fuseness of the electron distribution and it makes a lesser contribution to the total energy: the inversion barrier is raised slightly due to correlation effects.

Figure 4 is a density difference plot for one point on the minimum-energy path of the H^- plus vinylidene reaction. Again, correlation pulls in the diffuse electron density of the hydride. The beginning of charge transfer in the formation of the vinyl anion is therefore likely to be predicted incorrectly at the SCF molecular orbital level.

The inversion barriers of allenic anions are low in comparison to vinyl anions because of the role of an acetylenic structure in the odd-numbered carbon system. But this also means that the inversion barrier is sensitive to substitution because substitution can control the role of the acetylenic structure. Halogen substitution increases the height of the barrier. As a result, ionization of a halogen-substituted allenic anion followed by re-formation of the carbene–anion pair may be more competitive with inversion than for the unsubstituted anion. The net effect of electron correlation seems to be small throughout.

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Isotope Exchange Reactions of OH^- or OD^- with Hydrogen and Water

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Abstract: Exchange between gaseous hydroxyl ion and hydrogen and water has been investigated by using two mass spectrometers and two modes of ionization. Exchange of OH^- and D_2 is a relatively slow reaction (collision efficiency = 2.9×10^{-2}), and its rate constant exhibits a small negative temperature coefficient, $k = CT^{-0.7}$. The exchange of OD^- with H_2 is 30% slower than $OH^- + D_2$, the difference becoming less as the temperature increases. Exchange of OD^- with H_2O is fast (collision efficiency ~ 1). Exchange of OD^- with CH_4 and i-C_4H_{10} has also been examined, but these reactions are very slow ($k \leq 3 \times 10^{-13}$ cm^3/molecule·s) and may well be zero.

A number of investigations of the OH^- negative chemical ionization mass spectrometry of various compounds have recently been made.[1-5] In these studies, unusual and interesting reactions of gaseous anions have been observed, and we plan to make studies using deuterium labeling to elucidate their mechanisms. However, since with a high-pressure chemical ionization apparatus the gaseous anions being investigated will suffer many collisions with gas molecules during the period of their residence in the ionization chamber, the stability of the labels with respect to exchange with the gas molecules must first be investigated before the mechanistic studies utilizing labels can properly be undertaken. We have made such investigations, using two mass spectrometers each operated in a different mode (continuous ionization in one and pulsed, time-resolved ionization in the other). We find that hydroxyl anion (OH^-/OD^-) exchanges with gaseous hydrogen (H_2/D_2). We here report our results.

Perhaps the first study of hydrogen–deuterium exchange under chemical ionization conditions was that of Hunt, McEwen, and Upham,[6] who pointed out that active hydrogens in positive ions would exchange with D_2O at 1 Torr pressure. The phenomenon was suggested as an analytical technique to determine the numbers of active hydrogens in small samples. Lin and Smith[7] have shown that the number of active hydrogens in positive ions can be determined by using ND_3, and Hunt, Sethi, and Shabinowitz[8] have shown that exchange occurs with active hydrogens in negative ions and that the number of active hydrogens can be determined by using a variety of deuterated reagent gases.

More general studies of exchange in positive ions have been made by Freiser, Woodin, and Beauchamp,[9] Martinsen and Buttrill,[10] and Hunt, Gale, and Sethi.[11] General studies of exchange in negative ions have been made by DePuy, Shapiro, and co-workers.[12-14]

To summarize these studies, it is found that both for positive and negative ions certain hydrogens in the ions will exchange with certain deuterated reagents. Under some conditions and for some compounds, multiple exchange occurs. Both Hunt and co-workers[8] and DePuy, Shapiro, and co-workers[13,14] point out that in positive ions the occurrence of exchange depends upon the relative strengths of the base initiating the exchange and the conjugate base of the protonated ion undergoing the exchange, and in negative ions the exchange analogously depends upon the relative acidities of the acid promoting the exchange and the conjugate acid of the anion undergoing the exchange. The exchange will not occur in positive ions if the difference in basicities is too great or in negative ions

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if the difference in acidities is too great. Hunt and co-workers[8] attempt to provide some quantitation for this idea, for they estimate that exchange will not occur if a difference of 20–25 kcal/mol exists between the proton affinities of the two bases involved in the exchange in positive ions. Presumably a similar difference in the acid strengths of the acids involved determines whether exchange occurs in negative ions.

Experimental Section

The two mass spectrometers used in this work were our Biospect quadrupole mass spectrometer manufactured by Scientific Research Instruments Co., Baltimore, Md., and the Rockefeller University chemical physics mass spectrometer. The apparatus and techniques used with the Biospect were very similar to those described by Smit and Field.[1] The Biospect was modified for negative ion detection, using the negative ion detection system previously developed in this laboratory.[15] The output signal from the mass spectrometer was introduced into a VG2040 data system for recording and storage of the mass spectra. The scan rate was such that 2 s was required to scan from zero mass to whatever upper mass limit was appropriate to the experiment being undertaken. Ionization was initiated by bombardment with electrons emitted from a filament; the emission current was maintained at 200 μA. The ion source temperature was 210 °C. The reagent gas consisted of 2 Torr of nitrous oxide and 1 Torr of either hydrogen, deuterium, or methane. In exchange studies mixtures of H_2 and D_2 or CH_4 and D_2 were used.

Measurements using the Rockefeller University chemical physics mass spectrometer were made in the pulsed ionization mode.[16,17] The ion source was operated at −3.5 kV, and the first dynode of the electron multiplier was operated at −2.5 kV. Thus the ions arrived at the multiplier with a kinetic energy of 1 kV, which was sufficient for their detection. In the pulsed ionization mode the OH^- ions were produced from a mixture of N_2O and CH_4 as described previously,[1] although in the present work the relative amount of CH_4 was varied to keep the concentration of OH^- within limits which permitted the determination of reaction constants. The pressure of N_2O ranged from 1.5 to 2.5 Torr, and the pressure of CH_4 ranged from 0.1 to 1.5 Torr. Exchange of OH^- with D_2 at appropriate rates was effected by adding small amounts of D_2 (typically 0.01–0.03 Torr) to the N_2O–CH_4 mixture.

For the reaction of OH^- with D_2, rate constants were obtained from time and intensity values in the conventional way. However, for the reaction of OD^- with H_2 it was more convenient to determine the rate constants by measuring the steady-state intensities (intensities at long reaction times) of OH^- and OD^- in mixtures of N_2O, H_2, and D_2. CH_4 was also added sometimes to facilitate initial production of OH^-. In a similar manner the rate constants for exchange of OD^- with CH_4, *i*-C_4H_{10}, and H_2O were determined from steady-state OH^- and OD^- intensities in mixtures of N_2O, D_2, and CH_4; N_2O, D_2, and *i*-C_4H_{10}; and N_2O, D_2, and H_2O. Typical concentrations were 0.81% D_2 and 5.4% CH_4 in N_2O at a total pressure of 3.0 Torr. For the exchange of OD^- with H_2O typical concentrations were 50% D_2 and 1% H_2O in N_2O at a total pressure of 2.2 Torr.

Reagent gases were obtained from Matheson Gas Products, East Rutherford, N.J., and their purities follow: nitrous oxide, 98.5%; hydrogen, 99.95%; methane, 99.97%; *i*-C_4H_{10}, 99.5%. Deuterium was obtained from Merck Sharpe and Dohme, purity 99.5%.

Results and Discussion

In a mixture containing N_2O and H_2 at moderately high pressures (P = 0.5–3.0 Torr), hydroxyl ions are produced by the reactions[1]

$$N_2O + e \rightarrow O^{-}\cdot + N_2 \qquad (1)$$

$$O^{-}\cdot + H_2 \rightarrow OH^- + H \qquad (2)$$

In much of the previous work done in this laboratory[1-3] and in some of the present work, methane is used as a hydrogen donor, and reaction 2 is replaced by the reaction

$$O^{-}\cdot + CH_4 \rightarrow OH^- + CH_3 \qquad (3)$$

In a mixture of N_2O and D_2, OD^- is produced by

$$O^{-}\cdot + D_2 \rightarrow OD^- + D \qquad (4)$$

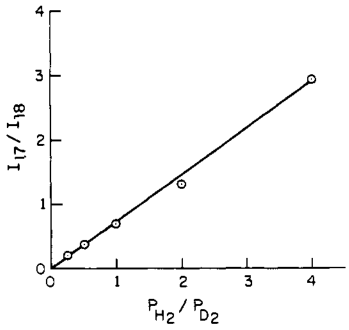

Figure 1. I_{17}/I_{18} vs. P_{H_2}/P_{D_2}. Biospect mass spectrometer.

We have investigated with the Biospect mass spectrometer the production of OH^- and OD^- in mixtures of N_2O and H_2 and N_2O and D_2, and we find that under identical experimental conditions of partial pressures, source temperature, instrumental electrical parameters, etc., the intensity of OH^- produced from N_2O–H_2 is approximately two times larger than the intensity of OD^- produced from N_2O–D_2. We conclude that an isotope effect is operating which makes reaction 4 slower than reaction 2.

When mixtures of H_2 and D_2 are added to N_2O, results are obtained that indicate exchange occurs between hydroxyl ion and hydrogen. Thus in a mixture containing 2.0 Torr of N_2O, 0.5 Torr of H_2, and 0.5 Torr of D_2, the intensity of OD^- (m/z 18) is 1.4 times larger than the intensity of OH^- (m/z 17), even though, as we saw above, reaction 2 is approximately twice as fast as reaction 4. We suggest that the exchange reactions occurring are

$$OH^- + D_2 \rightarrow OD^- + HD \qquad (5)$$

and

$$OD^- + H_2 \rightarrow OH^- + HD \qquad (6)$$

Still using the Biospect mass spectrometer, we have measured the amounts of OH^- and OD^- produced as a function of the relative pressures of H_2 and D_2. We give the results in Figure 1, which is a plot of the ratio I_{17}/I_{18} against the ratio P_{H_2}/P_{D_2}. The slope of this line is the quantity of interest to us, and it has the value 0.74. The reactions operating in the system are (2), (4), (5), and (6). Initial ionization is by reaction 1. Under the continuous ionization conditions that obtained in our experiments, the ion concentrations very probably achieved their steady-state values, and a steady-state kinetic analysis gives the result

$$\frac{I_{17}}{I_{18}} = \frac{(OH^-)}{(OD^-)} = \frac{[k_2(O^{-}\cdot) + k_6(OD^-)](H_2)}{[k_4(O^{-}\cdot) + k_5(OH^-)](D_2)}\,\frac{k_6(H_2) + k_L}{k_5(D_2) + k_L} \qquad (7)$$

where the k's are the rate constants for the subscripted reactions, and k_L is the rate constant for all of the ion-loss processes occurring in the system. As an acceptable simplification we assume that the loss processes for OH^- and OD^- are equal. We do not know the values of any of the rate constants involved in eq 7, and thus it is necessary to proceed in an approximate way. In none of the experiments reported in this paper have we observed the presence of $O^{-}\cdot$, presumably because it reacts rapidly enough to be below the limit of detectability in a time comparable with ion residence times in the mass spectrometer. Thus its steady-state concentration is negligibly small, and we neglect $k_2(O^{-}\cdot)$ with respect to $k_6(OD^-)$ and $k_4(O^{-}\cdot)$ with respect to $k_5(OH^-)$. We will also assume that k_L, the rate constant for all of the ion-loss processes occurring, is small compared with both $k_6(H_2)$ and $k_5(D_2)$. Then eq 7 reduces to the equation

$$I_{17}/I_{18} = k_6(H_2)/k_5(D_2) \qquad (8)$$

From eq 8 it may be seen that in a plot of I_{17}/I_{18} against P_{H_2}/P_{D_2} the slope will be k_6/k_5. Our experimental value for this slope (Figure 1) is 0.74, which gives us the result that exchange of OD^- with H_2 is 25% slower than the exchange of OH^- with D_2. We think that, at the 3-Torr pressure at which the experiments depicted in Figure 1 were made, the assumption that $k_6(H_2)$ and $k_5(D_2)$ are greater than k_L is reasonable, and we point out that

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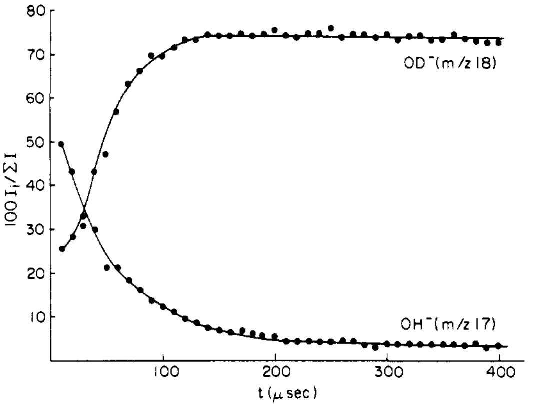

Figure 2. Ion intensities of m/z 17 (OH^-) and 18 (OD^-) as a function of reaction time, in a mixture of 0.81% D_2, 5.4% CH_4 in N_2O at a total pressure of 3.0 Torr, $T = 503$ K. Other ions observed in the system were m/z 32 (O_2^-), 46 (NO_2^-), and 60 (N_2O_2); their intensities were small and constant throughout the experiments.

Table I. Rate Constants for H/D Exchange Reactions

reaction	T, K	k, 10^{-10} cm^3/molecule·s^a
$OH^- + D_2 \rightarrow OD^- + HD$	447	0.37
	471	0.36
	522	0.32
	599	0.27
	632	0.29
$OD^- + H_2O \rightarrow OH^- + HDO$	480	15
	595	12
$OD^- + CH_4 \rightarrow OH^- + CH_3D$	560	≤0.000 32
$OD^- + i\text{-}C_4H_{10} \rightarrow OH^- + i\text{-}C_4H_9D$	560	≤0.000 29

^{a} Results represent average of two to four measurements. Precision, based on difference between replicates, is ±20%.

if the inverse assumption is made (ion-loss rates greater than exchange rates), eq 7 reduces to an expression wherein I_{17}/I_{18} will be proportional to the square root of P_{H_2}/P_{D_2}. Such behavior is not compatible with the experimental plot given in Figure 1.

Experiments were also made with mixtures of N_2O, CH_4, and D_2. In a mixture containing equal amounts of CH_4 and D_2 the OD^- intensity was approximately 11 times the OH^- intensity, and in an experiment wherein the ratio P_{CH_4}/P_{D_2} was varied the slope of the plot analogous to that in Figure 1 was 0.074. This shows that exchange between OD^- and CH_4

$$OD^- + CH_4 \rightarrow OH^- + CH_3D \qquad (9)$$

is much slower than that between OD^- and H_2. However, later experiments with the chemical physics mass spectrometer showed that the presence of trace amounts of H_2O affects the results, and we shall defer further discussion.

Turning now to the time-resolved experiments with the chemical physics mass spectrometer, a typical plot of the time variation of OH^- and OD^- concentrations in the exchange of OH^- with D_2 (reaction 5) is given in Figure 2, and rate constants for reaction 5 in the temperature range 447–632 K are given in Table I. We point out that ions at m/z 32 ($O_2^-\cdot$), 46 (NO_2^-), and 60 ($N_2O_2^-\cdot$) were observed in these mixtures containing N_2O, but their small relative intensities were constant with time in the reaction mixture at times greater than 10 μs, and thus they were not reacting.

The average of the five rate constants for reaction 5 in Table I is 3.2×10^{-11} cm^3/molecule·s. The Langevin rate constant for the collision of OH^- with D_2 is 1.12×10^{-9} cm^3/molecule·s, and therefore the reaction efficiency is 2.9×10^{-2}. Thus this is a rather slow ion–molecule reaction.

In these experiments concerning the exchange represented by reaction 5 the OH^- ion did not completely disappear at long reaction times, but remained as 10–20% of the intensity of OD^-. Since the experimental conditions were not such that the reverse of reaction 5 could occur, this residual OH^- indicated the occurrence of some other kind of reaction producing OH^-. Two possibilities to be considered are reaction of OD^- with H_2O impurity

$$OD^- + H_2O \rightarrow OH^- + HDO \qquad (10)$$

or the reaction of OD^- with CH_4 (reaction 9). In fact, passing the reactant gases through a P_2O_5 trap greatly reduced the residual OH^-, which showed that in the presence of water reaction 10 occurs. We point out that even with the use of the P_2O_5 trap some residual OH^- ion intensity existed, as may be seen from Figure 2, the data for which were taken with the use of a P_2O_5 trap.

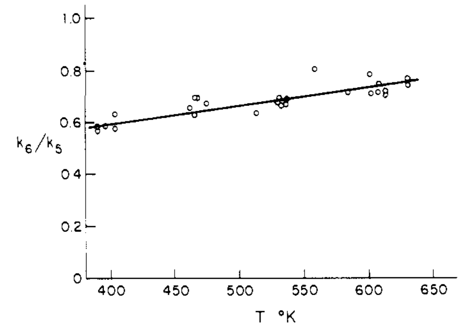

Figure 3. Ratios of rate constants k_6/k_5, as obtained from steady-state OD^-/OH^- ion intensity measurements, in the temperature range 380–640 K.

The fact that impurity amounts of H_2O produced significant amounts of OH^- indicated that (10) is a fast reaction and one of interest to the general problem of understanding exchange in hydroxyl ions. We therefore measured its rate constant at two temperatures by using a mixture of approximately equal amounts of D_2 and N_2O with 1% of added H_2O, which was much larger than the water present as an impurity. In this system OD^- is generated initially; reactions 10 and 5 then yield a constant steady-state ratio of OH^- to OD^- given by

$$(OH^-)/(OD^-) = k_{10}(H_2O)/k_5(D_2) \qquad (11)$$

The experimentally determined steady-state ion ratios when combined with experimental values for the H_2O and D_2 concentrations and the value of k_5 from preceding experiments yield values of k_{10}, which are given in Table I.

The values given in Table I show that (10) is a fast reaction. The Langevin rate constant for the reaction at 480 K is 20×10^{-10} cm^3/molecule·s, and thus one sees that the reaction is proceeding at nearly unit reaction efficiency.

Experiments in a mixture of N_2O, H_2, and D_2 were used to obtain the rate constant for the exchange of OD^- with H_2 (reaction 6). The steady-state concentrations of the ions at long reaction times are related to the rate constants by

$$(OD^-)/(OH^-) = k_5(D_2)/k_6(H_2) \qquad (12)$$

Experimental values of k_6/k_5 were determined in the temperature range 380–640 K, and measurements at each temperature were made on mixtures containing three different relative amounts of H_2 and D_2 in the range 5–25%. All the values of k_6/k_5 are plotted against temperature in Figure 3. The composition of the mixtures had no effect upon the results. From Figure 3 one observes that $k_6/k_5 = 0.59$, 0.66, and 0.73 at 400, 500, and 600 K, respectively. The value of k_6/k_5 at 483 K, which is the temperature at which our continuous ionization experiment with the Biospect mass spectrometer was made, is 0.66. The value of k_6/k_5 from our continuous-ionization measurement is 0.74, and the agreement between the two values is good. As a matter of interest the approach to the steady-state OH^- and OD^- intensities as a function of reaction time is shown in Figure 4. This experiment was carried out at lower concentrations of H_2 and D_2 (0.52% each) than the experiments for which the results are plotted in Figure 3 in order to show the approach to the steady state. At the higher concentrations used for the data in Figure 3, steady state was already established in the shortest reaction times measurable with our equipment.

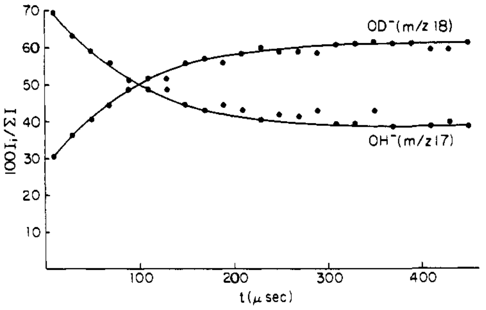

Figure 4. Ion intensities of m/z 17 (OH^-) and 18 (OD^-) as a function of reaction time, in a mixture of 0.52% H_2 + 0.52% D_2 + 15% CH_4 in N_2O at a total pressure of 2.3 Torr, $T = 456$ K.

We pointed out earlier that the use of a P_2O_5 trap with a mixture of nitrous oxide, D_2, and CH_4 markedly reduced, but did not completely eliminate, residual OH^- ion existing at long reaction times (see Figure 2). This could result from reaction 10 involving residual water in the ion source not removed even by the use of P_2O_5 trap, or it could result from reaction 9, i.e., exchange of OD^- with CH_4. If the latter be the case, the ratio k_9/k_5 can be obtained from the relation

$$(OH^-)/(OD^-) = k_9(CH_4)/k_5(D_2) \qquad (13)$$

and k_9 values can be obtained from this ratio and the k_5 values given in Table I. The k_9 value thus obtained is included in Table I, but it must be remembered that, since the occurrence of reaction 10 has not necessarily been completely eliminated, the value given in Table I is only an upper limit. In a similar manner, in a system containing $i\text{-}C_4H_{10}$ instead of CH_4 we obtained and give in Table I an upper limit for the rate constant for the reaction of OD^- with $i\text{-}C_4H_{10}$. Exchange of OD^- with these two hydrocarbons is very slow, and may well even be zero.

The average of the five rate constants for reaction 5 given in Table I is 3.2×10^{-11} cm^3/molecule·s, and the reaction efficiency is 2.9×10^{-2}. In the temperature range studied the rate constants exhibit a very weak negative temperature dependence, which can be expressed as

$$k = CT^n \qquad (14)$$

where $n \sim -0.7$. Indeed, the variation with temperature is of the order of the experimental error of the rate-constant measurements. However, no question exists that in reaction 5 one finds the combination of a low rate constant (low reaction efficiency) and a very small negative temperature dependence of the rate constant. A survey of temperature effects in ion-moecule reactions has recently appeared,[16] and for a very large majority of the reactions reported one finds that slow reactions ($k \leq 5 \times 10^{-10}$ cm^3/molecule·s) have relatively large negative temperature dependencies (n in eq 14 as large as -10). Conversely, fast reactions ($k \sim 10^{-9}$ cm^3/molecule·s) have zero or small temperature dependencies. Obviously, reaction 5 does not conform to this kind of behavior.

An inspection of the table of temperature dependencies in Table I of ref 16 gives the result that only six reactions have the combination of low rate and small temperature coefficient shown by reaction 5. Five of these are charge-transfer reactions, which are probably not directly comparable with reaction 5, and the other is a proton-transfer reaction:

$$N_2OH^+ + CO \rightarrow COH^+ + N_2O \qquad (15)$$

However, the rate constant for reaction 15 (3.2×10^{-10} cm^3/molecule·s at 620 K) is approximately ten times greater than that for reaction 5, which makes the comparison of the two less than perfect. Thus the behavior of reaction 5 is certainly unusual, and perhaps unique.

Slow ion-molcule reactions with negative temperature dependencies can be rationalized theoretically by using elementary transition state theory and RRKM concepts (see ref 16 for a summary of these methods). However, achieving a theoretical understanding of the factors involved in reaction 5 may well require a detailed calculation.

A possible way of reconciling a low negative dependence with a low rate is by postulating a small positive activation barrier for the reaction. We think it reasonable to assume that a four-center transition complex is operative in reaction 5, and transition-state theory predicts a T^{-1} temperature dependence for a reaction involving the formation of such a transition complex from two diatomic reactants. The close agreement of the calculated T^{-1} dependence with our observed $T^{-0.7}$ dependence will permit the existence of only a small activation barrier to account for the observed temperature dependence. We estimate 0.3–0.5 kcal/mol. However, a barrier of this small magnitude would produce a reaction efficiency of 0.5 compared with our experimental value of 2.9×10^{-2}. We are unable to find a positive activation barrier which will account for both our experimental temperature dependence and reaction efficiency. Thus we do not think that the explanation of our results for reaction 5 should be formulated in terms of the presence of a positive barrier.

The remainder of our experimental observations can be fairly well understood in terms of accepted concepts. The ratio of rate constants k_6/k_5 exhibits a small positive temperature coefficient (Figure 3). Rate constants from ion-molecule reactions may be written as the products of Langevin collision rate constants and collision efficiencies, p, and thus we may write

$$k_6/k_5 = (k_{L_6}/k_{L_5})(P_6/P_5) \qquad (16)$$

Using calculated values of k_L and rearranging, (16) becomes

$$P_6/P_5 = 0.74(k_6/k_5) \qquad (17)$$

At $T = 483$ K the average of the values of k_6/k_5 obtained by our two methods of measurement is 0.70, and substituting this value in (17) gives $P_6/P_5 = 0.52$. We suggest that the lower reaction probability in reaction 6 is the result of an activation barrier. Using tabulated energy values[18,19] one calculates that reaction 5 is 0.42 kcal/mol exothermic and reaction 6 is 0.58 kcal/mol endothermic. If we assume that reaction 5 has no activation barrier and in reaction 6 the activation barrier is equal to the endothermicity, we calculate

$$P_6/P_5 = e^{-E_6/RT} = 0.55 \qquad (18)$$

at 483 K, which agrees well with the experimental value.

The exchange of OD^- with H_2O (reaction 10) is very fast (1.2×10^{-9} and 1.5×10^{-9} cm^3/molecule·s at 595 and 480 K, respectively). Proton-transfer reactions with exothermicities greater than about 5 kcal/mol are known to be fast with small temperature coefficients, but slow proton-transfer reactions are observed when the exothermicities are smaller.[16] The transfer of D^+ from CH_4D^+ to CH_4 is virtually thermoneutral, but unfortunately different workers have obtained contradictory results for this reaction. Fast exchange has been found recently[20] in the hydronium ion–water system at 300 K, but the reactions are reported to be quite complex. It appears that the number of known essentially thermoneutral proton transfer reactions with which reaction 10 can be compared is not large.

It has been suggested[8,13,14] (see Introduction) that the occurrence or nonoccurrence of exchange is related to the energy required to remove a proton from one exchanging partner and attach it to the other exchanging partner. The proton-transfer reaction pertinent to the exchange of OD^- with H_2 is

$$OD^- + H_2 \rightarrow ODH + H^- \qquad (19)$$
$$\Delta H = 9 \text{ kcal/mol}$$

and that for the exchange of OD^- with CH_4 is

$$OD^- + CH_4 \rightarrow ODH + CH_3^- \qquad (20)$$
$$\Delta H = 25 \text{ kcal/mol}$$

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The energies used in these calculations are taken from the compilation of Rosenstock and co-workers[18] and the compilation given by McIver and co-workers.[21] The appreciably higher endothermicity in reaction 21 compared with that in (19) would result in a lower (and perhaps zero) rate of exchange of OD^- with CH_4 compared with that for exchange with H_2. Similar considerations apply to the absence of exchange between OD^- and i-C_4H_{10}.

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Photoelectrochemical Behavior of n-GaAs Electrodes in Ambient-Temperature Molten-Salt Electrolytes

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Abstract: Photoelectrochemical (PEC) characterization of n-GaAs electrodes was carried out in room-temperature molten-salt electrolytes by using the aluminum chloride–butylpyridinium chloride ($AlCl_3$–BPC) system as a representative example. The working potential limits for the above electrodes in the melts, containing varying ratios of $AlCl_3$ and BPC, were established by cyclic voltammetry. Flat-band potential (V_{fb}) measurements on n-GaAs in the same melts enabled location of the semiconductor band edge positions relative to the melt stability windows. In electrolytes containing $AlCl_3$ and BPC in the 1:1 molar ratio, the available range of potential was wide enough to probe the entire band-gap region. On the other hand, the potentials corresponding to the conduction band edges of n-GaAs were beyond the cathodic stability limit of both the 2:1 and 0.75:1 $AlCl_3$–BPC compositions. The electrode dissolution behavior of illuminated n-GaAs electrodes was investigated by cyclic voltammetry in melts of varying composition containing no intentionally added electroactive species. The onset of photoanodic corrosion currents was significantly positive of the values observed in aqueous electrolytes. The redox behavior of ferrocene–ferricenium ion couple ($Fe(Cp)_2/Fe(Cp)_2^+$) was studied by cyclic voltammetry on vitreous carbon electrodes in the 2:1, 0.75:1, and 1:1 $AlCl_3$–BPC electrolytes. This couple was electrochemically reversible in the above melts. Photogenerated holes on n-GaAs electrodes were competitively captured by the electrochemically active ferrocene species in the 1:1 $AlCl_3$–BPC electrolyte. This redox reaction occurred quite efficiently at the expense of the parasitic electrode dissolution process as judged by the constancy of photocurrents in a n-GaAs |1:1 $AlCl_3$–BPC||$Fe(Cp)_2/Fe(Cp)_2^+$|C PEC cell under short-circuit conditions for periods up to ~1 month. The underpotentials developed for the photoanodic process on n-GaAs relative to the reversible (dark) thermodynamic values on vitreous carbon were direct evidence for the sustained conversion of light energy to electrical energy. Rectifying behavior was observed on n-GaAs electrodes, with the reduction waves corresponding to the dark reduction of ferricenium chloride. The occurrence of this process at potentials positive of V_{fb} indicated the mediation of surface states in the electron-transfer process. Nonoptimized n-GaAs|1:1|$AlCl_3$–BPC||$Fe(Cp)_2/Fe(Cp)_2^+$|C PEC cells typically showed open-circuit potentials of 680 mV, fill factors around 0.49, and a net optical-to-electrical conversion efficiency of ~1% under illumination with a tungsten lamp at 40 mW/cm^2.

Introduction

Considerable attention has been focused in recent years on photoelectrochemical (PEC) conversion of light to electrical and chemical forms of energy.[1] The key element of PEC cells is the semiconductor photoelectrode. A perennial problem in the efficient operation of PEC devices has been the deleterious corrosion reactions undergone by the semiconducting electrodes, particularly in PEC cells employing aqueous electrolytes. Various approaches have been adopted to tackle this problem, and the parasitic reactions have been supressed to varying degrees of success (for a review of the literature on this topic, see ref 1h). The majority of these studies involve aqueous electrolytes which have at least three major disadvantages when compared with nonaqueous electrolytes: (a) a limited potential range (1.23 V) to work with, (b) the unfavorable shift in anodic decomposition potentials toward more negative values, and (c) fewer reversible one-electron redox couples that can be used without kinetic complication.

Therefore, a more profitable approach hinges on the use of nonaqueous electrolytes in PEC cells in place of aqueous electrolytes.[2-5] The feasibility of converting sunlight to electricity in PEC cells employing nonaqueous solvents has been demonstrated for at least two electrolyte systems, i.e., acetonitrile[2] and ethanol[3] although the reported conversion efficiencies are poor. A recent paper also reports on the photogeneration of solvated

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