A Laser Flash Photolysis Study of a Carbene−Ether Ylide

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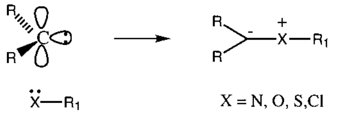
Laser flash photolysis (308 nm) of carbomethoxy-2-naphththyldiazomethane in deoxygenated Freon-113 (CF_2-$ClCFCl_2$) solution containing tetrahydrofuran (THF) produces a transient spectrum with a sharp absorption maximum at 330 nm and a shoulder at 375 nm. The observed rate constant of formation of transient absorption is the same at 330 and 400 nm. The transient spectrum is the same 100 ns, 1 μs, and 10 μs after the laser pulse at ambient temperature and is attributable to a single carrier. The transient shows little decay over 10 μs in the presence and absence of oxygen. Similar results were obtained at −60° C. This pattern of observations is not consistent with assigning the transient to triplet carbomethoxy-2-naphthylcarbene or its related radical. The rate constant of formation of the transient, k_{THF}, is first order in the concentration of THF; thus, the transient is attributed to a carbene−ether ylide. To our knowledge, this is the first direct observation of a carbene-ether ylide. An Arrhenius plot of k_{THF} is nonlinear due to a change in mechanism of the reaction of the carbene with THF or to reversion of the ylide to carbene and THF at elevated temperatures.

I. Introduction

Singlet carbenes react with compounds containing heteroatoms to form ylides.[1] These ylides are usually easier to detect in laser flash photolysis (LFP) experiments than the carbenes themselves. Typically, ylides derived from pyridine, nitriles, ketones, and thioketones have been detected.[2] Although ethers are believed to form ylides with carbenes and have been widely postulated, they have not been previously detected directly.[1,2] This motivated the present study with the well-known carbene carbomethoxy-2-naphthylcarbene and tetrahydrofuran. Herein we are pleased to report the results of that study and the first direct observation of a carbene−ether ylide.



II. Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 200, 200 MHz NMR spectrometer. DEPT and proton spin decoupled spectra were obtained on a Bruker AC 500 MHz NMR spectrometer. The chemical shifts are reported in δ (ppm) with tetramethylsilane as internal standard. Infrared spectra were recorded using a Perkin-Elmer 1700 series FTIR interfaced with a Perkin-Elmer 3700 data station. Exact mass measurements were made at The Ohio State University using a Q-TOF2 electrospray mass spectrometer. UV/Vis spectra were recorded on a Milton Roy Spectronic 3000 diode array spectrophotometer. Gas chromatographic analyses were obtained with a Perkin-Elmer 8500 gas chromatograph equipped with a flame ionization detector, using a Supelco fused silica capillary column cross-linked with methyl silicone (column i.d. 0.32 mm, column length 30 m, phase film thickness 3 μm). GC/MS mass spectral analysis was performed on a Hewlett-Packard 6889 gas chromatograph using a 30 m × 0.25 mm × 0.25 μm column packed with 5% phenylmethylsiloxane and an HP 5973 MS detector. Samples for laser flash photolysis studies were contained in quartz cells for excitation at 308 nm. The sample cells were fabricated from square tubing purchased from Vitro Dynamics. Excitation with the Nd:YAG picosecond laser required Suprasil quartz fluorescence-free static cells purchased from Scientific Products. Low-temperature LFP experiments were performed using a Fluorescence-free cell in a variable-temperature sample holder and a NESLAB RTE-110 proportional temperature controller to regulate temperature.

All reagents were purchased from commercial sources and used without purification, unless noted otherwise. 2,3-Dimethyl-2-butene and $CF_2ClCFCl_2$ (Freon-113) were purified by passage through a neutral alumina column, just prior to use. Diethyl ether and tetrahydrofuran were distilled over sodium and benzophenone. The distillations were performed under an inert atmosphere.

A Lambda Physik LPX-100 excimer laser (308 nm, 120 mJ, 17 ns) was used to obtain kinetics and transient spectra. The intensity of the laser remained stable for a period of several hours to meet the experimental requirement of constant laser output. For experiments involving the Lambda Physik excimer laser, the cells were made from square quartz tubing and were approximately 1 cm in length. An almost perfectly flat surface of this type of quartz cell results in the minimum scattering of laser light. The spectrometer has been described in detail elsewhere.[3]

The stock solutions of the 2-diazo-2-(2-naphthyl)acetate were prepared just prior to the LFP experiments. For experiments with the Lambda Physik excimer laser, the absorbance of the diazo samples used in the kinetic studies was close to 0.5 at 308 nm, which was the wavelength of laser emission. The LFP studies were carried out in Freon-113 as the solvent. A constant volume (1 mL) of stock solution was added to the cuvette. To each cuvette were added varying amounts of trapping agent (THF), and Freon-113 was added to each cuvette to maintain a total volume of 2 mL. In LFP experiments that required the use of the Nd:YAG laser, the diazo solution was prepared in neat trapping agent, THF. For all LFP experiments, the

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appropriate sample cells were fitted with a rubber septum and the solutions were deaerated by passing a stream of argon through the samples for 2 min.

Synthesis. The preparation of 2-diazo-2-(2-naphthyl) acetate (**D**) has been described.[4]

Characterization of Products Derived from Photolysis of 2-Diazo-2-(2-naphthyl) Acetate in the Presence of Tetrahydrofuran. In a continuous photolysis experiment, 300 mg of **D** in 25 mL of tetrahydrofuran was placed in a Pyrex tube, and the solution was deoxygenated for 5 min with an argon flow. The solution was photolyzed at 320−380 nm using a Ray-O-Net reactor equipped with 16 RPR-3500 bulbs for 20 h, at 15 °C. The photolytic reaction gave four carbene-trapped adducts, **1**−**4**, which were isolated by column chromatography using 2:1 petroleum ether and dichloromethane.

Methyl-α-(3-butenyloxy)-2-naphthalene Acetate (1). Compound **1** was isolated in a pure state as an oil (50 mg). ^{1}H NMR ($CDCl_3$, TMS, δ (ppm)) 2.45 (q, 2H), 3.55 (dd, 2H), 3.70 (s, 3H), 5.1 (m, 3H), 5.8 (m, H), 7.5 (m, 3H), 7.8 (m, 4H). ^{13}C NMR (δ (ppm)) 34.25, 52.50, 69.49, 81.44, 116.90, 124.77, 126.52, 126.60, 126.90, 127.93, 128.35, 128.70, 133.36, 133.67, 134.16, 134.89, 171.50. DEPT spectra revealed that δ 34.25, 69.49, and 116.90 are the methylene carbons. MS *m*/*e* (relative intensity) M^+ 270 (3), 211 (61), 181 (17), 171 (21), 157 (32), 155 (25), 129 (35), 127 (33), 55 (100). HRMS calcd 293.1154, found 293.1145.

Methyl Tetrahydro-2-(2-naphthyl)-2*H*-pyran-2-carboxylate (2). Compound **2** was isolated in a pure state as a yellow solid (90 mg), mp 62 °C. ^{1}H NMR ($CDCl_3$, TMS, δ (ppm)) 1.7 (m, 4H), 1.8 (m, 1H), 2.6 (m, 1H), 3.72 (s, 3H), 3.85−4.0 (mdd, 2H), 7.4 (m, 2H), 7.65 (dd, 1H), 7.8 (m, 3H), 8.0 (d, 1H). ^{13}C NMR ($CDCl_3$, TMS, δ (ppm)) 20.80, 25.13, 33.68, 52.59, 65.18, 80.94, 123.13, 124.44, 126.17, 126.21, 127.54, 128.21, 128.40, 132.84, 133.21, 138.41, 173.14. DEPT spectra revealed that δ 20.8, 25.13, 33.68, and 65.18 are the methylene carbons. MS *m*/*e* (relative intensity) M^+ 270 (0.65), 211 (100), 155 (73), 127 (54). HRMS calcd 293.1154 found 293.1167.

Methyl 1,3,4,6-Tetrahydro-2*H*-naphth[2,1-*c*]oxocin-6-carboxylate (3). Compound **3** was isolated in a pure state as a colorless oil (10 mg). ^{1}H NMR ($CDCl_3$, TMS, δ (ppm)) 1.65 (m,2H), 1.85 (m, 2H), 3.30 (m, 1H), 3.70 (s, 3H), 3.75 (m, 3H), 5.49 (s, 1H), 7.32 (d, 1H), 7.56 (m, 2H), 7.75, (d, 1H), 7.80 (m, 1H), 8.15, (m, 1H). ^{13}C NMR (δ (ppm)) 26.005, 27.496, 28.113, 52.832, 69.365, 80.348, 124.312, 126.176, 126.463, 126.855, 127.342, 129.181, 132.089, 132.348, 134.393, 138.002, 171.923. DEPT spectroscopy revealed that the bands at δ 26.005, 27.495, 28.112, and 69.365 are the methylene carbons. MS *m*/*e* (relative intensity) M^+ 270 (40), 211 (84), 193 (20), 169 (57), 152 (25), 141 (100), 115 (39). HRMS calcd 293.1154, found 293.1144.

Methyl Tetrahydro-α-2-naphthyl-2-furanacetate (4). Compound **4** was isolated in a pure state as a colorless oil (12 mg). ^{1}H NMR ($CDCl_3$, TMS, δ (ppm)) 1.55 (m, 3H), 2.15 (m, 1H), 3.66 (s, 3H), 3.80 (m, 3H), 4.6 (dd, 1H), 7.50 (m, 3H), 7.80 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS, δ (ppm)) 25.86, 30.42, 52.27, 57.15, 68.57, 80.18, 126.06, 126.24, 126.71, 127.82, 127.96, 128.15, 128.41, 133.10, 133.61, 134.30, 172.76. DEPT spectra revealed that δ 25.86, 30.42, and 68.57 are the methylene carbons. MS *m*/*e* (relative intensity) 270 (3), 200 (58), 141 (24), 71 (100), 43 (43). HRMS calcd 293.1154, found 293.1154.

Control Experiment. Photolysis (350 nm) of **4** (12 mg) in THF (12 mL) at 15 °C in a Pyrex tube for 20 h gave no traces of compound **1**, **2**, or **3**. The starting compound appeared unchanged.

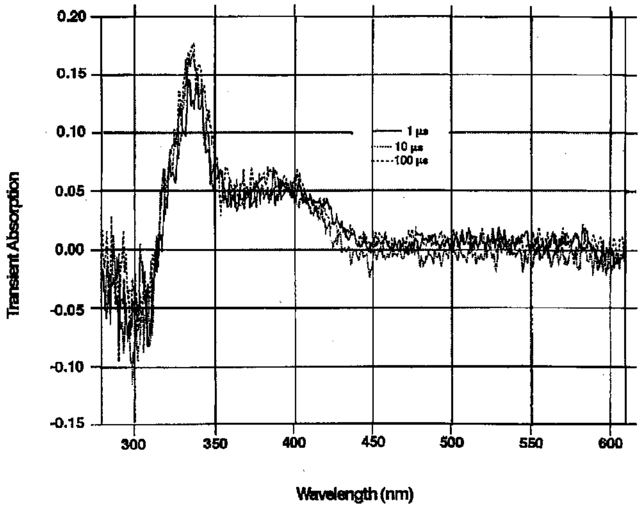


Figure 1. Transient spectrum produced upon LFP (308 nm) of diazo precursor **D** in deoxygenated THF at ambient temperature. The spectrum was recorded over a window of 200 ns, 1, 10, and 100 µs after the laser pulse.

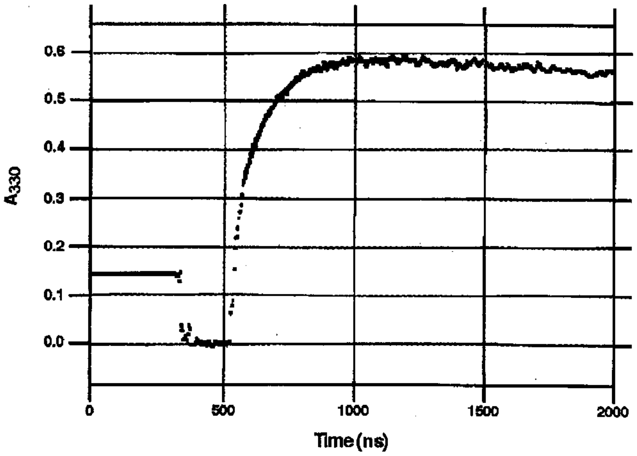


Figure 2. Rate of formation of transient absorption of ylide **Y** following LFP (308 nm) of diazo precursor **D** measured at 330 nm.

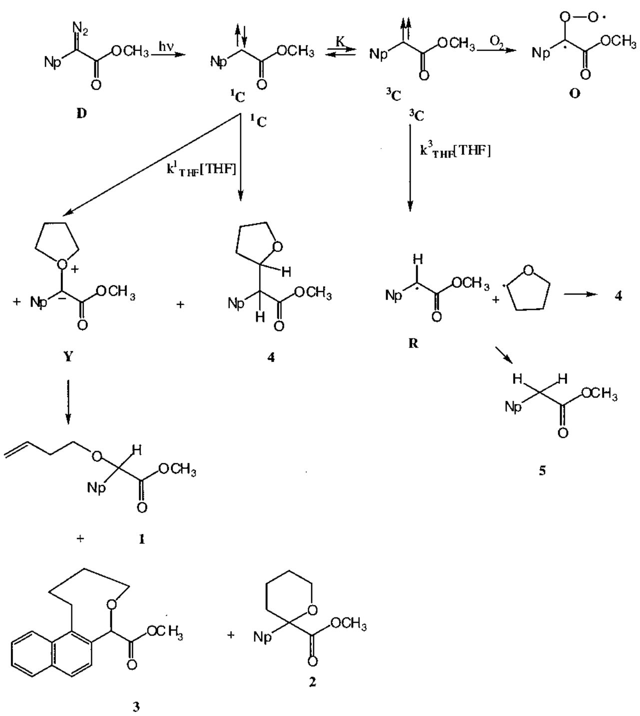
III. Results

Laser flash photolysis (XeCl excimer laser, 308 nm, 17 ns) of carbomethoxy-2-naphthyldiazomethane (**D**) in neat, deoxygenated, tetrahydrofuran produces a transient spectrum with a sharp absorption at 330 nm and a shoulder at 375 nm (Figure 1). The same spectrum is observed upon LFP of **D** in a 0.05 M THF solution in $CF_2ClCFCl_2$ (Freon-113). The transient spectrum observed in the presence of oxygen, is very similar to that in argon purged samples, however, the shoulder in oxygenated samples is more intense relative to the sharp band and is red shifted by about 10−15 nm.

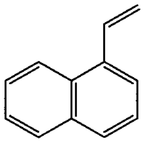
The transient spectrum remains unchanged over hundreds of microseconds and shows little decay over this time interval in the presence or absence of oxygen. The observed rate constant of formation of transient absorption (Figure 2) is the same at both 330 and 400 nm in the presence ($\tau = 115 \pm 10$ ns) and absence ($\tau = 165 \pm 10$ ns) of oxygen in Freon-113 containing 0.05 M THF.

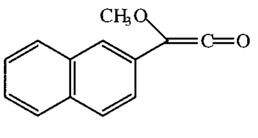
This pattern of observations is consistent with both absorption bands arising from a common carrier which does not react with oxygen but is derived from a species which does react with oxygen. Thus, the carrier of the transient cannot be triplet carbene ^{3}**C** ($\lambda_{max} = 363$ nm, Scheme 1) or radical **R** ($\lambda_{max} = 382$ nm, Scheme 1) both of which decay on the microsecond

SCHEME 1



time scale in Freon-113 and react with oxygen at a diffusion controlled rate.[4,5] Because the transient spectrum is dependent on the presence of THF it is neither 2-vinylnaphthalene nor ketene **K**, which can also be formed on photolysis of **D**.[4,5] In fact, the spectra of neither of these compounds matches that of the transient.[5,6]





K

Triplet carbenes react with oxygen to form carbonyl oxides (**O**, Scheme 1). The carbonyl oxide probably contributes slightly to the transient spectra observed in aerated THF in the 350–400 nm spectral region.

A plot of k_{obs} versus [THF] is linear (Figure 3) with slope equal to k_{THF} which is 1.5×10^8 M^{-1} s^{-1} at 293 K. The transient is assigned to ylide **Y** because the observed rate constant of formation of the transient (k_{obs}) is linearly related to the concentration of [THF]. The intercept of this plot is 1.4×10^6 s^{-1}. This indicates that the species which reacts with THF to form the transient has a lifetime of 714 ns in Freon-113 at 293 K. This is comparable to the lifetime of carbene **C**, but is too short to be that of ketene **K**. Thus, the transient is not a ketene–THF ylide. Values of k_{THF} were measured between 251 and 293 K. An Arrhenius treatment of the data is presented in Figure 4 and exhibits considerable curvature.

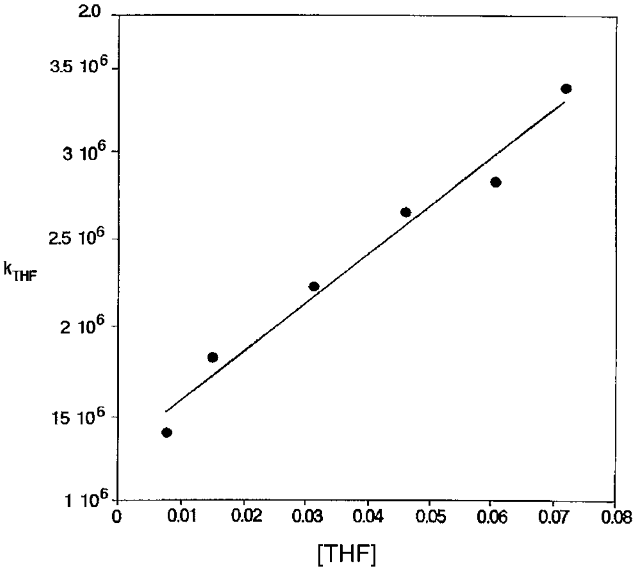


Figure 3. A plot of the observed rate constant of formation (k_{obs}) of ylide **Y**, as a function of [THF] in Freon-113 at 269 K.

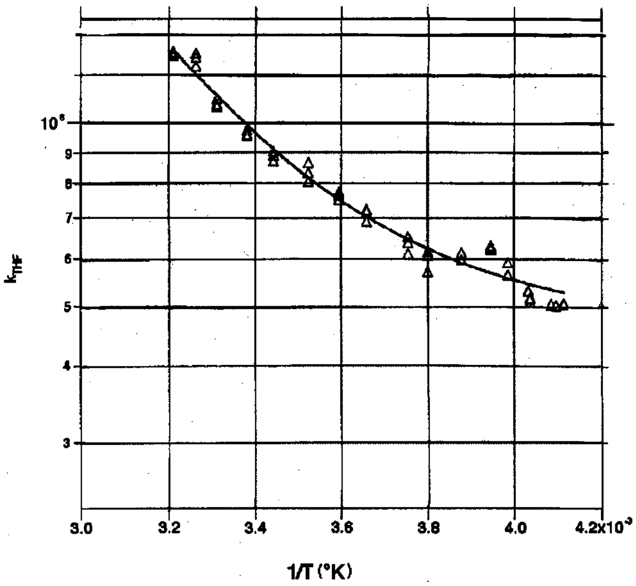
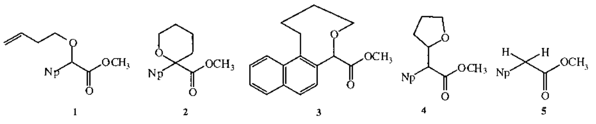


Figure 4. An Arrhenius plot of k_{THF}.

Chemical Analysis of Photolyzate Mixtures. The ether ylide assignment of the transient spectrum is consistent with chemical analysis of reaction mixtures. Photolysis of diazo precursor **D** in neat THF produces three adducts, **1**–**3**, which are consistent with rearrangements of ylide **Y**. Reaction of either singlet (^{1}**C**) or triplet (^{3}**C**) carbene with THF can produce adduct **4** as shown in Scheme 1. Triplet carbene reaction with THF forms a radical pair which can form adduct **4** or reduced ester **5** as shown in the scheme. The products were formed in the following proportions. Compound **4** was isolated and photolyzed in THF under the same conditions used to photolyze diazo compound **D**. No traces of **1**–**3** were observed. Ylide like products do not form upon secondary photolysis of **4**.



	1	2	3	4	5
11^0 C	26%	40%	12%	16%	1%
- 78^0 C	22%	26%	11%	24%	4%

Lowering the temperature favors the formation of products (**4**, **5**) formed from the triplet state of the carbene.

Other Carbene–Ether Ylides. The laser flash photolysis of diazo precursor **D** was also studied in other ethereal solvents. Carbene-ether ylide spectra were observed upon LFP of **D** in neat 1,4 dioxane (Figure 5), 1,2-dimethoxyethane (Figure 6) and 15-crown-5 (Figure 7). Very weak transient spectra were

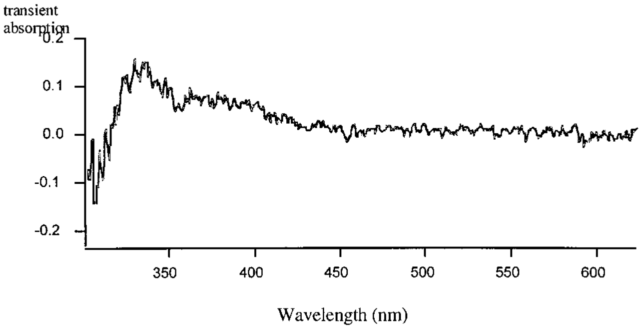


Figure 5. Transient absorption spectrum obtained upon LFP (308 nm) of diazo compound **D** in deaerated neat 1,4-dioxane at ambient temperature. The spectrum was recorded 400 ns after the laser excitation, over a window of 200 ns.

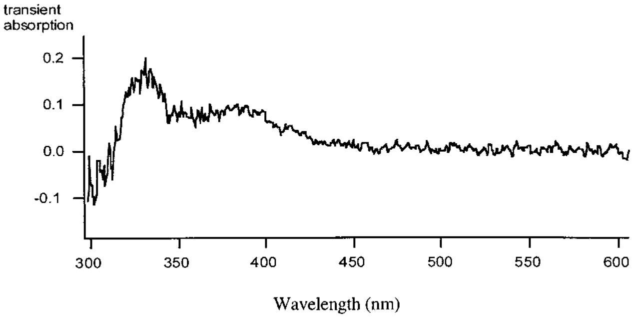


Figure 6. Transient absorption spectrum obtained upon LFP (308 nm) of diazo compound **D** in deaerated neat 1,2-dimethoxyethane at ambient temperature. The spectrum is recorded 400 ns after the laser excitation, over a window of 200 ns.

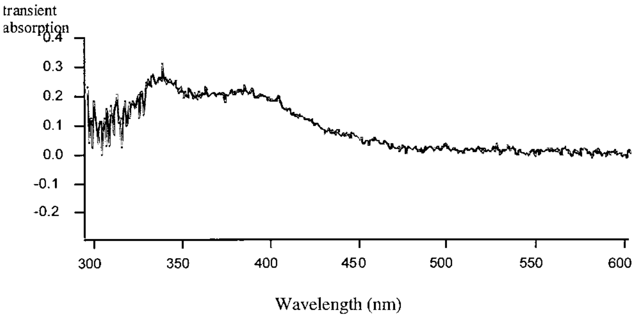
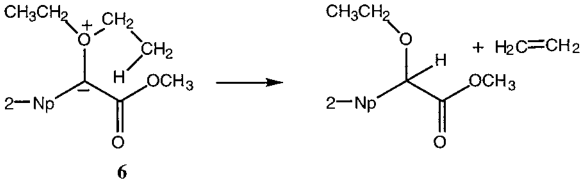


Figure 7. Transient absorption spectrum obtained upon LFP (308 nm) of diazo compound **D** in deaerated neat 15-crown-5 at ambient temperature. The spectrum is recorded 400 ns after the laser excitation, over a window of 200 ns.

observed in neat trimethylene oxide and diethyl ether. The putative ylides derived form the latter two ethers are either not formed or isomerize too rapidly to allow detection. This is easily envisaged with the ylide **6** derived from carbene and diethyl ether.



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IV. Discussion

Carbomethoxy-2-naphthylcarbene has been studied previously by low-temperature matrix spectroscopy.[5] The singlet (^{1}**C**) and triplet (^{3}**C**) states of the carbene, the carbonyl oxide (**O**) and ketene (**K**) have been characterized by both infrared and ultraviolet spectroscopy.[5,6] The triplet state (^{3}**C**) has been studied by matrix EPR spectroscopy.[5]

The carbene, its related radical (**R**) and carbonyl oxide (**O**) have also been detected in solution phase by laser flash photolysis.[4] It is clear that the transient detected in THF is neither carbene, nor radical, nor oxide on the basis of their spectroscopy and kinetics, although the oxide may contribute slightly to the transient absorption between 350 and 400 nm in aerated Freon-113.[4,5]

Time-resolved infrared spectroscopy (TRIR) was able to detect both ^{1}**C** and ^{3}**C** in Freon-113.[6] Toscano and co-workers demonstrated that both ^{1}**C** and ^{3}**C** are in rapid equilibrium as they react with methanol, an excellent trap of singlet carbenes, with the same rate constant. The singlet−triplet separation is very small in Freon-113 ($\Delta G_{ST} = 0.2$ kcal/mol, 298 K) with the triplet being the ground state.[6] Femtosecond spectroscopy has demonstrated that spin equilibration between ^{1}**C** and ^{3}**C** is complete within 20 ps.[7]

Thus, it is clear that it is an equilibrium mixture of singlet and triplet carbene which reacts with THF. The experimental rate constant k_{THF} is thus a composite of elementary rate constants (defined in Scheme 1) as shown in eq 1.[8]

$$k_{THF} = k^1{}_{THF}K + k^3{}_{THF} \qquad (1)$$

It is important to note that $k^1{}_{THF}$ is itself a composite term which is the sum of the absolute rate constant of singlet carbene with ethereal oxygen to form ylide **Y**, and of reaction of the singlet carbene with a C−H bond of the ether to form adduct **4**. Changes in the proportion of singlet carbene reaction pathways (ylide versus adduct formation) with THF, or the weighting of the contribution of ^{1}**C** and ^{3}**C** in the reaction of the carbene with THF as a function of temperature, are evident in the nonlinear Arrhenius plot. It is also possible that there is a Griller−Nazran−Scaiano surface crossing mechanism[9] at low temperatures. Another complication to the kinetics is the possibility of reversion of the ylide to carbene and THF,[10] particularly at higher temperatures. All of these factors may contribute to the nonlinear Arrhenius plot. The data indicates that the contribution of the $k^3{}_{THF}$ term to k_{THF} increases as the temperature decreases. Nevertheless, it is clear that there is a barrier of at least 6 kcal/mol to the reaction of the singlet carbene with the lone pair of electrons on the ethereal oxygen. This value is surprisingly large considering that the barrier to singlet carbene reactions with pyridine is typically 0−2 kcal/mol.[11] Clearly THF is less nucleophilic than pyridine and singlet carbene ^{1}**C** is particularly well stabilized by the naphthalene and carbomethoxy substituents and has relatively low absolute reactivity.[4]

V. Conclusions

Laser flash photolysis of **D** in neat THF or in a solution containing dilute THF in $CF_2ClCFCl_2$ produces a carbene−ether ylide (**Y**) at ambient temperature. The rate constant of ylide formation k_{THF} is equal to $1.5 \pm x\ 10^8\ M^{-1}s^{-1}$ at 293 K. The intermediacy of the carbene−ether ylide is consistent with chemical analysis of the stable products formed on photolysis of the diazo precursor **D** in THF. Values of k_{THF} were measured between 251 and 293 K where k_{THF} is an experimental rate constant equal to elementary rate constant $k^1{}_{THF}K$ plus $k^3{}_{THF}$. An Arrhenius treatment of the data is curved reflecting variation of $k^1{}_{THF}$, $k^3{}_{THF}$, and K with temperature. The curvature in the Arrhenius plot may also result from a surface crossing mechanism at low temperature or reversion of the ylide to carbene and THF at higher temperature.

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