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Ionic Photodissociation and Picosecond Solvation Dynamics of Contact Ion Pairs

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We report picosecond spectroscopic studies of the ionic photodissociation dynamics of malachite green leucocyanide (MGCN). The photoexcitation of MGCN in polar solvents forms malachite green (MG⁺) carbonium ion and cyanide (CN⁻). The lowest excited state of MGCN has ionic dissociation lifetimes of 0.1-5 ns which are controlled by solvation of an ionic transition state. Classical dielectric solvation models give reasonable transition state parameters for low-viscosity aprotic solvents and alcohol solvents. A higher energy excited state of MGCN rapidly dissociates into ions after radiationless conversion. The recombination yields of the vibrationally excited contact ion pair depend on dielectric constant and are related to vibrational relaxation and longitudinal dielectric relaxation. The initial contact ion pair has MG⁺ in a tetrahedral geometry which subsequently reorganizes to form planar MG⁺ with a delocalized charge. The times of this conversion are observed by transient absorption spectroscopy, and in aprotic solvents they increase with increasing dielectric constant from 6 to 13 ps. This rate behavior in aprotic solvents is characteristic of an activation energy defined by the solvent energetics. However, charge reorganization rates in alcohol solvents are determined by alcohol monomer reorientation times. This is an unusual solvent effect in which a specific solvent motion controls a transition state barrier crossing. The individual steps of ionic dissociation yield an experimental model for solvent effects in nucleophilic reactions. We give a brief, critical review of solvent dielectric relaxation and its application to charge reorganization phenomena.

I. Introduction

The interaction of charged molecules and electrons with solvent is important in many chemical systems. The dynamics of such interactions has become increasingly accessible to experimental measurement through a wide variety of techniques. Various picosecond experiments on phenomena ranging from electron solvation rate measurements to molecular ion reorientation measurements have provided some insights into solvent dynamic effects, although a great many fundamental questions remain. In this paper we concentrate on a model system whose behavior gives direct insight into solvent effects on ionic transition states. In particular, we study the picosecond solvent dynamics of an ionic photodissociation. This process of charge formation is initiated from a known neutral geometry and is the reverse of nucleophilic recombination, a major class of chemical reactions. As we shall see, these data help resolve questions of dielectric relaxation around a suddenly created dipole and how solvent dielectric properties and motions can control rates of charge reorganization processes. The analysis presented in this paper uses the contributions of solvation energetics and solvent dynamics to characterize charge stabilization and charge reorganization. These two factors have not been separately identified in previous experimental studies of ionic systems, despite the common identification of solvent effects on reaction kinetics.

The experimental work discussed here was briefly reported in two conference proceedings.^{1,2} The molecular starting material is a neutral compound made from a triarylmethyl carbonium ion, malachite green (MG⁺), and cyanide anion (CN⁻). The ionic photodissociation only occurs in polar solvents, and our preliminary report for malachite green leucocyanide (MGCN) showed that ionization to MG⁺ and CN⁻ occurred from the first excited state.² This process had rates that logarithmically correlated with inverse dielectric constant, characteristic of transition state solvation effects. In that report we also noted a strong nonexponential rise in MG⁺ absorbance that we could not explain with a simple excited state ionization mechanism. In parallel with our work, another group has recently provided some additional insight into the ionic photodissociation by measuring transient absorption of MG⁺ in two solvents of widely different viscosity.³

We will discuss the experimental history for MGCN and MG⁺ in the next section, along with a description of our experimental methods. The experimental results are presented in section III, the interpretation of the results is discussed in section IV, and the relation of these results to theoretical and experimental models of ion-solvent processes is discussed in section V.

II. Background and Experimental Methods

A. Structure and Photophysics. Malachite green leucocyanide (bis(4-(dimethylamino)phenyl)phenylacetonitrile) belongs to the triarylmethane group of compounds. Reaction of the highly colored malachite green carbonium ion with cyanide leads to the colorless "leuco" compound. Structures of the carbonium ion and the leucocyanide are shown in Figure 1. The malachite green leucocyanide is a tetrahedral structure around a central carbon atom while the malachite green carbonium ion has a planar central carbon atom with phenyl rings out of plane in a "propeller" conformation.4

The electronic absorption spectrum of MGCN is essentially the sum of three aryl groups because of the tetrahedral bonding at the central carbon. The room-temperature absorbance is peaked at 275 nm with a shoulder at 310 nm, and the maximum extinction coefficient is $4 \times 10^4 \ M^{-1} \ cm^{-1}.$ The fluorescence emission of MGCN peaks at 350 nm and is an approximate mirror image of the absorption. In solvent glasses at 77 K, MGCN phosphoresces with an emission at 400 nm.⁵ The intersystem crossing and

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Figure 1. Structure of malachite green leucocyanide (1) and malachite green (2). Malachite green has the sites of charge delocalization indicated by δ^+ .

fluorescence quantum yields of 0.11 in low-polarity solvents⁶ are characteristic of the photophysical behavior of the parent chromophore, dimethylaniline (DMA). In solvents having some polarity, the photophysics changes to include ionic photodissociation.

The spectroscopy of triarylmethyl carbonium ions has been extensively studied both theoretically⁷ and experimentally.⁴ The absorption spectrum of MG⁺ has an excitation coefficient of 1 $\times 10^5$ M⁻¹ cm⁻¹ at 620 nm and a much weaker absorbance in the 300-nm region. The photophysical behavior of electronically excited MG⁺ has generated much research interest because of its unusual excited state relaxation to the ground state. The fluorescence yields depend on solvent viscosity,8,9 and picosecond studies show excited state relaxation rates for MG⁺ as fast as 1.2 ps in low-viscosity solvents like water and alcohols.^{10,11} A number of models have been used to explain the fast internal conversion rates.¹²⁻¹⁴ The fast-recovery property of excited MG⁺ has been useful as a saturable absorber in picosecond laser technology.

The ionic photodissociation of MGCN and related compounds has been an active area of study since the first report of photochromic behavior in 1919.¹⁵ Dissociation yields have been measured in a number of studies.¹⁶⁻¹⁸ Some effort at identifying a free radical component of photochemistry has also been conducted¹⁹ in analogy to DMA cleavage,²⁰ although this seems to be a minor pathway compared to ionic photodissociation. The steady state yields of ionic photodissociation are difficult to obtain because of the problems of inner-filter effects and reactivity of MG⁺ with impurities in solvents or with water in solvent mixtures. The ionic dissociation yields by various workers range from 0.91 to 1.0, and in polar solvents such as ethanol and acetonitrile the yields are certainly very large and are probably 0.95-1.0. The mechanistic studies of Herz¹⁶ used fluorescence yields and ionization yields to show that ionic photodissociation probably occurred

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from the MGCN singlet state and that aryl substituents can affect the singlet-triplet conversion rate in competition with ionic dissociation. A comparative study of dimethylaniline and MGCN was reported by Brown and Cosa.⁶ They showed similar behaviors between these compounds in cyclohexane and reported fluorescence lifetimes of <200 ps for MGCN in ethanol and acetonitrile. They also concluded that the MGCN singlet state was the precursor of dissociation, but they could not resolve the transient risetime of MG⁺ absorption with a nanosecond apparatus. In parallel with our work, Cremers and Cremers³ used a picosecond transient absorption apparatus to observe the MG⁺ appearance in ethanol and glycerol solutions of MGCN. Their apparatus showed \sim 100-ps risetime for MG⁺ in ethanol but could not resolve any faster components. In viscous glycerol they observed a \sim 50-ps component plus a \sim 1-ns component, although no curve fitting was done to characterize these times. These workers also measured the absorbance spectrum over the 550-680-nm range at delays of 250 ps and 5.7 ns to identify the MG⁺ spectrum. They found no evidence for excited states of MG⁺ in glycerol by probing for stimulated emissions at 750 nm.

In summary, the published data for MGCN ionic photodissociation suggest that there is a dielectric constant dependence of yield and that the singlet state is directly dissociating in competition with fluorescence and intersystem crossing. The work by Cremers and Cremers³ which paralleled our earlier reports^{1,2} showed that this is a reasonable mechanistic path. The full understanding of the solvent dependence of the ionic photodissociation is the object of this report.

B. Experimental Methods. 1. Preparation of MGCN and Solvents. Malachite green leucocyanide was synthesized according to the method of Holmes¹⁶ with some minor modifications to the procedure. Purification was done by adding methanol to induce crystallization from a mixed solvent of acetone and chloroform (1:10 by volume). The final product was a white powder with a melting point of 186-7 °C.

The solvents were all obtained from Burdick and Jackson (Distilled in Glass grade) except for absolute ethanol produced by U.S. Industrial Chemicals. All solvents were used as received to prepare stock solutions of 1×10^{-4} M concentration in MGCN. All solutions were stored in the dark prior to experiment.

2. Spectra and Fluorescence Yields. The absorption spectra of MGCN were obtained for all solvents on a Cary 219 spectrophotometer. Fluorescence spectra of MGCN were recorded on a Perkin-Elmer MPF-44A fluorometer, and fluorescence excitation spectra were obtained for MCGN in a number of selected solvents. Fluorescence quantum yields were obtained in separate experiments designed to minimize the photodecomposition. A Perkin-Elmer MPF-2A fluorometer was used to excite the MCGN at 270 nm over a 5-nm bandwidth. Sensitivity calibration was done with MGCN in cyclohexane, and only a few seconds exposure at a single detection band of 6-nm width was used to obtain relative yields without decomposition effects. Absorbance and refractive index corrections were used to obtain the final fluorescence yields relative to the cyclohexane solvent.

3. Fluorescence Lifetimes. The technique of time-correlated photon counting, as used in this laboratory, has been described previously.²¹⁻²³ The mode-locked dye laser excitation gives a fwhm autocorrelation trace of 4.8 ps, which converts to 2.4 ps by assuming of a single-sided exponential pulse. Ultraviolet excitation at 300 nm was obtained by second harmonic generation (SHG) with a temperature-tuned crystal.²⁴ The precise definition of an instrument response function (IRF) at the correct fluorescence wavelength was obtained by using a reference fluorescence from benzo(b)ideno(1:2-e)pyran (BIP). This compound absorbs in the 250-380-nm region and fluoresces in the 340-500-nm region. Published yields²⁵ and fluorescence lifetimes²⁶ suggest that its

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Photodissociation Dynamics of Contact Ion Pairs

The Journal of Physical Chemistry, Vol. 90, No. 5, 1986 781

lifetime is <8 ps. We used the procedure of Boyd and Ellis²⁷ to synthesize BIP and used 1×10^{-4} M in cyclohexane to generate a pseudo-IRF from 350 to 360 nm. The fluorescence fwhm was 350 ps, and the light-scattering fwhm at 600-nm excitation was 270 ps.

The MGCN was used at 1×10^{-4} M for all lifetime studies, and the sample cuvette was stirred continuously. A fresh sample was used for each lifetime measurement, and several gain settings were used to characterize the short-time and long-time behavior. The BIP fluorescence was collected prior to and immediately after each sample lifetime to monitor system stability. Fluorescence polarization was collected at 54.7° with respect to excitation,²² and attempts to detect differences between parallel and perpendicular polarizations were unsuccessful because of the apparently rapid reorientation of the dimethylaniline chromophores. The calculation used deconvolution techniques, and we computed the correct IRF from the observed BIP fluorescence by assuming a lifetime of 5 ps for BIP. The results are not very sensitive to the precise value selected for BIP, and the resultant reduced χ^2 values were generally good.

4. Transient Absorption. The transient absorption experiment used a pump-probe geometry. The pump beam and probe beam were developed from a single large energy pulse at 600 nm. The large energy pulse was developed in a three-stage dye amplifier, which amplified a single pulse from the pulse train of a synchronously pumped dye laser. The amplifier was similar to others^{28,29} and used a 10-Hz Nd³⁺:YAG laser (Quanta-Ray) to provide 80 mJ at 532 nm as a source of pump energy. The dye amplifier used two transversely pumped stages and a final longitudinal pumped stage. Each gain stage was separated by saturable absorbers composed of malachite green jet streams at the focus of a telescope lens pair. The amplifier output was 0.4 mJ with $\pm 15\%$ fluctuation characteristic of 90% of the pulses. The amplified spontaneous emission was only 0.1% of the total pulse energy, and an autocorrelation pulse width measurement done by background-free SHG agreed reasonably well with the input laser pulse. We have previously² published a comparison of the input pulse shape with the amplified pulse shape. The transverse profile of the output pulse was nonuniform due to pump beam nonuniformities. We used an output coupler that gave concentric diffraction rings for the Nd³⁺:YAG laser pulse, although spatial fluctuations were transmitted to the last gain stage of the amplifier. These fluctuations represented the largest source of noise in our absorption experiment, especially after SHG conversion to the 300-nm pump beam.

The transient absorption experiment was done by splitting the 600-nm beam into a weak probe beam and a pump beam. The pump beam was delayed with a 20-cm precision translation stage before being frequency doubled to 300 nm in an angle-tuned KDP crystal. The probe beam was equally divided to provide two sample probe beams, one for measuring absorbance and a second beam displaced to the side for a reference beam. The pump beam was focused with a 25-cm focal length lens and was directed into the sample cell by a 45° pick-off mirror placed slightly below the plane of the probe beams. The probe beams were focused by an 18 cm focal length, achromatic lens and could be oriented at arbitrary polarization and intensity by a double fresnel rhomb polarization rotator and calcite polarizer. The focused beam diameters changed slightly across the 1-mm path of the absorption cell, and the probe beam diameters were smaller than the pump beam diameter. Depending on intensity, the effective beam diameters of 0.2-0.5 mm at the cell were achieved by varying the sample cell position.

The absorption cell provided complete sample interchange at the 10-Hz excitation rate. A syringe pump and reservoir were mounted with a reversible motorized plunger to cycle 5 mL of solution between reservoir and syringe. Contact switches prevented laser Q switching during the direction change of the syringe. The sample cell was connected with Teflon tubing that slip fit over 18-gauge stainless needles. The cell was machined from a length of 6.3-mm square brass that had a 2-mm hole. The brass piece was relieved on opposite faces to provide a 1-mm optical path over a 2-mm-long opening. The optical path was enclosed with pieces of quartz microscope cover slips bonded by high-strength silicon rubber (GE RTV 157). The inlet and outlet openings used diversion inserts to create turbulence at the windows, and 18-gauge stainless tubing was silver soldered into the ends.

The detection electronics was operated by a microcomputer to obtain three photodiode signals on each shot of the laser. We used EG&G FND-100 photodiodes with quartz windows at -100-V bias to collect complete beam cross sections (weakly focused) after multiple reflections from wedged windows oriented to monitor the 300-nm pump beam (I_p) , the 600-nm transmitted beam (I_t) , and the 600-nm reference beam (I_0) . The photodiodes were digitized by a time-gated, 12-channel ADC (Lecroy 2249W) whose CAMAC interface was directly operated by a special interface. The 11-bit digitized signals were read by a Commodore 32 N microcomputer, and the computer was interfaced to the stepper motor drive of the delay stage. Software allowed real time comparison of photodiode outputs with energy acceptance ranges. Multiple ranges could be recorded, and ratios of signals were computed in real time. The ratios $I_t/I_0/I_p$ and I_t/I_0 were averaged along with individual signals that met the desired range criteria. Two scans were obtained with an extended time range of 2.2 ns at 10 s/point and an expanded time range of 220 ps at 3 ps/point. The longer time scale used 20 shot averages per time point while the shorter time scale used 40 shot averages.

The instrument performance was tested by several methods. The I_t/I_0 measurements had 0.1% fluctuation in the absence of a pump beam; however, fluctuations in the pump beam were responsible for the greater noise in the transient absorption data. A laser dye, cresyl violet, was used to simulate our experiment. Cresyl violet absorbs 300- and 600-nm light, which allows an intense 300-nm pump beam to reduce the 600-nm absorbance with an instantaneous risetime. The resultant instrument response function agreed with the integration of the autocorrelation trace, as expected from published work.³⁰ This measurement was used to provide a true response function adequate for precise deconvolution of risetimes. It should be noted that $\sim 3\%$ reduction in MGCN due to ionization occurred in the experiments. This loss of MGCN slightly reduced the MG⁺ absorbance curves at longer delay times. This reduction could be corrected in calculations, although it was small enough to be ignored in many cases.

Typical excitation power densities at 300 nm were equivalent to 30 photons per MGCN molecule.

III. Experimental Results

Typical fluorescence decays of MGCN in different solvents have been published previously for MGCN in a number of solvents.² The fluorescence lifetimes were calculated by using the deconvolution techniques described in the previous section. The lifetimes (τ_f) and fluorescence quantum yields (ϕ_f) are tabulated in Table I along with the calculated radiative lifetimes (τ_r) , ionization lifetimes (τ_{ip}) , and ionization yields (ϕ_{ip}) . The acetonitrile $(\eta = 0.36 \text{ cP})$ and ethyl acetate $(\eta = 0.46 \text{ cP})$ mixtures were used to create a variable dielectric constant at a low, nearly constant viscosity. The yields in Table I are more accurate than the earlier work,^{1,2} and the fluorescence lifetimes are more precisely deconvoluted by our improved methods.

The fluorescence quantum yields of MGCN were measured relative to cyclohexane solutions, and the published absolute yield of 0.11 for cyclohexane was used to provide absolute calibration. The MGCN absorption and photophysics in cyclohexane were very similar to that of DMA as shown by the lifetime and quantum yields.^{6,31} Consequently, we have assumed a singlet-triplet rate

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TABLE I: MGCN Ionic Photodissociation Time Constants and Yields^a

solvent	e	τ_{ip} , b ns	ϕ_{ip}^{c}	$ au_{ m f}$, ns	ϕ_{f}^{d}	τ_r , ens	
cyclohexane	2.0			2.45	0.11	22.3	
benzene	2.3			2.62	0.10	26.2	
EtOAc	6.0	4.70	0.40	1.86	0.069	27.0	
90/10 EtOAc/MeCN	9.1	1.48	0.68	1.00	0.033	30.3	
62/38 EtOAc/MeCN	18.0	0.375	0.89	0.334	0.012	27.8	
31/69 EtOAc/MeCN	27.7	0.193	0.94	0.182	0.0060	30.3	
MeCN	37.5	0.130	0.96	0.125	0.0042	29.8	
EtOH	24.6	0.167	0.95	0.158	0.0057	27.7	
MeOH	32.7	0.098	0.97	0.095	0.0035	27.1	

^{*a*} Fluorescence lifetime (τ_f), fluorescence yield (ϕ_f), radiative lifetime (τ_r), ion pair yield (ϕ_{ip}), and ion pair formation lifetime (τ_{ip}). ^{*b*} $1/\tau_{ip} = 1/\tau_f$ - 1/28 ns - 1/3.46 ns. ^{*c*} $\phi_{ip} = \tau_f/\tau_{ip}$. ^{*d*} Absolute yields obtained by referencing relative yields to literature values for cyclohexane. ^{*e*} Radiative lifetime equal to τ_f/ϕ_f .

behavior for MGCN that is similar to that for DMA in cyclohexane, ethanol, and acetonitrile. In DMA the radiative rate varies slightly with solvent from its value in cyclohexane, but the ratio of radiative rate, k_r , to nonradiative rate, k_{nr} , was approximately constant. The data in Table I show an average radiative lifetime of about 28 ns for the solutions with greater dielectric constant. The ratio of measured radiative and nonradiative rates for MGCN in cyclohexane was used with a 28-ns average radiative lifetime to compute an average singlet-triplet conversion lifetime of 3.46 ns. By applying the average radiative lifetime of 28 ns and nonradiative lifetime of 3.46 ns, we computed ionization rates and yields for MGCN in the more polar solvents.

The calculations for Table I assume that the ionization process had first-order kinetics from the MGCN singlet state. The proof of this assumption will be shown in the analysis of the transient absorption results. The rates and yields for photoionization in Table I clearly depend on the dielectric constant of the EtOAc and MeCN solvent systems. The large yields for photoionization in ethanol and acetonitrile are compatible with literature values. Fisher et al.¹⁷ obtained a yield of 0.91 with 95% ethanol. Yields in absolute ethanol varied from 0.9 to 1.0.16,32,33 The reported yield of 0.93 for MGCN in acetonitrile²⁸ also is in good agreement with our data. In general, quantum yield accuracies of 5-10% are difficult to obtain and minimizing solvent water content has been shown³⁴ to be important in obtaining good quantum yields by nonrate methods. Our ionization yields are probably quite precise because they are derived from rate constant measurements with an assumption of a constant ratio of radiative and nonradiative rate.

The formation kinetics for MG⁺ from MGCN by ionic photodissociation was observed on a picosecond time scale in a series of transient absorption experiments. The absorption was monitored with a wavelength of 600 nm, and the excitation wavelength was 300 nm. As discussed in the previous section, the experimental technique used the ratio of a reference and probe transmittance to define absorbance. In addition, a photodiode measurement of the 300-nm pump pulse energy was used to select pulses having a narrow range of excitation power. The system response to our 2.4-ps excitation pulse was determined by measuring the transient absorption change of an ethanol solution of cresyl violet with the identical wavelengths and powers used for MGCN.

The curves in Figure 2 show MGCN transient absorbance changes recorded for the first 2 ns at 10 ps/point. The curves in Figure 2 are not smoothed or corrected for scan nonuniformities but are plotted as "connected dots" to show experimental noise. A solution of MGCN in benzene showed no transient absorbance, and MGCN degradation effects for the scans in Figure 2 gave minor, correctable changes in absorbance under the flowing sample conditions. These curves show nonexponential risetime behavior at shorter times. All solvents were measured for the first 200 ps at 3 ps/point, and they are shown in Figures 3 and 4. Figure 3 shows typical data for the alcohol solvents along with a smoothed



Figure 2. Transient absorbance at 600 nm following photoexcitation at 300 nm of malachite green leucocyanide: A, acetonitrile (MeCN); B, 31/69% ethyl acetate (EtOAc)/MeCN; C, 62/38% EtOAc/MeCN; D, 90/10% EtOAc/MeCN; E, EtOAc. Benzene and cyclohexane solutions show no absorbance change.

Figure 3. Transient absorbance following photoexcitation at 300 nm of malachite green leucocyanide: A, methanol; B, ethanol. The dotted curve is an average of system responses obtained from cresyl violet studies (see text). The lines through data A and B are calculated fits.

and averaged trace of several instrumental response functions obtained from cresyl violet experiments.

The data were sufficiently good to allow accurate fitting of the curves with a double-exponential function of the following form:

$$f(t) = C_1(1 - \exp(-t/\tau_1)) + C_2(1 - \exp(-t/\tau_2))$$
(1)

The f(t) function and instrumental response were used to fit the data by a least-squares process. Calculated fits for the expanded absorbance scans of 3 ps/point are shown in Figures 3 and 4. The

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Figure 4. Transient absorbance at 600 nm following photoexcitation at 300 nm of malachite green leucocyanide: A, MeCN; B, 31/69 Et-OAc/MeCN; C, 62/38 EtOAc/MeCN; D, 90/10 EtOAc/MeCN; E, EtOAc. The lines through data A-E are calculated fits. The dotted curve is the integrated system response.

 TABLE II: Comparison of Relative Ionic Photodissociation Yields

 from Fluorescence and Absorbance Methods

	relative yield			
solvent	$\overline{\phi_{ip}(\mathrm{fluor})^a}$	$\phi_{ip}(absorb)^b$		
EtOAc	0.42	0.15		
90/10 EtOAc/MeCN	0.71	0.65		
62/38 EtOAc/MeCN	0.93	0.91		
31/69 EtOAc/MeCN	0.98	0.97		
MeCN	1	1		

^a Values taken from fluorescence data in Table I. ^b Calculated from C_2 absorbance values relative to acetonitrile value.

reduced χ^2 statistic, χ^2_r , was <2.0 for all data except for MGCN in ethanol which had a χ^2_r of <4.0. The ethanol data may have a slightly faster exponential component in addition to the dominant fitted components, but additional data with a smaller increment of scan and shorter excitation pulse duration will be needed to refine the fit. The results of these fits are given in Tables II and III. While the experimental time resolution is not adequate to precisely examine the first 3 ps of response, there is a dominant fast component, τ_1 , that is determined in our fits with a precision of 5% or ±0.5 ps. The τ_2 values shown in Table III were set equal to the more precise values from the fluorescence data so that accurate values of τ_1 , C_1 , and C_2 could be obtained. Table III also tabulates the total absorbance of MG⁺ via $C_1 + C_2$ and the ratio C_2/ϕ_{ip} , which is a normalization of the measured absorbance to the expected yield of ions computed from ϕ_{ip} in Table I.

The long component, τ_2 , of transient absorbance was directly compared with the fluorescence decay by analysis of the 2-ns range of transient absorbance. The values of τ_1 were so short that the 2-ns range of data was fit at later times with the fast contribution treated as a constant contribution. While we do not show these results, the fits to the 2-ns range data were within 2% of the

fluorescence lifetimes in Table I, except for EtOAc which was 5% smaller. This excellent agreement between fluorescence decay and one component of absorbance risetime, even for the ethyl acetate data where the 2-ns range is not a large fraction of the decay time, establishes that MG+ is created directly from the MGCN singlet state. The short risetime component is not seen in the fluorescence kinetics and is apparently due to a new photoionization process created by the high-intensity excitation in the absorption experiment. The relative yields of ionization expected from the S₁ decay kinetics (Table I) are compared in Table II with relative ionization yields measured from absorbance values in Table III (C_2 values). Acetonitrile solution was used for normalization of the C_2 values. The relative MG⁺ yields from absorbance data are in excellent agreement with expectation from fluorescence decay for all solvents, except for ethyl acetate and 90/10 EtOAc/MeCN. This reduction of yields in the absorbance measurement is related to enhanced ion recombination for the low dielectric constant environments.

The fast transient absorbance data at 600 nm is interpreted as originating from MG⁺ and not another transient species. The data in Table III show that the fast component of the risetime is in large yield. This yield of fast component would have been very obvious if it also existed in the fluorescence data. Our use of a reference compound to obtain an accurate instrumental response was important for confirming the absence of a large component of fast decay in fluorescence. Our earlier report² was inconclusive on this point because a good response function was not available at that time. Consequently, there is a new, very fast process occurring under the high-power 300-nm excitation. We are working at absorbance values that correspond to 40% conversion of 5×10^{-5} M MGCN to MG⁺ ions. The large extinction coefficient of MG⁺ also implies that any transient species such as solvated electrons or cation radicals would also need a large extinction as well as a reproducible creation mechanism (note C_1) $+ C_2$ in Table III) to not have problems with mole balance. The discussion and rejection of possible artifactual absorbing species are done in the Appendix. As discussed later, the absorbance at 600 nm is probably a normal MG⁺ ion that results from relaxation of an intermediate ionic transient.

The data in Table III are remarkable in the consistency of $C_1 + C_2$ for high-dielectric solvents. This consistency was only experimentally possible by using a narrow window of excitation energy at 300 nm. We have not yet compared transient curves at different energy windows, but the $C_1 + C_2$ values at longer times do scale linearly with excitation energy over a twofold change in energy. This result is consistent with saturation of the one-photon absorption to S₁ followed by a second absorption to a higher energy state, S₂, that is not in full saturation. Additional work is necessary to identify the complete pumping mechanism and power dependence of the data, but the reproducible values of $C_1 + C_2$ suggest a simple mechanism. As discussed in the next section, the fast process probably originates from a higher excited state that has a much lower barrier to ionic dissociation.

IV. Interpretation of Results

A. Introduction. The results show that two separate processes can lead to MGCN photoionization. The lowest energy excited singlet state of MGCN is ionized to form MG^+ and CN^- in polar solvents. The rate for this ionization greatly increased with

TABLE III: Kinetic Parameters from the Calculated Fits to the Transient Absorption Data^a

solvent $(\epsilon)^e$	τ_1 , ^b ps	C_1^c	τ_2 , ^b ps	C_2^c	$C_2/(C_1 + C_2)$	$\overline{C_2/\phi_{ m ip}}^d$	$C_1 + C_2$
EtOAc (6)	6	0.043	1860	0.017	0.28	0.043	0.060
90/10 (9.1)	9	0.049	1000	0.077	0.61	0.113	0.126
62/38 (18.0)	11	0.084	334	0.107	0.56	0.120	0.191
31/69 (27.7)	12	0.080	182	0.114	0.59	0.121	0.194
MeCN (37.5)	13	0.077	125	0.118	0.61	0.122	0.195
EtOH (24.6)	18	0.110	158	0.088	0.44	0.093	0.198
MeOH (32.7)	11	0.122	95	0.077	0.39	0.080	0.199

 ${}^{a}f(t) = C_{1}(1 - \exp(-t/\tau_{1})) + C_{2}(1 - \exp(-t/\tau_{2}))$. b The error in τ_{1} is approximately $\pm 5\%$; τ_{2} was fixed at the fluorescence value. Fits from data with a 200-ps range. ${}^{c}C_{1}$ and C_{2} are given in absorbance. d Absolute ϕ_{ip} from fluorescence data in Table I. The solvent mixtures are for Et-OAC/MeCN, and dielectric constants, ϵ , are included.

TABLE IV: Rate Constants and Changes in ΔG_{ip}^{\dagger} for the Ionic Photodissociation of MGCN

solvent	$10^8 k_{\rm ip}, {\rm s}^{-1}$	$\delta\Delta G_{ m ip}{}^{*,a}$ kcal/mol	$\Delta G_{ip}^{*,b}$ kcal/mol
EtOAc	2.13	2.14	6.08
90/10 EtOAc/MeCN	6.76	1.45	5.40
62/38 EtOAc/MeCN	26.7	0.63	4.59
31/69 EtOAc/MeCN	51.8	0.24	4.20
MeCN	76.9	0.0	3.96
EtOH	59.9	0.15	4.11
MeOH	102.0	-0.17	3.79

^aThe change in ΔG_{ip}^{*} has been calculated from $\delta \Delta G_{ip}^{*} = -RT \ln (k_1/k_2)$ where k_2 is the rate constant in actionitrile. ^bComputed from the Eyring equation with a preexponential of 6.2×10^{12} s⁻¹ for 298 K.

increasing dielectric constant in aprotic solvents. We will show that this data can be interpreted as a rate-limiting behavior controlled by solvation of an ionic transition state. A second process, from a high excited state of MGCN, also formed MG⁺ and CN⁻. However, this fast process had kinetics with rates that slightly decreased with increasing dielectric constant in aprotic solvents. This process will be interpreted as a fast radiationless process leading to a transient contact ion pair, which then relaxes to form an equilibrium contact ion pair that has normal charge delocalization in MG⁺.

Two earlier reports^{3,34} hypothesized that ionization could proceed from the tetrahedral geometry of MGCN, which is then followed by geometrical relaxation of MG⁺ to its spectroscopically planar form. This ionization mechanism requires a reaction coordinate that involves C-CN stretching and development of ionic charge because of a curve crossing with a higher energy ionic state. An alternative mechanism is that the reaction coordinate contains tetrahedral distortion and C-CN stretching to allow curve crossing with an ionic state. The quantum calculations have not been done to identify which type of reaction coordinate is most likely. The slow rates for the lowest excited state process may favor a transition state that involves distortion of the tetrahedral angle in MGCN to effect a *concerted* charge separation and C-CN bond lengthening. This transition state will be a very localized dipolar transition state and should be insensitive to small changes in viscosity and very sensitive to small changes in dielectric stabilization.

For the highest excited state process we must hypothesize a geometrical change compatible with the observed very fast rates. The data for the higher excited state process will be explained by using the concept of ion pair formation from the tetrahedral geometry of MGCN.

B. Lowest Excited State Ionization of MGCN. The ionic photodissociation of MGCN from its lowest singlet state has rates that are relatively slow but quite dependent on the solvent dielectric behavior. The tetrahedral MGCN structure ultimately leads to a planar MG⁺ carbonium ion. Consequently, the transition state is likely to be ionic. This hypothesis of an ionic transition state is compatible with the observed dielectric constant behavior in that stabilization of the transition state will lower the rate-limiting activation energy.

The rate constants, k_{ip} , for ionic dissociation can be interpreted from transition state theory as

$$k_{\rm ip} = \frac{k_{\rm B}T}{h} \exp(-\Delta G_{\rm ip}^*/RT)$$
(2)

where ΔG_{ip}^{*} is the free energy of activation and $k_{\rm B}$ is Boltzmann's constant. No temperature studies have been completed, but relative changes, $\delta \Delta G_{ip}^{*}$, can be computed from the data if we assume a constant frequency factor. Table IV contains the calculated results for our solvents, with acetonitrile as the reference solvent. A computed frequency factor of $6.2 \times 10^{12} \text{ s}^{-1}$ at 298 K can be used to estimate an absolute ΔG_{ip}^* from the observed rate constants. This assumption yields a ΔG_{ip}^* for excited MGCN in acetonitrile of 3.96 keel/mel in acetonitrile of 3.96 kcal/mol.

A model of the transition state solvation should allow explanation of the $\delta \Delta G_{ip}^{*}$ in Table IV. The simplest solvation model

Figure 5. Natural logarithm of the ionization rate constant obtained from fluorescence plotted vs. a dielectric function $(\epsilon - 1)/(2\epsilon + 1)$. The circles refer to ethyl acetate and acetonitrile solvents, and the squares refer to methanol and ethanol.

is a classical calculation^{35,36} of the free energy for transfer of a dipole moment, μ , into a medium with a dielectric constant, ϵ . The solvation energy of a dipole moment has a free energy change

$$\Delta G = \frac{-\mu^2}{r^3} \left[\frac{\epsilon - 1}{2\epsilon + 1} \right] + \phi \tag{3}$$

where r is the radius of the dipole cavity and ϕ represents all nonelectrostatic terms. Consider the initial state of MGCN* as having a small dipole moment, μ_1 , and the final activated complex as having a dipole moment, μ_2 . The activation energy ΔG^* is then given by

$$\Delta G^* = \left[\frac{\epsilon - 1}{2\epsilon + 1}\right] \left[\frac{\mu_2^2}{r_2^3} - \frac{\mu_1^2}{r_1^3}\right] + \phi_2 - \phi_1 \qquad (4)$$

By substituting eq 4 into eq 2, we can write $\ln k_{\rm ip} =$

$$\ln\left(\frac{k_{\rm B}T}{h}\right) + \left[\frac{\mu_2^2}{r_2^3} - \frac{\mu_1^2}{r_1^3}\right] \left[\frac{\epsilon - 1}{2\epsilon + 1}\right] \left[\frac{1}{RT}\right] + \frac{\phi_1 - \phi_2}{RT}$$
(5)

The simplifying assumption that $\mu_1 \approx 0$ leads to a prediction that a plot of $\ln k_{ip}$ vs. $(\epsilon - 1)/(2\epsilon + 1)$ should be a straight line of slope μ^2/RTr^3 . Figure 5 shows that our data for aprotic solvents are very well represented by such an equation with an intercept of 4.77 ± 0.07 and a slope of 37.2 ± 1.9 , although methanol and ethanol show slightly faster rates than expected from purely electrostatic solvation. The slope of 37.2 for aprotic solvents is quantitatively compatible with the MGCN geometry. Possible values for the solvation radius, r, correspond to van der Waals distance from 2 to 2.5 Å. This range of r, when used with the observed slope, yields transition state dipole moments of 3.5-5 D. If we use C-CN bond length data to estimate a 2.1-2.5-Å charge separation, then the dipole moments are created from partial charge formation of 0.54-0.70 unit. Quantum calculations of molecular geometries will be necessary to test these estimates; however, the results are reasonable.

The continuum calculations using eq 4 have also been used to correct energetic changes in rate expressions for electron transfer.³⁷ However, within the electrostatic derivation³⁶ the dielectric constant of the ion has been set equal to unity. We can test the accuracy of this approximation by using the square of the refractive index (1.88) instead of unity in eq 4 (we must also divide by 1.88).

⁽³⁵⁾ Scatchard, G.; Kirkwood, J. G. Phys. Z. 1932, 33, 297.
(36) Kirkwood, J. G. J. Chem. Phys. 1934, 2, 351.

⁽³⁷⁾ Weller, A. Z. Phys. Chem. (Munich) 1982, 133, 93.

The resultant plot is a good linear fit which yields a modest increase in μ of 9%. It also should be noted that a $1/\epsilon$ correlation of the MGCN data, rather than $(\epsilon - 1)/(2\epsilon + 1)$, will give an excellent correlation, with a different interpretation of slope, because these two functions are self-correlated over our range of data. A $1/\epsilon$ type correlation is usually considered with Coulombic or dipole-dipole electrostatic models and has been successfully used in exciplex studies where plots of $1/\epsilon$ were correlated with ionic yields.³⁸

The recombination of MG^+ and CN^- is not kinetically measurable as a separate step because of the long time scales for ionic dissociation from the MGCN excited singlet state. The relative yields measured in the transient absorption experiments showed that in ethyl acetate the MG⁺ yield was only 36% of its expected yield while in 90/10 EtOAc/MeCN the MG⁺ was 92% of its expected yield. The data are consistent with a contact ion pair intermediate having a recombination path that is dramatically affected by a change in solvent dielectric constant from 6 to 9.

The fast recombination kinetics from the activated complex is controlled by a transient contact ion pair, its vibrational relaxation, and its stabilization by solvent dielectric constant. The slow rate-limiting ionization obscures these important processes. In addition, the time scale of ≤ 2 ns is too fast to observe gross effects from geminate recombination processes. For example, in ethyl acetate the Debye radius is 93 Å while in acetonitrile it is 15 Å. On our experimental time scale we only observe significant recombination for MGCN in ethyl acetate, which we attribute to rapid recombination of the transient ion pair, not a diffusional recombination of geminate ion pairs. If the latter mechanism were very important, our transient absorbance curves for MG⁺ in ethyl acetate would have shown deviation from an exponential rise. Data for MGCN in ethyl acetate will need to be completed over much longer time scales to test models of geminate recombination.

In summary, the lowest excited state of MGCN undergoes ionic dissociation into MG⁺ and CN⁻ by direct activation through an ionic transition state. For aprotic solvents, the solvent dielectric constant controls the stabilization of the ionic transition state, and therefore the ionization rate. The rates of ionization were modeled by using classical solvation energies of a dipole in a dielectric, and a partial charge formation of 0.54-0.70 unit was computed for the transition state dipole moment. The yields of ionization in ethyl acetate ($\epsilon = 6$) and a solvent mixture ($\epsilon = 9$) were only 36% and 92% of the expected yields. This ion recombination occurs on time scales fast compared to the 1-ns ionization rate and is probably enhanced by the poor ionic stabilization in low dielectric constant solvents. The ionic transition state probably develops by tetrahedral distortion of excited MGCN, although a viscosity study at constant dielectric constant will be necessary to prove this point.

C. High Excited State Ionization of MGCN. 1. Introduction. The issues to be discussed are the origin of the fast process, molecular and ion pair geometries, vibrational energy relaxation, ion recombination, solvent dielectric response, solvent reorganization, and time evolution of the charge distribution in the ion pair. Kinetic modeling will be used to establish self-consistency of rate estimates with the observed transient absorption kinetics. We develop a model that begins with fast ion pair formation from tetrahedral MGCN. Recombination competes with vibrational relaxation into a localized contact ion pair. This ion pair then evolves, with solvent reorganization, into a contact ion pair with a delocalized positive charge on MG⁺. The relaxation process is essentially a kinetic process resulting from a "sudden dipolar perturbation" by a contact ion pair in conformational nonequilibrium.

2. Fast Ion Pair Creation. The originating electronic state of the fast ion pair formation process cannot be identified from existing spectroscopic data. However, the data in Table III can be used to propose a very likely process. The key experimental observations from Table III are that $C_1 + C_2$ is constant for all solvents that do not have ion recombination effects ($\epsilon > 9$). The relative amounts of C_1 and C_2 appear to be nominally constant in the aprotic solvent mixtures, but in the alcohols more of the fast process is contributing. This suggests that a solvent-dependent branching ratio exists between the two processes. In addition, the data suggest that $C_1 + C_2$ is probably constant for all solvents. By assuming a constant $C_1 + C_2$, we can compute relative recombination yields for each process. The column labeled C_2/ϕ_{ip} in Table III correlates with a relative recombination yield for the lowest energy process, while the average C_1 value of 0.08 for the three mixtures of acetonitrile and ethyl acetate with greatest dielectric constant is reduced to 0.049 and 0.043 in dielectric constants of 9 and 6, respectively.

The data are consistent with a mechanism in which a second photon is absorbed from the first excited singlet state, S_a , to a second state, S_b , which then undergoes very rapid radiationless conversion to high vibrational levels of S_a . The high vibrational levels of S_a then undergo both vibrational relaxation and fast ionization. This mechanism establishes a branching process for fast vibrational relaxation and fast ion pair formation in which the nonionized molecules still reach S_a , where the slow ionization can eventually occur.

When we consider that recent measurements of vibrational relaxation in electronically excited MG⁺ have values of $\sim 1.2 \text{ ps}^{10,11}$ for 16000-cm⁻¹ energy relaxation, then a fast ion pair formation process which yields vibrationally excited ions would be followed by vibrational relaxation, recombination, and solvent stabilization of a contact ion pair. A very fast formation of the ion pair could retain MG⁺ in a tetrahedral configuration, with excess vibrational energy content mostly present in MG⁺. The hypothesis that a very fast ionization event occurs, essentially without any need to surmount an activation barrier, is essential for understanding of the weak dielectric constant dependence of the fast rates. If an activated process from excited MGCN existed that had a transition state with increased ionic character, then we should observe a dramatic rate change with dielectric properties just like we observed for the lowest excited state process. In fact, we observe a weak dependence on dielectric constant for the fast rates with a decreasing rate for increasing dielectric constant.

3. Ion Pair Time Evolution. The discussion of a mechanism now focuses on the time evolution of a vibrationally excited contact ion pair that was created in a short time (≤ 1 ps). We essentially must understand how solvent properties control ion recombination and also control ion-solvent evolution to our spectroscopically observed MG⁺ absorption signal. We label the initial transient contact ion pair as CIP^v, to denote vibrational content of the carbonium ion system. This state will evolve into a relaxed contact ion pair in times of ≤ 1 ps to achieve a contact ion pair state, CIP¹, denoted as a localized contact ion pair. This concept is compatible with the idea that a nearly tetrahedral MG⁺ structure will have a blue-shifted absorption spectrum compared with the normal delocalized MG⁺ cation because the charge is still "localized" on the central carbon atom. We do not have theoretical calculations that can resolve the degree of delocalization onto a single dimethylaniline group in the presence of cyanide. However, the final step for our observation of a normal MG⁺ absorption spectrum is achievement of a planar MG⁺ structure and a fully delocalized carbonium ion. This final state is symbolized as a delocalized contact ion pair, CIP^d. This last step of conversion from CIP¹ to CIP^d apparently is the "slow" step that we observe as a single-exponential rise in the transient absorbance. The data for the lowest dielectric constant solvents show an increasing yield of final MG⁺ signal with a *decreasing* rate of formation. This establishes that recombination occurs from states other than the precursor state, CIP¹, that leads to final MG⁺ signal. Substantial recombination must be occurring from the vibrationally excited contact ion pair, CIP^v, although the localized ion pair, CIP^l, may contribute to recombination in the lowest dielectric constant solvent.

4. Initial Recombination. The kinetics of recombination involves solvent effects because we find that the fast process $(C_1$ in Table III) has significant recombination at $\epsilon = 6$ and 9 while the slow process $(C_2$ in Table III) only has significant recombi-

⁽³⁸⁾ Mashuhara, H.; Hino, T.; Mataga, N. J. Phys. Chem. 1975, 79, 994.

nation at $\epsilon = 6$. The nearly tetrahedral geometry of MG⁺ in the transient contact ion pairs CIP^v and CIP^l is more capable of facile recombination than the distorted tetrahedron hypothesized to be present in the lower excited state process. However, the key question for the CIP^v and CIP^l ion pairs is to understand how the *solvent dielectric properties* affect recombination and reduce it to a noncompetitive process.

The transient contact ion pair CIP^v has been identified as a likely precursor of recombination. This vibrationally excited ion pair will sample a large degree of internal vibrational phase space, including motions such as torsional motions of the dimethylaniline groups that can perturb the electronic structure of tetrahedral MG⁺ and reduce the likelihood of charge localization. The solvent is apparently responsible for controlling the branching between recombination and stabilization on very fast time scales. The solvent will respond to the "sudden dipolar perturbation" of CIP^v by a short-time, nearest-neighbor polarization response leading to *energetic stabilization*. In recent *continuum* theories of dielectric relaxatio³⁹⁻⁴¹ a term called the longitudinal response time, $\tau_{\rm L}$, is related to the dielectric constant, ϵ , the normal dielectric response time, $\tau_{\rm D}$, and the infinite-frequency dielectric constant ϵ_{∞} . The relation is

$$\tau_{\rm L} = \frac{\epsilon_{\infty}}{\epsilon} \tau_{\rm D} \tag{6}$$

If only optical frequency polarization effects were important for transient stabilization of the "sudden dipole", we would expect rapid stabilization that is nearly independent of dielectric constant, followed by further stabilization through normal dielectric response. The variation of $\tau_{\rm L}$ with static dielectric constant has the qualitatively correct behavior to explain how an increasing dielectric constant can change the rate of energy stabilization into a time scale that competes with vibrational relaxation. We interpret the longitudinal response time $\tau_{\rm L}$ as appropriate for considering transient stabilization because the time-dependent electric field emanating from the "sudden dipole" must include successive layers of solvent to establish a net reaction field at the "sudden dipole" site. As we shall discuss in more detail later, the $\tau_{\rm L}$ is effectively a polarization propagation time that is shorter for larger static dielectric constants. For noncontinuum liquids, this "longitudinal" solvent relaxation creates a solvent stabilization energy in time $\tau_{\rm L}$ that is a fraction of the larger solvent stabilization energy achieved at longer times.

The theoretical understanding of molecular reorientation, spectroscopic line shape, and dielectric response is an active area of research. Reviews of available data for acetonitrile⁴² give some appreciation of the issues, although the kinetic consequences of these issues are not discussed. Both ethyl acetate⁴³ and acetonitrile⁴⁴ have dielectric relaxation times of \sim 3.8 ps at 303 K from microwave dielectric data. We use the square of the refractive index for an extrapolated ϵ_{∞} . For ethyl acetate we have an ϵ_{∞} of 1.88, and if we assume this value for all mixtures, we calculate $\tau_{\rm L}$ values of 1.2 ($\epsilon = 6$), 0.79 ($\epsilon = 9$), 0.40 ($\epsilon = 18$), 0.26 ($\epsilon =$ 28), and 0.19 ps ($\epsilon = 38$). These τ_1 values are on the correct time scale to allow significant solvent dielectric stabilization to proceed in parallel with vibrational relaxation processes, especially for the larger dielectric constant liquids. More theoretical effort must be done to compute the degree of ion pair stabilization achieved on a particular time scale, as well as first solvent layer orientation effects. This discussion of available concepts strongly suggests that longitudinal dielectric relaxation is important for transiently stabilizing ion pairs, and it may be important for understanding solvent effects upon reactions of other ionic intermediates in which

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Figure 6. Classical activation barriers and their dependence on a change in dielectric constant when the product species is stabilized less than the reactant by the solvent dielectric. The activation barrier in the lower dielectric constant solvent will be slightly less than in the larger dielectric constant.

vibrational relaxation and dielectric stabilization proceed on similar time scales. Furthermore, these results implicate vibrational excitation and related conformation changes as activation processes for recombination from a localized contact ion pair, CIP¹.

5. Delocalization of Charge. The discussion in the previous paragraph has given possible reasons for recombination to be present from CIP^v, although the net environmental energy relaxation to an equilibrated, localized contact ion pair, CIP¹, continues for times on the order of τ_D , the full dielectric relaxation. Useful questions are, why does CIP¹ evolve to CIP^d and how do solvent dielectric and viscosity properties affect the rate? We must consider environmental origins for barriers to the transformation of CIP¹ to CIP^d. Viscosity effects could be present, although the tetrahedral to planar transformation of MG⁺ can be achieved by small translational motions of the aryl groups "pulling" the central carbon into a planar position. In addition, the tetrahedral to planar transformation in MG⁺ involves extensive charge reorganization. This factor can be analyzed with simple electrostatic ideas, and we conclude that the final charge distribution in CIP^d has slightly less total ion-dielectric energy contribution than the initial localized CIP¹. The observed times for achieving CIP^d in MeCN are 13 ps, much longer than the 3.8-ps dielectric relaxation time and much longer than the time of 6 ps in ethyl acetate. These values qualitatively show that viscosity effects and dielectric relaxation effects could make up a reasonable fraction of the ethyl acetate rate. However, in the very similar viscosity, but larger dielectric, environment of acetonitrile, the slower rate must be due to effects other than viscosity. This rate difference is probably due to a solvent reorganization barrier created by the need to change internal charge distribution in MG⁺.

6. Solvent Reorganization Barriers. The hypothesis of a solvent reorganization barrier for converting CIP¹ to CIP^d can be simply understood by considering a classical barrier with a reaction coordinate consisting of charge reorganization coupled to geometric change from tetrahedral to planar MG⁺. The CN⁻ follows the motion of a positively charged carbon atom in this model, and the solvent must reorganize from an orientation stabilizing a localized dipole to an orientation stabilizing a more delocalized charge system. As shown in Figure 6, a change in dielectric constant from low to high values increases the barrier to reorganization [$E^{*}(\epsilon)$], even though the absolute energies are reduced. The role of dynamic effects in defining such a reaction barrier will be discussed later.

The differences between the data for aprotic solvents and the alcohols yield further insight into the reorganization process. Analysis of microwave relaxation in alcohols shows three-component relaxations composed of slow reorientation, τ_1 , in hydrogen-bonded clusters, medium speed, overall reorientation, τ_2 , of unassociated monomer, and fast rotation of OH groups, τ_3 . For the case of methanol and ethanol the literature values⁴⁵⁻⁴⁷ for τ_1

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Mol. Phys. 1979, 38, 699. (43) Srivastava, G. P.; Mathur, P. C.; Krishna, Mrs. J. Chem. Phys. 1974, 60, 1894.

⁽⁴⁴⁾ Srivastava, G. P.; Mathur, P. C.; Tripathi, K. N. Indian J. Pure Appl. Phys. 1971, 9, 364.

⁽⁴⁵⁾ Gary, S. K.; Smyth, C. P. J. Phys. Chem. 1965, 69, 1294.

⁽⁴⁶⁾ Kenney-Wallace, G. A.; Jonah, C. D. J. Phys. Chem. 1982, 86, 2572.

and τ_2 are somewhat variable, although τ_3 of ~ 2 ps is quite independent of alcohol chain length. We use τ_1 values at 20 °C from Saxton et al.⁴⁷ and the estimates of Kenney-Wallace and Jonah⁴⁶ for τ_2 values at 27 °C. The estimated τ_1 and τ_2 values for methanol are 53 and 12 ps and for ethanol 170 and 20 ps. In contrast, the acetonitrile dielectric relaxation time of 3.8 ps also has an unresolved faster component, although the overall tumbling motion has been determined by NMR and spectral band analysis as ~ 1.5 ps.^{42,48} Arbitrarily extending the continuum solvent concept of a longitudinal relaxation time for the alcohol solvents requires that one of the three dielectric relaxation times be selected. If we retain the physical picture of electric field propagation for τ_{1} , then τ_{3} would seem to be an upper limit to the appropriate dielectric relaxation time, which also could include time for slight orientational response. This interpretation is consistent with our observation of negligible recombination in alcohols. Our use differs from other calculations⁴⁹ that make no distinction among the relaxation times, although the appropriate analogy of the continuum concept is subject to further theoretical work.

We can use the τ_1 values in Table III as approximate measures of the CIP¹ \rightarrow CIP^d conversion lifetime. A kinetic model is developed later to show that this is nearly correct, especially for larger times. The values range from 6 to 13 ps for the aprotic solvent dielectric constant range of 6-38 while methanol ($\epsilon = 33$) is 11 ps and ethanol ($\epsilon = 25$) is 18 ps. The ethyl acetate/acetonitrile times increase to 13 ps which suggests a solvent reorganization barrier that is activated in an adiabatic sense, where the longitudinal dielectric relaxation times do not directly control the rate of barrier crossing.

An Arrhenius analysis of the rate would be especially useful in characterizing the activation energies and preexponential factors. For the ethyl acetate/acetonitrile solvents we see little rate change among the larger dielectric constants so that the energetic component of rate may be very similar. The dielectric properties of methanol and ethanol are sufficiently similar that rate differences should be similar to the three largest dielectric mixtures in the aprotics. Recall that our data in Table IV and Figure 5 showed that the alcohols were not very different from the aprotics in a more extreme case of solvation of an ionic transition state. Consequently, we tentatively interpret the differences between methanol and ethanol to solvent-specific features of the barriercrossing dynamics. This effect could be demonstrated by comparing preexponential Arrhenius factors. The times observed for charge reorganization in alcohols are very similar to τ_2 times for the dielectric response, which are qualitatively identified with overall molecular reorientation of nonassociated alcohol molecules.⁴⁶ This suggests that charge reorganization is directly controlled by molecular reorientation times for ethanol and larger alcohols. This type of activation barrier is a dynamic barrier, where charge delocalization can only occur with concurrent solvent reorientation. This is an activation barrier that includes solvent motion as an intimate part of the reaction coordinate, and it will be discussed in more detail later.

For our data, the observed relaxation times are largely associated with the contact ion pair interchange, $CIP^{I} \rightarrow CIP^{d}$, rather than a solvent molecule insertion between MG⁺ and CN⁻. The solvent insertion into the CIP^d is certainly an eventual step in the creation of a solvent-separated ion pair. In addition, solvent insertion into CIP^d is expected to have a smaller activation energy than CIP¹. The energy needed to separate CIP^d is largely electrostatic and can be roughly estimated by simple electrostatic calculations. The expected rate constants are much smaller than we observe and are on the order of published measurements for ion pair solvation.⁵⁰ These studies of a contact ion pair, created by electron transfer, have given ethanol insertion times as a function of ethanol concentration. In pure ethanol the observed rate was 149 ps, much longer than our time scales. Those studies involve different molecular ions, but the Coulombic effects and times are probably similar to those of our systems. A more general support for excluding solvent insertion kinetics from our interpretation is the roughly similar relaxation times for methanol and ethyl acetate, an observation that is not compatible with solvent insertion barriers of these two systems.

It is interesting to consider the effect of increasing viscosity on the mechanistic steps. Experimentally, the MGCN ionic dissociation was studied at a very high viscosity of 11 P in glycerol.³ As expected from our discussion, these workers found a long component for MG⁺ absorption of ~1-ns risetime which they interpreted as a hindered motion due to viscous drag in the CIP¹ \rightarrow CIP^d conversion. This was apparently supported by data on brilliant green leucocyanide, although more data will be needed to separate viscosity effects from solvent relaxation effects at the high viscosities. We also expect viscosity effects on vibrational relaxation of excited MGCN and CIP^v. However, for our lowviscosity range we do not expect dramatic effects because a recent study of MG⁺ excited state relaxation shows no viscosity effects in methanol-water mixtures.¹⁰

7. *Kinetic Model*. The preceding sections can be summarized in the following kinetic model.

$$S_{b} \xrightarrow{k_{1}} S_{a}^{v} \xrightarrow{k_{3}} CIP^{v} \xrightarrow{k_{4}} CIP^{1} \xrightarrow{k_{6}} CIP^{d}$$

$$\begin{vmatrix} k_{2} \\ k_{2} \\ k_{5} \\ k_{7} \\ k_{7$$

The initial radiationless conversion of S_b to vibrational levels of S_{a}^{v} and the subsequent competition of vibrational relaxation and contact ion pair formation are treated as simple rate processes rather than via a master equation. Theory exists for vibrational relaxation in the presence of a competing rate although our goal is to model the observed exponential rise in absorbance with reasonable rates. The vibrational relaxation of the initially created contact ion pair, CIP^v, to CIP¹ also results in recombination via k_5 . We could also include recombination from CIP¹ via k_7 , although it may not be very important except in the lowest dielectric constant solvent. Our kinetic model is not testing the recombination rate, but the effective rate of forming CIP^d, so we have omitted k_7 from our model. We have solved the kinetic model exactly, excluding k_7 , and programmed the solutions into a computer. Inspection of the kinetic scheme and trial calculations suggest that a single, rate-dominating term must be present to explain the excellent agreement between the data and a fast component of risetime that has one exponential component (see Figures 3 and 4). This fact was used to test individual estimates of various rate constants for compatible absolute values.

The kinetic model uses k_2 and k_3 to simulate the ionization branching and vibrational relaxation from $S_a^{\,v}$. Experimental measurements of vibrational relaxation in MG⁺ can be used as a guide to vibrational relaxation rates in MGCN. Values of 1.2 ps for internal conversion and relaxation were found in methanol for the first excited state of MG^{+.10} In our scheme we are using k_2 and k_3 to correspond with the effective branching ratio of C_1 and C_2 in high dielectric constant solvents. The absolute value of k_3 is probably quite large for very high vibrational levels, and we must have an effective k_3 large enough to maintain reasonable exponential behavior for the final product CIP^d. We have selected k_1 as 10 ps⁻¹ and k_2 as 2 ps⁻¹ and used the $k_2/(k_2 + k_3)$ ratio as 0.6 to derive $k_3 = 1.333$ ps⁻¹. The data in Table III have $C_2/(C_1$ + C_2) ~0.6 for high dielectric constant mixtures of EtOAc/ MeCN. The values of k_4 and k_5 are constrained by the data in Table III to correspond to relative yields of recombination in the fast channel. The value of C_1 is reduced from an average of 0.08 in high dielectric constant mixtures of EtOAc/MeCN to 0.049 and 0.043 in 90/10 mixtures and pure ethyl acetate. The ratio of $k_4/(k_4 + k_5)$ defines the yield of final CIP^d, and we can assign k_4 as a fast rate composed of vibrational relaxation and dielectric response. The value of k_4 is probably weakly dependent on dielectric constant and must always be large enough to maintain a good exponential rise in CIP^d. The recombination rate, k_5 , is

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Figure 7. Schematic of the intermediates involved in ionic photodissociation from MGCN excited states S_a and S_b. The rate constants correspond to the kinetic scheme in the text, and the vibrationally excited, localized, and delocalized contact ion pairs (CIP) are denoted by supercripts v, l, and d, respectively. The solvent-separated ion pair, SSIP, is also indicated.

TABLE V: Model Rate Constants with k_6 as the Best Fit to Experiment^a

e	k_1	\tilde{k}_2	<i>k</i> ₃	k_4	k5	k_6	k_{e}^{b}
6	10	2	1.333	2	1.70	0.175	0.167
9	10	2	1.333	2	1.26	0.115	0.111
18	10	2	1.333	2	0.02	0.095	0.091
28	10	2	1.333	2	0.02	0.086	0.083
38	10	2	1.333	2	0.02	0.081	0.077

^a All rate constants in ps⁻¹. ^b Effective rate from experiment, $1/\tau_1$ in Table III.

also directly affected by dielectric constant because local polarization response will stabilize the local contact ion pair and create an activation barrier to recombination. The barrier will increase with increasing dielectric constant, and therefore k_5 will have a decreasing exponential relationship with dielectric constants. This exponential relation explains why recombination is suddenly reduced in changing from $\epsilon = 9$ to $\epsilon = 18$, although the yield of recombination for $\epsilon = 9$ would be less if a pure exponential rate dependence was present. By assuming a constant value for k_4 of 2 ps⁻¹, we can use the yield data to define k_5 . An overview of the approximate energetics for the activated steps of our kinetic scheme is shown in Figure 7. Note that the intermediates for ionization from the lowest energy electronic state are not shown in Figure 7. We do not know if the transition state is tetrahedral or distorted; if it is distorted, then the vibrational excited contact ion pair and localized ion pair are geometrically different from CIP^v and CIP¹. Ultimately, the lowest energy process should also lead to CIPd.

The results of computer simulation with these rate constants are shown in Table V. The key computational result is that reasonable approximations to an exponential rise are found for all calculations, with the most deviation at $\epsilon = 6$. The values of k_6 are similar to the measured values of $1/\tau_1$ in Table III.

8. Summary. The fast transient absorbance rise of MG⁺ in our experiment has been modeled by ionization from high vibrational levels of the lowest singlet state in <1 ps. The data suggest that the initial, vibrationally excited, contact ion pair, CIP^v, has a more localized charge in tetrahedral MG⁺ and that recombination occurs in competition with transient solvent stabilization of the ion pair. The longitudinal dielectric relaxation time is proposed as the important solvent parameter in this competition. The dielectric constant dependence of our observed recombination yields is consistent with branching between recombination and stabilization into CIP¹, a localized contact ion pair of tetrahedral MG⁺ geometry. The localized contact ion pair is further stabilized by solvent relaxation, and this intermediate then reorganizes to a delocalized contact ion pair, CIP^d, in which MG⁺ has its normal

spectroscopic charge distribution. In aprotic solvents the solvents with larger dielectric constant have slower rates of charge reorganization than the dielectric relaxation times, which implies that motion over the activation barrier is controlled by energetic effects. In alcohol solvents of greater size than methanol the charge reorganization rates are comparable to overall solvent monomer reorientation times (τ_2) , which suggests that motion over the activation barrier is directly coupled to a specific solvent relaxation. These results show an unusual separation of energetic and dynamic effects in kinetic rates.

V. Discussion of Results

A. Introduction. The preceding sections have developed a number of fundamental issues in solution chemistry that are essential for understanding ionic photodissociation dynamics. Many phenomena provide insights into our data, and we have analyzed electron-transfer studies,⁵¹⁻⁵³ intramolecular chargetransfer experiments,49,54 transition state theory,40,55 photoionization studies,46 radiation chemistry,56 and exciplex photophysics.57 Theoretical⁵⁸⁻⁶⁰ and experimental⁵⁰ studies of ion pair separation dynamics relate to the final steps of ionic photodissociation while its reverse process encompasses nucleophilic reaction chemistry.61-65 In the following sections we extend our earlier discussion of dielectric relaxation and its role in charge stabilization and transition state models of the dynamics. In addition, we briefly relate our results to nucleophilic reactions of ion pairs.

B. Dielectric Response and Transition State Models. We partially discussed an interpretation of $\tau_{\rm L}$ in an earlier section in which we emphasized its importance in understanding ion recombination at very short times. The concept has been derived from continuum liquid models in several theoretical works³⁹⁻⁴¹ and plays an important role in theories of ionic relaxation⁶⁰ and solvent effects on ionic transition states.⁴⁰ In the continuum approximation, Friedman has discussed the meaning of $\tau_{\rm L}$ using a capacitor model.⁶⁶ The relation of his ideas to a physical picture of the solvation energy vs. time and how it relates to molecular motions are not explicitly developed by a capacitor treatment. The method of Friedman⁶⁶ does show that the concept of an electric field propagation time relates to $\tau_{\rm L}$. In addition, the theory of Calef and Wolynes⁶⁷ is suggestive in developing a molecular view of dielectric relaxation. If we view $\tau_{\rm L}$ from the point of view of a suddenly created charge in solution, the radial propagation of the polarization has a time dependence that is represented with a characteristic time, $\tau_{\rm L}$. From the point of view of molecular relaxation and polarization in a radial direction, the longitudinal relaxation time, $\tau_{\rm L}$, is the time to develop the radial electric field at a point far from the perturbation. Transverse relaxations, often characterized by the longer time $\tau_{\rm D}$, develop a final electric field at the site of the perturbation. From the point of view of energetics, there is a time spectrum of solvation energy development

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in a dielectric which is controlled by more than $\tau_{\rm D}$.

In our data analysis we have found evidence that a significant fraction of the final solvation energy develops in a time that functionally is similar to τ_L . We have used τ_L in our discussion even though it is not clear how to define the degree of solvation energy development or if $\tau_{\rm L}$ is the best representation of the physical concept. For liquids in which multiple relaxations can occur in τ_D , a single definition of τ_L becomes difficult. For our specific use of $\tau_{\rm L}$ we prefer to exclude molecular motions which induce correlated motions in adjacent (i.e., transverse) volume elements of the liquid. Accordingly, we only consider the fastest component of τ_D as useful for defining τ_L . In this qualitative description, τ_1 is the time for achieving a significant fraction of solvation energy, a fraction which might be called the longitudinal solvation component. Some physical processes may be sensitive to the times for more complete solvation energy development, and these processes will include longer time scale relaxations. The longer time scale relaxations will define a second (or third) relaxation time, τ_{L}' , which also can involve static dielectric effects in a form like eq 6.

We have examined the charge reorganization process of converting CIP¹ to CIP^d in terms of transition state theory to obtain a much clearer understanding of how molecular and continuum dielectric models operate in our system. Transition state models of Calef and Wolynes⁶⁷ and van der Zwan and Hynes^{40,55} directly incorporate solvent dynamics. The transition state for our system has solvent configurational changes coupled to a potentially fast intramolecular electron transfer which involves molecular framework motions. If the solvent reorganization dynamics either dominate or are negligible compared to framework dynamics, we expect a nearly one-dimensional reaction coordinate. For intermediate situations a multidimensional reaction coordinate may be necessary. For the aprotic solvents we observed reorganization lifetimes of CIP^l greater than 6 ps when the solvents have $\tau_{\rm L} \leq$ 0.9 ps and $\tau_{\rm D}$ = 3.8 ps. The fast solvent relaxation suggests that a continuum concept, with negligible solvent perturbation, of the framework dynamics is a good one-dimensional model in aprotic solvents. The rates in the aprotic solvents largely reflect energetic differences.

For the alcohol solvents we have multiple solvent relaxation times (12 and 53 ps for methanol and 20 and 70 ps for ethanol) that are much slower than our initial creation of CIP¹. In analogy with the dipolar aprotic solvents, we expect the energetic barrier for framework conversion in $CIP^{l} \rightarrow CIP^{d}$ to show little difference between ethanol and methanol. However, a solvent dynamical component to the transition state crossing should reflect the motional relaxation times of the alcohol solvents. The observed lifetimes were very similar to the 12- and 20-ps dielectric relaxation components, which implies that specific solvent motions control the charge reorganization in alcohol solvents. More alcohols, such as propanol, are important to confirm our interpretation. This particular behavior is similar to the theoretical model of polarization caging.55 However, our reaction coordinate is somewhat more complex because the initial state of CIP¹ does not have equilibrium solvation and a pure one-dimensional coordinate may not be a good description of the transition state dynamics. Understanding why these particular motions control the transition state is an important question for model calculations.

The kinetic behavior of MGCN is an especially clear example of transition state dynamic effects because of the contrasting behavior in alcohol and aprotic solvents. Other examples of solvent reorientation effects on the rate of charge reorganization occur in large displacement charge reorganizations of excited states.^{49,54} Recent interpretations of these data by Kosower and Huppert⁴⁹ have suggested that τ_L is the controlling time for charge reorganization in the alcohols. These authors use τ_1 , the longest component of alcohol dielectric relaxation, to calculate τ_L . We do not feel that this choice of relaxation component is unique for approximating τ_L , a continuum fluid concept. While there is no general definition of τ_L for molecular liquids, our data require emphasis of the fastest component of solvation energy development, a time which only allows small librational and translational motions. The published data^{49,54} for time-dependent spectral shifts in alcohol solvents show behavior characteristic of solvent reorganization effects. Unlike MGCN, the observed times are not directly correlated with particular relaxation motions and seem to be intermediate between the two longest times. The correlation of τ_L , computed with the longest component of relaxation, and the observed spectral shifts suggests that the experiment is measuring the time evolution of complete solvation. These systems differ from our system because they involve a transition state proceeding from a state of no charge development to a final charge-transfer state having a spatially displaced charge development. The solvation energy effects on spectra must also be explicitly modeled in these systems in order to separate energetic and dynamic effects.

The case of electron stabilization rates in alcohols⁴⁶ presents a slightly different example in that a transition state for a nonclassical species is totally defined in terms of the solvent reorganization. These data have been successfully correlated with τ_2 in alcohols, which shows the importance of this overall reorientation motion in achieving a major component of solvation energy. The fact that we obtain very similar times in alcohols suggests a common element in both processes and supports our interpretation of a transition state controlled by alcohol reorganization dynamics.

In summary, the observed data show how the longitudinal relaxation time, τ_L , is important for controlling ion recombination. In addition, the nonadiabatic solvent control of charge reorganization has been demonstrated for alcohol solvents and connected to specific solvent reorientations. For solvents not having a good continuum approximation, we define τ_L in a way that changes our concept of the time development of solvation energy.

C. Contact Ion Pairs and Nucleophilic Reactions. Our kinetic and yield studies of MGCN support the concept of a reasonably stable contact ion pair where the rate of evolution from $CIP^{l} \rightarrow$ CIP^d is only slightly dependent on solvent stabilization energy (in aprotic solvents). However, the recombination yield for $CIP^{v} \rightarrow$ CIPⁱ was very dependent on dielectric constant which implies that the reverse recombination from CIP¹ has a rate that is controlled by both internal activation of the MG⁺ molecule and solvent activation that reduces stabilization of the ion pair. In Figure 7 we diagram the overall view of recombination, starting with a solvent-separated ion pair (SSIP). The recombination begins with the desolvation of anion and cation to form a delocalized contact ion pair. The delocalized contact ion pair, CIPd, must be activated to form a localized ion pair, a step that probably has little solvent dependence of rate as indicated from the modest dependence of the reverse rate, $CIP^{i} \rightarrow CIP^{d}$, on solvent dielectric constant. The final step of activating the localized ion pair to achieve ion recombination appears to have a significant dependence on ion solvation energetics, as judged by our dissociation yield data. However, the activation energy of recombination is likely to be much smaller than the earlier step of desolvation.

If we consider the standard kinetic measurement of ion recombination, the desolvation of anion and cation is probably rate limiting. This suggests that the solvation energies of the ions control the rates, with secondary contributions from relative stabilities of the cations. The contribution of final bond strength is indirect for the desolvation step, and it operates through charge delocalization for different cations. In addition, the planar to tetrahedral conformation change ($CIP^d \rightarrow CIP^l$) also relates to bond energy. If we compare published data^{62,63} for recombination of CN^- with MG⁺ and CV^+ ((Me₂NC₆H₄)₃C⁺) in water, we find respective activation enthalpies of 13.4 and 14.8 kcal/mol and activation entropies of -16 cal/(K mol) for both cations. The thermodynamic free energy change is not known for CN-, but for OH- with MG+ or CV+ the respective values are -11.3 and -6.6 kcal/mol. These data suggest that activation energies for recombination are not greatly correlated with thermodynamic parameters. The work of Kessler and Feigel⁶⁸ used temperature and solvent variations to study the thermodynamics for conversion

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of neutral to contact ion pair in trityl chloride, $(MeOC_6H_4)_3C-NCS$, and $(Me_2NC_6H_4)_3C-N_3$. The last compound, crystal violet azide, is very similar to MGCN, and it had a ΔS^* of -11.5 eu and a $\Delta S^\circ = -12.7$ eu which suggests strong solvent ordering in the transition state. The overall thermodynamics also suggests that significant activation energy is needed for the reverse recombination of contact ion pairs to neutral product. Because these studies required nearly equilibrium conditions, no systematic solvent studies could be accomplished on a single compound.

The analysis of nucleophilic reaction kinetics by Ritchie and co-workers⁶⁴ has been completed for a large number of systems. These studies used MG⁺, CV⁺, and a number of other cations with a wide variety of nucleophiles. The kinetic results were interpreted with a nucleophilic reaction parameter N_+ which correlates with observed rate constants for any specific cation with a nucleophile X as log $(k_X/k_{H_2O}) = N_+$. The N_+ values are characteristic of the nucleophile, and different cations do have different reactivities for a specific nucleophile. While very few comparisons of solvent effects are available, the existence of a rate constant largely determined by the nucleophile is characteristic of ion solvation energy dominating the rate-limiting initial step. there has been one attempt to rationalize the Ritchie correlation in terms of solvation vs. thermodynamic effects.65 This work uses the classical Marcus model of electron transfer to attempt a transition state separation of solvent reorganization effects and thermodynamic effects. This work concludes that solvation effects are similar for the same nucleophile and different cations, but thermodynamic effects dominate the reactivity. Figure 7 and our kinetic data have shown that a single transition state picture is oversimplified. In addition, the final bond energy of the system may be indirectly related to solvation energy of the cation.

Our model for nucleophilic reactions and contact ion pair interactions in triphenylmethyl cation systems is consistent with the data on nucleophilic reactivity. In most cases the rate-limiting step is ion desolvation leading to a contact ion pair which then undergoes its own activation processes to recombination. We have identified the processes involved in the contact ion pair and what steps are likely to be solvent sensitive and also depend on final bond stability.

D. Summary. The ionic photodissociation of electronically excited MGCN has been shown to occur by two different mechanisms. The lowest excited state ionizes from an ionic transition state with an activation free energy that depends on the solvation energy. Continuum dielectric approximations for solvation energy successfully correlate the rate behavior in aprotic solvents and allow reasonable estimates of the transition state bond lengths and charge displacement. Only modest effects of hydrogen bonding are observed in the rates, and the absolute rates are too small to reveal kinetic details of transition state solvation or ion recombination. The picosecond ionic photodissociation from a high excited state of MGCN is explained by formation and subsequent geometric and charge reorganization of a contact ion pair. We identify how solvent dielectric relaxation and vibrational relaxation of the initial ion pair control the ion recombination yield. In addition, the charge reorganization of the initial contact ion pair demonstrates both energetic and solvent dynamic control of rates. Aprotic solvents have energetic control while alcohol solvents of larger size than methanol have rates controlled by the overall reorientation time of the alcohol monomer.

There are many more experiments yet to be done on MGCN and related systems that will check some of our hypotheses and provide more detailed understanding of ion pair solvation dynamics. At this stage of the experiments we have been able to understand how solvent dielectric relaxation processes affect reaction transition states. these insights are important for understanding nucleophilic reactions and the time dependence of solvent reorganization behavior. Further experiments and more detailed comparison with theory will be needed to allow testing and extrapolating our current understanding about effects in ionic reaction chemistry.

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Appendix

The single wavelength monitor of transient absorption has been ascribed to MG^+ . The one published work³ with a transient spectrum from 550 to 680 nm supports this conclusion for delay times of 250 ps, and we can find no strongly absorbing species that could provide an alternative to this interpretation at earlier times. Obviously, several complete absorption spectra over the first 20 ps would confirm the proposed mechanistic conversion of $CIP^{l} \rightarrow CIP^{d}$. We have explicitly assumed that the absorbance of CIPⁱ is weak at 600 nm because it is a partially resonant species, presumably with an absorbance that is significantly blue-shifted. An artifactual absorbance at 600 nm which converted to MG⁺ at 250-ps delay time would need a product of number density and extinction coefficient that equaled MG⁺. Because MG⁺ is a large fraction of the initial MGCN, any proposed artifact will need an extinction of $\sim 1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ and a very high yield. The candidates for artifacts are reviewed below. None have a large extinction coefficient.

Direct photoionization is a potential source of alternative transients at the high pump power levels. Solvated electrons in acetonitrile from anions⁶⁹ absorb at 1450 nm while in the alcohols the extinction coefficient is only 10⁴ M⁻¹ cm⁻¹⁷⁰ at ~600 nm. Photoionization of MGCN to form the MGCN⁺ radical cation may be an alternative. While no spectral data exist for MGCN⁺, the cation from N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD) has bands at 575 and 630 nm that are solvent sensitive with an extinction coefficient of about ~10⁴ M⁻¹ cm^{-1.71}

Similarly, the radical cation of DMA has weak absorption bands,^{72,73} but these occur below 500 nm. Another analogue, N,N,N',N'-tetramethyl-1,6-pyrenediamine, weakly absorbs at 590 nm in MeCN.⁷⁴

Registry No. 1, 4468-56-8; 2, 14426-28-9; CN^- , 57-12-5; MeCN, 75-05-8; EtOAc, 141-78-6; benzene, 71-43-2; cyclohexane, 110-82-7; methanol, 67-56-1; ethanol, 64-17-5.

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