acetonitrile/acetone mixtures. Since no increase in the 640-nm carbonyl ylide absorption was observed it can be concluded that 7 does not undergo photochemical fragmentation. This photostability may reflect the limitation to bond rotation and a structure more closely approaching linearity in the nitrile ylide compared with the carbonyl ylide. In fact these limitations may also be reflected in the slow thermal decay of the nitrile ylide.[8,9]

Finally we note that efficient (~80%) photobleaching of the carbonyl ylide does not necessarily reflect high quantum yields. The measurement of quantum yields in biphotonic ("three-beam") experiments remains a challenging problem.

Acknowledgment. Thanks are due to S. E. Sugamori for technical assistance and to M. Tanner and N. H. Werstiuk for their help with some of the early experiments.
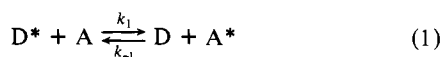

Figure 1. (Top) Representative traces for the chrysene–naphthalene system at 335 K, monitored at 580 (A) and 425 nm (B) where chrysene (A) and naphthalene (B) show preferential absorption. The concentrations are [naphthalene] = 0.39 M and [chrysene] = 1.02 mM. (Bottom) Ratio of the two traces (A/B) showing essentially no time dependence; in this particular system and time-scale equilibrium is essentially complete at point "C". The scattered points at the left result from the division of two near-zero (i.e., base line) signals.

Importance of Entropy Terms in Triplet Energy Transfer Equilibria[1]

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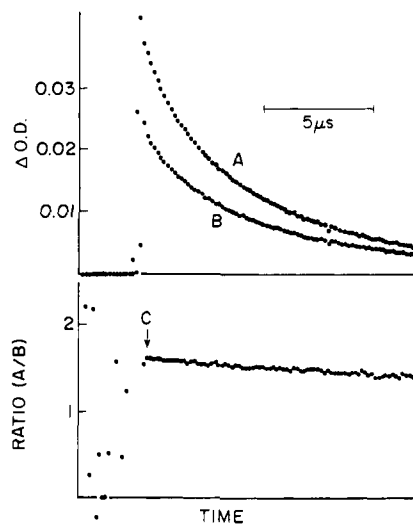*National Research Council of Canada*
Ottawa, Ontario, Canada K1A 0R6

It has been known for over 20 years[3] that triplet-state equilibria can be readily established in solution if the corresponding excited states are sufficiently long lived (micro- to milliseconds) and the excited-state energies do not differ by more than a few kcal/mol, reaction 1, where D and A refer (rather arbitrarily) to donor and

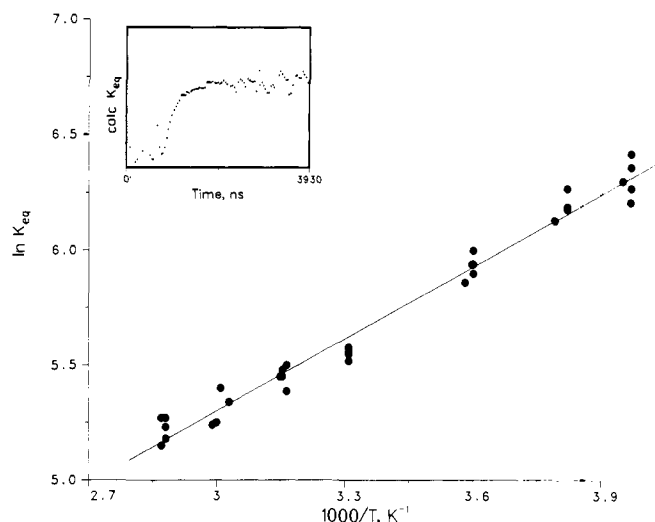$$D^* + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} D + A^* \qquad (1)$$

acceptor, respectively, and the asterisk denotes a thermally equilibrated triplet state. Studies of such equilibria have been carried out using emission spectroscopy,[3,4] product studies,[5] pulse radiolysis,[6–9] and laser flash photolysis[6,9] techniques. These studies usually yield the equilibrium constant ($K_{eq} = k_1/k_{-1}$) and from it the free energy change, ΔG. Since all data have hereto been obtained only at room temperature it was generally assumed that ΔG could be compared directly with the spectroscopic energy difference, ΔE, and any difference was discussed in terms of nonvertical energy transfer. In other words, ΔS, the entropy change associated with reaction 1, was neglected. In a recent treatment of energy-transfer processes,[10] where ΔS^*, the entropy of excitation, was introduced explicitly, only the trivial multiplicity term was actually taken into account, largely because other contributions are difficult to evaluate.

In the last few years time-resolved energy-transfer studies have clearly indicated that entropic terms can play an important role in determining rates of endothermic[11] and exothermic[12] energy

Figure 2. Semilogarithmic plot of the equilibrium constant against the reciprocal temperature for the benzophenone–triphenylene system in $CF_3C_6H_5$ covering the 251–348 K temperature range and (inset) calculated equilibrium constant based on traces at 535 and 400 nm for a solution containing [benzophenone] = 0.046 M and [triphenylene] = 5.35 $\times 10^{-4}$ M at 348 K. Note the time evolution illustrating the approach to equilibrium.

transfer; to a certain extent this was already evident from quenching studies that showed the relevance of steric/conformational factors.[13,14]

In this paper we report preliminary results of the temperature dependence of energy-transfer equilibria, from which ΔS (along with ΔH) for three systems have been obtained. To the best of our knowledge these are the first direct measurements of entropy

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Table I. Energy Transfer Data

donor	acceptor	$\lambda_D{}^a$	$\lambda_A{}^b$	K_{eq}(25 °C)	ΔH^c	ΔS^d
chrysene	naphthalene	580	420	1.1×10^{-3}	4.0 ± 0.1	0.04 ± 0.3
benzophenone	biphenyl	535	395	12.0	-2.0 ± 0.2	-1.8 ± 0.5
benzophenone	triphenylene	535	400	260	-2.1 ± 0.1	4.3 ± 0.4

^{a} Wavelength (nm) where donor absorbance predominates. ^{b} Wavelength (nm) where acceptor absorbance predominates. ^{c} In kcal/mol. ^{d} In gibbs/mol.

changes resulting from excitation. Our results show that entropic terms can account for differences of over an order of magnitude in K_{eq}; further, the entropy changes observed can be interpreted in terms of the relative conformational freedom of the ground and excited states involved. The systems (solvent) examined are chrysene–naphthalene (toluene), benzophenone–biphenyl (CF_3-C_6H_5), and benzophenone–triphenylene ($CF_3C_6H_5$). The measurements were carried out by using laser photolysis techniques[15] and the same analytical approach described by Kira and Thomas,[6] based on transient absorption measurements at two selected wavelengths where the excited donor and acceptor absorb preferentially. In order to establish that the equilibrium condition is met one obtains the ratio of the two traces at both wavelengths or calculates the equilibrium constant as a function of time; a time-independent value indicates that equilibrium has been achieved. Figure 1 illustrates a pair of traces and their ratio. The values of ΔS and ΔH can then be determined from a plot of log K_{eq} vs. T^{-1}, Figure 2. Table I summarizes the data. The enthalpy changes do not hold any significant surprises; in the case of naphthalene–chrysene the value of ΔH coincides with the spectroscopic energy difference,[6] and the other examples agree with reports already in the literature.[5,6] They will be discussed in detail in a full report. The equilibrium constant for the benzophenone–biphenyl system (12.0) is in reasonable agreement with values of 7 and 23 reported by Wagner[5] and Thomas.[6] For the benzophenone–triphenylene system, our value of 260 should be compared with the reported one of 133.[5]

It is noteworthy that the value of ΔS for the chrysene–naphthalene system is essentially zero, as one would expect for a pair of rigid molecules, where no significant changes in conformational freedom are expected upon excitation. On the other hand, in the benzophenone–triphenylene system ΔS = 4.3 gibbs/mol; here, if we assume that triphenylene is essentially rigid, then the entropy of benzophenone must decrease by 4.3 gibbs/mol (apart from the multiplicity term) upon excitation, indicating a substantial decrease[16] in conformational freedom. Similarly, if we combine the last two entries in Table I, biphenyl must lose about 6.1 gibbs/mol upon excitation. It should be noted that these entropy differences refer to the relaxed triplet and ground state, rather than to the states involved in a "vertical" transition. We propose that this large entropy loss is the result of the freezing of the C–C bond between the biphenyl rings in a nearly planar conformation. Wagner[13b] has pointed out that "there exists a gross geometric difference between the ground state and the excited triplet state" of biphenyl. Interestingly, an entropy change of this magnitude will introduce a change of a factor of ca. 21 in an equilibrium constant.

We find the small value of ΔS in the benzophenone–biphenyl system rather surprising, since literature discussions of these molecules usually emphasize conformational effects in biphenyl, not in benzophenone. However, Kearns and Case[17] have observed a substantial separation between the O–O absorption and phosphorescence bands of benzophenone; further, the O–O phosphorescence band of aromatic ketones is known to be different for relaxed and unrelaxed triplets.[18]

Finally, it is interesting to consider a ΔS^* scale, of entropies of excitation, in much the same way in which we use triplet or

singlet excitation energies. This could be useful in thermodynamic calculations, energy-transfer studies, and conformational effects in photochemistry. For example, the entropy effects observed for benzophenone and biphenyl provide a straightforward interpretation to the inefficiency of energy transfer in this system.[5] We are currently trying to measure sufficient examples to establish the basis for such a scale.

Monomeric Tungsten(IV) Phenoxide and Thiolate Complexes

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To our knowledge there is no example in the literature of a complex of the type WX_4 where X is a monodentate anionic ligand.[1] We believe such 10e, d^2 species will be of interest in terms of their ability to bind and activate small molecules. The small molecule we are most interested in activating (using *two* such W(IV) centers) is molecular nitrogen. We now have firm evidence that $W^{IV}W_2(\mu\text{-}N_2)$ complexes can be prepared, either from W(VI) and hydrazine or directly from molecular nitrogen by reducing W(V).[2] It is thought that $W_2(\mu\text{-}N_2)$ complexes can be formed more easily than the more relevant $Mo_2(\mu\text{-}N_2)$ complexes owing to the expected greater reducing power of W(IV) vs. Mo(IV).

Blue, diamagnetic $W(DIPP)_4$ (DIPP = O-2,6-C_6H_3-i-Pr_2) can be prepared by heating $WCl_4(Et_2S)_2$ and 4 equiv of LiDIPP in a mixture of toluene and ether at 40 °C overnight.[3] An X-ray structural study[4] shows $W(DIPP)_4$ to be nearly square planar (Figure 1) with trans-O–W–O angles of 168° and cis angles of 90–91°. W–O–C angles vary from 154° to 159°. W–O bond lengths vary from 1.85 to 1.87 Å. The four phenyl ring systems

(1) (a) $W(CH_2C_6H_5)_4$ appears to be well characterized[1b] although no structure has been reported. The benzyl ligand, however, may behave as a benzallyl ligand and therefore does not qualify as an unambiguously monodentate ligand. (b) Thiele, K. H.; Russek, A.; Opitz, R.; Mohai, B.; Brüser, W. *Z. Anorg. Allg. Chem.* **1975**, *412*, 11.

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(3) A solution of $WCl_4(Et_2S)_2$ (0.59 mmol, 0.300 g) in 3 mL of toluene at −30 °C was added to LiDIPP(ether) (2.37 mmol, 0.613 g) in 20 mL of ether at −30 °C. The mixture was stirred for 1.5 h at 25 °C then heated in a sealed vessel at 40 °C for 14 h. The precipitated salts were filtered off and the solvents removed in vacuo. The crude product was recrystallized from pentane to give dark blue crystals (0.25 g, 47%). Anal. Calcd for $WC_{48}H_{68}O_4$: C, 64.57; H, 7.68. Found: C, 64.48; H, 7.75.

(4) $W(DIPP)_4$ crystallizes in the space group $C2/c$ with a = 30.557 (5) Å, b = 13.434 (2) Å, c = 22.312 (3) Å, β = 91.99 (1)°, V = 9153.6 Å^3, Z = 8, ρ(calcd) = 1.296 g cm^{-3}, and μ = 24.23 cm^{-1}. Data were collected at −50 °C on an Enraf-Nonius CAD4F-11 diffractometer by using Mo Kα radiation. A total of 8054 reflections (±h, +k, +l) were collected in the range 3° ⩽ 2θ ⩽ 50° with the 5006 having $F_o > 6\sigma(F_o)$ being used in the structure refinement, which was by full-matrix least-squares techniques (241 variables) using SHELX-76. Final R_1 = 0.042 and R_2 = 0.046. An empirical absorption correction was applied.

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