D_2O to give HD (mass spectrum).

(11) 1-Methyl-3-butylcyclohexane (12%) was also formed in this reaction, no doubt analogously to the 1-methyl-3-butylcyclopentane formed from 1,5-hexadiene (J. J. Bahl, R. B. Bates, W. A. Beavers, and N. S. Mills, *J. Org. Chem.*, **41**, 1620 (1976)).

(12) ^{1}H NMR showed the deuteriums to be in the methylene and methyl groups as expected for **11b**.

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Amendment of the CIDNP Phase Rules. Radical Pairs Leading to Triplet States[1]

Sir:

One of the assumptions in the radical-pair theory of chemically induced dynamic nuclear polarization (CIDNP)[2,3] is that the probability of annihilation of the radical pair is proportional to the singlet character of the pair. This assumption is certainly valid when the radical pair is destroyed by a pair combination or disproportionation reaction. In these cases the triplet state of the product is generally antibonding or at least energetically inaccessible. In this communication we want to discuss and demonstrate an important ambiguity in the interpretation of CIDNP spectra which may arise in cases where the radical pair is of higher energy than the triplet state of the reaction product.

Inclusion of this possibility leads to four reaction sequences

$$S_r \rightarrow RP \rightarrow S_{pr} \qquad (1)$$

$$T_r \rightarrow RP \rightarrow S_{pr} \qquad (2)$$

$$S_r \rightarrow RP \rightarrow T_{pr} \rightarrow S_{pr} \qquad (3)$$

$$T_r \rightarrow RP \rightarrow T_{pr} \rightarrow S_{pr} \qquad (4)$$

Sequences 1 and 2 describe the conventional CIDNP experiments where S_r and S_{pr} are the singlet states of reactant and product, respectively, and T_r is the triplet reactant and RP is the radical pair. If the radical-pair state lies above the triplet state of the product, two other pathways (3 and 4) become available where T_{pr} is the triplet state of the product. Since sequences 1 and 4 involve no intersystem crossing in the radical pair, they give the same CIDNP spectra. Similarly, sequences 2 and 3 give indistinguishable spectra because each involves intersystem crossing in the pair state. For a given experimental spectrum the precursor multiplicity cannot be assigned unless the multiplicity of the exit channel is also defined. It is therefore necessary to amend the qualitative polarization phase rules formulated by Kaptein[4] by an "exit channel" factor, γ, which is positive for the singlet exit channel and negative for triplet. All other parameters remain the same.

It has been recognized for some time[5] that the fluorescence quenching of photoexcited aromatic hydrocarbons by electron donors proceeds by charge transfer and may lead to the triplet hydrocarbon faster than can be rationalized by either intersystem crossing in unquenched singlet hydrocarbon or diffusional recombination of hydrocarbon radical anions with donor radical cations in the bulk solution. A well-studied system exhibiting this behavior is pyrene as acceptor with aniline derivatives as donors.[5-7] We have chosen this system to investigate the CIDNP effect as a case where the predominant exit channel of the radical pair has been clearly established to be the triplet state of pyrene.

When a 10^{-2} M solution of pyrene containing 10^{-1} M *N,N*-diethylaniline in acetonitrile-d_3 is irradiated in the probe of an FT NMR spectrometer, the pyrene transitions broaden[8] and appear in enhanced absorption (Figure 1). The aromatic and methylene protons of diethylaniline are also broadened while the methyl protons remain sharp. The broadening of the pyrene signals is caused by electron exchange between pyrene radical anion and ground-state pyrene[10] resulting in a reduction of the T_2 of the pyrene protons. Similarly, exchange between the diethylanilinium radical ion and diethylaniline causes broadening of the diethylaniline signals. Because CIDNP is related to T_1 it is possible[11] to eliminate the broadening but retain the polarization by sampling the magnetization after the light has been shut off. Thereby, the radicals decay within milliseconds while the CIDNP effect remains observable for seconds (T_1). The result is shown in Figure 1. Besides the strong enhanced absorption of the pyrene signals, a weak enhanced absorption of the diethylaniline methylene protons (~30%) is noticeable as well as a reduction in the aromatic proton intensities.[12]

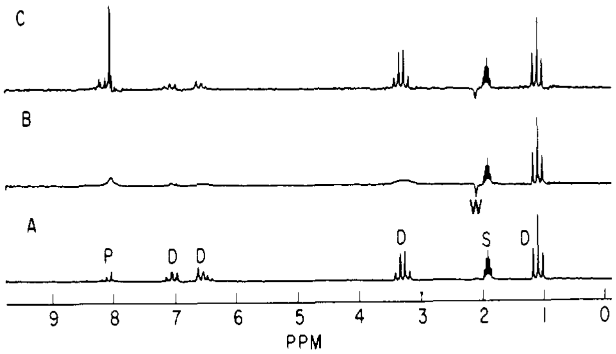

Figure 1. 90-MHz ^{1}H FT NMR spectra of 10^{-2} M pyrene and 10^{-1} M *N,N*-diethylaniline in CD_3CN (P = pyrene, D = diethylaniline, W = water[9] and S = solvent): (A) initial dark; (B) during irradiation; and (C) 0.5 s after termination of irradiation as explained in text.

If one were to interpret the results using the conventional rules,[4] one would deduce from the *g*-factor difference and signs of the hyperfine interaction[13] that triplet pyrene was undergoing charge-transfer quenching with diethylaniline via pathway 2. This is unacceptable for two reasons. First, electrochemical potentials for the reduction[14] of pyrene and oxidation[15] of diethylaniline put the radical-ion pair 0.7 V above triplet pyrene[16] making charge transfer to the triplet state several orders of magnitude slower than its decay rate. Second, fluorescence studies carried out in our laboratory and elsewhere[17] show that under the conditions of the NMR experiments >95% of the singlet pyrene is quenched. Consequently, in line with the conclusions of previous investigators,[5-7] the reaction sequence occurs via pathway 3, where the radical-ion pair is formed from the singlet state of pyrene and is predominantly annihilated via the triplet state. Interestingly, although the energetics allow the ion pair to exit to either the singlet or triplet state of the product, the latter is preferred.[18] Other donors such as 3,5-dimethoxy-*N,N*-dimethylaniline[7] behave the same way. We obtained similar results in the photochemical charge transfer between naphthalene and 1,4-diazabicyclo[2.2.2]octane (Dabco).

In conclusion, it appears necessary to supplement CIDNP results with information such as quenching kinetics, redox potentials, and excited-state energies before conclusions on the electronic multiplicity of the intercepted state in charge-transfer reactions can be reached.[19]

References and Notes

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(6) M. E. Michel-Beyerle et al., *Chem. Phys.*, **17**, 139 (1976).

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(8) Paramagnetic broadening in CIDNP spectra has also been observed by Roth. See H. D. Roth and A. A. Lamola, *J. Am. Chem. Soc.*, **96**, 6270 (1974); H. D. Roth and M. L. Manion, *ibid.*, **97**, 6886 (1975).

(9) The polarization of water is assumed to arise from proton exchange between water and the pyrene radical anions which escape the singlet pair. The net reaction leads to ground state pyrene.

(10) The broadening may also contain a contribution from the exchange of triplet excitation between triplet pyrene and ground state pyrene. See M. Cocivera, *Chem. Phys. Lett.*, **2**, 529 (1968); S. G. Boxer and G. L. Closs, *J. Am. Chem. Soc.*, **97**, 3268 (1975).

(11) The method described was first executed in a similar study by S. G. Boxer formerly of this laboratory.

(12) The weaker polarization of diethylaniline compared to pyrene arises, at least in part, from more effective exchange which leads to cancellation of geminate and escape polarization.

(13) Pyrene$^{-}\cdot$: $g = 2.0027$ included in M. S. Blois, Jr., M. W. Braun, and J. E. Maling, *Arch. Sci.*, **13**, Spec. No. 243–255 (1960); *Chem. Abstr.*, **57**, 1770e (1960). The hyperfine coupling constants (hfcs) are $A^{H}{}_{1} = -4.75$ G, $A^{H}{}_{4} = -2.08$ G and $A^{H}{}_{2} = +1.09$ G. See G. J. Hoijtink, J. Townsend, and S. I. Weissman, *J. Chem. Phys.*, **34**, 507 (1961). *N,N*-Diethylaniline$^{+}\cdot$(D$^{+}\cdot$): estimated $g = 2.0040$. The hfcs are expected to be similar to those of *N,N*-dimethyl-*p*-toluidinium radical cation where $A^{H}{}_{CH_3} = 12.20$ G (to be used for the methylene groups of D$^{+}\cdot$), $A^{H}{}_{ortho} = 5.30$ G, and $A^{H}{}_{meta} = 1.35$ G. See E. T. Seo et al., *J. Am. Chem. Soc.*, **88**, 3498 (1966); B. M. Latta and R. W. Taft, *ibid.*, **89**, 5172 (1967). The methyl groups of D$^{+}\cdot$ are expected to have $A^{H}{}_{CH_3} < 1$ G; see ref 8.

(14) $E_{red} = -2.05$ V vs. SCE (CH_3CN): R. Dietz and M. E. Peover, *Trans. Faraday Soc.*, **62**, 3535 (1966).

(15) $E_{ox} = +0.76$ V vs. SCE (CH_3CN): D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).

(16) E_T (pyrene) = 2.09 eV as determined from the 0–0 phosphorescence band: D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

(17) H. Schomburg, H. Staerk, and A. Weller, *Chem. Phys. Lett.*, **22**, 1 (1973).

(18) For a plausible explanation of this effect, see ref 6.

(19) H. D. Roth (*Mol. Photochem.*, **5**, 91 (1973)) reports an experiment by G. N. Taylor on charge transfer of naphthalene and *trans*-1,2-dicyanoethylene where the products, *cis*- and *trans*-dicyanoethylene, show opposite polarization. He interprets this result by assuming a triplet exit channel for the rearranged compound while the reactant is regenerated from the singlet radical-ion-pair state. While this interpretation may be correct, little evidence was advanced in support of this scheme.

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Photolysis of Aryldiazomethanes in Alcoholic Matrices. Temperature and Host Dependences of Phenylcarbene Processes in Alcohols

Sir:

It is generally accepted that carbene generated in alcohols inserts into the O–H bond rather than the C–H bonds of the alcohol to give ether,[1] and hence the detection of the ether in an alcoholic reaction system in which carbene seems to be involved has been strong evidence[2] for the intervention of carbene intermediate. In the present communication we wish to report, however, that the O–H insertion reaction of carbene is highly temperature dependent and the C–H insertion products become dominant at the expense of the O–H insertion product in low temperature alcoholic matrices. Interestingly, we also found that carbene processes in low temperature matrix are highly sensitive to host effects.

Irradiation[3] of phenyldiazomethane **1** in degassed 2-propanol in a quartz tube at 20 °C gave 2-propyl benzyl ether (77%) as a main product. In contrast, irradiation[3] of **1** in frozen 2-propanol matrix at −196 °C resulted in the C–H insertion products (**5α** and **5β**) in high yield (78%) and the yield of the ether was greatly reduced (15%). Toluene **3** and bibenzyl **4** were also formed as minor products in each experimental condition.

Table I. Temperature Dependence of Product Distributions in the Photolysis[a] of **1** in Alcohols

ROH	*T*, °C	Relative product yields,[b] %				
		2	**3**	**4**	**5α**	**5β**
MeOH	0	92.6	3.4	2.8	1.1	
	−72	90.3	2.3	3.5	3.9	
	−110	74.0	4.3	1.0	20.7	
	−196	52.9	6.0	0.8	40.3	
EtOH	0	87.1	5.0	3.3	4.6	Trace
	−72	82.7	4.6	2.0	10.7	Trace
	−110	74.1	5.0	1.9	17.8	1.2
	−196	20.8	9.8	0.4	64.2	4.8
i-PrOH	0	72.4	3.8	6.7	16.6	0.5
	−72	51.6	5.8	13.7	28.1	0.9
	−110	35.7	5.2	2.0	46.3	10.8
	−196	14.7	5.6	1.3	63.8	14.7

[a] All products were identified by gas chromatography (2.5 m × 5 mm 5% OV-17 column) comparisons with authentic samples and by GC–mass spectroscopy techniques. Control experiments demonstrated that product distributions were essentially independent of irradiation time as well as wavelength of light. [b] Total product yields are ~70–80%. Other products (<5%) were benzaldehyde, the azine, and stilbenes derived from **1**.

$$\underset{\mathbf{1}}{PhCH{=}N_2} \xrightarrow[ROH]{h\nu} \underset{\mathbf{2}}{PhCH_2OR} + \underset{\mathbf{3}}{PhCH_3} + \underset{\mathbf{4}}{(PhCH_2)_2}$$

$$+ \underset{\mathbf{5\alpha}}{PhCH_2CR_1R_2(OH)} + \underset{\mathbf{5\beta}}{PhCH_2CH_2CHR_3(OH)}$$

a, R = Me; $R_1 = R_2 = H$
b, R = Et; R_1 = Me; $R_2 = R_3 = H$
c, R = *i*-Pr; $R_1 = R_2 = R_3$ = Me

The product distributions in other alcohols (i.e., methanol and ethanol) were also examined as a function of temperature in more detail and the results shown in Table I demonstrated that the temperature dependence of regioselectivity of carbene insertion reactions is quite general in each system studied. Diphenyldiazomethane (**6**) showed analogous behavior. A parallel series of irradiations[3] with 1-phenyldiazoethane in 2-propanol, however, showed that the C–H insertion products were also formed only in solid run at −196 °C, but as minor components (20%), and a main product was styrene (72%). From Table I it can be seen that the ethers decrease monotonously as the temperature is lowered in solution phase and drastic alterations in product distributions are observed when the reaction phase is changed from liquid to solid. Also striking is the significant increase in the C–H insertion product (**5**) yield in solid-phase experiments as temperature is lowered to −196 °C, although these reaction mixtures (in methanol and 2-propanol) appear solid at −110 °C.[4]

It has been proposed[1a] that the O–H insertion is the characteristic reaction of singlet phenylcarbene. There are ample examples,[1,5] on the other hand, that triplet phenylcarbene abstracts hydrogen in hydrocarbon solution to give toluene and bibenzyl via free benzyl radical. We suggest here that the key intermediate leading to the C–H insertion products in the solid-phase experiments is also triplet phenylcarbene since there have been spectroscopic[6] and chemical[5] evidences for the presence of the ground-state triplet carbene in the low temperature matrix photolysis of **1** at −196 °C.[7,8] The presence of triplet carbene also accounts for the observed selective[9] insertion into the secondary and tertiary C–H bonds compared with the primary. Thus we suggest the abstraction-recombination mechanism rather than the direct insertion to rationalize formation of **5** in the matrix experiments. The observed difference in the chemical behavior of triplet carbenes generated in the liquid and solid phases, then, reflects, at least in part, on the mobility of members of radical pairs. It is possible that the triplet carbene formed in the solid-phase abstracts hydrogen