the absence of hydrogen. Within the range of conditions in which eqn. (4) is valid, the accessible values of $F.E._{Fe^{3+}}$ when H₂ is used are not large (due to the low solubility and small k_1) and are only increased by about 25 % by a 10-deg. rise in temperature. Since, moreover, substitution of hydrogen by deuterium decreases F.E._{Fe³⁺}, high precision is necessary if reliable values of $A_1^{D_2}/A_1^{H_2}$ and $E_1^{D_2} - E_1^{H_2}$ are to be obtained. Experiments were carried out independently at Chalk River by T. J. H. and at Leeds. At Chalk River the F.E._{Fe³⁺} was increased by reducing the ferrous ion concentration. Under these conditions, corrections are necessary for the variation of [Fe²⁺] during the reaction and for the competition between Fe^{2+} and Fe^{3+} for HO₂. In Leeds, the conditions for these two complications to have a negligible effect were met by keeping [Fe2+]/ $[H_2O_2]_0 > 20$. Here it was found that, whilst the analytical technique used previously was adequate to obtain the precision required, day-to-day variations in the small amounts of organic impurity, which were not removed efficiently by the purification methods given in ref. (1), constitute a major difficulty in obtaining accurate values of $k_{1}^{\text{H}_2}/k_{1}^{\text{D}_2}$ and $E_{1}^{\text{D}_2} - E_{1}^{\text{H}_2}$. Much of the experimental work in Leeds was therefore directed towards destroying this impurity or allowing for its effect on F.E. Fe3+.

EXPERIMENTAL

REAGENTS

(a) IN CHALK RIVER

PERCHLORIC ACID.—Merck 72 % perchloric acid was vacuum-distilled at 100°C, the middle 80 % being retained.

FERROUS PERCHLORATE.—" Pure" iron wire was dissolved in 3 N perchloric acid.1

WATER.-Laboratory-distilled water, redistilled from alkaline permanganate, was used throughout.

HYDROGEN PEROXIDE.—Merck 30 % superoxol was suitably diluted with purified water.

GASES.—Hydrogen and oxygen were taken from cylinders through absorbent cotton wool. The hydrogen was further passed through a liquid nitrogen trap. Tank deuterium (99.8 %) was used without further purification. Hydrogen deuteride was prepared by the addition of pure D_2O to lithium hydride.

(b) IN LEEDS

PERCHLORIC ACID.—A.R. 72 % perchloric acid was vacuum-distilled at 100°C from freshly precipitated and exhaustively washed silver oxide. The middle 80 % was redistilled, the initial 10 % of the redistillate being rejected.

FERROUS PERCHLORATE.—Because of the manganese impurity in the iron wire used by Dainton and Hardwick,¹ pure iron granules, obtained from the Bureau of Analyzed Samples Limited, with a maximum impurity of 0.023 % in manganese, were used for the preparation of ferrous perchlorate.

WATER.—Water prepared in the manner described in the previous paper still contained organic impurities in amounts which varied from sample to sample and which prevented the attainment of the necessary accuracy especially in the deuterium experiments. The quantitative results quoted in this paper were all obtained using water which had been further purified as follows. It was first irradiated with 60 Co γ -rays from a 1000-Curie source in order to produce a concentration of hydrogen peroxide of about 2×10^{-4} M and then irradiated with light from a mercury resonance lamp filtered through 2 cm of 10 % aqueous acetic acid in a quartz cell. The ultra-violet irradiation was generally sufficient to reduce the hydrogen peroxide content to $\sim 10^{-7}$ M.

HYDROGEN PEROXIDE.—Solutions were prepared by re-irradiation of the purified water with 60 Co γ -rays.

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GASES.—In the earlier work the gases were drawn directly from cylinders, but were later prepared by electrolysis of purified light or 99.77 % heavy water containing 10 % of carefully dried sodium sulphate. The electrolysis cell was designed to operate with 15 ml of solution, and was water-cooled. A current of 150 mA was used, the Pt foil electrodes being ~ 20 sq. cm in area. Both the hydrogen (or deuterium) and the oxygen were collected and stored over distilled de-aerated water.

PROCEDURE

The procedure used was as described in part 1 with the following minor modifications. An improved form of reaction vessel (fig. 1) was found to permit extremely vigorous shaking without risk of premature mixing of the solutions. The hydrogen (or deuterium) + oxygen mixture was admitted at a pressure slightly greater than atmospheric and reduced



FIG. 1.—Gas-equilibration and mixing vessel —all dimensions in cm. to the latter after thermal equilibration. At the lower temperature ($\sim 0^{\circ}$ C) an excess pressure of about 8 cm was generally required in order to allow for the fall in the vapour pressure of water and the reduction in gas pressure due to Charles's law. Reactions were carried out at temperatures controlled to ± 0.05 deg. between 0° and 35°C. The solubilities and temperature coefficients of solubility for hydrogen, hydrogen deuteride and deuterium in 0.1 N and 0.2 N perchloric acid were assumed to be not substantially different from the values for hydrogen in pure water.

All spectrophotometric measurements were made at the temperature of the room containing the spectrophotometer. In Leeds, the change in ferric ion concentration was determined, as previously described, by measuring the optical density at 3040 Å in the presence of 0.8 N sulphuric acid. At Chalk River, the alternative procedure was adopted of measuring the initial and final concentrations of ferrous ion by the *o*-phenanthroline method (cf. ref. (3)),

the percentage change in the ferrous ion concentration being very much greater in these experiments. In both cases, control flasks were set up containing the same volumes of ferrous perchlorate + perchloric acid and hydrogen peroxide solutions as in the mixing vessels. These were allowed to react in the presence of air, the increase in the ferric ion concentration or the decrease in ferrous ion concentration providing a measure of the initial hydrogen peroxide concentration. "Blanks" were also set up containing the shore of the ferrous perchlorate + perchloric acid solution diluted with water in place of the hydrogen peroxide solution. These provide the initial ferric ion concentration for the procedure in which ferric ion production is measured and the initial ferrous ion concentration of less than 1 μ M has no relevance for the determination of F.E.Fe³⁺ by the latter method and was neglected in the calculations of k_1/k_2 .

The importance of a scrupulous washing technique has been emphasized in part 1, but an even more rigorous procedure than that described in the earlier paper was used for all the Leeds experiments reported here. All glass-ware was rinsed with a freshly prepared solution of potassium permanganate in concentrated sulphuric acid and, after a thorough rinsing with distilled water, with a mixture of hydrogen peroxide and nitric acid. A minimum of five washings with distilled water and three washings with redistilled water followed and at this stage those flasks which were to be used for the determination of the initial hydrogen peroxide concentration and for the determination of the initial ferric ion concentration were steamed out. The vessels were thoroughly drained, dried for 20 min at 150°C in an oven reserved for this particular purpose and closed while still hot.

RESULTS

(a) IN CHALK RIVER

Increasing the value of F.E._{Fe³⁺}, with the aim of increasing the accuracy of the method, by reducing the initial ferrous ion concentration to $100 \,\mu\text{M}$ or less has two complicating effects. First, the ferrous ion concentration can no longer be considered to be essentially constant during the reaction, nor can a mean value be used satisfactorily in the calculations. Secondly, the ferric ion concentration builds up to values which are of the same order of magnitude as the residual ferrous ion concentration. Reduction of ferric ion by the hydroperoxyl radical,

$$\mathrm{Fe}^{3+} + \mathrm{HO}_2 \xrightarrow{\kappa_c} \mathrm{Fe}^{2+} + \mathrm{H}^+ + \mathrm{O}_2, \qquad (c)$$

in competition with the oxidation of ferrous ion,

$$Fe^{2+} + HO_2 \rightarrow Fe^{3+} + HO_2^{-}, \qquad (b)$$

must therefore be taken into account. The appropriate differential equation involving steady-state concentrations of the radicals (cf. method A, part 1) now defies integration. A method of successive approximations was therefore used to obtain k_1/k_2 from the experimentally observed value of F.E._{Fe³⁺}.

The calculation is based upon the approximation that the overall change in the system is the summed effect of a series of incremental changes in each of which a small amount of hydrogen peroxide is destroyed and ferric ion is produced. If the increments are sufficiently small, the fractions f_b and f_c of the HO₂ radicals which react respectively with Fe²⁺ and Fe³⁺ may be calculated for each increment from the expression,

$$f_b = 1 - f_c = \frac{(k_b/k_c) [\text{Fe}^{2+}]}{[\text{Fe}^{3+}] + (k_b/k_c) [\text{Fe}^{2+}]},$$

using mean values for $[Fe^{2+}]$ and $[Fe^{3+}]$ for the incremental change and the value of k_b/k_c appropriate to the hydrogen ion concentration and the temperature. k_b/k_c was obtained by interpolation from the data of Barb, Baxendale, George and Hargrave.⁴ For each molecule of hydrogen peroxide disappearing by reaction (0),

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH,$$
 (0)

a total of $2(1 - f_1 f_c)$ ferric ions are produced as a result of reactions (0), (1), (2), (b) and (c), and $f_1 f_b$ molecules of H₂O₂ are regenerated in reaction (b), where f_1 is the fraction of OH radicals reacting with H₂ and is given by

$$f_1 = \frac{(k_1/k_2) [\text{H}_2]}{[\text{Fe}^{2+}] + (k_1/k_2) [\text{H}_2]}$$

It follows that for every two molecules of ferric ion formed in any given increment, $(1 - f_1 f_b)/(1 - f_1 f_c)$ molecules of hydrogen peroxide will have disappeared.

TABLE 1.--CHALK RIVER EXPERIMENTS

gas	Т (°С)	[Fe ²⁺] ₀ (µM)	[H ₂ O ₂] ₀ (µM)	$[Fe^{2+}]_{\infty}$ (μ M)	[gas] (µM)	k_1/k_{2} calc.
${\rm H}_2$	0.1	99•4	10.82	63.4	781	0.0698
	8.8			61.4	717	0.0845
	20.2			58.3	652	0.109
	29.4			56-2	606	0.1274
HD	0.1	69.8	10.80	33.8	7 79	0.0419
	8.8			33.0	710	0.0200
	20.2			29.1	652	0.0678
	29.8			28.3	595	0 ·0796
\mathbf{D}_2	0.1	99•4	10.80	73.8	774	0.0207
	8.8			72.6	712	0.0272
	20.2			72-2	646	0.0358
	29.4			71.3	602	0.0415

[HC1O₄] in all cases = 0.1 N

REACTION OF OH WITH H_2 AND D_2

The amount of hydrogen peroxide lost during each successive increment in which 2 mole/1. of ferric ion are formed was calculated using an assumed value for k_1/k_2 . The series of increments terminates when the total loss of hydrogen peroxide is identical with the experimental initial peroxide concentration, and the calculated amount of ferric ion formed in the series of increments will then match the experimental yield if the correct value of k_1/k_2 has been used in the calculation. Successive values of k_1/k_2 were inserted into the calculations until agreement between calculated and experimental yields was achieved.

The conditions and the results of this series of experiments are given in table 1. The best straight lines for the variation of $\log (k_1/k_2)$ with 1/T were determined by the method of least squares. The kinetic parameters thereby obtained are presented in table 2. From

TABLE 2

isotopic compound	$E_1 - E_2$ (kcal/mole)	$\log \left(A_1/A_2\right)$
H_2	3.41 ± 0.09	1.57 ± 0.07
HD	3.67 ± 0.20	1.55 ± 0.15
D_2	3.92 ± 0.28	1.46 ± 0.21

the uncertainties in the slopes and intercepts as given by the usual standard deviation formulae, the standard deviations from the mean square values for $E_1 - E_2$ and $\log (A_1/A_2)$ were obtained. In view of the limited number of observations in each run these assessments may not be reliable indications of the overall uncertainty in the quoted values.

(b) IN LEEDS

(1) USING DOUBLY-DISTILLED UNIRRADIATED WATER

Excellent straight lines passing through the origin were always obtained when F.E._{Fe³⁺} was plotted against $[H_2]/[Fe^{2+}]$ (cf. fig. 2 of ref. (1)) and an Arrhenius plot of the logarithm of the slope of these lines against T^{-1} gave excellent straight lines. However, it was found that this slope varied from one set of experiments to another, corresponding to values of $E_1 - E_2$ lying in the range 3.0 to 4.0 kcal mole⁻¹ and the good Arrhenius plots were only obtained if *all* the experiments were carried out on the same day. If replicate experiments were performed at one temperature on one day, excellent agreement was obtained on different days at different temperatures did not give a good Arrhenius plot. Those mean values of k_1/k_2 which lay off the " best" Arrhenius line were frequently off the line by an amount greater than the standard deviation within the set of replicates which they represented.

This kind of irreproducibility seemed to be consistent with the effect of an organic impurity which could be present in (small) amounts determined by the laboratory conditions from day to day. The origin of such impurities can only be conjectured; as a result of experience with this system and with the photolysis of solutions of ferric perchlorate we regard organic vapours from floor and bench polishes as suspect. Since attempts to avoid irreproducibility by scrupulous cleanliness and standardized techniques were all unsuccessful attention was directed to the possibility of diminishing the effect by destroying the organic impurities which might have been present in the doubly-distilled water and all subsequent work utilized irradiated water.

(2) USING DOUBLY-DISTILLED IRRADIATED WATER

A set of experiments using deuterium as the substrate at three different temperatures gave an excellent straight line corresponding to $(A_1/A_2)^{D_2} = 53$ and $E_1^{D_2} - E_2 = 4.09$ kcal When hydrogen was the substrate it reacted 2.8 times more rapidly than deuterium However, a large number of repeat experiments carried out on different days indicated tha the irreproducibility had not been eradicated and that, although the ratios of $k_1^{H_2}/k_1^{D}$ might be of the right order of magnitude, the values of $E_1^{D_2} - E_1^{H_2}$ and hence $A_1^{D_2}/A_1^{H_2}$ could not be obtained with the necessary precision without making allowance for the effect of irremovable impurity.

We denote the impurity by RH and assume that it competes significantly with ferrous ions and dissolved hydrogen for hydroxyl radicals according to reaction (5),

$$\mathbf{R}\mathbf{H} + \mathbf{O}\mathbf{H} \to \mathbf{R} + \mathbf{H}_2\mathbf{O}.$$
 (5)

The organic radicals R are likely to be able to reduce both oxygen and ferric ion (eqn. (6) and (7)):

$$\mathbf{R} + \mathbf{O}_2 \to \mathbf{R}\mathbf{O}_2,\tag{6}$$

$$\mathbf{R} + \mathbf{F}\mathbf{e}^{3+} + \mathbf{O}\mathbf{H}^{-} \rightarrow \mathbf{R}\mathbf{O}\mathbf{H} + \mathbf{F}\mathbf{e}^{2+},\tag{7}$$

and the RO_2 radicals will either oxidize ferrous ion or reduce ferric ions :

$$RO_2 + Fe^{2+} + H^+ \rightarrow RO_2H + Fe^{3+}, \qquad (8)$$

$$RO_2 + Fe^{3+} + OH^- \rightarrow ROH + O_2 + Fe^{2+}.$$
 (9)

The hydroperoxide will be destroyed by ferrous ion to form the alkoxy radical (RO),

$$RO_2H + Fe^{2+} \rightarrow Fe^{3+} + OH^- + RO, \qquad (10)$$

which will in turn be competed for by ferrous ion and impurity,

$$RO + Fe^{2+} + H^+ \rightarrow ROH + Fe^{3+}, \tag{11}$$

$$RO + RH \rightarrow ROH + R.$$
 (12)

From other experiments in these laboratories with known organic compounds RH it would appear that $k_{12}/k_{11} < k_5/k_1$ and that little error will be introduced by neglecting reaction (12) and assuming that *all* the R radicals are produced in reaction (5). This latter assumption is further justified by mathematical analysis which shows that the concentration of RO₂H and therefore the rate of formation of RO radicals rise to maximum values which are not attained until amounts of hydrogen peroxide have reacted corresponding to considerable depletion of impurity. Nothing is known of the relative rates of reactions (8) and (9), but if it is assumed that substitution of RO₂ by HO₂ does not enormously alter this ratio, the fact that $[Fe^{3+}] \ll [Fe^{2+}]$ in all the experiments performed suggests that reaction (9) may safely be ignored. Reactions (8) to (12) inclusive may thus be replaced by

$$\mathrm{RO}_2 + 3\mathrm{Fe}^{2+} + 2\mathrm{H}^+ \rightarrow \mathrm{ROH} + \mathrm{OH}^- + 3\mathrm{Fe}^{3+}. \tag{13}$$

In aerated solution where $k_6[O_2] \gg k_7[Fe^{3+}][OH^-]$, which is always likely to be the case at pH 2, reaction (7) may be neglected and the presence of the impurity would be expected to have two consequences. First, the concentration of ferric ion formed in the "control" experiment (no H₂ or D₂ present) will be greater than twice the concentration of hydrogen peroxide initially present. Secondly, the concentration of ferric ion formed in those experiments with H₂ or D₂ present will be larger than eqn. (4) would indicate; the error is more serious at low hydrogen pressures and more marked with deuterium than with hydrogen. We will consider these effects in turn.

It is known that chloride ions react very rapidly with hydroxyl radicals ⁵ converting them into chlorine atoms (eqn. 14)),

$$OH + Cl^{-} \rightarrow OH^{-} + Cl, \qquad (14)$$

and that $k_{15}/k_{16} \ll k_1/k_2$ for all organic substances investigated : ⁶

$$Cl + RH \rightarrow HCl + R,$$
 (15)

$$Cl + Fe^{2+} \rightarrow Fe^{3+} + Cl^{-}.$$
 (16)

The presence of chloride ion in millimolar concentration would therefore be expected to suppress reaction (5) and make the ferric ion formed in the control experiments strictly equivalent to the hydrogen peroxide initially present.^{4, 7} 3×10^{-3} M chloride ion sufficed to decrease the yield of ferric ion in the control experiments to a reproducible value $(\Delta[Fe^{3+}]Cl^{-}]$ and all subsequent measurements of $[H_2O_2]_0$ were therefore carried out with this concentration of chloride ion present. In confirmation of the stoichiometric relation $\Delta[Fe^{3+}]Cl^{-} = 2[H_2O_2]_0$, it was found that when the control experiments were carried out in de-aerated system the yield of ferric ion was less than in aerated solution (due to reaction(7) following reaction (5)) but that the addition of chloride ion raised the former and lowered the latter to the *same* value.

The excess ferric ion concentration produced by the impurity in the absence of chloride ion and hydrogen may be expressed as a fraction of the ferric ion produced when chloride ion is present and represented by $F.E._{Fe^{3+}(RH)}$. Then

$$F.E._{Fe^{3+}(RH)} = k_5[RH]/(k_5[RH] + k_2[Fe^{2+}]).$$
(17)

REACTION OF OH WITH H₂ and D_2

The observed fractional excess when hydrogen and impurity are present and the control experiments have been made with chloride ion present may be denoted by $F.E._{Fe^{3+}(RH, H_2)}$ and is given by

$$F.E._{Fe^{3+}(RH, H_2)} = (k_1[H_2] + k_5[RH])/(k_2[Fe^{2+}] + k_5[RH]).$$
(18)

In all our experiments F.E._{Fe³⁺(RH)} $\ll 1$ and consequently $k_2[Fe^{2+}]/(k_2[Fe^{2+}]+k_5[RH]) \approx 1$. It follows from eqn. (17) and (18) that

$$k_1[H_2]/k_2[Fe^{2+}] = F.E._{Fe^{3+}(RH, H_2)} - F.E._{Fe^{3+}(RH)},$$
 (19)

provided that the fractional excesses are measured on the same reagents and as nearly simultaneously as possible. Eqn. (19) incorporates the approximation $k_2[\text{Fe}^{2+}]/(k_2[\text{Fe}^{2+}])$ + $k_5[\text{RH}]$ = 1 which will lead to an error, depending upon the magnitude of the correction, of between 1 and 4 % in k_1/k_2 . (Although this apparent error is easily assessible, allowance has not been made for it in the calculation of k_1/k_2 because an alternative theoretical treatment in which reaction (12) is not neglected indicates that eqn. (19) would be exact if $k_{12}/k_{11} \approx k_5/k_2$.)

The magnitude of the correction term, $F.E._{Fe^{3+}(RH)}$, in (19) generally increases with temperature and is therefore (relatively) largest for the deuterium experiments at the highest temperatures. The effect of the correction is illustrated by the representative deuterium run analyzed in table 3.

TABLE 3

<i>T</i> (°C)	$P_{\mathbf{D}_2}(mm)$	F.E.Fe ³⁺ (RH, D ₂)	F.E.Fe ³⁺ (RH)	$k_1[D_2]/k_2[Fe^{2+}]$
4.70	565.8	0.198	0.020	0.178
15.85	560.5	0.232	0.027	0.205
30.60	545-9	0.277	0.038	0.239

 $[Fe^{2+}] = 149 \ \mu M$; $[H_2O_2]_0 = 6.70 \ \mu M$;

[HC1O₄] = 0.202 N; $P_{O_2} = 182$ to 189 mm according to temp.

[Cl⁻] in control experiments = 3×10^{-3} M.

The results of eleven experiments at Leeds on the hydrogen and deuterium systems are summarized in table 4 which gives the mean values and the deviation from the mean for the Arrhenius parameters derived from the best lines in individual sets of experiments, each covering several temperatures.

The values of the ratio k_1/k_2 are the *observed* values (mean and standard deviation from the mean) for hydrogen and deuterium respectively. The values in the last two columns are obtained from those listed in columns (1) and (3).

DISCUSSION

The results presented in the preceding section illustrate very strikingly the major problems to be solved in measuring k_1/k_2 for a relatively unreactive solute such as deuterium. The most satisfactory course, short of using partial pressures of H₂ or D₂ of several atmospheres, is (a) to minimize the impurity content by ${}^{60}\text{Co} \gamma$ and 2537 Å irradiation, (b) to determine the magnitude of the residual impurity effect by measuring the effect of chloride ion on the control experiments within each set and then (c), if this effect is sufficiently small, to apply the correction procedure given in § b(2) of the experimental part. Application of this method greatly reduces the standard deviation of $E_1 - E_2$ and at the same time reduces the values of A_1/A_2 and $E_1 - E_2$.

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A correction for impurity was not made in that part of this work which was carried out at Chalk River. The effect of chloride ion upon the controls was tested on several occasions and it was deemed that, under the conditions of these experiments, impurity effects were not important. The results from the two laboratories are not completely concordant, the differences being greater than the apparent uncertainty in the separate results.* The values for $E_1 - E_2$ and A_1/A_2 calculated from the Chalk River experiments fall within the spread of values obtained in Leeds from experimental data *before correction* for impurity, e.g. for H₂ the uncorrected Leeds results give $(E_1 - E_2)_{apparent} = 3.4 \pm 0.5$ kcal and $1 < A_1/A_2 < 100$ (mean value, 43). On the other hand, the discrepancy between the Chalk River values in table 2 and the *corrected* Leeds values (table 4) is not easily dismissed as being due to impurity effects in the former because the corresponding values of k_1/k_2 (table 1) are *lower* than those calculated from the Leeds data. Both sets of data, however, lead to essentially the same value for the reactivity-ratio for OH capture by H₂ and D₂, viz. $(k_1^{H_2}/k_{12}^{D_2})^{25^{\circ}C} = 2.8 \pm 0.5$ and, within the experimental error, are in agreement that the difference in activation energies, $E_{12}^{D_2} - E_{14}^{H_2}$, is about 700 cal.

The data are sufficiently precise to leave little doubt that the reaction (1) involves bond breakage rather than electron transfer. The frequency factor ratio and the difference in energy of activation are almost identical with those found by Majury and Steacie⁸ for the gas-phase reactions of CD₃ radicals with H₂ and D₂. It would be of interest to know the influence on k_1/k_2 of changing the solvent to D₂O, since no large effect on k_1 would be expected whereas the electron-transfer reaction (2) might be significantly slower.⁹

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* The two sets of data relate to different perchloric acid concentrations, 0.1 N and 0.2 N respectively. Although $(k_1/k_2)_{calc.}$ varies with pH (unpublished experiments by G. A. S.) the difference in medium could not account for more than a 7 % difference in k_1/k_2 at 20°C.

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