ON THE PROTON AFFINITY OF HYDROGEN AND SATURATED HYDROCARBONS

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Abstract

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The affinity of molecules for the proton P is a very important thermochemical constant. Meanwhile, direct experimental data on proton affinity, obtained by the electron-impact method, were until recently known only for unsaturated compounds.

The existence of a positive affinity of hydrogen and methane for the proton follows from the existence of the stable ions H_3^+ (1) and CH_5^+ (2). There is no information in the literature concerning the "onium" ions of the homologues of methane. In a paper by one of the authors (3) it was shown that, upon collision of the molecular ions of ethane, propane, and butane with molecules of these substances, the corresponding "onium" ions are not formed. In that work, and also in the work of Stevenson and Schissler (13), the lower limit of P_{H2} was estimated. Hirschfelder (4) and Barker and Eyring (5) carried out a theoretical calculation of the energy of the H_3^+ ion. Simons et al. obtained the value P_{H2} on the basis of Hirschfelder' s calculations from the interaction law of H^+ with H_2, obtained in experiments on the scattering of protons in hydrogen (6). The present communication sets forth the results of experiments on determining the proton affinity of hydrogen, methane, ethane, and propane by the ion-impact method developed by the authors (7).

Experiments to detect reactions leading to the formation of secondary H_3^+ ions were carried out on an MS-1a mass spectrometer (8). The energy of the ionizing electrons was 50 eV. In experiments with variation of the gas pressure in the ion source, the following reactions were investigated:

$$(1)\ H_2^+ + H_2 \to H_3^+ + H; \quad (2)\ H_2^+ + C_2H_2 \to H_3^+ + C_2H; \quad (3)\ H_2 + C_2H_2^+ \to H_3^+ + C_2H;$$

$$(4)\ H_2^+ + C_2H_6 \to H_3^+ + C_2H_5; \quad (5)\ H_2 + C_2H_6^+ \to H_3^+ + C_2H_5.$$

It was shown that addition of acetylene to an ion source containing hydrogen at a pressure of $\sim 10^{-4}$ mm Hg does not increase the yield of H_3^+ ions. Under these conditions H_3^+ ions are formed only in process (1). However, addition of ethane to the ion source under analogous conditions increases the current of H_3^+ ions; this indicates that, in addition to (1), at least one of the processes

(4) or (5) takes place. To estimate the limiting values of the affinity of the H_2 molecule for the proton, the authors used the following values of the dissociation energies and ionization potentials of the molecules: $D(H_2) = 103.2$ kcal/mole, $D(C_2H_5—H) = 96$ kcal/mole (9), $D(C_2H—H) = 121$ kcal/mole (9), $I(H_2) = 15.43$ eV, $I(C_2H_2) = 11.43$ eV (10), $I(C_2H_6) = 11.76$ eV (10).

Since, in accordance with the rule underlying the ion-impact method, the heat effect of ion-molecule reactions detectable mass-spectrometrically is positive or equal to zero, whereas that of undetectable reactions is negative, the use of the experimental information on reactions (1)-(5) and of the energy quantities given above makes it possible to write the following series of inequalities determining the limits of the permissible values of the proton affinity: 1) $P_{\mathrm{H2}} \geqslant 61$ kcal/mole; 2) $P_{\mathrm{H2}} < 79$ kcal/mole; 3) $P_{\mathrm{H2}} < 171$ kcal/mole; 4) $P_{\mathrm{H2}} \geqslant 54$ kcal/mole.

Inequalities 1) and 2) determine the narrowest interval of possible values of P_{H2}: 61 kcal/mole $\leqslant P_{\mathrm{H2}} < 79$ kcal/mole. Taking the mean of the two

of the extreme possible values, we obtain $P_{\mathrm{H_2}} = 70 \pm 9$ kcal/mole. It is interesting that calculation of this quantity on the basis of data (4) and (5) and the experimental value $D\_(H_2)$ gives 81 and 77 kcal/mole, while Simons' experiments give 69.2 kcal/mole.

All subsequent experiments were carried out on a special mass spectrometer possessing increased sensitivity and the capability of accurately measuring ion appearance potentials (11). To determine the proton affinity of the methane molecule, the following processes were studied, in which the ion CH_5^+ can be formed:

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3; \tag{6}$$

$$CH_4 + C_2H_6^+ \rightarrow CH_5^+ + C_2H_5; \tag{7}$$

$$CH_4 + H_2O^+ \rightarrow CH_5^+ + OH; \tag{8}$$

$$CH_4^+ + H_2O \rightarrow CH_5^+ + OH; \tag{9}$$

$$CH_4 + H_2^+ \rightarrow CH_5^+ + H; \tag{10}$$

$$CH_4^+ + H_2 \rightarrow CH_5^+ + H; \tag{11}$$

$$C_3H_6^+ + CH_4 \rightarrow CH_5^+ + C_3H_5; \tag{12}$$

$$C_3H_6 + CH_4^+ \to CH_5^+ + C_3H_5. \qquad (13)$$

Fig. 1. Appearance curves of the ions CH_4^+ and CH_5^+ from methane. The number next to the CH_4^+ appearance curve is the coefficient by which the corresponding ordinates must be multiplied in order to compare the appearance curves with one another. $P_{\text{syst.}\,CH_4} = 10^{-4}$ mm Hg, $P_{\text{syst.}\,C_2H_6} = 2 \cdot 10^{-4}$ mm Hg.

The reaction (6) was identified by comparing the appearance potentials of the ions CH_4^+ and CH_5^+. The corresponding current appearance curves are shown in Fig. 1. When ethane is added to the ion source, the appearance potential of CH_5^+ ions does not change. This means that process (7) is endothermic.

Processes (8) and (9) were tested in an experiment with an increase in the pressure of water vapor in the ion source. Ionization was carried out by electrons with an energy of 14 eV. Under these conditions, in the ionization chamber the primary ions were only CH_4^+ and H_2O^+. An increase in the pressure of water vapor does not lead to an increase in the yield of CH_5^+ ions. The current of ions of 17 a.m.u. remains constant and is due to isotopic ions of methane and secondary CH_5^+ ions formed in process (6). Addition of hydrogen to an ion source containing methane increases the yield of CH_5^+ ions (Fig. 2). This increase is evidently caused by at least one of the processes (10) or (11). An analogous experiment was carried out with propylene added to the ion source (Fig. 3). The increase in the current of CH_5^+ ions in this case is associated with at least one of the processes (12) or (13).*

Calculation of the limiting values of the proton affinity of methane, P_{CH_4}, performed on the basis of the information obtained on the processes of formation of CH_5^+ ions, gives the following inequalities: 6) $P_{CH_4} \geq 114$ kcal/mole; 7) $P_{CH_4} < 139$ kcal/mole; 8) $P_{CH_4} < 129$ kcal/mole; 9) $P_{CH_4} < 139$ kcal/mole; 10) $P_{CH_4} \geq 61.2$ kcal/mole, 11) $P_{CH_4} \geq 91$ kcal/mole.

Inequalities 6) and 8) determine the narrowest limits:

$$114 \text{ kcal/mole} \leq P_{CH_4} < 129 \text{ kcal/mole}.$$

In the calculation, along with the values $D(H_2)$, $D(C_2H_5\text{—}H)$, $I(H_2)$, $I(C_2H_6)$ given above, the following quantities were used: $D(CH_3\text{—}H) = 101$ kcal/mole (9), $D(HO\text{—}H) = 116$ kcal/mole (9), $D(C_3H_5\text{—}H) = 77$ kcal/mole (12), $I(CH_4) = 13.04$ eV (10), $I(H_2O) = 12.62$ eV (10), $I(C_3H_6) = 9.84$ eV (10).

* Since processes (10) and (11), as well as (12) and (13), were not each studied separately, we are justified in confidently ascribing the increase in the secondary-ion current only to the process that gives the smaller value of P_{CH_4}.

Searches for "heavier" $C_2H_7^+$ ions were carried out in collisions of ethane ions or molecules with molecules and ions of various hydrocarbons, as well as of

Fig. 2

Figure 1: Fig. 2

hydrogen. The following collision processes were investigated:

$$C_2H_6^+ + H_2; \quad C_2H_6 + H_2^+; \quad C_2H_6^+ + CH_4;$$

$$C_2H_6 + CH_4^+; \quad C_2H_6 + C_3H_8^+; \quad C_2H_6^+ + C_3H_8;$$

$$C_2H_6 + \text{n-}C_4H_{10}^+; \quad C_2H_6^+ + \text{n-}C_4H_{10};$$

$$C_2H_6 + \text{iso-}C_4H_{10}^+; \quad C_2H_6^+ + \text{iso-}C_4H_{10}; \quad C_2H_6^+ + C_2H_6.$$

Fig. 2. Dependence of the yield of CH_5^+ ions on the hydrogen pressure. In the ion source, a CH_4—H_2 mixture. The gas pressure in the ion source is $\sim 10^6$ times smaller than the pressure in the inlet volume.

Adding to an ion source containing ethane any of the indicated gases does not lead to an increase in the ratio of the currents of ions of 31 and 30 a.m.u.; the latter remains equal to the ratio of the currents of the corresponding isotopic ethane ions (2.3%). Consequently, in none of the processes are $C_2H_7^+$ ions formed. The smallest possible value of the upper limit for the proton affinity of the ethane molecule is given by use of the process $C_2H_6 + H_2^+$. In this case one obtains

$$P_{C_2H_6} < 61 \text{ kcal/mol}.$$

Searches for $C_3H_9^+$ ions were carried out in the ionization of propane, and also in the ionization of mixtures of propane with hydrogen, with methane, and with ethane. It was shown that $C_3H_9^+$ ions are not detected as products of the processes

$$C_3H_8^+ + H_2, \quad C_3H_8 + H_2^+, \quad C_3H_8^+ + CH_4,$$

$$C_3H_8 + CH_4^+, \quad C_3H_8^+ + C_2H_6, \quad C_3H_8 + C_2H_6^+, \quad C_3H_8 + C_3H_8^+.$$

The smallest possible value of the upper limit $P_{C_3H_8}$ is given by the process $C_3H_8 + H_2^+$. Thus,

$$P_{C_3H_8} < 61 \text{ kcal/mol}.$$

Fig. 3

Figure 2: Fig. 3

Fig. 3. Dependence of the yield of CH_5^+ ions on the propylene pressure. In the ion source, a CH_4—C_3H_6 mixture; $P_{\text{inlet } CH_4} = 50$ mm Hg.

Strictly speaking, the detection of all the ion-molecular processes cited in the article with the apparatus used by the authors is possible not only in the case of their thermoneutrality or exothermicity, but also when the process is endothermic by $1 \div 2$ kcal/mol. This leads to a lowering of the values found by 1—2 kcal/mol.

The observed sharp difference in proton affinity between methane and its homologues is quite unexpected and requires a theoretical explanation.

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