Re–Cl stretch. A small shift is expected as the Re–Cl bonding is relatively unaffected by the Re–Re axis localized $\delta \rightarrow \delta^*$ transition. We assign the 138-cm^{-1} excited-state Raman band as the Cl–Re–Re bending vibration. This mode has not been observed in the ground-state Re$_2$Cl$_8{}^{2-}$ Raman spectrum; the A$_{2u}$ Cl–Re–Re bend has been observed in the IR at 165 cm^{-1}.[20,21] The observation that the 366- and 138-cm^{-1} bands are the two most intense features in the excited-state spectrum is consistent with the assignment of the 390-nm transient absorption band as e$_u$(Cl) $\rightarrow \delta$ charge transfer.

We are left to assign the 204-cm^{-1} excited-state Raman band as the excited-state Re–Re stretch. Although we expect a decrease in Re–Re frequency in going from the ground state (bond order = 4) to the $\delta\delta^*$ excited state (bond order = 3), the 204-cm^{-1} frequency represents an unexpectedly large shift from the 272-cm^{-1} ground-state Re–Re stretch and also from the 248-cm^{-1} excited-state Re–Re stretch deduced from low-temperature absorption measurements.[19] There are several possible explanations for these results: (i) The *interpretation* of the 248-cm^{-1} progression in the low-temperature absorption experiment as the excited-state Re–Re stretch is incorrect and the true frequency is 204 cm^{-1}. (ii) The 248-cm^{-1} Re–Re stretch is for an excited state *eclipsed* geometry, due to the constraining effects of the low-temperature crystalline environment, while the 204-cm^{-1} assignment reflects the solution-phase, room temperature relaxed (possibly staggered) $^1\delta\delta^*$ geometry.[24] (iii) In our TR^3 experiment, we are observing a state other than the singlet $\delta\delta^*$, such as the triplet $\delta\delta^*$ state; this would require a reassignment of the emissive excited state since our TR^3 spectra *are* of the emissive excited state. Further TR^3 work is now being done to try to sort out the geometric and electronic properties of quadruply bonded metal dimers, which will lead to a more complete understanding of the excited-state structure of Re$_2$Cl$_8{}^{2-}$.

Acknowledgment. This work was supported by a Cottrell Research Grant from the Research Corporation. We thank Ann R. Cutler and Professor Richard A. Walton for generously providing a sample of tetrabutylammonium octachlorodirhenate.

(24) Simple group theory predicts three polarized Raman vibrations for both the eclipsed (D_{4h}) and staggered (D_{4d}) Re$_2$Cl$_8{}^{2-}$ geometries. Thus, we cannot easily deduce the excited-state geometry from group theory alone.

Photochemistry of the Carbonyl Ylide Produced by Reaction of Fluorenylidene with Acetone. A Comparison of Carbonyl and Nitrile Ylides[1]

J. C. Scaiano,* W. G. McGimpsey, and H. L. Casal

Division of Chemistry
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6

Received March 19, 1985

Fluorenylidene (2) forms unstable ylides with solvents such as acetone and acetonitrile.[2,3] In this work we investigate the photochemistry of the carbonyl ylide 3 formed by reaction of 2 with acetone in order to compare its photochemical and thermal decay processes. Ylide 3 was produced by nitrogen laser excitation (λ = 337.1 nm, ~8 ns, <10 mJ/pulse) of deaerated 1 × 10^{-3} M solutions of diazofluorene (1) in acetone at room temperature (Scheme I). The transient absorption spectrum of 3 exhibits[2,3] a broad band centered at 640 nm appearing within 10 ns (in pure acetone) after excitation[2] and decaying with a lifetime of ca. 3.4 μs.

(1) Issued as NRCC 24549.
(2) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6631–6635.
(3) Griller, D.; Nazran, A. S.; Scaiano, J. C. *Acc. Chem. Res.* **1984**, *17*, 283–289.
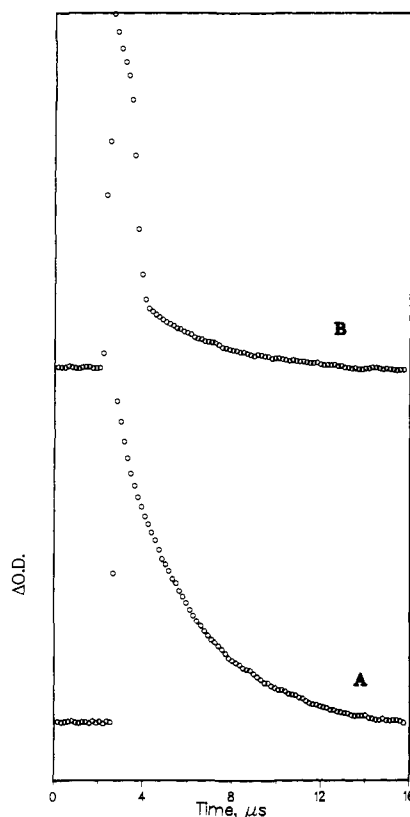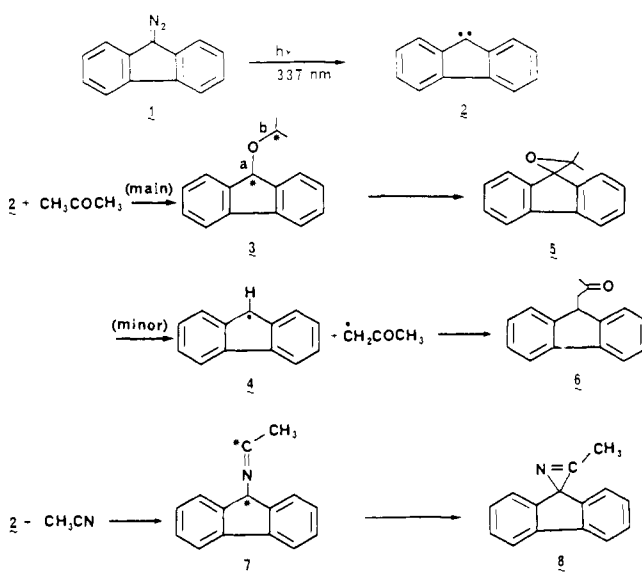
Scheme I

Figure 1. Comparison of the traces monitored at 640 nm from one- and two-laser experiments in the photodecomposition of 1 × 10^{-3} M diazofluorene (1) in acetone at 300 K. (A) Resultant trace after 337-nm laser excitation; (B) result of 337-nm laser excitation followed (after 1.5 μs) by 591-mm laser photolysis.

Excitation of 3 with the delayed pulse from a Candela UV-500 M flash-lamp pumped dye laser (λ = 591 nm, ~250 ns, 200–800 mJ/pulse) resulted in concurrent bleaching of the 640-nm absorption band;[4] the transient absorptions due to 3 are sufficiently small (typically ≤0.06) that only a small fraction of this energy is actually absorbed. Figure 1A shows the decay of the 640-nm ylide absorption produced by 337-nm laser excitation alone, while Figure 1B illustrates the effect of the second 591-nm excitation,

(4) A description of our setup for two-laser experiments has been published: Weir, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4396.
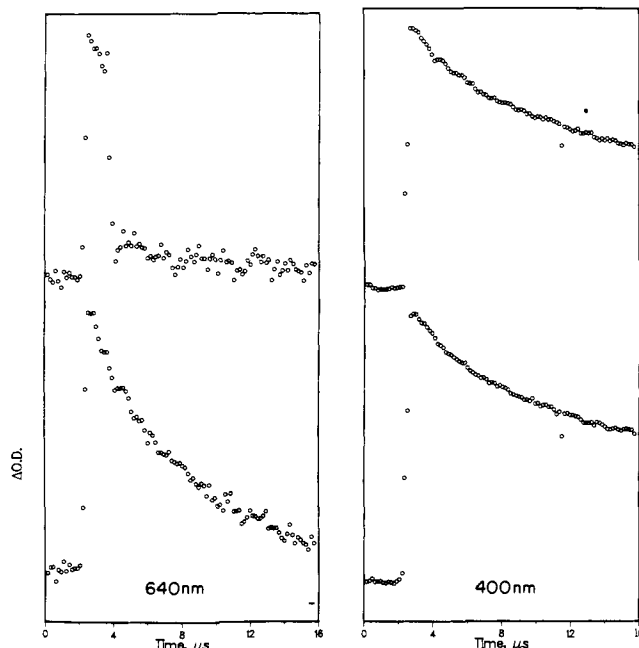
Communications to the Editor

J. Am. Chem. Soc., Vol. 107, No. 24, 1985 7205

Figure 2. Comparison of the decay traces monitored at 640 and 400 nm from one- and two-laser experiments in the photodecomposition of 1 × 10^{-3} M diazofluorene (**1**) in a 9:1 (vol/vol) acetonitrile/acetone mixture. Bottom trace show the resultant traces after 337-nm laser excitation only; top traces show the result of 337-nm laser excitation followed (after 1.5 μs) by 591-nm laser photolysis.

delayed by 1.5 μs. The lifetime and spectral characteristics of the residual signal remaining after the 591-nm pulse were identical with those in the one-laser experiment; the second laser pulse (591 nm) destroys over 80% of the ylide present at that time.

Theoretical studies[5,6] predict that carbonyl ylides may undergo fragmentation via an excited-state process, and, indeed, this is supported experimentally in some cases.[7] Fragmentation of **3** would lead to two possible sets of products depending on the C–O bond broken. Cleavage of bond **a** would regenerate the original reactants, i.e., fluorenylidene and acetone, while cleavage of the C–O bond (**b**) would yield fluorenone and dimethylcarbene. Since fluorenone was not produced (vide infra), this latter possibility may be ruled out.

In order to determine if the fragmentation of **3** regenerates fluorenylidene and acetone, photolysis was carried out in a 9:1 (v/v) acetonitrile/acetone mixture. Under these conditions **2** adds to both acetone and acetonitrile to form carbonyl and nitrile ylides[3,8,9] (λ_{max} = 640 and 400 nm, respectively), Scheme I. By use of the known rate constants for reaction with acetone and acetonitrile[2,8] (but neglecting hydrogen abstraction), 29% of the carbenes **2** will add to acetone and the rest to acetonitrile; in one of our experiments this led to transient optical densities of 0.0097 and 0.013 at 640 and 400 nm, respectively. Fragmentation of **3** to regenerate **2** (induced by the 591-nm laser) would increase the intensity of the 400-nm nitrile ylide absorption band, since **2** would once again be free to add to both substrates. In our case an 80% destruction of **3** should lead (on the basis of the known rate constants) to a 23% increase in optical density at 400 nm. Figure 2 shows that the decay traces (at 400 nm) of the nitrile

ylide **7** for one- (bottom) and two-laser (top) experiments are practically identical; plots of residuals for one- and two-laser experiments give a change <<2% in the transient optical density at 400 nm. This figure also shows the corresponding decay traces of **3** monitored at 640 nm; clearly, destruction of the carbonyl ylide **3** does not regenerate **2** which could form **7**. In summary, cleavage of bonds **a** or **b** is not a relevant process in the photodecomposition of **3**.[10]

A series of two-laser preparative experiments was performed in order to compare the final products from **3** with and without 591-nm excitation. For these experiments the 337-nm "synthesis" pulse was followed after a 1.5-μs delay by the 591-nm "photolysis" pulse. In control runs, the pulse sequence was reversed.[11]

Both preparative experiments led to the *same products*. GC–MS analysis after sample concentration and treatment with diethyl fumarate to destroy the unreacted diazo compound showed that the oxirane **5** or its rearranged product (9-acetyl-9-methylfluorene (**9**))[3] is the major product, with a minor contribution from the isomer resulting from radical recombination of 9-fluorenyl and $\dot{C}H_2COCH_3$.[12]

From the evidence presented above we conclude that photolysis of **3** leads to the rapid occurrence of the same processes that occur more slowly and with an activation energy of 11 kcal/mol in the spontaneous decay of **3**.[2] Theory[5] suggests that the requirement for decay is C–O bond rotation from the 0°,0° (edge-to-edge)[13] conformation to the 0°,90° conformer, which then can decay readily to form **5**. We suggest that excitation of the ylide actually leads to this rotation, perhaps an indication that the 0°,90° species is an energy minimum for the excited ylide.

The detection of oxirane formation by photocyclization of the carbonyl ylide is consistent with the behavior of ylides derived ·from stilbene oxides in glasses at 77 K.[14] Here the photoreversibility was attributed to the fact that the ylides were rigidly held in the proper geometry for cyclization.

The case of the fluorenylidene–acetonitrile ylide **7** contrasts with that of **3**. The former absorbs at ~400 nm and decays with $\tau > 100$ μs.[8,9] However, 429-nm dye laser excitation (~250 ns, ⩽150 mJ/pulse) of **7** fails to cause any bleaching.[15] In order to confirm this *surprising* photostability,[17] 337-nm photolysis of diazofluorene followed by 429-nm excitation was carried out in

(5) Houk, K. N.; Rondan, N. G.; Santiago, C.; Galls, C. J.; Gandour, R. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 1504–1512.

(6) Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1979**, *101*, 1095–1100; **1979**, *101*, 1101–1106.

(7) Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537–547.

(8) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, *104*, 6813–6814. Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227–2235.

(9) Brauer, B.-E.; Grasse, P. B.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6814–6816. Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833–6845.

(10) The quality of the 640-nm decay traces in Figure 2 is less than that of the traces shown in Figure 1; this is due to a smaller concentration of 3 in the mixed solvent due to competitive formation of 7.

(11) This type of experiment has the advantage that any photodecomposition of otherwise stable final products or thermal effects caused by the 591-nm pulse will be duplicated in both experiments, while the possibility of any transient photochemistry is eliminated.

(12) In preparative experiments 2 mL of a degassed 1 × 10^{-3} M solution of 1 in acetone was irradiated with 337.1-nm laser pulses followed after 1.5 μs by 591-nm pulses; a total of 1000 pairs of pulses led to conversions ~10%. The sample, concentrated to <100 μL, contained ⩽40 μg of 5; 20 μL of diethylfumarate were added to destroy the remaining 1. This yields a cyclopropane by GC–MS [m/e (relative abundance) 336 (29), 218 (25), 190 (24), 189 (100), 165 (18)], but does not obscure the identification of other products by NMR. The major product was oxirane 5 whose mass spectrum gave m/e 222 (13), 180 (18), 179 (100), 178 (36), and 176 (10) (the pattern suggests that rearrangement to 9 may be taking place; the ¹H NMR spectrum (CDCl₃) of the product mixture showed prominent signals at δ 1.62, due to the methyl groups in 5. Attempts to use IR were complicated by the signals due to the excess diethyl fumarate. Product 6 was identified from its mass spectrum [m/e 222 (50), 180 (17), 179 (100), 178 (47), 165 (43)] which was identical with that reported previously[2] (in that case 6 had been identified by ¹H NMR and infrared spectroscopy). Substitution of acetone by acetone-d_6 led to a marked decrease in the yield of 6 and the expected changes in the mass spectrum.

(13) The 0°,0° conformation refers to the "planar" one, having the two methyl groups in the plane of the C–O–C group. In the 0°,90° conformer the two methyls are in a plane perpendicular to that one.

(14) Trozzolo, A. M.; Leslie, T. M.; Sarpotdar, A. S.; Small, R. D.; Ferraudi, G. J. *Pure Appl. Chem.* **1979**, *51*, 261–270.

(15) Under identical conditions fluorenone oxide (λ_{max} ~ 450 nm)[16] is readily photobleached (>70%), making us confident of the detectability of similar changes when they occur to a significant extent.

(16) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616.

(17) Nitrile ylides (without fluorene moieties) are not photostable at 77 K: Orahovats, A.; Heingartner, H.; Schmid, H.; Heinzelmann, W. *Helv. Chim. Acta* **1975**, *58*, 2662. Siebu, W.; Gilgen, P.; Chaloupka, S.; Hansen, H.-J.; Schmid, H. *Helv. Chem. Acta* **1973**, *56*, 1679.

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.

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

F. Gessner[2] and J. C. Scaiano*

Division of Chemistry
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6

Received May 29, 1985

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

$$D^* + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D + A^* \qquad (1)$$
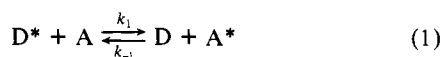
acceptor, respectively, and the asterisk denotes a thermally equilibrated triplet state. Studies of such equilibria have been carried out using emission spectroscopy,[3,4] product studies,[5] pulse radiolysis,[6–9] and laser flash photolysis[6,9] techniques. These studies usually yield the equilibrium 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
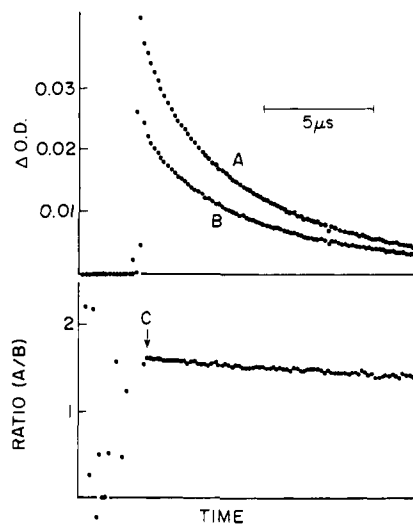

Figure 1. (Top) Representative traces for the chrysene–naphthalene system at 335 K, monitored at 580 (A) and 425 nm (B) where chrysene (A) and naphthalene (B) show preferential absorption. The concentrations are [naphthalene] = 0.39 M and [chrysene] = 1.02 mM. (Bottom) Ratio of the two traces (A/B) showing 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.
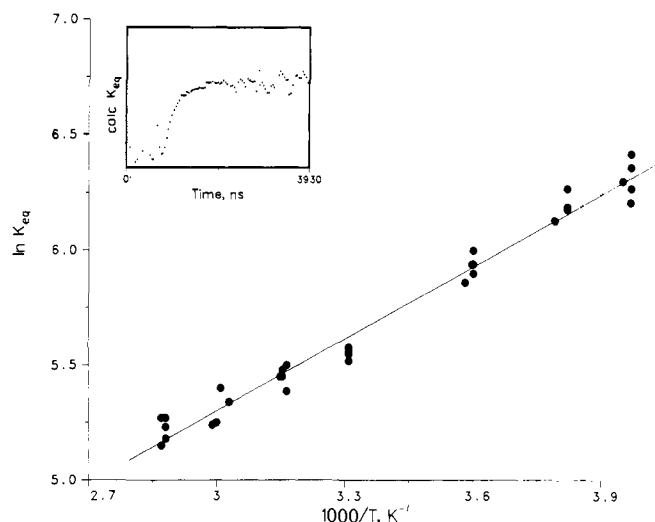

Figure 2. Semilogarithmic plot of the equilibrium constant against the reciprocal temperature for the benzophenone–triphenylene system in $CF_3C_6H_5$ covering the 251–348 K temperature range and (inset) calculated equilibrium constant based on traces at 535 and 400 nm for a solution containing [benzophenone] = 0.046 M and [triphenylene] = 5.35 × 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

(1) Issued as NRCC-24873.
(2) NRCC Visiting Scientist under the sponsorship of CIDA (Canada) and CNPq (Brazil).
(3) Sandros, K. *Acta Chim. Scand.* **1964**, *18*, 2355.
(4) Kikuchi, K.; Kokubun, H.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2732.
(5) Wagner, P. J. *Mol. Photochem.* **1969**, *1*, 71.
(6) Kira, A.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 196.
(7) Gorman, A. A.; Hamblett, I.; Harrison, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6952.
(8) Craig, B. B.; Gorman, A. A.; Hamblett, I.; Kerr, C. W. *Radiat. Phys. Chem.* **1984**, *23*, 111.
(9) Gorman, A. A.; Gould, I. R.; Hamblett, I. *J. Am. Chem. Soc.* **1981**, *103*, 4553.
(10) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.

(11) Saltiel, J.; Marchand, G. R.; Kirkor-Kaminska, E.; Smothers, W. K.; Mueller, W. B.; Charlton, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3144.
(12) Scaiano, J. C.; Leigh, W. J.; Wagner, P. J.; Meador, M. A. *J. Am. Chem. Soc.* **1985**, *107*, 5806.
(13) (a) Wagner, P. J.; Kochevar, I. E. *J. Am. Chem. Soc.* **1968**, *90*, 2232. (b) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820.
(14) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769.