For triethylgallium the molecular weights found in this study are consistent with the indirect evidence summarized in the preceding paragraph but not with two earlier molecular weight determinations.[2,16] We feel compelled to conclude that these earlier results must be rejected.

The behavior of the saturated trialkyl derivatives of the group III metals now appears much less capricious than it did when this work was begun, since it has been shown that the aluminum derivatives are the only ones which associate in solution. Granted the advantage of using hindsight, the situation is not too difficult to rationalize. It has been proposed[17] that four principal factors govern the stability of dimers held together by alkyl bridges. Association is favored by: (1) a large difference in electronegativity between the metal and carbon; (2) a low value for the energy required to promote an electron from an s to a p orbital in the valence shell of the metal; (3) a large bond energy for a normal, single bond between the metal and carbon; (4) a minimal amount of inner-shell repulsion between two metal atoms separated by an internuclear distance consistent with the geometry of the dimer. The first two of these are particularly unfavorable if the metal is boron. The last two are expected to become increasingly unfavorable as the atomic number of the metal increases, and hence they probably prohibit dimerization for the trialkyls of gallium, indium, and thallium. This leaves the aluminum compounds as the only ones in which the interplay of all four effects allows association by the kind of bridge bonding proposed in ref. 17.

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Iron(II) + Iron(III) Isotope Exchange in Dimethyl Sulfoxide

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The isotope exchange reaction between iron(II) and iron(III) in dimethyl sulfoxide has been studied. The reaction is first order with respect to total Fe(II) and to total Fe(III) concentration. The enthalpy and entropy of activation are 9.6 ± 0.6 kcal./mole and −20 ± 2 cal./deg. mole, respectively. The reaction was studied at various perchloric acid concentrations and ionic strengths and over the entire range of water concentrations from zero added water to purely aqueous solutions. At water concentrations less than approximately 0.1–0.2 *M* and at perchloric acid concentrations greater than approximately 7×10^{-6} *M*, the reaction appears to proceed between the hexakis(dimethyl sulfoxido)iron(II) and (III) complexes.

The iron(II) + iron(III) isotope exchange reaction and its catalysis by various anions has been rather extensively studied.[1] The exchange has also been studied in ice-like media,[2] in certain nonaqueous solvents,[3,4] and in nonaqueous solvent–water mixtures.[5] In isopropyl alcohol[4] the exchange rate was at least 10^8 times slower than in water; the effect of water on the exchange rate was not determined. In nitromethane[3] the effect of water was not determined, but the exchange in rigorously purified solvent was extremely slow. In mixtures of methanol, ethanol, 1-propanol, or acetone with water the rate of exchange decreased with decreasing water concentration down to mole fractions of approximately 0.5, as far as the variation was studied.[5] The results, to date, have tended to indicate that the exchange rate is very slow in nonaqueous solvents either because the mechanism of electron transfer changed or because the lower dielectric constants of the nonaqueous solvents resulted in large coulombic repulsion energies on formation of the activated complex. In dimethyl sulfoxide (DMSO) the exchange rate is not particularly slow and the present report describes a study of orders of reaction, effect of water from mole fraction ~0 to 1, effect of perchloric acid concentration, ionic strength, and temperature in this solvent.

Experimental

Chemicals.—The solvent, DMSO, was obtained either from the Crown Zellerbach Co. or as 99.9% pure Baker Analyzed reagent from the J. T. Baker Chemical Co. Both sources of DMSO were found to give identical results after purification. Purification consisted of a fractional distillation at 2–3 mm. pressure and ~50°, collection of the center two-thirds of the distillate, and shaking the latter with Alcoa alumina overnight followed by a fractional distillation at the same pressure and temperature as the first distillation with the center one-half of the distillate being retained for use. The purified solvent was stored in a cold room (5°) in a flask fitted with a magnesium perchlorate guard tube to prevent absorption of moisture. The freshly prepared solvent was analyzed for water content with Mallinckrodt Karl Fischer reagent[6] and found to contain approximately 0.015 *M* water.

Perchloric acid solutions in DMSO were prepared by a cation-exchange method. Dowex 50W-X8 cation-exchange resin (50–100 mesh) was converted to the hydrogen form with a 3 *M* HCl

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[1] To list all the references to past work singly would be prodigal of space. A complete set of references can be found in the two review articles (a) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961), and (b) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962), for literature prior to those two dates. Recent publications are (c) W. L. Reynolds and S. Fukushima, *Inorg. Chem.*, **2**, 176 (1963); (d) K. Bächmann and K. H. Lieser, *Z. physik. Chem.* (Frankfurt), **36**, 236 (1963); (e) J. C. Sheppard and L. C. Brown; *J. Phys. Chem.*, **67**, 1025 (1963); (f) R. L. S. Willix, *Trans. Faraday Soc.*, **59**, 1315 (1963); (g) S. Fukushima and W. L. Reynolds, *Talanta*, **11**, 283 (1964); (h) J. Menashi, S. Fukushima, C. Foxx, and W. L. Reynolds, *Inorg. Chem.*, **3**, 1242 (1964); (i) A. McAuley and C. H. Brubaker, Jr., *ibid.*, **3**, 273 (1964).

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solution, washed until the eluent gave a negative test for Cl^-, and dried at 115°. A slurry of the resin in DMSO was then packed into an ion-exchange column, and a solution of ammonium perchlorate (twice recrystallized from conductivity water and dried *in vacuo* over P_2O_5 for several weeks) in DMSO was passed through the column. Moisture from the atmosphere was excluded by fitting the eluting and eluent reservoirs at the top and bottom of the column, respectively, with magnesium perchlorate guard tubes. The ammonia-free eluent (negative test with Nessler's solution) containing perchloric acid was analyzed with standard sodium hydroxide solution. When not in use the acid solutions in DMSO were stored in a cold room.

Sodium and barium perchlorate, for maintaining constant ionic strength, were prepared by the action of Mallinckrodt A.R. perchloric acid on A.R. sodium carbonate and barium hydroxide, respectively. The perchlorate salts were recrystallized twice from conductivity water, dried in an oven at 250°, and stored in a desiccator over phosphorus pentoxide.

The DMSO solvates of $Fe(ClO_4)_2$ and $Fe(ClO_4)_3$ have been prepared and characterized by a number of workers.[7-9] In this work $Fe(ClO_4)_3 \cdot 6DMSO$ was prepared by the method of Selbin, Bull, and Holmes.[9] The corresponding Fe(II) compound, $Fe(ClO_4)_2 \cdot 6DMSO$, is an unstable solid and decomposes on standing.[9] Thus, except where otherwise stated, hydrated ferrous perchlorate, obtained from G. F. Smith and Co. and stored over phosphorus pentoxide, was used as the source of iron(II). Since the iron(II) concentrations required were of the order of 10^{-4} M, the amount of water introduced by the hydrated salt was very small compared to the amount which remained in the solvent after distillation. The $Fe(ClO_4)_2 \cdot 6H_2O$ was analyzed for perchloric acid content by the method of Silverman and Dodson.[10] The amount of perchloric acid added to the reaction mixture from this source was approximately $1\text{–}2 \times 10^{-6}$ M depending on the iron(II) concentration and was negligible compared to the added acid concentration in all the experiments in which perchloric acid was added separately.

The ^{59}Fe isotope was obtained from Oak Ridge National Laboratory as an iron(III) solution in HCl. The aqueous solution of iron(III) was freed of Cl^- by several cycles of evaporation to dryness with concentrated nitric acid. The radioactive precipitate was dissolved in DMSO to give a stock solution of radioactive iron(III).

Measurement of Isotope Exchange Rate.—The water bath with a temperature control of ±0.02°, reaction vessel, and thermostated pipets have been described previously.[1g] The required quantities of solvent, freshly prepared iron(III) perchlorate solution, and radioactive iron(III), all containing predetermined concentrations of perchloric acid and sodium perchlorate, were placed in the reaction vessel and deaerated by a N_2 gas flow. The N_2 gas was saturated with solvent vapor by passing the gas through a series of bubblers containing solvent at the required ionic strength and at the temperature of the water bath. A fresh solution of iron(II) perchlorate was prepared in deaerated solvent containing the same concentrations of perchloric acid and sodium perchlorate as required for the reaction mixture and brought to temperature in the water bath while being kept deaerated by passage of N_2 gas saturated with solvent vapor. The isotope-exchange reaction was started by adding the requisite amount of iron(II) solution. A vigorous flow of nitrogen was maintained throughout the entire reaction period, initially to mix the reactants and thereafter to maintain oxygen-free conditions while withdrawing samples for radioactivity determinations. At a time t approximately 5 ml. was withdrawn by means of either a thermostated pipet or syringe and delivered into a 25-ml. volumetric flask containing ice-cold quenching solution stirred by a magnetic stirrer. The thermostated pipet was used when the temperatures of the room and reaction vessel were different by more than a few degrees; when the temperatures were different by only a few degrees it was found that both syringe and thermostated pipets yielded identical results so that the former, being easier to manipulate, was used. The quenching solution contained 5 ml. of water, 1 ml. of 0.125 M 2,2'-bipyridine dissolved in a 50% ethanol–water mixture, 1 ml. of 0.9 M perchloric acid, and 1 ml. of 0.2 M aluminum nitrate. Within 5 sec. of mixing the 5-ml. aliquot and quenching solution 3.2 ml. of a solution containing 1 M sodium acetate, 1 M ammonia, and 3.3 M ammonium nitrate was added to adjust the pH to 8.7 for precipitation of the aluminum and iron(III) hydrated oxides. The resulting solution was diluted to volume and filtered. The radioactivity of 5.00-ml. samples of each filtrate was determined as described earlier.[1c]

When total iron concentrations of approximately 2×10^{-5} M were used the "infinite" time samples were withdrawn at about 10 hr. In such cases a small amount of oxidation of iron(II) to iron(III) occurred in the infinite time samples. To correct for this source of error and also to correct for small fluctuations in the volume of sample due to drainage of the pipet, the concentration of iron(II) in each filtrate was measured at 522 mμ with a Beckman DU spectrophotometer having a cell compartment thermostated at 25° and the radioactivity count corrected accordingly. The effect of DMSO on the extinction coefficient of the tris(2,2'-bipyridine)iron(II) complex was taken into account by comparing the absorbances of the filtrates to those on a standard curve. The standard curve was obtained from a set of standard iron(II) solutions having the same chemical composition as the filtrates but which had been made from aqueous iron(II) solutions and to which DMSO and the other chemicals had been added. In this way the drainage error due to the viscosity of DMSO solutions and oxidation of iron(II) by air in DMSO solutions was avoided.

The total iron concentration in the reaction mixture was determined spectrophotometrically as the tris(2,2'-bipyridine)iron(II) complex after reduction of iron(III) with hydroxylamine.

Results

Order of Reaction.—The McKay equation[11] as modified by Prestwood and Wahl[12] for zero-time exchange is

$$\ln (1 - F) = \ln (1 - F_0) - Rt(a + b)/ab \quad (1)$$

where a is the total iron(II), b is the total iron(III) concentration, F_0 is the separation-induced fractional exchange, F is the observed fractional exchange at time t, and R is the (unknown) rate law governing the rate of isotope exchange between the (II) and (III) oxidation states. F is equal to x/x_∞ where x is the radioactivity in counts/min. of the 5.00-ml. portion of the filtrate for the sample taken at time t and x_∞ is the same quantity for the infinite time sample. Plots of log $(1 - F)$ *vs.* t gave straight lines up to F values of 0.85 with slopes given by

$$S = -R(a + b)/2.303ab \quad (2)$$

If the exchange rate R is first order in each of the concentrations of total iron(II) and iron(III) then an apparent second-order rate constant, given by

$$k_{\text{app}} = -S/(a + b) \quad (3)$$

and independent of a and b, will be obtained. The values of k_{app} obtained for 15- and 10-fold variations

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TABLE I

ORDER OF REACTION WITH RESPECT TO [Fe(II)] AND [Fe(III)]
0.025 M H_2O, 2×10^{-5} M $HClO_4$, 0.2000 M $NaClO_4$;
$\mu = 0.20$; 20.0 ± 0.02°

10^4[Fe(II)], M	10^4[Fe(III)], M	$10^{-2}t_{1/2}$, sec.	k_{app}, l./mole sec.
2.79	1.03	1.13	16
1.46	1.03	1.52	18
1.37	0.10	2.64	18
0.83	0.30	2.74	22
0.78	0.67	2.98	16
0.53	0.94	2.91	16
0.42	1.05	2.47	19
0.106	0.41	2.56	18
			Av. 18 ± 2

of iron(II) and (III) concentrations, respectively, are listed in Table I. It is seen that the values of k_{app} are constant within approximately ±10% and that no trend is indicated.

It is also seen from the data for 0.0500 M perchloric acid and 0.1500 M sodium perchlorate in Table II on the effect of acid concentration that k_{app} = 20 l./mole sec., with a standard deviation for a single measurement of approximately 15%, over 10-fold variations of iron(II) and iron(III) concentrations.

Effect of Acid.—The effect of perchloric acid concentration on the apparent second-order rate constant, k_{app}, was examined at an ionic strength of 0.200 using anhydrous sodium perchlorate to maintain constant ionic strength. The results are summarized in Table II.

TABLE II

THE EFFECT OF $HClO_4$ ON EXCHANGE RATE
0.025 M H_2O; $\mu = 0.20$; 20.00 ± 0.02°

[$HClO_4$], M	10^5[Fe(II)], M	10^5[Fe(III)], M	$t_{1/2}$, sec.	k_{app}, l./mole sec.
1.5×10^{-6}	0.46	0.34	407	210[a]
2×10^{-6}	0.52	0.35	410	190[a]
2×10^{-6}	0.51	0.37	415	190[a]
7.0×10^{-6}	0.13	0.85	3380	21[a]
5.02×10^{-4}	0.32	0.34	4560	23[b]
5.00×10^{-3}	1.08	0.08	2390	25[c]
2.46×10^{-2}	8.50	3.80	301	19[d]
5.00×10^{-2}	10.8	4.40	224	20[e]
5.00×10^{-2}	1.57	0.36	1440	25[e]
5.00×10^{-2}	2.46	1.01	1120	18[e]
5.00×10^{-2}	1.04	0.43	1970	24[e]
5.00×10^{-2}	2.03	0.35	1480	20[e]
5.00×10^{-2}	2.63	0.34	1620	16[e]
5.00×10^{-2}	16.1	5.2	190	17[e]
0.122	9.4	6.4	273	16[f]

[a] 0.2000 M $NaClO_4$. [b] 0.1995 M $NaClO_4$. [c] 0.1950 M $NaClO_4$. [d] 0.1754 M $NaClO_4$. [e] 0.1500 M $NaClO_4$. [f] 0.0780 M $NaClO_4$.

It is readily seen that k_{app} was independent of perchloric acid concentration when the latter was greater than approximately 7×10^{-6} M.

At a perchloric acid concentration of approximately 2×10^{-6} M k_{app} shows a large increase. In the complete absence of perchloric acid, as when $Fe(ClO_4)_2 \cdot 6DMSO$ was used as the source of iron(II), the exchange rate was immeasurably fast even at total iron concentrations of 5×10^{-6} M. Thus under these conditions k_{app} was greater than approximately 6×10^4 l./mole sec.

Effect of Perchlorate Ions.—The perchloric acid concentration was maintained at 2×10^{-5} M and anhydrous barium perchlorate was substituted for anhydrous sodium perchlorate to give an ionic strength of 0.200. At 20.00° with 1.00×10^{-4} M iron(II), 0.15×10^{-4} M iron(III), and 0.0665 M barium perchlorate the value obtained for k_{app} was 20 l./mole sec., in good agreement with the average value for 0.2000 M perchlorate ion and perchloric acid concentrations greater than about 7×10^{-6} M. The water content of the solvent was unchanged.

Effect of Water.—Since the DMSO used in this work contained about 0.015–0.025 M water it was necessary to determine the dependence of k_{app} on water concentration. The effect of water was investigated mainly at 2×10^{-5} and 5.00×10^{-2} M perchloric acid concentration, although three perchloric acid concentrations were used at 0.463 mole fraction of water. The results are summarized in Table III.

TABLE III

THE EFFECT OF WATER ON THE APPARENT RATE CONSTANT
20.00 ± 0.02°; $\mu = 0.200$

[H_2O], M	X_{H_2O}[e]	10^4[Fe(II)], M	10^4[Fe(III)], M	$t_{1/2}$, sec.	k_{app}, l./mole sec.
0.025	0.002	1.05	0.26	288	18[a]
0.108	0.008	0.44	0.486	416	18[a]
0.425	0.029	1.07	0.26	248	21[a]
0.425	0.029	1.56	0.34	156	20[a]
0.825	0.058	0.73	0.33	272	24[a]
1.63	0.106	1.00	0.35	238	29[a]
3.23	0.194	0.73	0.39	119	52[a]
0.025	0.002	1.29	0.16	268	18[b]
0.125	0.009	0.92	0.36	279	19[b]
0.225	0.016	1.06	0.34	256	19[b]
0.425	0.029	0.67	0.44	331	17[b]
0.825	0.057	0.83	0.64	276	17[b]
1.63	0.106	0.86	0.67	330	14[b]
3.23	0.194	0.86	0.62	389	12[b]
6.43	0.340	0.88	0.65	481	9.4[b]
10.03	0.463	0.85	0.58	866	5.6[b]
10.03	0.463	1.17	0.25	761	6.4[b]
10.03	0.463	0.58	1.16	568	7.1[b]
16.03	0.615	0.85	0.34	1390	4.2[b]
22.03	0.712	0.84	0.40	1600	3.5[b]
28.03	0.800	1.23	0.29	1140	4.0[b]
36.03	0.875	1.14	0.33	763	6.8[b]
42.03	0.924	1.14	0.30	364	13[b]
48.03	0.962	1.02	0.36	192	26[b]
54.03	0.994	0.71	0.25	148	48[b]
55.5	1.000	0.81	0.07	143	55[b]
10.03	0.463	1.33	0.24	382	4.7[c]
10.03	0.463	1.08	0.35	510	9.5[d]

[a] [$NaClO_4$] = 0.2000 M, [$HClO_4$] = 2×10^{-5} M. [b] [$NaClO_4$] = 0.1500 M, [$HClO_4$] = 5.00×10^{-2} M. [c] [$NaClO_4$] = 0.0220 M, [$HClO_4$] = 1.78×10^{-1} M. [d] [$NaClO_4$] = 0.1900 M, [$HClO_4$] = 1.00×10^{-2} M. [e] The mole fraction of water was based on the weights of water and DMSO only; the presence of solutes was neglected.

At water concentrations less than approximately 0.425 M the apparent rate constant is the same for 2×10^{-5} and 5.00×10^{-2} M perchloric acid within the experimental error of approximately 15%. At the lower of the two acid concentrations k_{app} increases very slowly with increasing water concentration at

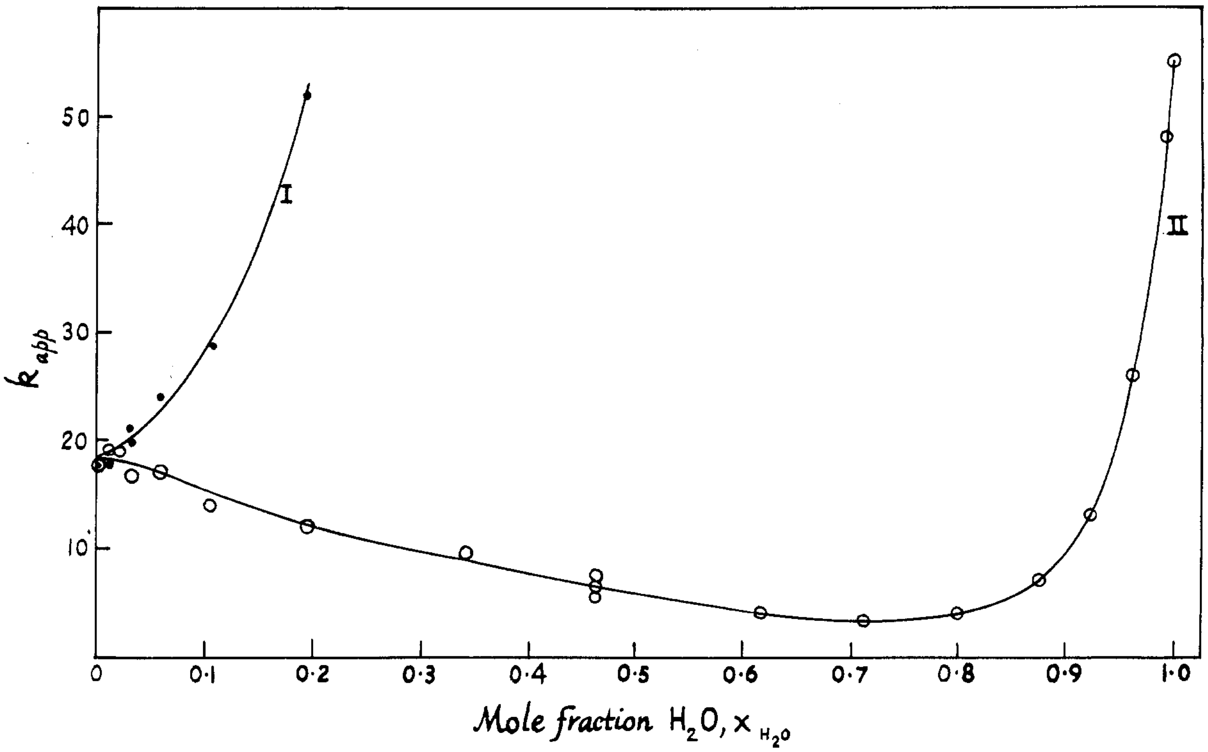

Figure 1.—Plot of k_{app} *vs.* mole fraction of water, X_{H_2O}, at $\mu = 0.200$ and at 20.0°: I, ●, experimental points at $[HClO_4] = 2 \times 10^{-5}$ *M;* II, ○, experimental points at $[HClO_4] = 5.00 \times 10^{-2}$ *M.*

water concentrations below 0.825 *M*, but above this water concentration it increases very rapidly as shown in Figure 1. A plot of log k_{app} *vs.* log $[H_2O]$ showed that the apparent order of the reaction with respect to water concentration increased rapidly above 0.825 *M* water, *i.e.*, the resulting curve was decidedly concave upward at water concentrations above this value. Empirically it was found that log k_{app} depended linearly on water concentration up to 3.23 *M* according to the equation

$$\log k_{app} = 1.25 + 0.146[H_2O]$$

At 0.0500 *M* perchloric acid the apparent rate constant remained virtually unchanged up to 0.825 *M* water as shown in Figure 1, decreased gradually with increasing water concentration up to approximately 22 *M* water (= mole fraction 0.7) passing through a very broad minimum and increased rapidly above water concentrations of 36 *M* (= mole fraction 0.875) until in pure water a value of 55 l./mole sec. was reached, in good agreement with that which would be expected in 0.0500 *M* perchloric acid at 20° from previous measurements.[1g,10]

At 10 *M* water k_{app} increased with decreasing perchloric acid concentration but the relationship between k_{app} and $[H^+]$ was not determined. Further work remains to be done on the nature of the species present over the very broad range of water concentrations where k_{app} is less than it would be in purely aqueous solutions at the same acid concentration and temperature.

Effect of Ionic Strength.—The values of k_{app} obtained at various ionic strengths between 0.0016 and 0.75 are summarized in Table IV. They are independent of ionic strengths below approximately 0.200 and increase at ionic strengths above this value. The ionic strength was always adjusted with anhydrous sodium perchlorate.

Effect of Temperature.—The temperature dependence of k_{app} was determined at an ionic strength of 0.200 and 0.0500 *M* perchloric acid over the range 20–45°. The results are summarized in Table V and plotted in Figure 2. A least-square treatment of the data gave $\Delta H^* = 9.6 \pm 0.6$ kcal./mole and $\Delta S^* = -20 \pm 2$ cal./deg. mole.

Discussion

The fact that k_{app} at small water concentration, for example, less than 0.1 to 0.2 *M*, is independent of perchloric acid concentration over the range (2–5000) $\times 10^{-5}$ *M* shows that no iron species involving OH^-

TABLE IV

EFFECT OF IONIC STRENGTH ON THE APPARENT RATE CONSTANT

0.025 *M* H_2O; 20.00 ± 0.02°

μ, *M*	$10^4[Fe(II)]$, *M*	$10^4[Fe(III)]$, *M*	$t_{1/2}$, sec.	k_{app}, l./mole sec.
0.0016	1.00	0.24	318	18[a]
0.0016	0.88	0.28	300	20[a]
0.0016	1.05	0.26	266	19[a]
0.0106	1.23	0.25	275	17[b]
0.0106	0.98	0.24	359	16[b]
0.200	...	...	...	19[c]
0.500	1.12	0.19	174	30[d]
0.500	1.14	0.20	147	35[d]
0.750	0.31	0.17	290	50[e]

[a] 0.0010 *M* $HClO_4$. [b] 0.0100 *M* $HClO_4$. [c] Average value for this ionic strength. [d] 0.0500 *M* $HClO_4$ + 0.4500 *M* $NaClO_4$. [e] 0.0500 *M* $HClO_4$ + 0.7000 *M* $NaClO_4$.

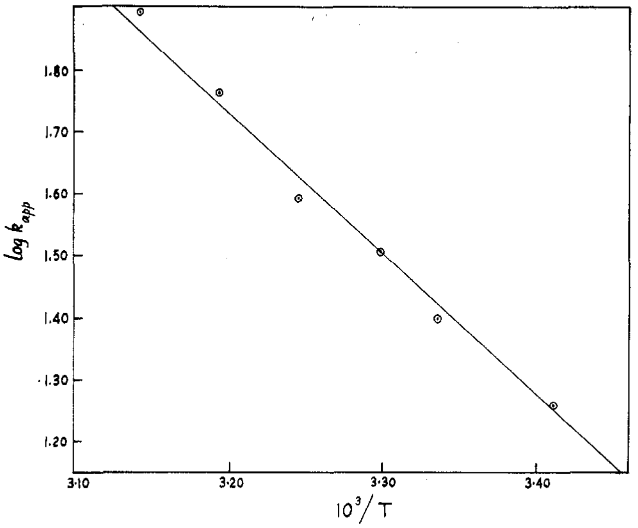

Figure 2.—Plot of log k_{app} *vs.* ($10^3/T$): $[H_2O] = 0.025\ M$, $[HClO_4] = 0.0500\ M$, $[NaClO_4] = 0.1500\ M$, $\mu = 0.200$.

TABLE V

DEPENDENCE OF k_{app} UPON TEMPERATURE

$0.025\ M\ H_2O$, $0.1500\ M\ NaClO_4$, $0.0500\ M\ HClO_4$; $\mu = 0.200$

t, °C.	10^4[(FeII)], M	10^4[Fe(III)], M	$t_{1/2}$, sec.	k_{app}, l./mole sec.
20	...	...	...	19[a]
25	1.12	0.30	198	25
30	1.13	0.30	151	32
35	0.96	0.28	143	39
40	0.64	0.17	148	58
45	0.37	0.13	177	78

[a] Average value from Tables I and II for $0.0500\ M\ HClO_4$.

or a solvent anion, S^-, are involved in the rate-determining step of the over-all electron-transfer reaction over this range. This does not prove that mixed-ligand complexes such as $Fe(DMSO)_{6-n}(H_2O)_n^{+2,+3}$ do not appear in the activated complex at these water concentrations, but it does strongly suggest that these species are unimportant. If such species existed in appreciable concentration, dissociation of a proton from a water molecule in the inner coordination sphere in the basic solvent, DMSO, would be expected with a contribution to k_{app} from the resulting hydroxo complex. Certainly at larger water concentrations, for example, above approximately 0.5 M, k_{app} does become dependent on acid concentration, being smaller at 0.0500 M perchloric acid than at 2×10^{-5} M. Furthermore, the larger the water concentration the greater the difference in the k_{app} values at the two acid concentrations. This fact implies that at the higher water concentrations the mixed-ligand complexes are becoming important and that at low acid concentration the dissociation of protons from these complexes yields hydrolyzed species capable of reacting more rapidly than the unhydrolyzed species.

It is also significant that as water content increased at 0.0500 M acid k_{app} *decreased.* At 10 M water, where k_{app} is a minimum, the value of k_{app} has contributions from hydrolyzed species because k_{app} decreased as acid concentration increased at this water content. Thus the rate constant for the unhydrolyzed species in 10 M water is much less than the value of k_{app} at the very small water concentrations. If the reaction at the very small water concentrations involved the hexaaquo species then it would be expected that the exchange rate between these species would increase with increasing water concentration, rather than decrease, because the macroscopic dielectric constant of the solvent is increasing with increasing water content. Thus far the most successful theory[13] of electron-transfer reactions predicts that the coulomb repulsion free energy and the outer-solvation-sphere reorientation free energy would be decreased by an increase in the macroscopic dielectric constant. Although it is true that the theory relates specifically to outer-sphere activated complexes and it is not known whether outer-sphere or inner-sphere mechanisms prevail in the present instance, nevertheless one might expect similar qualitative behavior for inner-sphere activated complexes. Hence it may be tentatively concluded that the reactant species at the very small water concentrations were not the hexaaquo ions and that they probably did not contain water in the first-coordination spheres.

At sufficiently small acid concentration, for example 2×10^{-6} M, the value of k_{app} increases rapidly. It is not known whether the change of rate is due to formation of solvolyzed species, to a change of reaction order, or both. Further work is necessary on this aspect. It is difficult to get reproducible results, however, because the rate of exchange is now dependent on acid concentration and it is difficult to control acid concentrations in this region of very low acid concentration.

The enthalpy and entropy of activation are equal, within the standard deviations given, to the corresponding quantities for the $Fe(H_2O)_6^{+2} + Fe(H_2O)_6^{+3}$ exchange reaction in ordinary water media.[1g] This is a rather surprising result. Even if the exchanging species in DMSO were $Fe(H_2O)_6^{+2}$ and $Fe(H_2O)_6^{+3}$ (due to presence of water as an impurity), the enthalpy of activation in DMSO would not be expected to be the same as it was in H_2O. The observed entropy of activation, approximately −20 cal./deg. mole, is not surprising since very many electron-transfer reactions with both inner-sphere and outer-sphere mechanisms have similar values for ΔS^*. This entropy of activation is associated mainly with motional entropy loss on formation of the activated complex.

A net hydrogen atom transfer mechanism between $Fe(OS(CH_3)_2)_6^{+2}$ and $Fe(OS(CH_3)_2)_6^{+3}$ ions is very unlikely and may be disregarded. The chief mechanisms for electron transfer remaining are the inner-sphere and outer-sphere mechanisms. The results obtained do not permit any firm conclusions. However, of the two possibilities the former is certainly the more attractive one for the following reasons. The S–O bond in DMSO contains considerable double bond character[14] and is suitable for transferring elec-

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(13) R. A. Marcus, *Discussions Faraday Soc.*, **29**, 21 (1960).

(14) W. Moffitt, *Proc. Roy. Soc.* (London), **A200**, 409 (1950).

trons between the iron ions when one iron is bonded to the oxygen end and one iron is bonded, by means of the lone pair on sulfur, to the sulfur end of the S–O bond. The sulfur atoms, rather than the oxygen, appear to bond DMSO ligands to Pd(II)[8,9] so that transition metal–$SO(CH_3)_2$ bonds are not highly improbable although they are not observed in most of the stable DMSO complexes. The essentially tetrahedral configuration[15] of the oxygen atom, two methyl groups, and the lone pair of electrons around the sulfur atom, would not be expected to permit a sufficient close approach of two S–O bonds, one in each iron complex with the oxygen atoms bonded to the iron ions, so as to make overlap of S=O bonds between metal complexes in an outer-sphere activated complex a ready path for electron conduction.

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[15] O. Bastiansen and H. Viervoll, *Acta Chem. Scand.*, **2**, 702 (1948).

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The Thermal Decomposition of Lithium Aluminum Hydride

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The thermal decomposition of lithium aluminum hydride has been investigated utilizing a Perkin-Elmer differential scanning calorimeter. The decomposition was found to occur in three stages; two endothermic and one exothermic change with evolution of hydrogen. A reversible phase change and an exotherm related to sample purity were also noted. The results obtained are at variance in several aspects with studies previously reported.

Introduction

Garner and Haycock[2] investigated the isothermal decomposition of $LiAlH_4$ by measurement of hydrogen evolution and electrical conductivity at several temperatures in the range 100–150°. They found a three-stage reaction, consisting of a rapid initial evolution of gas amounting to less than 1% of the ultimate hydrogen evolved, an accelerating reaction corresponding to the formal equation

$$LiAlH_4 \longrightarrow LiAlH_2 + H_2 \qquad (1)$$

and a slow final step represented formally by

$$LiAlH_2 \longrightarrow LiH + Al + {}^1/_2H_2 \qquad (2)$$

The initial reaction was interpreted as occurring at defects on the surface, which were thought to collapse to a limited number of nuclei from which the decomposition proceeds by a specific interface reaction, yielding the observed cubic time dependence of the second stage. The behavior of the last stage was found to be erratic and was not investigated in detail.

Mikherva, Selivokhina, and Kryukova[3] investigated $LiAlH_4$ utilizing differential thermal analysis with simultaneous collection and measurement of evolved hydrogen. In any such temperature-scanning technique, the influence of steadily increasing temperature is superimposed on the effect of increasing reaction time, so that reactions which are essentially consecutive under isothermal conditions occur at successively higher temperatures in the program. The apparent reaction temperatures for the individual steps will depend upon their reaction rates, their activation energies, and the instrumental temperature-scanning rate. At sufficiently fast scanning rates, consecutive reactions are often "resolved" on the temperature axis, and the general character of the reaction sequence is thereby obtained in an experiment of short duration which is comparatively easy to interpret. Mikherva, *et al.*, report three endothermic maxima in their thermograms, corresponding to evolution of one-half the theoretical hydrogen at 154–161°, one-quarter at 197–227°, and the remaining one-quarter at 580–586°.

We have re-examined the thermal decomposition of $LiAlH_4$, utilizing a Perkin-Elmer differential scanning calorimeter (DSC-1).[4] This instrument provides direct differential power read-out as opposed to differential temperature, and areas consequently are directly related to transition energies. This facility, coupled with the integral thermal conductivity effluent analyzer, allows an unambiguous interpretation of the thermal events accompanying the decomposition of $LiAlH_4$.

Experimental

Lithium aluminum hydride, obtained from Metal Hydrides, Inc., Beverly, Mass., was recrystallized from ethyl ether and dried under vacuum at 60–70°. Elemental analyses of the recrystallized product indicated a minimum purity of 98% $LiAlH_4$, with less than 0.5% residual ether. Samples of 1–4 mg. were accurately weighed with a Cahn Model G electrobalance in aluminum dishes, which were standard sample containers supplied with the Perkin-Elmer differential scanning calorimeter. With an empty pan in the reference holder, the sample was placed in the instrument, both holders covered with loosely fitting gold caps, and the entire assembly enclosed with the O-ring-sealed cover provided with the instrument. The enclosed holder space was flushed continuously with an inert gas (usually argon) prior to and during the scan. The effluent gas was monitored with the thermistor thermal conductivity detector provided with the instrument. The thermal read-out was recorded with a Texas In-

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[2] W. E. Garner and E. W. Haycock, *Proc. Roy. Soc.* (London), **A211**, 335 (1952).

[3] V. I. Mikherva, M. L. Selivokhina, and O. N. Kryukova, *Proc. Acad. Sci. USSR, Chem. Sect.*, **109**, 439 (1956).

[4] E. S. Watson, M. J. O'Neill, J. Justin, and N. Brenner, *Anal. Chem.*, **36**, 1233 (1964).