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Interpretation of Reaction and Activation Volumes in Solution

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The importance of the reaction volume ΔV_{cc} of contact complex formation for the interpretation of reaction and activation volumes is quantitatively investigated on the basis of literature data. The deactivation of singlet oxygen $O_2(^1\Delta_g)$ via electronic to vibrational energy transfer is used as a probe for the study of the influence of the liquid structure on rate constants and activation volumes. ΔV_{cc} reaches values up to about -10 cm^3 mol^{-1} for the formation of contact complexes of O_2 with polyatomic quenchers in alkanes. The same volume effect but with opposite sign contributes to the reaction volume of the fragmentation of diphenylcyclopropenone, in which the diatomic CO dissociates apart from a polyatomic fragment. Reaction volumes of excimer and exciplex formation are exemplarily reinterpreted on the basis of these results. The consideration of ΔV_{cc} leads to very different mechanistic conclusions in comparison to earlier interpretations.

Introduction

Until now, a rather simple hypothesis is mostly used for the interpretation of reaction volumes ΔV and activation volumes $\Delta V^\ddagger$. Each is to a first approximation considered as the sum of an intrinsic and a solvational component.[1] For the reaction volume, for example, eq 1 should hold true.

$$\Delta V = \Delta V_{intr} + \Delta V_{solv} \tag{1}$$

V_{intr} is assumed to be the result of the net motion of the nuclei of the reacting species, i.e., changes in bond lengths and angles during the formation of the products. Thus, ΔV_{intr} should be equivalent to the changes of the pure van der Waals volumes V_{vdW}. ΔV_{solv} is believed to represent all volume changes associated with changes in polarity, electrostriction, and dipole interactions during the reaction. However, it was already shown in 1984 by Yoshimura and Nakahara that due to the structure of liquids already in the complete absence of any attractive interaction the formation of a contact complex is accompanied by a volume contraction.[2] This negative reaction volume ΔV_{cc} of the contact complex formation is of considerable magnitude and is not comprised in the above definition of ΔV_{solv}. Yoshimura and Nakahara developed a theoretical model allowing the calculation of ΔV_{cc} for the reaction of hard spheres.[2] Studies of the deactivation of singlet oxygen $O_2(^1\Delta_g)$ by solvent molecules via electronic-to-vibrational (e−v) energy transfer and of the fragmentation reaction of diphenylcyclopropenone (DPCP) lead to a strong support of this theory.[3−5] In the present paper these results and other findings are discussed in more detail in a common context. It will be shown that the application of eq 1 is not justified. Instead, it is absolutely necessary to consider the value of ΔV_{cc} in the interpretation of reaction volumes as well as activation volumes. Exemplarily, the formation of excimers and exciplexes is investigated. Very different mechanistic conclusions are obtained from experimental ΔV data whether or not values of ΔV_{cc} are considered.

Discussion

Nonelectrostatic Solvational Contributions to ΔV and $\Delta V^\ddagger$. The approximation that reaction volumes ΔV and activation volumes $\Delta V^\ddagger$ can be considered as sums of only two components, an intrinsic part and a solvational part, whereby the latter represents all volume changes associated with changes in polarity, electrostriction, and dipole interactions during the reaction,[1,6] is an oversimplification, which leads to misinterpretations of the overall reaction volume effects. The reason is the complete neglect of the solvent structure and the changes of the packing fraction in the solvent due to solvation of the reactants and products or the transition state, respectively.[2] Based on Kirkwood's theory on the free enthalpy of electrostatic interaction of the dissolved species with the surrounding solvent,[7] which is considered as a continuum with dielectric constant ϵ, the volume effects ΔV_{el} resulting from electrostatic interactions should vanish in a hypothetical solvent with a pressure-invariant dielectric constant, i.e., $(d\epsilon/dP)_T = 0$. Therefore, linear extrapolations of correlations of values of ΔV or $\Delta V^\ddagger$ with the solvent parameter $q_P = 3(2\epsilon + 1)^{-2}(d\epsilon/dP)_T$ to the value $q_P = 0$ are thought to yield directly realistic estimates of ΔV_{intr} or $\Delta V^\ddagger{}_{intr}$, assuming $\Delta V_{solv} = \Delta V_{el}$ or $\Delta V^\ddagger{}_{solv} = \Delta V^\ddagger{}_{el}$, respectively.[1,6,8,9] However, in the analysis of the pressure dependence of rate constants of Menschutkin reactions, it was already shown in 1967 by Heydtmann that a large solvational contribution to the activation volume exists, which is not comprised by the electrostatic model.[10] Extrapolations of values of $\Delta V^\ddagger$, determined at different pressures, to $q_P = 0$ resulted in values of $\Delta V^\ddagger{}_{intr}$ that were strongly dependent on pressure. Values of $\Delta V^\ddagger{}_{intr}$ varied from -26 (1 bar) to -18 cm^3 mol^{-1} (1500 bar) for the reaction of triethylamine with ethyliodide and from -21 (1 bar) to -11 cm^3 mol^{-1} (1500 bar) for the reaction of pyridine with methyl iodide. Since the pure van der Waals volumes V_{vdW} are only slightly compressible, this large pressure effect undoubtly demonstrates that nonelectrostatic solvational contributions must also be part of $\Delta V^\ddagger{}_{intr}$, if it is the result of eq 1 and this extrapolation, in which the solvent structure is neglected.

The Radial Distribution Function. The structure of a liquid is described by the radial distribution function $g(R)$, which gives the local density of molecules dependent on the distance R from a central molecule, normalized to the average density value.

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$g(R)$ is a function of the number density n of the molecules of the system. $g(R)$ has its maximum value $g(\sigma)$ at the collisional distance σ. For the simple model of a hard-sphere (HS) liquid $g_{HS}(R)$ falls off rapidly with increasing R, in a way similar to a damped oscillation, to finally reach the value of unity.

There are no attractive interactions between the particles of a hard-sphere liquid. At $R = \sigma$ the intermolecular potential changes from zero to infinity. However, real liquids are distinguished by weak long-range attractive and strong short-range repulsive interactions, which are described by the intermolecular potential $U(R)$. The validity of the hard-sphere model for real liquids depends mainly on the hardness of the repulsive interaction between the molecules. For a real liquid, consisting of spherical particles, $g(R)$ is well simulated by the product $\exp(-U(R)/(k_BT))g_{HS}(R)$, where k_B and T are the Boltzmann constant and the temperature in kelvin. However, most liquids consist of strongly nonspherical molecules, further complicating the situation. Therefore, it first has to be investigated, under which conditions the simple hard-sphere liquid model can be used to describe structural properties of real liquids.

According to Einwohner and Alder, eq 2 holds for the collision frequency Z in liquids, where μ is the reduced mass of the colliding pair.[11]

$$Z = 4n\sigma^2 g(\sigma)(\pi k_B T/\mu)^{0.5} \qquad (2)$$

The quenching of singlet oxygen $O_2(^1\Delta_g)$ by ground-state oxygen $O_2(^3\Sigma_g^-)$ occurs as electronic-to-vibrational (e−v) energy transfer. This physical process can be used as a probe for the determination of the value of the radial distribution function $g(\sigma_{OO})$ at the O_2-O_2 collision distance σ_{OO}. Its second-order rate constant k^Δ_D is given by the product of the normalized collision frequency Z/n and the deactivation probability per collision, which is constant for a given temperature. As was shown by Chatelet et al. in a high-pressure investigation of the quenching of $O_2(^1\Delta_g)$ in pure gaseous as well as in pure liquid O_2, k^Δ_D is directly proportional to $g(\sigma_{OO})$.[12] The determination of k^Δ_D for the quenching of $O_2(^1\Delta_g)$ by $O_2(^3\Sigma_g^-)$ can even be used to get information about $g(\sigma_{OO})$ in polyatomic solvents. We investigated the e−v deactivation of $O_2(^1\Delta_g)$ by $O_2(^3\Sigma_g^-)$ in perhalogenated solvents at 295 K and obtained values of k^Δ_D of 2600 (perfluorohexane, PFH), 3200 (Freon 113, FRE), 3900 (tetrachloromethane, TET), and 4100 M^{-1} s^{-1} (perfluorodecalin, PFD).[13] Plötz and Maier determined at 295 K in the low-density O_2 gas, where $g(\sigma_{OO}) = 1$, $k^\Delta_D = 1020$ M^{-1} s^{-1}.[14] Using the relation $k^\Delta_D \sim g(\sigma_{OO})$ we calculate from these results the experimental values of $g(\sigma_{OO})$ of 2.5 (PFH), 3.1 (FRE), 3.8 (TET), and 4.0 (PFD).

These data are used to test analytical expressions of the radial distribution function for hard-sphere liquids. The eq 3 of Grundke and Henderson gives the value of the radial distribution function at the contact distance of molecules A and B in the solvent S.[15]

$$g_{HS}(\sigma_{AB}) = (1-\eta)^{-1} + 1.5\eta(\sigma/\sigma_S)(1-\eta)^{-2} + 0.5\eta^2(\sigma/\sigma_S)^2(1-\eta)^{-3} \qquad (3)$$

Here σ_A, σ_B, and σ_S are the diameters of the spheres A, B, and S; $\sigma_{AB} = (\sigma_A + \sigma_B)/2$ and $\sigma = \sigma_A\sigma_B/\sigma_{AB}$. $\eta = \pi n_S \sigma_S^3/6$ is the packing fraction of the solvent. The compressibility β of the hard-sphere liquid is given by eq 4, with liquid molar volume V_m and gas constant R.[4]

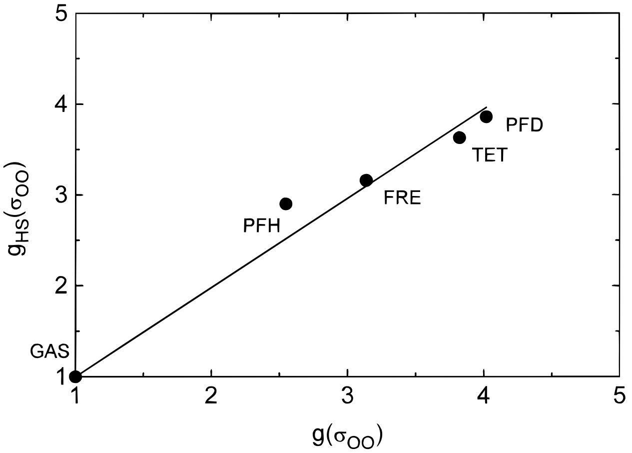

Figure 1. Correlation of calculated and experimental values of the radial distribution function at the O_2-O_2 contact distance σ_{OO}. Straight line represents the linear least-squares fit through the gas-phase value with slope 0.98 ± 0.05.

$$\beta = (V_m/RT)(1-\eta)^4(1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4)^{-1} \qquad (4)$$

The diameters of the spherically assumed solvent and oxygen molecules are derived from V_{vdW} values calculated according to Bondi.[16] For the O_2-O_2 collision $\sigma_A = \sigma_B = \sigma_{O_2} = 3.45$ Å. If η is chosen for each solvent such that eq 4 reproduces the experimental value of the solvent compressibility, eq 3 yields realistic values of $g_{HS}(\sigma_{OO})$, as can be seen from the correlation of Figure 1, which has a slope of unity. Then, η is about 15% smaller than calculated as $\eta = V_{vdW}/V_m$. If $\eta = V_{vdW}/V_m$ is used in eq 3, the agreement is lost. Then, the calculated values $g_{HS}(\sigma_{OO})$ are by about 50% larger and the calculated values β 2−3-fold smaller than the experimental data. Thus, the principal parameter describing the liquid structure of real solvents, $g(\sigma)$, is well reproduced by the hard-sphere liquid model in combination with eqs 3 and 4.

Volume of Contact Complex Formation. Yoshimura and Nakahara demonstrated that already in the complete absence of any attractive interaction the formation of a contact complex is accompanied by a volume contraction.[2] They derived eq 5, which allows the calculation of the reaction volume of contact complex formation ΔV_{cc} for hard spheres.

$$\Delta V_{cc} = -\beta RT(1 + \eta(\mathrm{d}\ln g_{HS}(\sigma_{AB})/\mathrm{d}\eta)_T) \qquad (5)$$

The quenching of singlet oxygen $O_2(^1\Delta_g)$ by e−v energy transfer to terminal bonds of a quencher molecule Q is a purely physical bimolecular process, which is particularly suited to test whether ΔV_{cc} is a real effect. The overall rate constant k^Δ_D is additively composed of rate constants k^Δ_{XY} of deactivation of $O_2(^1\Delta_g)$ by single terminal bonds X−Y of the quencher.[17] A strong exponential correlation of k^Δ_{XY} with the fundamental energy E_{XY} of the X−Y stretching vibration has been found.[18] However, deviations from the correlation with E_{XY} to increasingly larger values of k^Δ_{XY} occur in the series k^Δ_{C-Cl}, k^Δ_{C-Br}, and k^Δ_{C-I}, which reveals that a strong heavy atom effect operates on the spin-forbidden deactivation, if $O_2(^1\Delta_g)$ collides with the corresponding halogen atoms.[19] Therefore, a small but finite overlap of the electron clouds of $O_2(^1\Delta_g)$ and terminal atom of the quenching bond must take place in the deactivation step. Values of k^Δ_{XY} depend not on the solvent polarity and increase with the square root of the temperature.[20] Actually, the rate constant k^Δ_D is proportional to the value of the radial distribution function at the contact distance of O_2 and Q, as was shown by Hild and Brauer using a correlation similar to the one given in

TABLE 1: Activation Volumes $\Delta V^{\ddagger}_{D}$ of the e−v Deactivation of $O_2(^1\Delta_g)$ by Quenchers Q and Corresponding Reaction Volumes of Contact Complex Formation ΔV_{cc} and Activation Volumes $\Delta V^{\ddagger}_{isc}$ of the Intersystem Crossing $^1C \rightarrow {}^3C$[a]

Q	$\Delta V^{\ddagger}_{D}$	ΔV_{cc}	$\Delta V^{\ddagger}_{isc}$
n-pentane	−11.9	−10.0	−1.9
tetrachloromethane	−10.6	−7.9	−2.7
carbon disulfide	−10.5	−6.4	−4.1
toluene	−10.3	−7.3	−3.0
perfluorobenzene	−9.9	−8.7	−1.2
cyclohexane	−9.9	−8.5	−1.4
dichloromethane	−8.7	−6.6	−2.1
acetone	−8.2	−7.6	−0.6
trichloromethane	−8.0	−7.1	−0.9
benzonitrile	−7.2	−5.1	−2.1
acetonitrile	−7.0	−5.9	−1.1
formamide	−4.1	−3.2	−0.9

[a] All data in $cm^3\ mol^{-1}$.[4]

Figure 1.[21] Thus, deactivation occurs as a pure collisional process without intermediate bond formation or charge transfer, which can be used to quantitatively verify the volume of contact complex formation.

In the first step of deactivation $O_2(^1\Delta_g)$ and Q reversibly form a singlet excited collision complex ^1C. Intersystem crossing (isc) in ^1C via e−v energy transfer from $O_2(^1\Delta_g)$ to Q produces with rate constant k_{isc} the triplet ground-state collision complex ^3C, which consists of vibrationally excited $O_2(^3\Sigma_g^-)$ and Q. Since backward isc to ^1C is energetically not feasable, ^3C can only dissociate to form $O_2(^3\Sigma_g^-)$ and Q. k^{Δ}_{D} is much smaller than the diffusion-controlled rate constant. Therefore, $k^{\Delta}_{D} = K_{cc}k_{isc}$, with K_{cc} being the equilibrium constant of contact complex formation, and $\Delta V^{\ddagger}_{D} = \Delta V_{cc} + \Delta V^{\ddagger}_{isc}$ hold true.[4]

The pressure dependence of the e−v deactivation of $O_2(^1\Delta_g)$ in solution was independently studied by Okamoto and us.[3,4] Only the broader investigation will be discussed here. We measured the pressure dependence of k^{Δ}_{D} in 12 neat liquids (Q = S) up to 1500 bar.[4] The quenchers and the corresponding activation volumes $\Delta V^{\ddagger}_{D}$ are listed in Table 1. Large negative values ranging from −4.1 (formamide) to −11.9 $cm^3\ mol^{-1}$ (*n*-pentane) have been determined, although no bond formation or charge transfer occurs. Already these results qualitatively demonstrate the reality of the reaction volume of contact complex formation.

For the quantitative test of the Yoshimura Nakahara model, we compare the experimental $\Delta V^{\ddagger}_{D}$ data with values of ΔV_{cc} calculated for the formation of the O_2−S contact complex by eq 5 with $\sigma_A = \sigma_{O_2}$ and $\sigma_B = \sigma_S$. η is chosen such that eq 4 reproduces the experimental value of the solvent compressibility. With these values of η the hard-sphere model yields realistic values of $g_{HS}(\sigma_{OS})$ by eq 3. $(d \ln g_{HS}(\sigma_{OS})/d\eta)_T$ is calculated by numerical differentiation. The second column of Table 1 lists the results of ΔV_{cc} and the third $\Delta V^{\ddagger}_{isc} = \Delta V^{\ddagger}_{D} - \Delta V_{cc}$. Values of $\Delta V^{\ddagger}_{isc}$ are small and negative. The average is 1.6 ± 0.7 $cm^3\ mol^{-1}$, if the rather uncertain value of CS_2 is neglected. This finding is in very satisfying agreement with the conclusions concerning the heavy atom effect. Values of ΔV_{cc} are large and negative and range from −3.2 (formamide) to −10.0 $cm^3\ mol^{-1}$ (*n*-pentane), demonstrating convincingly the reality and the magnitude of the effect of ΔV_{cc}. A linear correlation of ΔV_{cc} with β is observed (see Figure 2), which is a consequence of the only slight variation of $\eta(d \ln g_{HS}(\sigma_{AB})/d\eta)_T$ with solvent and the direct proportionality of ΔV_{cc} with β in eq 5.

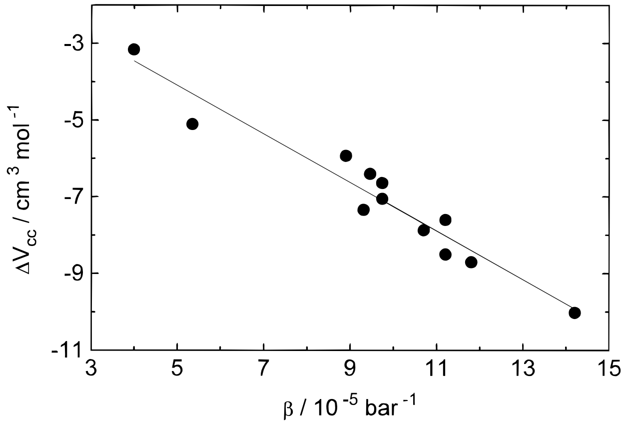

Figure 2. Correlation of ΔV_{cc} for the formation of contact complexes O_2−Q with the isothermal compressibility β for the solvents Q of Table 1. Straight line represents the linear least-squares fit with slope (−6.3 ± 0.5) × 10^4 $cm^3\ mol^{-1}$ bar and intercept −0.9 ± 0.5 $cm^3\ mol^{-1}$.

Volume of Contact Complex Dissociation. The addition of a solute to a solvent leads to a perturbation of the packing of the solvent molecules in the liquid, causing a reduced packing fraction in the direct solvent shell of the solute molecules in the absence of electrostriction. This effect is exemplarily illustrated by the partial molar volumes of CO in different solvents of 29 (H_2O),[22] 39 (C_7H_{16}),[23] 52 (C_6H_6),[22] and 53 $cm^3\ mol^{-1}$ (CCl_4)[22] compared with the pure van der Waals molecular volume of only 16.2 $cm^3\ mol^{-1}$.[16] Therefore, the main reason for the negative volume of contact complex formation is the decrease of the overall volume of the solvent shells of lower packing fraction of the colliding species. Thus, a very similar effect, but with just the opposite sign, has to be expected for a fragmentation process. Immediately after bond breakage the fragments form a contact complex, which subsequently dissociates into the free components. Since hereby the overall volume of the solvent shells with lower packing fraction increases, a positive contribution $-\Delta V_{cc}$ to the reaction volume should result. Actually, this effect was found for the photoinduced fragmentation of diphenylcyclopropenone (DPCP) into diphenylacetylene and carbon monoxide, which we studied by photoacoustic calorimetry.[5] We obtained the reaction volume as $\Delta V = 22.3 \pm 2.5$ $cm^3\ mol^{-1}$ in a homologous series of alkanes at constant temperature. In micellar solution (sodium dodecyl sulfate) we determined $\Delta V = 22.1 \pm 0.8$ $cm^3\ mol^{-1}$.

Following the above arguments, the reaction volume of the fragmentation of DPCP should be given by $\Delta V = \Delta V_{vdW} + \Delta V_{el} - \Delta V_{cc}$. ΔV_{vdW} can be estimated from increments for the calculation of van der Waals volumes given by Bondi to be about 10 $cm^3\ mol^{-1}$.[16] ΔV_{el} has been estimated to about 4 $cm^3\ mol^{-1}$ in alkanes.[24] ΔV_{el} is certainly smaller in the micelles because of the larger polarity of this solvent. Thus, the average value of the difference $\Delta V - \Delta V_{vdW} - \Delta V_{el}$ of about 9 $cm^3\ mol^{-1}$ is obtained, which has to be attributed to $-\Delta V_{cc}$. In fact, the fragmentation reaction of DPCP is accompanied by an increase of the molecular surface of the solutes exposed to the solvent, which leads to an increase of the perturbation of the liquid structure. Since a small diatomic fragment dissociates apart from a polyatomic fragment, this dissociation process is just the opposite of the formation of the contact complex of O_2 and a polyatomic quencher in an alkane solvent for which values of −10 (pentane) and −8.5 $cm^3\ mol^{-1}$ (cyclohexane) have been found (vide infra). Therefore, the results of both different experimental studies are complementary and confirm impressively the effect and importance of the reaction volumes of formation and dissociation of contact complexes. Actually, already for the contact complex of a large molecule with a small diatomic molecule, the absolute value of ΔV_{cc} can even be as large as ΔV_{vdW} for a 2-fold bond cleavage. Thus, it is absolutely necessary to consider the value of ΔV_{cc} in the interpretation of both reaction and activation volumes. This has been exemplarily done in the study of the dimerization reaction of 2-methyl-2-nitrosopropane by Yoshimura et al. and in recent investigations of Hild and Brauer concerning the physical and chemical deactivation of $O_2(^1\Delta_g)$.[21,25−27]

Contributions to the Partial Molar Volume. Yoshimura and Nakahara demonstrated by an analysis of molar volumes of alkanes that in the absence of any attractive interactions between solvent and solute molecules the partial molar volume V of the solute is given by eq 6, where S_{vdW} and $\mathrm{d}\gamma/\mathrm{d}P$ are the molar surface of the hard core (van der Waals) solute molecules and the pressure derivative of the interfacial tension between the solvent and the hard walls of the solute molecules.[28−30]

$$V = V_{\mathrm{vdW}} + (\mathrm{d}\gamma/\mathrm{d}P)S_{\mathrm{vdW}} + \beta RT \qquad (6)$$

βRT is the translational contribution to the partial molar volume. $(\mathrm{d}\gamma/\mathrm{d}P)S_{\mathrm{vdW}}$ represents the increase of the void volume in the direct solvent shell due to the perturbation of the solvent structure by the solute, which increases with the surface of the solute molecules. If a contraction of the solvent around the solute takes place because of electrostatic interactions, an additional negative contribution ΔV_{el} to the partial molar volume has to be considered. Since ΔV is the difference of the partial molar volumes of product(s) and reactant(s), eq 7 holds for the reaction volume in solution, with $\Delta\nu$ being the sum of the stoichiometric numbers.

$$\Delta V = \Delta V_{\mathrm{vdW}} + (\mathrm{d}\gamma/\mathrm{d}P)\Delta S_{\mathrm{vdW}} + \Delta\nu\beta RT + \Delta V_{\mathrm{el}} \qquad (7)$$

Equation 7 reveals that the volumes of contact complex formation, ΔV_{cc}, and dissociation, $-\Delta V_{\mathrm{cc}}$, contain also a translational contribution in addition to the solvent structure perturbation term, eq 8.

$$\Delta V_{\mathrm{cc}} = (\mathrm{d}\gamma/\mathrm{d}P)\Delta S_{\mathrm{vdW}} + \Delta\nu\beta RT \qquad (8)$$

If eqs 7 and 8 are compared with the very simplifying eq 1, it becomes evident that besides ΔV_{el} also ΔV_{cc} contributes to ΔV_{solv}. As will be shown below, wrong conclusions about reaction mechanisms can result, if ΔV_{cc} is not considered in the evaluation.

Comparison of Calculated and Experimental Results. Only a few years after the discovery of the pyrene excimer by Förster and Kasper,[31] reaction volumes of excimer formation have been determined for several nonpolar aromatic molecules in high-pressure investigations. These reactions are particularly suited to study the effect of ΔV_{cc}, since excimers have no permanent dipole moments,[32] and $\Delta V_{\mathrm{el}} = 0$ can be assumed.

The following reaction volumes of excimer formation have been reported. In stationary emission experiments: naphthalene in alkanes and alcohols $\Delta V = -16$ cm^3 mol^{-1},[33] 1,6-dimethylnaphthalene in hexane and methanol $\Delta V = -15$ cm^3 mol^{-1},[33] 1,6-dimethylnaphthalene in hexane at 20 °C and in pure 1,6-dimethylnaphthalene at 110 °C $\Delta V = -19$ cm^3 mol^{-1},[34] and pyrene in methylcyclohexane at 115 °C $\Delta V = -21$ cm^3 mol^{-1};[34] in time-resolved emission experiments: pyrene in toluene $\Delta V = -11$ cm^3 mol^{-1} [35] and $\Delta V = -24$ cm^3 mol^{-1}.[36] There is some scatter in the data, indicating the experimental uncertainty. However, without any doubt, the large negative values of ΔV are significant.

The earlier interpretations of these data are based on eq 1. Assuming $\Delta V_{\mathrm{el}} = 0$, $\Delta V = \Delta V_{\mathrm{intr}} = \Delta V_{\mathrm{vdW}}$ was concluded.[33,34] It is generally supposed that excimers have a sandwich conformation. In the first step of excimer formation the singlet excited and ground state molecules approach the collision distance. As soon as the excimer bond is formed, a further reduction of the distance between both parallel planar aromatic molecules by about 0.5 Å was assumed, which would be sufficient to explain the overall reaction volumes of excimer formation quantitatively.[33,34] This vivid mechanistic interpretation is at first sight convincing. However, if the weakness of the excimer bond and the strong increase of the repulsive potential below the collision distance are considered, the interpretation becomes doubtful. In fact, the contribution of the reaction volume of contact complex formation, which was not known at that time, to the overall reaction volume is, of course, not considered. The values of ΔV_{cc} could be calculated by eq 5. However, the treatment of planar molecules forming a sandwich excimer by a model considering the reaction of hard spheres leads only to unsatisfactory results. Although the planar surface of pyrene is distinctly larger than that of naphthalene, practically the same values of ΔV_{cc} result from eq 5 for pyrene (-13 cm^3 mol^{-1}) and naphthalene (-12 cm^3 mol^{-1}) in hexane.

Equation 8 offers an alternative way for the estimation of ΔV_{cc}, which considers the particular conformation of the reacting contact complex. In the case of excimers, only those contact complexes can react in which both planar molecules take the sandwich conformation. For these contact complexes the reduction ΔS_{vdW} of the solute surface exposed to the solvent is calculated as the area of the flat surface of the aromatic molecule per mole. Yoshimura and Nakahara derived for alkanes dissolved in carbon tetrachloride at 25 °C the value $\mathrm{d}\gamma/\mathrm{d}P = 3.6 \times 10^{-11}$ m.[30] In default of other data we take this as a general value for nonpolar organic systems. The diameter of the disk-shaped benzene molecule amounts to about 6 Å. Thus, we calculate for the formation of a benzene sandwich contact complex at room temperature $\Delta S_{\mathrm{vdW}} = 3.4 \times 10^5$ m^2 mol^{-1}, $\Delta\nu\beta RT = -2.6$ cm^3 mol^{-1} and $\Delta V_{\mathrm{cc}} = -15$ cm^3 mol^{-1}. The planar surface of naphthalene is about 1.5-fold, and that of pyrene is about 2-fold larger than the planar surface of benzene. Thus, we arrive at estimates of $\Delta V_{\mathrm{cc}} = -21$ (naphthalene) and $\Delta V_{\mathrm{cc}} = -27$ cm^3 mol^{-1} (pyrene), which can be compared with the corresponding reaction volumes of excimer formation. In the limits of the uncertainties of experimental results and theoretical estimates these data agree, indicating that none or only a negligible contribution ΔV_{vdW} of bond formation to ΔV exists. Therefore, we conclude that no further reduction of the distance of the planar aromatic molecules in the sandwich configuration occurs upon formation of the weak excimer bond. Thus, a much more realistic interpretation is obtained, if the volume of contact complex formation is considered.

An alternative method for the determination of reaction volumes of excited complexes offers the time-resolved PAC. Recently, Braslavsky et al. investigated the intramolecular formation of an exciplex from a semiflexible bridged donor (aniline) acceptor (cyanonaphthalene) compound in a series of *n*-alkane solvents.[37] The reaction volume for the formation of the exciplex from the ground-state molecule was determined to be $\Delta V = -40 \pm 5$ cm^3 mol^{-1}. The contribution of electrostriction was estimated as $\Delta V_{\mathrm{el}} = -15$ cm^3 mol^{-1}. According to eqs 7 and 8, we have to interpret the difference $\Delta V - \Delta V_{\mathrm{el}} = -25$ cm^3 mol^{-1} as the sum $\Delta V_{\mathrm{vdW}} + \Delta V_{\mathrm{cc}}$. A drastic conformational change accompanies the formation of the intramolecular exciplex. The ground-state molecule has a conformation like an open bag and is supposed to fold to a conformation like a closed bag.[37] Hereby, the molecular surface exposed to the solvent decreases strongly. Since in this case three ring systems—the benzene, the naphthalene, and the piperidene ring—are concerned, the value $(d\gamma/dP)\Delta S_{vdW}$ of the reaction volume for the intramolecular "contact complex formation" (closing of the molecular bag) could even be as large as the value of ΔV_{cc} of the formation of the naphthalene excimer although for the intramolecular reaction $\Delta\nu\beta RT = 0$ holds true. Therefore, it is concluded that in the case of exciplex formation at maximum a small negative contribution ΔV_{vdW} of bond formation to ΔV exists.

Conclusions

Using model reactions, we have quantified the reaction volume of contact complex formation or dissociation. It is demonstrated that the value of ΔV_{cc} can even be as large as -25 cm^3 mol^{-1} if two planar molecules such as pyrene form a sandwich contact complex. This volume effect is much larger than the volume change ΔV_{vdW} caused by the formation of several single bonds. The consideration of ΔV_{cc} leads to very different mechanistic conclusions for the excimer and exciplex formation process compared with earlier interpretations. Thus, we conclude that it is generally necessary to consider the value of ΔV_{cc} in the interpretation of reaction volumes and activation volumes.

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