The Reactions of Neutral Iron Clusters with D_2O: Deconvolution of Equilibrium Constants from Multiphoton Processes[a]

B. H. Weiller, P.S. Bechthold[b], E.K. Parks, L. G. Pobo, and S.J. Riley

Argonne National Laboratory
Chemistry Division
Argonne, IL 60439

Abstract

    The chemical reactions of neutral iron clusters with D_2O are studied in a continuous flow tube reactor by molecular beam sampling and time-of-flight mass spectrometry with laser photoionization. Product distributions are invariant to a four-fold change in reaction time demonstrating that equilibrium is attained between free and adsorbed D_2O. The observed negative temperature dependence is consistent with an exothermic, molecular addition reaction at equilibrium. Under our experimental conditions, there is significant photodesorption of D_2O ($Fe_n(D_2O)_m + h\upsilon \longrightarrow Fe_n + m\, D_2O$) along with ionization due to absorption of multiple photons from the ionizing laser. Using a simple model based on a rate equation analysis, we are able to quantitatively deconvolute this desorption process from the equilibrium constants.

[b] Permanent address: KFA Jülich, Postfach 1913, D-5170 Jülich, Federal Republic of Germany.

DISCLAIMER

Chemical reactivity is one of the most informative probes of transition metal clusters, especially for revealing variations with size in the properties of neutral clusters.[1-6] A significant advance in chemical reactivity studies is the ability to examine cluster reactions under equilibrium conditions.[5] This allows the measurement of fundamental thermodynamic quantities rather than phenomenological kinetics parameters. The present work describes the determination of equilibrium constants for the reaction of iron clusters with D_2O using a method to treat quantitatively the ubiquitous problem of multiphoton fragmentation/ionization.[7]

The experimental apparatus[1a,6] uses a laser vaporization cluster source coupled to a flow tube reactor. Continuous reagent and carrier gas (He) flows assure that the pressure, temperature, and reaction time are all well defined and reproducible. Source temperature can be varied with resistance heaters. Unless noted, the total source pressure for all experiments was 20.0 torr and the temperature $23\pm3°C$. Upon exiting the reactor, the clusters and products are formed into a molecular beam and detected by pulsed laser ionization (ArF excimer laser, photon energy 6.4 eV) and time-of-flight mass spectrometry.

To derive thermodynamic parameters, it must be shown that the system is at equilibrium. For the reactions of iron clusters (Fe_n, $7<n<34$) with D_2O, mass spectra show that relative product intensities for a particular Fe_n do not change when the reaction time is increased five-fold at a D_2O pressure that gives a significant extent of reaction (>20 %). Such behavior is consistent with a series of equilibria, i.e.:

$$Fe_n \; \overset{D_2O}{\rightleftharpoons} \; Fe_n(D_2O) \; \overset{D_2O}{\rightleftharpoons} \; Fe_n(D_2O)_2 \; \overset{D_2O}{\rightleftharpoons} \; \ldots \ldots \tag{1}$$
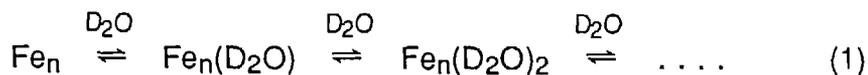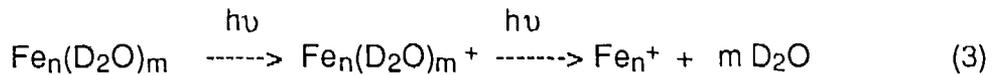
These reactions are expected to be exothermic and therefore should show a negative temperature dependence. Indeed, when the temperature of the reactor is increased from 20° to 55° C at constant D_2O pressure, the molecular addition products decrease in intensity relative to the bare clusters.

The equilibrium constant expression gives a simple relation between product and reactant densities. Assuming that the intensity of an ion signal is proportional to the corresponding neutral density in the flow tube, and that the ionization efficiency is independent of the number of D_2O's on an iron cluster, then in terms of ion signals: $I_{m+1}/I_m = K_{m+1}[D_2O]$. Here I_m is the integrated intensity of the $Fe_n(D_2O)_m^+$ peak and K_m is the corresponding equilibrium

constant. Figure 1 shows these ratios for $Fe_{14}(D_2O)_m$ ($m = 0$ - 2) versus D_2O pressure. The expected linear relationship is not seen for I_1/I_0, yet does seem to hold for I_2/I_1. In general, similar behavior is observed for all iron clusters studied in the range Fe_9 to Fe_{34}.

This deviation from linearity for I_1/I_0 appears to be a consequence of D_2O desorption following multiphoton absorption/ionization:

$$Fe_n(D_2O)_m \xrightarrow{\quad h\upsilon \quad} Fe_n + m\, D_2O \xrightarrow{\quad h\upsilon \quad} Fe_n^+ + m\, D_2O \qquad (2)$$

$$Fe_n(D_2O)_m \xrightarrow{\quad h\upsilon \quad} Fe_n(D_2O)_m^+ \xrightarrow{\quad h\upsilon \quad} Fe_n^+ + m\, D_2O \qquad (3)$$
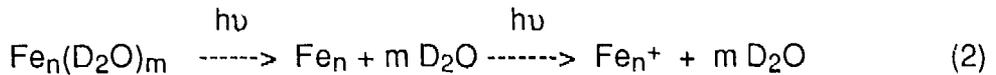
The principal evidence for these processes is a quadratic fluence dependence of I_0 as expected for two-photon generation of bare cluster ion. Under conditions of high D_2O pressure, such that all bare cluster has reacted away (as evidenced by the absence of bare cluster signal at low laser fluence), log-log plots of I_0 versus laser fluence (1.2 to 7.2 mJ/cm^2) are linear with slopes of 2.0 ± 0.2. However, I_2/I_1 is found to be independent of laser fluence. Together with the linear dependence of I_2/I_1 on D_2O pressure, this observation suggests that if desorption occurs, all of the D_2O adsorbates are lost. This is expected for a photon energy much greater than the cluster-D_2O bond energies.

To account for these processes, we use a rate equation analysis[8] of eqs. (2) and (3). If we assume (in addition to the above assumptions) that desorption probabilities are the same for ionized and neutral species and independent of m, then we can define a photodesorption yield, Ω, that is simply the average fraction of $Fe_n(D_2O)_m$ and $Fe_n(D_2O)_m^+$ that fragment to give Fe_n and Fe_n^+, respectively. Then the observed ion intensities (I_m) are given by: $I_m = (1-\Omega)I_m^0$ and $I_0 = I_0^0 + \Omega \sum I_m^0$, where I_m^0 is the ion intensity in the absence of fragmentation. At low D_2O pressures we need only consider the first two equilibria and the following expressions for I_1/I_0 and I_2/I_1 result:

$$\frac{I_1}{I_0} = \frac{(1 - \Omega)K_1[D_2O]}{1 + \Omega K_1[D_2O] + \Omega K_1 K_2[D_2O]^2} \qquad \qquad \frac{I_2}{I_1} = K_2[D_2O]$$

$$(4)$$

The smooth curves in Fig. 1 are least squares fits of the data to the above equations showing that the model can readily explain the data. The resulting values for K_1, K_2, and Ω are $5.9 \pm 0.2 \times 10^5$ atm^{-1}, $1.35 \pm 0.04 \times 10^5$ atm^{-1}, and 0.17 ± 0.04, respectively. K_1 and K_2 are fluence independent, and Ω is roughly linear with laser fluence, as expected. These results indicate that 17% of $Fe_{14}(D_2O)$ and $Fe_{14}(D_2O)_2$ suffer multiphoton fragmentation/ionization, even at the relatively low fluence of 2.4 mJ/cm^2. The equilibrium constants give enthalpies (bond energies) of $\Delta H \sim -18$ kcal/mol assuming that the translational contribution dominates the entropy change. A future article will present equilibrium constants and derived bond energies for Fe_8 through Fe_{22} along with more details of the above analysis.

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Figure Captions

Figure 1. Ratios of $Fe_{14}(D_2O)_m^+$ signals (I_m) versus D_2O pressure in the flow tube reactor. The solid lines are least squares fits to the equations in (4). The ionizing laser fluence was 2.4 mJ/cm^2. The error bars (± 1 sigma) are propagated from individual ion intensities.