Ab initio CALCULATION OF THE EQUILIBRIUM CONSTANT OF THE REACTION Na + H_2O ⇌ NaOH + H

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Theoretical prediction of the equilibrium constant of the title reaction was obtained by a standard statistical-thermodynamic treatment for which all necessary molecular constants were generated by the *ab initio* SCF calculations. The experimental value at 2 030 K is quantitatively reproduced. Comparison with experiment is also made for geometry parameters and vibrational frequencies of NaOH.

Previously we have treated[1] the chemical equilibrium Li + H_2O ⇌ LiOH + H, which is of importance for the determination[2,3] of the dissociation energy of LiOH. Knowledge of the dissociation energy of LiOH is needed in order to apply the Li/LiOH method of measuring the free H-atom concentration in flames[4]. Lithium differs greatly from the other alkali metals[2]: the dissociation energy (MOH → M + + OH) is considerably higher and the equilibrium M + H_2O ⇌ MOH + H is not shifted so markedly to the left. Our previous calculations[1] on the equilibrium constant of the Li + H_2O ⇌ LiOH + H reaction were in excellent agreement with the experimental value at 2 370 K, though they were only of SCF type and of double zeta quality. Next calculations[5] showed that the success of that treatment was due to a cancellation of basis set and correlation effects. Since this cancellation might also be expected in the analogous reaction of the sodium atom, we decided to apply the same theoretical approach to the equilibrium Na + H_2O ⇌ NaOH + H with the aim of giving a theoretical account of the observed difference in the behaviour of lithium and sodium.

CALCULATIONS

Equilibrium constants were calculated by a standard statistical-thermodynamic procedure assuming ideal gas behaviour of all reaction components and the rigid rotator and harmonic oscillator approximation in the construction of partition functions. All necessary energy data and molecular constants were generated by the *ab initio* SCF calculations. For oxygen and hydrogen we useDd unning's[6] (9*s*5*p*)/[4*s*2*p*] and (4*s*)/[2*s*] double zeta basis sets. The hydrogen functions

were scaled by a factor of $(1{\cdot}2)^2 = 1{\cdot}44$. For sodium we used the $(12s7p)/[7s4p]$ basis set developed by us previously[7], but with the changed exponent for the most diffuse p-function (0·05 instead of 0·04).

RESULTS AND DISCUSSION

The first task of any nonempirical theoretical approach to equilibrium constants is the determination of optimum molecular geometries for all reaction components. The total SCF energies at the optimum geometries are then used for the evaluation

TABLE I

Predicted temperature dependence of the equilibrium constant and thermodynamic functions for the reaction Na + $H_2O \rightleftarrows$ NaOH + H

T, K	log K_p	ΔG°, kJ mol^{-1}	ΔH^0, kJ mol^{-1}	ΔS^0, J mol^{-1} deg
700	−10·47	140·5	145·9	7·7
800	− 9·12	139·6	147·4	9·7
1 000	− 7·18	137·4	150·3	12·9
1 200	− 5·86	134·6	152·9	15·2
1 500	− 4·51	129·5	156·4	17·9
2 000	− 3·13	119·9	161·3	20·7
2 030	− 3·07	119·3	161·9	21·0
2 500	− 2·28	108·9	165·4	22·6
3 000	− 1·70	97·5	168·9	23·8

TABLE II

Spectroscopic constants for NaOH

Observable quantity		Calculated	Experimental
Geometry parameters[a]:	r_{NaO}	1·923	1·95[b]
	r_{OH}	0·950	
	$\sphericalangle$ NaOH	180·0	180[b]
Vibrational wavenumbers[c]:	Σ^+	4 120	
	Σ^+	615	431[d]
	Π	461	337[d]

[a] In 10^{-10} m and degrees; [b] ref.[8]; [c] In cm^{-1}; [d] ref.[9].

of the heat of reaction. In our case the obtained SCF energies are the following (expressed as E/E_h, $E_h = 2\,625{\cdot}5$ kJ/mol): $-161{\cdot}844564$ for Na, $-76{\cdot}010999$ for H_2O, $-237{\cdot}293328$ for NaOH and $-0{\cdot}497637$ for H. Next, quadratic force constants for NaOH and H_2O were calculated from which harmonic vibrational frequencies were obtained. The latter were then used for the evaluation of zero-point energies and vibrational partition functions. The final results of the whole treatment are presented in Table I. Experimentally, the equilibrium constant is known[2] at 2 030 K and its value is reproduced precisely by our calculations. The perfect agreement need not be overestimated, but it shows that a justifiable use of modest scale *ab initio* calculations may give quantitative predictions. It appears that a cancellation of basis set and correlation effects is a general feature of the series of reactions $M + H_2O \rightleftharpoons \rightleftharpoons MOH + H$ so that we may also expect a realiable prediction for potassium by using the same type of calculations.

Since gaseous alkali metal hydroxides are not easily accessible to spectroscopic measurement, we considered it expedient to present in Table II the calculated spectroscopic constants for NaOH. One cannot of course expect highly accurate results from SCF calculations of double zeta quality but the data of this kind may be useful for confirming the assignment of the observed bands. The prediction of vibrational frequencies may be improved considerably by applying scaling factors[10,11] to the computed force constants. No such improvement was however attempted, because the computed equilibrium constants are affected rather little by the accuracy achieved in the evaluation of vibrational frequencies.

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