the number of molecules in that level at V–V steady state vs. the number at complete V–T/R equilibrium. As the temperature increases, high-energy states will retain a larger fraction of the overall vibrationally excited-state population at V–V steady state because their Boltzmann factors are increasing most rapidly with temperature. Thus, the V–T/R amplitude should increase with increasing temperature for levels fluorescing at 5.3 μm. The observed rate for this process, corresponding to 30 collisions, is about what would be expected for a medium-sized molecule with a low-lying vibrational frequency.

The decrease in 5.3-μm fluorescence intensity with the addition of argon is in marked contrast to the behavior of laser-pumped small molecules such as CH_3F, SO_2, CH_3Cl, or COF_2 which often show an increase in fluorescence intensity as rare gas is added. There are several possible explanations for this observation. While the most tempting is to suggest that argon collisions "kick" $(COF)_2$ molecules which would ordinarily fluoresce at 5.3 μm into background vibrational states with no oscillator strength at this wavelength, the fact that the overall decay rate does not change significantly with argon pressure argues against this explanation. Argon does not seem to compete favorably with parent gas in causing vibrational relaxation. This suggests that much of the collisional vibrational relaxation in $(COF)_2$ is controlled by resonant V–V energy transfer processes. Another explanation is that the argon simply broadens the spectral absorption lines causing a decrease in the absorption coefficient per unit frequency range. This assumes that a majority of the excitation arises from transitions in which the laser frequency is near the center of a vibration–rotation line. Although this assumption cannot be corroborated in $(COF)_2$ because of the unresolved and unassigned spectral features, the probability of such a coincidental match is clearly much higher for a molecule with a dense vibration–rotation spectrum than for a small relatively light molecule. Thus, adding a rare gas simply broadens the lines without adding any new absorbers. In contrast, a small molecule with less dense vibration–rotation levels usually does not have a

good laser–molecule match so that the addition of rare gas frequently broadens lines into coincidence with the laser.

Conclusions

(1) Intermode vibrational relaxation rates in $(COF)_2$ are extremely rapid.

(2) The observed temperature dependence of infrared fluorescence intensity and the overall rapid equilibration of the very large number of vibrational levels in $(COF)_2$ are consistent with an excitation mechanism in which the laser pulse produces excess population in a large number of vibrational levels by hot band pumping.

(3) While the observed fast risetime of all infrared fluorescence emissions in $(COF)_2$ is tantalizing evidence for collision-free intermode relaxation, the excitation of a ladder of levels with a spacing of the order of 120 cm^{-1} ($(COF)_2$ torsional frequency) followed by fast resonant collisional relaxation could also explain the rapid fluorescence risetimes.

(4) The relaxation behavior of nonrigid $(COF)_2$, in which intermode equilibration is complete in roughly five collisions, is in marked contrast to the behavior observed in rigid COF_2 where more than 300 collisions are required to fully equilibrate the vibrational levels.[13,14] The presence of a low-frequency torsional mode in $(COF)_2$, which leads to a very high density of vibrational levels at relatively low energy, appears to enhance intermode equilibration processes in $(COF)_2$.

COMMENTS

Photochemistry in Ultrahigh Laboratory Magnetic Fields. Photolysis of Micellar Solutions of Dibenzyl Ketones and Phenylbenzyl Ketones at 145 000 G. Observation of a $\Delta g\vec{H}$ Effect on the Cage Reaction

Sir: Although singlet ⇄ triplet intersystem crossing (isc) in *molecules* usually occurs via spin–orbit coupling,[1] the latter interaction is often so weak for many commonly encountered carbon-centered *radical pairs* (RP) that some mechanism other than spin–orbit coupling determines the rate of $^1RP \rightleftarrows {}^3RP$ processes. For example, the electron–nuclear hyperfine interaction (hfi) which contributes to the intersystem crossing of geminate radical pairs provides

the basis for the phenomenon of chemically induced dynamic nuclear polarization[2] and magnetic isotope effects on chemical reactions.[3]

A magnetic field dependence of reactions involving radical pairs is expected when the pairs are produced or encounter in a state of definite electronic spin multiplicity:[4] if the spin state of the pair is a singlet, *cage reactions* such as combination or disproportionation dominate, and if the spin state of the pair is a triplet, *escape reactions* such as

(1) (a) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978; pp 46 ff and 266 ff. (b) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(2) Reviews: (a) Buchachenko, A. L.; Zhidomov, F. M. *Russ. Chem. Rev.* **1971**, *408* 801. (b) Kaptein, R. *Adv. Free Radical Chem.* **1975**, *58* 381. (c) Lawler, R. G. *Acc. Chem. Res.* **1972**, *58* 25. (d) Closs, G. *Proc. Int. Congr. Pure Appl. Chem., 23rd* **1971**, *4*, 19.
(3) Buchachenko, A. L. *Russ. J. Phys. Chem.* **1977**, *55*, 1445.
(4) Reviews: (a) Buchachenko, A. L. *Russ. Chem. Rev.* **1976**, *45*, 375. (b) Hayashi, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2862. (c) Sagdeev, R. Z.; Salikhov, K. N.; Molin, Y. M. *Russ. Chem. Rev.* **1977**, *46*, 297. (d) Atkins, P. W.; Lambert, T. P. *Annu. Rep. Chem. Soc., Sect. A: Phys. Inorg. Chem.* **1975**, 67.
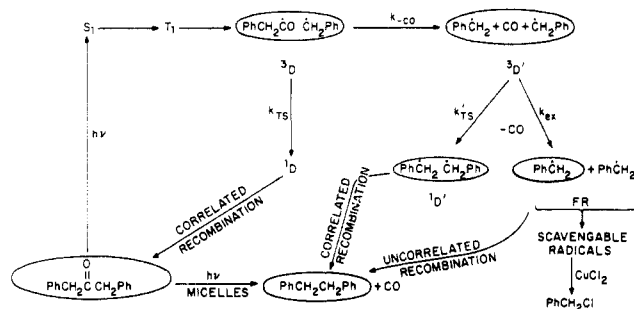
Figure 1. Working mechanism for the photolyses of DBK in micellar solution.

radical pair separation or radical pair transformation to another (triplet) radical pair dominate. Intersystem crossing (isc) may occur via coupling of the electronic spins of the pair to an "external" magnetic field (such as that provided by a laboratory magnet) or by an "internal" field (such as that provided by nearby magnetic nuclei or by the orbital motion of electrons). As the magnitude of an applied external field is increased from low field (i.e., the earth's magnetic field to several hundred Gauss) to high field (i.e., several thousand to tens of thousands of Gauss), the mechanism of triplet–singlet mixing in a triplet radical pair may switch from hyperfine induced $[T_+,T_-,T_0]$–S mixing at "low fields" to a hyperfine induced T_0–S mixing at "high fields", i.e., at sufficiently "high field" T_0–S mixing is still hyperfine induced, but $[T_+,T_-]$–S_0 mixing is inhibited by Zeeman splitting. Under "high field" conditions the rate of T_0–S mixing (ω_{T_0-S}) is approximated[9e] by eq 1,

$$\omega_{T_0-S} \sim \tfrac{1}{2}(\Delta g \mu_B \vec{H} + \Sigma a_i m_i - \Sigma a_j m_j) \qquad (1)$$

where $\vec{H}$ is the strength of the applied laboratory magnetic field, Δg is the difference in g factors of the individual odd electron centers of the radical pair, μ_B is the electron Bohr magneton, and a_i and a_j refer to the pertinent hyperfine coupling constants in radical i (with nuclear magnetic moments m_i) and in radical j (with nuclear magnetic moments m_j) of the radical pair.

Equation 1 indicates that at "ultrahigh" magnetic fields (i.e., when $\Delta g \mu_B \vec{H} \gg \Sigma a_i m_i - \Sigma a_j m_j$) the rate of T_0–S mixing will be given by eq 2. In such a situation T_0–S

$$\omega_{T_0-S} \sim \tfrac{1}{2}\Delta g \mu_B \vec{H} \qquad (2)$$

mixing is no longer induced by hyperfine interactions but is, instead, induced by Zeeman interactions. In the case of geminate radical pairs, if the rate of cage reactions (such as recombination or disproportionation) are much faster than the rate of T_0–S mixing, the latter will be the rate-determining process in the formation of cage products from triplet radical pairs. Hence, at "ultrahigh" fields the rate of formation of cage products may be determined by a Zeeman-induced mixing mechanism. The experiments reported here were initiated to determine whether the reactions of selected triplet radical pairs in micelle cages are determined by Zeeman-induced mixing at ultrahigh magnetic fields.

The working mechanism employed to interpret the results is given in Figure 1 for dibenzyl ketone as a prototype. For $C_6H_5CH_2COCH_2C_6H_5$ (DBK), $C_6H_5CH_2{}^{13}COCH_2C_6H_5$ (DBK-1-^{13}C) and $C_6H_5{}^{13}CH_2CO^{13}CH_2C_6H_5$ (DBK-$2,2'$-^{13}C), the pertinent radical pairs will be $C_6H_5\dot{C}H_2$ $\dot{C}H_2C_6H_5$, $C_6H_5\dot{C}H_2$ $\dot{C}H_2C_6H_5$, and $C_6H_5{}^{13}\dot{C}H_2$ ${}^{13}\dot{C}H_2C_6H_5$, respectively. Since each of these pairs possesses $\Delta g = 0$, the percent cage is expected to decrease and to possibly result in a limiting value determined by the competition between escape from the micelle and intersystem crossing. Indeed,

TABLE I: Laboratory Magnetic Field Effects on the Cage Reactions of Para-Monosubstituted Dibenzyl Ketones

| X	name	field strength,[a] G	cage,[b] %	Δg^c
CH_3	4-CH_3DBK	0	48 ± 3	3×10^{-5}
		14 500	25 ± 1	
		145 000	21 ± 1	
F	4-FDBK	0	34 ± 2	2.3×10^{-4}
		3 000	15 ± 1	
		145 000	16 ± 1	
Cl	4-ClDBK	0	52 ± 3	5.5×10^{-4}
		13 500	31 ± 1	
		145 000	37 ± 1	
Br	4-BrDBK	0	58 ± 4	2.1×10^{-3}
		13 500	58 ± 4	
		145 000	57 ± 1	
H	DBK	0	32 ± 2	0
		14 500	16 ± 1	
		145 000	13 ± 1	

[a] Experiments were conducted by photolyzing 0.002 M ketone in 0.05 M HDTCl samples either (1) within the gap of an Alpha Model 4500, 4-in. adjustable gap electromagnet (magnetic field below 15 000 G) or (2) within the 5-cm bore of a Bitter water-cooled solenoid capable of providing a field of 15 T at about 5 MW. [b] The cage effect is computed by product ratio. An asymmetrical ketone ACOB yields products AA, AB, and BB after decarbonylation; the cage effect is given by AB – (AA + BB)/AB + AA + BB. [c] A reference to Δg data: Berndt, A.; Fischer, H.; Paul, H. "Magnetic Properties Properties of Free Radicals"; Landolt-Bornstein, Springer-Verlag: Berlin, 1977; Group II, Vol. 9, part b.

this is the behavior for each of these ketones with a limiting value of 13 ± 1% cage being observed at 145 000 G.

In Table I, it is seen that substitution in the 4 position of the benzene ring of DBK leads to various results. For the radical pairs with the smallest values of Δg (X = CH_3, $\Delta g = 3 \times 10^{-5}$ and X = F, $\Delta g = 2.3 \times 10^{-4}$) the situation is similar to that for the parent DBK, i.e., a value of the cage effect is reached which approaches that expected for complete elimination of $[T_+,T_-]$–S mixing. In the case of X = Cl, the magnitude of Δg is relatively large, and an *increase* in percent cage occurs upon going from high fields to ultrahigh fields. In the case of X = Br, the radical pair possesses largest value of Δg for systems studied, *yet the percent cage is the same at low field and at ultrahigh fields*. We interpret this result to mean that a new mechanism, e.g., spin–orbit coupling, dominates isc. This result is consistent with the observation that the ^{1}H CIDNP spectrum of photoexcited BrDBK is very weak compared to those of DBK and CIDNP.

In Table II the influence of applied field strength on the percent cage produced in the photolysis (eq 3) of 1,2-di-

$$PhCOC(CH_3)_2Ph \xrightarrow[\text{micelles}]{h\nu} PhCHO + PhC(CH_3){=}CH_2 \qquad (3)$$
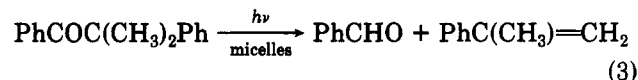
phenyl-2-methylpropanone (DPMP) and some isotopically substituted derivatives is summarized. In this case it has been shown that benzaldehyde and α-methylstyrene are produced exclusively in micellar cages.[7] It is found that, as for dibenzyl ketone, the cage effect is larger at 0 G than in a moderately strong field of 10 000 G. However, in the case of DPMP and the deuterated derivatives, DPMP-d_3 and DPMP-d_6, the cage effect displays a measurable *increase* at the ultrahigh fields at 145 000 G. These results, which are qualitatively similar to those for 4-ClDBK, also

(5) Atkins, A. *Chem. Br.* **1976**, *12*, 214.
(6) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369.
(7) Turro, N. J.; Mattay, J. *J. Am. Chem. Soc.* **1981**, *103*, 4200.

TABLE II: Effect of Laboratory Magnetic Fields on the Photolysis of 1,2-Diphenyl-2-methylpropanone and Its Isotopically Substituted Derivatives[a]

ketone	name	field strength,[b] G	cage,[c] %
$C_6H_5COC(CH_3)_2C_6H_5$	DPMP	0	30 ± 2
		10 000	19 ± 1
		145 000	23 ± 1
$C_6H_5COC(CH_3)(CD_3)C_6H_5$	DPMP-d_3	0	26 ± 2
		10 000	17 ± 1
		145 000	21 ± 1
$C_6H_5COC(CD_3)_2C_6H_5$	DPMP-d_6	0	23 ± 2
		10 000	14 ± 1
		145 000	20 ± 2
$C_6H_5{}^{13}COC(CH_3)_2C_6H_5$	DPMP-^{13}C	0	40 ± 2
		10 000	29 ± 1
		145 000	23 ± 1

[a] Δg for the $C_6H_5\dot{C}O\ \dot{C}(CH_3)_2C_6H_5$ radical pair is 1.4×10^{-3}; see ref c, Table I. [b] Photolysis conditions, see footnote a in Table I except [ketone] = 0.005 M. [HDTCl] = 0.15 M. [c] The cage effect is the yield of PhCHO (or $PhC(CH_3)=CH_2$) based on DPMP consumed.[7]

may be interpreted in terms of a ΔgH mechanism for isc at ultrahigh fields. Interestingly, the carbonyl ^{13}C-substituted derivative, DPMP-^{13}C, does not show a comparable effect. This may be because ^{13}C hyperfine induced isc still dominates at 10 000 G. Experiments at intermediate field strength are in progress to examine this possibility.

In summary, the extent of cage recombination of benzyl radical and/or substituted benzyl radical pairs produced in micelle aggregates depends on the strength of the external laboratory field applied to the sample. In the earth's magnetic field the percent cage is maximal, as expected if triplet benzyl radical pairs are produced initially and if (rate and product determining) intersystem crossing to a singlet benzyl radical pair is induced by electron–nuclear hyperfine interactions. In moderate to strong fields ($\sim$1000–20 000 G), the percent decreases because the T_+ and T_- states of radical pairs are inhibited, by Zeeman splitting, from intersystem crossing to singlet radical pairs. At ultrahigh fields, for systems with sufficiently large values of Δg and with sufficiently slow relaxation mechanisms, the ΔgH mechanism for intersystem crossing dominates and leads to an *increase* in the percent cage.[9]

(8) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Weed, G.; Kraeutler, B. *J. Am. Chem. Soc.* **1980**, *102*, 4843.

(9) Other systems have been examined in search of the ΔgH effect: (a) Buchachenko, A. L.; Markarian, S. A. *React. Kinet. Catal. Lett.* **1974**, *157*, 1. (b) Turro, N. J.; Chow, M.-F. *J. Am. Chem. Soc.* **1979**, *101*, 3701. (c) Broomhead, E. J.; McLauchlan, K. A. *J. Chem. Soc., Faraday Trans. 2* **1977**, *74*, 775. (d) Sagdeev, R. Z. et al. *Org. Magn. Reson.* **1973**, *5*, 599, 603. (e) Sakuragi, H. et al. *Chem. Lett.* **1975**, 231. *Chem. Phys. Lett.* **1976**, *41*, 267. (f) Chidsey, C. E. D.; Roelofs, M. G.; Boxer, S. G. *Ibid.* **1980**, *74*, 113.

Chemistry Department   **Nicholas J. Turro***
Columbia University   **Chao–Jen Chung**
New York, New York 10027
Chemistry Department   **Guilford Jones, II***
Boston University   **William G. Becker**
Boston Massachusetts 02215

ADDITIONS AND CORRECTIONS

1981, Volume 85

William G. Valance: Diatomic Molecule Dissociation. A Vibrating-Rotor Theory Including Nonequilibrium Effects.

Page 1306. The units of α in Table I are reciprocal Ångstroms.

Page 1307. The expression for E_a in footnote b of Table II should be identical with eq 25, p 1309. Note that eq 25 does not depend on the interaction potential parameters.

Page 1307. When the magnitudes in the original Table III are recalculated by using $q = 0.10$ (except where otherwise indicated) and indicated values of $\bar{A}$, the results in the enclosed Table III were obtained.

Page 1309, eq 20. While the activation energies do not depend significantly on the potential parameters (cf. eq 25 and Table II), the potential parameters q and $\bar{A}$ control the magnitude of the rate constant. The parameters q and L (cf. eq 16) for each diatomic molecule were not varied

TABLE III: Magnitudes of the Theoretical Rate Constant at Selected Temperatures

X_2	$\bar{A}$	T, K	$k_d/(Ar)$ cm^3 molecule^{-1} s^{-1}
H_2	1.0	2699	2.1×10^{-7}
		3479	1.4×10^{-15}
N_2	100	5764	1.2×10^{-17}
		9164	0.7×10^{-14}
O_2	51	4819	2.3×10^{-15} [a]
Cl_2	140	1968	1.0×10^{-15}
Br_2	2.0	1145	2.2×10^{-18} [b]
F_2	2.5	1773	2.2×10^{-14}

[a] $q = 0.20$ for O_2. [b] $q = 0.07$ for Br_2.

to find the values of these parameters and precise expressions for k_d which best fit experimental values for each diatomic. Instead physically reasonable values for q and L were selected to obtain the magnitudes of Table III. A value of $q = 0.10$ reasonably reproduces the experimental values. Smaller (more in line with the classical results of