should be qualitatively reliable for the nonconjugated cations (entries 4–6, 13, 14, 16, 17, 19, and 20).

The π-donor effect of the cyano group is rapidly attenuated with successive introduction of methyl groups (entries 1–3). That is, the most stable cations are destabilized most by the cyano group. This occurs since the inductive effect drops off only slowly as the cation is stabilized whereas the π-donor effect is rapidly diminished as the cation LUMO is destabilized by donor alkyl groups.

Each methyl group attenuates the stabilization due to π donation of the cyano group by 4–5 kcal/mol. Reduced π donation is reflected in a shortening of the CN bond length by ~0.013 Å, and a lengthening of the C–C$^+$ bond by 0.025 Å per methyl group. For $^+CH_2CN$, π donation is stabilizing by 15–20 kcal/mol, assuming that the inductive destabilization of $^+CH_2CN$ is about 5 kcal/mol greater than that for the β-cyanomethyl cation.

With the formyl substituent, calculations at the STO-3G level predict an unrealistic stabilization of 16 kcal/mol (entry 7) in the formylmethyl cation whereas the 4-31G calculation predicts destabilization, but to a lesser extent than is observed with cyano. When the formyl group is rotated 90° out of planarity, an additional 5 kcal/mol destabilization results (entry 8). This is to be expected since π-conjugated effects are now absent. Introduction of methyl groups again attenuates the π donation of the formyl group by ca. 3 kcal/mol (entries 7, 9, and 11; 4-31G results) per methyl group. Although the geometry of the $^+CH_2CHO$ species reflects substantial π donation by the formyl group, the C=O bond length of $^+(CH_3)_2CCHO$ is lengthened by only 0.009 Å with respect to that in 2-methylpropanal, which indicates little or no π delocalization in this cation. These data, together wth those of entries 13 and 14, indicate that the inductive effect of the formyl group destabilizes the methyl cation by ≥19 kcal/mol, and π donation stabilizes the same group by ≥13 kcal/mol.

Thus, the smaller destabilization of an α cation by formyl than by cyano is a result of the larger σ-electron withdrawal by cyano, which is only partially counteracted by the greater π donation by cyano. Geometric changes, charge densities, and overlap populations as well as energetic estimates made earlier for the cations confirm the greater π donation by cyano. For example, the $^+C_\alpha$–C bond length contracts by 0.098 Å in the cyanomethyl cation but only by 0.047 Å in the formylmethyl cation (Figure 1). The π charge at the cationic center is +0.71 in the cyanomethyl cation and +0.83 in formylmethyl although the total charges on the CH_2 groups are in the opposite direction, +0.71 and +0.67, respectively.

A substituent usually thought to be purely inductively electron withdrawing, CF_3, has a larger destabilizing influence on cations than CN or CHO, but calculations performed at the STO-3G level imply that even CF_3 shows abnormally low destabilization of an α cation as compared to a more remote cation. Our results indicate that CF_3 is intermediate between CN and CHO in σ-withdrawing ability (as reflected in σ^* values)[15] but provides much less resonance stabilization when α to a cationic center. The 2,2,2-trifluoromethyl cation is distorted in exactly the same fashion as the ethyl cation.[16] However, very little π density (0.04 electron density) resides in the cation p orbital compared with the cyano and formyl cations (0.21 and 0.24 electrons, respectively). At the 4-31G level, the 2,2,2-trifluoroethyl cation is destabilized by 37 kcal/mol. This result indicates that there is no hyperconjugative stabilization by the trifluoromethyl group.

The potential π-donor[6] effect of the ammonio substituent is suggested at the STO-3G level by the typical hyperconjugatively distorted geometry of the dication, especially the shortened CN bond as compared to that in the methylammonium cation. However, this effect is small energetically: pure coulombic interactions between two plus charges located at the distance separating N and C$^+$ in the γ, β, and α ammonio cations would destabilize these species by 87, 135, and 209 kcal/mol; calculations with the STO-3G basis set indicate destabilizations of 105, 135, and 172 kcal/mol, respectively.

In summary, we emphasize again that the π-donor effect of CN and carbonyl substituents is only manifested when these substituents are attached to very unstable cations. For this reason, the π-donor effect of groups is not easily detected in "classical" systems designed to prove substituent effects. For example, σ_p and σ_p^+ constants for CN, CO_2Et, and CF_3 are quite similar (σ_p = 0.66, 0.45, and 0.54; σ_p^+ = 0.66, 0.48, and 0.61, respectively).[6b] Since the cyclohexadienyl cation is highly stabilized, the π-donor effects of these substituents are largely suppressed.

Hydrogen bonding of hydroxylic solvents to the heteroatoms of groups such as cyano, formyl, or trifluoromethyl should exacerbate the destabilization of cations. For example, the CH_3C-HO···HOH hydrogen bond has an energy of 6 kcal/mol, whereas no stable hydrogen-bonding minimum is found for the corresponding cation. On the other hand, polar solvents will stabilize cations through direct (electrostatic or overlap) effects on the cationic center, and this will level differences in stabilization of cations. Schleyer et al. found that approximately 40–50% of the stabilization of the allyl cation caused by methyl groups appears in the transition state of solvolysis reactions.[11]

The strong acceleration of S_N2 reactions by α-cyano and carbonyl substituents[17] may also be related to the phenomena described here. That is, in a transition state where little or no plus charge is built up on the center undergoing substitution, but considerable p-orbital character develops, then cyano and carbonyl groups can provide large conjugative stabilization of the transition state, just as a vinyl substituent does, without the necessity of secondary orbital interactions.

In the full account of this work, the optimized structures of many of these species will be reported, along with a more complete survey of electron-withdrawing group effects on cations.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and to Professor R. A. More O'Ferrall for stimulating discussions.

(14) For example, STO-3G calculations overestimate the stabilization of $^+CH_2F$ by 30 kcal/mol but of $^+CH_2CH_3$ by only 1 kcal/mol, relative to 4-31G calculations: Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291.

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(17) See the references given in footnote 1 of ref 1 and footnote 3 of ref 3.

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Dynamics and Energetics of the Singlet–Triplet Interconversion of Diphenylcarbene

Sir:

Numerous calculations of the energy spacing separating the lowest singlet and triplet states of carbenes have been reported.[1] In contrast, almost no quantitative experimental information is available concerning the dynamics of interconversion or the energetic separation of the triplet and singlet states of carbenes, although many investigations of the products arising selectively from one of the two spin states have appeared. From competition experiments and kinetic analysis of the reactions of diphenylcarbene (DPC), it has been suggested that singlet diphenylcarbene

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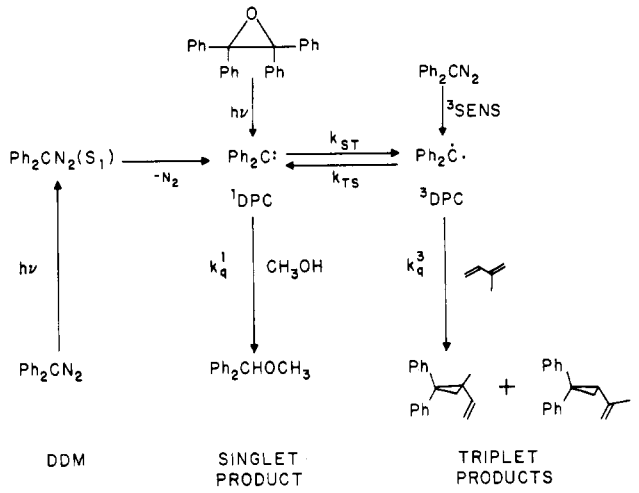
Scheme I



(^{1}DPC) and triplet diphenylcarbene (^{3}DPC), the ground state, exist in rapid equilibrium during most reactions (Scheme I).[2] A pioneering flash spectroscopic study of DPC by Closs and Rabinow[3] has supplied an estimate of the upper limit for the equilibrium constant; however, the absolute rate constants for interconversion of the spin states of DPC were not measured due to the ultrafast rate constant (k_{ST}) of the ^{1}DPC $\rightarrow$ ^{3}DPC process, which was estimated to be on the order of 10^{10} s^{-1}. It is therefore necessary to employ picosecond laser methods to measure k_{ST}. We have combined picosecond laser measurements with quenching experiments, nanosecond flash measurements, and triplet sensitization experiments to evaluate both k_{ST} and the rate constant (k_{TS}) for the ^{3}DPC $\rightarrow$ ^{1}DPC process in acetonitrile solvent at ambient temperature. From knowledge of k_{ST} and k_{TS}, the equilibrium constant and free energy of the ^{1}DPC $\rightleftarrows$ ^{3}DPC system have been evaluated.

We have investigated the system described in Scheme I by using methanol and isoprene (IP) as selective ^{1}DPC and ^{3}DPC traps, respectively. Alcohols are generally accepted to react with ^{1}DPC to yield ethers by OH insertion,[3,4] and 1,3-dienes[3,5] have been shown to be efficient traps of triplet carbenes. We have found that the ratio of the two isomeric cyclopropanes formed upon reaction of DPC with isoprene is independent of isoprene concentration in the range 10^{-1}–10 M. Furthermore, the same ratio of cyclopropanes is produced by direct excitation or triplet sensitization[6] of diphenyldiazomethane in the presence of a high concentration of CH_3OH and a low concentration of isoprene. These results define isoprene as a selective trap of ^{3}DPC.

The occurrence of a rapid equilibrium and the spin state selective reactions predict the ratio of the quantum yield of triplet products ($^3\phi$) to the quantum yield of singlet products ($^1\phi$) will obey eq 1. Thus, if the equilibrium ^{1}DPC $\rightleftarrows$ ^{3}DPC is rapid

$$^3\phi/^1\phi = \frac{k_{ST}}{k_{TS} + k_q^3[\mathrm{IP}]}\,\frac{k_q^3[\mathrm{IP}]}{k_q^1[\mathrm{CH_3OH}]} \qquad (1)$$

relative to reactions with CH_3OH and isoprene, a plot of $^3\phi/^1\phi$ vs. the concentration of isoprene, [IP], is expected to exhibit two

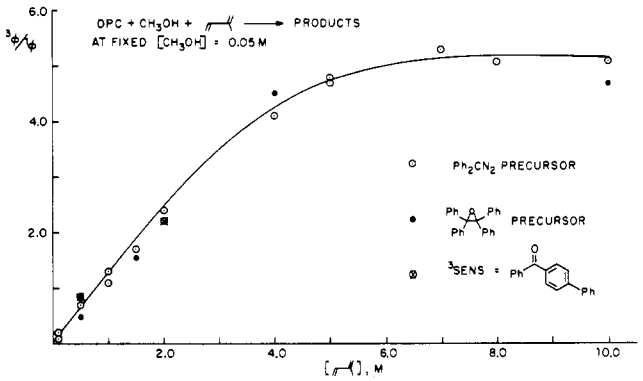


Figure 1. The ratio of cyclopropanes to ether ($^3\phi/^1\phi$) formed by reaction of DPC in acetonitrile solvent, at fixed (0.05 M) concentration of methanol and variable concentrations of isoprene.

limiting domains. In the first domain for which $k_{TS} \gg k_q^3[\mathrm{IP}]$, eq 1 reduces to eq 2.

$$^3\phi/^1\phi = \frac{k_{ST}}{k_{TS}}\,\frac{k_q^3[\mathrm{IP}]}{k_q^1[\mathrm{CH_3OH}]} \qquad (2)$$

In this domain, the slope of a plot of eq 2 yields a value for the quantity $(k_{ST}/k_{TS})(k_q^3/k_q^1[\mathrm{CH_3OH}])$. In the second domain, $k_{TS} \ll k_q^3[\mathrm{IP}]$ and eq 1 reduce to eq 3.

$$^3\phi/^1\phi = \frac{k_{ST}}{k_q^1[\mathrm{CH_3OH}]} \qquad (3)$$

DPC was generated by the direct photochemical excitation of either diphenyldiazomethane (DDM)[7] or tetraphenyloxirane (TPO)[8] in the presence of a fixed concentration of methanol (0.05 M) and with varying amounts of isoprene. From the yields of cyclopropanes and diphenylmethyl methyl ether (Scheme I), the ratio $^3\phi/^1\phi$ was computed as a function of [IP]. From Figure 1, it can be seen that a plot of the form expected from eq 1 is obtained. Support for the intermediacy of free DPC is provided by the observation that direct irradiation of either DDM or TPO yields experimentally indistinguishable values of $^3\phi/^1\phi$. Evidence for a rapid ^{1}DPC $\rightleftarrows$ ^{3}DPC equilibrium relative to reaction (in the first domain) is provided by the observation that triplet sensitization of the decomposition of DDM yields the same values of $^3\phi/^1\phi$ as direct photolysis of DDM.[6]

From the data in Figure 1 and use of eq 2 and 3 for the appropriate domains, we compute $(k_{ST}/k_{TS})(k_q^3/k_q^1) = (5.5 \pm 0.8) \times 10^{-2}$, $k_{ST}/k_q^1 = 0.26 \pm 0.04$ M, and $k_q^3/k_{TS} = 0.21 \pm 0.03$ M^{-1}. The absolute rate constant k_q^3 was determined to be $(3.5 \pm 0.5) \times 10^5$ M^{-1} s^{-1} by nanosecond laser flash spectroscopy.[9] Thus, k_{TS} is calculated to be $(1.7 \pm 0.3) \times 10^6$ s^{-1}.

The magnitude of k_{ST} was determined by picosecond laser induced fluorescence.[10] A frequency-quadrupled (266 nm) Nd^{3+}:YAG laser pulse (fwhm $\leq$ 25 ps) was used to generate ^{1}DPC by photodissociation of DDM. A weak picosecond probe pulse at 266 nm was used to monitor the buildup of ^{3}DPC by laser-

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(6) Triplet photosensitized reactions were conducted with solutions containing appropriate amounts of methanol and isoprene and DDM ($\sim 2 \times 10^{-3}$ M) and 4-phenylbenzophenone ($\sim 1.5 \times 10^{-2}$ M). Light from a 150-W high-pressure xenon lamp was passed through a combination of Corning filters 7-51 and 0-52.

(7) (a) Direct irradiation of diphenyldiazomethane ($\sim 2.5 \times 10^{-3}$ M) in a nitrogen-purged acetonitrile solution containing methanol (0.05 M) and isoprene (0.10–10 M) gave the products indicated in Scheme I (VPC analysis). In addition, minor amounts of diphenylmethane and benzophenone were detected, but no benzophenone azine, tetraphenylethylene, or tetraphenylethanes. (b) We have assumed that direct irradiation of diphenyldiazomethane leads initially to ^{1}DPC quantitatively. This is strongly supported by our picosecond studies.

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(9) For the nanosecond flash experiments, [DDM] equals $\sim 1 \times 10^{-4}$ M in vacuum-degassed acetonitrile. The spectroscopic setup is of a standard design, and employed a Lambda Physik excimer laser as the excitation source (KrF lasing medium, 249 nm, $\sim$200 mJ/pulse, fwhm 18 nanosecond). For a more detailed description of the setup, see: Turro, N. J.; Aikawa, J.; Butcher, J. A., Jr. *IEEE J. Quantum Electron.*, in press.

(10) Korenowski, G. M.; Dupuy, C.; McAuliffe, M. J.; Hetherington, W.; Eisenthal, K. B., unpublished results.

induced fluorescence. The buildup of triplet fluorescence intensity was measured as a function of the time separation between the excitation and the probe pulses, and allowed analysis of the appearance of ^{3}DPC. The value of k_{ST} measured by this method was found to be $(9.1 \pm 1) \times 10^9$ s^{-1}.

Combining the value of k_{ST} with that for k_{ST}/k_q^1 (measured from Figure 1) allows evaluation of $k_q^1 = (3.5 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1}. The latter is very close to the value for diffusion-controlled reaction in acetonitrile. From knowledge of k_{ST} and k_{TS}, the equilibrium constant for the process ^{1}DPC $\rightleftarrows$ ^{3}DPC is computed to be $(5.4 \pm 1) \times 10^3$, with an associated free-energy difference of 5.1 ± 1 kcal/mol at 25 °C.

These values may be compared to the estimates of Closs and Rabinow,[3] who, with the assumption of a diffusional quenching constant of 5×10^9 M^{-1} s^{-1} of ^{1}DPC by methanol in benzene, computed an equilibrium constant of 5×10^2. The difference between our direct experimental value and the indirect measurement of Closs and Rabinow[3] may reflect a small solvent effect on the equilibrium constant.[11] Our steady-state data for the quantity $k_{ST}/(k_q^1 k_{TS})$ was found to be 1.6×10^{-7} Ms in acetonitrile, and we compute a value of 1.0×10^{-7} Ms for this quantity from published data.[3]

Acknowledgment. We thank the National Science Foundation and the Air Force Office of Scientific Research for their generous support of this research. K.B.E. also acknowledges the support of the Joint Services Electronic Program.

(11) **Note Added in Proof**: Equation 1 may be inverted to yield an expression for $^1\phi/^3\phi$ which is a linear function of 1/[IP] at constant methanol concentration. Evaluation of the rate constants of Scheme I by fitting this expression leads to values which are in even closer agreement to the estimates of Closs and Rabinow[3] than the values achieved employing eq 1.

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Mobility of Solvent Molecules in a Nonaqueous Lyotropic Liquid Crystal

Sir:

The binary system composed of phosphatidylcholines (lecithins) and water is known to exhibit several phases,[1] and this system has been studied by a variety of techniques,[2] including NMR.[3] Recently, we have found[4] that the important aqueous lyotropic liquid crystalline phase, exhibited by lechithins, has a nonaqueous counterpart, and we are currently undertaking a research program to delineate and characterize this new phase.

Deuterium NMR quadrupole splittings and spin–lattice relaxation times have been found to be very useful for characterizing the aqueous lecithin phases,[5] and we have made preliminary ^{2}H NMR studies on the lamellar liquid crystalline phase formed by dilinoleyllecithin (L) and ethylene glycol-d_4 (EG) at 20 °C. The ^{2}H NMR parameters are presented in Table I for sample compositions that span the range of stability of the phase. The results shown in Table I are indicative of increased motion, on the average, with increased EG content. However, we wish to analyze both the concentration dependence and the magnitude of the splittings in terms of models. It is of interest that a very simple model appears to account for the concentration dependence of the splittings in Table I. Consider EG interacting with the L head group to form a 1:1 complex, in which all L sites are filled, and the remaining EG exists in a "free" state. Rapid exchange between "bound" and "free" EG is assumed so that NMR parameters are weighted averages over the two sites. The splittings in bound and free sites are $\Delta\nu_B$ and $\Delta\nu_F$, respectively, and the fraction of bound EG is p_B = [mol of EG/mol of L]$^{-1}$. The observed splitting $\Delta\nu$ is given by eq 1. If both $\Delta\nu_B$ and $\Delta\nu_F$ are concentration independent, then a plot of $\Delta\nu$ vs. p_B will be linear. Such a plot is shown in Figure 1, wherein it can be seen that the plot is linear within experimental error. An analogous treatment for spin–lattice relaxation predicts eq 2, and the appropriate plot is also shown in Figure 1. It can be seen that this plot is linear within experimental error. The parameters characterizing bound and free sites are obtained from the intercepts in Figure 1, and these are shown in Table II.

$$\Delta\nu = p_B(\Delta\nu_B - \Delta\nu_F) + \Delta\nu_F \quad (1)$$

$$1/T_1 = p_B(1/T_{1B} - 1/T_{1F}) + 1/T_{1F} \quad (2)$$

There are several interesting results that are obtained within the context of this simple model. First, $\Delta\nu_B$ and $\Delta\nu_F$ are inde-

Table I. Deuterium NMR Parameters[a] for Lecithin/Ethylene Glycol-d_4 Liquid Crystalline Phase

wt percentage L:EG	mol of EG/ mol of L	quadrupole[b] splitting, Hz	T_1,[c] ms
90:10	1.32	1750	6.2
80:20	2.97	928	14.7
70:30	5.04	630	24.0
60:40	7.91	461	33.3

[a] Parameters refer to methylene deuterons. [b] Experimental uncertainty ±3%. [c] Experimental uncertainty ±10%.

Table II. Parameters for "Bound" and "Free" Sites in Lecithin/Ethylene Glycol-d_4 Liquid Crystalline Phase

quadrupole splitting, Hz		relaxation time, ms	
bound	free	bound	free
2240	230	5.1	140

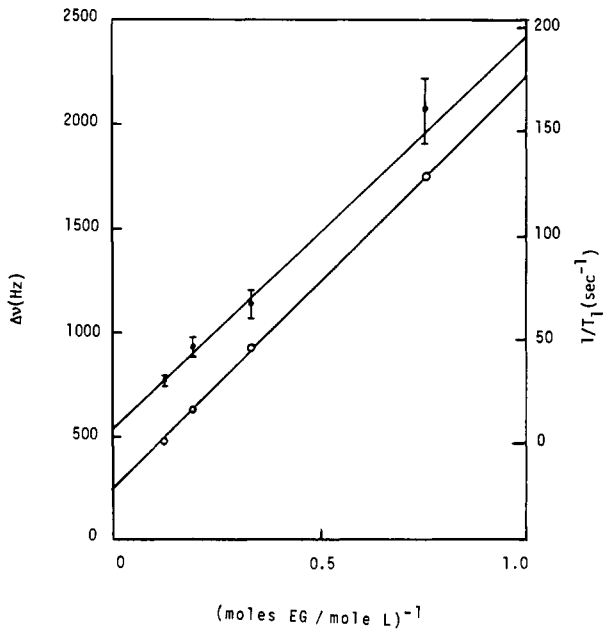

Figure 1. Deuterium NMR quadrupole splittings ($\Delta\nu$) (O) and spin–lattice relaxation rates ($1/T_1$) (·) vs. fraction bound for lecithin/ethylene glycol-d_4 liquid crystalline phase at 20 °C.

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