J. Am. Chem. Soc. **1982**, *104*, 5899-5902 5899

Basicities of Methyl-, Methylphenyl-, and Phenylphosphines in the Gas Phase

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Abstract: The relative gas-phase basicities of the methyl-, methylphenyl-, and phenylphosphines were measured with a pulsed electron high ion source pressure mass spectrometer. The kinetics leading to the equilibria and the equilibria $B_0H^+ + B = B_0 + BH^+$ were observed and the equilibrium constants K determined. These led to standard free energy changes $\Delta G°$. For a constant $B_0 = Me_3P$, these were: $B = Me_2PhP$, $\Delta G° = -2.5$ kcal/mol; $B = MePh_2P$, $\Delta G° = -3.2$ kcal/mol; $B = Ph_3P$, $\Delta G° \approx -3.2$ kcal/mol. Also the vertical ionization potentials of the phosphorus lone pairs were measured by photoelectron spectroscopy. These were found to decrease in the order $Me_3P \rightarrow Ph_3P$ as expected from the measured basicity changes. The observed increase of basicity with phenyl substitution in the gas phase is opposite to the order in solution where the basicity decreases in the order $Me_3P \rightarrow Ph_3P$. The latter must be due to adverse solvation of the phenylphosphonium ions. The observation that the gas-phase basicities increase when methyl is replaced by phenyl is very interesting. A decrease is observed for the analogous amines where the basicity of Me_2PhN is lower than that of Me_3N. Part of this difference of behavior can be attributed to stabilization in the phenylphosphonium ions by π-conjugation of the aromatic ring with empty orbitals of the phosphorus. Such a stabilization is not available to the nitrogen compounds.

Introduction

An experimental determination[1] of the proton-transfer equilibrium (eq 1) in the gas phase showed that trimethylamine is a

$$Me_2PhNH^+ + Me_3N = PhNMe_2 + Me_3NH^+ \quad \Delta G°_1 = -1.6 \text{ kcal/mol} \quad (1)$$

stronger Brønsted base then *N,N*-dimethylaniline. By analogy with the result for reaction 1, one may expect that the basicities will continue to decrease in the series Me_3N, Me_2PhN, $MePh_2N$, Ph_3N. A recent measurement of the proton affinity of Ph_3N by Munson,[2,3] which puts the basicity of Ph_3N some 14 kcal/mol below that for Me_2PhN, is in agreement with that expectation.

Considering that nitrogen and phosphorus differ in size, electronegativity, and availability of orbitals, the interesting question arises as to whether replacement of methyl by phenyl will also lead to a weakening of the gas-phase basicity in the phosphine series $Me_3P \rightarrow Ph_3P$. The basicities in solution do show a regular decrease with phenyl substitution;[4] however, the basicity order in solution may be strongly influenced by solvation effects. Recently one of us (R.J.P.), in connection with a discussion of the σ donor abilities of tertiary phosphines, suggested that the intrinsic, i.e., gas-phase, basicity of the methylphosphines should increase with phenyl substitution.[5] The present work describes measurements of the gas-phase basicities of the tertiary phosphines and the ionization potentials for the lone-pair electrons on the phosphorus, which were undertaken in order to determine the basicity order of the methyl-, methylphenyl-, and phenylphosphines.

Experimental Section

(a) Gas-Phase Basicity Measurements. The basicity measurements were performed with a pulsed electron beam high ion source pressure mass spectrometer of design similar to that described previously.[6,7] A suitable reaction mixture is irradiated with short (10 μs) electron pulses. The resulting ions react, and, when conditions have been chosen properly, proton-transfer equilibria between two neutral bases B_0 and B present at known concentrations become established. The ion concentrations are observed by bleeding a small part of the reaction gas mixture into a vacuum system where the ions are captured by electric fields and mass analyzed in a mass spectrometer. The detected ion intensities B_0H_+ and BH^+ are assumed proportional to the concentrations of the ions in the reaction chamber.

The reaction mixtures used for the measurements consisted of methane as the major gas and the two bases B_0 and B. These mixtures, as usual, were prepared in a thermostated 5-L glass bulb at ~1 atm of CH_4 and known partial pressures of B_0 and B. The mixtures were then passed through the ion source reaction chamber in slow flow regulated by means of an all-metal valve between the bulb and ion source. Some difficulties were experienced because of the very low vapor pressure of Ph_3P. This base was introduced as a solid in the evacuated bulb, thermostated at ~130 °C. The saturation pressure (over the solid) was measured with a capacitance manometer (MKS Baratron). In order to ascertain that the saturation pressure does not consist largely of high vapor pressure impurities, the vapor in the bulb was pumped out once or twice until a visible amount of the solid had been used up. Then, the saturation pressure read on the manometer (~10 mtorr) was assumed to be the Ph_3P vapor pressure. We estimate that the error in the Ph_3P pressure determination is less than ±50%.

In order to check that pyrolysis of the bases B was not occurring in the glass storage bulb, measurements at different bulb temperatures were made. The equilibrium constants were found to be independent of the bulb temperature.

b. Time Dependence of Ion Concentrations in Proton Transfer Equilibria Measurements. A typical result obtained in the course of measurements of the equilibrium 2 is shown in Figure 1. Electron irradiation

$$Me_3PH^+ + Me_2PhP = Me_3P + Me_2PhPH^+ \quad (2)$$

of the major gas, methane (3 torr), leads to CH_5^+ and $C_2H_5^+$ as final ions. Both CH_5^+ and $C_2H_5^+$ are strong Brønsted acids so that each can protonate the two phosphines Me_3P and Me_2PhP which are present at a ratio of 7.9. For the given phosphine concentrations these protonations are very fast such that both CH_5^+ and $C_2H_5^+$ disappear completely within some 20 and 30 μs reaction time. Initially a much higher concentration of Me_3PH^+ is observed (see Figure 1) since the neutral base Me_3P is present at much higher concentration than Me_2PhP and the rate of protonation by CH_5^+ and $C_2H_5^+$ is essentially proportional to the concentration of the bases. A little later the intensity of Me_3PH^+ is seen to decrease rapidly owing to proton transfer to Me_2PhP, i.e., reaction 2. After about 200 μs, equilibrium 2 is established. The equilibrium con-

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(1) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 3504.

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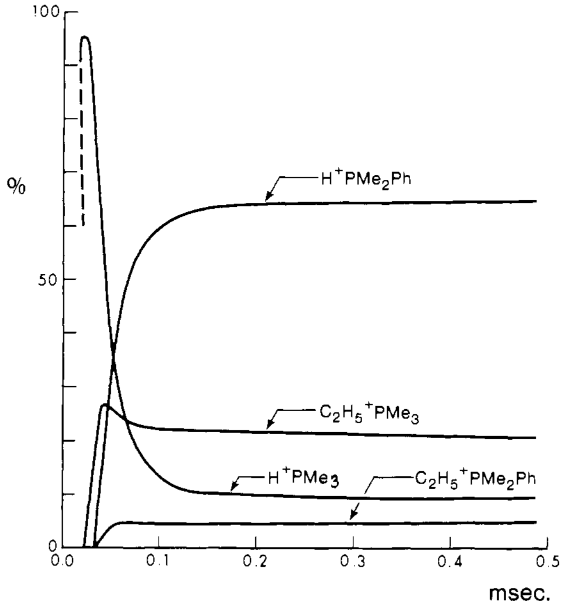

Figure 1. Time dependence of ions observed in a typical measurement of equilibrium 2: $Me_3PH^+ + Me_2PhP = Me_3P + Me_2PhPH^+$. Abscissa gives time after electron pulse, which corresponds to reaction time in the ion source. Ordinate gives relative abundance in percent of observed ions. The observed ion percent corresponds approximately to the relative ion concentrations in the ion source. The reaction mixture used consisted of methane as the major gas containing small amounts of the two phosphines (CH_4 = 3 torr, Me_3P = 9 mtorr, Me_2PhP = 1.1 mtorr). The ions due to methane, CH_5^+ and $C_2H_5^+$, disappear rapidly (~30 μs) owing to reactions with the phosphines; therefore, the concentration changes of CH_5^+ and $C_2H_5^+$ are not shown. Proton transfer from CH_5^+ and $C_2H_5^+$ leads to Me_3PH^+ and Me_2PhPH^+. The Me_3PH^+ is initially produced in larger amounts since the Me_3P is present in larger concentration. However, at longer reaction times equilibrium 2 leads to a preponderance of Me_2PhPH^+. This clearly shows that the basicity of Me_2PhP is higher. A side reaction observed is the oxidative addition of $C_2H_5^+$ to the two phosphines.

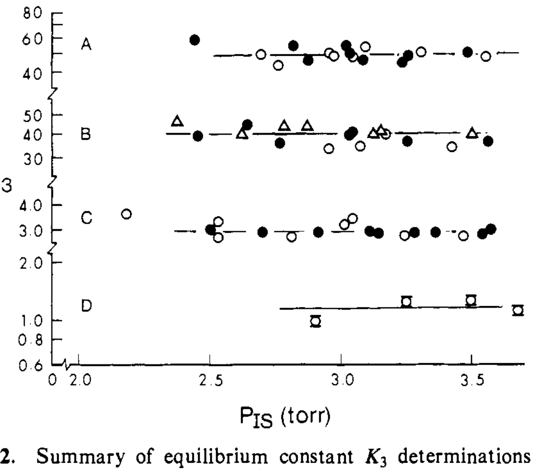

Figure 2. Summary of equilibrium constant K_3 determinations for equilibria 3, $B_1H^+ + B_2 = B_1 + B_2H^+$, involving methyl-, methylphenyl, and phenylphosphines. The B_1H^+ and B_2H^+ at equilibrium were taken from runs like that shown in Figure 1 at long reaction times where B_1H^+ and B_2H^+ had become constant. Increase of ion source pressure increases neutrals B_1 and B_2 concentrations at constant ratio $R = [B_1]/[B_2]$. (A) $B_1 = Me_3P$; $B_2 = Me_2PhP$: ion source temperature 47 °C; ○, R = 7.9; ●, R = 6.7. (B) Same as above, but temperature 75 °C; ○, R = 2.3; ●, R = 7.9; △ R = 15.5. (C) $B_1 = Me_2PhP$, $B_2 = MePh_2P$: 71 °C; ○, R = 2.8; ●, R = 1.3. (D) $B_1 = MePh_2P$, $B_2 = Ph_3P$: 72 °C; R = 28.

stant K_2 for the run in Figure 1 is $K_2 = 52 \pm 4$. Other determinations of K_2 are shown in Figure 2.

The forward rate reaction (eq 2) was measured in one run. A rate constant $k_2 \approx 0.8 \times 10^{-9}$ molecule^{-1} cm^3 s^{-1} was observed. Thus, the rate for the exothermic direction of the proton-transfer reaction is near the collision rate as is common for many proton-transfer reactions.

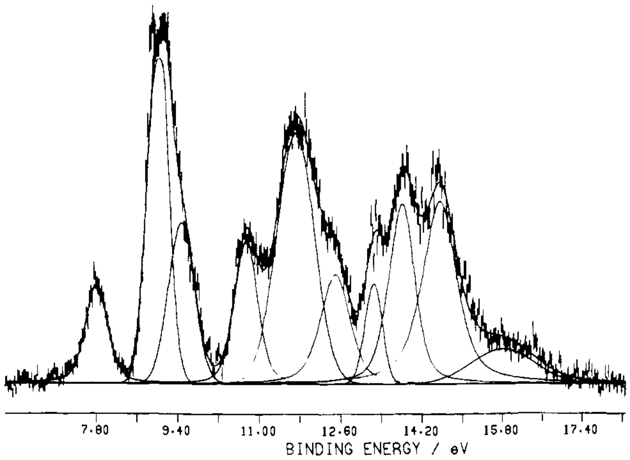

Figure 3. Photoelectron spectrum of Ph_3P.

$C_2H_5^+$ does not engage only in proton transfer to the phosphines. Evidently (see Figure 1) the following alkylations (oxidative additions) also occur.

$$Et^+ + Me_3P = EtPMe_3^+$$

$$Et^+ + Me_2PhP = EtPPhMe_2^+$$

The initial $C_2H_5^+$ concentration in methane is ~40%, the rest being CH_5^+. The total amount of ethylphosphonium ions observed after the $C_2H_5^+$ has disappeared is ~26%; thus ethylation of the phosphines occurs with slightly greater probability than proton transfer from $C_2H_5^+$.

c. **Photoelectron Spectra.** The He I and He II photoelectron spectra were recorded in the gas phase with a McPherson ESCA 36 spectrometer and a hollow cathode lamp as the source.[8] The phosphines Me_3P, Me_2PhP, and $MePh_2P$ were sufficiently volatile that their PE spectra could be recorded at room temperature using the gas inlet system; sample pressure was maintained at $\sim 5 \times 10^{-6}$ torr. For the less volatile Ph_3P, a copper-tipped stainless steel sample tube was used together with a heated inlet system[9] in which the temperature was kept at ~120 °C. All spectra were calibrated with the argon $^2P_{3/2}$ line at 15.729 eV and computer fitted to symmetric Lorentzian-Gaussian line shapes using an iterative procedure.[10] Both He I and He II spectra were obtained, and the measured binding energies were equal within ±0.05 eV. Selected data are given in Table I and a typical spectrum is shown in Figure 3. Table I also includes lone-pair ionization potentials from the literature. There is reasonable agreement, but the new values (especially relative to one another) are considered more reliable since they were obtained and calibrated in the same way on the same spectrometer. Vertical ionization potentials are given since these can be measured more accuately. The lone-pair ionization bands for all phosphines had similar shapes and similar full widths (0.55 ± 0.1 eV) at half-height. Therefore, it is very likely that the ordering of the adiabatic ionization potentials will be the same as that for the vertical ones.

Results and Discussion

The results of the measurements of the proton-transfer equilibria 3 involving the methyl-, methylphenyl-, and phenylphosphines are

$$B_1H^+ + B_2 = B_1 + B_2H^+ \qquad (3)$$

summarized in Figure 2. The equilibrium constants $K_3 = [B_2H^+][B_1]/[B_1H^+][B_2]$ obtained from the figure were used to obtain the free-energy change $\Delta G^\circ_3 = -RT \ln K_3$. For $B_1 = Me_3P$ and $B_2 = Me_2PhP$, determinations at two different temperatures T were performed (see Figure 2): $\Delta G^\circ_3(320\text{ K}) = -2.48$ kcal/mol, $\Delta G^\circ_3(348\text{ K}) = -2.49$ kcal/mol. The identical result indicates that ΔS°_3 for this pair is approximately zero, i.e. $\Delta G^\circ_3 \approx \Delta H^\circ_3$. This result is expected if the entropy change is assumed to be due to changes of rotational symmetry only. For the other base pairs determinations were made at a single temperature. It is likely that for these pairs also $\Delta S^\circ_3 \approx 0$ and $\Delta G^\circ_3 \approx \Delta H^\circ_3$ since the

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Table I. Gas-Phase Basicities and Ionization Potentials of Methyl-, Methylphenyl-, and Phenylphosphines and Related Amines[a]

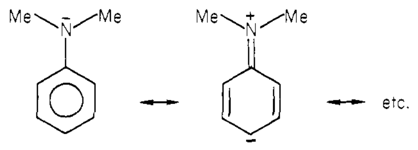
base B	$\Delta G° \sim \Delta H°$ [b]	PA[c]	IP (B)[d]	IP (B)[e]	pK_a (HB^+)[l]
Me_3P	0	223.5[f]	184.7[f]	197.9,[g] 198.8[h]	7.85
Me_2PhP	−2.5	226.0[i]		193.0,[g] 191.9[h]	6.25
$MePh_2P$	−3.2	226.7[i] ~228.0[m]		186.1,[g] 190.9[h]	4.65
Ph_3P	~(−3.2)	~226.7[i]		186.8,[g] 179.9[h]	3.05
PH_3		187.4[f]	229.5[f]		
Me_3N		223.1[j]	181.5[f]		
Me_2PhN		221.5[k]			
NH_3		202.3[c]	234.3[f]		

[a] All values in kcal/mol. [b] Experimental measurement, present work (see Figure 2), for the reaction $Me_3PH^+ + B = Me_3P + BH^+$, estimated error ±0.2 kcal/mol; the error for Ph_3P could be larger (see Experimental Section). [c] Proton affinities based on $PA(NH_3) = 202.3$ kcal/mol.[9,11] [d] Adiabatic ionization potential of one pair of B. [e] Vertical ionization potentials; IP (B) refers to lone pair of B, estimated error ±2 kcal/mol. [f] Data from Beauchamp et al.[11] [g] Data from several sources, quoted in ref 5. [h] Present experimental work. [i] Based on $\Delta G°_3 \approx \Delta H°_3$, present work, and PA $(Me_3P) = 223.5$ kcal/mol from Wolf et al.[11] [j] Data from Yanıdagni.[9] [k] Data from Yamdagni.[2] [l] Data from Henderson and Streuli.[4] [m] Data from Munson.[3]

rotational symmetry numbers cancel. The data are summarized in Table I. Also given in Table I are the ionization potentials for the lone pairs on the phosphorous atoms determined in the present work and literature data for basicities and ionization potentials of the corresponding amines.[11,12]

The relationship between the proton affinity PA(B) and the ionization potential of the lone pair in B has been considered in several papers.[13] In general, it is observed that for a related series of compounds containing the same heteroatom base, the ionization potential decreases monotonically with increase of the PA. For example a near-linear relationship is observed[13a] for the series NH_3, $MeNH_2$, Me_2NH, and Me_3N. Examining the present data one finds that the observed order of proton affinities $PA(Me_3P) < PA(Me_2PhP) < PA(MePh_2P) \approx PA(Ph_3P)$ is supported by the measured ionization potentials. The relative magnitudes of the ΔIP correlate approximately with the corresponding $\Delta G°_3$ values, except the ΔIP (present work, Table I) for the pair $MePh_2P$–Ph_3P which is much larger than the $\Delta G°_3 \approx 0$ kcal/mol. This latter result is probably due to an unfavorable combination of errors in the IP determinations. The ΔIP values are of lower accuracy than the $\Delta G°$ measurements; earlier IP values give a $\Delta IP \approx 0$ kcal/mol for this pair (see Table I).

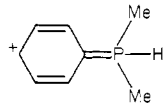
The Brønsted basicities of the methyl-, methylphenyl-, and phenylphosphines increase with phenyl substitution, as suggested earlier by Puddephatt.[5] It was mentioned in the Introduction (see also Table I) that the behavior of the amines is exactly the opposite; i.e., the basicity of the methyl amines decreases with phenyl substitution. The amine basicity decrease is caused by resonance stabilization *R* of the neutral base, as shown in structure I, and inductive destabilization *I* of the onium ion by the electron-withdrawing phenyl group. However, these effects are partially offset by the stabilization *P* of the onium ion, which is due to the large polarizability of the phenyl group. Taft[14] has analyzed these effects for the closely analogous reaction 4 and obtained, $R_4 \approx -5.5$ kcal/mol, $I_4 \approx -4$ kcal/mol, and $P \approx +7$ kcal/mol. One might expect that for reaction 1, involving Me_2PhN and Me_3N with $\Delta G°_1 = -1.6$ kcal/mol, the relative magnitudes for *R*, *I*, and *P* should be similar to those above, with the absolute values being uniformly smaller.



I

$$PhNH_3^+ + MeNH_2 = PhNH_2 + MeNH_3^+ \quad \Delta G°_4 = -2.5 \text{ kcal/mol} \quad (4)$$

Turning to the phosphine pair, Me_3P and Me_2PhP, one might expect the following changes. The *R* term should be much smaller, probably down to one-third, because of the mismatch of the phosphorous bonding orbitals with the 2p orbitals of the aromatic system. The destabilizating inductive effect *I* in the onium ion is probably somewhat smaller, while the stabilizing effect *P* should be considerably smaller because of the larger distance present in the phosphines. The decrease of *R* may well be the dominant effect, and it is conceivable that the combined changes of *R*, *I*, and *P* outlined above might be sufficient to explain the experimentally observed increase of basicity with phenyl substitution. However, an additional effect may be involved also, namely, stabilization of the phosphonium ion by conjugation of π electrons from the benzene ring with empty orbitals of the phosphorus, structure II.



II

Another example where back-donation into empty phosphorus orbitals may be involved can be found in the comparison of methyl substituent effects for NH_3 and PH_3. The proton affinity of phosphine is much lower than that of ammonia $(PA(NH_3) - PA(PH_3) \approx 15$ kcal/mol). Methyl substitution increases the proton affinities of both phosphines and amines. However, the methyl substituent effect is very much larger for the phosphines than for the amines. This results in a proton affinity for Me_3P which is higher than that for Me_3N (see Table I). The stronger methyl effect on the phosphines could be due to stabilization of the phosphonium ion by hyperconjugation, i.e., conjugation of π-like orbitals of the methyl group with empty orbitals of the phosphorus. This is a stabilization analogous to that proposed in structure II but involving methyl rather than phenyl. Staley and Beauchamp[11] have examined the possible factors involved in the stronger substituent effect of methyl in the series $PH_3 \rightarrow Me_3P$. These authors also consider π-donation by methyl as one possibility. However, they point out other factors that can be involved also. There appears to be a decrease in sp^3 hybridization in the series $NH_3 \rightarrow NMe_3$ such that the p character of the lone pair decreases. On protonation rehybridization to sp^3 must occur. For the higher methylated species, the rehybridization change is larger and leads to a larger energy requirement. The favorable energy change due to the stabilization of the onium ions by the polarizability of the methyl groups is reduced by the rehybridization so that the observed net basicity increase is smaller. In the phosphine series, $PH_3 \rightarrow PMe_3$, there is no change of hybridization. The lone-pair orbital remains throughout largely of s character. Therefore, on protonation, the energy required for rehybridization to sp^3 remains constant through the series, so that the observed methyl substituent effect is larger.[11]

Considering that alternate explanations can be found, the importance of the stabilization of phenyl- and methylphosphonium ions by π-conjugation as in structure II cannot be easily assessed without additional information. Theoretical calculations at the STO-3G*, 4-31G, and 4-31G* levels together with additional

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experimental determinations of the proton affinities of some key phosphines will be reported in a future publication.[15] The calculations indicate that the conjugation in II does make a significant contribution to the stabilization of the phenylphosphonium ion (calculations were made for $PhPH_3^+$ rather than $PhMe_2PH^+$). The phosphorus orbitals involved are mostly π^*; i.e., the participation of dπ orbitals is smaller. The role of methyl hyperconjugative stabilization of the $MePH_3^+$ ion is found to be relatively small. The much stronger basicity increasing effect of phenyl for the phosphines relatively to the amines is found to be caused primarily by the basicity decreasing stabilization of the neutral amine base (aniline, conjugation like in structure I). The stabilization of the phenylphosphonium ion by conjugation in II while sizable, is less important.[15]

The basicities of the phosphines in solution (see Table I) decrease with phenyl substitution, i.e., show a behavior opposite to that observed in the gas phase. Obviously, this must be due to adverse solvation effects. The positive charge delocalization onto the phenyl groups and the large size of these groups corresponds to a large effective increase of the phosphonium ion radius. Thus an adverse effect of phenyl on the solvation of these ions is to be expected.

Registry No. Me_3P, 594-09-2; Me_2PhP, 672-66-2; $MePh_2P$, 1486-28-8; Ph_3P, 603-35-0.

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Solution Thermodynamic Studies. 7.[1a] A Thermodynamic Study of Solvent Effects on the Relative Stability of *cis*- and *trans*-Dichloroethylene: Importance of the Quadrupolar and Octupolar Electric Moments in the Reaction Field Model

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Abstract: Calorimetric measurements of heats of solution on the title compounds clearly show a similar solvent effect on both isomers even though the cis isomer is a dipolar molecule and the trans isomer a quadrupolar molecule. Interaction energies of both isomers with various solvents can be described by a reaction field model in which higher moments than the dipole moment are taken into account. The quadrupolar contribution is as important for the trans isomer as for the cis, and even the octupolar contribution to the interaction energy is not negligible in the case of the cis isomer.

It is interesting to note that in organic chemistry a polar molecule is generally considered to be a molecule with a dipole moment. The moments of higher order are generally ignored. In this work we point out that a quantitative or even a semiquantitative description of the so-called "solvent effect" in organic chemistry cannot be developed if the quadrupole moment and, in some cases, the octupole moment of the solute is not explicitly taken into account. The electric component of the interaction energy of a polar solute in various solvents can be estimated by using the reaction field theory. Often, the calculation is limited to a point dipole located at the center of a spherical cavity. As was pointed out many years ago by Böttcher,[2] the application of this model to real dipolar molecules leads to a very crude estimation of intermolecular electrostatic interactions. The interaction energy changes considerably when the dipole is not at the center of the cavity, as was proved by Böttcher[2] in his calculation of the work required to bring a point dipole from an infinite distance to an excentric position inside a spherical cavity surrounded by a homogeneous dielectric. In this case, the energy of interaction is given by an infinite series of terms. It must be noted that this series is reduced to its first, i.e., dipolar term, when the dipole is at the center of the cavity. In 1954, Wada[3] published an evaluation of the energy difference between rotational isomers in various solvents. To improve the estimation of interaction energies, this author introduced two refinements to the original reaction field theory. The shape of the cavity of the solute molecule is taken as an ellipsoid, and the reaction field is evaluated at the two focuses where the two point dipoles are considered to be located.

In 1966, Abraham and his co-workers[4] extended Böttcher's calculation to several point dipoles in a spherical cavity. Wada and Abraham were the first to show the importance of the second term of the series, which can be described as quadrupolar. In a series of works devoted to stereochemical problems, Abraham et al.[4] demonstrated the significance of the quadrupolar term not only for solute molecules without permanent dipoles but also for solute molecules with permanent dipoles.

In 1976, Rivail and co-workers calculated a multipolar expansion of interaction energy. As far as we know, these authors were the first to show that a *n*-polar contribution higher than quadrupolar has to be considered in order to estimate interaction energy. Unfortunately, the expressions they used to calculate them[5] present some typographic errors.

In 1959, Buckingham[6] gave an expression for the reaction field gradient inside a spherical cavity containing a central point quadrupole, the cavity being immersed in a continuum of a given

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