LASER PHOTOLYSIS OF TRIMETHYLGALLIUM AT 193 nm: QUANTUM YIELDS FOR METHYL RADICAL AND ETHANE PRODUCTION

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Quantum yields for the products from trimethylgallium (TMG) photolysis were determined via a new method involving isotopic analysis using TMG-acetone- d_6 mixtures. The following model-dependent quantum yields were obtained: monomethylgallium (MMG), 0.5; dimethylgallium (DMG), 0.2; gallium, 0.3; molecularly eliminated ethane, 0.3; free methyl, 1.5. Two new electronic absorptions at 216 and 220 nm were found and are tentatively ascribed to DMG⁺.

1. Introduction

Organometallic compounds are of great interest for the production of thin films on semi-conductor materials. Metal deposition may be achieved by thermal vapor phase fragmentation of these compounds. Laser-induced chemical vapor deposition has also been applied successfully as an alternative method when lower substrate temperature or deposit along the beam line is desired [1]. The principal objectives of numerous studies on both thermal and photochemical dissociation have been to establish the chemistry and physics of the pathways leading to deposition.

The laser-induced photochemistry of gallium compounds has been investigated in several laboratories. Mitchell et al. [2] derived a dissociation mechanism for visible and UV multiphoton dissociation of trimethylgallium (TMG). Their model is that of TMG photolysis producing two methyls and monomethylgallium (MMG) with some of the MMG further photolyzing to produce methyl and free gallium. Dimethylgallium (DMG) was not considered an important fragment. Baughcum and Oldenborg [3] photolyzed TMG at 193 nm and used laser-induced fluorescence to determine the production mechanism of Ga atoms. They also interpreted their results in terms of a two-photon sequential process. The first photon produces DMG and CH₃ or alternatively MMG and ethane. Absorption of a second photon gives excited DMG (DMG*) decomposing to ethane and Ga, or MMG*, decomposing to CH₃ and Ga. More recently Zhang et al. [4] detected both MMG and free gallium atoms by laser mass spectrometry. Since DMG was observed in minor amounts, the authors assumed that MMG was the major product along with significant "primary" production of the free metal atoms. Beuermann and Stuke [5], in working with trimethylaluminum as a model for the group III trimethyl compounds in general (Al, Ga, and In) propose a single photon mechanism involving molecular ethane elimination,

 $AI(CH_3)_3 \rightarrow AI + C_2H_6 + CH_3,$ $\rightarrow AICH_3 + CH_3 + CH_3,$

for $\lambda < 230$ nm photolysis. They further note that their experimental data do not support the reaction

 $Al(CH_3)_3 \rightarrow AlCH_3 + C_2H_6$.

In view of the general importance of the photolysis of metal alkyls for metal film production we report here a new approach to the experimental determination of the major photodecomposition products in the TMG system. Detection of free gallium atoms has not been undertaken at this time. The main focus is on the direct and indirect detection of free methyl radicals and molecular ethane. The relative importance of the direct elimination of one or more methyl radicals in the primary photolytic process has been assessed. Relatively low light flux was employed to minimize multiple photon processes.

2. Methodology

It is useful in a quantitative determination of the quantum yields of methyl in the photolysis of TMG, to compare the TMG photolysis with that of acetone or azomethane as actinometric standards. Acetone and azomethane have quantum yields of approximately two for production of methyl radicals at the 193 nm ArF excimer laser wavelength [6,7]. Their reaction products are almost exclusively CO and ethane, and N₂ and ethane. The procedure for the measurements involves first the accurate measurements of the absorption cross sections centered at 193.3 nm for acetone, azomethane and TMG. Each of these compounds is subjected to multiple laser pulses, and the time history of the methyl radicals, as determined by the methyl absorption at 216.4 nm, is recorded and analyzed. Second, the total ethane produced in the process is obtained chromatographically. By comparing acetone and azomethane with TMG, the absolute value for the quantum yield for methyl production in TMG can be determined.

A discrepancy between ethane production and methyl concentration for TMG led to the finding that the 216.4 nm wavelength used for the CH_3 analysis is not valid for the TMG photolysis because a species

other than methyl also absorbs strongly at 216.4 nm (at 220 nm as well). Therefore, a novel procedure for the determination of the quantum yields for TMG is introduced while still taking advantage of comparison with a primary standard. This procedure involves the photolysis of measured mixtures of TMG and completely deuterated acetone (acetone- d_6). Completely deuterated azomethane would be equally satisfactory. The rationale is that in the photolysis, CD₃ and CH₃ are produced from the photolysis of an acetone- d_6 and TMG mixture. Recombination of these methyl groups gives C_2D_6 , CH_3CD_3 and C_2H_6 which can be analyzed mass spectrometrically. As we will show, the application of this procedure leads to a convenient and reliable determination of quantum vields for TMG.

3. Experimental procedure

An excimer laser with an ArF-He mixture is employed. The laser intensity can be controlled through focusing, the use of neutral density filters, and by some adjustment of the laser voltage. Laser fluence determinations are made by way of analysis of ethane produced by azomethane or acetone photolysis (actinometry). Laser fluences were always restricted to 3 mJ/cm^2 or less in order to minimize multiple photon processes and still ensure sufficient CH₃ radical absorption at 216.4 nm for spectrometric determinations. Absorption signals of about 5% could be easily analyzed with the accumulation of about 100 laser pulses.

Absorption cross sections were measured with a 1 m normal incidence vacuum monochromator with either 0.05 or 0.1 nm resolution. Wavelengths were calibrated using both the 253.7 nm Hg and the 121.6 nm Lyman- α H lines. Absorption cross sections were determined at various pressures to a precision of better than 5%. In table 1 is a list of the cross sections for the various compounds used at 193.3 nm. For acetone and acetone- d_6 the absorption cross sections represent averages around a quasi-triangular band approximately 0.5 nm wide centered at 193.3 and representing the ArF band as reported by Hoffman et al. [8], fig. 1. Some of the ArF radiation is absorbed by atmospheric oxygen [9]. However, its effect on the results of the calculation of the acetone

Table 1Absorption coefficients at 193.3 nm

Compound	Absorption coefficient $(\text{cm atm})^{-1}$	
azomethane (AM)	450 ± 20	
trimethylgallium (TMG)	680 ± 20	
acetone-h ₆	85± 5	
acetone- d_6	116±10	



Fig. 1. Absorption cross sections for light and fully deuterated acetone at 0.05 nm resolution. Schematic intensity distribution of 193.3 nm ArF laser line also shown.

absorption cross section was negligible.

Gas sample purity was checked either chromatographically or by mass spectrometry. Gas mixtures were prepared using a calibrated capacitance manometer. A chromatographic tracer, cyclopropane, was added at pressures less than 1% of the compound to be photolyzed. Ethane was referenced to cyclopropane and hence there was no need to reproduce injection sample sizes. Absolute ethane determinations required (i) knowing the precise volume of the photolysis cell and the rest of the sample system, (ii) the number of laser pulses, and (iii) the absorption cross sections for the sample. Standard chromatographic procedures were employed. However, the analysis of ethane from TMG mixtures poses a special problem in that most chromatographic columns result in some TMG destruction with methane formation. Some ethane is also produced. To eliminate this problem (rather than correct for it) the TMG was cryogenically removed prior to chromatographic analysis.

For methyl quantum-yield determinations, the

TMG and either the azomethane or the acetone pressures were adjusted in the inverse ratio of their absorption cross sections. Any inhomogeneities in the laser beam then did not affect the accuracy of the data.

In the isotope experiments acetone- d_6 was used. Mixtures of acetone- d_6 with TMG were always kept below a total pressure of these compounds of 7 Torr. It was found that higher pressures resulted in liquid condensation. This is remarkable in that the vapor pressures of each of these substances is approximately 200 Torr at 30°C. At the pressures employed no association complex between acetone- d_6 and TMG could be detected in the gas phase.

4. Results

Methyl radicals and ethane are first compared from separate photolysis of azomethane and acetone, each diluted with helium. The pressures of the compounds were chosen in the inverse ratio of their absorption cross sections (table 1) and the results given in table 2 were obtained. Within the experimental error, ethane and the initial methyl concentrations are in agreement. The initial CH₃ concentration was obtained by extrapolating the methyl radical absorption at 216.4 nm to zero time on a reciprocal methyltime (second-order) plot, fig. 2. Reproducibility of such plots has been found to be within 5% and are adequate for methyl radical intercomparisons.

For the use of acetone- d_6 -TMG mixtures some elementary analysis is required to furnish the guidelines necessary for the treatment of the data. The isotopic ethanes in a mixed system formed by methyl radical combination are formed according to the following kinetic equations,

Table 2

A comparison of the quantum yields of methyl formation from azomethane and acetone- h_6 at 193 nm

Sample	C ₂ H ₆ (chromatographic)	CH ₃ (spectroscopic)
0.500 Torr azomethane	2.0	2.0
2.64 Torr acetone	1.96±0.15 *)	2.12±0.15 ^a)

^{a)} Relative to azomethane (azomethane assumed to be 2).



Fig. 2. Typical methyl radical determination: acetone at a pressure of 3.12 Torr with 46.9 Torr added helium. S_{Abs} is absorption signal at 216.4 nm.

$$d[C_2H_6]/dt = k[CH_3][CH_3],$$
 (1a)

$$d[CH_3CD_3]/dt = 2k[CH_3][CD_3],$$
 (1b)

$$d[C_2D_6]/dt = k[CD_3][CD_3].$$
 (1c)

This leads to

$$[CH_3]/[CD_3] = [CH_3CD_3]/2[C_2D_6],$$
 (2)

$$[CH_3]/[CD_3] = 2[C_2H_6]/[CH_3CD_3]$$
 (3)

and

$$[CH_3CD_3]^2/[C_2D_6][C_2H_6] = 4.$$
(4)

Methyl radical loss processes other than (1a)-(1c), provided they do not produce ethane, do not perturb eqs. (2)-(4) since they influence the [CH₃] and [CD₃] similarly. If ethane is formed by reactions other than by simple combination (via eqs. (1a)-(1c), by molecular ethane elimination for example, eqs. (2) and (3) will necessarily yield different values for the [CH₃]/[CD₃] ratio. Alternatively, eq. (4) will not yield the value 4. Finally, eqs. (2) and (3) can be applied to the calculation of quantum yield ratios, ϕ (CH₃)/ ϕ (CD₃). Thus, in the case of the photolysis of a mixture of acetone- d_6 and TMG,

$$\frac{\phi(\mathrm{CH}_3)}{\phi(\mathrm{CD}_3)} = \frac{[\mathrm{CH}_3\mathrm{CD}_3]P_\mathrm{D}\epsilon_\mathrm{D}}{2[\mathrm{C}_2\mathrm{D}_6]P_\mathrm{H}\epsilon_\mathrm{H}},\tag{5a}$$

$$\frac{\phi(\mathrm{CH}_3)}{\phi(\mathrm{CD}_3)} = \frac{2[\mathrm{C}_2\mathrm{H}_6]P_{\mathrm{D}}\epsilon_{\mathrm{D}}}{[\mathrm{CH}_3\mathrm{CD}_3]P_{\mathrm{H}}\epsilon_{\mathrm{H}}},$$
(5b)

where P_D and P_H are the pressures of acetone- d_6 and TMG, and ϵ_D and ϵ_H are the corresponding absorption coefficients.

Eqs. (5a) and (5b) were applied to several intercomparisons involving acetone- d_6 , acetone and acetone- d_6 , azomethane. Representative results are presented in table 3 and are in accord with processes in which there is no molecular elimination of ethane.

On the other hand, in the case of TMG-acetoned₆ mixtures cq. (4) is not satisfied as will be shown later. Molecular elimination of ethane is a likely explanation. We model this case here and consider other possibilities later. Let in the photolysis, D=2 be the number of CD₃ radicals from acetone-d₆ (CD₃ quantum yield), Q the quantum yield of total methyl from TMG, R the number of free CH₃ radicals from TMG, M the total number of CH₃ units from TMG, free methyl radicals plus molecularly eliminated ethane (two methyls) ($M=Q\epsilon_{TMG}P_{TMG}/\epsilon_{Ac}P_{Ac}$), F the fraction of M produced as free CH₃, 1-F the fracTable 3

Table 4

Representative examples of the CH_3/CD_3 ratios obtained from the photolysis of various isotopic mixtures

Mixture composition	$\frac{\phi(\mathrm{CH}_3)^{\mathrm{a}}}{\phi(\mathrm{CD}_3)}$	$\frac{\phi(\mathrm{CH}_3)^{\mathfrak{b})}}{\phi(\mathrm{CD}_3)}$
$P_{Ac-d_6} = 1.0$ Torr $P_{Ac-d_6} = 1.42$ Torr $P_{He} = 17.6$ Torr	1.2 ±0.13 °)	1.14±0.12 ^{c)}
$P_{Ac-d_6} = 1.02$ Torr $P_{Az} = 0.30$ Torr $P_{He} = 20.7$ Torr	0.98 ± 0.07 °)	0.99 ± 0.07 ^{c)}

^{a)} Calculated from eq. (5a).

^{b)} Calculated from eq. (5b).

^{c)} Errors derived from error estimates listed in table 1.

tion of M as the methyl equivalent of molecularly formed ethane, and S the number of molecules of ethane eliminated molecularly. It follows that,

(A)
$$[CH_3-CD_3]^2/[C_2D_6]([C_2H_6]-S)=4$$
,

(B) $D=2=[CH_3CD_3]+2[C_2D_6]$,

(C)
$$R = MF = [CH_3CD_3] + 2([C_2H_6] - S),$$

(D) M - R = M(1 - F) = 2S.

Solving these mass balance conditions leads to the following:

$$X = \frac{[CH_3CD_3]\epsilon_{Ac}P_{Ac}}{[C_2D_6]\epsilon_{TMG}P_{TMG}} = QF, \qquad (7)$$

where the quantity X represents the quantum yield of free CH₃ radicals and is mixture independent, and

 $Y = \frac{4\epsilon_{\rm Ac}P_{\rm Ac}[C_2H_6]}{\epsilon_{\rm TMG}P_{\rm TMG}[\rm CH_3CD_3]} = Q + \frac{2(1-F)\epsilon_{\rm Ac}P_{\rm Ac}}{F\epsilon_{\rm TMG}P_{\rm TMG}}.$ (8)

Thus the quantity Y is a linear function of P(Ac)/P(TMG) in which Q and F may be determined by the intercept and the slope of the linear plot. Eq. (8) leads to

$$F = \frac{(QF)\epsilon_{\mathrm{TMG}}P_{\mathrm{TMG}}/\epsilon_{\mathrm{Ac}}P_{\mathrm{Ac}}+2}{4[C_2H_6]/[\mathrm{CH}_3\mathrm{CD}_3]+2}.$$
(9)

Eqs. (7) and (8) together define the value of Qand F. Obviously if all the data were error free, the data plotted according to eq. (8) would yield Q and F, derived from the slope and the intercept, that would match the requirement that the quantity QFmust be a constant equal to that derived from eq. (7). Since this is not the case, eq. (8) is rearranged to give eq. (9) where F is shown as a function of QFand $P_{\rm TMG}/P_{\rm Ac}$. Eq. (9) applied to each appropriate data point leads to a set of F's and Q's, the latter obtained from the constraint OF = 1.5. These are listed in table 4. Once the average values of F and Q are determined the line Y may be constructed, fig. 3, which then serves as a consistency check on the method. We ascribe a better fit of the data to X than Y because the accuracy of mass 36 and 33 determinations are considerably better than that of mass 30 which requires cross corrections.

The procedure described above is valid provided that there are no unknown effects that invalidate the

F °) $Q^{(d)}$ P_{Tot}^{a)} [CH₃CD₃] ^{b)} [C₂D₆] ^{b)} [C2H6] b) Run PAC-do PTMG 1.70 0.50 20.0 33 13 36.5 0.72 2.08 1 2 1.0 1.0 20.0 33 3 102 0.75 2.00 1.99 40.3 23.5 _ c) 91 2.42 3 2.02 0.62 _ •) 108 0.98 40.4 2.63 4 1.09 23 0.57 _ e) 5 1.0 1.05 41.4 23.5 95 0.58 2.60 0.94 2.02 21.4 45 11.5 58.2 0.85 1.76 6 22.6 64 39 43.4 2.07 7 0.54 3.36 0.72 8 0.85 3.95 30.2 75 36.5 45.6 0.84 1.78 0.71 ± 0.1 ⁽¹⁾ 2.15 ± 0.4 f)

Isotopic ethanes from 193 nm photolysis of TMG-acetone- d_6 mixtures

^{a)} Represents total pressure with added He (all pressure units Torr). ^{b)} Arbitrary units.

^{c)} F is the fraction of total methyls that are free as calculated from eq. (9).

^{d)} Q is the quantum yield total methyl calculated from F with QF = 1.5 (see fig. 3).

*) Too small to be accurately measured. () Errors in each quantity represent the σ of set of eight runs.



Fig. 3. Plots of X(eq. (7)) and Y(eq. (8)) versus mixture composition. Line for Y calculated from average F and Q (table 4).

above model. We list several of these here.

(i) $CD_3 + TMG(h_9) \rightarrow CH_3 + TMG(h_6, d_3)$,

(ii) $CD_3 + TMG \rightarrow CH_3CD_3 + DMG$, $\Delta H = -102.5$ kJ/mol,

(iii) F (and 1-F) and Q are functions of pressure,

(iv) different production rates for CH_3 and CD_3 .

All of these require variation in the quantity QF with composition. Fig. 4 shows no evidence that this is the case and we thus treat all of the runs listed in table 4 as independent and average the F's and Q's accordingly.

While molecular ethane elimination has previously been postulated on energetic grounds the results shown in table 4 clearly demonstrate that this occurs.

Having considered quantum yields of methyl and ethane derived from the isotopic studies we now explore quantum yields pertinent to gallium containing species in table 5. In the model shown, two steps give molecular ethane, namely (b) and (d). While (b) implies TMG dissociation to DMG* plus CH₃ followed by DMG* \rightarrow C₂H₆+Ga, step (d) requires molecular ethane elimination from TMG. Step (b) is favored on the basis of the work of Beuermann and Stuke [5] who cite evidence favoring production of DMG followed by ethane elimination and gallium



Fig. 4. (A) Quenching plot of newly observed transient species by argon, log $[S_{Abs}(P) - S_{Abs}(P = \infty)]$ versus *P*, at 5.0 µs delay, $S_{Abs}(P)$ is absorption signal at 216.4 nm and pressure *P*. Quenching rate constant, $k_Q = 4.3 \times 10^{-14}$ cm³/molecule s. (B) Transient species signal decay at 220 nm with 48.7 Torr argon present. Quenching rate constant $k_Q = 4.2 \times 10^{-14}$ cm³/molecule s.

Table 5

Gallium, monomethyl gallium and dimethyl gallium quantum yields derived from the free CH₃ and molecular ethane quantum yields. Q=2.15 is the quantum yield of total methyl eliminated from TMG photolysis, F=0.71 is the fraction of total methyl which is free, QF is the quantum yield of free CH₃ eliminated from TMG photolysis, Q(1-F) is twice the quantum yield of molecular C₂H₆ formed from TMG photolysis

$Ga(CH_3)_3 \stackrel{a}{\rightarrow} CH_3 + Ga(CH_3)_2$ $Ga(CH_3)_3 \stackrel{b}{\rightarrow} C_2H_6 + CH_3 + Ga$	a+b+c=1 $a+b+2c=OF$	a=0.16 b=0.31	
$Ga(CH_3)_3 \stackrel{<}{\rightarrow} CH_3 + CH_3 + Ga(CH_3)$ $Ga(CH_3)_3 \stackrel{d}{\rightarrow} C_2H_6 + Ga(CH_3)$	$a+3b+2c=Q$ $d\approx 0^{a}$	$c = 0.53$ $d \approx 0$	

a) Based on other considerations (see text) this step is considered to be small.

formation. Also Baughcum and Oldenborg [3] note the participation of a long-lived intermediate responsible for gallium production. Such an intermediate is not likely to be MMG* as produced via step (d) where 137 kcal [10] must be partitioned between MMG and C_2H_6 . This excess energy is likely to lead to immediate fragmentation of MMG*. However, if TMG is photolysed to yield CH₃ and DMG only about 88 kcal [10] need be partitioned in the fragments. This can possibly lead to a long-lived electronically excited DMG*, and eventually to the products of step (b).

Previously we noted an electronic metastable absorption in the vicinity of both 216 and 220 nm. It has been postulated by a number of workers [2,3] that there is a long-lived electronically excited precursor to the production of gallium. It is clear from our direct spectroscopic observations that such an intermediate exists. Its identity, however, is a matter of speculation at this time. We suggest that it is DMG from arguments such as cited above. The quenching of the absorption system at 216 nm (attenuation of the absorption signal as a function of added argon) gives the same relaxation rate constant as that measured at 220 nm through the decay measured in real time. This suggests that the two absorption systems are to be ascribed to the same carrier. These results are shown in fig. 4.

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