AB INITIO CALCULATIONS OF THE EQUILIBRIUM CONSTANTS OF THE GAS-PHASE REACTIONS $C_2H_2 + OH^- \rightleftharpoons C_2H^- + H_2O$ and $Li + H_2O \rightleftharpoons LiOH + H$

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Preliminary results of ab initio calculations for the two title reactions are reported. Temperature dependences of equilibrium constants were obtained by a standard statistical-thermodynamic treatment for which all necessary molecular constants were generated by the ab initio SCF calculations of double zeta quality. For enthalpy terms the SCF energies were corrected for correlation effects by using known correlation energies of H_2O, OH^- and Li and by making justifiable assumptions about the correlation energies in C_2H_2, C_2H^- and LiOH.

1. Introduction

If the ability to provide estimates of rates and equilibrium constants of "chemical" accuracy is considered as a final state in the development of the theory of chemical reactivity, a provocative question may be asked as to how close we are at present to this ultimate goal.

It is difficult to answer this question because of the scarcity of MO studies in that an explicit evaluation of rate and equilibrium constants was attempted. Semi-empirical methods of the CNDO, INDO and MINDO types have been successful in energy predictions for many chemical problems and they might therefore seem suitable for calculations of rate and equilibrium constants.

In actual applications of the latter we encountered [1—3] however a typical difficulty with the use of semi-empirical methods viz. that one is never sure whether the method is sufficiently reliable for a particular reaction. For example, MINDO/2 gives generally good estimates of heats of formation. We found, however, that it unexpectedly fails badly for some ordinary molecules.

Since the semi-empirical methods do not give the upper bound of energy, it is not possible — in contrast to ab initio calculations — to check the results by performing refined calculations for selected points of the energy hypersurface (e.g. by making use of a larger basis set or/and by estimating the correlation energy in some way).

With ab initio calculations, we found in the literature several papers [4—7] devoted to the estimation of equilibrium constants. As they treat reactions hardly accessible experimentally, the accuracy of calculated equilibrium constants cannot be quantitatively checked.

For this reason we considered it expedient to start an ab initio study for a series of simple gas-phase chemical equilibria. The prime aim of these calculations is to establish how much confidence one may have in equilibrium constants determined by ab initio calculations with a medium sized basis set and a simple statistical-thermodynamic treatment for reactions

for which no experimental data are available.

It is possible to argue that if use is made of experimental geometries, vibrational fundamentals, and heats of formation, one can arrive at more accurate equilibrium constants than by means of ab initio calculations. Ordinarily, however, the complete set of necessary experimental data is not available; if the equilibria involve unstable species then calculations are often the sole source of information. Moreover, a thorough MO study may establish that the assumptions of experimentalists about the nature of a known and simple equilibrium are wrong: our previous semiempirical studies [2,3] can be taken as examples.

Finally, a notable feature of the calculations should be emphasized. Since they are completely independent of experiment, they turn chemistry into an exact science based on postulates of quantum mechanics.

2. Theoretical approach

Equilibrium constants were calculated by a standard statistical-thermodynamic procedure which is described in our earlier paper [1]. Ideal gas behavior was assumed for all reaction components and the partition functions were constructed in the rigid rotator and harmonic oscillator approximation. First the minima on the energy hypersurface were searched for and the equilibrium geometries were determined. Then the force constants were evaluated by a quadratic fit to points corresponding to internal coordinate displacements $\Delta R = \pm 0.05$ bohr and $\Delta \vartheta = \pm 3°$.

The vibrational frequencies, obtained by the Wilson matrix analysis, were used for the construction of vibrational partition functions and for the zero-point energies of the reaction components. Since the accuracy of equilibrium geometries and vibrational frequencies used for the construction of partition functions affects the quality of the latter rather little [8], geometry optimization and evaluation of force constants may be performed with a small or medium-sized basis set and the correlation effects may be disregarded.

The crucial point for a successful estimation of the equilibrium constant is the evaluation of the heat of reaction. Since one can arrive at reasonable equilibrium constants only with highly accurate heats of reaction, the energies of reaction components must be

calculated with a large basis set and correlation effects must be accounted for. Refinement of the calculations along these lines for the two reactions studied will be presented in a full communication.

The basis set used throughout in this paper is of double zeta quality. For carbon, oxygen, and hydrogen we used the [4s2p/2s] contracted gaussian basis set proposed by Dunning [9]. The hydrogen functions were scaled by a factor of 1.2. The contracted [4s2p] set was also used for lithium [10]. Its selection was based on the recommendation of Schaefer [11] that if minimum or double zeta basis sets are to be used for Li, the 2s–2p near degeneracy should be recognized and at least a 2p function added to the basis set.

Estimates of correlation energy changes in the reactions were based on the following assumptions. Correlation energies in C_2H_2 and C_2H^- were assumed to be the same because of the same number of electron pairs and their mutual orientation in the two systems. Since the calculations suggest that LiOH is almost completely ionic [12], its correlation energy was taken as a sum of correlation energies for Li^+ and OH^-. For H_2O and OH^- we employed the correlation energies given by IEPA calculations [13], for Li and Li^+ we took values from ref. [14].

3. Results and discussion

In this paper we restrict ourselves to equilibrium constants; the results on equilibrium geometries, force constants, and other details about calculations will be given in a full communication. The results on the two equilibria studied are summarized in table 1 and fig. 1.

With the $C_2H_2 + OH^- \rightleftharpoons C_2H^- + H_2O$ process, meaningful results are obtained only if correlation effects on ΔH_0^0 are accounted for. At 296 K the error in ΔH^0 is 2.8 kcal/mole, which brings about the error of two orders for the equilibrium constant. For temperatures above 1000 K the computed equilibrium constants are believed to be accurate within one order.

With the $Li + H_2O \rightleftharpoons LiOH + H$ reaction, the SCF data are markedly superior, presumably because of a fortuitous cancelation of basis set and correlation effects. A deeper insight into this equilibrium requires refined calculations. These are in progress and will be reported in a full communication.

Table 1
Thermodynamic functions

Reaction	Origin of data [a]	ΔH_0^0 (kcal/mole)	ΔH_T^0 (kcal/mole)	ΔS_T^0 (eu)	ΔG_T^0 (kcal/mole)	$\log K_p$
$C_2H_2 + OH^- \rightleftharpoons C_2H^- + H_2O$	SCF	−21.10	−20.90	4.20	−22.14	16.35
($T = 296$ K)	SCF + ΔE^{corr}	− 9.20	− 9.00	4.20	−10.24	7.56
	experiment [15]		− 6.2	3.6	− 7.3	5.40
$Li + H_2O \rightleftharpoons LiOH + H$	SCF	9.40	14.65	3.75	5.77	− 0.53
($T = 2370$ K)	SCF + ΔE^{corr}	− 1.40	3.85	3.75	− 5.03	0.46
	experiment [16]					− 0.57

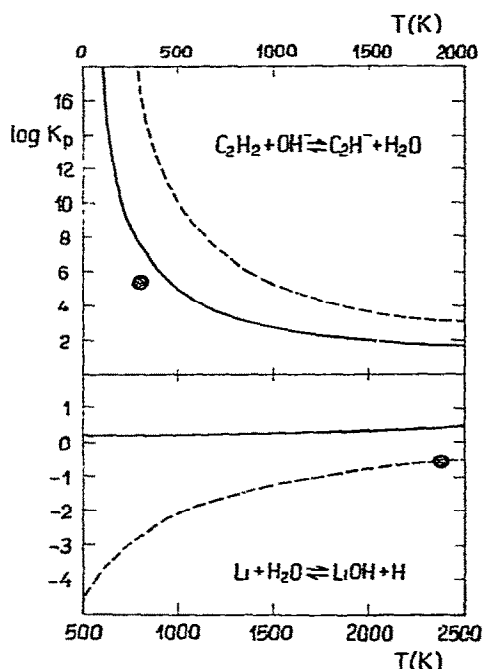[a] The two theoretical treatments differ in the evaluation of the energy changes (see text).

Fig. 1. Temperature dependence of the equilibrium constants. Dashed lines correspond to SCF calculations. Full lines refer to treatments based on heats of reaction corrected for correlation effects. Experimental data are indicated by full circles (for references see table 1).

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