CONDENSED PHASE PHOTOCHEMISTRY OF ACETIC ACID IN THE VACUUM UV

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Summary

The vacuum ultraviolet (VUV) photolysis of acetic acid (HAC) in Ar, N_2, CO and CO-doped argon matrices was performed at 10 K by systematically exciting into specific absorption bands with various VUV resonance line sources. The major overall processes which occur as a reuslt of photoexcitation are (1) $CH_3COOH + h\nu \rightarrow CH_4 + CO_2$, (2) and (3) $CH_3COOH + h\nu \rightarrow CH_3 + CO_2 + H$ and (4) $CH_3COOH + h\nu \rightarrow CH_3OH + CO$. All three of these overall processes occur to varying extents as a result of excitation into the four VUV bands of HAC. The results of experiments performed in CO and N_2 matrices suggest that reactions (2) and/or (3) dissociate from triplet states corresponding to $n' \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ (3s) transitions. Isotopic CD_3COOH experiments were performed and assisted in confirming previously proposed gas phase mechanisms.

Introduction

The recent application of cryogenic photochemistry in ascertaining the photochemical roles played by specific electronic states has proved very successful for carefully selected systems [1 - 5]. The aim is to add detail to kinetic mechanisms derived from the spectral observation of stable products and intermediates resulting from primary photochemical processes. The study of relative product yield as a function of exciting wavelength is particularly important in the determination of predominant processes, where competitive decomposition modes may occur from a common initially excited state.

Acetic acid (HAC) is one of a series of small organic molecules containing a $>C=O$ chromophore that we have selected for these photochemical studies. The electronic states of this species are somewhat further complicated by the influence of the hydroxyl group as compared with the states of formaldehyde [5] and cyclobutanone [4]. The vacuum ultraviolet (VUV) absorption spectrum (2500 - 1250 Å) has been reported by Barnes and Simpson [6]. Consequently, excitation of particular transitions with appropriate resonance line sources could be correlated with relative product yields.

The photolysis of HAC has been studied previously with ultraviolet (UV) sources by several investigators [7 - 11]. The first vapor phase photolysis was reported by Farkas and Wansborough-Jones [11] who proposed the primary process
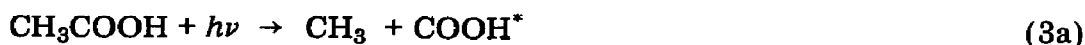
$$CH_3COOH + h\nu \rightarrow CH_4 + CO_2 \tag{1}$$

Burton [9, 10] proposed the additional primary process

$$CH_3COOH + h\nu \rightarrow CH_3COO^* + H \tag{2a}$$
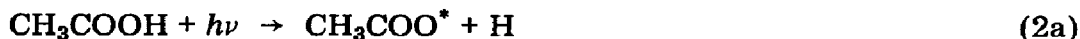
Ausloos and Steacie [7] suggested the subsequent dissociation

$$CH_3COO^* \rightarrow CH_3 + CO_2 \tag{2b}$$

as well as the following process

$$CH_3COOH + h\nu \rightarrow CH_3 + COOH^* \tag{3a}$$

first proposed by Clusius and Schanzer [8], and subsequently

$$COOH^* \rightarrow CO_2 + H \tag{3b}$$

$$CH_3COOH + h\nu \rightarrow CH_3CO^* + OH \tag{4a}$$

$$CH_3CO^* \rightarrow CH_3 + CO \tag{4b}$$

More recently, the Hg photosensitized decomposition of HAC was studied by Kebarle and Lossing [12] by leaking the reaction mixture into a mass spectrometer for direct *in situ* analysis. The results indicated the identification of CH_3 and strong indirect proof for the primary formation of CH_3COO, $COOH$ and CH_3CO via reactions (2a), (3a) and (4a) respectively. Therefore, the matrix-isolated VUV photolysis of HAC should be an ideal means of producing these species at low temperatures for spectroscopic investigation, provided that the excited radicals do not undergo further fragmentation. In this paper we present the first study of the photolysis of HAC in the VUV.

Experimental

Glacial acetic acid (Mallinckrodt, 99.7%) was used without further purification. No impurities other than water were observed in the matrix-isolated infrared spectrum of HAC. Partially deuterated acetic acid (CD_3COOH) was prepared from CD_3COOD (Aldrich, 99.5%) by exchange with water and subsequent drying over copper sulfate. The matrix gases, argon (Matheson, 99.995%), nitrogen (Liquid Air Inc., 99.99%) and carbon monoxide (Scientific Gas Products, ultrapure), were also used without further purification. A typical M/A ratio of matrix to active material was 1500:1 or greater in order to minimize formation of the acetic acid dimer.

The matrix-isolated samples of HAC were deposited onto a CsI window at 10 K, which was cooled by an Air Products closed-cycle helium Displex

refrigerator. Samples were deposited from a glass manifold of approximately 2.5 l volume through a Granville–Phillips leak valve at a rate of 2.5 mmol h^{-1} over a period of 3 - 5 h with simultaneous photolysis.

The photolysis of matrix-isolated acetic acid was accomplished by subjecting samples on the cold CsI window to direct irradiation through LiF (approximately 1050 Å cut-off), CaF_2 (approximately 1250 Å cut-off) or Suprasil II (approximately 1650 Å cut-off) windows. The appropriate combination of VUV window (used as a filter) and resonance lamp provided the means for selective excitation into the desired absorption band. The characteristics of these sources have been discussed previously [13]. As an example of the notation used in this manuscript for the combination of a given lamp and window, the combination of a Br_2 resonance lamp and a CaF_2 window is Br_2/CaF_2. The resonance line sources used in this study were N (1743 - 1745 and 1493 - 1495 Å), Br (1634, 1582 and 1577 Å), O (1302 - 1306 Å) and H (1215 Å). The use of these lamps in this type of experiment has been discussed previously [1].

The identification of the photochemically produced species was obtained from the infrared spectra after photolysis with a Perkin–Elmer 180 IR spectrophotometer. The resolution in these experiments was estimated to be 3 cm^{-1} between 4000 and 3000 cm^{-1} and 1 cm^{-1} between 3000 and 500 cm^{-1}. Below 500 cm^{-1} the resolution decreased to approximately 4 cm^{-1}. The appropriate infrared absorptions were examined under higher resolution (approximately 1 cm^{-1}) after identification and were converted to absorbance. The areas under these peaks were integrated by the triangular approximation and were ratioed to that of methane (see Results) to obtain the relative yields listed in Table 3.

Results

The VUV spectrum of HAC in the gas phase has been studied by Barnes and Simpson [6]. The spectrum consists of a very weak absorption centered at about 2150 Å, two broad intense bands centered at about 1724 and about 1587 Å and an intense structured band at about 1500 Å. An additional intense band centered at about 1350 Å and extending to about 1250 Å was also observed. The assignments of these bands are shown in Table 1. Most of the spectrum is diffuse with overlapping bands having little fine structure to assist in the detailed interpretation. The tentative assignments shown in Table 1 were in general made on the basis of transition energies, band structure and intensity, but principally by comparison with known band assignments of a large group of similar molecules [6]. The VUV photolysis of HAC in Ar and N_2 matrices was performed by systematically matching appropriate resonance line sources to known VUV absorption bands listed in Table 1.

Initial experiments to effect photochemical conversion of HAC by excitation into the weakly absorbing n → π^* transition with a medium pressure mercury lamp and a selenium resonance lamp were not very successful. The

TABLE 1

Transition assignments in the VUV spectrum of HAC

Transition (Å)	$\sim \lambda_m$ (Å)	Assignment
2000 - 2500	2150	$n \rightarrow \pi^*$
1900 - 1667	1724	$n' \rightarrow \pi^*$
1667 - 1538	1587	$n \rightarrow \sigma^*$
1538 - 1389	1500	$\pi \rightarrow \pi^*$
1389 - 1250	1350	$n \rightarrow \sigma^*$
		$n \rightarrow R^*$

conversions obtained after prolonged photolysis were insufficient to obtain meaningful optical density measurements.

The infrared spectrum of matrix-isolated HAC (Ar, 1500) is shown in the solid curve in Fig. 1. Studies of matrix-isolated HAC and of (HAC)$_2$ in Ar and N$_2$ indicated that M/A ratios of 1000 or greater were necessary to prevent significant dimerization of HAC in these experiments [14 - 16]. Nevertheless,
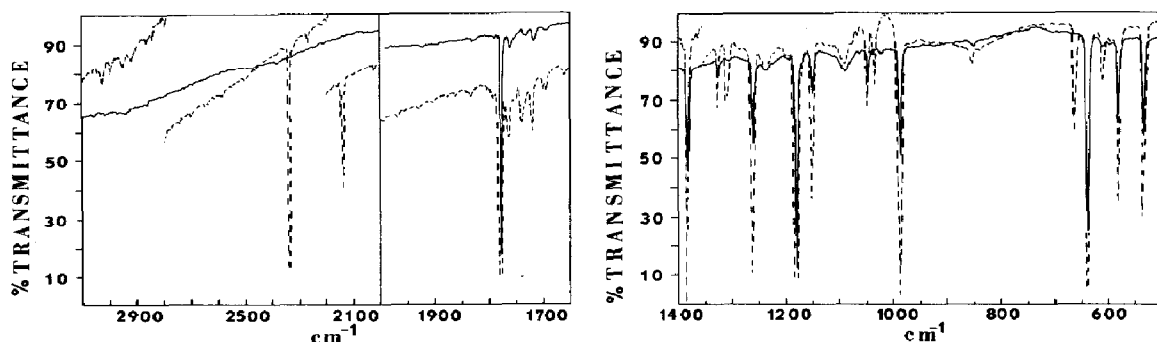

Fig. 1. Acetic acid (Ar, 1500) at 12 K: — 1.0 μM acetic acid deposited at 0.03 μM min^{-1}; ---- 3 μM additional acetic acid deposited at 0.02 μM min^{-1} with simultaneous N$_2$/S II irradiation.

in our experiments with M/A ratios of about 1500 very weak absorptions due to the (HAC)$_2$ were observed, indicating the presence of an acceptably low concentration of the dimer. The dotted curve in Fig. 1 is the spectrum recorded after simultaneous photolysis (N$_2$/S II) and deposition for 5 h of an additional 3.0 μM of HAC. This lamp and window combination provides excitation into the $n' \rightarrow \pi^*$ band (1900 - 1667 Å), with the 1743 - 45 Å resonance lines. On the basis of previous photolytic work, we may immediately assign new absorptions appearing at 2347 and 665 cm^{-1} to CO$_2$, 2140 cm^{-1} to CO, and 3022 and 1305 cm^{-1} to CH$_4$. An absorption at 1033 cm^{-1} appearing after photolysis is assigned to methanol. This assignment was further confirmed by recording the infrared spectrum of matrix-isolated methanol. A new absorption at 611 cm^{-1} is assigned to the methyl radical, on the basis of work performed in this laboratory and the work of Milligan and

Jacox [17]. In experiments where the concentration of CO was high and significant H atom production occurred, absorptions detected at 2488, 1861 and 1087 cm^{-1} were assigned to the formyl radical HCO [18]. These results are summarized in Table 2.

TABLE 2

Summary of the absorptions appearing in the acetic acid (Ar, 1500) experiments

Before photolysis (cm^{-1})	After photolysis (cm^{-1})	Assignment
3566		HAC
	3022	CH$_4$
	2488	HCO
	2347	CO$_2$
	2140	CO
	2095[a]	CH$_2$N$_2$
	1861	HCO
1779		HAC
1750 - 1700		HAC dimer
1439		HAC
1434		HAC
1380		HAC
	1305	CH$_4$
1259		HAC
1181		HAC
1152		HAC
	1087	HCO
1044		HAC
	1033	CH$_3$OH
987		HAC
	737[b]	C$_2$H$_2$
	665	CO$_2$
642		HAC
	611	CH$_3$
581		HAC
534		HAC

[a] Observed after irradiations in N$_2$ matrices (see text).
[b] Observed after O$_2$/CaF$_2$ and H$_2$/LiF irradiations (see text).

Since the relative optical densities of the products is used as a measure of the relative importance of the various processes as a function of exciting sources, the possible occurrence of secondary photolysis is extremely important. Major products which might undergo secondary photolysis are CO$_2$, CH$_4$ and CH$_3$OH. Therefore, each of these species was separately investigated to determine their efficiency of conversion in the VUV.

In a series of experiments films of Ar:CO$_2$ = 1000:1 were subjected to radiation from N$_2$/CaF$_2$, Br$_2$/CaF$_2$ and H$_2$/LiF sources. Significant concentrations of CO were formed with photolysis from each lamp, with H$_2$/LiF and

Br$_2$/CaF$_2$ yielding the greatest conversion of CO$_2$ to CO. The concentration of CO formed was sufficient to interfere with any interpretation of HAC photolysis yields based on CO$_2$/CO ratios.

Matrix-isolated methane photolysis has been investigated by Milligan and Jacox [17] with H and Kr VUV resonance line sources. The length of photolysis time, the initial concentration of parent absorptions and the intensity of product absorptions (CH$_3$, C$_2$H$_2$) reported suggest that methane photodecomposition is rather inefficient. This observation has been further confirmed by methane photolysis experiments performed in this laboratory. Therefore we exclude the possibility of significant methane photodecomposition as a secondary photolysis process.

The photolysis of matrix-isolated methanol in the VUV was also investigated by Milligan and Jacox [19]. Using the 1470 Å resonance line of Xe, they found the principal products of photodecomposition to be formaldehyde, the formyl radical and a species tentatively identified as CH$_2$OH. The strongest absorption reported for CH$_2$OH, 1183 cm^{-1} in an N$_2$ matrix, occurs very near an intense absorption of HAC, making its identification doubtful in our experiments. No formaldehyde was observed in any of the photolysis experiments of HAC, and the intensity of the HCO absorptions correlated with the amount of CO present and H atoms produced from HAC photodecomposition. Finally, VUV photolysis experiments of matrix-isolated CH$_3$OH in our laboratory confirmed the inefficient conversion of methanol, except in cases of low M/A ratios.

The possible photodecomposition of CH$_3$ in the VUV is unknown, although an absorption near 1500 Å was reported by Milligan and Jacox [17] in matrices containing this species. Since we know of no further evidence to the contrary, we shall assume that CH$_3$ is not extensively photolyzed by secondary photolysis in these experiments. Other very weak absorptions assigned to acetylene and diazomethane provide a measure of the possible importance of the HAC methyl group photofragmentation. Therefore, the species whose absorptions appear to be best suited for the analysis of HAC photodecomposition characterizing reactions (1), (2) and/or (3) and (4) respectively are CH$_4$, CH$_3$ and CH$_3$OH.

The relative extent to which each of the products, corresponding to reactions (1) through (4), occurs at the various exciting wavelengths in Ar and N$_2$ matrices is summarized in Table 3. Since CH$_4$ had the most intense absorption (1304 cm^{-1}) in all of the photolysis experiments, the optical densities of CH$_3$ (611 cm^{-1}) and CH$_3$OH (1033 cm^{-1}) are normalized relative to CH$_4$. It is to be emphasized that these tabulated results represent qualitive comparisons which are representative of the average spectrum in each case. Although each of these cases will be discussed in the following section, photochemical decomposition of HAC producing CH$_4$, CH$_3$ and CH$_3$OH occurred with all of the VUV photolysis sources. The relative conversion efficiencies in Ar and N$_2$ do not appear to have a clearly discernible pattern. The most striking features of Table 3 are the significantly decreased optical densities of CH$_3$ produced in N$_2$ matrices with the N$_2$/SII and N$_2$/CaF$_2$ sources.

TABLE 3

Optical densities of CH_4, CH_3 and CH_3OH as a function of exciting sources, normalized to CH_4

Exciting source	Matrix	CH_4	CH_3	CH_3OH
N_2/SII	Ar	1.00	0.52	0.71
	N_2	1.00	0.13	0.81
Br_2/CaF_2	Ar	1.00	0.71	0.94
	N_2	1.00	0.44	0.72
N_2/CaF_2	Ar	1.00	0.33	0.51
	N_2	1.00	0.14	0.60
O_2/CaF_2	Ar	1.00	0.47	0.20
	N_2	1.00	0.55	0.30
H_2/LiF	Ar	1.00	0.60	0.63
	N_2	1.00	0.57	0.68

It is interesting to note (and not indicated by Table 3) that the percentage of photolysis conversion was a function of the exciting wavelength. The yields with the N_2/SII source relative to parent absorptions were consistently lower than with any other lamp and window combination. The highest relative conversion was realized, not with the highest energy source H_2/LiF, not with the most intense lamps H and N, but with the O resonance source. This observation is not totally surprising since this band not only involves the greatest extinction coefficient, but also appears in the VUV spectrum to be continuous over most of the band. Such spectra are not unusual for overlapping $n \rightarrow \pi^*$ and $n \rightarrow R$ transitions.

Photolysis of HAC in CO and in CO-doped Ar matrices was also performed. In addition to the expected parent frequency shifts in CO matrices, the identification of CH_4 as a product was complicated by a strongly absorbing and overlapping HAC absorption at 1304 cm^{-1}. Thus, with the low energy sources N_2/SII and N_2/CaF_2, where little or no conversion via $CO + h\nu \rightarrow C + O$ and $O + CO \rightarrow CO_2$ occurs, the production of CO_2 serves as a qualitative measure of reaction (1). This assumption is further predicated on the observations of these experiments that very weak absorptions due to CH_3 are observed. Thus, we assume quenching of (2) and/or (3), with a corresponding quenching of CO_2 production. The conclusion, as in previous studies of this nature, is that the CO matrix effectively quenches (2) and/or (3), as observed in N_2 also. Further confirmation is provided by the extremely weak HCO absorptions as compared with the CO-doped Ar experiments where they (HCO) are significantly more intense.

In anticipation of stabilizing uncharacterized radical species, matrix photolysis of CD_3COOH was performed. In addition to the non-isotopically

shifted products CO and CO_2, absorptions due to the various deuterated stable products were also identified, such as CD_3OH, CD_3H and an absorption at 471 cm^{-1}, tentatively assigned to some deuterated form of the methyl radical. However, the most important result from the photolysis of CD_3COOH was the sole formation of HCO in CO-rich experiments and no corresponding absorptions due to DCO. The implication with respect to the photofragmentation mechanism is the confirmation that the hydroxyl hydrogen is the one dissociated from the parent molecule.

Discussion

Systematic excitation of HAC across the VUV with various resonance line sources results in four major processes according to reactions (1) - (4) discussed above. Since these processes are conducted in condensed media, entrapment in the matrix cage allows the subsequent reaction of photochemically produced radicals. Thus, CH_3 and OH in the same site can react to produce methanol

$$CH_3 + OH \rightarrow CH_3OH \tag{4c}$$

in the same site where a CO molecule is present. Since CO is produced as a product of the overall reaction (4) as well as by the secondary photolysis of CO_2 with the resonance sources with wavelengths less than about 1500 Å, an additional reaction which occurs to a varying extent is

$$H + CO \rightarrow HCO \tag{5}$$

One of the primary aims of this study was to stabilize one or more of the radical species previously proposed in the introduction to this paper. We were unsuccessful in these attempts, apparently because the electronically excited radical fragments readily decomposed upon formation. However, identification of the major products in these photolyses strongly implies the decomposition modes of reactions (1) - (4). The primary formation of CH_4 and CO_2 (reaction (1)) are confirmed by spectral observation. The occurrence of the net process

$$CH_3COOH + h\nu \rightarrow CH_3 + CO_2 + H \tag{2 and 3}$$

is confirmed by the stabilization and identification of CH_3, CO_2 and subsequent H atom reactions with CO. We were not, however, able to distinguish between the two routes involving either CH_3COO or $COOH$. The net decomposition process

$$CH_3COOH + h\nu \rightarrow CH_3OH + CO \tag{4}$$

suggests an unstable surface involving $CH_3CO^* + OH$, unless of course the net products of reaction (4) are formed directly from CH_3COOH, which would appear to be unlikely.

Since we were able to excite selectively into the specific bands listed in Table 1 with a variety of VUV line sources, it is interesting to note the relative

product yields as a function of exciting frequency. The very weak n → π^* absorption was excited in a series of experiments by a medium pressure mercury lamp and a selenium resonance lamp (2060 Å). The photochemical conversion in these cases was at best minimal under prolonged exposure (about 5 h) of Ar/HAC films to these sources. The major products which appeared to be formed are consistent with the previously cited gas phase studies: CH_4, CH_3 and CH_3OH. The paucity of photochemical conversion in this case is probably due to the extremely low extinction coefficient, which is a factor of about 100 smaller than the other bands in the VUV spectrum.

Exclusive excitation into the n′ → π^* band with the N_2/S II (1742 - 45 Å) combination gives rise to the major products corresponding to the overall reactions (1), (2) and/or (3) and (4). Since CO_2 can be photochemically converted to CO by secondary photolysis, neither of these products could confidently be used in ascertaining relative product yields. Furthermore, since we were not successful in stabilizing CH_3COO or COOH for spectroscopic investigation, we are unable to distinguish between (2) and (3). If we make the reasonable assumption that reaction (4) results in the quantitative production of CH_3OH and CO, regardless of the mechanism, then the CH_3 concentration may be used as a measure of reactions (2) and/or (3). Thus, the product absorptions used as a relative measure of the competitive processes (1), (2) and/or (3) and (4) are CH_4 (3022 and 1305 cm^{-1}), CH_3 (611 cm^{-1}) and CH_3OH (1033 cm^{-1}) respectively. In a N_2 matrix reactions (2) and/or (3) are significantly reduced as compared with an Ar matrix. The same effect is observed in a CO matrix, although the interpretation is somewhat more complicated since an HAC absorption shifts to 1304 cm^{-1} and overlaps the strong CH_4 absorption. A qualitative measure of the occurrence of (1) is, however, ascertained by the relative intensity of CO_2 (2347 cm^{-1}) and the weak 3022 cm^{-1} absorption of CH_4. We have previously observed this quenching effect in the study of other species [1, 2, 4, 5], and attribute the quenching of reactions (2) and/or (3) to triplet (guest)–triplet (host) energy transfer. Both CO and N_2 have low lying triplet states with wavelengths greater than about 1550 and about 1400 Å respectively, which presumably quench the triplet state of the guest molecule and in essence quench the reaction(s) occurring from this state. A qualitative measure of the relative conversions of reactions (1), (2) and/or (3) and (4) is shown in Table 3 based on the optical densities of representative products.

Exclusive excitation into the n → σ^* (3s) band is accomplished by the three major lines (1634, 1582 and 1577 Å) of the Br resonance lamp. The relative efficiencies of the major processes are similar to the n′ → π^* band, with the exception of a slight relative increase in processes (2) and/or (3) and (4). Although the CH_3 production is also reduced in the N_2 matrix, it is difficult to make a strong case for triplet state quenching, in spite of the fact that the wavelength of the excitation source is still above the first N_2 singlet onset at about 1400 Å. A similar relative reduction in the CH_3 optical density was observed in the experiments involving a CO matrix.

Excitation into the structured π → π^* band is accomplished by the N_2/CaF$_2$ source, which allows transmission of the 1473 - 95 Å lines of N.

These lines have approximately 60% of the intensity of the 1743 - 45 Å lines. Therefore, any photochemistry occurring from this band would have to be obtained as the difference between the overall conversion and that obtained from the $N_2/S II$ source. Without taking the relative ratios of the optical densities between the two types of experiments to be too quantitatively meaningful, we can again observe the quenching of CH_3 production, at least from the $n' \rightarrow \pi^*$ absorption. As a result of the uncertainties involved in the optical densities, we are really unable to make definitive statements about the photochemistry resulting from the $\pi \rightarrow \pi^*$ excitation alone.

Excitation into the center of the overlapping $n \rightarrow \sigma^*$ and $n \rightarrow R$ transitions by the O resonance lines (1302 - 1306 Å) resulted in the most efficient conversion of HAC to products according to reactions (1) - (4). As shown by Table 3, the relative production of CH_3 (reactions (2) and/or (3)) increased measurably as compared with CH_3OH (reaction (4)). There was also a corresponding significant increase in the production of HCO as a result of the increased H production and subsequent reaction with CO produced from reaction (4).

Excitation of matrix-isolated HAC with the 1215 Å resonance line of H atoms resulted in very efficient parent to product conversion. The relative ratios of reactions (1) - (4) are indicated by the optical densities in Table 3. It is interesting to note that the VUV spectrum reported by Barnes and Simpson [6] did not include spectral absorptions beyond 1250 Å. Nevertheless, the 1215 Å radiation is undoubtedly absorbed by Rydberg transitions.

The experiments involving the matrix photolysis of CD_3COOH resulting in relatively intense HCO absorptions and no observable DCO counterparts is important in establishing the fact that the hydroxyl hydrogen is the primary (if not the total) source of H atoms in the primary photodecomposition of HAC. This indirect observation provides further support for reactions (2a) and/or (3b).

Conclusion

Excitation of HAC into the four major VUV absorption bands with various VUV resonance line sources results in photodecomposition according to the three overall processes discussed in this paper: processes (1), (2) and/or (3) and (4). Previously proposed primary gas phase photodecomposition processes are confirmed to occur also in the VUV photolysis of HAC. As in previous studies [1, 2, 4, 5] reactions (2a) and/or (3a) appear to occur from triplet states corresponding to the $n' \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ (3s) transitions.

Acknowledgment

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