

# Unsaturated Carbenes from Primary Vinyl Triflates. V.<sup>1</sup>

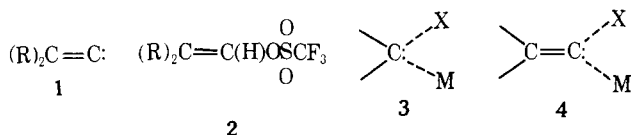
## The Nature of Vinylidene Carbene Intermediates

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**Abstract:** The electrophilicity of vinyl triflate derived unsaturated carbenes was established by means of competitive reactivities with substituted styrenes. The relative rates (relative to styrene) were found to be: *p*-CH<sub>3</sub>O, 1.51; *p*-CH<sub>3</sub>, 1.28; *p*-Cl, 0.63. Hammett correlation of these data gives a  $\rho = -0.75$  with  $r = 0.997$ . Crown ethers were used to establish that these species are the free carbene rather than some sort of carbenoid.

Although unsaturated carbenes (1) have been known<sup>2</sup> for a decade or so, the exact nature of these intermediates and in particular their spin multiplicity, electronic selectivity, and the question of free carbene or carbenoid have not been extensively investigated and ascertained. Recently we have shown<sup>3</sup> that primary vinyl triflates (2) serve as progenitors par excellence for such species and, by means of the stereochemistry of addition to olefins, indicated<sup>4</sup> that they are singlets.



Carbenes generally show electrophilic selectivity of differing degrees, usually assessed by their behavior toward various olefins.<sup>5</sup> Therefore, it was of interest to determine if unsaturated carbenes (1) conform to this general carbene behavior and in particular to ascertain the exact magnitude of unsaturated carbene electrophilicity or nucleophilicity. Hence, in this paper we report the results of a careful investigation of the relative reactivity of isopropylidene carbene (1, R = CH<sub>3</sub>) as generated from the appropriate vinyl triflate, toward a series of substituted styrenes and the resultant Hammett analysis.

One of the more interesting and important aspects of carbene chemistry has been the question of the "freeness" of the carbenic species. An entire spectrum of carbene intermediates is possible ranging from the completely free species<sup>6</sup> to ones strongly associated with either the leaving group or the metal of the base used in their generation, or both as in 3. The former are usually encountered in the thermal or photochemical gas phase generation of carbenes, while the latter, termed a carbenoid,<sup>5b,7</sup> are most often seen in intermediates resulting from base induced  $\alpha$ -elimination.<sup>5</sup> A correspondingly wide range of chemical behavior, such as differing stereochemical and relative reactivities toward olefins, is generally encountered as a function of the exact character of the divalent carbon intermediate. Hence, it was once again of interest to ascertain the precise nature of unsaturated carbenes in terms of their being free (1) or carbenoid (4) and, in this paper, we report the results of our investigation into this question as well.

### Results and Discussion

In order to assess the electrophilicity or nucleophilicity of unsaturated carbenes, we carried out a Hammett study of a series of ring substituted styrenes with isopropylidene generated from  $\beta,\beta$ -dimethyl vinyl triflate with potassium *tert*-butoxide at  $-20^\circ$ . In these experiments, equimolar amounts of the vinyl triflate and base were reacted with a 20-fold ex-

cess of a known mixture of two styrenes, and the reaction mixture was analyzed for product adducts by direct injection into a GC. Authentic adducts were obtained by preparative GC and fully characterized by spectral means as given in the Experimental Section. Relative reactivities of the styrenes were calculated by means of the well-established equation<sup>8</sup>

$$k_{\text{rel}} = \frac{k_X}{k_H} = \frac{P_X}{P_H} \frac{O_H}{O_X}$$

where  $k$  is the rate constant for reactions of the carbene with olefins of mole fraction  $O$ , and  $P$  is the mole fraction of adduct products. Control experiments established that the starting styrenes as well as the methylene cyclopropane adducts were stable to the reaction conditions employed. Reactions were carried out in duplicate or triplicate, and the results are presented in Table I.

In order to assess the importance of possible carbene-metal interactions, the above relative styrene reactivities were also determined in the presence of a 10% molar excess of crown ethers as well as the relative reactivity of cyclohexene and styrene, and these results are also given in Table I.

To determine the internal consistency and accuracy of the styrene reactivities, a cross-check experiment was performed. The *direct* experimental relative reactivity of *p*-methoxystyrene toward *p*-chlorostyrene was determined to be  $(k_{\text{CH}_3\text{O}}/k_{\text{Cl}})_{\text{expt}} = 2.20 \pm 0.02$ , while their mutual calculated relative reactivity is  $(k_{\text{CH}_3\text{O}}/k_{\text{Cl}})_{\text{calcd}} = 1.51/0.63 = 2.40 \pm 0.07$ , in good agreement with the experimental value.

Figure 1 is a computer-plotted least-squares Hammett correlation of the experimental data in Table I with  $\sigma$ ,<sup>9</sup> resulting in  $\rho = -0.75$  with a correlation coefficient  $r = 0.997$ . Examination of the data in Table I and Figure 1 clearly indicates that unsaturated carbenes (1) behave as electrophiles with electrophilic attack at the C=C bond. The magnitude of  $\rho$  deserves further comment and, for comparisons, a number of relevant carbene selectivities toward styrenes are summarized in Table II.

The large discrepancies in isopropylidene selectivities between the triflate derived species and the oxazolidone and vinyl halide derived species are particularly disconcerting. A  $\rho$  of  $-3.4$  in the case of the oxazolidone derived species and  $-4.3$  in the case of the vinyl halide derived intermediate implies a very large degree of electrophilicity and a highly polar transition state with nearly a fully developed charge such as is the case with electrophilic addition to styrenes or arylacetylenes. Hydration<sup>16</sup> of substituted styrenes, for example, has a  $\rho = -4$ , bromination<sup>17</sup> a  $\rho$  of  $-4.3$ , and hydration of substituted arylacetylenes<sup>18</sup> a  $\rho$  of  $-3.8$  to  $-4.3$ . In fact, the  $\rho$  values obtained by Newman and Pat-

Table I. Relative Reactivity of  $(\text{CH}_3)_2\text{C}=\text{CHOTf}$  Derived Isopropylidene with Styrenes ( $\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$ ) in the Presence and Absence of Crown Ethers at  $-20^\circ$

Substrate	$k_{\text{rel}}$ (substrate/styrene)	$k_{\text{rel}}$ (crown ethers)
<i>p</i> - $\text{CH}_3\text{O}$	$1.51 \pm 0.02^a$	$1.50 \pm 0.01$
<i>p</i> - $\text{CH}_3$	$1.28 \pm 0.04$	$1.26 \pm 0.03$
H	1.0	1.0
<i>p</i> -Cl	$0.63 \pm 0.01$	$0.62 \pm 0.01$
Cyclohexene	$1.74 \pm 0.14$	$1.78 \pm 0.13$

<sup>a</sup> Average of deviations.

rick are comparable to the  $\rho$  value of  $\rho = -4.1$  obtained in the aqueous ethanol solvolysis of substituted styryl triflates<sup>19</sup> with a fully developed vinyl cation intermediate.<sup>20</sup> Such a highly polar transition state and high degree of charge development in the addition of a neutral divalent carbon species to styrenes, therefore, seem extremely unusual.<sup>21</sup> Interestingly, the related allenidenecarbene  $[(\text{CH}_3)_2\text{C}=\text{C}=\text{C}]$  seems to be much less electrophilic with a  $\rho$  value of only  $\rho = -0.95$ .<sup>12</sup>

Results of the present work with a  $\rho$  of  $-0.75$  imply that vinyl triflate derived unsaturated carbenes are mildly electrophilic with a concerted addition to olefins with but a slightly polar transition state. In fact, as the data in Table II indicate,  $(\text{CH}_3)_2\text{C}=\text{C}:$  seems about as electrophilic as the halocarbenes or cyclopentadienylidene. Moreover, as has been pointed out by Seyferth and coworkers<sup>13</sup> singlet state divalent carbon species (such as  $\text{X}_2\text{C}:$  and  $\text{C}=\text{C}:$ ) are isoelectronic with trigonal boron compounds that have been shown to react with styrenes<sup>22</sup> and other olefins<sup>23</sup> by means of a relatively nonpolar  $\pi$  complex-like transition state.

There remains, of course, the possibility that the triflate derived carbene and the halide and oxazolidone derived carbene are different species with one being a carbenoid and the other a free carbene that exhibit qualitatively similar but quantitatively different behavior.

Table II. Representative Carbene Selectives toward Styrenes


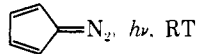
Carbene	Reaction conditions	$\rho$	Ref
$(\text{CH}_3)_2\text{C}=\text{C}:$	$(\text{CH}_3)_2\text{C}=\text{CHOTf}$ , <i>t</i> -BuOK, $-20^\circ$	$-0.75$ ( $\sigma$ )	This study
$(\text{CH}_3)_2\text{C}=\text{C}:$	<i>N</i> -Nitrosooxazolidone, $+40^\circ$	$-3.4$ ( $\sigma^+$ )	11
$(\text{CH}_3)_2\text{C}=\text{C}:$	$(\text{CH}_3)_2\text{C}=\text{CHBr}$ , <i>t</i> -BuOK, $-10^\circ$	$-4.3$ ( $\sigma^+$ )	12
$(\text{CH}_3)_2\text{C}=\text{C}=\text{C}:$	$(\text{CH}_3)_2\text{C}=\text{C}=\text{CHBr}$ , <i>t</i> -BuOK, $-10^\circ$	$-0.95$ ( $\sigma^+$ )	12
$\text{Cl}_2\text{C}:$	$\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$ , $\text{C}_6\text{H}_6$ , $80^\circ$	$-0.62$ ( $\sigma^+$ )	13
$\text{F}_2\text{C}:$	$\text{C}_6\text{H}_5\text{HgCF}_3$ , $\text{C}_6\text{H}_6$ , $80^\circ$	$-0.57$ ( $\sigma^+$ )	14
	 , $h\nu$ , RT	$-0.76$ ( $\sigma$ )	15

Table III. Spectral Properties of Isopropylidenearylcyclopropanes<sup>a</sup>

X	Ir <sup>b</sup>	NMR <sup>c</sup>						X	Mass spec <sup>d</sup>
		1	2	3	4	5	6		
X = H <sup>e</sup>	1782	0.85 (m)	1.35 (m)	2.27 (m)	1.67 (m)	1.57 (m)	6.82		158 (31), 143
X = <i>p</i> - $\text{CH}_3\text{O}$ - <sup>f</sup>	1779	0.62 (m)	1.28 (m)	2.09 (m)	1.48 (m)	1.40 (m)	6.37 (d), 6.27 (d)	3.08 (s)	188 (8), 173
X = <i>p</i> - $\text{CH}_3$ - <sup>g</sup>	1780	1.00 (m)	1.47 (m)	2.39 (m)	1.83 (m)	1.73 (m)	6.83 (s)	2.15 (s)	172 (16), 157
X = <i>p</i> -Cl- <sup>h</sup>	1775	0.98 (m)	1.55 (m)	2.42 (m)	1.87 (m)	1.73 (m)	7.07 (d), 6.83 (d)		192 (0.6), 157

<sup>a</sup> All the spectral data are in agreement with the available literature data, see ref 11. <sup>b</sup> Exocyclic  $\text{C}=\text{C}$  in  $\text{cm}^{-1}$ , neat. <sup>c</sup> Assignments of protons 1 and 2 might be reversed as may be the assignments of methyls 4 and 5. <sup>d</sup> First peak, molecular ion (%), second number is the base peak. <sup>e</sup> NMR in  $\text{CCl}_4$  with external  $\text{Me}_4\text{Si}$ . <sup>f</sup> NMR neat with external  $\text{Me}_4\text{Si}$ . <sup>g</sup> NMR in  $\text{CCl}_4$  with internal  $\text{Me}_4\text{Si}$ . <sup>h</sup> NMR neat with internal  $\text{Me}_4\text{Si}$ .

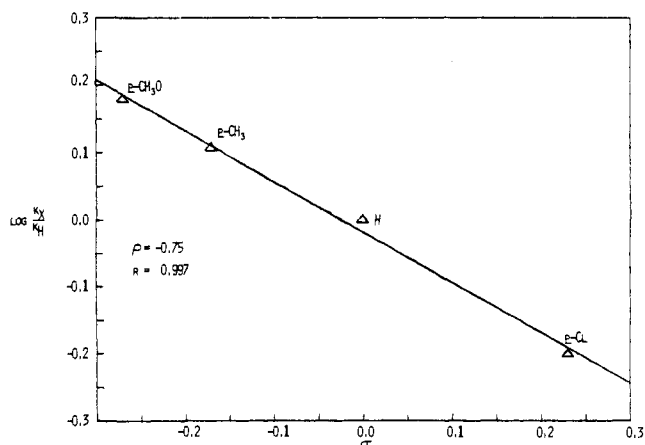


Figure 1. Hammett  $\sigma$ - $\rho$  plot of  $(\text{CH}_3)_2\text{C}=\text{C}:$  Addition to  $\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$ .

In order to assess the "freeness" of the vinyl triflate derived carbenic species, relative rate studies were carried out in the presence of crown ethers.<sup>24</sup> Crown ethers are known to strongly complex various cations, and  $\text{K}^+$  is particularly well complexed by the 18-crown-6 ethers.<sup>24,25</sup> With crown ethers, *t*-BuOK can be readily solubilized in nonpolar solvents and its reactivity and dissociation are significantly increased,<sup>26</sup> and reagents such as  $\text{KMnO}_4$ ,<sup>27</sup>  $\text{KF}$ ,<sup>28</sup> and  $\text{KOH}$ <sup>29</sup> can be handled in organic solvents. Hence, there is no question but that the  $\text{K}^+$  ion would be preferentially complexed by the crown ether rather than the carbene.

As the data in Table I show, the relative reactivities are within experimental error identical regardless of the presence or absence of 18-crown-6 ethers, precluding the possibility of a carbene metal association. Moss and Pilkiewicz<sup>30</sup> in a recent elegant study have shown that significant rate

differences are observed in the selectivity of benzal halide derived phenylhalocarbenes in the presence and absence of crown ether and with the aid of supporting data ascribed the differences to the behavior of the free carbene and the corresponding carbenoid, respectively. Therefore, we believe that the vinyl triflate derived unsaturated carbene is free of any association with  $K^+$  and, since we have previously shown<sup>3</sup> that it is free of association with the leaving group, it must be the free carbene itself.

In summary, in this paper we have shown by means of selectivity studies with styrenes that unsaturated carbenes (1) are electrophilic in their behavior toward olefins and are comparable in their electrophilicity to dihalocarbenes. We have also established by means of crown ethers that the vinyl triflate derived species is the free unsaturated carbene.<sup>31</sup>

## Experimental Section

**General.** All boiling points are uncorrected. NMR spectra were recorded on a Varian A-60 spectrometer, and data are given in  $\delta$  (ppm) relative to internal or external tetramethylsilane ( $Me_4Si$ ,  $\delta$  0) as indicated. All IR spectra were recorded on a Beckman IR5-A and are reported in wave numbers ( $cm^{-1}$ ) calibrated to the 1603  $cm^{-1}$  line of polystyrene. Mass spectra were recorded on a AEI-MS-30 spectrometer. Preparative GC was carried out on a Varian-Aerograph 90P chromatograph and analytical GC on a Hewlett-Packard 700 flame ionization chromatogram equipped with a Hewlett-Packard 3370B digital integrator. The following columns were employed: A, 0.25 in.  $\times$  5 ft 10% SF-96 on 60-80 Chrom. W; B, 0.125 in.  $\times$  6 ft 10% UC W-98 on 80-100 Chrom. W; C, 0.125 in.  $\times$  10 ft 10% Apiezon J on 100-120 Chrom. W.

**Materials.** 2-Methylpropenyl triflate (2, R =  $CH_3$ ) was prepared from isobutyraldehyde, and potassium *tert*-butoxide and cyclohexene were purified as previously described.<sup>3</sup> Dicyclohexyl-18-crown-6 ether was purchased from PCR and 18-crown-6 ether was obtained from E. I. DuPont and Co., and used without further purification. Styrene (99%) was purchased from Aldrich and redistilled immediately prior to use. Substituted styrenes were prepared<sup>32</sup> according to the procedure of Walling and Wolfstirn<sup>33</sup> from the appropriate cinnamic acids: *p*- $CH_3OC_6H_4CH=CH_2$ , 63%, bp 63-64° (4 mm) [lit.<sup>33</sup> 53-53.8° (2 mm)]; *p*- $CH_3C_6H_4CH=CH_2$ , 38%, bp 35-36° (2.7 mm); *p*- $ClC_6H_4CH=CH_2$ , 43%, bp 47-48° (2 mm) [lit.<sup>33</sup> 60-62° (6.5 mm)].

**Preparation of Styrene Isopropylidene Addition Products (Isopropylidenearylcyclopropanes).** Into a dry 15-ml round-bottomed flask equipped with a magnetic stirrer and serum cap were added 5-10 mmol of *t*-BuOK (10% excess) and 4-6 ml of the appropriate styrene, and the mixture was precooled to -20°. To the stirred cold mixture was added 4.5-9 mmol of  $(CH_3)_2C=CHOTf$  with the aid of a syringe, and the mixture was allowed to react for 24 hr. At the end of this period, the mixture was diluted with 10 ml of pentane and extracted once with 3 ml of  $H_2O$ , and the organic layer was dried over  $MgSO_4$  and concentrated by vacuum distillation of the solvent. The products were collected by preparative GC on column A at 95° for the parent adduct, at 105° for the *p*-methylstyrene adduct, 110° for the *p*- $CH_3O$  adduct, and 120° for the *p*-Cl adduct. The spectral data of each adduct are given in Table III. These fully characterized adducts were then used as "authentic" compounds for product identification by coinjection for the relative rate studies.

**General Procedure for the Competition Experiments.** Into each of two or three dry 10-ml round-bottomed flasks equipped with a magnetic stirrer and serum cap were added 0.0672 g (0.6 mmol) of *t*-BuOK and 3 ml of the appropriate mixture of substituted styrene and styrene, and the mixture was precooled to -20°. To each of the stirred cold mixtures was added 80  $\mu$ l (0.5 mmol) of  $(CH_3)_2C=CHOTf$  by means of a syringe. The reaction was allowed to proceed at  $-20 \pm 1.0^\circ$  for 20 to 24 hr and then analyzed directly without work-up for the two product adducts on a flame ionization GC equipped with a digital electronic integrator. Each reaction mixture was analyzed four to six times and averaged. Previous experience with internal standards has demonstrated that re-

sponse factors on a flame ionization detector for closely related compounds were, within experimental error, the same and, hence, no internal standards were used. Relative rates were calculated with the aid of eq 1 and are reported in Table I.

***p*- $CH_3OC_6H_4CH=CH_2/C_6H_5CH=CH_2$  Selectivity.** The solvent mixture consisted of 20.95 g of *p*-methoxystyrene and 24.07 g of styrene for an  $O_H/O_{CH_3O}$  mole ratio of 1.48. The reaction mixture was analyzed on column C by manual programming from 130 to 190°.

***p*- $CH_3C_6H_4CH=CH_2/C_6H_5CH=CH_2$  Selectivity.** The solvent mixture was made up of 47.21 g of *p*-methylstyrene and 41.62 g of styrene for an  $O_H/O_{CH_3}$  mole ratio of 1.00. The reaction mixture was analyzed on column B by manual programming from 55 to 120°.

***p*- $ClC_6H_4CH=CH_2/C_6H_5CH=CH_2$  Selectivity.** The solvent mixture consisted of 13.51 g of *p*-chlorostyrene and 6.506 g of styrene for an  $O_H/O_{Cl}$  mole ratio of 0.641. The reaction mixture was analyzed on column C at 150°.

***p*- $CH_3OC_6H_4CH=CH_2/p$ - $ClC_6H_4CH=CH_2$  Selectivity.** The solvent mixture was made up of 7.157 g of *p*-chlorostyrene and 2.848 g of *p*-methoxystyrene for an  $O_{Cl}/O_{CH_3O}$  mole ratio of 2.43. The reaction mixture was analyzed on column C at 180°.

**Cyclohexene/Styrene Selectivity.** The solvent mixture consisted of 32.85 g of cyclohexene and 41.63 g of styrene for a  $O_C/O_S$  mole ratio of 1.00. The reaction mixture was analyzed on column B at 85°.

**Selectivity in the Presence of Crown Ethers.** These reactions were set up in a manner identical with the above described runs, using the same solvent pool, the same analyses conditions, etc., except that a 10% mol excess (over the *t*-BuOK used) of 18-crown-6 or dicyclohexyl-18-crown-6 ether was added to each reaction mixture prior to the addition of the triflate. In most instances, the two sets of experiments, i.e., with and without crown ether, were run simultaneously side by side. The results are reported in Table I.

**Acknowledgments.** This investigation was supported by Public Health Service Research Grant No. 1-RO-1-CA16903-01 from the National Cancer Institute. We are grateful to Dr. W. A. Sheppard for a sample of 18-crown-6 ether.

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- (31) At least free of association with the leaving group ( $^-OTf$ ) and with the metal ( $K^+$ ) of the base used to generate the carbene. Possible complexing with solvent and in particular *t*-BuOH cannot be ruled out. Furthermore, a rapid equilibrium between free carbene and carbenoid, with the free species reacting much faster than the carbenoid, also cannot be ruled out nor easily probed experimentally.
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## Temperature Dependence of the Relative Rate Constants for the Reaction of O(<sup>3</sup>P) Atoms with Selected Olefins, Monoterpenes, and Unsaturated Aldehydes

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**Abstract:** Using a competitive technique, rate constants for the gas phase reactions of O(<sup>3</sup>P) atoms with selected monoterpenes, unsaturated aldehydes, and olefins have been determined relative to that for the reaction of O(<sup>3</sup>P) atoms with cyclopentene over the temperature range 296–423 K. The Arrhenius expressions obtained, relative to cyclopentene as unity, when placed on an absolute basis using  $k(\text{propylene}) = 2.4 \times 10^9 e^{-76/RT}$  l. mol<sup>-1</sup> sec<sup>-1</sup> derived from the literature, were (l. mol<sup>-1</sup> sec<sup>-1</sup>): cyclopentene,  $5.6 \times 10^9 e^{(430 \pm 80)/RT}$ ;  $\alpha$ -pinene,  $7.5 \times 10^{10} e^{-(910 \pm 140)/RT}$ ;  $\beta$ -pinene,  $6.0 \times 10^{10} e^{-(820 \pm 140)/RT}$ ; *d*-limonene,  $1.1 \times 10^{11} e^{-(300 \pm 150)/RT}$ ; 1-methylcyclohexene,  $5.3 \times 10^9 e^{(1330 \pm 220)/RT}$ ; 1,3-cyclohexadiene,  $5.1 \times 10^9 e^{(1320 \pm 180)/RT}$ ; acrolein,  $1.4 \times 10^{10} e^{-(2400 \pm 270)/RT}$ ; crotonaldehyde,  $1.5 \times 10^{10} e^{-(1980 \pm 130)/RT}$ . The rate constants for acrolein and crotonaldehyde are compared and discussed with existing literature values.

Although there has been a large amount of reliable rate constant and product data reported in the literature for the reaction of O(<sup>3</sup>P) atoms with alkenes and alkanes, which have been reviewed by Cvetanovic<sup>1</sup> and by Herron and Huie,<sup>2</sup> there are little data available for the reaction of O(<sup>3</sup>P) atoms with unsaturated aldehydes and the naturally occurring monoterpene hydrocarbons.

These compounds are not only of interest from the fundamental grounds of structure and reactivity, but also because of their possible significance in the chemistry of polluted atmospheres, as pointed out in our previous study,<sup>3</sup> which reported the room temperature rate constants for the reaction of O(<sup>3</sup>P) atoms with several monoterpenes, unsaturated aldehydes, and alkenes using a competitive technique. In this work we have extended these measurements to elevated temperatures (296–423 K) in order to obtain the Arrhenius parameters. Propylene was again included in the compounds studied as its absolute rate constant is reliably known<sup>4–8</sup> over the temperature range used in this work.

### Experimental Section

The experimental apparatus and technique used have been described previously,<sup>3</sup> and hence only a brief summary will be given here. Ground state oxygen O(<sup>3</sup>P) atoms were generated by the mercury photosensitization of N<sub>2</sub>O in a circulating system of 1043 cm<sup>3</sup> volume. The reaction cell and circulating system was enclosed by a furnace whose temperature could be held constant to better than  $\pm 1$  K over the temperature range 296–423 K.

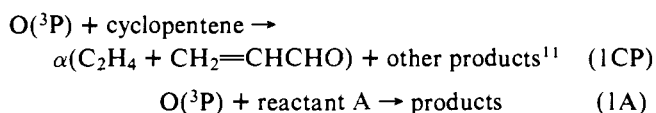
Samples (5 cm<sup>3</sup>) were periodically removed for analysis using a Carle gas sampling valve and split into two fractions. N<sub>2</sub> from the

N<sub>2</sub>O photosensitization was measured on a 5 ft  $\times$  0.25 in. Linde Molecular Sieve 13X column at  $296 \pm 2$  K by a thermal conductivity detector, while C<sub>2</sub>H<sub>4</sub> from the reaction of O(<sup>3</sup>P) atoms with cyclopentene was analyzed on a 6 ft  $\times$  1/8 in. Poropak Q column at  $296 \pm 2$  K by a flame ionization detector. Retention times and relative responses were periodically monitored using a calibrated mixture of N<sub>2</sub> in C<sub>2</sub>H<sub>4</sub>. In all cases, the N<sub>2</sub> yield served as an internal actinometer for the amount of O(<sup>3</sup>P) atoms produced during the reaction.

As reported previously,<sup>3</sup> in all cases, reactant purities were  $\geq 98\%$  and were further purified by thorough degassing at 196 or 77 K and bulb-to-bulb distillation in vacuum.

### Results

Relative rate constants were determined using the technique developed and used by Cvetanovic and coworkers.<sup>1,9,10</sup> From the reaction scheme:



with rate constants  $k_1^{\text{CP}}$  and  $k_1^{\text{A}}$ , respectively, then

$$\frac{(\text{C}_2\text{H}_4/\text{N}_2)^{\text{A}=\text{O}}}{(\text{C}_2\text{H}_4/\text{N}_2)^{\text{A}}} = 1 + \frac{k_1^{\text{A}}[\text{A}]}{k_1^{\text{CP}}[\text{CP}]} \quad (1)$$

where  $(\text{C}_2\text{H}_4/\text{N}_2)^{\text{A}=\text{O}}$ ,  $(\text{C}_2\text{H}_4/\text{N}_2)^{\text{A}}$  are the C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub> yield ratios in the absence and presence of reactant A, respectively. In all cases, experiments were carried out in the absence of cyclopentene to check that ethylene was not pro-