the smaller C-6 secondary allylic axial group at C-5 exerts a weaker positive effect.

Similar chirality contributions also account for the Cotton effects of other cyclohexadienes. For example, ORD and CD data for over 30 steroidal 5,7-dienes,[1,15] including a 19-nor-5,7-diene with an otherwise anomalous positive 280-nm Cotton effect,[15] show a direct dependence on chirality contributions of the substituents at C-9 and C-10 according to the amount of their axial character[16] and steric bulk (or polarizability).[17]

In the case of the conformationally rigid diene **1** and the other exceptions already cited,[6,7,15] the reversed sign of the long-wavelength Cotton effect suggests an inverse (or "dissignate" [18]) chirality contribution by allylic axial hydrogen. However, such a chirality effect does not appear to be very strong and, under some circumstances, can evidently be outweighed by normal (or "consignate" [18]) ring-chirality contributions corresponding to the helicity of the diene. This is indicated by the CD data of the following, conformationally flexible dienes, in which at least one of the two homoannular allylic axial hydrogens is secondary: estra-2,4-dien-17β-ol ($\Delta\epsilon_{260}$ + 2.1[2a]), palustric acid (abieta-8,13-dien-18-oic acid) ($\Delta\epsilon_{260}$ + 1.1[5b,19]), 3β-acetoxy-17α-ethyl-17^2-cyano-17^2,21-cyclo-D-homo-5α-pregna-17a,21-diene ($\Delta\epsilon_{304}$ +6.2[7]), and α-phellandrene [(−)-*p*-mentha-1,5-diene] ($\Delta\epsilon_{260-265}$ +5.5 at −186 °C[20]).

Obviously, further investigation of this problem is required. Nevertheless, the present findings clearly demonstrate that allylic chirality contributions play a key role in the Cotton effects of skewed 1,3-cyclohexadienes.

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Albert W. Burgstahler,* Leland O. Weigel
Department of Chemistry, The University of Kansas
Lawrence, Kansas 66045

Jacek K. Gawroński
Institute of Chemistry, A. Mickiewicz University
60-780 Poznań, Poland

Received December 15, 1975

Diffusion in Mixed Solvents. 3. The Heat of Mixing Parameter and the Soret Coefficient[1]

Sir:

Diffusion processes[2-12] and intermolecular interactions[13-16] in binary solvents are of strong fundamental interest to scientists in several disciplines. Reactions are performed in mixed solvents to facilitate solvation. Biological reactions and fluid flow processes always take place in complex solvents which are at least binary.[10,14] Diffusion processes and intermolecular interactions in the mixed solvent system are responsible for reported anomalous peaks and valleys in the entropies and enthalpies of activation for numerous reactions[7,10] and fluorescence phenomena.[10,11] Anomalies in several sets of solvated electron reaction rate constants,[3] ground[6,8] and triplet[2] states electron transfer reaction rate constants, and diffusion coefficient data[9] for entire solvent mixture ranges are due to the intermolecular interactions in the binary solvent.[2,15,16] The heat of mixing parameter (HMP) plots reported earlier,[2,15,16] which strongly implicate thermal diffusion[17] as being important to the explanation of these processes, successfully correlates the above mentioned anomalies. Further, the HMP theory as conceptually outlined[15] appears to be supported by recent magnetic relaxation results for protein-water interactions.[14]

Presented here is new evidence which demonstrates that for aqueous glycerol solutions, the Soret coefficient of glycerol,[17] $\sigma_1 = D_1^T/D_1$ (where D_1^T and D_1 are the thermal and self-diffusion coefficients of glycerol, respectively, in aqueous solution), is an integral part of the HMP, defined as $(-\partial\Delta H^M/\partial n_2)/X_2$ for this system, where X_2 is the mole fraction of water.[2,15,16] Figure 1A shows that the HMP plot for the self-diffusion coefficients of glycerol[18] is linear for $0 < X_1 < 0.44$; further, it nearly superimposes on similar plots for the data for two different reactions[6,8,19] in aqueous glycerol solvent. Figure 1B demonstrates that both the HMP and the diffusion parameter, DP, $(k\eta\epsilon/(k\eta\epsilon)_2$ where k represents the diffusion coefficient or second-order reaction rate constant, plotted against $\partial \ln a_1/\partial \ln c_1$ exhibit curves which appear

Table I. Calculation of Glycerol Soret Coefficients[a] in Aqueous Glycerol Solutions from Equation 2

X_1	0.021	0.047	0.072	0.115	0.164	0.227	0.312	0.439	0.500	0.638
$10^3\sigma_1$, $\deg^{-1}$	17.2	7.7	4.9	3.0	2.2	1.7	1.5	(1.6) (−10.8)	−15.6	−19.1

[a] Values for the glycerol self-diffusion coefficient, $(\partial \Delta H^M/\partial n_2)$, and $(d \ln a_1/d \ln c_1)$ are at 25 °C (i.e., slopes in Figure 1C). Values for the partial molar volumes are at 20 °C since values at 25 °C were not available. Consequently, errors derived from this use of approximate values appear in σ_1 values. The data point at $X_1 = 0.439$ appears to lie on both slopes so the sign and magnitude are uncertain. Due to the unavailability of precision partial molar volume data, resolution of this minor point is unwarranted.

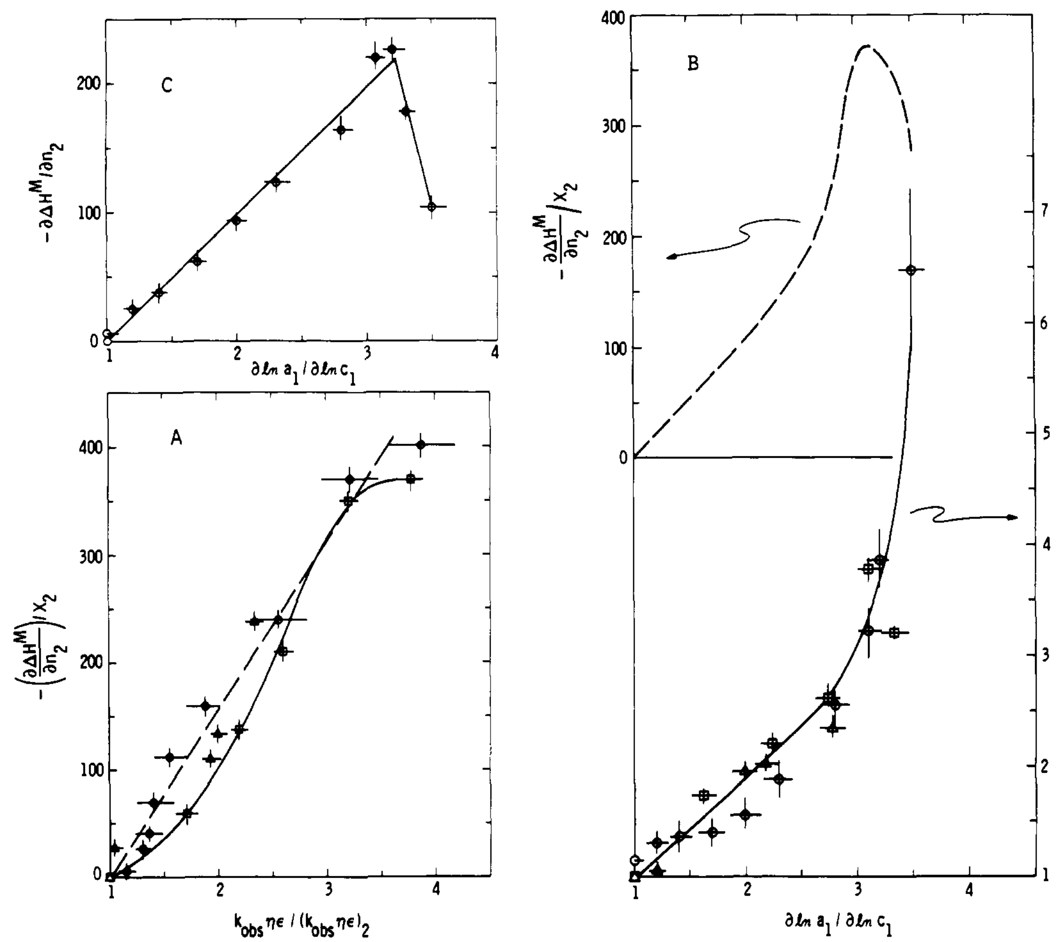

Figure 1. Correlations for diffusion processes in glycerol water solvents: self-diffusion coefficients of glycerol (circles), ref 18, data taken from enlarged graph; neutralization of bromocresol green, $H^+ + BG^{2-} \rightarrow (HBG)^-$ (triangles), ref 8 for second-order rate constants, 25 °C; electron transfer reaction $CH_3(C_6H_5)CO\cdot^- + (C_6H_5)_2CO \rightarrow CH_3(C_6H_5)CO + (C_6H_5)_2CO\cdot^-$ (squares), ref 6 and 19 for second-order rate constants, 21 °C. (A) Heat of mixing parameter plot: HMP in calories per mole calculated from ref 25; dielectric constant, ϵ, calculated from ref 26, p 318; viscosity, η, calculated from ref 26, p 279. Representations: n, number of moles; X, mole fraction. (B) Heat of mixing parameter, calories per mole, vs. activity factor and diffusion parameter vs. activity factor plots. Activity factor, $d \ln a_1/d \ln c_1$, data, ref 18. (C) Partial heat of mixing of water, calories per mole, with glycerol vs. activity factor.

linear for $0 < X_1 < 0.23$. Figure 1C shows a definite discontinuity in the plot of $-\partial\Delta H^M/\partial n_2$ vs. $\partial \ln a_1/\partial \ln c_1$ for the self-diffusion coefficient of glycerol. The importance of the Soret coefficient to these plots is demonstrated by the following. If $X_1 = 0$ is the reference composition, $\partial \ln a_2/\partial T = (-\partial\Delta H^M/\partial n_2)/RT^2$;[20] division by $\partial \ln X_2$ and substitution of $dX_2/dT = X_1X_2\sigma_2$,[21] yields

$$\frac{\partial \ln a_1}{\partial \ln X_1} = \frac{(-\partial\Delta H^M/\partial n_2)}{X_2}\frac{1}{RT^2}\frac{X_2}{X_1}\frac{1}{\sigma_1} \tag{1}$$

since $\partial \ln a_2/\partial \ln X_2 = -\partial \ln a_1/\partial \ln X_1$ by Gibbs-Duhem equation, and $\sigma_1 = -\sigma_2$. Conversion to concentration units from mole fraction units and equation reorganizations yield:

$$\frac{-\partial\Delta H^M}{\partial n_2} = \frac{\partial \ln a_1}{\partial \ln c_1}RT^2X_1\sigma_1\left(\frac{\bar{v}_2}{X_1\bar{v}_1 + X_2\bar{v}_2}\right) \tag{2}$$

and

$$\frac{-(\partial\Delta H^M/\partial n_2)}{X_2} = \frac{\partial \ln a_1}{\partial \ln c_1}RT^2\frac{X_1}{X_2}\sigma_1\left(\frac{\bar{v}_2}{X_1\bar{v}_1 + X_2\bar{v}_2}\right) \tag{3}$$

Application of eq 2 also represents another method by which Soret coefficients can be computed from thermodynamic data for type III solvent[15] systems. The usefulness of eq 2 for calculation of σ_1 from the slopes of Figure 1C is indicated by the values in Table I. Figure 1C yields a positive slope for $0 < X_1 \leq 0.44$ and a negative slope for $0.44 \leq X_1 \leq 0.64$, resulting in positive and negative values, respectively, for σ_1. The variation in σ_1 with X_1 is consistent with those for several binary solvent systems both aqueous and nonaqueous.[22] Measured values for σ_1 for aqueous sugars are similar to those reported here for aqueous glycerol; the variation with concentration is also evident.[23] The linear relationship of $\partial \ln a_1/\partial \ln c_1$ with the DP (Figure 1B) for $0 < X_1 < 0.23$ further suggests that diffusion processes in binary solvents are directly related to thermal diffusion processes.[24] Equation 3 may be sometimes more useful as it expresses the HMP for a system (a type III solvent)[15] directly in terms of the Soret coefficient and the activity factor, $\partial \ln a_1/\partial \ln c_1$, a function which indicates mixed solvent nonideality as does the heat of mixing, ΔH^{M}.

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P. A. Carapellucci

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

Received November 3, 1975

Nitroso Compounds and Azo Dioxides as Quenchers of Singlet Oxygen ($^1\Delta_g$) and Sensitizer Triplet States

Sir:

We recently reported that 3,3,4,4-tetramethyl-1,2-diazetine-1,2-dioxide (**1**) was a useful triplet quencher.[1] It absorbs at short wavelengths, efficiently quenches triplets of energies $\geqslant$42 kcal/mol, and does not quench aromatic singlet states. We now describe some unexpected quenching properties of other azo dioxides and nitroso compounds.

Quenching of sensitizer triplets was monitored by the effect of quenchers on the rate of sensitized formation of O_2 ($^1\Delta_g$) in 95% ethanol. The reaction was followed by the disappearance of $\sim 9 \times 10^{-5}$ M 1,3-diphenylisobenzofuran (DPIF). Linear Stern–Volmer plots were obtained from which quenching rate constants were calculated.[2] The sensitizer triplet lifetimes required for these calculations were estimated from the product of the oxygen concentration in air-saturated ethanol (1.57×10^{-3} M)[3] and the rate constants for oxygen quenching of aromatic triplet states. The latter ($1\text{-}3 \times 10^9$ M^{-1} s^{-1}) were either known or estimated from the triplet energies of the sensitizers.[4]

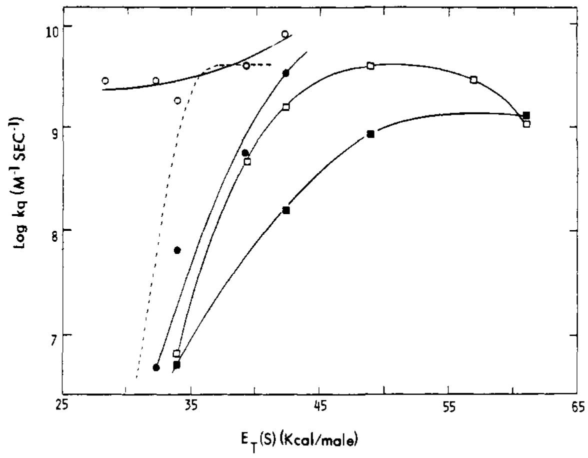
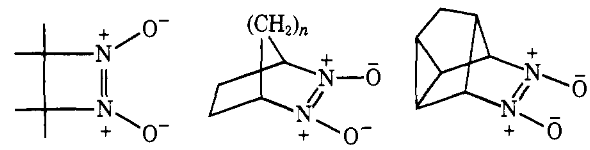
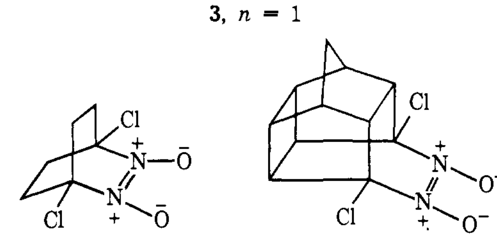


Figure 1. Rate constants for quenching sensitizer triplets by azo dioxides in ethanol: ■, **1**; □, **2**; ●, **4**; ○, apparent k_q for **5** ignoring possible quenching of O_2 ($^1\Delta_g$). Dashed line is calculated for a classical quencher ($E_T(Q)$ = 34 kcal/mol). Sensitizers, ascending order of $E_T(S)$, are chlorophyll a and b, methylene blue, rose bengal, anthracene, pyrene, chrysene, and naphthalene.

Representative quenching rate constants are compared in Table I with the longest wavelength absorption maxima of azo dioxides **1–6**.[5] The absorption maxima of the unchlorinated azo dioxides **1–4** decrease in energy as the quenching efficiencies increase. The accompanying structural changes suggest that the orbitals of the increasingly strained transannular 5,6-σ bonds in the series **1** (no bond), **2**, **3**, and **4**, may mix with the π^*-azo dioxide orbitals and lower the excited state energies.



1 **2**, n = 2 **3**, n = 1 **4**



5 **6**

The introduction of α-chlorine atoms in the azo dioxides should contribute to Coulombic destabilization of their ground states relative to their less polar excited states. Thus the absorption maxima of **5** and **6** are red-shifted relative to their unchlorinated analogues **2** or **3** and **4**, respectively. Although the greater quenching efficiencies of **5** and **6** suggest that Coulombic destabilization is also relieved in their lowest triplet states, significantly, the parallel relationship between absorption maxima and quenching rates found in the unchlorinated compounds was not observed.

The effect of sensitizer triplet energy on the azo dioxide quenching rate constants was compared with that expected in a classical energy transfer model (eq 1)

$$S^* + Q \underset{k_{-\text{diff}}}{\overset{k_{\text{diff}}}{\rightleftarrows}} |S^* + Q| \overset{K}{\rightleftarrows} |S + Q^*| \xrightarrow{k_{-\text{diff}}} S + Q^* \quad (1)$$