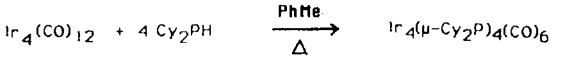
$Ir_4(CO)_{12}$ with $Cy_2PH$ under similar conditions gives deep red $[Ir(\mu\text{-}Cy_2P)(CO)]_4(CO)_2$ (**3**) in 65% yield.[13] The structures of



$$Ir_4(CO)_{12} + 4\ Cy_2PH \xrightarrow[\Delta]{PhMe} Ir_4(\mu\text{-}Cy_2P)_4(CO)_6 \quad (\underline{3})$$

these complexes have been determined by X-ray crystallography.[14] The dimer $[Ir(\mu\text{-}t\text{-}Bu_2As)(CO)_2]_2$ (**2**) has two planar 16-electron Ir atoms, each bearing two CO ligands and bridged by two $t\text{-}Bu_2As$ units. It will be described fully in another paper.[15] **1** is a black crystalline material which is air stable for short periods in the solid state but decomposes in solution when exposed to the air.

There are several unique features of the molecular structure of **1** (Figure 1). The central $Ir_4$ core is planar due to a crystallographically imposed center of inversion at the midpoint of Ir(2)–Ir(2)′. The two central Ir atoms Ir(2) and Ir(2)′ are separated by a relatively short distance (2.592 (6) Å) which is consistent with an Ir=Ir double bond. The distance is similar to those observed in $[Ir(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ (2.545 (1) Å)[5] and $[Ir(\mu\text{-}Ph_2P)(CO)(PPh_3)]_2$[4] (2.551 (1) Å) which both have Ir=Ir double bonds. The Ir=Ir double bond is bridged by two notably asymmetric CO ligands (Ir(2)–C(2) = 2.08 (4) Å, Ir(2)′–C(2) = 2.36 (4) Å).

The Ir–Ir distances around the outer edges of the $Ir_4$ parallelogram are typical of single bonds (Ir(1)–Ir(2) = 2.807 (3) Å, Ir(1)–Ir(2)′ = 2.866 (3) Å). The $t\text{-}Bu_2As^-$ groups are virtually coplanar with the $Ir_4$ core and occupy slightly asymmetric bridging positions (Ir(1)–As(av) = 2.373 Å, Ir(2)–As(av) = 2.409 Å). The two Ir atoms at the far corners of the parallelogram (Ir(1) and Ir(1)′) each bear a terminal CO ligand and have formal electron counts of 16. Of related interest to **1** is $Rh_6(CO)_{11}(\mu\text{-}t\text{-}Bu_2As)_2(\mu_4\text{-}t\text{-}BuAs)$ in which the use of the bulky $t\text{-}Bu_2As^-$ ligand results in a planar array of five rhodium atoms.[17]

The structure of the $Cy_2P^-$ complex $[Ir(\mu\text{-}Cy_2P)(CO]_4(\mu\text{-}CO)_2$ (**3**) is quite different from that of **1** (Figure 2). The central $Ir_4$ core consists of a fairly regular closed tetrahedron. Four $Cy_2P^-$ units bridge four edges of the tetrahedron and each Ir atom bears a terminal CO ligand. The two remaining edges of the $Ir_4$ tetrahedron are bridged by CO groups. Ir–Ir distances range from 2.769 (2) to 2.882 (2) Å and are typical of Ir–Ir single bonds. The $Cy_2P^-$ units occupy fairly symmetrical bridging positions with the Ir–P distances ranging from 2.259 (11) to 2.341 (11) Å. These values may be compared to similar ones found in $[Ir(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$[5] [2.324 (2) Å] and $[Ir(\mu\text{-}Ph_2P)(CO)(PPh_3)]_2$ [2.288 Å (av)]. The $^{31}P\{^1H\}$ NMR of **3** shows four second-order multiplets with downfield shifts relative to 85% $H_3PO_4$ (aq).[13] This is consistent with the phosphido groups bridging metal–metal bonding distances.[18] The spectrum is consistent with the X-ray structure since all four P atoms are magnetically inequivalent and it has been successfully simulated.[19]

These results indicate that it should be possible to rationally synthesize unsaturated transition-metal clusters with a variety of open or planar central cores by using suitably bulky ligands. Further studies are in progress.

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**Supplementary Material Available:** Complete listings of bond lengths, angles, atomic coordinates, thermal parameters, structure factors, complete ORTEPs for **1** and **3**, observed and simulated $^{31}P\{^1H\}$ NMR spectra of **3**, and details of the characterization and X-ray structures of **1** and **3** (68 pages). Ordering information is given on any current masthead page.

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(14) Details of the X-ray structures of **1** and **3** are provided as supplementary material.[19]

(15) Jones, R. A.; Whittlesey, B. R., manuscript in preparation.

(16) For **1**, deviations (Å) from the least-squares plane containing Ir(1), Ir(2), Ir(1)′, Ir(2)′, As(1), As(2), and C(1) are As(1) 0.179 (10), As(2) 0.028 (11), C(1) 0.234 (98). Deviation (Å) from the Ir(2)–Ir(2)′–C(2) plane for O(2) is 0.110 (76).

(17) Jones, R. A.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 1078.

(18) (a) Petersen, J. L.; Steward, R. P. *Inorg. Chem.* **1980**, *19*, 186. (b) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163. (c) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(19) See paragraph at end of paper regarding supplementary material.

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## Kinetic Evidence for a Critical Hydrophobic Interaction Concentration

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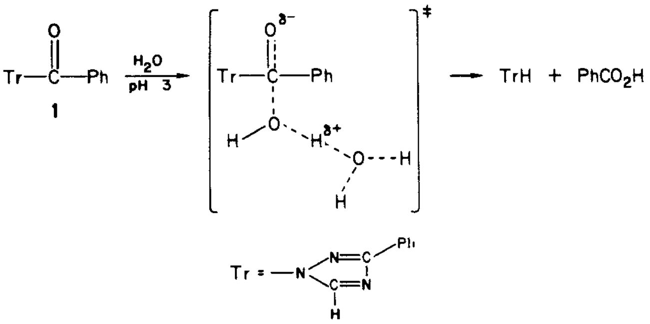
Isobaric and isothermal activation parameters of organic reactions in water-rich mixtures of water with a relatively hydrophobic cosolvent have often shown complex, if not capricious, behavior upon variation of the solvent composition.[1,2] These intriguing effects have been attributed to the unique solvent structural properties of water.[3] In particular, the large and partially compensatory changes in enthalpies and entropies of activation are caused by initial state solvation effects and are believed to reflect hydrophobic interactions with the cosolvent.[1,2] Much emphasis has been placed on the $t\text{-}BuOH\text{–}H_2O$ system. In a recent theoretical study, Grunwald[4] has analyzed the partial molar thermodynamic properties of this mixture in terms of two additive terms. The first "isodelphic", term refers to effects under conditions where the solvent network theoretically remains constant upon addition of *t*-BuOH; the second, "lyodelphic", term describes the effect of the change in the solvent network upon changing the molality of the cosolvent. In this paper we describe kinetic evidence in support of Grunwald's analysis and we introduce the concept of "critical hydrophobic interaction concentration" (chic).

Rate constants and isobaric activation parameters for the pH-independent hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole (**1**)



in highly aqueous $t\text{-}BuOH\text{–}H_2O$ are summarized in Table I. The hydrolytic process, which occurs via rate-determining water-catalyzed nucleophilic attack of water on the carbonyl moiety,[5] is slowed down by the cosolvent. The plots of $\Delta^{\ddagger}H^{\ominus}$ and $\Delta^{\ddagger}S^{\ominus}$ vs. mole fraction of water ($n_{H_2O}$) exhibit the usual extrema at about 5 mol % of *t*-BuOH (Figure 1), attributable to lyodelphic solvent effects. The important observation is *that the large changes in* $\Delta^{\ddagger}H^{\ominus}$ *and* $\Delta^{\ddagger}S^{\ominus}$ *set in only below* $n_{H_2O} = 0.98$. It is only at $n_{H_2O} = 0.97$ that these changes are accompanied by a large heat capacity of activation[6] ($\Delta^{\ddagger}C_p^{\ominus} = -1200 \pm 200$ J mol$^{-1}$ K$^{-1}$).

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(3) (a) Eisenberg, D.; Kauzmann, W. "The Structure and Properties of Water"; Oxford University Press: London, 1969. (b) Mirejovsky, D.; Arnett, E. M. *J. Am. Chem. Soc.* **1983**, *105*, 1112.

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**Table I.** Pseudo-First-Order Rate Constants and Isobaric Activation Parameters[a] for the Neutral Hydrolysis of 1-Benzoyl-3-phenyl-1,2,4-triazole in Water-Rich $t$-BuOH–$H_2O$ Mixtures

| $n_{H_2O}$ | $k_{obsd} \times 10^4$,[a,b] $s^{-1}$ | $\Delta^{\ddagger}G^{\ominus}$, kJ $mol^{-1}$ | $\Delta^{\ddagger}H^{\ominus}$, kJ $mol^{-1}$ | $\Delta^{\ddagger}S^{\ominus}$, J $mol^{-1}$ $K^{-1}$ |
|---|---|---|---|---|
| 1.00 | 12.53 ± 0.17 | 89.65 ± 0.02 | 45.9 ± 0.5 | −147 ± 2 |
| 0.99 | 11.10 ± 0.10 | 89.93 ± 0.03 | 48.1 ± 0.9 | −140 ± 3 |
| 0.98 | 8.80 ± 0.06 | 90.46 ± 0.02 | 48.7 ± 0.8 | −140 ± 3 |
| 0.97[c] | 7.04 ± 0.05 | 91.06 ± 0.02 | 41.7 ± 0.9 | −166 ± 3 |
| 0.96 | 5.02 ± 0.05 | 91.85 ± 0.01 | 37.1 ± 0.3 | −184 ± 1 |
| 0.95 | 3.27 ± 0.06 | 92.91 ± 0.01 | 37.2 ± 0.4 | −187 ± 2 |
| 0.94 | 2.23 ± 0.02 | 93.86 ± 0.02 | 38.4 ± 0.6 | −186 ± 2 |
| 0.93 | 1.62 ± 0.03 | 94.63 ± 0.02 | 45.7 ± 0.9 | −164 ± 3 |
| 0.92 | 1.34 ± 0.02 | 95.21 ± 0.02 | 48.4 ± 0.9 | −157 ± 3 |

[a] At 25 °C. [b] Activation parameters were calculated (Eyring equation) from $k_{obsd}$ values at seven temperatures in the range 19–37 °C. [c] $\Delta^{\ddagger}C_p^{\ominus} = -1200 \pm 200$ J $mol^{-1}$ $K^{-1}$ (Valentiner equation).[6a]

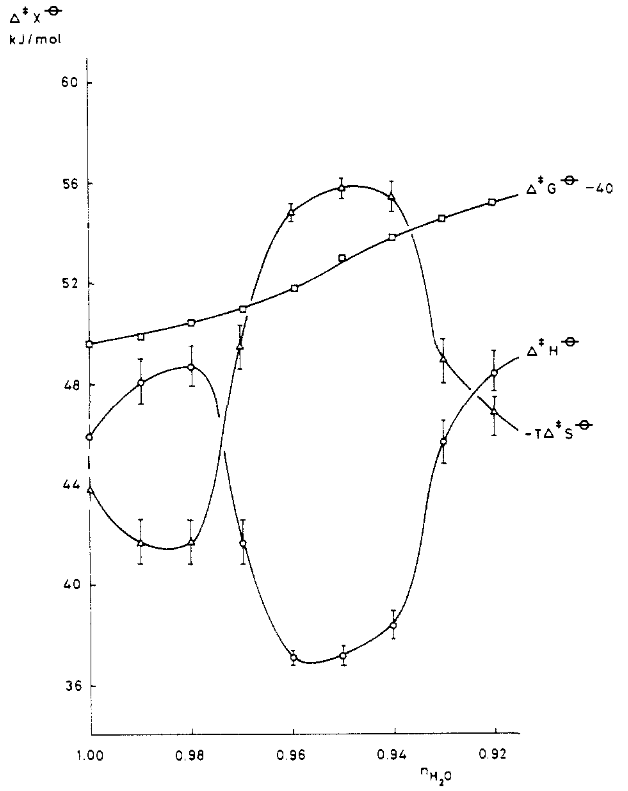

**Figure 1.** Plot of $\Delta^{\ddagger}G^{\ominus}$, $\Delta^{\ddagger}H^{\ominus}$, and $-T\Delta^{\ddagger}S^{\ominus}$ for the neutral hydrolysis of **1** in water-rich $t$-BuOH–$H_2O$ as a function of solvent composition (25 °C).

We contend that the solvent effects on $\Delta^{\ddagger}H^{\ominus}$ and $\Delta^{\ddagger}S^{\ominus}$ in highly aqueous $t$-BuOH–$H_2O$ are not primarily caused by hydrophobic interactions between the substrate and individual $t$-BuOH molecules (as previously assumed)[1,2] but instead involve substrate binding to *clusters*[7] of $t$-BuOH. There is strong experimental[8] and theoretical evidence[4,9] that aggregated domains of $t$-BuOH molecules start to form when there is not sufficient water for the development of complete hydrophobic hydration shells of the alcohol. Under these conditions these hydrophobic hydration shells interpenetrate leading to microheterogeneity in the solution. This cooperative solvent-driven association has the characteristics of a multiple effect and is akin to micellization of surfactant molecules. By analogy with the critical micelle concentration (cmc) of surfactants,[10] we propose that the cosolvent concentration where hydrophobic cosolvents start to aggregate in a cooperative manner may be called critical hydrophobic interaction concentration (chic). Thus for $t$-BuOH the chic is 1.4 ± 0.3$m$ at 25 °C. In Grunwald's isodelphic/lyodelphic analysis of the solution thermodynamics of aqueous binaries,[4] the solvent network has been characterized by a single microscopic variable $\alpha$. If $m_2$ denotes the cosolvent molality, the chic is the concentration for which $\partial\alpha/\partial m_2$ changes sign. For $t$-BuOH–$H_2O$, Grunwald made a rough estimate of the chic, and the value (0.4$m$) is in satisfactory agreement with our result. Microheterogeneity or pseudophase separation has been detected for a variety of water-rich aqueous solutions.[11] It is clear that the larger the hydrophobic part of the cosolvent molecule and the more waters are necessary for complete hydrophobic hydration, the more sharply defined and the lower the chic will be.[12]

The concept of the chic is useful in the analysis of solvent effects on organic reactions in typically aqueous (TA) solutions[13] under conditions that the solvent hydrogen-bonded network only depends on the cosolvent and is (nearly) independent of the substrate.[10] It emphasizes the importance of pseudophase separation and the notion that the solvent composition dependence of $\Delta^{\ddagger}H^{\ominus}$ and $\Delta^{\ddagger}S^{\ominus}$ is merely governed by cosolvent aggregation. Only the magnitude of the changes in these activation parameters depends on substrate hydrophobicity.[14] Binding of the substrate at the chic to cosolvent aggregates then leads to highly temperature-dependent solvation changes and the observation of appreciable heat capacities of activation ($\Delta^{\ddagger}C_p^{\ominus}$).[15] Since the chic is temperature-dependent, the $\Delta^{\ddagger}C_p^{\ominus}$ may change sign depending on the temperature range for which $\Delta^{\ddagger}C_p^{\ominus}$ has been determined.[14,16] Below the chic, hydrophobic interactions appear to exert only minor effects on reagent properties.[17] For example, in the region between $n_{H_2O}$ = 1.00 and 0.98 the changes in $\Delta^{\ddagger}H^{\ominus}$ and $\Delta^{\ddagger}S^{\ominus}$ for hydrolysis of **1** are rather similar for $t$-BuOH–$H_2O$ and MeCN–$H_2O$ mixtures[2c] despite the great difference in hydrophobicity of the cosolvent. It is only above the chic that the widely different lyodelphic solvent effects in typically aqueous (TA)[13] and typically nonaqueous (TNA) solutions[13] come into play.

**Acknowledgment.** We thank Prof. E. Grunwald for helpful correspondence and Prof. F. Franks for stimulating discussion.

**Supplementary Material Available:** Table II showing pseudo-first-order rate constants as a function of temperature for the neutral hydrolysis of **1** in $t$-BuOH–$H_2O$ ($n_{H_2O}$ = 0.92–1.00) (3 pages). Ordering information is given on any current masthead page.

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(10) The same situation prevails in surfactant aggregation. Although hydrophobic interactions between surfactant molecules do occur below the cmc, it is only at the cmc that extensive cooperative association to form micelles sets in.

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(12) An extreme case is *N*-cyclohexylpyrrolidone for which the chic is <0.3$m$. Neutral ester hydrolysis in these mixtures even exhibits Michaelis-Menten-type kinetics, see: Van Warners, A.; Engberts, J. B. F. N., unpublished results.

(13) For definitions and examples of TA and TNA solutions, see: Franks, F. In "Water. A Comprehensive Treatise"; Franks, F., Ed.; Plenum Press: New York, 1973; Vol. 2, Chapter 1; 1975; Vol. 4, Chapter 1.

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(16) Kanerva, L. T.; Euranto, E. K. *J. Am. Chem. Soc.* **1982**, *104*, 5419.

(17) Nonpolar solute–cosolvent pair interactions are dominated by hydrophobic effects: Tucker, E. E.; Christian, S. D. *J. Phys. Chem.* **1979**, *83*, 426.