

The rate of formation of EDA complexes from their unassociated components is not known, but presumably it is close to the diffusion-controlled limit.<sup>8-10</sup> Under our conditions,  $k_{\text{diff}} \approx 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  which is calculated by assuming  $k_{\text{diff}} = 8RT/3000^{35a}$  where  $\eta = 0.437 \text{ cP}$  at 298 K.<sup>36</sup> Therefore, with a system consisting of 0.05 M indene and 0.05 M TCNE, the rate of diffusional encounter ( $2.6 \times 10^9 \text{ s}^{-1}$ ) would be of the same magnitude as the rate found for the regeneration of the EDA complex ( $>2 \times 10^9 \text{ s}^{-1}$ ). The latter may exceed somewhat the rate of diffusional encounter, owing to the proximity of indene and TCNE following the decay of the ion pair. This explanation, if valid, would indicate that (a) the formation of the ground-state EDA complex is diffusion limited and (b) the electron transfer in the formation and/or decay of the radical ion pairs may lead to a geometry different from that favored at equilibrium for the ground-state EDA complex. Furthermore, in the case of a diffusion-controlled reaction, there should be a temperature dependence that decreases the rate of regeneration,  $k_{\text{diff}}$ , to about  $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  at 262 K because  $\eta$  increases to 0.59 cP.<sup>36b,c</sup> Unfortunately, the resolution of the spectra (Figure 7) does not permit a quantitative experimental differentiation between the regeneration rates of the EDA complexes at 262 and 293 K. The picosecond spectroscopic data indicate regeneration rates of  $0.5-1.0 \times 10^{10} \text{ s}^{-1}$  which are somewhat greater than those expected for purely diffusional encounter in this temperature range. The resulting IN and TCNE may recombine or undergo reorientation within the solvent cage to reform the EDA complex. We expect that the breaking of the

bridging  $\sigma$  bond between indene and TCNE in either iv or v also should represent a process with low activation energy. Thus the temperature dependence of the rate of bond breaking may be small.

### Summary and Conclusions

Specific photochemical excitation of electron donor-acceptor complexes involving meso-substituted anthracenes or indene as electron donors and TCNE as the common electron acceptor establishes the direct population of an ion singlet state. The rise times of the transient absorptions of the radical ion pairs are limited by the width of the laser pulse (25 ps). These results represent in these systems a direct confirmation of Mulliken theory, the CT excitation involving essentially complete transfer of an electron from the donor to the acceptor.<sup>11</sup> The radical ion pairs rapidly decay within  $\sim 60$  ps to ultimately regenerate the original electron donor-acceptor complex. No products are formed irreversibly. However, in the case of indene, an intermediate is formed which does not absorb in the visible region. We are currently investigating the transient absorption spectra at wavelengths less than 420 nm in an effort to observe and to identify spectroscopically this intermediate. We are also extending our studies to include systems which afford stable photoproducts.<sup>14b</sup>

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**Registry No.** 1 (X = CN; Y = H)-TCNE, 86885-44-1; 1 (X = NO<sub>2</sub>; Y = H)-TCNE, 93350-34-6; 1 (X = CHO; Y = Cl)-TCNE, 93350-35-7; 1 (X = CHO; Y = H)-TCNE, 29844-15-3; 1 (X = MeOCO(O); Y = H)-TCNE, 93350-36-8; 1 (X = Y = Ph)-TCNE, 64914-69-8; 1 (X = Y = MeO)-TCNE, 36336-02-4; 1<sup>+</sup> (X = Y = H), 34512-28-2; 1<sup>+</sup> (X = NO<sub>2</sub>; Y = H), 84367-93-1; 1<sup>+</sup> (X = CHO; Y = Cl), 93350-37-9; 1<sup>+</sup> (X = CHO; Y = H), 91547-89-6; 1<sup>+</sup> (X = CN; Y = H), 84985-64-8; IN-TCNE, 7378-72-5; TCNE<sup>-</sup>, 34512-48-6.

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## Picosecond Photochemistry of 2,3-Diphenyloxiranes: Reaction from a Vibrationally Unrelaxed Electronic Excited State

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**Abstract:** Picosecond photochemistry of *trans*-1,2-diphenyloxirane (Ia) and *cis*-1,2-diphenyloxirane (Ib) is studied in cyclohexane and acetonitrile after 266-nm excitation by a 25-ps laser pulse. Carbonyl ylides, IIa and IIb, are formed by disrotatory opening of the singlet electronic excited state of Ia and Ib, respectively. The carbonyl ylides arise in  $450 \pm 250$  ps after excitation in either solvent. After formation, the carbonyl ylides (IIa and IIb) disappear with lifetimes of  $>250$  and  $40 \pm 20$  ns, respectively. Photolysis of Ib in either solvent leads to significant amounts of IIa, the symmetry-forbidden product formed in a conrotatory fashion. It is suggested that the symmetry-forbidden product arises from the vibrationally unrelaxed electronic excited state of Ib.

The photochemistry of diaryloxiranes (I) has received considerable attention.<sup>1</sup> Griffin and co-workers have shown that room-temperature steady-state photolysis of many diaryloxiranes leads to efficient cycloelimination yielding arylcarbenes and carbonyl compounds.<sup>2,3</sup> Low-temperature photolysis of diaryloxiranes at 77 K by Griffin et al.<sup>4-6</sup> and Trozzolo et al.<sup>6,7</sup> has established that carbonyl ylides (II) form along with the carbenes.

The opening of diaryloxiranes to carbonyl ylides occurs with conservation of orbital symmetry. Thermally, diaryloxiranes open

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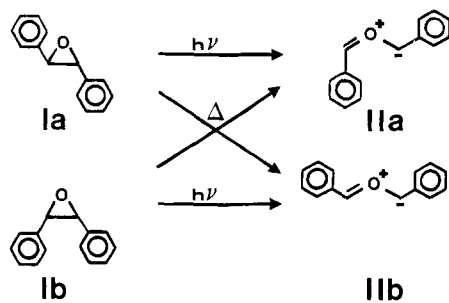
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**Table I.** Kinetic and Spectroscopic Data for Ia and Ib in Cyclohexane and Acetonitrile

solvent	oxirane, ylide	$1/k_{\text{appear}}$ , ps	$1/k_{\text{disappear}}$ , ns	$\lambda_{\text{max}}$ , nm
cyclohexane	Ia, Ia	$350 \pm 50$	$>250$	478
cyclohexane	Ib, Ib	$580 \pm 100$	$40 \pm 10$	495
acetonitrile	Ia, Ia	$320 \pm 50$	$>250$	471
acetonitrile	Ib, Ib	$300 \pm 50$	$40 \pm 20$	497

in a conrotatory fashion<sup>8</sup> as predicted in accordance with the Woodward–Hoffman rules.<sup>9</sup> After thermal formation of the carbonyl ylide, the major path for its disappearance is reclosure in a conrotatory mode to give back the diaryloxirane. This fact has been experimentally demonstrated by the observation that optically active *trans*-2-phenyl-3-*p*-tolylloxirane racemizes 172 times faster than it isomerizes from *trans* to *cis*.<sup>10</sup> Photochemically the diaryloxiranes open in a disrotatory fashion.<sup>8</sup> However, the orbital symmetry restrictions are less stringent in the photochemical reaction (as compared to the thermal reaction) as indicated by chemical trapping of photochemically generated carbonyl ylides. Interception of the photochemically produced carbonyl ylide from *trans*-2,3-diphenyloxirane (Ia) by the dipolarophile methyl acrylate leads to ~90% of the product expected by trapping of carbonyl ylide Ia (formed through a disrotatory mechanism) and ~10% of the product from trapping carbonyl ylide Ib (formed through a conrotatory mechanism).<sup>11</sup> It is not



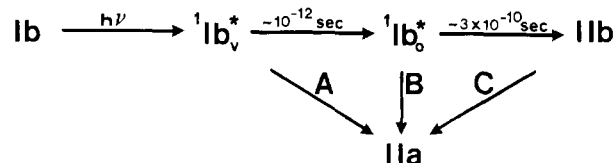
known when after photolysis this breakdown in orbital symmetry restrictions takes place. In this paper we report our results from room temperature, 266 nm, picosecond flash photolysis of *trans*-2,3-diphenyloxirane (Ia) and *cis*-2,3-diphenyloxirane (Ib). Carbonyl ylides are formed from both of the oxiranes studied. The carbonyl ylide formation is highly stereospecific and as expected leads to transients with different absorption<sup>7</sup> spectra namely IIa and IIb with  $\lambda_{\text{max}}$  at ~475 and ~500 nm, respectively. Furthermore for Ib, the symmetry-forbidden product arises from the initially formed, thermally unrelaxed singlet excited state; whereas, the allowed product is formed from the vibrationally relaxed singlet excited state.

### Experimental Section

The picosecond absorption spectrometer has been previously described.<sup>12</sup> Briefly, it consists of a mode-locked Nd<sup>3+</sup>-YAG (Quantel International, YG-400), 10 Hz, laser with pulse duration of 25 ps. A 0.5-mJ pulse at 266 nm is used for photolysis. The probing continuum, 450–750 nm, is dispersed by a spectrograph (JY-200) and detected by an OMA II (PAR 1215-1216-1205I) Vidicon system. Spectra reported at time delays longer than 500 ps are obtained by delaying the interrogation beam with the use of fiber optics (Math Associates).

*trans*-2,3-Diphenyloxirane was purchased from Aldrich. *cis*-2,3-Diphenyloxirane was prepared by *m*-chloroperbenzoic acid oxidation of *cis*-stilbene in methylene chloride. All solutions were  $\sim 1 \times 10^{-3}$  M in diaryloxirane. The solutions were N<sub>2</sub> saturated and the sample continuously flowed (single pass) through the photolysis cell to ensure that no photoproducts accumulated.

### Scheme I



### Results and Discussion

Photolysis of Ia in cyclohexane at 266 nm produces a transient with  $\lambda_{\text{max}}$  at 478 nm. Similarly photolysis of Ib produces a transient with  $\lambda_{\text{max}}$  at 495 nm. We assign the spectra of the carbonyl ylides IIa (from Ia) and IIb (from Ib), respectively. These assignments are based on the similarity to the  $\lambda_{\text{max}}$  reported at 77 K for IIa and IIb of 490 and 500 nm, respectively.<sup>6,7</sup> The carbonyl ylides appear at similar rates,  $1/k = 350 \pm 50$  ps for  $^1\text{Ia}^* \rightarrow \text{IIa}$  and  $1/k = 580 \pm 100$  ps for  $^1\text{Ib}^* \rightarrow \text{IIb}$ , Table I. The appearance of IIa and IIb on this time scale ensures that the vibrationally relaxed singlet excited state ( $^1\text{I}_0^*$ ) is the precursor to the carbonyl ylides.<sup>13</sup> Subsequent to formation, both IIa and IIb decay on the nanosecond time scale with lifetimes of  $>250$  and  $40 \pm 20$  ns, respectively. The carbonyl ylides can disappear by separation to carbene and carbonyl, or by reclosure to oxirane. It is not obvious why IIb should dissociate to carbene and carbonyl faster than IIa, especially since IIb should be more stable than IIa; furthermore, thermal opening of 2,3-diaryloxiranes to carbonyl ylides does not lead to carbenes.<sup>10</sup> It is apparent from these observations that the major path for disappearance of the carbonyl ylides is reclosure to the oxirane. Since recyclization is a thermally activated reaction, we anticipate that it would occur in a conrotatory manner; therefore, IIa will form Ib and IIb will form Ia. The observed rates for disappearance of IIa and IIb (IIb decays more than six times faster than IIa) are consistent with IIa closing to the less stable *cis* isomer Ib and IIb closing to the *trans* isomer Ia. At 125 ns most of IIb has decayed; however, small amounts of IIa ( $\lambda_{\text{max}}$  at 478 nm) remain from the photolysis of Ib.

The amount of IIa observed from photolysis of Ib in cyclohexane is 15–20% that obtained when Ia is photolyzed. This is a direct observation of the loss of stereospecificity in these photochemical reactions. The loss of stereospecificity can occur during any of several steps after photolysis, Scheme I. Path A indicates formation of IIa from the initially formed excited state,  $^1\text{Ib}_v^*$ , prior to relaxation to  $^1\text{Ib}_0^*$ . In path B, IIa formation occurs from the vibrationally relaxed singlet excited state,  $^1\text{Ib}_0^*$ , a result that would be in direct conflict with the principles of conservation of orbital symmetry. Finally, path C suggests *cis*–*trans* isomerization can occur after carbonyl ylide formation. Path C is inconsistent with the observation that there is little *cis*–*trans* isomerization from the thermally generated carbonyl ylide.<sup>10</sup>

Photolysis of Ia or Ib in acetonitrile produced the corresponding carbonyl ylides IIa and IIb with  $\lambda_{\text{max}}$  at 471 and 497 nm, respectively. The spectra are similar to those obtained in cyclohexane except for a greater difference in peak  $\lambda_{\text{max}}$  (26-nm difference in acetonitrile vs. 17-nm difference in cyclohexane). The kinetics for appearance and disappearance of IIa and IIb are essentially identical with those seen in cyclohexane. Figure 1 shows the results obtained upon 266-nm excitation of Ib in acetonitrile. Within

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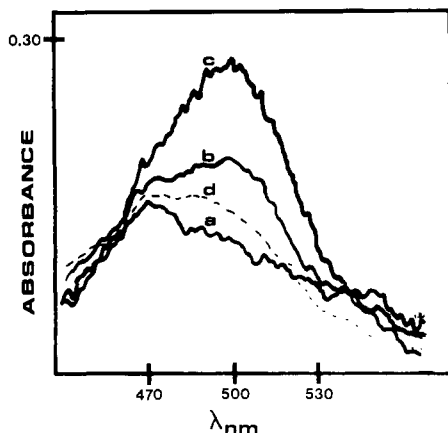
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(13) It has been shown by chemical trapping experiments that triplet-sensitized carbonyl ylide formation from Ia or Ib gives the same ratio of IIa to IIb independent of which oxirane was the precursor.<sup>11</sup> In our case, photolysis of Ia strongly favors carbonyl ylide IIa, while photolysis of Ib favors IIb. These observations ensure that we are not seeing triplet-state chemistry.



**Figure 1.** Appearance of carbonyl ylides IIa and IIb after photolysis of Ib in acetonitrile: (a) <50 ps; (b) 180 ps; (c) 9.1 ns; (d) (---) 125 ns.

50 ps some carbonyl ylide appears with  $\lambda_{\max}$  at 471 nm which corresponds to IIa, the symmetry-forbidden product! Within a few nanoseconds IIb appears ( $1/k = 320$  ps,  $\lambda_{\max} = 497$  nm) and then decays with a lifetime of  $\sim 40$  ns. At 125 ns (by which time most of IIb has decayed) the same amount of IIa remains as was present at 50 ps. This result indicates that most of the IIa formed by photolysis of Ib in acetonitrile is formed within 50 ps and suggests path A (formation of IIa from the unrelaxed excited state  $^1\text{Ib}^*$ ) is the major source of the "forbidden" product in this case. Further analysis of the data reveals that IIa is the major product to appear in the first 50 ps (>90%). Path A simply indicates a loss of orbital symmetry control due to carbonyl ylide formation from a vibrationally excited state. We might anticipate that such a path would give similar amounts of IIa and IIb (possibly favoring the more stable ylide IIb), but we observe mostly IIa formation. It seems that the fast process leading to carbonyl ylide occurs stereospecifically in a conrotatory fashion. One explanation is that IIa arises via an upper electronic excited state of Ib from

which conrotatory opening is allowed. In this case the upper excited state would have to be the result of a two-photon absorption process. This possibility is eliminated by the observation that the ratio of IIa to IIb (after photolysis of Ib in acetonitrile) is independent of laser power. Furthermore the amount of ylide formed from Ib is linear with laser power (determined over an 8-fold range of power).

It seems that the excess energy from 266-nm excitation of Ib causes efficient population of a vibrational level which is strongly coupled to the motion leading to carbonyl ylide. The 0,0 band for Ib occurs at  $271 \pm 3$  nm<sup>5</sup> which results in  $800$  to  $3100$  cm<sup>-1</sup> of excess energy being added by the 266-nm excitation. The oxirane ring of Ib has three infrared active absorptions between  $850$  and  $1250$  cm<sup>-1</sup> which indicates that the excess energy added by the 266-nm excitation could reasonably be expected to excite some oxirane ring vibrations.<sup>14</sup>

Establishment that strongly coupled vibration levels can control the course of concerted reactions would help explain in some instances why photochemical reactions generally occur with less stereospecificity than thermal reactions. Future plans to examine this phenomenon include the study of wavelength and temperature effects on the ratio of IIa and IIb. Also, faster time resolution experiments will help elucidate the actual source of stereochemical loss.

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**Registry No.** Ia, 1439-07-2; Ib, 1689-71-0; IIa, 93041-28-2; IIb, 93041-29-3.

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## Theoretical Study of Phosphate Interaction with $\text{NH}_4^+$ , with $\text{Na}^+$ , and with $\text{Mg}^{2+}$ in the Presence of Water

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**Abstract:** The interactions of the phosphate anion with ammonium, sodium, and magnesium cations are studied by ab initio molecular orbital theory. Regions of the potential energy surfaces for anion-cation complex formation with two water molecules present are investigated. The theory predicts that the most stable structures for the monocation complexes have the water molecules partially between the anion and the cation. These bridging water molecules increase the separation distance between the ionic species in order to optimize the water-ion interactions. The addition of two water molecules is not predicted to affect the geometry of the magnesium phosphate complex. Implications for the association of cations with nucleic acids are discussed.

### Introduction

The structure, function, and physical properties of nucleic acids are, to a large extent, determined by their polyanionic nature. The electrostatic repulsion resulting from the proximity of many negatively charged phosphate groups imposes severe constraints on the conformation of these polyions. In addition, the interaction of nucleic acids with regulatory proteins, drugs, or other molecules is affected by the very high charge density on the surface of the nucleic acid. The stability of these macroions is maintained by the association of small cations that are attracted to the very negative electrostatic potential near the nucleic acid surface. These

counterions shield the phosphate-phosphate repulsions, affecting the intrapolymer energy and the stability of various conformations of DNA. In this way changes in the ionic environment can induce sequence-specific conformation changes in DNA.<sup>1</sup>

The nature of the DNA-cation interaction still remains unresolved. The formation of a "Stern layer"<sup>2</sup> on the immediate surface of the polyion may result from phosphate-cation ion-pair formation. Although simple phosphate-cation salts would be

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