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"Inverted" Solvent Effect on Charge Transfer in the Excited State**

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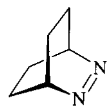
The mechanism of charge-transfer (CT) processes[1, 2] is vital to the understanding of many photochemical[3] and photobiological[4] reactions. It is paradigmatic for CT-induced photoreactions that their rates increase with solvent polarity, a phenomenon which has been most extensively examined through the fluorescence quenching of singlet-excited states.[5–7] The faster quenching in polar solvents is attributed to a stabilization of the primary reaction intermediates resulting from CT.[8] When free ions are formed, this stabilization derives from the reduced Coulombic attraction between ions in polar solvents which decreases with the inverse of the dielectric constant (ε) according to the Born formula.[8–10] When excited CT complexes or exciplexes are involved, the stabilization is related to the large induced dipole moment[11–14] and follows a $(\varepsilon-1)/(2\varepsilon+1)$ dependence according to the Kirkwood–Onsager continuum model.[5, 8–10, 15, 16]

The quenching of n,π^*-excited ketones by amines and sulfides is a well-examined case of a CT-induced photoreaction,[17, 18] which displays the expected solvent effect. Herein, we have examined the fluorescence quenching of the n,π^*-excited azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO)[19] by amines and sulfides, which presents a closely related example of a CT-induced photoreaction. This photoreaction is slowed down in polar solvents. To the best of our knowledge, this is the first observation of an "inverted" solvent effect on the rate constants for CT-induced quenching. It is presumed that the initial reaction step involves the formation of an exciplex with partial CT character. Counterintuitively, the exciplex is stabilized to a lesser degree by polar solvents than the reactants.



DBO

The rate constants for fluorescence quenching of DBO by triethylamine and diisopropyl sulfide in different solvents (Table 1) were on the order of 10^6–$10^8\,M^{-1}s^{-1}$ and varied over one order of magnitude for each quencher. Linear Stern–Volmer behavior was observed in the steady-state experiments, and time-resolved measurements (for benzene and acetonitrile) gave consistent results. Most interesting, the quenching rates decreased with increasing solvent polarity (cf. Reichardt's E_T parameter[20] in Table 1), that is, they were *highest* in perfluorohexane and cyclohexane and *lowest* in acetonitrile.[21] The peculiar solvent effect of singlet-excited DBO is opposite to that established in the literature, both for n,π^*-excited ketones (cf. data for triplet-excited benzophenone in Table 1) and π,π^*-excited aromatic molecules as acceptors.[5–7]

Table 1. Rate constants k_q for the quenching of singlet-excited DBO and triplet-excited benzophenone by amines and sulfides in different solvents.

		k_q $[10^7\,M^{-1}s^{-1}]$			
		NEt_3		$SiPr_2$	
Solvent	E_T[a]	$^1DBO^*$[b]	$^3Ph_2CO^*$[c]	$^1DBO^*$[b]	$^3Ph_2CO^*$[d]
perfluorohexane	30.4	24		23	
cyclohexane	33.2	14	14	6.7	9.0
Freon-113	33.2	18		5.0	14
benzene	34.8	7.2	170	1.8	19
ethyl acetate	38.1	5.6		1.4	
1,4-dioxane	36.0	6.1		1.3	
acetone	42.2	6.2		1.0	
acetonitrile	46.0	4.4	380	0.67	59

[a] Data from: C. Reichardt, E. Harbusch-Görnert, *Lieb. Ann. Chem.* **1983**, 721–743 except for Freon-113 (C. Laurence, P. Nicolet, M. Lucon, T. Dalati, C. Reichardt, *J. Chem. Soc. Perkin Trans. 2* **1989**, 873–876) and perfluorohexane (estimated from Equation (4) of the latter reference). [b] Determined from steady-state or time-resolved fluorescence quenching; error in data is 10%. [c] From: A. A. Gorman, C. T. Parekh, M. A. J. Rodgers, P. G. Smith, *J. Photochem.* **1978**, *9*, 11–17. [d] From: S. Inbar, H. Linschitz, S. G. Cohen, *J. Am. Chem. Soc.* **1982**, *104*, 1679–1682.

A mechanistic interpretation of the "inverted" solvent effect must take three pertinent features into account: a) The fluorescence quenching involves CT from the donor molecule to the excited DBO, as evidenced by the dependence of the quenching rate constant on the ionization potential of the donor (Table 2). The CT nature of the fluorescence quenching of DBO has also been firmly established for the weaker olefin donors.[22–24] Incidentally, a first indication for the unusual solvent effect (isooctane and acetonitrile) was noted by Engel et al. for olefin quenching,[23] but the underlying reasons were not discussed. b) Ion pair formation is unlikely to occur with

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Table 2. Dependence of the rate constants k_q for fluorescence quenching of DBO on the ionization potential of the donor.

Donor	IP [eV][a]	k_q [$10^7\,\text{M}^{-1}\,\text{s}^{-1}$][b]
tetrahydrofuran	9.42	0.23[c]
diisopropylsulfide	8.26[d]	0.67
triethylamine	7.50	7.2
tri-*n*-propylamine	7.23	8.5
tri-*n*-butylamine	7.15[e]	9.2
N,*N*-dimethylaniline	7.12	24
triphenylamine	6.86	21

[a] Adiabatic ionization potentials taken from: R. C. Weast, D. R. Lide, M. J. Astle, W. H. Beyer, *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, **1990**. [b] Determined from time-resolved fluorescence quenching in benzene; error in data is 10%. [c] From: W. Adam, J. N. Moorthy, W. M. Nau, J. C. Scaiano, *J. Org. Chem.* **1997**, *62*, 8082–8090. [d] Vertical ionization potential taken from: G. Wagner, H. Bock, *Chem. Ber.* **1974**, *107*, 68–77. [e] From: X. Allonas, P. Jacques, *Chem. Phys.* **1997**, *215*, 371–378.

the examined quenchers since full electron transfer between singlet-excited DBO and triethylamine should be *endergonic* by about 38 kJ mol^{-1}.[25] The same reaction is *exergonic* by about 25 kJ mol^{-1} for triplet-excited benzophenone.[25] This energetics is consistent with the absolute quenching rate constants of DBO, which fall 2–3 orders of magnitude below the diffusion-controlled limit.[26] The formation of free ions was also excluded (< 1%) by time-resolved photoconductivity measurements in acetonitrile,[27] and, most importantly, the observed solvent effect argues against rate-determining electron transfer. c) The reaction quantum yields for DBO with triethylamine are very low, for example, 4.4% in benzene and 2.7% in acetonitrile, which demonstrates that deactivation of singlet-excited DBO predominates.

The combined arguments point to the involvement of an exciplex with partial CT character in the fluorescence quenching of DBO. Such exciplexes are well-established for other photoreactions,[28–32] including the quenching of DBO by olefins,[22–24] and that of triplet-excited azoalkanes by amines.[33] In keeping with the present mechanistic understanding of related photoreactions,[6, 7, 34] we propose a reversible formation and subsequent deactivation of this exciplex (Scheme 1).

$$^{1}\text{DBO}^{*} + \text{NEt}_3 \xrightleftharpoons{K} {}^{1}[\text{DBO}^{\delta-}\cdots\text{NEt}_3^{\delta+}]^{*} \xrightarrow{k_d} \text{DBO} + \text{NEt}_3$$

Scheme 1. Exciplex-induced deactivation of DBO by triethylamine.

The kinetics of quenching k_q according to Scheme 1 increases with the equilibrium constant for exciplex formation K and the rate of deactivation k_d.[6, 7, 23, 26] When dissociation of the exciplex occurs faster than deactivation, a typical preequilibrium and steady-state scenario results,[7] where $k_q = K k_d$. We will now demonstrate that the equilibrium constant for exciplex formation K may display an "inverted" solvent effect, which suffices to account for the experimental results, regardless of any superimposed solvent dependence and the nature of the deactivation step. This finding contrasts the general presumption that exciplex formation is facilitated in polar solvents.[5, 8–11, 13, 14]

According to the full expression of the Kirkwood–Onsager solvation model,[15, 16, 20, 35, 36] the polar solvent stabilization ($\Delta G_{\text{solvent}}$) of an exciplex (or generally an adduct) AB relative to the reactants (A and B) is proportional to a structural constant C, which incorporates the difference of the square of the individual dipole moments μ divided by the cube of the corresponding molecular radii r [Eq. (1)].

$$\Delta G_{\text{solvent}} = \frac{N_A}{4\pi\varepsilon_0}\left(\frac{\mu_A^2}{r_A^3}+\frac{\mu_B^2}{r_B^3}-\frac{\mu_{AB}^2}{r_{AB}^3}\right)\left(\frac{\varepsilon-1}{2\varepsilon+1}\right) = C\left(\frac{\varepsilon-1}{2\varepsilon+1}\right) \qquad (1)$$

The reaction constant C may be negative or positive, resulting in a relative stabilization or destabilization of the exciplex with increasing solvent polarity, or it may vanish as in the case of the pyrene excimer ($\mu_{AB} = \mu_A = \mu_B = 0$) to result in an insensitivity on the solvent.[11] Most aromatic exciplexes have much higher dipole moments than the reactants and in these cases the normal solvent dependence is expected (negative C), since $\mu_{AB} \gg \mu_A$ and $\mu_{AB} \gg \mu_B$.[11, 13, 14] In fact, the dipolar solvent stabilization of the reactants is neglected in most treatments of solvent effects on exciplex formation.[5, 8–11] However, the possibility of an inverted solvent dependence becomes a real one, when the reactant has a significant dipole moment and when the dipole moment of the exciplex falls short of its maximum value of about 14 D[11, 13, 14] due to partial CT, that is, $\mu_{AB} \geq \mu_A$. In such cases, the molecular size effect will tend to offset any increase in dipole moment, since $r_{AB} > r_A$, and when a small reactant (small r_A) is involved, the inverted solvent effect may become sizable. These boundary conditions, namely a small, strongly dipolar reactant, and an exciplex with only partial CT are unquestionably met in the fluorescence quenching of DBO by amines and sulfides.

The absence of exciplex emission[37] precluded an experimental estimate of the exciplex dipole moment.[11, 38, 39] Hence, we have used the semiempirical UHF-PM3 method[40] to assess the resulting dipole moments of the exciplexes between n,π*-excited states and amines. CT interaction entails molecular orbital overlap between the donor HOMO and the acceptor LUMO or, in the case of an excited acceptor, its lowest SOMO. In the case of n,π*-excited states and amines, CT interaction should take place between the lone pair of the amine and the electron-deficient, singly occupied lone pair orbital of the carbonyl oxygen or azo nitrogen atoms. The minimized exciplex structures (in the triplet state due to the restriction of the UHF method) confirmed this mode of CT interaction (Figure 1). These are the first calculated exciplex structures between n,π*-excited states and amines.[41]

The UHF-PM3 geometries were employed in single-point CI-PM3 calculations[40] (including the lone pairs and closest π and π* as active orbitals) to obtain estimators for the dipole moments of singlet-excited DBO (3.2 D), triplet-excited benzophenone (2.2 D), triethylamine (1.0 D), the singlet exciplex of DBO (4.4 D), and the triplet exciplex of benzophenone (7.3 D). We contend that the pertinent trends of the dipole moments produced by the semiempirical method are meaningful. First, the calculated and experimental dipole moments for the ground states of triethylamine (1.0 versus 0.86 D)[42] and DBO (3.4 versus 3.5 D),[43] but also the triplet-excited state of benzophenone (2.2 versus 2.1 D)[44] are in excellent agreement. Second, the calculated dipole moment of

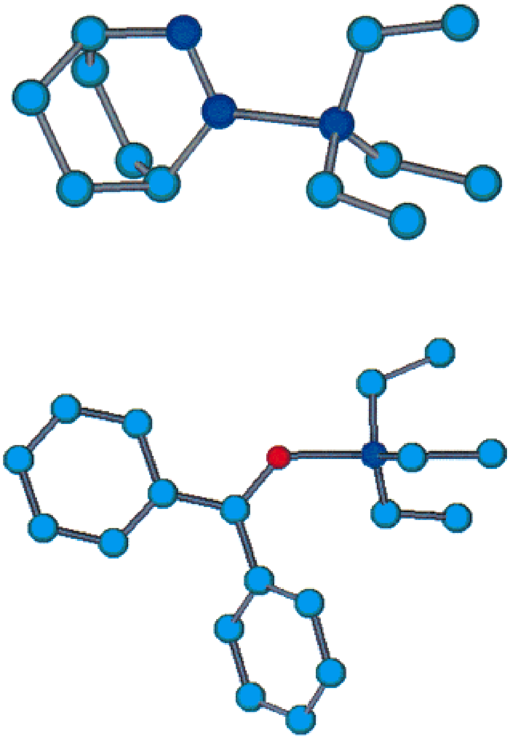

Figure 1. Calculated geometries (UHF-PM3 method) of the triplet exciplexes between DBO and triethylamine (top) and benzophenone and triethylamine (bottom).

the DBO exciplex (4.4 D) meets the expectation for a partial CT.[5, 36] Third, the larger increase in dipole moment for the benzophenone exciplex (7.3 D) agrees with the more favorable energetics for electron transfer (see above). The molecular radii of the reactants can be taken from the literature[45] or calculated accordingly by using 1,4-diazabicyclo[2.2.2]octane as a model for DBO ($r_A = 3.07$ Å). Those of the complexes were estimated by volume additivity, that is, $r^3_{AB} = r^3_A + r^3_B$.

The use of the above parameters in Equation (1) affords a positive reaction constant for singlet-excited DBO ($C = +0.101\ D^2\,Å^{-3}$), that is, a relative destabilization of the exciplex in polar solvents, but a stabilization for triplet-excited benzophenone ($C = -0.466\ D^2\,Å^{-3}$). These results are in agreement with the experimentally observed "normal" solvent effect for benzophenone and the "inverted" solvent effect for DBO (Table 1). Note that the solvent effect for exciplex formation of benzophenone operates in the same direction as that expected for electron transfer, such that a mechanistic discrimination is not possible on the basis of the observed solvent dependence alone. The calculated differential solvation energy ($\Delta\Delta G_{solvent}$) of the DBO–NEt$_3$ exciplex in acetonitrile versus cyclohexane amounts to 1.7 kJ mol^{-1} (factor of 2 difference), while the experimental data (factor 3.2) suggest a value of 2.9 kJ mol^{-1}. Given the simplicity of the solvation model (e.g., spherical approximation, continuum model), this agreement between experiment and theoretical expectation is satisfactory, but reveals also the limitations for making accurate quantitative predictions.

The applicability of the simple Kirkwood–Onsager Equation (1) for assessing solvent effects on the CT-induced quenching of singlet-excited DBO was subject to additional computational and experimental tests. The reaction constant C should decrease for better donors as a consequence of increased CT in the exciplex, which should result in a larger μ_{AB} in Equation (1). Indeed, triethylamine exhibits a smaller solvent effect than the weaker donor diisopropylsulfide, for example, the ratio of rate constants in cyclohexane and acetonitrile decreases from 10 for the sulfide to 3.2 for the amine (Tables 1 and 2). The expected effect is also reproduced by the computational method described above:[46] The calculated C value for diisopropylsulfide ($+0.234\ D^2\,Å^{-3}$) is larger than for triethylamine ($+0.101\ D^2\,Å^{-3}$), although the molecular radii of the donors are virtually the same ($r_B = 3.49$ versus 3.44 Å).[47]

In conclusion, the fluorescence quenching of the azoalkane DBO by amines and sulfides provides an example for an "inverted" solvent effect on a CT-induced photoreaction. The effect, which can be semiquantitatively rationalized by the Kirkwood–Onsager solvation model [Eq. (1)], appears to be related to the large dipole moment and small molecular size of DBO and the partial degree of CT in the exciplex intermediate. Similar effects must be considered when predicting solvent effects in related CT-induced photoreactions. They are particularly important when exciplexes with partial CT character are involved, which have been postulated for an increasing number of photoreactions and may precede the electron transfer step.[8, 28–32]

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[47] In an effort to observe a "normal" solvent effect we examined also triphenylamine, which is a better donor than triethylamine (Table 2). However, the solvent effect for this better amine donor was very similar as for triethylamine. Although this result may be in part related to the increase in molecular size of triphenylamine, which would tend to balance the donor strength effect in Equation (1), a *C* value could not be estimated. The UHF-PM3 calculation does not produce minimum exciplex structures in the case of aromatic amines, which differ from aliphatic amines in that they act as "π" rather than "n" donors (cf. P. Jacques, X. Allonas, *Chem. Phys. Lett.* **1995**, *233*, 533–537).

An Inorganic Tire-Tread Lattice: Hydrothermal Synthesis of the Layered Vanadate $[N(CH_3)_4]_5V_{18}O_{46}$ with a Supercell Structure**

Bryan E. Koene, Nicholas J. Taylor, and Linda F. Nazar*

There has been much recent interest in preparing new vanadium oxides owing to their promise as anodes in secondary lithium batteries and electrochromic devices.[1–3] The catalytic properties of vanadium oxides also make these materials viable candidates as heterogeneous catalysts. An inviting synthetic route that deviates from traditional solid-state high-temperature synthesis is hydrothermal chemistry at relatively low temperatures (120–250 °C) and pressures with organic cations as templating agents. Recent developments in this field have proven that it is a viable method for the preparation of many novel two-dimensional materials, especially vanadium oxides. To date, only five truly unique host inorganic lattices have been synthesized, although each lattice can be formed with one of several organic cations in most cases. The lattices, indicated by square brackets, include $[V_4O_{10}]^-$ in the presence of tetramethylammonium (TMA) ions;[4] $[V_4O_{10}]^{2-}$ in the presence of ethylenedamine (en), piperazine (pip),[5] or diaminopropane;[6] and $[V_6O_{14}]^{2-}$ in the presence of 1,4-Diazabicyclo[2.2.2]octan (dabco).[7] Other frameworks that are very closely related to $[V_6O_{14}]^{2-}$ were also recently reported, namely, $(TMA)_2[V_6O_{14}]$[8] and $[Zn(en)_2]^{2+}[V_6O_{14}]$.[9] The mechanism by which these inorganic and organic components assemble under hydrothermal conditions is currently the subject of intense research but is not yet understood. Cooperative organization of organic and inorganic phases has been alluded to in some cases. The organic cation also acts as a reducing agent in the synthesis of transition metal oxides, and this complicates the dissolution and nucleation processes.

We report here the highly unusual layered vanadate $(TMA)_5V_{18}O_{46}$, whose structure is sufficiently distinct from of those other metal oxides that it has no precedent in the literature. The lattice is self-assembled from two distinct $[V_9O_{23}]$ building blocks, neither of which is known to form repeating lattices on its own, to form a supercell arrangement. One building block is neutral, and the other carries localized electrons and is negatively charged. The organic cations reside between the layers. Formation of this unusual lattice arrangement appears to be driven by thermodynamic factors that minimize strain in the "mixed" alternating lattice.

$(TMA)_5V_{18}O_{46}$ was prepared by mixing V_2O_5 (182 mg, 1.0 mmol), V_2O_3 (50 mg, 0.33 mmol), $[N(CH_3)_4]Cl$ (110 mg,

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