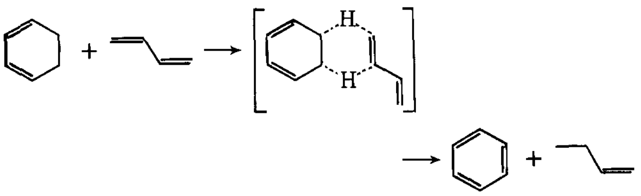
mediate species, as Kwiatek[3] has postulated, i.e., a σ-bonded intermediate gives 1-butene, while π-adsorbed intermediates give 2-butenes. However, this may not be the case in reaction b. The only factor that could account for the different products is the source of hydrogen. Thus, favorable formation of 1-butene in reactions a and b suggests the possible formation of an intermediate of the form



in which two H atoms are transported *simultaneously* to one end of the diolefin, which is an allowed process according to the Woodward–Hoffmann rules. In reaction c, which yields predominately 2-butenes, the process may occur via the reactive adsorption of dihydrogen from the gas phase directly onto adsorbed 1,3-butadiene.[1] ^{13}C NMR analysis revealed that the two D atoms from D_2 are located almost exclusively on the 1 and 4 carbon atoms of *trans*-2-butene.

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Site of Protonation in Aromatic and Acyclic Amines and Acyclic Amides Revealed by N_{1s} Core Level Electron Spectroscopy

Sir:

Considerable gas phase proton affinity data has been collected in recent years by means of high pressure mass spectrometry and ICR techniques[1] and the data indicates that the behavior of the free molecule is frequently quite different from that in solution. Neither of the principally used proton affinity methods is capable of directly identifying the site of protonation in the molecule and those methods traditionally used to deduce this information (e.g., NMR) are done in solution in which the compound may behave differently. Alternatively, theoretical calculations[2] may be used to determine the most probable site of protonation.

A recent excellent correlation[3] of the proton affinity of aniline and other substituted benzenes (C_6H_5X, X = F, Cl, H, CH_3, C_2H_5, NH_2) with STO-3G calculated shifts and Hammett σ^+ values in this series suggested that aniline might suffer protonation on the ring rather than at nitrogen, although a recent chemical ionization study[4] and solution p*K* trends[5] suggest preferential nitrogen protonation in this molecule.

We have measured the N_{1s} core ionization energy for a number of gaseous amines extending previous data[6-8] to these systems wherein the site of protonation may be ambiguous. The data (Table I) were obtained with a McPherson ESCA-36 instrument on gaseous samples of the amines at ~100-μ pressure intimately mixed with similar amounts of Ar for calibration.[9] The Mg Kα x ray was used for excitation. Gas phase proton affinity data for the amines given primarily by Kebarle and coworkers[10,11] has been corrected to the present prevailing value of 202.3 kcal for NH_3[12] as were the few other values taken from other work.[13,14] The proton affinity data (Table I) correlated well with the N_{1s} binding energies as has been established for similar and related systems,[7,15,16] as illustrated in Figure 1, especially if we assign generous limits of accuracy of ±1.0 kcal to the proton affinities (although, if the differences have been obtained by constructing a "ladder",[10-14] they are probably better than this) and ±0.1 eV to the E_B (N_{1s}) values. The straight line is an arbitrary unit slope

Table I

Compd	E_B (N_{1s}), eV		Proton affinity, kcal
	This work,[a]	Other work	
Et_3N (**1**)	404.36	404.3[b]	231.3[e]
Et_2NH (**2**)	404.58	404.54[b]	225.2[e]
$EtNH_2$ (**3**)	404.93	404.95[b]	217.2[e]
Me_3N (**4**)		404.79[b,c]	225.6[f]
Me_2NH (**5**)		404.90[b,c]	220.6[f]
$MeNH_2$ (**6**)		405.14[b,c]	213.1[f]
NH_3 (**7**)		405.6[b]	202.3[g]
Pyrrole (**8**)	406.18	406.1[d]	209.45[f]
Piperidine (**9**)	404.58		226.8[f]
Pyrrolidine (**10**)	404.60		223.3[e]
Pyridine (**11**)	404.82		220.9[f]
Aniline (**12**)	405.31		211.2[f]
N-Monomethylaniline (**13**)	405.01		217.4[f]
N,N-Dimethylaniline (**14**)	405.06		224.0[f]
Cyclohexylamine (**15**)	404.72		222.0[f]
Formamide (**16**)	406.30		
N-Monomethylformamide (**17**)	405.8		204.0[h]
N,N-Dimethylformamide (**18**)	405.8		209.9[h]

[a] Relative to $Ar_{2p(3/2)}$ 248.62 eV.[9] [b] Reference 7. [c] Reference 6. [d] Reference 8. [e] Value given in ref 13 has been corrected to a PA(NH_3) of 202.3 kcal.[12] [f] Value given in ref 10 has been corrected to a PA (NH_3) of 202.3 kcal.[12] [g] Reference 12. [h] Reference 14 converted to PA (NH_3) of 202.3 kcal.[12]

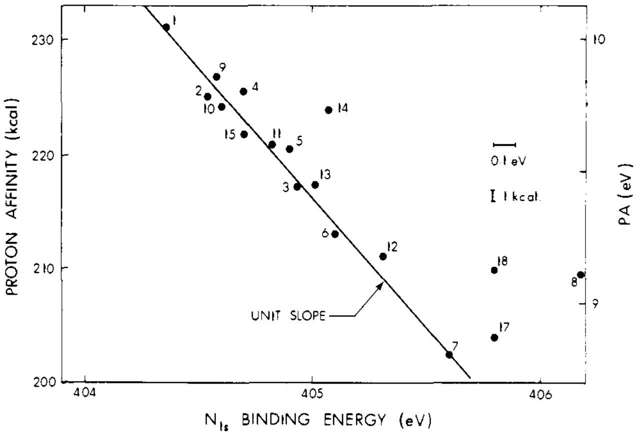
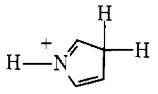
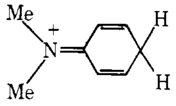


Figure 1. Correlation of N_{1s} binding energy with proton affinity of various amines and amides. The numbers refer to the compounds in Table I. The straight line has unit slope (23.1 kcal/eV) and is arbitrarily drawn through the NH_3 data point (compound 7).

line (23.1 kcal/eV) drawn through the NH_3 point (thus representing $\Delta E_B = -\Delta PA$)[7,15,16] and is *not* a best fit. It is notable that aniline (**12**) and *N*-monomethylaniline (**13**) agree with the trend defined by ammonia (**7**), the methylamines (**4–6**), ethylamines (**1–3**), and amines such as piperidine (**9**), pyrrolidine (**10**), cyclohexylamine (**15**) and pyridine (**11**), and we would suggest that the *site* of protonation in all these molecules is the nitrogen atom. Large deviations are demonstrated by *N,N*-dimethylformamide (**18**) and *N*-methylformamide (**17**) and it is reasonable to suggest that the site of protonation is oxygen in these cases rather than nitrogen; this proposal is supported by the good correlation of the proton affinities for these molecules with E_B (O_{1s})[17] and NMR evidence in solution.[18] Pyrrole (**8**) and *N,N*-dimethylaniline (**14**) are the only amines in the present set which deviate significantly. The former probably protonates on a ring carbon rather than the nitrogen, perhaps because of a stabilization of the ion structure I which increases the proton affinity of the parent molecule.



I



II

It is interesting to note that NMR solution data suggest that exclusive ring protonation occurs in pyrrole (and its methylated derivatives).[19] The deviation of *N,N*-dimethylaniline from the correlation is not so readily rationalized. Ring protonation may be more likely for this compound compared to aniline and *N*-monomethylaniline, perhaps as the result of stabilization of the ion structure **II**, although it seems unlikely that the basic site is drastically different in such closely related derivatives. It is possible that E_B (N_{1s}) of *N,N*-dimethylaniline is higher than expected because of a destabilization of the N_{1s} hole state in this compound relative to the hole states in **12** and **13** (i.e., the final states differ more than might be expected[15,16]) or a stabilization of the ground state of *N,N*-dimethylaniline relative to those of *N*-monomethylaniline and aniline (assuming similar hole state stabilities for all three anilines) or a combination of both effects.

Our electron spectroscopic data suggests that aniline protonates at nitrogen in the gas phase. The calculated proton affinities for ring (210.9 kcal)[20] and nitrogen (208.7 kcal)[21] sites are very close indeed and this molecule may well offer two equally probable protonation sites. Since theoretical calculations[22] suggest that *N*-methyl substitution favors protonation at nitrogen, it seems unlikely that the behavior of *N,N*-dimethylaniline is due to enhancement of ring protonation and we suggest that either stabilization of the ground state or destabilization of the N_{1s} hole state of this compound is responsible for the deviation from the correlation. This discrepancy suggests that conclusions derived from a correlation such as the present one should be treated with caution. Further study of the gas phase system by means of structurally specific techniques is clearly warranted but meanwhile the use of N_{1s} binding energies to deduce the site of protonation is a convenient aid to interpretation.

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