Heats of Formation for Third-Period Hydrides: Test of an Extended Basis Set

Mark S. Gordon
John Heitzinger
Heats of Formation for Third-Period Hydrides: Test of an Extended Basis Set

Mark S. Gordon* and John Heitzinger

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

(Received: September 23, 1986)

The extended basis set developed by McLean and Chandler for third-period atoms is combined with the -311G hydrogen basis and augmented by polarization functions to predict the heats of formation of third-period hydrides at the full MP4 computational level. The calculated heats of formation are at least as accurate as those predicted for second-row hydrides by using MP4/6-311G(d,p) wave functions, with a root mean square error of approximately 4 kcal/mol.

Introduction

In a recent paper, Pople, Luke, Frisch, and Binkley3 (PLFB) described a procedure for using accurate electronic structure calculations to predict heats of formation of small molecules. In that work the method was applied to a series of hydrides containing one heavy atom from the first three periods of the periodic table, and the results for several basis sets were compared. For second-period atoms (Li–F) all basis sets used contained the 6-311G(d,p) basis set, as a subset, since a sensible starting point for generating a highly correlated wave function, especially for small molecules, is the use of a triple zeta plus polarization (TZP) basis set. Since a comparably systematic basis set was not available for third-period atoms (Na–Cl), for these atoms the authors used 6-31G(d,p)3 as a starting point instead.

We have recently made use of the McLean–Chandler4 (MC) basis set, augmented by the standardd polarization functions, for the prediction of the energetics for reactions of silicon-containing compounds.5 MC is a segmentally contracted basis set with fewer raw Gaussians but more basis functions than one would have in a 6-311G basis for the same atom. For example, for Si, P, S, and Cl, the s basis functions have a 631111, rather than a 66311, contraction with the sets of 6 and 3 Gaussians sharing one common function (i.e., a segmented contraction). Similarly, the p basis functions have a segmental 52111, rather than a 6311, contraction.6 Since the limited applications of the MC basis set have produced reasonably accurate predictions,7 in the present note we use this basis to predict the heats of formation for the same hydrides of Si, P, S, and Cl as those considered by PLFB.

Computational Method

The McLean–Chandler basis set4 was used for all calculations. For third-row atoms, this basis was augmented by a set of six d functions with the exponents developed for the 6–31G basis.3 For hydrogen, the –311G(p) basis5 was used. The net basis set is then referred to as MC-311G(d,p).

Following PLFB,8 all calculated reaction energies were obtained by using full fourth-order perturbation theory (MP4), including triples and excluding correlation of the core electrons, at the 6-31G(d) geometries quoted in ref 1. The procedures suggested in that paper for obtaining heats of formation at 298 K were used here as well. All calculations were carried out on the ground states of each species (with restricted or unrestricted wave functions as appropriate) using GAUSSIAN82.7

Results and Discussion

The calculated heats of formation and their deviations from the experimental values8 are summarized in Table I. The results for the 6-31G(d,p) and extended basis sets used by PLFB are included for comparison. While the heats of formation predicted by MP4/MC-311G(d,p) are not quite as accurate as those estimated by using the 6-31G(2df,p) basis, they clearly represent a significant improvement relative to 6-31G(d,p), with a root mean square (RMS) error of just over 4 kcal/mol. (This error would be smaller for all basis sets if the more recent experimental heat of formation for SH2 of 65.3 kcal/mol were used.) For comparison, the RMS deviation of the MP4/6-31G(d,p) heats of formation from experiment for second-period hydrides (excluding BH2)9 is 5.4 kcal/mol.

We conclude that the MC basis set is consistently at least as accurate as 6-31G and that use of these two basis sets (6-31G for first- and second-period atoms, MC for third-period atoms, augmented by appropriate polarization functions) to obtain accurate reaction energetics with correlated wave functions is a reasonable procedure. The MC basis set has now been incorporated into the most recent version11 of GAMESS.12

Acknowledgment. This work was supported by grants from

---

(4) (a) McLean, A. D.; Chandler, G. S. J. Chem. Phys. 1980, 72, 5639. (b) For Si, the p orbital contraction is an unsegmented 42111.

---

TABLE I: Heats of Formation for Third-Period Hydrides (kcal/mol)*

<table>
<thead>
<tr>
<th>Hydride</th>
<th>6-31G(d,p)</th>
<th>MC-311G(d,p)</th>
<th>EXTa</th>
<th>EXTb</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH</td>
<td>91.3</td>
<td>1.3</td>
<td>90.0</td>
<td>0.0</td>
</tr>
<tr>
<td>SiH2</td>
<td>68.7</td>
<td>10.8</td>
<td>66.1</td>
<td>8.2</td>
</tr>
<tr>
<td>SiH3</td>
<td>52.6</td>
<td>6.2</td>
<td>50.0</td>
<td>3.6</td>
</tr>
<tr>
<td>SiH4</td>
<td>33.4</td>
<td>5.2</td>
<td>34.3</td>
<td>1.7</td>
</tr>
<tr>
<td>PH</td>
<td>61.9</td>
<td>10.4</td>
<td>60.1</td>
<td>4.6</td>
</tr>
<tr>
<td>PH2</td>
<td>54.5</td>
<td>7.5</td>
<td>50.7</td>
<td>3.8</td>
</tr>
<tr>
<td>PH3</td>
<td>12.1</td>
<td>11.0</td>
<td>7.1</td>
<td>5.4</td>
</tr>
<tr>
<td>PH4</td>
<td>3.5</td>
<td>7.4</td>
<td>3.7</td>
<td>4.0</td>
</tr>
<tr>
<td>SH</td>
<td>38.8</td>
<td>5.5</td>
<td>37.2</td>
<td>3.9</td>
</tr>
<tr>
<td>SH2</td>
<td>2.5</td>
<td>7.4</td>
<td>0.9</td>
<td>4.0</td>
</tr>
<tr>
<td>SH3</td>
<td>-17.5</td>
<td>4.6</td>
<td>-23.6</td>
<td>-1.5</td>
</tr>
<tr>
<td>SH4</td>
<td>0.7</td>
<td>7.4</td>
<td>0.9</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*All calculations were performed at the MP4(SDTQ) level. DEV denotes deviation from experiment, defined as theory – experiment. EXTa refers to the results for the 6-31G(2df,p) basis set, estimated as described in ref 1. EXTb = root mean square deviation from experiment.
Collisional Energy Transfer in the Two-Channel Thermal Unimolecular Reaction of Bromoethane-2-d

Kyung-Hoon Jung,* Sung Hoon Kang, Chul Un Ro, and E. Tschulakov-Roux

Department of Chemistry, Korea Advanced Institute of Science and Technology, Chongyangni, Seoul 131, Korea

Department of Chemistry, University of Calgary, Alberta, Canada T2N 1N4 (Received: August 15, 1986)

Unimolecular thermal decomposition in the two-channel bromoethane-2-d system was studied over the temperature range of 660–706 K in the presence of CF<sub>4</sub> and He bath gases. The C<sub>2</sub>H<sub>5</sub>Br system was also studied as a reference process. The average energy removed per collision from energized bromoethane-2-d by a bath gas (ΔE<sub>down</sub>) is as follows: by the substrate, 1100 cm<sup>-1</sup> (stepladder model); by CF<sub>4</sub>, 675 cm<sup>-1</sup> (exponential model, EXP); by He, 215 cm<sup>-1</sup> (EXP). Comparison is made with recent studies of direct measurements. The relative rate ratio of two-channel reaction has been expressed in terms of microscopic rate ratio and distribution function of the reacting molecule. Arrhenius parameters, i.e., log A and E<sub>kcal/mol</sub>, at ca. 50 Torr of total pressure were found to be as follows: for C<sub>2</sub>H<sub>5</sub>Br, 13.37 ± 0.18, 53.36 ± 0.55; for CH<sub>2</sub>DCH<sub>2</sub>Br, 13.16 ± 0.16 and 53.30 ± 0.51 (HBr elimination) and 12.83 ± 0.30 and 54.29 ± 0.92 (DBr elimination).

I. Introduction

The multichannel thermal unimolecular reaction systems have attracted considerable interest in elucidating more reliable and significant information about intermolecular energy-transfer process in thermal reactions. The measurements of the ratio of rate constants of competitive reactions have canceling effects of unpredictable experimental error and produces a marked difference between weak and strong collision systems at low pressures. Since the usefulness was first recognized by Chow and Wilson, successful utilizatons of two-channel systems have been demonstrated for the isomerization of cyclopropane-1,1-d<sub>2</sub> in He bath gas systems<sup>2</sup> and for the decompositions of C<sub>5</sub>H<sub>9</sub>I, CH<sub>2</sub>DCH<sub>2</sub>Cl, and CHD<sub>2</sub>CD<sub>2</sub>Br at very low pressure. The work extended to the three-channel system of cyclopropane-l-t-2,2-d<sub>2</sub> by Rabinovitch et al.<sup>4</sup> has shown a rather marked decline of both the relative collision efficiency, β<sub>r</sub>, and the average energy removed per collision, (ΔE)<sub>down</sub> for several bath gases with temperature rise. These indirect measurements of the collisional energy-transfer parameters require the explicit knowledge of kinetic parameters of reference process, while recent direct measurements<sup>5</sup> by transient spectroscopy do not employ the unimolecular reaction system. However, an accurate evaluation of the microscopic rate constant k(E) and critical energy E<sub>k</sub> of the unimolecular reaction from thermal or external activation study renders it possible to obtain more reliable information on energy transfer.

In the present study, intermolecular energy transfer has been investigated in two-channel competitive HBr/DBr elimination reactions of CH<sub>2</sub>DCH<sub>2</sub>Br. The experiments have been carried out both in the neat system and in the presence of He and CF<sub>4</sub> as collisional partners. The energy-transfer parameters of weak colliders He or CF<sub>4</sub> have been deduced from differential dilution experiments by collision partners at constant pressure of parent gas. Concomitant work on thermal reaction of C<sub>2</sub>H<sub>5</sub>Br has been used to determine the rate constant parameters for CH<sub>2</sub>DCH<sub>2</sub>Br and to obtain supplementary information on vibrational energy transfer of neat system.

Measurement of the relative rate ratio as a function in H(D)Br elimination reactions of CH<sub>2</sub>DCH<sub>2</sub>Br has permitted the reliable evaluation of intermolecular energy-transfer parameters. We have presented an explicit expression for the macroscopic rate ratio of two-channel reaction in terms of the energy-dependent microscopic rate ratio and the normalized distribution function of reacting molecule dissociating into each reaction path. This approach has permitted a useful interpretation on the pressure dependence of the relative rate ratio in weak and strong collision systems of thermal unimolecular reaction.

II. Experimental Section

The experiment was performed in a static system with a 887.0-cm<sup>2</sup> (65 mm i.d. × 30 cm length) cylindrical quartz vessel, which had been seasoned by a number of runs at higher pressure and temperature than the actual run prior to the experiment. The reaction vessel was placed in the middle zone of the tubular furnace, Electroglass, equipped with three separated heating zones. The temperature of the furnace was controlled by internal thermocouples within ±1 °C along the length of the furnace. The fluctuation of temperature in the reaction vessel was kept less than ±0.5 °C throughout the entire experiment. The dead volume of the reaction was less than 1% of the total volume.

The reaction product analysis was carried out with a two-stage gas chromatograph equipped with a single flame ionization detector (FID). The first stage high temperature column, 1/8 m length × 1/8 in. o.d. stainless steel Porapak S, was operated at 80 °C to separate the reaction product from the reactant. The reaction product portion from the first stage separation was then