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Progress in the Theory of Acids and Bases†

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Published data on the acid-base properties of organic substances in the gaseous phase have been reviewed. The proton affinity (PA) of bases is taken as the enthalpy of the gaseous reaction $M + H^+ \rightarrow MH^+$, with the opposite sign, and the basic strength of the bases (GB) is taken as the change in the standard free energy of this reaction (again with opposite sign). Correspondingly, the acidity in the gaseous phase is taken to be the enthalpy of the reaction $AH \rightarrow A^- + H^+$ or the change in the standard free energy of this reaction.
The dependence of the acid strength and base strength in the gaseous phase on the structures of the molecules of the acids and bases has been examined, and the lack of agreement between the observed facts and the classical electronic interpretation based on the inductive and mesomeric effects of the groups has been discussed. Attention has been drawn to the change in the acid-base properties of organic molecules on going from the gaseous to the liquid phase, and the energetic effects of the solvation of the molecules and ions have been examined.
The bibliography contains 78 references.

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I. INTRODUCTION

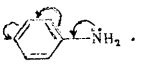
The modern electronic theory of organic chemistry, developed in the early nineteen-thirties on the basis of the classical theory of chemical structure, uses an electronic description of the structure of molecules and their reactivity[1].

The description of the structure has two sources and, correspondingly, two languages. The first is the theory of electronic effects (inductive and mesomeric), developed mainly by the efforts of the English school of chemists, and the second is quantum chemistry. The establishment of a satisfactory correspondence between these two descriptive systems was the greatest achievement of theoretical organic chemistry.

The electronic theory of *reactivity* has not reached this high level. The situation is better in the theory of radical reactions. The free valency indices and the energy of homolytic bond rupture can be calculated theoretically and made the basis of an examination. In the theory of ionic reactions, an important role is played by a fundamental principle: "nucleophilic reacts with electrophilic". Although there are exceptions to this principle, it works well in the great majority of cases. The determination of the degree of nucleophilic or electrophilic character of molecules and their fragments and complexes has therefore become an important task of theory. This degree of nucleophilic or electrophilic character is not equivalent to the distribution of the effective charges on the atoms, which can be calculated theoretically. Here, therefore, it is necessary to resort to the use of hypotheses and ideas constructed on the basis of so-called common sense. They appear to be reasonable, although in fact they are often somewhat doubtful. These hypotheses and ideas have in fact been accepted without proof as the only possible translation of the familiar regular features of the classical theory of chemical structure into the language of electronic theory. Since there has been no doubt that the classical theory adequately describes objective reality, these hypotheses have acquired the appearance of principles.

This applies particularly to the acid–base properties of substances, that is to proton transfer reactions. These reactions represent the simplest illustration of the principle "nucleophilic combines with electrophilic". This will therefore be the subject of the subsequent discussion, which begins with several examples of well known facts and their explanations to which we have become accustomed and whose possible revision we have not considered.

First example. The long familiar fact that the base strength of ammonia decreases on the successive attachment of phenyl groups, that is the series $NH_3 > C_6H_5NH_2 > (C_6H_5)_2NH > (C_6H_5)_3N$, has always been explained by stating that in aniline, the unshared pair of electrons is partly transferred to the ring (+*M*-effect):



The mesomeric stabilisation of the base and the partial positive charge on the nitrogen are the factors responsible for the decrease in the base strength of aniline compared with ammonia, where these effects are not found. In diphenylamine, which has two phenyl rings, this effect is stronger, and triphenylamine is not basic at all. All appears sufficiently convincing and clear!? It is not quite so clear, however, why the resonance effect in the aniline molecule should produce such a marked decrease in the proton affinity of the molecule that aniline becomes a much weaker base than ammonia.

Second example. It is well known that pyridine is a much weaker base than ammonia and aliphatic amines. The lower base strength of pyridine has been attributed to the nature of the hybridisation of the unshared pair of electrons of the nitrogen atom. Its hybrid orbital has more *s*-character than in the case of ammonia and amines. In

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pyridine the hybridisation is sp^2, and in ammonia and amines sp^3. Since s-electrons are more firmly bound to the nucleus of the atom, the basic strength decreases with increase in the s-component[1]. Again, all appears logical. Not altogether, however! Why can it be assumed that the greater strength of attachment of the unshared pair to the nucleus alone can produce a much smaller proton affinity of the molecule? The attachment of a proton to two comparable molecules leads to extensive and different changes in their entire energetics, which primarily determine the magnitude of the relative proton affinity! Until recently, this has not been taken into account.

Third example. The introduction of methyl (and in general alkyl) groups in the series $NH_3 < CH_3NH_2 < (CH_3)_2NH$ leads to an increase in base strength, which we readily attribute to the $+I$-effect, that is the positive inductive effect of the methyl groups. On going from dimethylamine to trimethylamine, however, the basic strength decreases: $(CH_3)_2NH > (CH_3)_3N$ ($pk_{a(H_2O)}$ 10.77 and 9.80 respectively). To explain this anomaly, Brown[2] proposed his B-strain hypothesis. Later, under the influence of modern ideas, Condon[3] attributed it to be a change in solvation. In either case, special additional hypotheses were introduced, the aim of which was to save the *a priori* view of the decisive role of the $+I$-effect of the methyl groups.

Fourth example. The acidity of alcohols. We are accustomed to the fact that trimethylcarbinol is an incomparably weaker acid than ethanol. Alcohols can be arranged in the following order of acid strength[4]: $H_2O > CH_3OH > C_2H_5OH > (CH_3)_2CHOH > (CH_3)_3COH$; $H_2O > CH_3OH > C_2H_5OH > C_3H_7OH > C_4H_9OH$..... These series we explain without strain in terms of the inductive $+I$-effect of the alkyl groups. Clear and obvious! Really!? In exactly the same way we used the $+I$-effect to explain the course of the change in the acid strength of the carboxylic acids ($pK_{a(H_2O)}$ values in parenthesis): HCOOH (3.75) $>$ CH_3COOH (4.76) $>$ C_2H_5COOH (4.87) $>$ C_3H_7COOH (4.82) $\geqslant$ C_4H_9COOH (4.86) $\geqslant$ $C_5H_{11}COOH$ (4.86), and the $-I$-effect to explain the change in the strength of the halogenoacetic acids: FCH_2COOH (2.57) $>$ $ClCH_2COOH$ (2.86) $>$ $BrCH_2COOH$ (2.90), recalling that the electronegativities of the halogens decrease in the familiar order: F (4.0) $>$ Cl (3.0) $>$ Br (2.8).

These facts, which can easily be multiplied, are apparently fairly well interpreted by theory. If we were not convinced of this, we would not tell the students. The trouble is not that our arguments are not sufficiently logical. The trouble is that many of the facts which we can explain so successfully in fact are incorrect (in the context in which they are interpreted). This means that our explanations are also incorrect.

To anticipate, it may be said that this error has arisen because absolutely correct results on the measurement of acid or base strengths in the liquid phase have always been assigned only to the actual molecules of the substance being studied. In fact, however, these data should be related to the system consisting of the molecules of the substance being studied and the surrounding molecules of the medium. The acid–base properties of the actual molecules of the substance — outside the medium —are often quite different.

The lack of correspondence between our explanations and the data being explained and the actual state of affairs became clear with the development of high-pressure mass spectroscopy and, somewhat later, ion-cyclotron resonance spectroscopy. These methods made it possible to study the properties of molecules in the gaseous phase, that is when they are not distorted by the influence of surrounding molecules. It is the properties of the molecules in the gaseous and not the liquid phase that must be related to their electronic structure, various electronic effects, etc; in the liquid phase the distortions produced by the environment may be very great.

Here it should be specially stated that the subsequent treatment will deal not with any one or even several studies but with a large number of studies by various workers. Thus the data presented below are now firmly established. Reviews of the new results have been published, for example by Agami[5], Taft[6], and Kebarle[7].

II. PRINCIPLES OF THE EXPERIMENTAL METHODS

In high-pressure mass spectrometry[8–11], a pressure of $\sim 10-10^{-4}$ mmHg is used. Since ions in the gaseous phase are unstable (they disappear rapidly as a result of recombination or discharge on the walls), they must be continually created by the action of radiation. The apparatus must be constructed in such a way that it is possible, within the limited lifetime of the ions, to observe the interaction of the ions with molecules, leading to ion–molecular equilibrium.

The direct mass-spectrometric method of measuring the proton affinity of a molecule M involves the measurement of the appearance potential of the ion MH^+ as a fragment of the degradation of another molecule. From the appearance potential of the ion it is possible to calculate its enthalpy of formation, that is $\Delta H^\circ(MH^+)$, and hence the proton affinity (PA).

$$PA = \Delta H^0(H^+) + \Delta H^0(M) - \Delta H^0(MH^+)$$

The enthalpy of formation of hydrogen ions is calculated from the ionisation potential of atomic hydrogen, and the enthalpy of formation of the molecules M from thermochemical data. It is thus possible to calculate the proton affinity of the molecules M.

The method is one of the few giving absolute results. Its disadvantage is the frequently encountered difficulty of assigning the peaks to a specific ion and the occasional impossibility of obtaining a known given protonated species MH^+ of definite structure[12,13].

Soon after the first publications in this field[14,15], various methods were developed for determining the relative basic strength of molecules in the gaseous phase by high-pressure mass spectrometry. In all cases, a mixture of gases M_1 and M_2 is placed in the reaction cell. Positive ions are generated by electron collision, and the ratio of the concentrations of the ions M_1H^+ and M_2H^+ is measured by a suitable method. The results are used to calculate the equilibrium constant and standard free energy:

$$M_1H^+ + M_2 \rightleftarrows M_1 + M_2H^+$$
$$K = [M_2H^+] \cdot [M_1]/[M_1H^+] \cdot [M_2]$$
$$-\Delta G^0 = RT \ln K$$

To determine the relative acid strength of organic acids A_1H and A_2H in the gaseous phase by high-pressure mass spectrometry, various special methods for generating negative ions are used. An example is provided by the determination of the relative acid strength of two benzoic acids, developed in the University of Alberta in Canada[7]. A gas mixture consisting of the carrier gas methane

(5 mmHg), a weaker acid A_2H (0.050 mmHg), and a smaller quantity of a stronger acid A_1H is irradiated in a compartment by a beam of electrons (e); SO_2F_2 (0.1 mmHg) is added to the mixture for the formation of negative ions. The following principal reactions take place:

$$e + SO_2F_2 = SO_2F + F^-,$$
$$F^- + A_2H = HF + A_2^-,$$
$$A_1H + A_2^- \rightleftarrows A_2^- + A_2H.$$

The capture of an electron by sulphuryl fluoride is exothermic, since the electron affinity of fluorine is greater than the dissociation energy of the F–SO_2F bond. The reaction of the fluoride anion with A_2H is practically irreversible, since benzoic acids in the gaseous phase are much stronger than HF.

The resulting gaseous mixture is "withdrawn" continuously by a fast-acting vacuum pump into the compartment of the mass spectrometer, in which a high vacuum is maintained, and the usual separation according to mass is then carried out. This gives the ratio of the equilibrium concentrations of the ions A_2^- and A_1^- and hence the equilibrium constant:

$$K = [A_1^-] \cdot [A_2H]/[A_2^-] \cdot [A_1H].$$

K can be used to calculate the free energy of proton transfer ΔG°.

The generation of negative ions in the gaseous phase is often carried out using the radiolysis of methyl nitrite or NF_3 [24];

$$e + CH_3ONO = CH_3O^- + NO$$
$$e + NF_3 = F^- + NF_2.$$

The principles of ion-cyclotron resonance spectroscopy are as follows[16,17]. The ion MH^+ with charge q_1 and mass m_1, entering the uniform magnetic field H of the cyclotron, begins to move around a circular orbit of radius r^1, with velocity v_1 and angular frequency ω_1:

$$\omega_1 = v_1/r_1 = q_1H/m_1c.$$

On the applications of a variable electric field E_1 having a frequency ω, resonance occurs when $\omega = \omega_1$. The energy of the electric field is then absorbed, and the ions MH^+ obtain additional kinetic energy. The absorption of the energy of the electric field is reflected on the oscilloscope screen (scanning along the frequency scale ω) by an absorption peak.

To determine the relative proton affinity by the double resonance method, the ions M_1H^+ are generated by a suitable method in the cell of the ion-cyclotron spectrometer; these ions then react with the molecules M_2:

$$M_1H^+ + M_2 \rightleftarrows M_1 + M_2H^+.$$

On the application of two variable electric fields E_1 and E_2 having frequencies corresponding to the angular velocities ω_1 and ω_2 ($\omega_2 = q_2H/m_2c$), two signals are produced on the oscilloscope screen. From these two signals, using appropriate procedures, it is possible to calculate the proton affinity of the molecules M_2 relative to the molecules M_1.

A number of versions of the ion-cyclotron resonance method have been developed and are being used successfully, including the highly effective pulsed method[18–23]. In all cases the experiments are carried out at a low pressure ($p \leq 10^{-4}$ mmHg) and only at room temperature. The method makes it possible, however, to determine the relative concentrations of ions in situ, and has a high accuracy[21].

Basic strength in the gaseous phase is often expressed by the proton affinity of the molecule M, that is by the enthalpy of the reaction $M + H^+ \rightarrow MH^+$, taken with opposite sign: $PA = \Delta H^\circ(MH^+)$ kcal mole^{-1}. The acid strength in the gaseous phase is given by the enthalpy of the reaction $AH \rightarrow A^- + H^+$, again in kcal mole^{-1}. The higher the numerical value of the proton affinity, the stronger the base, and hence the weaker the acid. Strictly speaking, the negative enthalpy of the reaction $M + H^+ \rightarrow MH^+$ gives not the basic strength but the proton affinity. The basic strength GB (Gas-phase Basicity) is given by the change in the standard free energy of this reaction (again taken with negative sign). In practice, however, these quantities are equal or almost equal, since the entropy contribution here is very small. In fact, most published data have been obtained by relative measurements. Since proton transfer reactions are practically isentropic (free energies independent of temperature), the enthalpies for the equilibria measured are equal (or almost equal) to the free energies. Here the entropy term usually does not exceed 2 e.u., which at 298 K is 0.6 kcal mole^{-1}, and hence often lies within the limits of error of the measurement.

In most relative measurements, the standard used is ammonia, that is the equilibrium constant of the proton transfer: $NH_4^+ + M \rightleftharpoons NH_3 + MH^+$, is measured experimentally and used to calculate the free energy of proton transfer ($-\delta\Delta G^\circ$, kcal mole^{-1}) or the enthalpy of proton transfer ($-\delta\Delta H^\circ$, kcal mole^{-1}), which is equal to the latter.

In order to use these data to calculate quantities characterising the equilibrium $M + H^+ \rightleftharpoons MH^+$, namely the basic strength of the molecules $GB(M) = -\Delta G^\circ$ or their proton affinity $PA(M) = -\Delta H^\circ$, it is necessary to know the values of the basic strength and proton affinity of ammonia, that is the values of $-\Delta G^\circ$ and $-\Delta H^\circ$ for the equilibrium $NH_3 + H^+ \rightleftharpoons NH_4^+$. These values have been verified repeatedly, and it has been established that at 298 K they are: $GB(NH_3) = -\Delta G^\circ = 198 \pm 3$ kcal mole^{-1} and $PA(NH_3) = -\Delta H^\circ = 207 \pm 3$ kcal mole^{-1}.[8,9] The entropy term $T\Delta S^\circ$ includes a correction for the change in the symmetry on protonation (for ammonia, $\Delta S^\circ_{symm} = 0.82$ e.u.) and for the translational entropy of the ion H^+[$\Delta S^\circ(H^+) = 26.1$ e.u.].[25] ‡

Thus the published values of the basic strength of the molecules M are $GB(M) = -\Delta G^\circ = -\delta\Delta G^\circ + 198$ kcal mole^{-1}, and the values of the proton affinity of the molecules M are $PA(M) = -\Delta H^\circ = -\delta\Delta H^\circ + 207$ kcal mole^{-1}. These quantities naturally differ by approximately 9 kcal mole^{-1}.

Finally, it should be noted that both methods — high-pressure mass spectrometry and ion-cyclotron resonance spectroscopy — are based on the determination of the ions MH^+ or A^- from their masses. The question of the structure of the ion (protonation position) must be resolved independently by other methods, for example by isotopic substitution.

This entire field has developed comparatively recently. The first pioneer work of the late nineteen-fifties and early nineteen-sixties was carried out by Tal'roze[14]. Since 1965, after the work of Munson[15], the field began to develop rapidly. There are now five main centres in which proton transfer reactions in the gaseous phase are being studied.

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‡ A new and more accurate value, $-\Delta H^\circ(NH_3) = 202$ kcal mole^{-1}, has been reported[26]. If these data are confirmed, all the numerical values of the relative thermodynamic parameters, related to ammonia as standard substance, are altered by 5 kcal mole^{-1}.

1. Kebarle's group[7,10,24,27-31] in the University of Alberta, Edmonton, Canada. Here, high-pressure (~1 mmHg) mass spectrometry is used; the experiments are carried out at 600 K (at this temperature it is possible to avoid the formation of higher aggregates, which is unavoidable at the given pressure and room temperature). The group is studying the basic and acid strength of organic compounds in the gaseous phase and also the products of the attachment of neutral molecules to gaseous ions, which are regarded as a model of "supermolecules" — solvated molecules in the liquid phase.

2. Bowers, Aue, and coworkers[21,23,32] in the University of California at Santa Barbara. They use ion-cyclotron resonance at varying pressure. The experiment is carried out at room temperature and medium pressure ($\sim 10^{-4}$ mmHg). The group is studying the relative basic strength of organic compounds in the gaseous phase and the relationship between gas-phase and liquid-phase basic strengths.

3. McIver and coworkers[18,20,22,33-37] in the University of California at Irvine; this group is using pulsed ion-cyclotron resonance, suitable for accurate measurements at room temperature and low pressure ($\sim 10^{-6}$ mmHg). Both the basic and acidic properties of molecules in the gaseous phase are being studied. In the discussion of the results obtained in relation to the structure of the molecules and in comparison with the acid-base properties in the liquid phase, the group is cooperating with Taft, a well-known specialist in the correlation analysis of organic reactions, and Arnett, a specialist in the theory of solutions.

4. Beauchamp and coworkers[19,38] in the California Institute of Technology at Pasadena are studying the basic strength of organic compounds by ion-cyclotron resonance at low pressure ($\sim 10^{-6}$ mmHg) and room temperature.

5. Bohme and coworkers[11,39] at York University, Ontario, Canada are using a flow method to measure the rate constants and equilibria for proton transfer at room temperature.

The groups of McIver, Beauchamp, Bowers, and Aue have achieved a high accuracy in their measurements (±2 kcal mole^{-1}).

III. BASIC STRENGTH IN THE GASEOUS PHASE

1. Basic Strength of Various Simple Molecules in the Gaseous Phase[9,11]

Of the hydrides of the elements, ammonia has the highest proton affinity: $PA = 207 \pm 3$ kcal mole^{-1}.[9] In the first period of the periodic system, the lowest basic strength is naturally shown by methane §, so that it is possible to write the series (proton affinities in parentheses):

$$CH_4\ (126) < NH_3\ (207) > H_2O\ (165) > HF\ (137)\ .$$

In the second period, phosphine has the highest proton affinity: SiH_4 (146) < PH_3 (186) > H_2S (170) > HCl (141).

In the halogen series the basic strength of the hydrides increases from HF to HI:

$$HF\ (137) < HCl\ (141 \pm 3) \approx HBr\ (140 \pm 3) < HI\ (145)\ .$$

§ The proton affinity of methane was first measured by Tal'roze in 1958. The value obtained, $PA = 122$ kcal mole^{-1}, is close to the presently accepted value.

2. Basic Strength of Amines in the Gaseous Phase¶

a) Aromatic and heterocyclic amines

In contrast to all measurements in the liquid phase, in the gaseous phase aniline has been found to be a stronger base than ammonia, and only a slightly weaker base than methylamine. Diphenylamine has been found to be an even stronger base, of approximately the same strength as methylamine, and triphenylamine is the strongest of these bases, its strength being greater than that of methylamine[41]. Everything is reversed! Table 1 shows that the proton affinity of aniline in the gaseous phase is 8.9 kcal mole^{-1} greater than that of ammonia. According to other authors[42], the relative basic strength of aniline in the gaseous phase, that is the free energy of the proton transfer: $NH_4^+ + C_6H_5NH_2 \rightleftharpoons NH_3 + C_6H_5NH_3^+$, is slightly less than that, $-\delta\Delta G^\circ = 6.70$ kcal mole^{-1}.[6] According to these data also, however, aniline is a much stronger base than ammonia.

Table 1. Basic strength of various aromatic amines and ammonia in the gaseous phase and in water[41].

Basic strength	NH_3	$C_6H_5NH_2$	$(C_6H_5)_2NH$	$(C_6H_5)_3N$
PA, kcal mole^{-1}	207	215.9[29]	~218	225>PA>218*
pK_a (H_2O)	9.27	4.58	0.9	<0

* Estimated by us from the data in Ref. 41.

Table 2. Basic strength of methylanilines in the gaseous phase and in water[29,30].

Basic strength	$C_6H_5NH_2$	$C_6H_5NHCH_3$	$C_6H_5N(CH_3)_2$
PA, kcal mole^{-1}	215.9	222.1	228.7
pK_a (H_2O)	4.58	4.85	5.06

Dzidic[41], who was the first to observe this phenomenon, wrote that the results which he obtained made it necessary to re-examine our ideas on the mesomeric effect. In fact, it is apparently necessary to re-examine not the idea of the mesomeric effect but the view that it plays a role in determining the basic strength of molecules.

An interesting feature is that the basic strength of N-alkyl derivatives of aniline in the gaseous phase increases with increasing replacement of the hydrogen atoms attached to nitrogen, in the same way as the basic strength increases in a liquid medium. Table 2 gives as an example the data for methylanilines[29,30]. In contrast to the previous case, the ratios of these quantities here have their usual values.

¶ The numerical values of the proton affinity given below are related to ammonia as standard [$PA(NH_3) = 207 \pm 3$ kcal mole^{-1}].

The usual change is also observed in the basic strength of aniline on hydrogenation. Table 3 shows that the basic strength of cyclohexylamine is greater than that of aniline both in the gaseous phase and in water[6,30]. According to Taft and coworkers[6,42], the free energy of proton transfer from the anilinium to the cyclohexylammonium ion

$$(C_6H_5NH_3^+ + \text{cyclo-}C_6H_{11}NH_2 \rightleftarrows C_6H_5NH_2 + \text{cyclo-}C_6H_{11}NH_3^+,$$

measured by ion-cyclotron resonance, is $-\delta\Delta G^\circ = 9.6$ kcal mole^{-1}. The order of the basic strength of heterocyclic bases was completely unexpected (Table 4). In water and in any other liquid medium, pyridine is incomparably weaker than ammonia, not to mention methylamine. In the gaseous phase, however, and hence by itself, its "intrinsic basic strength" is much greater than that of ammonia (by 18.9 kcal mole^{-1}) and is similar to that of dimethylamine. Thus the explanation of the lower basic strength of pyridine compared with ammonia, based on the type of hybridisation of the unshared pair of electrons of the nitrogen in pyridine, hangs in mid-air: pyridine is intrinsically a stronger base than ammonia.

Table 3. Basic strength of aniline and cyclohexylamine in the gaseous phase and in water[8,30].

Basic strength	$C_6H_5NH_2$	cyclo-$C_6H_{11}NH_2$
PA, kcal mole^{-1}	215.9	226.7
$pK_{a\ (H_2O)}$	4.58	10.64

Table 4. Basic strength of various heterocyclic bases in the gaseous phase and in water.

Basic strength	NH_3				
PA, kcal mole^{-1} (Ref.30)	207	214.15	225.6	228.7	231.5[21] 230.1
$-\delta\Delta H^\circ$ ($-\Delta H^\circ_{NH_3} = 0$) (Ref.30)	0	7,1	18,0	21.7	24.5
GB, kcal mole^{-1} (Ref.26)	198	205	216,9	220.4	221.5
$pK_{a(H_2O)}$	9.27	−0.27	5.23	11.27	11.22

At the same time, the influence of γ-substituents in the pyridine ring on the basic strength in the gaseous phase was studied. A good linear correlation is observed between the data for the gaseous phase and for water, with constants σ_I and σ_{R^+}[43]:

$$[\Delta H^0/\Delta H^0_0]^\dagger = 16{,}7\sigma_I + 10{,}3\sigma_R^+ \text{ (in the gaseous phase);}$$
$$\lg(K/K_0) = 5{,}15\sigma_I + 2.69\sigma_R^+ \text{ (in water).}$$

The basic strength in the gaseous phase is much more sensitive to change in the parameters σ, that is to the influence of substituents, than the basic strength in water. Water, as a medium for acid–base equilibria, shows a clearly defined levelling action compared with the gaseous phase.

† In log K units.

Thus the influence of substituents in the pyridine ring on the basic strength in both the gaseous phase and a liquid obeys the Hammett equation, and it seems that here there is no anomaly. It should be noted that quantum-chemical calculation by the CNDO/2 method also gives a similar result. Recently, Aue and coworkers[44] extended this correlation (with slight exceptions) to pyridine derivatives having substituents in the three positions, α, β, and γ.

b) Aliphatic amines[15,23,30,32,33,45]

A large number of studies have been devoted to amines. As alkyl groups are introduced into the ammonia molecule there is a monotonic increase in the basic strength in the gaseous phase, without any deviation for tertiary amines (Table 5). The basic strength in the gaseous phase also increases with increased length of the normal chain in the amine (Table 6). Moreover, it can be seen that, beginning from C_3–C_4, the increase in the basic strength in the gaseous phase becomes less marked. In water, all primary amines have the same basic strength, within the limits of experimental error.

Table 5. Basic strength of primary, secondary, and tertiary aliphatic amines in the gaseous phase and in water.

Basic strength	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$	$(C_2H_5)_2NH$	$(C_2H_5)_3N$
PA, kcal mole^{-1}	207	218.4	224.9	229.1	221.1	230.1	235.8
GB, kcal mole^{-1} (Ref.26)	198	210.0	216.6	220.8	213.0	221.2	227.7
$pK_a(H_2O)$	9.27	10.62	10.77	9.80	10.63	10.93	10.87

Table 6. Dependence of the basic strength of aliphatic amines on the length of the normal chain in the gaseous phase and in water.

Basic strength	CH_3NH_2	$C_2H_5NH_2$	$C_3H_7NH_2$	$C_4H_9NH_2$	$C_5H_{11}NH_2$	$C_6H_{13}NH_2$
PA, kcal mole^{-1}	218.4	221.1	222.3	222.8	223.1	223.2
ΔPA, kcal mole^{-1}	11.0	3.1	1.2	0.5	0.3	0.1
GB, kcal mole^{-1} (Ref.26)	210.0	213.0	214.4	214.9	—	—
$pK_a(H_2O)$	10.62	10.63	10.53	10.60	10.63	10.64

The basic strength of amines in the gaseous phase also increases with branching in the substituent (Table 7). An interesting feature is that in aqueous solution the basic strength decreases in this case; this was attributed to *B*-strain. In general, however, the order of the change in the basic strength of amines agrees with the inductive $+I$-effect of the alkyl groups. It appears that here it is possible to retain the explanation based on this effect. This would be the case if there were no data on the acid strength of amines in the gaseous phase. To anticipate, it may be noted that the relative acid strength of alcohols and amines in the gaseous phase, which Brauman and Blair studied by semi-quantitative ion-cyclotron resonance[46,47] also

increases with increased number of alkyl groups on the nitrogen, the number of carbon atoms in them, and the degree of branching of their hydrocarbon skeleton, that is under the influence of the factors which led to an increase in the basic strength of amines:

$$(C_2H_5)_2NH > H_2O > NH_3;$$
$$(C_2H_5)_2NH > (CH_3)_2NH > NH_3;$$
$$C_3H_7NH_2 > C_2H_5NH_2 > CH_3NH_2 > NH_3;$$
$$(CH_3)_3CCH_2NH_2 > (CH_3)_3C{-}NH_2 > (CH_3)_2CH{-}NH_2 > C_2H_5{-}NH_2 > CH_3{-}NH_2 .$$

At the same time, naturally, the $+I$-effect also increases. According to all our ideas, however, the $+I$-effect cannot increase the acid strength; it can only decrease it. This means that the concept of the $+I$-effect cannot be used to explain the acid–base properties of amines. It is necessary to look for other ways of interpreting the experimental data.

Table 7. Dependence of the basic strength of aliphatic amines on the degree of branching of the carbon chain in the gaseous phase and in water.

Basic strength	n-$C_4H_9NH_2$	iso-$C_4H_9NH_2$	s-$C_4H_9NH_2$	t-$C_4H_9NH_2$
PA, kcal mole^{-1}	222.8	223.2	224.4	225.4
GB, kcal mole^{-1} (Ref.26)	214.9	215.4	216.4	217.3
$pK_{a(H_2O)}$	10.60	10.49	10.56	10.45

c) Aliphatic cyclic amines

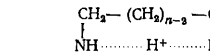
The basic strengths of several cyclic amines have been measured in the gaseous phase. Here, the basic strength increases with increase in the size of the ring, whereas in water it is practically constant[21] (Table 8).

Table 8. Basic strength of various saturated heterocyclic bases in the gaseous phase and in water[20,30].

Base			
PA, kcal mole^{-1}	231.5 230.1[21]	228.7	227
$pK_{a(H_2O)}$	11.22	11.27	11.29

d) Aliphatic diamines

Unexpected results were obtained in the study of the basic strength of alkylenediamines[30,32]. These substances were found to be very strong bases in the gaseous phase; they show a greater (by 10–20 kcal mole^{-1}) proton affinity than the corresponding monoamines. This is not observed in the liquid phase (Table 9). Proton transfer to the monoamine molecule in the gaseous phase is almost isentropic, that is $\Delta G^\circ = \Delta H^\circ$, whereas in the case of diamines there is a considerable decrease in entropy. This is related to the formation of an intramolecular hydrogen bond[32], which is assumed to be linear:



Studies of aqueous solutions of diamines have not detected hydrogen bonds of this type in monoprotonated diamines.

Table 9. Basic strength of mono- and diamines in the gaseous phase and in water[30,32].

Basic strength	*n* = 2	3	4	5	6	7
Monoamines $CH_3(CH_2)_nNH_2$						
PA, kcal mole^{-1}	222.3	222.8	223.1	223.2	—	—
$pK_{a(H_2O)}$	10.53	10.60	10.63	10.64	10.66	10.65
Diamines $NH_2(CH_2)_nNH_2$						
PA, kcal mole^{-1}	232;234.9	238.3;243.3	243.3;	241.3;	242.1;	—;
			—	243.3	—	243.2
$-\Delta S^\circ$, e.u.	12.7	20.6	—	20.0	—	20.0
$pK_{a(H_2O)}$	10.09	10.62	10.80	10.86	—	—

3. Basic Strength of Oxygen Bases in the Gaseous Phase

This question will not be dealt with in detail. The regular features here are in principle the same as in the case of amines. The basic strength of all oxygen compounds in the gaseous phase is greater than that of water; with increase in the number of carbon groups, their size, and their degree of branching, the basic strength increases in all cases[15,48,49].

1. Alcohols				
a) the effect of homology	H_2O	CH_3OH	C_2H_5OH	C_3H_7OH
PA, kcal mole^{-1}	165	182, 180[51]	187, 186[51]	189
b) the effect of branching	CH_3OH	CH_3CH_2OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$
PA, kcal mole^{-1}	182	187	193, 195[51]	198, 206[51]
2. Esters of carboxylic acids	$HCOOCH_3$	CH_3COOCH_3	$C_2H_5COOCH_3$	$CH_3COOC_2H_5$
PA, kcal mole^{-1}	188	202	205	205
3. Carboxylic acids	HCOOH	CH_3COOH	C_2H_5COOH	
PA, kcal mole^{-1}	175	188	190	
4. Oxo compounds	CH_2O	CH_3CHO	CH_3COCH_3	
PA, kcal mole^{-1}	168[51, 52]	183[49, 53]	202[48], 190[51]	

Table 10. Basic strength of various alkyl halides in the gaseous phase[50].

Basic strength	CH_3F	CH_3Cl	CH_3Br	CH_3I	C_2H_5F	C_2H_5Cl	C_2H_5Br	C_2H_5I
PA, kcal mole^{-1}	151	160	163	170	163	167	170	175

4. Basic Strength of Alkyl Halides and Alkenes in the Gaseous Phase

Alkyl halides are protonated according to the equation:

$$RX + H^+ \rightleftarrows (R{-}X{-}H)^+ .$$

In general, the readily understood order given in Table 10 [50]

is observed. An interesting feature is that the basic strength of alkyl halides in the gaseous phase is comparable with that of alkenes, benzene, and acetylene (Table 11).[51] This should be borne in mind for the study of the mechanism of gaseous reactions.

Table 11. Basic strength of various alkenes, benzene, and acetylene in the gaseous phase[51].

Basic strength	$CH_2{=}CH_2$	$CH_3CH{=}CH_2$	$C_2H_5CH{=}CH_2$	$(CH_3)_2C{=}CH_2$	C_6H_6	$CH{\equiv}CH$
PA, kcal mole^{-1}	160	179	183	195	183[a]	151

IV. RATIO OF THE BASIC STRENGTHS IN THE GASEOUS AND LIQUID PHASES

The study of the basic strength of organic substances in the gaseous phase and comparison with the basic strength in solutions lead to contradictory results. On the one hand, there is a marked lack of correspondence. between the values of the basic strength (ammonia–aniline, ammonia–pyrrole, ammonia–pyridine, trimethylamine–dimethylamine, etc.), and this undoubtedly requires a change in existing ideas regarding the factors determining basic strength in the liquid phase. On the other hand, there are cases where the structure of molecules influences the basic strength in the liquid and in the gaseous phases in qualitatively the same way (and sometimes quantitatively, with linearity of the free energies). Thus in some cases the liquid medium changes only the scale of the differences in the basic strength for a series of substances, leaving the order of the changes unaltered; in other cases, however, the actual order of the basic strength is altered. In these latter cases, the change from the gaseous phase, in which the basic strength of *isolated* molecules is measured, to the liquid phase, where the basic strength of molecules in a liquid environment, that is *solvated* molecules, is measured, has such a marked effect that the ratio of the basic strengths of the substances being compared is reversed. This question has been examined in detail by Taft and Arnett and coworkers[6,54,55], Aue and coworkers[23,26,56], and others; good reviews have been published by Arnett[55,57].

The basic strength in the liquid phase is determined by two factors: the "intrinsic" or "internal" basic strength, measured in the gaseous phase as the proton affinity (more accurately as $-\Delta G$ for the attachment of a proton), which is a property of the molecules themselves; and an external factor, the solvation factor, which is a property of the "molecule of the base + molecule of the medium" system[58]. The effect of the external factor may be stronger than the influence, to which we are accustomed, of the structure of the molecules of the base with their characteristic inductive and mesomeric effects; the effect of this factor often masks everything completely. Thus our explanations of the acid–base properties of substances in the liquid phase only by means of inductive effects (aliphatic amines, alcohols, esters), mesomerism (aniline and its derivatives, naphthylamines, etc.), and hybridisation (pyridine, quinoline, pyrimidine) are primitive and often simply incorrect.

It should be said that the theory of the gas-phase and liquid-phase basic strength of organic substances is still in the development stage. Many questions, not at all of secondary importance, are still disputed. These include the understanding of the essential features and role of the inductive effect of alkyl groups, polarisability in the stabilisation of ions, resonance and hyperconjugation effects, the effect of hybridisation, etc. The research groups of Aue and Kebarle on the one hand, and of Taft and Arnett on the other, have different views. The application of electrostatic concepts, widely used by Aue, is not favoured by other workers. Taft's efforts to break down all thermodynamic functions according to the additive contributions of the effects is not supported either, however. Some selections from the literature on this topic, which seem more correct to the present author, are discussed below.

The basic strength of organic substances is determined by the difference between the free energies of the neutral molecules and the corresponding protonated forms, in most cases onium ions. The main contribution is made by the stability of the ion MH^+. Ions are unstable in the gaseous phase. Once formed, they rapidly disappear by recombination with oppositely charged ions or on the walls. In the liquid phase, ions are stabilised by solvation, the energy of which may exceed the energy of formation of the ion from the molecule. The least stable in the gaseous phase are the simplest ions: H_3O^+, NH_4^+, NH_2^-, OH^- . . . . The replacement of a hydrogen atom in these ions by organic groups stabilises the ions by delocalisation of the ionic charge. Kebarle calls this "internal solvation" [7]. The greater the "capacity" of the organic group for delocalisation of the charge (in this sense, the higher its polarisability ‡), the greater the delocalisation, the more stable the ion, and, other conditions being equal, the higher the base strength.

Aniline in the gaseous phase is a stronger base than ammonia, so that the ammonium ion is unstable, and the anilinium ion is stabilised by delocalisation of the onium charge, possibly by an inductive–mesomeric mechanism. For an analogous reason, pyridine is a stronger base than ammonia, trimethylamine is a stronger base than dimethylamine, and the base strength (and acid strength) of aliphatic amines increases with increase in the number, size, and degree of branching of the hydrocarbon groups present[59–61]. This is confirmed by theoretical quantum-chemical calculations[62–65], although, as pointed out by Huheey[61], it would have been better if these calculations had not been carried out a posteriori.

Nevertheless, in the examination of the questions of base strength it is also necessary to take account of factors stabilising the neutral molecules of the base. Taft and coworkers[42] drew attention to the fact that comparison of the base strength of amines is justified only if they have equal numbers of carbon atoms and a similar skeleton. In this case aniline should be compared not with ammonia but with cyclohexylamine. The base strength of the latter is greater than that of aniline in the gaseous phase by

‡ Here and subsequently the concept of the polarisability of a group will be used only in the sense of the ability of this group, when attached to an ionic centre, to delocalise its charge.

9.6 kcal mole^{-1}. Taft[6] considers that the main contribution to this difference is made by the mesomeric stabilisation of the neutral aniline molecules (~ 5.5 kcal mole^{-1} according to Taft) §.

Similarly, according to Taft, pyridine should be compared not with ammonia but with, for example, N-methylpyrrolidine ($-\delta\Delta G^\circ$ in the gaseous phase 7.5 kcal mole^{-1}). In this case the role of the hybridisation effect is distinguished (the weighting of the *s*-orbital of the unshared pair of electrons of the nitrogen is greater for pyridine). Arnett points out that Aue[66] attributes too much importance to the hybridisation effect in the examination of the base strength of ethyleneimine (compared with dimethylamine). The question of the role of hybridisation has also been dealt with by Brauman and Blair[67].

Taft and, following him, Arnett probably overestimate the role of electronic effects in neutral molecules and underestimate their role in protonated ions (the polarisation effect according to Taft). In any case, our view that the mesomeric effect and the effect of hybridisation play a definite role in determining the base strength of organic substances is not refuted by the results of measurements in the gaseous phase. Those comparisons and conclusions unjustifiably based on incorrectly understood facts have been refuted.

The relationships change most significantly on going to the liquid phase. Appropriate thermodynamic studies were carried out by Arnett[55] by applying the Born cycle[68]:

$$\begin{array}{ccc} MH^+_{(gas)} & \xrightarrow{\Delta G^\circ_{ion(gas)}} & (M + H^+)_{(gas)} \\ \uparrow -\Delta G^\circ_{solv\ (MH^+)} & & \downarrow \Delta G^\circ_{solv\ (M+H^+)} \\ MH^+_{(liquid)} & \xrightarrow{\Delta G^\circ_{ion(liquid)}} & (M + H^+)_{(liquid)} \end{array} .$$

In this cycle, the ionisation of the cation MH^+ in the liquid phase takes place in two ways: the first is the ionic dissociation in the liquid phase, for which $\Delta G^\circ_{ion(liquid)} = -RT \ln K_{a(liquid)}$. The second is the desolvation of the cation (transfer to the gaseous phase, free energy of solvation $-\Delta G^\circ_{solv\,(MH^+)}$), dissociation in the gaseous phase ($\Delta G^\circ_{ion(gas)}$), followed by reverse transfer to the liquid phase ($\Delta G^\circ_{solv(M + H^+)}$).

The two routes naturally lead to the same free energy change, so that:

$$\Delta G^\circ_{ion(liquid)} = \Delta G^\circ_{ion(gas)} - \Delta G^\circ_{solv\,(MH^+)} + \Delta G^\circ_{solv\,(M+H^+)} .$$

If $\Delta G^\circ_{ion(liquid)}$ is known from the ionisation constant in the liquid phase, $\Delta G^\circ_{ion(gas)}$ from measurements in the gaseous phase, and $\Delta G^\circ_{solv(M + H^+)}$ from thermochemical measurements, it is possible to calculate $\Delta G^\circ_{solv(MH^+)}$. Similar cycles can be constructed for ΔH° and $T\Delta S^\circ$.

In fact, these calculations are carried out as relative calculations (usually relative to ammonia as reference standard). In this case the difficulties associated with the choice of standard states disappear, and, in addition, the terms relating to the proton are eliminated. In fact, this relative calculation is related not to the simple equilibrium $MH^+ \rightleftharpoons M + H^+$ but to the double equilibrium $MH^+ + NH_3 \rightleftharpoons M + NH_4^+$. Thus from the Born cycle:

$$\delta\Delta G^\circ_{ion(liquid)} = \delta\Delta G^\circ_{ion(gas)} - \delta\Delta G^\circ_{solv\,(MH^+)} + \delta\Delta G^\circ_{solv(M)} ,$$

where the latter δ denotes the relative change in the free energy (relative to the ionisation of NH_4^+).

The free energy of solvation of ions is very high. Its relative value may be only slightly less than the relative free energy of ionisation in the gaseous phase, but may be equal to it and even exceed it. If the difference in the free energies of solvation of the ions M_1H^+ and M_2H^+ being compared is less than the difference in the energies of ionisation in the gaseous phase, no anomalies are observed in the qualitative order of the change in base strength in the gaseous phase and in solution. If however the difference in the free energies of the solvation of the ions is greater than the difference in the free energies of ionisation in the gaseous phase, the above-mentioned lack of agreement will be observed between the base strength in the gaseous phase and the base strength in solution.

This is the case, for example, for aniline and ammonia. The protonation of aniline in the gaseous phase is energetically more favourable than the protonation of ammonia, by 7–8 kcal mole^{-1}. This means that the protonation constant of aniline is greater than that of ammonia by 5–6 orders of magnitude. When the ammonium ion is transferred to the aqueous phase, however, the large energy of solvation $-\Delta G_{solv(NH_4^+)} = 77.1$ kcal mole^{-1} is gained, and this is much greater than that for the transfer of the anilinium ion. As a result, the ammonium ion becomes energetically much more favourable than the anilinium ion in the aqueous phase. As a consequence, in the aqueous phase the protonation of aniline is less favourable by 6.5 kcal mole^{-1} than the protonation of ammonia (pK_a 9.27 and 4.58 respectively). Thus the fact that in the liquid phase aniline is weaker than ammonia is due to the less extensive solvation of the anilinium ion compared with the ammonium ion, and not to the basic properties of the unshared pair of electrons of the nitrogen atom in the aniline molecule.

A complete thermodynamic calculation has been carried out for many primary, secondary, and tertiary amines[26,54]. It has been found, for example, that in the case of trimethylamine, the protonation in the gaseous phase ($\delta\Delta G^\circ_{ion(gas)}$) is more favourable by 20.4 kcal mole^{-1} than in the case of ammonia, and the free energy of solvation of the trimethylammonium ion ($\delta\Delta G_{solv(MH^+)}$) is lower by 20.7 kcal mole^{-1}. In the gaseous phase, trimethylamine is a stronger base than ammonia, as a result of the inductive effect of the three methyl groups, but in the liquid phase this advantage is almost completely quenched by the less extensive solvation of the ion. Thus the basic strength of trimethylamine in the aqueous phase is only slightly greater than that of ammonia (by 0.8 kcal mole^{-1}).

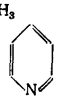
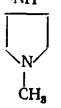
This quenching does not take place in the case of dimethylamine, which in water is a stronger base than trimethylamine. Here, the following results have been obtained for the MH^+ ion: $\delta\Delta G^\circ_{ion(gas)} = 15.8$ kcal mole^{-1}, $\delta\Delta G^\circ_{ion(liquid)} = 2.1$ kcal mole^{-1}, $\delta\Delta G^\circ_{solv(M)} = 0$, and

§ Here there may be one objection. Quantum-chemical calculation of the effective charges on the atoms in alkylammonium molecules[56] shows that the positive charge of the ion is distributed to the extent of more than 90% on the hydrogen atoms. It may therefore be doubted if it is justifiable to assign the observed differences to the resonance effect when comparing amines which satisfy only the requirement that the numbers of carbon atoms be equal and the skeleton similar, but for which the numbers of hydrogen atoms differ to such a great extent.

$\delta\Delta G^\circ_{solv(MH^+)}$ = 13.7 kcal mole^{-1}. In the gaseous phase, dimethylamine is weaker than trimethylamine $\delta\Delta G^\circ_{ion(gas)}$= 15.8 kcal mole^{-1} for $(CH_3)_2NH_2^+$ and 20.4 kcal mole^{-1} for $(CH_3)_3NH^+$, the difference in favour of trimethylamine being 4.6 kcal mole^{-1}). In aqueous solution, however, $\delta\Delta G^\circ_{ion(liquid)}$ = 0.8 kcal mole^{-1} for $(CH_3)_3NH^+$ and 2.1 kcal mole^{-1} for $(CH_3)_2NH_2^+$. The difference in favour of dimethylamine is 1.3 kcal mole^{-1}, in spite of the increased +*I*-effect in the case of trimethylamine from the introduction of the third methyl group. The difference in the hydration energies is greater.

Extensive data have been published[26] on the terms of the Born cycles for a number of bases. Of particular interest, for example, are the ratios[26] of the free energies of dissociation and solvation of the molecules and ions of pyridine, N-methylpyrrolidine, and piperidine, given in Table 12 (as before, the protonation of ammonia is taken as standard). Here, $-\Delta H^\circ_{solv(NH_4^+)}$ = 83.8 kcal mole^{-1}, $-\Delta G^\circ_{solv(NH_4^+)}$ = 77.1 kcal mole^{-1}¶.

Table 12. Born cycle data for pyridine, N-methylpyrrolidine, and piperidine[26] ($\delta\Delta G^\circ$, kcal mole^{-1}).

Compound	$\delta\Delta G^\circ_{ion(liq.)}$	$\delta\Delta G^\circ_{solv.(MH^+)}$	$\delta\Delta G^\circ_{ion(gas)}$	$\delta\Delta G^\circ_{solv.(M)}$
NH_3	0	0	0	0
	—5.49	26.9	18.9	1.99
	2.69	22.9	23.5	1.58
	1.65	27.9	26.4	2.71

In the gaseous phase, the protonation of pyridine is more favourable by 18.9 kcal mole^{-1} than the protonation of ammonia, but in aqueous solution, as a consequence of the loss of 26.9 kcal mole^{-1} for solvation, the protonation of pyridine is less favourable by 5.5 kcal mole^{-1} than that of ammonia. The relationships between pyridine and N-methylpyrrolidine are different. The protonation of the latter is more favourable both in the gaseous phase and in solution, by 7.5 kcal mole^{-1} in the gaseous phase and by 7.14 kcal mole^{-1} in solution. The effect of solvation is approximately the same in both cases (the difference is ~1.0 kcal mole^{-1}), and does not alter anything. This equality of the solvation effects apparently lies at the basis of Taft's rule[42], mentioned above.

¶ The change in the standard free energy for the transfer of 1 mole of NH_4^+ at a pressure of 1 atm from the gaseous phase to a hypothetical molal aqueous solution[69].

The free energy of solvation of an ion can be calculated approximately from the Born equation[68]:

$$-\Delta G^\circ_{solv} \quad \frac{z^2e^2}{2r}\left(1-\frac{1}{D}\right).$$

According to this equation, the standard free energy of the transfer of a spherical ion of radius r, having a charge ze, from a vacuum to a medium with a dielectric constant D is proportional to the square of the charge and inversely proportional to the radius of the ion. The solvation energy decreases with increase in the radius of the ion. Moreover, on delocalisation of the charge, when $ze = \Sigma q_i$, the solvation energy decreases, since $\Sigma q_i^2 < z^2e^2$ (the sum of the squares is always less than the square of the sum). The purely electrostatic picture of solvation is naturally insufficient for an adequate description, but the relationships given are nevertheless useful for a qualitative examination of the part played by solvation. The greater the size of the ion and the more extensively delocalised the charge, the less extensive the solvation. It should be noted that the effect of decrease in solvation on delocalisation of the charge was first noted by Mason[70].

Thus the part played by the hydrocarbon groups attached to the atom which acts as protonation centre is appreciably different in the gaseous phase and in solution. In the gaseous phase, increase in the polarisability (in the sense of delocalisation capacity) of the groups — their number, size, degree of branching, etc. — stabilises the ions and hence makes the base stronger. In the liquid phase, increase in the volume and polarisability of the groups decreases solvation, destabilises the ion, and hence decreases the strength of the base.

In the liquid phase, it is also necessary to take account of the volume effect: increase in the volume of the ion in all cases requires the expenditure of work to create a cavity in the solvent; this work decreases the energy of solvation, particularly in highly associated solvents; the steric hindrance of solvation also decreases the solvation energy. On the other hand, it is also necessary to take account of the possible formation of hydrogen bonds or other complexes with the solvent, since this leads to a significant increase in the solvation energy. The effect of this factor is effectively illustrated by the decrease in the exothermic character of the hydration of primary, secondary, and tertiary substituted ammonium ions compared with the unsubstituted NH_4^+ ion.[55] For primary ammonium ions, $\delta\Delta H^\circ_{solv(MH^+)}$ has an average value of ~6.8 kcal mole^{-1}, for the secondary ions ~13 kcal mole^{-1}, and for the tertiary ions ~19 kcal mole^{-1}, that is there is a decrease of ~6 kcal mole^{-1} for each hydrogen bond lost. Within each type, however, the decrease in the solvation energy increases with the volume of the ion (±20% of the average value). Thus the effect of hydrogen bonds predominates in this case.

Aue and coworkers[26] consider that the number of hydrogen bonds formed by the alkylammonium ions with water does not play such an important role in determining the solvation energy. They attribute more importance to the strength of the hydrogen bonds, which decreases with decreased charge on the NH_X^+ group. Since the charge decreases with increased number of alkyl groups attached to nitrogen, the illusion is created that a part is played by the number of hydrogen bonds, which also decreases with increased number of alkyl groups. In Aue's opinion, hydrogen bonds produce only a slight change in the solvation energy; the main contribution to the solvation energy of ammonium ions is made by the hydrophobic solvation of the alkyl groups and the electrostatic effects in the spirit of the Born theory.

It can be seen that the question of the dependence of the solvation energy on the structure of a molecule is fairly complex. No rational approach has yet been developed for its complete interpretation or more particularly its theoretical calculation.

V. ACID STRENGTH IN THE GASEOUS PHASE

1. Acid Strength of Alcohols in the Gaseous Phase

The first qualitative results of the study of the acid strength of alcohols in the gaseous phase were obtained by Brauman and Blair in 1968.[46] They immediately attracted the attention of chemists, since they contradicted the accepted conclusions and ideas of theoretical organic chemistry. This was followed by the publication of a number of papers by different authors, confirming the results of Brauman and Blair. Qualitatively, they reduce to the following: the acid strengths of alcohols having a normal chain increase in the order[46,59]: $H_2O < CH_3OH < CH_3.CH_2OH < CH_3CH_2CH_2OH < CH_3CH_2CH_2CH_2OH < CH_3CH_2.CH_2CH_2CH_2OH$, that is the acid strength in the gaseous phase increases with increase in the chain length. Branching of the group also leads to an increase in the acid strength, the effect being greater than the effect of the increase in its size: $CH_3OH < CH_3CH_2OH < (CH_3)_2.CHOH < (CH_3)_3COH < (CH_3)_3CCH_2OH$; $(CH_3)_3COH \geqslant n\text{-}C_5H_{11}OH$ †.

Increase in the formal $+I$-effect of the alkyl groups is accompanied by an increase in their electron-acceptor effect, that is the $-I$-effect. Similar relationships were observed for the acid strength of amines, as noted above.

Within the framework of the concept of the $+I$-effect, which is fixed for the alkyl groups, this sounds paradoxical. It can be shown, however, that we ourselves have created this paradox. The fact is that a constant $+I$-effect, characteristic of alkyl groups, is one of the dogmas characteristic of present-day work in organic chemistry. A dogma which has appeared from nowhere! Ingold, one of the founders of the electronic theory of organic chemistry, wrote in the early nineteen-thirties[71]: "It can be deduced from the premises stated above that the inductive effect of all alkyl groups *is zero* ... (They) will merely exert those polar effects which are impressed on them by the other polar groups ... The important property of alkyl groups is that they are more polarizable than hydrogen ... Since the majority of substituents commonly encountered are attractors of electrons, alkyl groups generally function as feebly electron-repelling groups: the possibility of the other type of behaviour can, however, be foreseen..."

Thus the direction of the inductive effect of alkyl groups depends on whether they are attached to an atom (or group) with a greater or lesser electronegativity than the alkyl groups. The first case leads to the relationships called the $+I$-effect, and the second to the relationships called the $-I$-effect.

This very perspicacious warning of Ingold was forgotten, and we teach students that alkyl groups exhibit a $+I$-effect. In fact, this is not the case. In proton attachment reactions, the principal role is played by the stabilisation of the cation formed, for example R_3N^+H or RO^+H_2. Here, the alkyl groups "deliver" electrons, since they are attached to an atom carrying a positive charge, that is an atom which is much more electronegative than the alkyl groups. Here, the larger the alkyl group, the greater its polarisability in the sense of "delocalisation capacity", the greater the $+I$-donor power and the greater the basic strength.

In the acidic dissociation of amines and alcohols, the principal role is played by the stabilisation of the resulting anion RNH^- or RO^-. Here, the alkyl groups "withdraw" electrons, since they are attached to an atom carrying a negative charge, that is an atom which is less electronegative than the alkyl groups. In this case, the larger the alkyl, the stronger its $-I$-effect, leading to greater acidity. Thus the t-butyl and neopentyl groups are both the strongest donors and the strongest acceptors among the alkyl groups, since they have the greatest ability, among alkyl groups, to delocalise any charge (Brauman and Blair[59–61]). Later, Arnett and coworkers[37] supported this view. The acid strength of alcohols in the vapour phase was also examined theoretically by MINDO and CNDO/2 methods and calculated *ab initio*. The results confirmed these suggestions. Reversal of the order of acid strength of the alcohols is observed on going to the liquid phase. The factors responsible are the same as in the case of the basic strength of amines. The smaller the anion, the stronger the effect of solvation. The order is reversed, not because of the $+I$-effect, which is not present in this case, but because of the solvation effect.

2. Acid Strength of Carboxylic Acids in the Gaseous Phase

The acid strength of carboxylic acids in the gaseous phase is expressed as the free energy change in the dissociation:

$$RCOOH \rightleftarrows RCOO^- + H^+ ,$$

When a standard acid AH is used, relative measurements are made for the reaction:

$$RCOOH + A^- \rightleftarrows RCOO^- + AH ,$$

In these reactions, the entropy change is small and does not exceed 1–2 e.u., so that it is usually assumed that $\Delta G^\circ = \Delta H^\circ$, and the acid strength is measured by the proton affinity of the anion, that is the enthalpy of the reaction

$$A^- + H^+ \rightarrow AH,$$

taken with the opposite sign ($-\Delta H^\circ$).

It is possible to write:

$$\Delta H^\circ = D\,(A{-}H) + IP\,(H) - EA\,(A),$$

where $D(A-H)$ is the energy of rupture of the bond, O–H, $IP(H)$ the ionisation potential of atomic hydrogen, and $EA(A)$ the electron affinity of the radical $RCO\dot{O}$. Since $IP(H)$ is a constant equal to 313.6 kcal mole^{-1}, a measure of the acid strength is usually obtained by calculating the quantity

$$\delta\Delta H^\circ = D\,(A{-}H) - EA\,(A), \text{ that is } \delta\Delta H^\circ = \Delta H^\circ - IP\,(H) = \Delta H^\circ - 313{,}6$$

(kcal mole^{-1}). For water, $D(A-H) - EA(A) = D(HO-H) - EA(OH^\cdot) = 77$ kcal mole^{-1}. In the gaseous phase, water is a very weak acid. All other oxygen acids are stronger,

† McIver's group[37] carried out quantitative measurements of the acid strength of various alcohols in the gaseous phase relative to methanol The following values were obtained for $-\delta\Delta G_{ion(ROH)}$ in kcal mole^{-1} (at 298 K; an increase in the numerical value indicates an increase in the acid strength): CH_3OH 0, C_2H_5OH 2.9, iso-C_3H_7OH 4.8, t-C_4H_9OH 5.6, neo-$C_5H_{11}OH$ 6.9. These data confirm the qualitative conclusions of Brauman and Blair.

that is their $\delta\Delta H^\circ$ values are less than 77 kcal mole^{-1}, and the smaller the numerical value of $\delta\Delta H^\circ$, the stronger the acid.

In the homologous series of carboxylic acids, the value of $\delta\Delta H^\circ$ for ionisation decreases with increase in the number of carbon atoms (Table 13 [24]). Thus butyric acid is stronger than propionic acid, and propionic acid is stronger than acetic acid; the order is reversed compared with the acid strength in water or other liquid media. Formic acid is the strongest acid in this series, however. To enable the reader to estimate the numerical values of the strength of acids in the gaseous phase ($\delta\Delta F^\circ$), the gaseous acid strength of the hydrogen halides is given (Table 14).

Table 13. Acid strength of various carboxylic acids in the gaseous phase and in water[24].

Acid strength	CH_3COOH	C_2H_5COOH	C_3H_7COOH	HCOOH
$\delta\Delta H^0$, kcal mole^{-1}	31.8	30.6	29.7	28.6
pK_a (H_2O)	4.76	4.87	4.82	3.75

Table 14. Acid strength of hydrogen halides in the gaseous phase and in water[24,74].

Acid strength	HF	HCl	HBr	HI
$\delta\Delta H^0$, kcal mole^{-1}	56.3	20.0	10.0	0.7
pK_a (H_2O)	+3.2	−7	−9	−11

The study of the gas-phase acid strength of halogen-substituted carboxylic acids gave unexpected results. They are of course stronger than the unsubstituted acids (Table 15).

Table 15. Acid strength of chloroacetic acids in the gaseous phase and in water[24].

Acid strength	CH_3COOH	$ClCH_2COOH$	$Cl_2CHCOOH$
$\delta\Delta H^0$, kcal mole^{-1}	31.8	19.0	12.0
pK_a (H_2O)	4.76	2.86	1.25

The order of the halogens is here reversed, however, compared with the liquid phase (Table 16). Bromoacetic acid in the gaseous phase (that is in itself) is stronger than chloroacetic acid, and the latter in turn is stronger than fluoroacetic acid; the concept of the *-I*-effect does not apply. The electronegativities of the halogens decrease in the order F > Cl > Br. This means that there are other factors in addition to the *-I*-effect (which is observed in the comparison with the unsubstituted acid). In fact, in the XCH_2COO^- anion, bromine is apparently more readily polarised, and its polarisation by the anionic charge stabilises the anion (the negative charge is delocalised). In an aqueous or in general liquid medium, on the other hand, in least polarisable fluorine-containing anion, in which the negative charge is concentrated in a small volume, is most effectively stabilised by the liquid medium; in the liquid phase, fluoroacetic acid is stronger than the others.

Table 16. Acid strength of various halogenoacetic acids in the gaseous phase and in water[75].

Acid strength	FCH_2COOH	$ClCH_2COOH$	$BrCH_2COOH$
$\delta\Delta H^0$, kcal mole^{-1}	21.0	19.0	17.9
pK_a (H_2O)	2.57	2.86	2.90

If however the carboxylic acid molecule contains substituents which each exhibit inductive and mesomeric effects, but which produce only slight changes in the total "delocalisation capacity" of the acid residue, the usual influence of electronic effects on the acid strength are observed satisfactorily in this series of derivatives. This is the case for the benzoic acid derivatives XC_6H_4COOH (X = NH_2, CH_3O, HO, CH_3, Cl, F, CN, NO_2). In this series, satisfactory correlations were obtained between ΔG° for dissociation in the gaseous phase (and pK_a in liquid phases) and the constants σ of Brown and Taft[31].

3. Acid Strength of Phenols in the Gaseous Phase

Here, reference may be made to the literature[35,75].

Table 17. Acid strength of thiols in the gaseous phase and in water[76].

Acidity	H_2S	t-C_4H_9SH	iso-C_3H_7SH	n-C_3H_7SH	C_2H_5SH	CH_3SH
$\delta\Delta H^0$, kcal mole^{-1}	37.5	39.4	40.3	41.1	41.7	43.2
pK_a (H_2O)	7.02	11.05	10 89	10.78	10.61	10.33

4. Acid Strength of Thiols in the Gaseous Phase[76]

Here, very interesting relationships are observed (Table 17). Hydrogen sulphide is a stronger acid than thiols both in the gaseous phase and in aqueous solution. In the gaseous phase, however, the strongest acid among the thiols is t-butyl mercaptan, which is the weakest acid in water. On the other hand, methanethiol, which is the

weakest acid in the gaseous phase, is a stronger acid than the other thiols in water. These relationships show a greater resemblance to those for the carboxylic acids than to those for the alochols (where water is weaker than all alcohols). The explanation for these phenomena is apparently similar to the explanation of the influence of alkyl groups on the strength of carboxylic acids (see below).

5. CH Acid Strength of Hydrocarbons and Their Derivatives

Carbon atoms in the hybridisation states sp^2 or sp have a greater electronegativity than in the state sp^3. Thus the bond $C_{(sp^3)} - C_{(sp^2)}$ should have a dipole moment directed from the sp^3- to the sp^2-hybridised carbon atom:

$$C_{(sp^3)} \longrightarrow C_{(sp^2)} .$$

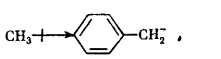
Thus alkyl groups should exhibit the familiar donor $+I$-effect. In this connection, the acid strengths of various unsaturated and aromatic hydrocarbons were studied in the gaseous phase[67]. The following series were obtained (some of the quantitative data are given in Ref. 36):

$$C_2H_5OH > C_6H_5CH_3 > CH_3OH > n\text{-}(CH_3C_6H_4CH_3 > H_2O;$$
$$CH \equiv CH > n\text{-}C_4H_9C \equiv CH > CH_3C \equiv CH > H_2O.$$

Here everything is remarkable!

1. Toluene is found to be a stronger acid than water. This indicates that the benzyl anion $C_6H_5CH_2^-$ is intrinsically more stable than OH^-. This is understandable, since the OH^- anion in the gaseous phase, that is when there is no solvation, is very unstable.

2. The fact that *p*-xylene is less acidic than toluene indicates that the methyl group has a destabilising action in the anion, since here the methyl "delivers" electrons ($+I$-effect):



3. Similarly, aklylacetylenes are less acidic than acetylene itself. A destabilising effect is present:

$$R \longrightarrow C \equiv O^- .$$

4. It is much more difficult to explain why t-butylacetylene is nevertheless a stronger acid than methylacetylene (by 3.4 kcal mole^{-1}). For this case, an apparently justified explanation has been put forward. In the general case, the stability of an anion is influenced by the dipole

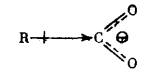
$$C_{(sp^3)} \longrightarrow C_{(sp)}$$

but in the butyl derivative the charge on the positive end of the dipole is assigned to the butyl group, which has a greater volume and polarisability. This decreases slightly the destabilising action of the alkyl group compared with the methyl group.

The question of the strength of carboxylic acids can now be considered:

$$HCOOH > C_3H_7COOH > C_2H_5COOH > CH_3COOH .$$

Here it is necessary to consider the system



containing the bond

$$C_{(sp^3)} \longrightarrow C_{(sp^2)} .$$

The action of an alkyl group produces a dipole, which is directed from the carbon atom of the alkyl group to the carbon atom of the carboxylate anion and destabilises the anion‡. This destabilisation, which is greatest for the methyl group, decreases slightly with increase in the size of the alkyl group, as a consequence of the delocalisation of the charge at the positive end of the dipole.

In an aqueous medium, however, the stability of the anion decreases with increase in its volume: $HCOOH^- > CH_3COO^- > C_2H_5COO^- > C_3H_7COO^-$, since there is a decrease in solvation, and the familar order of acid strengths is obtained:

$$HCOOH^- > CH_3COOH^- > C_2H_5COOH^- > C_3H_7COOH^- \ldots$$

This explanation naturally requires verification, but in any case this order cannot be attributed to the $+I$-effect of the alkyl groups (as is done in the most recent and best textbooks of organic chemistry).

6. Acid Strength of Ketones in the Gaseous Phase

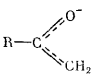
Recently, Brauman and coworkers[77] determined the acid strength of various ketones in the gaseous phase. The following order of acid strength was obtained:

$$C_6H_5COCH_3 > (CH_3)_3CCOCH_3 > CH_3COCH_3.$$

This differs from the order of acid strength in the liquid phase[78]:

$$C_6H_5COCH_3 > CH_3COOH_3 > (CH_3)_3CCOCH_3.$$

Here, the factors operating are apparently the same as in the case of carboxylic acids. In the anion



compared with the anion of acetaldehyde (R =H), the alkyl groups have a destabilising action (the dipole is directed to the anionic centre).

$$R \longrightarrow C_{(sp^2)}$$

This destabilising action is least for R = t-Bu, and greatest for R = CH_3. In the liquid phase, for reasons which are readily understood, acetone and methyl t-butyl ketone change places.

VI. SUMMARY

The intrinsic acid–base properties of molecules are observed only in the gaseous phase. In a liquid medium, these properties are distorted; they are deformed by the very strong interaction with the medium. In the examination of acid–base properties (and chemical properties in general) in the liquid phase, that is properties which necessarily belong to the system "molecule of the reactant plus surrounding molecules of the medium", these properties have been assigned only to the molecule of the

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‡ It should be noted that the effect of the dipole $C_{sp^3} - C_{sp^2}$ or $C_{sp^3} - C_{sp}$ is also observed in other cases. Thus prōp-2-ynylamine in the gaseous phase is a weaker base than propylamine by 6.3 kcal mole^{-1}; diprop-2-ynylamine is weaker than dipropylamine by 10.5 kcal mole^{-1}, and triprop-2-ynylamine is weaker than tripropylamine by 13.7 kcal mole^{-1} [6]. This results from the fact that in the corresponding cations $(CH \equiv C\text{-}CH_2)_nNH_{4-n}^+$ the dipole $C_{sp^3} \rightarrow C_{sp}$ destabilises the cation. Taft calls these hybridisation–inductive effects.

reactant, and very beautiful but incorrect explanations have been constructed from the non-existent consequences of the action of inductive and mesomeric effects. These ideas have been re-examined in recent years.

The present review has dealt with only proton transfer reactions. The same situation is observed in reactions of other types. Extremely interesting results have been obtained by Kebarle's group[7] in the study of ionic clusters in the gaseous phase. These products of the attachment of neutral molecules to ions provide models of short-range order on solvation ("supermolecule" formation). Reactions involving addition to multiple bonds, nucleophilic substitution at a saturated carbon atom, and other reactions have also been studied in the gaseous phase. In these fields it has been found that the role of intramolecular effects in neutral molecules has been exaggerated and frequently distorted, and the problems of the stability of ions in relation to the influence of solvation have been insufficiently analysed. It is now time for a painstaking re-examination and correction of all the errors made in theoretical organic chemistry in the last 40 years. We are standing on the threshold of great events in the theory of heterolytic reactions in organic chemistry, which will be realised in the near future.

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§ According to a personal communication from McIver, the results of this work will be revised; see Ref. 6.

¶ These data were subsequently refined; see R. W. Taft and M. Taagepera, Abstracts of the 167th ACS National Meeting, Los Angeles, April, 1974.

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