ployed in the model are described in detail elsewhere.<sup>32</sup> Reaction 12 was included in the mechanism with a rate constant of either  $3.0 \times 10^{-12}$  or  $1.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The operator RO<sub>2</sub> in the LCC chemical mechanism represents both large and small peroxy radicals. The use of  $k_{12} = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ thus probably represents an upper limit on the importance of reaction 12. The impact of  $k_{12}$  on the predicted  $H_2O_2$  levels depends upon the initial concentration ratio of non-methane organic compounds (NMOC) to the sum of NO and NO<sub>2</sub> (NO<sub>2</sub>) used in the simulation). For NMOC/NO<sub>x</sub> ratios of 10-20 (typical of the rural Eastern US) increasing  $k_{12}$  over the range stated reduces the predicted  $H_2O_2$  formation by 25-30%. The increase in  $k_{12}$  had little effect on the predicted ozone concentrations (<2%), principally because the production of ozone requires the presence of significant quantities of NO<sub>x</sub> and under such circumstances  $RO_2 + HO_2$  reactions are unimportant. As illustrated above, and previously noted by Dodge,33 the predicted concentrations of H<sub>2</sub>O<sub>2</sub> are sensitive to the choice of  $k_{12}$ . At the present time, in the absence of experimental data concerning the reactions of a variety of structurally diverse peroxy radicals with HO<sub>2</sub>, it is unclear as to the best way in which to incorporate these reactions into computer models of atmospheric chemistry.

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Registry No. neo-C<sub>5</sub>H<sub>11</sub>O<sub>2</sub>, 27947-64-4; HO<sub>2</sub>, 3170-83-0; O<sub>2</sub>, 7782-44-7; neo-C<sub>5</sub>H<sub>11</sub>O<sub>2</sub>H, 999-80-4; neo-C<sub>5</sub>H<sub>12</sub>, 463-82-1; CH<sub>3</sub>OH, 67-56-1; Cl, 22537-15-1; Cl<sub>2</sub>, 7782-50-5; H<sub>2</sub>, 1333-74-0; t-C<sub>4</sub>H<sub>9</sub>CHO, 630-19-3.

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# Photochemistry of Group V Ethyl-Containing Systems: Enhancing H-Atom Production via 248-nm Ethyl Radical Photolysis

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We report on the photolysis of triethylarsenic, monoethylamine, and monoethylarsine with respect to H-atom formation. For all three molecules, 193-nm excitation followed by a 248-nm laser pulse produces an H-atom signal that is enhanced relative to the signal derived from the sum of the two lasers operating alone. The use of the selectively-deuterated compounds  $C_2D_5NH_2$  and  $C_2H_5ND_2$  clearly demonstrates that significant H-atom enhancement occurs via the ethyl group, at least in the case of monoethylamine. The importance of such photolysis reactions is discussed in terms of the laser-enhanced growth of III-V semiconductor materials.

## Introduction

An understanding of the fundamental photochemistry of group V ethyl-containing compounds is important, especially when such knowledge can be applied to photoassisted semiconductor growth. A perpetual problem associated with the use of organometallic compounds in III-V semiconductor growth environments is unwanted carbon incorporation.<sup>1-3</sup> For group V ethyl compounds,

the offending species is presumably the ethyl radical, due in part to its "sticky" nature. Ethyl radicals attached to a surface during film growth can dissociate, ultimately appearing as unwanted carbon impurities lodged within the bulk material. As a partial remedy for this problem, we submit that converting  $C_2H_5$  into  $C_2H_4$  and H is a desirable reaction that is beneficial in two ways. First of all, the closed-shell  $C_2H_4$  molecule should not be as "sticky"

as the ethyl radical. In addition, the H atom is thought to act as a good scavenger of  $C_2H_5$  radicals,<sup>4</sup> the net reactive result being a closed-shell  $C_2H_6$  molecule which should in turn leave a hot growth surface with greater ease than the  $C_2H_5$  radical can leave the surface.

Although  $AsH_3$  is still used extensively by the semiconductor community for the growth of III–V semiconductor materials, its extreme toxicity and the fact that it is a gas at room temperature and thus more difficult to contain than a condensed material make alternative sources of As atoms especially attractive. Because they are liquids, compounds such as tertiarybutylarsine (TBAs) triethylarsenic (TEAs), and monoethylarsine (MEAs) have emerged as replacement candidates.<sup>5–8</sup> However, the presence of the alkyl group can still create problems, for example, the introduction of unwanted carbon impurities into the bulk material as discussed above.<sup>7</sup> From a photochemical standpoint, one can ask whether or not the proper use of excimer laser radiation in these systems can help alleviate the carbon impurity problem by (1) generating atomic hydrogen and (2) converting ethyl radicals into ethylene and atomic hydrogen.

The possible importance of  $(C_2H_5)_3As$  and  $C_2H_5AsH_2$  as organometallic precursors for GaAs growth has recently been identified.<sup>7,8</sup> and in general, an understanding of the photoreactivity of compounds of the form  $(C_2H_5)_{\nu}XH_{3-\nu}$  (X = N, P, or As; y = 0, 1, 2, or 3) is desirable for improving laser-assisted methods applied to III-V semiconductor growth environments. With respect to H-atom formation, previous work in our laboratory on triethylarsenic<sup>9</sup> and monoethylarsine<sup>10</sup> has shown that 193-nm laser radiation can result in significant H-atom generation. In the current paper, we demonstrate that a second laser operating at 248 nm can enhance H-atom production for each of these two systems. In other words, H-atom production resulting from both lasers is greater than the sum of the two lasers operating alone. For the simplest ethyl-containing group V compound, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, we also show that 193-nm excitation followed by 248-nm excitation results in enhanced H-atom production. Furthermore, through the use of the selectively-deuterated compounds C<sub>2</sub>H<sub>5</sub>ND<sub>2</sub> and  $C_2D_5NH_2$ , we show unequivocally that significant H-atom (or D-atom) enhancement is derived via the ethyl group. Such observations suggest that the targeted transformation,  $C_2H_5 \rightarrow C_2H_4$ + H, is being achieved.

## **Experimental Section**

The experimental apparatus for these studies has been described previously.<sup>11,12</sup> The outputs from two excimer lasers (Questek 2720 and 2520, 193 and 248 nm) function as photolysis sources and pass antiparallel to the probe laser beam, an excimer-pumped dye laser (Lambda Physik LPX 105; 3002) operating at 364.7 nm. A small fraction ( $\sim 10^{-6}$ ) of the 364.7-nm probe radiation is frequency tripled in a Kr cell, creating a tunable vacuum-ultraviolet source operating at  $\sim$ 121.6 nm. All beams pass through the ionization region of a time-of-flight mass spectrometer (TOFMS). The 193- and 248-nm laser beams are made collinear by utilizing a dielectric optic (Newport) that reflects 193-nm light but transmits 248-nm radiation. The operating pressure for each of the compounds, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> (Aldrich, 99% purity), C<sub>2</sub>D<sub>5</sub>NH<sub>2</sub> (MSD, 98% D-atom enriched), C<sub>2</sub>H<sub>5</sub>ND<sub>2</sub> (MSD, 98% D-atom enriched), (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>As (Strem, 99+% purity), and C<sub>2</sub>H<sub>5</sub>AsH<sub>2</sub> (Morton, 99.999% purity), was kept constant at  $2 \times 10^{-4}$  Torr within the TOFMS during all studies. When all three laser beams are utilized, the following sequence is employed to generate and then monitor H atoms: fire 193-nm pulse, delay 60 ns, fire 248-nm pulse, delay 20 ns, fire probe pulse. Sequential absorption of 121.6and 364.7-nm photons produces H<sup>+</sup> ions from neutral H atoms,<sup>13</sup> the H<sup>+</sup> ions being detected within the TOFMS via standard extraction/drift techniques. H-atom Doppler profiles at 121.6 nm (Lyman- $\alpha$ ) are readily obtained, and D-atom profiles are detected analogously, except in this case the resonance lies 22 cm<sup>-1</sup> higher in energy.

Both the 193- and 248-nm photolysis beams are focused by a lens with a focal length of 250 mm, but a definitive determination of photolysis photon intensities is very difficult due to uncertainties



Figure 1. H-atom Doppler profiles resulting from  $(C_2H_5)_3As$  photolysis using three different excitation schemes: 193 nm alone, 248 nm alone, and 193 nm followed by 248 nm. It is clear that significant enhancement of the H-atom signal occurs when both lasers are used. Here,  $\nu_0$  is equal to Lyman- $\alpha$  (82 259 cm<sup>-1</sup>).

in the focal geometries and their spatial overlap within the ionization region of the TOFMS. We estimate that typical intensities are roughly on the order of tens of  $MW/cm^2$ .

#### **Results and Discussion**

Triethylarsenic. Previously, we have observed that the 193-nm photolysis of TEAs can produce a reasonable H-atom signal, but the laser power regime for maximizing the signal is rather narrow.<sup>9</sup> Here, too little photolysis power simply does not excite many TEAs molecules, but too much photolysis power accesses ion channels at the expense of the neutral H-atom formation channel(s). Figure 1 shows H-atom Doppler profiles at Lyman- $\alpha$  produced via TEAs photolysis using several different photolysis schemes. It is apparent that H-atom formation arising from a combination of 193- and 248-nm laser pulses is enhanced significantly if compared with H-atom generation resulting from the sum of the two photolysis lasers acting alone. Since the absorption cross sections for TEAs at 193 and 248 nm are considerable  $(1.76 \times 10^{-17} \text{ and } 1.2 \times 10^{-18})$ cm<sup>2</sup>, respectively),<sup>14</sup> it is not surprising that H-atom formation is observed in each individual case. However, the H-atom signal increases dramatically when a 248-nm pulse follows a 193-nm pulse, the net H-atom signal having been enhanced by a factor of 5 when compared with the H-atom signal resulting from the sum of the two lasers acting alone. Mechanistically, we suggest that the reaction

$$As(C_2H_5)_3 + h\nu (193 \text{ nm}) \rightarrow As(C_2H_5)_2 + C_2H_5$$
 (1)

is most likely the dominant initial step. Those  $C_2H_5$  radicals possessing sufficient internal energy  $(\geq 1.7 \text{ eV})^9$  can proceed to react and form  $C_2H_4$  and H. However,  $C_2H_5$  photofragments lacking sufficient internal energy have a reasonable chance of absorbing a photon when the 248-nm pulse occurs, since the absorption cross section for  $C_2H_5$  at 248 nm is  $\sim 2 \times 10^{-18} \text{ cm}^{2.15}$ Direct evidence for such a process using  $\text{Cl}C_2H_5$  as a precursor for the ethyl radical has already been demonstrated in our laboratory,<sup>12</sup> and we submit that, in the case of TEAs, the desired reaction ( $C_2H_5 \rightarrow C_2H_4 + H$ ) is being photolytically enhanced by the 248-nm laser pulse.

Although we assume that for TEAs photolysis the initial photochemical step is straightforward As-C bond cleavage, it must be noted that  $\beta$ -hydrogen elimination (i.e.,  $(C_2H_5)_3As \rightarrow (C_2-H_5)_2AsH + C_2H_4$ ) is a valid alternative step thought to occur pyrolytically.<sup>16</sup> As discussed, the H-atom enhancement observed at 248 nm is consistent with photolysis of an ethyl radical intermediate, but we have no evidence for invoking the  $\beta$ -elimination mechanism as an alternative route although it cannot be ruled out.

Monoethylamine. The simplest group V ethyl-containing compound is monoethylamine, and Figure 2 shows the results of



**Figure 2.** H-atom Doppler profiles resulting from  $C_2H_5NH_2$  photolysis using two different excitation schemes: 193 nm only and 193 nm followed by 248 nm. (When only 248-nm radiation was used, there was no discernible H-atom signal.) It is clear that significant enhancement of the H-atom signal occurs when both lasers are used. Here,  $\nu_0$  is equal to Lyman- $\alpha$  (82 259 cm<sup>-1</sup>).



Figure 3. D-atom Doppler profiles resulting from  $C_2D_5NH_2$  photolysis using two different excitation schemes: 193 nm only and 193 nm followed by 248 nm. (When only 248-nm radiation was used, there was no discernible D-atom signal.) It is clear that significant enhancement of the D-atom signal occurs when both lasers are used, suggesting that 248-nm excitation of the ethyl radical may play an important role. Here,  $\nu_0$  is equal to Lyman- $\alpha$  (82 281 cm<sup>-1</sup>).

photolysis studies on  $C_2H_5NH_2$ . In this case, photolysis using solely 248-nm radiation produced *no* discernible H-atom signal. In contrast and as observed previously,<sup>17</sup> 193-nm radiation produces a significant H-atom signal at this wavelength. Previous studies have also shown that the dominant pathway for H-atom formation using low power 193-nm excitation is via N-H (not C-H) bond cleavage.<sup>17</sup> For convenience, we distinguish between H atoms arising via N-H or C-H routes as  $H_N$  or  $H_C$ , respectively.

Inspection of Figure 2 clearly indicates that the H-atom signal generated by 193-nm radiation can be enhanced by combining 193- and 248-nm pulses. Moreover, through the use of selectively-deuterated monoethylamines, the chemical site(s) (be it  $H_N$ or  $H_{\rm C}$ ) that leads to increased H-atom production can be readily identified. In Figure 3, results using both 193- and 248-nm pulses on C<sub>2</sub>D<sub>5</sub>NH<sub>2</sub> demonstrate that the D-atom signal is increased by a factor of 2 over the sum of the two lasers acting alone. Note that the profiles in all figures have been normalized, the absolute intensity of the maximum D-atom signal in Figure 3 being 0.25 times that of the maximum H-atom signal in Figure 2. Nonetheless, Figure 3 shows that  $H_C$  production can be improved significantly by adding 248-nm radiation to the photolysis scheme even though this photolysis wavelength induces no discernible chemistry alone due to monoethylamine's vanishingly small absorption cross section at 248 nm.<sup>1</sup>

Mechanistically, it is very likely that a significant number of ethyl radicals and NH<sub>2</sub> fragments are generated by the 193-nm pulse, and as noted the ethyl radical possesses an appreciable absorption cross section ( $\sim 2 \times 10^{-18}$  cm<sup>2</sup>).<sup>15</sup> Consequently, a logical step in the overall process should be C<sub>2</sub>D<sub>5</sub> +  $h\nu$  (248 nm)  $\rightarrow$  C<sub>2</sub>D<sub>4</sub> + D. As previously mentioned, studies on haloethane molecules have indicated that this route is certainly viable.<sup>12,19</sup> In Figure 4, we show that the reaction ND<sub>2</sub> +  $h\nu$  (248 nm)  $\rightarrow$ ND + D does not appear to be important in the enhancement



Figure 4. D-atom Doppler profiles resulting from  $C_2H_3ND_2$  photolysis using two different excitation schemes: 193 nm only and 193 nm followed by 248 nm. (When only 248-nm radiation was used, there was no discernible D-atom signal.) It is clear that *no* significant enhancement of the D-atom signal occurs when both lasers are used, suggesting that 248-nm excitation of the ND<sub>2</sub> is not an important pathway under these experimental conditions. Here,  $\nu_0$  is equal to Lyman- $\alpha$  (82 281 cm<sup>-1</sup>).



**Figure 5.** H-atom Doppler profiles resulting from  $C_2H_5AsH_2$  photolysis using two different excitation schemes: 193 nm alone and 193 nm followed by 248 nm. (When only 248-nm radiation was used, there was no discernible H-atom signal.) It is clear that some enhancement of the H-atom signal occurs when both lasers are used. Here,  $\nu_0$  is equal to Lyman- $\alpha$  (82 259 cm<sup>-1</sup>).

process, at least under the experimental conditions studied.

Monoethylarsine. In contrast to TEAs, note that MEAs has direct H-atom formation channels available. Nonetheless, we expect that 193-nm excitation of C<sub>2</sub>H<sub>5</sub>AsH<sub>2</sub> would induce significant As-C dissociation in addition to As-H bond cleavage, since the As-C bond is significantly weaker than the As-H bond.<sup>10</sup> If As-C bond cleavage does occur, then ethyl radical formation is expected. Can 248-nm radiation enhance H-atom formation following MEAs photolysis in a fashion similar to the case of TEAs? The results of such an experiment can be found in Figure 5, where the experimental procedure was the same as in the case of TEAs photolysis as shown in Figure 1. The main difference for MEAs in Figure 5 is the fact that 248-nm radiation alone produced no discernible H-atom signal, most likely due to a low absorption cross section at this wavelength. However, the H-atom signal is enhanced albeit slightly when both 193- and 248-nm pulses are used as opposed to 193-nm radiation acting alone. The actual increase is by  $\sim 50\%$ . Is this enhancement occurring via an ethyl radical intermediate? If the answer is "yes", then the desired photochemistry is once again being achieved.

It must be emphasized that typical H-atom production from MEAs using 193-nm radiation is roughly an order of magnitude larger than that from TEAs under comparable experimental conditions. Consequently, normalized H-atom enhancement using 248-nm radiation is not nearly as dramatic in the case of MEAs. However, absolute H-atom production (193 nm + 248 nm) is still much larger for MEAs compared with TEAs, and the enhancement in the *absolute* number of H atoms produced is in fact comparable to that for TEAs shown in Figure 1.

In order to test for "site-specific" H-atom production in MEAs, selectively-deuterated MEAs compounds must be utilized. Unfortunately, compounds such as  $C_2H_5AsD_2$  or  $C_2D_5AsH_2$  are not yet readily available, so work is still underway toward finding a definitive understanding of H (or D) atom formation in these systems. We close by noting once again that understanding the photochemistry of group V ethyl-containing compounds may ultimately prove important in enhancing III-V semiconductor growth processes. In this area, monoethylarsine is a particularly attractive candidate, since only one ethyl group is present.

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## On the Loewenstein Rule and Mechanism of Zeolite Dealumination

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The reason for and the peculiarities of dealumination of aluminum-rich zeolites are explained on the basis of ab initio SCF MO calculations of the energies of local chemical interactions in the zeolite lattice. As distinct from Dempsey-Mikovsky-Marshall electrostatic approach (DMM), a conclusion is made that simultaneous extraction of the most closely situated



structural elements from the lattice takes place. The first step of this reaction is their mutual extracoordination according to the scheme



This step and the subsequent formation of large nuclei of hydroxoaluminum phases are regarded as a transformation of the lattice into a most energetically favorable state corresponding to the chemical composition  $nSiO_2 \cdot mAl_2O_3 \cdot kH_2O$ .

### Introduction

According to the Loewenstein rule,<sup>1</sup> the existence of >Al-O-Al< fragments in zeolite lattices is virtually excluded.<sup>29</sup>Si NMR data for faujasites<sup>2-4</sup> indicate a tendency for Al atoms toward even greater isolation from each other in the course of lattice growth: at a given Si/Al ratio, the distribution of Al atoms corresponds to a minimum number of



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fragments in the unit cell (Dempsey's rule). As shown<sup>4.5</sup> this peculiarity may be explained within the scope of the hypothesis that the mechanism of lattice growth should provide minimum energy for the local electrostatic repulsion between Al atoms (formally, between Al<sup>3+</sup> cations) in 4- and 6-membered rings. A mechanism of dealumination that follows logically from such a model is based on the assumption<sup>6-8</sup> that (i) extraction of one of the two most closely located Al atoms from the lattice is energetically preferential (on account of mutual repulsion between the Al atoms) and (ii) removal of one of these atoms stabilizes the state of the remaining atom of the pair in the lattice. In principle, this makes it possible to explain some important peculiarities of the dealumination processes, primarily, the experimental results of Beaumont and Barthomeuf.<sup>9</sup> According to their results, dealumination of faujasite-like zeolites starts with removal

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