volved must be at least this long. This state is also insensitive to quenching by up to about 70 collisions by  $N_2$ or CO molecules.<sup>9</sup> The excited state of VO<sup>+</sup> in these processes could involve either vibrational or electronic excitation. The available evidence does not provide a basis to choose between these possibilities. Reaction of Ti<sup>+</sup> with  $N_2O$  or  $O_2$  also appears to give an excited-state species of TiO<sup>+</sup>. With Fe, Zr, and Nb there is no evidence for production of a long-lived excited-state metal oxide product in the present results.

The VO<sup>+</sup> system affords an interesting opportunity to explore the photochemistry and spectroscopy of a gasphase ionic species. Photodissociation and photodetach-

(9) If we assume a Langevin rate of  $5 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, a quench gas pressures of  $2 \times 10^{-5}$  torr correspond to about 70 collisions within a typical 200-ms experiment.

# ARTICLES

ment experiments have been carried out by several groups using ICR techniques.<sup>10</sup> In no case, however, has photoexcitation led to observable changes in bimolecular reaction chemistry. Irradiation of VO<sup>+</sup> produced by reaction of  $O_2$  with V<sup>+</sup> in the presence of  $CH_4$  could provide an example of this type of process. Reaction of VO<sup>+</sup> to VOH<sup>+</sup> would be expected in this system only if VO<sup>+</sup> absorbs the photon energy producing an excited-state species similar to the one involved in the present results.

Acknowledgment. This work was supported by the National Science Foundation by Grant CHE-76-17304.

# Photolysis of Gaseous Tetramethylethylene between 185 and 230 nm

#### Guy J. Collin,\* Hélène Deslauriers, and Andrzej Więckowski<sup>†</sup>

Département des Sciences Pures, Université du Québec à Chicoutimi, Chicoutimi, Québec, Canada G7H 2B1 (Received: April 16, 1980; In Final Form: October 15, 1980)

The far-UV photolysis of gaseous tetramethylethylene was carried out at 184.9 (mercury line), 202.4–213.8 (zinc lines), and 214.4-228.8 nm (cadmium lines). The photoproducts may be divided into two groups. In the first one, the quantum yield of each product decreases with an increase in the total pressure. The proposed mechanism involves the  $\alpha$ (C–CH<sub>3</sub>) or the  $\beta$ (C–H) fragmentation of the photoexcited molecule. Excited (CH<sub>3</sub>)<sub>2</sub>CC(CH<sub>3</sub>)CH<sub>2</sub>\* radicals decompose further at 185.9 nm, and 2,3-dimethyl-1,3-butadiene and 3-methyl-1,2-butadiene are the products. Excited  $(CH_3)_2C = CCH_3^*$  radicals decompose further, and 2-butyne and isoprene are the products. Isomers 2,3-dimethyl-1-butene, 1,1,2-trimethylcyclopropane, and 3,3-dimethyl-1-butene are products of the second group; its quantum yield increases with an increase in the total pressure. The results support a collisionally induced preisomerization mechanism. Finally, it seems that both groups of products are formed from a different set of excited states.

## Introduction

The photolysis of gaseous olefins in the 147-174-nm region is now relatively well-known.<sup>1</sup> The fate of the photoexcited molecule is to decompose through the breaking of a C–C or a C–H bond. For example, in the case of olefins having a  $\beta(C-C)$  bond, the main fragmentation process is to split this  $\beta$ (C–C) bond:  $\Phi \simeq 0.85 \pm 0.10$  at 163 nm.<sup>2</sup> In olefins where there is no  $\beta$ (C–C) bond, the fragmentation occurs by splitting of either a  $\beta$ (C–H) bond or a  $\alpha$ (C-CH<sub>3</sub>) bond.<sup>3</sup> The probability of these two splits is similar, although a decrease in the photon energy favors the  $\beta$ (C–H) split.<sup>4</sup> This behavior is thought to be linked to the formation of transient  $\pi,\pi^*$  excited molecules. Methylated ethylenes show a strong absorption band ( $\epsilon =$ 3000–5000) whose maximum peaks around 174 nm (57 000  $cm^{-1}$ ).<sup>5</sup>

At 185 nm, the photolysis of gaseous 2-butene was studied by Borrell et al.<sup>6,7</sup> They observed fragmentation, cis-trans isomerization of the photoexcited molecule, and positional migration of the double bond. The results were explained "in terms of the singlet Rydberg and the singlet  $\pi,\pi^*$  state which act as intermediates. The Rydberg state breaks down into a variety of products and the V state leads only to (the cis-trans) isomerization".6

<sup>(10)</sup> For examples, see (a) Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. In "Advances in Laser Chemistry"; Zewail, A. H., Ed.; Springer Series in Chemical Physics, Springer: Berlin, 1978. (b) Dunbar, R. C.; Teng, H. H.; Fu, E. W. J. Am. Chem. Soc. 1979, 101, 6506-6510. (c) Janousek, B. K.; Reed, K. J.; Brauman, J. I. Ibid. 1980, 102, 3125-3129.

<sup>&</sup>lt;sup>†</sup>On leave from the Chemistry Department, Warsaw University, Warsaw, Poland.

<sup>(1)</sup> G. J. Collin, Rev. Chem. Int., 2, 377 (1979).

<sup>(2)</sup> G. J. Collin, H. Deslauriers, and S. Auclair, Can. J. Chem., 57, 863 (1979).

<sup>(3)</sup> G. J. Collin, H. Deslauriers, and J. Deschênes, Can. J. Chem., 57, 870 (1979).

 <sup>(4)</sup> A. Więckowski and G. J. Collin, J. Phys. Chem., 81, 2592 (1977).
 (5) M. B. Robin in "Higher Excited States of Polyatomic Molecules",

<sup>(6)</sup> N. B. Robin m. Higher Excited States of Polyaciant invertigation.
(6) P. Borrell and F. C. James, *Trans. Faraday Soc.*, 62, 2452 (1966).
(7) P. Borrell, P. Cashmore, A. Cervenka, and F. C. James, *J. Chim. Phys.*, 229 (1970); P. Borrell and A. Cervenka, *J. Chem. Soc., Faraday* Trans. 1, 68, 345 (1972).



Figure 1. Absorption spectrum of gaseous tetramethylethylene (from ref 5).

Similar studies at longer wavelengths are very scarce. cis-2-Hexene was photolyzed at 202.6-206.2 nm and the main products observed were isomers: trans-2-hexene, 3-methyl-1-pentene, and 1-hexene. The formation of trans-2-hexene and of 1-hexene was explained in terms of the isomerization of a photoexcited molecule; a combination of ethyl and  $\alpha$ -methallyl radicals was proposed for the formation of 3-methyl-1-pentene.<sup>8</sup> Lower molecular weight products were also measured with much lower yields.

In the same work, the photolysis of *cis*-2-butene was also investigated. Results were similar except a strong pressure effect was observed: the formation of trans-2-butene increased with the total pressure.<sup>8</sup>

More recently, Kropp et al. have studied the photolysis of several alkenes in aprotic media. In the case of tetramethylethylene, the observed photoproducts were 2,3-dimethyl-1-butene (18%), 3,3-dimethyl-1-butene (17%), and 1,1,2-trimethylcyclopropane (4%).<sup>9,10</sup>

This molecule is very interesting. Its absorption spectrum shows a strong  $V \leftarrow N$  absorption band with its maximum centered at 185 nm. Another weak band, well separated from the previous one, located between 210 and 240 nm (48000-42000 cm<sup>-1</sup>), corresponds to a  $\pi \rightarrow R(3s)$ transition.<sup>5</sup> Thus, it is tempting to look at the behavior of the photoexcited molecule in this region (Figure 1).

#### **Experimental Section**

Experimental details were essentially the same as those reported in previous studies from this laboratory.<sup>2-4</sup> The tetramethylethylene is an API product (99.97  $\pm$  0.02%) previously degassed under high vacuum and at low temperature. The analysis of the starting material shows only the presence of 2,3-dimethyl-1-butene (0.0226%) and 1,1,2-trimethylcyclopropane (0.0018%).  $D_2S$  and DI are products of Merck Sharp and Dohme of Canada, and other additives are Research Grade from Matheson of Canada.<sup>2-4</sup>

Three lamps have been used regularly throughout this work. Bought from Philipps, they are a mercury lamp, 184.9 nm (100%), a zinc lamp, 202.4:206.2:213.8 nm (1:5:27:4), and a cadmium lamp, 214.4:226.5:228.8 nm (1:2:24). The reactor was a Pyrex tube (25 cm long, 2.5 cm diameter) equipped with two spectrosil quartz windows sealed with an epoxy cement. All emission lines from each lamp and light transmitted by the gaseous samples were measured with a 0.5-m McPherson monochromator equipped with a grating blazed at 150 nm (no corrections were made for the sensitivity of the system). For example, the absorption coefficient of tetramethylethylene is  $\epsilon \simeq$  $1.0 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup> between 214 and 229 nm. Thus, a pressure of 1300 N m<sup>-2</sup> (10 torr) of tetramethylethylene absorbs more than 99% of the incident light (pathlength 25 cm). Chemical actinometry was made at 185 nm and at 202-214 nm. With the mercury lamp, the gaseous photolysis of 20 torr (2660 N m<sup>-2</sup>) of ethylene was made, and the *n*-butane ( $\Phi \simeq 0.21$ ) peaks observed on the chromatogram were compared with those obtained in the photolysis of the monomer under various conditions.<sup>11</sup> The same procedure was used with the zinc lamp, except that ethanethiol was exchanged for ethylene:  $\Phi(C_2H_8) =$  $0.28 \pm 0.03$ <sup>12</sup> In each case, corrections were applied in order to take account of the transmitted light, if necessary. The intensity output of the lamps was established at  $1 \times$  $10^{14}$  and  $4.1 \times 10^{13}$  photon s<sup>-1</sup> at 185 and 202–214 nm, respectively.

All analyses were made chromatographically.<sup>2,4</sup> A squalane column (25% on firebrick) was used at 67 °C.<sup>13</sup> Several products were trapped at the exit of the chromatograph (thermal conductivity detection) and were injected on a Varian mass spectrometer in order to check their identification.

#### Results

The photolysis of tetramethylethylene (TME) yields a number of hydrocarbon products which, along with their quantum yields, are given in the tables and figures. In all experiments the amount of conversion was kept below 1%. Neither a photolytic time effect nor an intensity effect were observed. No decrease in the intensity of the light beam with the number of experiments was observed, except in the cases where DI or D<sub>2</sub>S were used as radical scavengers.<sup>14</sup> In DI experiments, a large amount of 2,3-dimethyl-1-butene was formed. For example at 184.9 nm, the photolysis of the TME:DI (5:1 torr) results in a  $\Phi$ -(2,3-dimethyl-1-butene) value of 2.6; at a total pressure of 12 torr, the same mixture produces the same product with a quantum yield of 5.1. The formation of this compound is probably the result of the presence of iodine atoms. The following equilibrium has been studied elsewhere, and the formation of 2.3-dimethyl-1-butene in the presence of DI need not be discussed anymore:<sup>15</sup>

2,3-dimethyl-2-butene + I  $\Rightarrow$  I + 2,3-dimethyl-1-butene (1)

In addition to the results given in the tables and figures, the following information should be reported.

At 184.9 nm, the  $\Phi(\text{isoprene})/\Phi(2\text{-butyne})$  ratio is constant whatever the pressure is, and its value is  $0.90 \pm 0.12$ . In the same experiments, the  $\Phi(2,3-\text{dimethyl-1},3-\text{butadi-}$ ene)/ $\Phi$ (3-methyl-1,2-butadiene) radio is 3.5 ± 0.4. Addition of either methanol (0 < P < 50 torr) or sulfur hexafluoride (0 < P < 250 torr) to a TME:O<sub>2</sub> (8.0:1.0 torr) mixture has a similar effect on the quantum yield of iso-

<sup>(8)</sup> J. P. Chesick, J. Chem. Phys., 45, 3934 (1966).
(9) P. J. Kropp, E. J. Reardon, Jr., Z. L. F. Gaibel, K. F. Williard, and J. H. Hattaway, Jr., J. Am. Chem. Soc., 95, 7058 (1973).

<sup>(10)</sup> P. J. Kropp, H. G. Gravel, Jr., and T. R. Fields, J. Am. Chem. Soc., 98, 840 (1976).

<sup>(11)</sup> P. Potzinger, L. C. Glasgow, and G. Von Bünau, Z. Naturforsch. A, 27, 628 (1972).

<sup>(12)</sup> L. Bridges, G. H. Hemphill, and J. M. White, J. Phys. Chem., 76, 2668 (1972).

<sup>(13)</sup> R. A. Hively and R. E. Hipton, J. Gas Chromatogr., 6, 203 (1968).

G. J. Collin and K. Bukka, J. Photochem., 6, 381 (1976/77).
 A. S. Rodgers and M. C. R. Wu, J. Am. Chem. Soc., 95, 6913

<sup>(1973).</sup> 

TABLE I: Photolysis of Tetramethylethylene at 184.9 nm

[TME], <sup>a</sup> torr	5.0	9.5	19.0	12	<b>24.4</b>	5.0	10.4
$[O_2]$ , torr	0.55	1.1	<b>2.2</b>				
[DI], torr						1.0	2.0
$[D_2S]$ , torr				2.5	5.0		
$\Phi(CH_{\ell})$	0.010	0.015	0.009	0.54	0.54	b	ь
$\Phi((CH_{1}), CHCH=CH_{1})$	0.00	0.00	0.00	0.0015	0.002	0.006	0.006
$\Phi(CH_2 = C(CH_1)C_2H_2)$	0.00	0.00	0.00	0.003	0.004	0.015	0.015
$\Phi((CH_{1}), C = CHCH_{1})$	0.00	0.00	0.00	0.07	0.07	0.42	0.42
$\Phi((CH_3)_2CHCH(CH_3)_2)$	0.00	0.00	0.00	0.34	0.35	b	b

<sup>a</sup> 1 torr = 133 N m<sup>-2</sup>. <sup>b</sup> Not measured.



Figure 2. Photolysis of tetramethylethylene in the presence of 10% oxygen at 184.9 nm.

mers. In all these experiments a  $\Phi(2\text{-methyl-}2\text{-pentene})$  value of 0.020 ± 0.005 was measured.

At 202.4–213.8 or 214.4–228.8 nm and in the presence of 10% oxygen, isoprene, 3-methyl-1,2-butadiene, and methylbutenes are not detected at pressures higher than 5 torr (665 N m<sup>-2</sup>).

#### Discussion

At 184.9 nm. Figure 2 shows the quantum yields of several products and their dependence upon the pressure. These products may be arranged in two groups. In the first one 2,3-dimethyl-1,3-butadiene, 3-methyl-1,2-butadiene, 2-butyne, and isoprene have quantum yields that decrease with an increase in total pressure. In the second one are isomers whose quantum yields increase with total pressure. The addition of  $D_2S$  or DI reveals the presence of several radical intermediates through the following process:<sup>16-18</sup>

$$DX + R \rightarrow RD + X (X \equiv DS \text{ or } I)$$
 (2)

Thus, methane and 2,3-dimethylbutane result from the presence of  $CH_3$  or  $C_6H_{13}$  radicals, respectively. The latter are probably formed through the addition of a hydrogen atom to the double bond of the starting material. It is worthwhile to note the larger increase in the yield of me-

thylbutenes upon addition of DI than in the presence of  $D_2S$  (Table I). It is well-known that  $D_2S$  is an inefficient allylic radical scavenger and that DI is a much better one.<sup>19</sup> Thus, the precursors of these methylbutenes are probably the vinylic ( $\Phi \simeq 0.09$ ) and allylic ( $\Phi \simeq 0.35$ )  $C_5H_9$  radicals. It follows that two primary fragmentation processes may be identified as

$$TME + h\nu \to TME^{**} \tag{3}$$

TME\*\* →

 $CH_3^* + (CH_3)_2 C = \dot{C}CH_3^*$  (vinylic structure) (4)

 $\Delta H \simeq 370 \text{ kJ mol}^{-1} \text{ (ref 20)}$ 

$$TME^{**} \rightarrow H + (CH_3)_2 \dot{C} \dot{C} (CH_3) \dot{C} H_2^* \quad (allylic structure) (5)$$

$$\Delta H = 326 \text{ kJ mol}^{-1} \text{ (ref 15)}$$

M\*\* is the photoexcited molecule (unknown excited state(s)), and M\* is a primary fragment which bears away part of the excess energy of the incident photon. A simple RRKM calculation (Whitten–Rabinovitch formula) shows that  $k_4$  and  $k_5$  are of the order of  $10^8-10^9 \text{ s}^{-1}$  at 184.9 nm. Thus, provided the total pressure is above 10 torr (1330 N m<sup>-2</sup>), both processes are in competition with the stabilization by collision. At 184.9 nm, 644 kJ einstein<sup>-1</sup> are available and the energy beyond that required to induce the primary split must appear among the fragments, and some of them have sufficient internal energy for further fragmentation.

$$(CH_3)_2\dot{C}\dot{C}(CH_3)\dot{C}H_2^* \xrightarrow{k_{6a}} CH_2 = C(CH_3)C(CH_3) = CH_2 + H \quad (6a)$$
$$\Delta H \simeq 232 \text{ kJ mol}^{-1}$$
$$(CH_3)_2\dot{C}\dot{C}(CH_3)\dot{C}H_2^* \xrightarrow{k_{6b}} (CH_3)_2C = C = CH_2 + CH_3 \quad (6b)$$

$$\Delta H \simeq 227 \text{ kJ mol}^{-1}$$

$$(CH_3)_2 C = CCH_3 * \xrightarrow{k_{7a}} CH_3 C \equiv CCH_3 + CH_3 \quad (7a)$$

$$\Delta H \simeq 118 \text{ kJ mol}^{-1}$$

$$(CH_3)_2C = \dot{C}CH_3^* \xrightarrow{k_{7b}} \dot{C}H_2C(CH_3)\dot{C}HCH_3^*$$
 (7b)

$$\Delta H \simeq -63$$
 kJ mol<sup>-</sup> (ref 15)

$$E_{A} \simeq +146 \text{ kJ mol}^{-1} \text{ (ref 22)}$$
  
$$\dot{C}H_{2}\dot{C}(CH_{3})\dot{C}HCH_{3}^{*} \rightarrow CH_{2} = C(CH_{3})CH = CH_{2} + H$$
(8)

<sup>(16)</sup> P. Ausloos and S. G. Lias, J. Chem. Phys., 44, 521 (1966).

<sup>(17)</sup> G. J. Collin, P. M. Perrin, and C. M. Gaucher, Can. J. Chem., 50, 2391 (1972).

<sup>(18)</sup> Z. Diaz and R. D. Doepker, J. Phys. Chem., 81, 1442 (1977).

<sup>(19)</sup> P. Ausloos, R. E. Rebbert, and S. G. Lias, J. Photochem., 2, 267 (1973/74).

<sup>(157)(4).</sup> (20) (a)  $\Delta H_1^{e}[(CH_3)_2C \doteq \dot{C}CH_3]$  was estimated to be 171 kJ mol<sup>-1</sup>:  $\Delta H_1^{e}[(CH_3)_2C \doteq \dot{C}CH_2] = \Delta H_1^{e}(\dot{C}H_2\dot{C}(CH_3)\dot{C}H_2)^{20b}$  + increment for a  $CH_2$ group<sup>20e</sup> + allylic resonance energy.<sup>15</sup> (b) A. B. Trenwith and S. P. Wrigley, J. Chem. Soc., Faraday Trans. 1, 73, 817 (1977). (c) This value corresponds to a  $D(C-CH_3)$  value of 89 kcal mol<sup>-1</sup> (372 kJ mol<sup>-1</sup>) in the tetramethylethylene.

TABLE II: Photolysis of Tetramethylethylene:Oxygen (100:10) at 184.9 nm

	a			$SF_6^{\ b}$ (40-250 torr)			$CH_4^b$ (60-260 torr)		
additive	Φ	$r^{2}c$	k <sup>d</sup>	Φ_	r <sup>2 C</sup>	$k^d$	$\Phi_{\infty}$	$r^{2}c$	k <sup>d</sup>
2,3-dimethyl-1-butene 1,1,2-trimethylcyclopropane 3,3-dimethyl-1-butene	0.45 0.07 <sub>5</sub> 0.07 <sub>0</sub>	0.99 0.97 0.93	$175 \\ 130 \\ 2800$	0.31 0.08 0.09	0.97 <sub>6</sub> 0.91 0.98 <sub>7</sub>	258 298 5740	0.27 0.09	0.99 0.96 0.98	$351 \\ 954 \\ 12000$

<sup>a</sup> Total pressure between 10 and 45 torr (1330-6000 N m<sup>-2</sup>). <sup>b</sup> TME:O<sub>2</sub> mixtures: 9.5 torr (1260 N m<sup>-2</sup>). <sup>c</sup> Correlation coefficient of the linear regressions. <sup>d</sup> k in units of (torr)<sup>-1</sup>.

These reactions are, of course, in competition with stabilization by collision.

$$(CH_3)_2\dot{C}\dot{C}(CH_3)\dot{C}H_2^* + M \xrightarrow{\kappa_*} M + (CH_3)_2\dot{C}\dot{C}(CH_3)\dot{C}H_2$$
(9)

If this mechanism is correct, the quantum yields of 2,3dimethyl-1,3-butadiene (process 6a), 2-butyne (process 7a), 3-methyl-1,2-butadiene (process 6b), and isoprene (process 8) must follow the Stern-Volmer law.<sup>23</sup> For example

# $[\Phi(2\text{-butyne})]^{-1} =$

 $[\Phi_0(2\text{-butyne})]^{-1} + [\Phi_0(2\text{-butyne})]^{-1}k_s[M]/k_{7a}$ 

where  $\Phi_0$  is the quantum yield at zero pressure,  $k_s$  is the second-order rate constant of the stabilization process (reaction 9) and  $k_{7a}$  is the first-order rate constant of the fragmentation process. The linearity of the plots of  $[\Phi-(X)]^{-1}$  vs. total pressure is good for 2,3-dimethyl-1,3-butadiene and 3-methyl-1,2-butadiene (Figure 2); however, those for isoprene and 2-butyne show a positive curvature. The above mechanism assumes that stabilization occurs at every physical collision. It might not be the case and two or several collisions may be needed to remove the excess internal energy and result in a positive curvature of the Stern-Volmer plot.<sup>23</sup>

The origin of 3-methyl-1,2-butadiene is assumed to be the fragmentation of the  $(CH_3)\dot{C}\dot{C}(CH_3)\dot{C}H_2^*$  radical and not the  $(CH_3)_2C=\dot{C}CH_3^*$  radical. The  $\Phi(2,3\text{-dimethyl-}1,3\text{-butadiene})/\Phi(3\text{-methyl-}1,2\text{-butadiene})$  ratio is constant (see Results). Although reaction 6b is less endothermic than process 6a, six hydrogen atoms are available for this last process against one C-CH<sub>3</sub> bond for process 6b. Finally, the isomerization process, reaction 7b has been included in order to explain the formation of allylic  $C_5H_9$ radicals and isoprene: see the relevant discussion in ref 1, 3, and 22 (Figure 3).

At this stage, the relative importance of the quantum yields of the two primary processes, reactions 4 and 5, may be estimated. Provided no other important process contributes to the formation of methyl radicals and hydrogen atoms:  $\Phi(\text{process 4}) = \Phi_{D_2S}(CH_4) - \Phi_{O_2}(CH_4) - \Phi_{O_2}(2-\text{butyne}) - \Phi_{O_2}((CH_3)_2C=C=CH_2) \simeq 0.50$  and  $\Phi(\text{process 5}) = \Phi_{D_2S}(C_6H_{14}) - \Phi_{O_2}(C_6H_{10}) - \Phi_{O_2}(\text{isoprene}) \simeq 0.22 (\Phi_{D_2S}-(CH_4))$  is the methane quantum yield measured in the presence of  $D_2S$ , ..., etc.). It is interesting to note that more than 90% of the  $(CH_3)_2\dot{CC}(CH_3)\dot{CH_2}^*$  radicals decompose further at low pressure; that means that the most of the excess energy is in the allylic radical and that the hydrogen atom has a small part of the excess energy content.

The second group of products, isomers, have low quantum yields that increase with an increase in the total pressure, except in the case of 2-methyl-2-pentene whose quantum yield is rather constant (see Results). The for-



**Figure 3.** Schematic potential energy diagram for reactions 7a, 7b, and 8:  $E_1 \simeq 34 \text{ kJ mol}^{-1}$ ;  $E_2 \simeq 144 \text{ kJ mol}^{-1}$ ;  $^{22}E_3 \simeq 5 \text{ kJ mol}^{-1}$ .



**Figure 4.** Photolysis of tetramethylethylene: $O_2$  mixtures (8.5:1.0 torr) at 185 nm in the presence of various amounts of methane or sulfur hexafluoride.

mation of these products is also observed when additives such as methane, methanol, or sulfur hexafluoride are added as inert gas (Figure 4, Table II). In each case, the quantum yield increases with the pressure. Provided the concentration of additive is sufficient, a linear relationship is observed between the reverse of the quantum yield value and the reverse of the pressure:  $[\Phi(X)]^{-1} = a + k[P]^{-1}$ . These relationships were used to determine the quantum yield values of each product at infinite pressure:  $\Phi_{\infty}(X) = a^{-1}$  (Table II).

In view of the observed effects of total pressure on quantum yield for the two groups of products, it seems apparent that the isomeric products arise via rearrange-

<sup>(21)</sup> F. H. Dorer and B. S. Rabinovitch, J. Phys. Chem., 69, 1952
(1965); P. J. Robinson and K. A. Holbrook in "Unimolecular Reactions",
Wiley-Intersciences, New York, 1972, Chapter 5.
(22) T. Ibuki, A. Tsaji, and Y. Takezaki, J. Phys. Chem., 80, 8 (1976).

<sup>(22)</sup> T. Ibuki, A. Tsaji, and Y. Takezaki, J. Phys. Chem., 80, 8 (1976).
(23) J. A. Barltrop and J. D. Coyle in "Principles of Photochemistry", Wiley, New York, 1978, Chapter 5.

 TABLE III: Photolysis of Tetramethylethylene in the 202.4-228.4 nm Region

[TME], torr	$202.4-213.8 \text{ nm}^{a}$					214.4-228.8 nm <sup>b</sup>						
	5.4 0.6	10.3 1.1	5.7	10	16.2	$\overline{4.3}\\0.45$	9.0 1.0	$\frac{17}{1.2}$	4.85	10.0	20.2	
$[D_2 S]$ , torr			1.0	2.0	3.2				1.0	2.0	4.0	
$ \begin{aligned} & \Phi(CH_4) \\ & \Phi((CH_3)_2 C = CHCH_3)^{g} \\ & \Phi((CH_3)_3 CC = CH_2) \\ & \Phi(TMC)^{c} \\ & \Phi(CH_2 = C(CH_3)CH(CH_3)_2) \\ & \Phi((CH_3)_2 C = CHC_2H_5) \\ & \Phi(CH_2 = C(CH_3)C(CH_3) = CH_2) \\ & \Phi((CH_3)_2 CHCH(CH_3)_2) \\ & R^{f} \end{aligned} $	$\begin{array}{c} 0.001\\ 0.00\\ 0.007\\ 0.019\\ 0.011\\ 0.004\\ 0.009\\ 0.00\\ 0.24 \end{array}$	$\begin{array}{c} 0.00\\ 0.00\\ 0.008\\ 0.020\\ 0.024\\ 0.003\\ 0.004\\ 0.00\\ 0.29 \end{array}$	$\begin{array}{c} 0.075 \\ 0.03 \\ 0.006 \\ 0.019 \\ 0.036 \\ 0.003 \\ d \\ 0.134 \end{array}$	$\begin{array}{c} 0.062\\ 0.03\\ 0.009\\ 0.020\\ 0.038\\ 0.003\\ d\\ 0.125 \end{array}$	$\begin{array}{c} 0.045\\ 0.025\\ 0.011\\ 0.021\\ 0.037\\ 0.002\\ d\\ 0.127\\ \end{array}$	$\begin{array}{c} 0.00\\ 0.00\\ 0.56\\ 1.0\\ 0.22\\ 0.08\\ 0.24\\ 0.00\\ 0.84 \end{array}$	$\begin{array}{c} 0.00\\ 0.00\\ 0.68\\ 1.0\\ 0.21\\ d\\ 0.14\\ 0.00\\ 0.94 \end{array}$	0.00 0.73 1.0 0.20 0.03 0.09 0.00 1.18	$\begin{array}{c} 0.59 \\ 0.36 \\ 0.54 \\ 1.0 \\ 0.34 \\ e \\ d \\ 1.62 \end{array}$	$\begin{array}{c} 0.55 \\ 0.26 \\ 0.68 \\ 1.0 \\ 0.30 \\ e \\ d \\ 1.50 \end{array}$	$\begin{array}{c} 0.36 \\ 0.18 \\ 0.77 \\ 1.0 \\ 0.30 \\ e \\ d \\ 1.29 \end{array}$	

<sup>a</sup> Quantum yields. <sup>b</sup> Relative yields only,  $\phi(\text{TMC}) = 1.0$ . <sup>c</sup> TMC = 1,1,2-trimethylcyclopropane. <sup>d</sup> Not measured. <sup>e</sup> Traces. <sup>f</sup>  $R = \phi(C_6H_{12})/[\phi(CH_3) + \phi(H)]$ . <sup>g</sup> Mass spectrometric analysis show that the majority of 2-methyl-2-butene is  $C_5H_9D$ : see reaction 2.

ment of the electronic excited state(s) formed, whereas the other products arise via competing fragmentation of the electronic excited state(s) made possible by the excess vibrational energy imparted to the molecule. This would explain the observed wavelength effect. Thus, the two groups of products arise from the same electronic states having different levels of vibrational energy. It is also interesting to note from Figure 2 that the quantum yields of formation of 1,1,2-trimethylcyclopropane and 3,3-dimethyl-1-butene respond in a parallel fashion to changes in the total pressure whereas the quantum yield for 2,3dimethyl-1-butene follows a quite different slope (see also Table II). This supports the involvement of the same excited state in the formation of the former two products and a different excited state in the case of the latter. A fourth isomeric product, 2-methyl-2-pentene, observed here, was not reported in the solution-phase work.<sup>9,10</sup> Its constant quantum yield, on a large pressure scale, supports also the involvement of a third different excited state. Finally, photoexcited cyclopropane derivatives are known to decompose through a  $CH_2$  elimination from the  $C_3$  ring, and 2-methyl-2-butene is an expected product.<sup>24</sup> Again, if an electronically excited cyclopropane molecule is formed, the excited state must be different from the one obtained by photoabsorption since there is no 2-methyl-2-butene formation.

In order to take the pressure effect into account, the following mechanism may be proposed:<sup>25</sup>

$$TME + h\nu \to TME^{\ddagger} \quad (\phi^{\ddagger}) \tag{10}$$

 $TME^{\ddagger} \rightarrow TME \quad (+ h\nu \text{ or radiationless conversion})$ (11)

$$TME^{\ddagger} + TME \rightarrow 2TME \quad (description) \quad (12)$$

$$1 \text{ME}^{\dagger} + 1 \text{ME} \rightarrow 21 \text{ME}$$
 (deactivation) (12)

 $TME^{\ddagger} \xrightarrow{TME} A^{\ddagger} \rightarrow A$  (induced preisomerization) (13)

$$\Gamma M E^{\ddagger} + M \to T M E + M \tag{14}$$

$$TME^{\ddagger} \xrightarrow{M} A^{\ddagger} \rightarrow A \tag{15}$$

where TME<sup>‡</sup> is one excited state of TME, A is one of the isomers, M is an added gas, and  $\phi^{\ddagger}$  is the quantum yield of primary process 10. In the absence of M, this scheme leads to the following expression for the quantum yields:

$$[\Phi(\mathbf{A})]^{-1} = (\phi^{\ddagger})^{-1} \frac{k_{11}}{k_{13} [\text{TME}]} + (\phi^{\ddagger})^{-1} \frac{k_{12} + k_{13}}{k_{13}}$$

This expression is similar to the previously indicated one. In the presence of a large amount of M, it becomes

$$[\Phi(\mathbf{A})]^{-1} = (\phi^{\ddagger})^{-1} \frac{k_{11}}{k_{15}[\mathbf{M}]} + (\phi^{\ddagger})^{-1} \frac{k_{14} + k_{16}}{k_{15}}$$

Thus, in each case, the previously defined  $\Phi_{\infty}$  value is smaller than or equal to the  $\phi^{\ddagger}$  value and has different values depending on the nature of M (Table II).

In the pure system, it happens that  $\phi^{\dagger} \geq \sum \Phi_{\infty}$  isomer and  $\phi^{\dagger} \geq 0.615$ . This value, when combined with the calculated  $\phi$ (process 4) and  $\phi$ (process 5) gives a total quantum yield for the primary processes equal to  $1.35_5$ . This value is not bad, taking into account the experimental error, although it is a little bit away from unity. It must be said that the above mechanism is a very simple one, and such a process

$$A^{\ddagger} + TME \rightarrow A + TME^{\ddagger}$$
 (16)

may explain the value higher than unity. This may also partly explain the lower quantum yield measured in the presence of sulfur hexafluoride.

At 202.4-213.8 and 214.4-228.9 nm. The chromatographic analysis obtained are much simpler when the photolysis is with either the zinc or the cadmium lamp. There are only traces of fragmentation products and the only measurable one is 2,3-dimethyl-1,2-butadiene:  $\Phi \simeq$ 0.009 at a total pressure of 5 torr (605 N m<sup>-2</sup>). However, the addition of D<sub>2</sub>S or DI shows the presence of methyl radicals and hydrogen atoms (Table II):  $\Phi(CH_3)$  and  $\Phi(H)$ are 0.06 and 0.125, respectively, at a total pressure of 12 torr (1 600 N m<sup>-2</sup>) in the 202.4-213.8-nm region. At 184.9 nm, the  $\beta$ (C-H) split/ $\alpha$ (C-CH<sub>3</sub>) split ratio was 0.44; at 202.4-213.8 nm, this ratio becomes 2.0 and 2.8 at 214.4-228.8 nm. Thus, a decrease in the photon energy favors the C-H split as it was previously noted in the photolysis of cis-2-butene.<sup>4</sup> The decomposition of the primary  $C_5H_9*$  radicals and  $C_6H_{11}*$  radicals is very limited, since only at shorter wavelength does it impart a sufficient quantity of energy in the starting molecule to produce 2,3-dimethyl-1,3-butadiene and 3-methyl-1,2-butadiene. The zinc lamp gives more energy than necessary to produce isoprene and 2-butyne. However, in the primary process (reaction 4) the methyl radical takes part of this excess energy, and the  $C_5H_9$ \* radicals are not capable of further decomposition.

Although no actinometry was made at 214.4–228.8 nm, it can be said that the longer the wavelength is, the less important the fragmentation of the photoexcited molecule is. Table III gives the values of the ratio of the quantum yield of isomers,  $C_6H_{12}$ , relative to the total  $\Phi(CH_3) + \Phi(H)$ . At 184.9 nm the same ratio is 0.10 and 0.14 at a total

<sup>(24)</sup> G. J. Collin, J. Chim. Phys., 74, 302 (1977), and references cited therein.

<sup>(25)</sup> J. Hagège, P. C. Roberge, and C. Vermeil, *Trans. Faraday Soc.*, 64, 3288 (1968).

pressure of 5.5 and 10.6 torr, respectively, and the longer the wavelength is the more important the isomerization processes are.

The Absorption Spectrum. It is time now to come back to the absorption spectrum of the starting material and to try to draw some conclusions on the relationship between the behavior of the photoexcited state (photolysis) and the electronic state formed upon absorption of light (spectroscopy). It is, of course, tempting to link the isomerization of the monomer to the formation of Rydberg excited states. This simple view does not take into account all the likely internal conversion of electronic energy, from one excited electronic state to another or to the fundamental one. The results obtained here are far from sufficient to draw any valid conclusion.

It is worthwhile to recall here a full discussion on the

different properties of  $\pi,\pi^*, \pi, R(3s)$ , and  $\pi,\sigma^*$  excited states in olefins given recently by Kropp.<sup>26</sup> The principal chemical property associated with the  $\pi,\pi^*$  state of alkenes is cis-trans isomerization; the  $\pi,R(3s)$  state undergoes a 1,2-methyl shift (skeletal isomerization); the positional migration of the double bond involves a [1,3]-sigmatropic hydrogen shift, and appears to be associated with neither  $\pi,\pi^*$  nor  $\pi,R(3s)$  excited states.<sup>26</sup>

Acknowledgment. We express our gratitude to Professor C. Sandorfy (Université de Montréal) for his encouragements throughout this work. The help of the Department of Chemistry of the Université de Montréal was also appreciated for the generous mass spectrometric analysis.

(26) P. J. Kropp, US ARO Report, ARO-12810-2, 1978.

# Resolution of the Fluorescence Lifetimes in a Heterogeneous System by Phase and Modulation Measurements

#### **Gregorio Weber**

Department of Biochemistry, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801 (Received: August 12, 1980)

A closed-form procedure is described for the determination of the decay constants and the relative contributing intensities of the N independent components of a heterogeneous fluorescence emission employing measurements of the phase shift and relative modulation of the total fluorescence at N appropriate harmonic excitation frequencies. At each frequency the phase and modulation measurements yield the real part of the Fourier transform of the fluorescence impulse response, G, and its imaginary part, S. It is shown that the moments of a distribution of the lifetimes are linear combinations of the Gs (zero and even moments) or the Ss (odd moments), and the rule for the construction of the coefficients of G and S in these linear combinations is derived. The classical de Prony method is used to obtain the lifetimes and fractional contributions of the components from the moments. For binary and ternary mixtures the numerical computations required are trivial. In the present state of the art, the lifetimes of the components of a binary mixture should be derivable with a loss in precision somewhat smaller than 1 order of magnitude with respect to the overall measured lifetimes.

## Introduction

The determination of fluorescence lifetimes by phase delay techniques goes back to Gaviola<sup>1</sup> (1927), and the effects expected in the overall phase and modulation by the presence of multiple fluorescence emissions were made clear by Dushinsky<sup>2</sup> in 1933. In spite of these early beginnings no general method has been proposed to determine the proportions and lifetimes of the fluorescence components utilizing the phase delay and relative modulation data obtained at different frequencies of the exciting light. This shortcoming has resulted in neglect of the phase techniques in favor of pulse fluorometry<sup>3</sup> which often permits resolution into components, although it is known that the phase methods are much faster in execution, and superior in precision in the measurements of overall decay, especially in the range of 100 ps to 3 ns.<sup>4</sup> We present here an exact solution of the problem of determination of the proportion and lifetimes of N independent, noninteracting fluorophores, starting from the values of the phase shifts and relative modulation of the overall fluorescence excited at N light-modulation frequencies.

The numerical computations required are sufficiently simple to be performed in line with data acquisition. Although present-day precision may not be sufficient to

E. Gaviola, Z. Phys., 42, 85 (1927). Improved instrumentation of the same kind was used by W. Szymanowsky, Z. Phys., 95, 460 (1936).
 Electronic detection of phase differences between photocurrents was introduced by E. A. Bailey and G. K. Rollefson, J. Chem. Phys., 21, 1315 (1953) and A. Schmillen, Z. Phys., 135, 294 (1953). Use of both phase and modulation to measure fluorescence lifetimes was first employed by J. B. Birks and W. A. Little, Proc. Phys. Soc., London, Sect. A, 66, 921 (1953). Cross-correlation techniques for phase and modulation measurements were introduced by R. D. Spencer and G. Weber, Ann. N.Y. Acad. Sci., 158, 361 (1969). Continuously variable frequency of excitation has been realized by H. P. Haar and M. Hauser, Rev. Sci. Instrum., 49, 632 (1978).

<sup>(2)</sup> F. Dushinsky, Z. Phys., 81, 7 (1933).

<sup>(3)</sup> Recent publications on pulse fluorometry that give an account of present state technology include the following: D. V. O'Connor, W. R. Ware, and J. C. Andre, J. Phys. Chem., 83, 1333 (1979); B. Valeur, Chem. Phys., 30, 85 (1978); R. L. Lyke and W. R. Ware, Rev. Sci. Instrum., 48, 320 (1977); A. Gafni, R. L. Moolin, and L. Brand, Biophys. J., 15, 273 (1975).

<sup>(4)</sup> R. D. Spencer and G. Weber, J. Chem. Phys., 52, 1654 (1970); H. P. Haar and M. Hauser, under ref 1.

<sup>(5)</sup> R. de Prony, J. Ec. Polytech. (Paris), 1, 24 (1795) appears to have used for the first time a method based on eq 27 to obtain the coefficients of dilation of an anisotropic solid. A modern description of Prony's method is given by F. B. Hildebrand, "Introduction to Numerical Analysis", McGraw-Hill, 1974, p 458.