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ESTIMATION OF THE OUTER SPHERE CONTRIBUTION TO THE ACTIVATION PARAMETERS FOR HOMOGENEOUS ELECTRON TRANSFER REACTIONS USING THE MEAN SPHERICAL APPROXIMATION

by

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Estimation of the Outer Sphere Contribution to the Activation Parameters for Homogeneous Electron Transfer Reactions Using the Mean Spherical Approximation

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Abstract

Estimation of the outer sphere contribution to the Gibbs energy and enthalpy of activation for homogeneous electron transfer is described on the basis of the mean spherical approximation (MSA). It is shown that these quantities for spherical reactants are significantly smaller than those estimated by the Born continuum model. MSA estimates and experimental values of the activation enthalpy for the cobaltacene/cobaltacenium cation redox couple are found to agree very well with one another. The assumptions used in applying the MSA in the present paper and in earlier work are discussed.

Introduction

In the Marcus treatment of thermally activated electron transfer [1], the Gibbs energy of activation is broken up into two components, an inner sphere activation energy describing the reorganization of the bonds within the reactant, and an outer sphere contribution related to changes in polarization of the solvent around the reactant. The latter component, ΔG^*_{OS}, has been most often estimated on the basis of dielectric continuum theory using the Born model. For this reason, the model used to estimate ΔG^*_{OS} has often been criticized as giving estimates which are too large. In fact, Marcus [1] considered the shortcomings of this model pointing out that it failed to consider effects of ion-ion interactions and partial dielectric saturation beyond the first coordination shell of the reactant. More recently, attempts have been made to improve the description of reactant solvation on the basis of a non-primitive model of the electrolyte solution, namely, the mean spherical approximation (MSA) [2-5].

In the MSA as usually applied, the electrolyte solution is assumed to be composed of hard spheres of two sizes, those representing the solvent with diameter σ_s and a central point dipole, and those representing ions of diameter σ_i with a central point charge. An important feature of the model is the polarization parameter λ which is related to the solvent's dielectric constant, and thus, to its dipole moment and polarizability. Although the MSA model recognizes the molecular nature of the electrolyte solution, as normally applied, it does not recognize the chemical forces which are so important in determining the solvation energy. Thus, in common with the Born model, the MSA estimates of the Gibbs energy of solvation of a cation and anion of equal size are the same. In practice, it is well known that this is not the case, the experimental Gibbs solvation energy of a monoatomic anion of a given radius being much greater than that of a monoatomic cation of the same size [6].

We have recently described a method of introducing chemical "stickiness" into the MSA model in which the polarization parameter λ is extracted from experimental data for monovalent monoatomic cations and anions [7]. It was shown that the value of λ for monoatomic anions in a given solvent is very different from the value appropriate for monoatomic cations. Moreover, the ratio of λ/σ_s estimated in a variety of polar solvents for cations correlates well with the donor number (DN), a well known empirical parameter characterizing the solvent's ability to act as a Lewis base. At the same time, the values of λ/σ_s appropriate for anions correlate with the E_T parameter which characterizes solvent acidity, that is, its ability to solvate anions. This extension of the MSA model is very successful in estimating the Gibbs energy of solvation of other ions provided they are spherical.

In the present paper, the MSA is applied to the estimation of the outer sphere contribution to the activation parameters for electron transfer. The theory is then used to estimate these parameters for electron transfer reactions involving cobaltacene, a system which has been studied recently in a number of solvents and which can be considered to be spherical to a good approximation [8].

The Model

The Gibbs activation energy for the homogeneous electron transfer reaction

$$A + B' \longrightarrow B + A' \qquad (1)$$

in which one electron is transferred is given by

$$\Delta G^*_{os} = \frac{N_o e^2}{16\pi \varepsilon_o}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)\left(\frac{1}{2r_A} + \frac{1}{2r_{B'}} - \frac{1}{r_{AB'}}\right) \qquad (2)$$

where N_o is Avogadro's constant, e, the fundamental electronic charge, ε_o, the permittivity of free space, ε_s, the static dielectric constant of the solvent, ε_{op}, its value at optical frequencies, r_A, the radius of reactant A represented as a sphere, $r_{B'}$, the corresponding radius of B', and $r_{AB'} = r_A + r_{B'}$, the distance between the centers of the two reactants at contact. For a self exchange reaction (A = A', B = B'), for which the radii of the two species A and B can be assumed equal, the expression for ΔG^*_{os} reduces to

$$\Delta G^*_{os} = \frac{N_o e^2}{32\pi \varepsilon_o r_i}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \qquad (3)$$

where r_i is now the radius of either reacting species. This expression can be regarded as giving the difference between the Gibbs solvation energy of the reacting system at optical frequencies and that at static frequencies, and can be physically related to the hypothetical two step charging process associated with thermally activated electron transfer described by Marcus [9]. Thus, if the Gibbs solvation energy of the reacting system at optical frequencies is

$$\Delta G_{s,op} = - \frac{N_o e^2}{8\pi \varepsilon_o r_i} \left(1 - \frac{1}{\varepsilon_{op}}\right) \tag{4}$$

and that at static frequencies

$$\Delta G_{s,st} = - \frac{N_o e^2}{8\pi \varepsilon_o r_i} \left(1 - \frac{1}{\varepsilon_s}\right), \tag{5}$$

it follows that

$$\Delta G^{*}_{os} = (\Delta G_{s,op} - \Delta G_{s,st}) / 4 \tag{6}$$

When one uses the MSA to estimate the static contribution to the Gibbs solvation energy, the expression for $\Delta G_{s,st}$ becomes [7, 10, 11]

$$\Delta G_{s,st} = - \frac{N_o e^2}{8\pi \varepsilon_o r_i} \left(1 - \frac{1}{\varepsilon_s}\right) \frac{1}{(1 + r_s / \lambda r_i)} \tag{7}$$

where r_s is the radius of the solvent represented as a sphere and λ, the polarization parameter discussed earlier. The ratio $r_s / \lambda r_i$ has values typically between 0.2 and 0.4 so that the MSA estimate of $\Delta G_{s,st}$ is from 55 to 70% of the Born estimate. However, the predominant contribution to ΔG^{*}_{os} comes from the term at optical frequencies because the optical permittivity in all polar solvents is much less than the static value. The MSA model which was derived for systems with permanent dipole moments embedded in hard spheres [10-12] is not appropriate at these high frequencies where the electrical property of importance is the molecular polarizability. Statistical mechanical models appropriate to systems which are polarizable but non-polar have been developed [13], one example being the perturbation theory of Logan and Madden [14]. This theory is applicable for high molecular densities and thus, could be applied to liquids. We assume here that deviations from the continuum model for the solvent are not so significant at optical frequencies , and therefore, that the Born model gives a good estimate of $\Delta G_{s,op}$ (eq. 4). Thus, the expression for ΔG^{*}_{os} for a homogeneous self-exchange reaction becomes

$$\Delta G^{*}_{os} = - \frac{N_o e^2}{32\pi \varepsilon_o r_i} \left[\left(1 - \frac{1}{\varepsilon_{op}}\right) - \left(1 - \frac{1}{\varepsilon_s}\right) \frac{1}{(1 + r_s / \lambda r_i)}\right] \qquad (8)$$

As applied here, the value of the MSA parameter λ depends on whether the reacting system involves cations or anions.

It is also interesting to estimate the enthalpy of activation, ΔH^{*}_{os}. To do this, one requires knowledge of the temperature dependence of the permittivities ε_{op} and ε_s from which one can estimate the outer sphere entropy of activation. Differentiating eq. (8) assuming that the parameter λ is independent of temperature, one obtains the following expression for ΔS^{*}_{os}:

$$\Delta S^{*}_{os} = \frac{N_o e^2}{32\pi \varepsilon_o r_i} \left[\frac{1}{\varepsilon_{op}^2} \frac{\partial \varepsilon_{op}}{\partial T} - \frac{1}{\varepsilon_s^2} \frac{\partial \varepsilon_s}{\partial T} \frac{1}{(1 + r_s / \lambda r_i)}\right] \qquad (9)$$

The corresponding expression for ΔH^{*}_{os} is

$$\Delta H^{*}_{os} = - \frac{N_o e^2}{32\pi \varepsilon_o r_i} \left[\left(1 - \frac{1}{\varepsilon_{op}} - \frac{T}{\varepsilon_{op}^2} \frac{\partial \varepsilon_{op}}{\partial T}\right) - \left(1 - \frac{1}{\varepsilon_s} - \frac{T}{\varepsilon_s^2} \frac{\partial \varepsilon_s}{\partial T}\right) \left(\frac{1}{1 + r_s / \lambda r_i}\right)\right] \qquad (10)$$

It is interesting to estimate ΔG^{*}_{os} for the redox reactions involving cobaltacene (COB). This system can be oxidized to form the corresponding cation radical or reduced to form the anion radical [15]. Assuming that the solvent radius is 0.37 nm [8], and using the solvent parameters given in Table 1, ΔG^{*}_{os} was first estimated for the reaction involving the oxidized form, COB^{+} in 17 different polar solvents. The results are shown in Fig. 1 as a plot of the estimate of ΔG^{*}_{os} against the Pekar factor, $1/\varepsilon_{op} - 1/\varepsilon_s$, for the given solvent. For solvents with Pekar factors varying between 0.387 (nitrobenzene) and 0.550 (water), the Born estimates of ΔG^{*}_{os} vary between 18.2 kJ mol^{-1} and 25.8 kJ mol^{-1}. The MSA estimates in each solvent are considerably smaller being about 65% of the Born estimate. When these values are plotted against the Pekar factor one obtains an approximately linear relationship with a slope slightly smaller than that for the

Born estimate. This result has two important consequences. Firstly, examination of estimates of ΔG^*_{os} from experimental data using the plot shown here should give a straight line from which reasonable estimates of the size-distance parameter, r_i, could be made. Secondly, the intercept of such a plot would be non-zero, and would yield a negative value of ΔG^*_{os} for a Pekar factor of zero.

Values of ΔG^*_{os} were also estimated for the redox reaction involving the couple COB/COB$^-$. Since the activated state involves a negatively charged species, the values of λ/σ_s appropriate for anions were used to estimate the MSA factor. The results shown in Fig. 2 demonstrate that there is much more scatter in the MSA estimates of ΔG^*_{os} with respect to the best linear correlation when these data are plotted against the Pekar factor. Since the values of λ/σ_s are much higher for anions than cations the MSA estimates are closer in magnitude to the Born estimates, varying between 13.9 kJ mol^{-1} in nitrobenzene and 23.4 kJ mol^{-1} in water. Because the slope of the best straight line through the MSA estimates is significantly higher than that for the Born model, interpretation of the data in terms of the Born model would lead to a low estimate of the effective radius of the reactant. However, failure of the Born model would be clear because the value of ΔG^*_{os} is not zero when the Pekar factor is zero. Unfortunately, one cannot obtain estimates of ΔG^*_{os} directly from experiment, and is always faced with the problem of separating the solvent dependence of the activation parameters from that of the pre-exponential factor. This subject is discussed further below.

Comparison with Experimental Data

Examination of the solvent dependence of the outer sphere activation energy is not straight forward because, when ΔG^*_{os} is large with respect to ΔG^*_{is}, the pre-exponential factor is also expected to be solvent dependent [16-18]. Nevertheless, the best way of examining the magnitude of the activation barrier is by determining the temperature dependence of the rate constant. Such a study has been carried out for the cobaltacene/cobaltacenium cation redox couple by Nielson et al. [19] in a large number of solvents using NMR line broadening methods. The rate constant for electron exchange varied from a low of 5.4 x 10^{-6} M^{-1} s^{-1} in hexamethylphosphoramide (HMPA) to a high of 8.9 x 10^7 M^{-1} s^{-1} in methylene chloride. At the same time, considerable variation in the experimental enthalpy of activation $\Delta H^{\ddagger}_{ex}$ was observed, from a low of 14.2 kJ mol^{-1} in methylene chloride to a high of 23.4 kJ mol^{-1} in HMPA. Data reported in solvents of reasonable polarity are recorded in Table 2.

Values of the outer sphere contribution to the enthalpy of activation, ΔH^{*}_{os} according to the MSA were estimated for the COB/COB⁺ reaction using eq. (10) with the parameters given in Table 1 and assuming $r_i = 0.37$ nm. These values together with the Born estimates ($\lambda = \infty$ in eq. (10)) are given in Table 2. It is immediately apparent that the Born estimate of ΔH^{*}_{os} is close to the experimentally observed quantity $\Delta H^{\ddagger}_{ex}$ for the solvents considered. However, since other effects contribute to the experimental activation enthalpy, it is clear that the Born model overestimates ΔH^{*}_{os} for this system.

A general way of writing the rate constant for a thermal electron transfer reaction with consideration of solvent dynamical effects in the pre-exponential factor is

$$k_{ex} = A\,\tau_L^{-\alpha} \exp(-\Delta G^*/RT) \qquad (11)$$

where ΔG^* is the Gibbs energy of activation, $A\tau_L^{-\alpha}$, the pre-exponential factor, τ_L, the longitudinal solvent relaxation time, and α, a fraction which depends on the degree of reaction adiabaticity, and the relative contributions of the inner and outer sphere reorganizational energies to ΔG^* [20]. Assuming that the factor A is temperature independent, it follows that the expression for the overall enthalpy of activation is

$$\Delta H^{*}_{t} = -R\frac{d\ln k_{ex}}{d(1/T)} = \Delta H^{*}_{is} + \Delta H^{*}_{os} + \alpha\,\Delta H_L \qquad (12)$$

where ΔH^{*}_{is}, is the inner sphere enthalpy of activation, and ΔH_L, the contribution from the temperature dependence of τ_L [20]. The estimate of ΔG^{*}_{is} for this system is 2.1 kJ mol^{-1} [19]. In the present calculations, ΔH^{*}_{is} has been assumed to be equal to ΔG^{*}_{is}. ΔH_L was estimated from data for the temperature dependence of the Debye relaxation time τ_D, static dielectric constant ε_s, and high frequency value ε_∞ using the relationship

$$\Delta H_L = R\left[\frac{\partial \ln\tau_D}{\partial(1/T)} + \frac{\partial \ln\varepsilon_\infty}{\partial(1/T)} - \frac{\partial \ln\varepsilon_s}{\partial(1/T)}\right] \qquad (13)$$

The value of the temperature coefficient of ε_∞ was assumed to be equal to that of the optical quantity ε_{op} which is tabulated for most solvents [21]. In the case of methanol for which dielectric relaxation involves multiple processes [22], estimation of ΔH_L is more involved and has been described elsewhere [23]. Finally, the best value of the adiabaticity parameter α was found to be 0.7, in agreement with results of an earlier analysis [24].

Values of ΔH_t^* estimated for the COB/COB$^+$ reaction in seven solvents are given in Table 2. The estimated quantities agree very well with the experimental values, especially in solvents in which the electron transfer process is slower. In fact, the estimate of ΔS_{os}^* should consider temperature dependence of the polarizability parameter λ which is expected to decrease with increase in temperature. In addition, eqs. (11) and (12) give an oversimplified account of the solvent effect on the pre-exponential factor [25] such that the parameter α may not be constant but change for a given reaction when this is studied in a series of solvents with a wide range of values of τ_L. Nevertheless, it is clear that the MSA estimates of ΔH_{os}^* appear much more reasonable than those estimated from the Born model. The present improvement in the estimates of the activation parameters should do much to reduce problems in the interpretation of experimental data.

Discussion

In assessing the present results, it should be kept in mind that the MSA estimates used here are only valid for spherical ions, and that the cobaltacene system can be considered spherical to a good approximation [8]. On the basis of solvation data for ions of other geometries, such as linear ions (CN^- and N_3^-) or tetrahedral ions (ClO_4^- and NH_4^+) it is clear that different values of the polarization parameter λ are needed depending on both the ion's charge and geometry. Thus, no attempt has been made to consider other systems, such as the diaminobenzenes studied by Grampp and Jaenicke [26], for which a spherical representation would be a poor approximation. These considerations are also relevant to estimates of ΔG_{os}^* based on the energy associated with optical electron transfer within symmetrical mixed-valence compounds, such as the biferrocenylacetylene cation [5]. These estimates are much closer to the continuum Born estimates than values calculated on the basis of the present approach using the MSA. A possible problem associated with using the optical data to estimate ΔG^*_{os} is related to differences in solvation of this dumbbell like system with respect to that of a simple sphere.

It should also be pointed out that the present approach to the MSA differs from that used earlier [2-5] in two important ways. Firstly, the polarization parameter used here takes chemical interactions into consideration, and is quite different from the value used in most earlier work which is obtained from the solvent's static dielectric constant using the equation [12]

$$\lambda^2 (1 + \lambda)^4 = 16\, \varepsilon_s \tag{14}$$

As a result, the values of λ used here are larger, the difference between the estimate based on eq. (14) and the data given in Table 1 being very large in the case of anions. The second point of difference is that we have used the MSA to estimate solvation under static conditions only, whereas previous workers [4, 5] have used it to estimate both the static and optical contributions to ΔG^*_{os}. In our opinion, the present approach is preferred since the molecular description of the system is less important at optical frequencies. It should be noted that these differences lead to very large differences in the estimates of ΔG^*_{os}. For instance, in the case of propylene carbonate the estimate of ΔG^*_{os} by the Born model is 22.6 kJ mol^{-1} and 13.7 kJ mol^{-1} by the MSA as applied here. On the other hand, McManis et al. [5] estimated ΔG^*_{os} to be 21 kJ mol^{-1} in this solvent using the MSA at both optical and static frequencies. In fact, the latter procedure leads to results which are only slightly smaller than the Born estimates in most solvents considered. On the basis of comparison with the experiment, it would seem that the present method of applying the MSA to estimating activation parameters is preferable.

In conclusion, the present study has shown that quite reasonable estimates of activation parameters for homogeneous electron transfer can be obtained using the MSA to estimate the static contribution to these quantities. Although it is tempting to apply this treatment to estimating the corresponding quantities for heterogeneous electron transfer, strictly speaking, it is not valid to apply the MSA in this situation because of the lack of spherical symmetry for the reacting system at the electrode/solution interface. This subject certainly merits further consideration. In addition, the role of reactant geometry in determining solvation energy needs to be considered more carefully. These subjects are currently under further investigation.

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Table 1. Solvent Parameters Relevant to the Estimation of the Gibbs Solvation and Outer Sphere Activation Energies

Solvent	Relative Permittivity		MSA Parameter $\lambda\sigma_s^{-1}$ /nm^{-1}	
	Static ε_s	Optical ε_{op}	Cations	Anions
Protic				
1. Ethanol (EtOH)	24.6	1.848	5.96	18.58
2. Formamide (F)	111.0	2.093	6.26	17.06
3. Methanol (MeOH)	32.7	1.760	6.04	20.48
4. N-methylformamide (NMF)	182.4	2.045	6.35	-
5. Propanol (PrOH)	20.3	1.915	6.02	17.36
6. Water (w)	78.3	1.776	6.06	24.00
Aprotic				
7. Acetone (AC)	20.7	1.839	6.27	11.01
8. Acetonitrile (AN)	37.5	1.800	5.74	12.20
9. Dimethylacetamide (DMA)	37.8	2.061	6.75	10.04
10. Dimethylformamide (DMF)	36.7	2.040	6.60	11.10
11. Dimethylsulfoxide (DMSO)	46.7	2.182	6.64	12.77
12. Hexamethylphosphoramide (HMPA)	30.0	2.123	6.89	9.61
13. Nitrobenzene (NB)	34.8	2.403	5.31	13.18
14. Nitromethane (NM)	35.8	1.903	5.33	12.76
15. N-methylpyrrolidinone (NMP)	32.0	2.155	7.01	11.04
16. Propylene carbonate (PC)	66.1	2.019	5.71	11.93
17. Tetramethylene sulphone (TMS)	43.3	2.196	6.24	11.01

Table 2. Contribution to the Enthalpy of Activation for Homogeneous Electron Transfer in the COB/COB+ System Compared to Experimental Data

Solvent	Outer Sphere Enthalpy of Activation ΔH^*_{os}/kJ mol^{-1}		Longitudinal Relaxation Enthalpy ΔH_L/kJ mol^{-1}	Total Estimated Enthalpy of Activation* ΔH^*_t/kJ mol^{-1}	Experimental Enthalpy of Activation ΔH^*_{ex}/kJ mol^{-1}
	Born	MSA			
Acetone	20.8	12.3	3.6	16.9	18.4
Acetonitrile	21.2	12.2	5.6	18.2	19.2
Benzonitrile**	16.4	7.6	11.9	18.0	19.7
Dimethylsulfoxide	18.1	10.2	10.7	19.8	19.9
Hexamethylphosphoramide	19.5	11.7	13.4	23.2	23.4
Methanol	23.0	14.3	7.5	21.7	18.0
Pyridine**	17.4	9.5	5.4	15.4	16.3

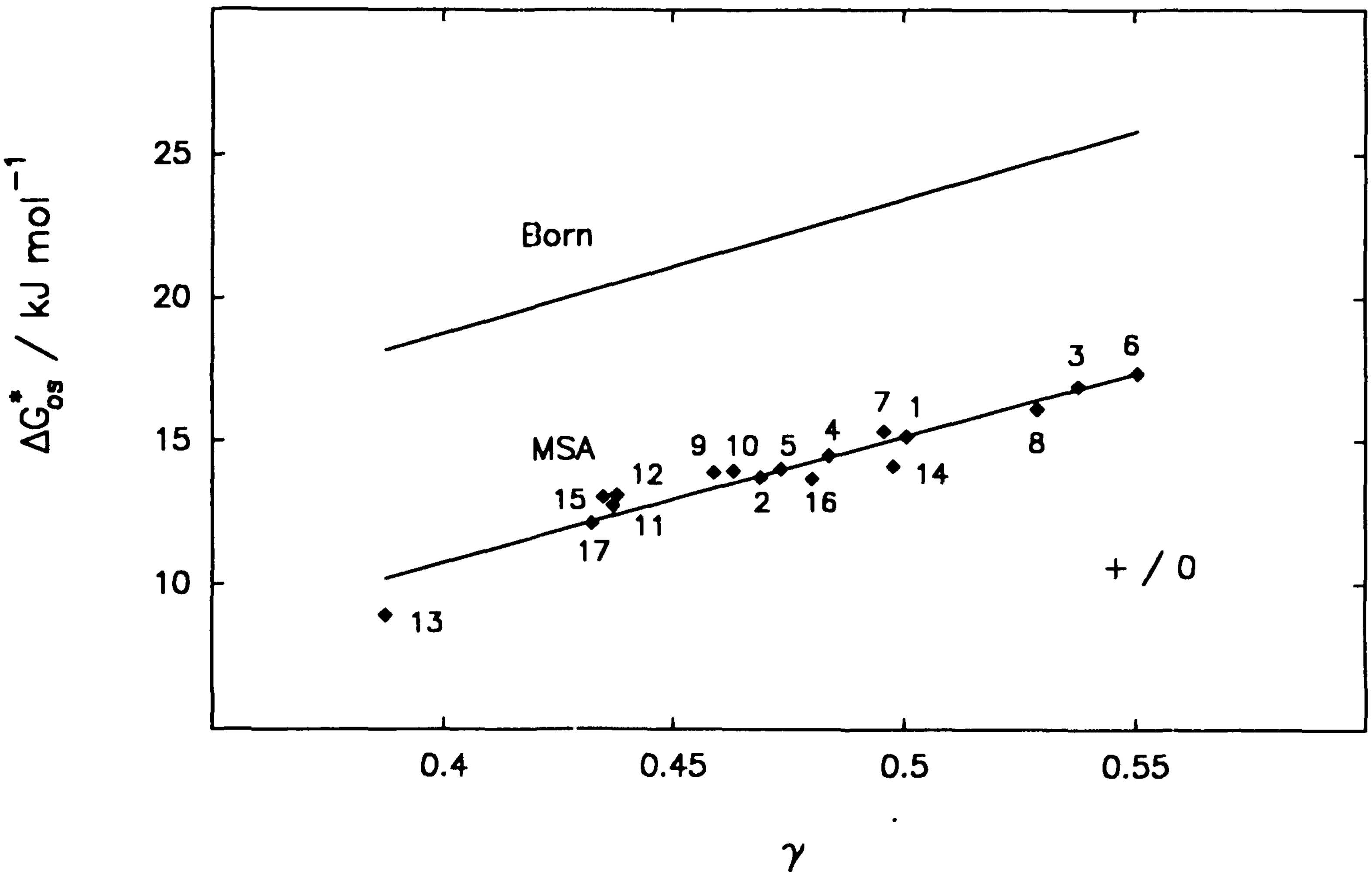
* Estimate based on ΔH^*_{os} according to the MSA and assuming $\alpha = 0.7$ (eq. 12).

** The estimates of the parameter λ/σ_s for benzonitrile (5.825) and pyridine (6.907) were based on the linear relationship between this parameter and the donor number as given elsewhere [7].

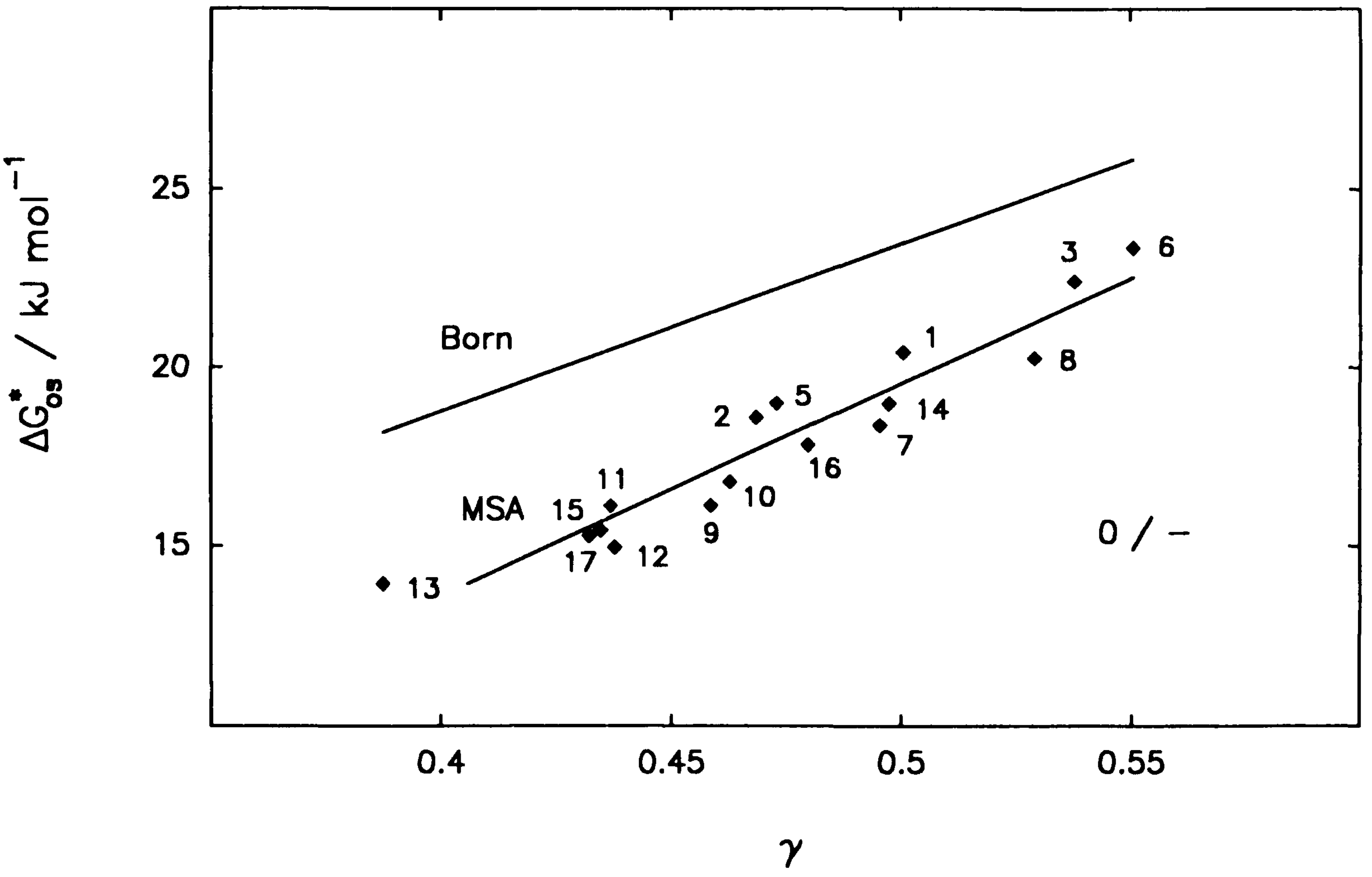
Legends for Figures

Figure 1. Plots of the outer sphere contribution to the Gibbs activation energy, ΔG_{os}^{*}, according to the Born model (upper line) and mean spherical approximation (MSA) against the Pekar factor γ for a reaction involving a spherical molecule with radius of 0.37 nm and its cation radical. The MSA estimates in each of 17 solvents are shown together with the best linear correlation. The integers refer to the solvents listed in Table 1.

Figure 2. Plots of the outer sphere contribution to the Gibbs activation energy, ΔG_{os}^{*} according to the Born model (upper line) and mean spherical approximation (MSA) against the Pekar factor γ for a reaction involving a spherical molecule with radius of 0.37 nm and its anion radical. The MSA estimates in each of 16 solvents are shown together with the best linear correlation. The integers refer to the solvents listed in Table 1.



ΔG^*_{os} / kJ mol^{-1}
25
20
15
10
Born
MSA
+ / 0
6
3
8
7
1
14
4
16
5
2
10
9
12
15
11
17
13
0.4
0.45
0.5
0.55
γ



ΔG^*_{os} / kJ mol^{-1}
25
20
15
0.4
0.45
0.5
0.55
γ
Born
MSA
0 / –
1
2
3
5
6
7
8
9
10
11
12
13
14
15
16
17