Intermediates Produced in the Flash Photolysis of Acetone and Amides in Aqueous Solution

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The flash photolysis of air-free aqueous acetone solutions was shown to produce $\dot{C}H_2COCH_3$ and $(CH_3)_2\dot{C}OH$ radicals. The acetonyl $\dot{C}H_2COCH_3$ radical has an absorption maximum at 295 nm and an extinction coefficient $\epsilon_{295} = 800 \pm 150 \ M^{-1} \ cm^{-1}$. No intermediates could be observed in the flash photolysis of air-free aqueous amide solutions. In presence of acetone, photosensitized decomposition of amides has been observed. Formamide (F), N,N-dimethylformamide (DMF), acetamide (A), N-methylacetamide (NMA), and N,Ndimethylacetamide (DMA) have been examined, and the transient species produced in the presence of acetone have been observed. These species are produced by H-atom abstraction by triplet excited acetone. With the N-methylated amides, abstraction takes place mainly from the N-methyl group producing HCONCH₂(CH₃), CH₃CONHCH₂, and CH₃CONCH₂(CH₃) radicals. With F and A, the main radicals are $\dot{C}ONH_2$ and $\dot{C}H_2CO-$ NH₂. It is interesting to note that the site of H-atom abstraction by triplet acetone is the same as that recently found for abstraction by OH radicals. This correlation is further discussed.

Introduction

Comprehensive spectroscopic studies of the optical absorption spectra of simple aliphatic amides in solution have recently been carried out.^{1,2} The effect of substitution on the intensity of the strong (molar extinction coefficient $\sim 8000 M^{-1} \sec^{-1}$, oscillator strength ~ 0.25) π, π^* transition of the amide band at ~ 190 nm, and the location of the n, π^* transition, were determined.¹ The photochemistry which these molecules undergo, however, is far from understood.⁸ Early work⁴ on the photochemistry of acetamide in aqueous solution indicated the formation of ammonia and acetic acid at temperatures higher than 60°; at room temperature, these products were not observed. The photolysis of aliphatic amides in organic solvents was suggested⁵ to occur by a molecular mechanism, not involving free radicals. In the gas phase,⁶ acetamide produced CH_4 , C_2H_6 , CO, and NH_3 .

To observe the primary intermediates produced on direct optical excitation of amides in aqueous solution, the flash photolysis and kinetic absorption spectrophotometry technique was used. On flash photolysis at $\lambda < 200$ nm of oxygen-free 10⁻⁴ to 1.0 *M* aqueous solutions of acetamide, dimethylformamide, dimethylacetamide, and formamide at pH ~5.0-6.0, no transient species could be observed in the wavelength region 250-700 nm, time resolution ~20 µsec. No intermediates were observed on flash photolysis of oxygenfree neat dimethylformamide or dimethylacetamide. In pulse radiolysis studies⁷ of the same amides in aqueous solution, a number of radicals were observed and characterized as due to the rupture of C-H and N-H bonds.

Amides and amino acids are known⁸ to decompose on exposure to sunlight in the presence of photosensitizers (TiO₂ and ZnO). In an attempt to pursue the reactions which simple amides undergo, the intermediates produced in the photosensitized decomposition of amides were examined. Acetone was chosen as the sensitizer since it had previously been used⁹ to produce esr spectra of amide radicals in solution.

Numerous investigations have been carried out on the photochemistry of acetone in the gas phase, but only a few in aqueous 10-12 or nonaqueous (see ref 3, 13-15, and references cited therein) solutions. This paper presents the results obtained on flash photolysis of acetone in aqueous solution, as well as the intermediates produced in the acetone-photosensitized decomposition

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of formamide (F), N,N-dimethylformamide (DMF), actamide (A), N-methylacetamide (NMA), and N,N-dimethylacetamide (DMA).

Experimental Section

The flash photolysis apparatus used has already been described.¹⁶ In the aqueous acetone-amide solutions, to prevent photolysis by light below ~ 200 nm, the chamber of the apparatus was not pumped down. Flashes of energies of about 2000-3000 J were normally used.

Water which was purified by triple distillation followed by radiolysis and photolysis was employed. Solutions were thoroughly deoxygenated by bubbling prepurified nitrogen, and the concentration of acetone in the solution was determined spectrophotometrically after the bubbling. Acetone, DMF, and DMA were Eastman Spectrograde solvents, acetamide was Mallinckrodt reagent grade, and formamide was purified⁷ by multiple distillation.

Pulse radiolysis work was carried out using a Febetron 705 (Field Emission Corp.) machine, and the details are described elsewhere.¹⁷ Quartz cells of 2-cm optical path were used.

Results

To interpret the results obtained in the acetonephotosensitized decomposition of amides, it was necessary to study first the intermediates produced in the flash photolysis of acetone in aqueous solution.

Figure 1a shows the transient absorption spectrum observed on flash photolysis of $\sim 30 \text{ m}M$ acetone in water at pH ~ 5.5 . Due to the absorption by acetone itself (quartz cells of 20-cm optical path were used) it was not possible to detect transient absorptions below $\sim 310 \text{ nm}$. The decay kinetics of the transient absorption showed the presence of two intermediates, decaying at somewhat different rates. On addition of an excess concentration of an efficient hydrogen donor, isopropyl alcohol, an increased absorption is found (Figure 1b) the transient decays faster, and clean second-order kinetics, apparently due to only one species, are observed.

Since one of the intermediates expected to be formed in the photolysis of acetone is the acetonyl radical, \cdot CH₂COCH₃, this species was produced independently, by pulse radiolysis of aqueous solutions of acetone. From known¹⁸ rate constants for OH, e_{aq}^{-} , and H radicals with acetone, under the conditions of the experiments and dose rate used (Figure 2) only \cdot CH₂COCH₃ radicals are considered to be formed by the reaction

$$OH + CH_3COCH_3 \longrightarrow \dot{C}H_2COCH_3 + H_2O$$

A transient with an absorption maximum at ~ 295 nm is observed, Figure 2, with an extinction coefficient $\epsilon_{295} = 800 \pm 150 \ M^{-1} \ \mathrm{cm}^{-1}$. The decay kinetics of the acetonyl radical were neither first nor second



(a)

0.10

Figure 1. Flash photolysis of air-free aqueous solutions of 30 mM acetone (top curve) and 30 mM acetone in presence of 3 M isopropyl alcohol (bottom curve) at pH 5.5. Square symbols represent spectrum of $\dot{C}H_2COCH_3$ and of ($\dot{C}H_2COCH_3$ + (CH_3)₂ $\dot{C}OH$) radicals, respectively.



Figure 2. Absorption spectrum of $\dot{C}H_2COCH_3$ (\odot) (obtained from the pulse radiolysis of $2 \times 10^{-2} M$ acetone, 0.2 MHClO₄) and CH₃ \dot{C} (OH)CH₃ radicals (\Box) (from pulse radiolysis of 0.1 M isopropyl alcohol, pH 6.0, 1 atm N₂O). Data (\Box) reproduced from ref 17a.

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System	λ _{max} , nm	$2k/\epsilon^a$	e, M ⁻¹ cm ^{-1b}	$2k, M^{-1} s_{2}c^{-1}$	Suggested radical
20 mM CH ₃ COCH ₃ + 3.2 M HCONH ₂	320	$5.1 imes 10^6 \ (3.7 imes 10^6)$	350	$1.9 imes 10^9$	ĊONH₂
$\begin{array}{c} 30 \text{ m}M \text{ CH}_8\text{COCH}_8 + \\ 1.0 M \text{ HCON}(\text{CH}_8)_2 \end{array}$	380	$2.0 imes 10^6~(1.4 imes 10^6)$	1600	$3.2 imes10^9$	HCONHĊH2
$\begin{array}{r} 20 \text{ m}M \text{ CH}_{\$}\text{COCH}_{\$} + \\ 5.0 M \text{ CH}_{\$}\text{CONH}_{2} \end{array}$	400	$3.0 imes10^{ extsf{6}}$ ($2.0 imes10^{ extsf{6}}$)	1050	$3.1 imes10^{9}$	ĊH2CONH2
10 mM CH ₃ COCH ₃ + $0.2 M$ CH ₃ CONHCH ₃	340	$9.0 imes10^{s}$ (7.0 $ imes10^{s}$)	2000	$1.8 imes10^{9}$	CH₂CONHĊH₂
$\begin{array}{c} 30 \text{ m}M \text{ CH}_{\$}\text{COCH}_{\$} + \\ 0.5 M \text{ CH}_{\$}\text{CON}(\text{CH}_{\$})_{2} \end{array}$	350	$7.5 imes 10^5 \ (8.0 imes 10^5)$	2000	$1.5 imes10^{9}$	CH₃CONĊH₂(CH₃)

 Table I: Intermediates Observed in the Acetone-Sensitized Photochemical

 Decomposition of Amides in Aqueous Solution, at pH 5.5

^a Figures given in brackets are the corresponding values for the same radicals produced from the reaction of OH radicals with amides by pulse radiolysis (ref 7). ^b Taken from ref 7.



Figure 3. Flash photolysis of oxygen-free aqueous solutions of 30 mM acetone, pH \sim 5.5, in presence of (a) 1.0 M DMF, OD read at 160 μ sec, and (b) 0.5 M DMA, OD read at 200 μ sec. Symbols (\square) represent the equimolar concentration of CH₃C(OH)CH₂ radicals produced under stated conditions. Dotted line represent absorption spectra of HCON(CH₂)(CH₃) and CH₃CON(CH₂)(CH₃) radicals reproduced from ref 7.

order. At high $[\cdot CH_2COCH_3]$ it approached secondorder decay, indicating presumably competition between dimerization and unimolecular decomposition to produce ketene ($CH_2=C=0$) and $CH_3 \cdot$ radicals. For comparison, the absorption spectrum of the (CH_3)₂C-(OH) radical, previously obtained,^{17a} is shown in Figure 2. On addition of amides to aqueous solutions containing acetone, new transient absorptions are observed, and different decay kinetics are obtained. Figure 3 shows the transient spectra produced on flash photolysis of air-free 30 mM acetone in presence of 1.0 M dimethylformamide and 0.5 M dimethylacetamide.

On flash photolysis of air-free aqueous solutions of 20 mM acetone in presence of 3.2 M F, 5.0 M A, and 3.0 M NMA weaker transient absorptions were observed, with maximum at \sim 320, 400, and 340 nm, respectively. All these intermediates decayed by second-order kinetics, and the values are given in Table I. From the decay kinetics, it is possible that $R_1 + R_1$ and $R_1 + R_2$ radical-radical reactions are occurring.

The flash photolysis of neat DMF in presence of $\sim 30 \text{ m}M$ acetone produced the same radicals as found in aqueous DMF-acetone solutions.

Discussion

Flash Photolysis of Acetone. The absorption band of acetone ($\lambda_{max} \sim 280 \text{ nm}, \epsilon_{280} \simeq 18 M^{-1} \text{ cm}^{-1}$) is related to a single-singlet ${}^{1}\text{n}-\pi$ transition involving the nonbonding electron of the oxygen atom. Borkman and Kearns¹⁴ have found that the excited singlet state of acetone in liquid acetone at 23° has a $\tau \simeq 25$ nsec and a $\phi_{\rm F} = 0.01$; it undergoes intersystem crossing to the triplet state ${}^{3}\text{n}-\pi$ with $\phi_{\rm Ic} \simeq 1.0$ and $k_2 = 4 \times 10^7 \text{ sec}^{-1}$. In pure acetone, 14 the triplet lifetime is >30 μ sec (k_4 can be estimated to be $\geq 2 \times 10^5 M^{-1} \text{ sec}^{-1}$), while in liquid hexane 19 it is $\sim 0.4 \mu$ sec. The following primary photodissociative processes are considered

$$CH_{3}COCH_{3} \xrightarrow{h\nu} CH_{3}COCH_{3^{1}}$$
 (1)

$$CH_{3}COCH_{3^{1}} \longrightarrow CH_{3}COCH_{3^{3}}$$
 (2)

$$CH_{3}COCH_{3}^{3} \longrightarrow CH_{3} + CH_{3}CO$$
 (3)

$$CH_{3}COCH_{3}^{3} + CH_{3}COCH_{3} \longrightarrow$$
$$\dot{C}H_{2}COCH_{3} + CH_{3}\dot{C}(OH)CH_{3} \quad (4)$$

The methyl radical produced can abstract hydrogen, and all the radicals undergo combination and disproportionation reactions. In presence of an efficient hydrogen donor, e.g., isopropyl alcohol, reaction 5 $CH_3COCH_3^3 + CH_3CH(OH)CH_3 \longrightarrow$

 $2CH_{\mathfrak{s}}\dot{C}(OH)CH_{\mathfrak{s}}$ (5)

occurs and dissociation of triplet excited acetone via reaction 3 can be almost completely suppressed.¹²

The transient absorption observed in the flash photolysis of acetone in water, Figure 1a, is suggested to be due to the CH_2COCH_3 and $(CH_3)_2\dot{C}(OH)$ radicals. The absorption spectra and extinction coefficients of these radicals are shown in Figure 2. Assuming the formation of equal concentrations of each radical, a transient absorption was reconstructed (based on the spectra in Figure 2) and is superimposed on Figure 1a. The agreement is satisfactory. Zeldes and Livingston¹¹ have observed the esr spectra of $\dot{C}H_2COCH_3$, $(CH_3)_2$ - $\dot{C}OH$, and CH_3 radicals on photolysis of aqueous acetone in the cavity of the esr spectrometer. Diacetone alcohol and the pinacol are among the products recently observed²⁰ in the liquid phase photochemistry of acetone.

In presence of excess isopropyl alcohol, only $(CH_3)_2$ - $\dot{C}(OH)$ radicals are produced, Figure 1b, and agreement with the spectrum obtained independently from pulse radiolysis^{17a} by the reaction OH radicals with isopropyl alcohol (OH + CH₃CH(OH)CH₃ \rightarrow CH₃ $\dot{C}(OH)CH_3$ + H₂O) is excellent. In 20 mM acetone and 3.0 M isopropyl alcohol, the decay at 320 nm is second order with $2k/\epsilon = 4.7 \times 10^6$, compared to $2k/\epsilon = 4.6 \times 10^6$ from pulse radiolysis work.^{17a} Taking the extinction coefficient given in ref 17a, $2k = 1.1 \times 10^9 M^{-1} \sec^{-1}$.

Flash Photolysis of Acetone and Amides. In the presence of amides, the triplet excited acetone can be expected to abstract H atoms at two sites, e.g.

In the flash photolysis of acetone containing A and DMA, the transient spectra observed and the decay kinetics are in accord with the formation of \cdot CH₂-CONH₂ and CH₃CONCH₂(CH₃) radicals, *via* reactions 6 and 9, with the CH₃C(OH)CH₃ radicals formed in all cases. It would appear that the extent of reaction 8 is quite small compared to 9, in agreement with esr observations.⁹ The presence of CH₃CONH could not be established since it absorbs below 310 nm and is masked by the absorption of ground state acetone.

In the photolysis of acetone plus formamide the amide radicals \cdot CONH₂ and HCONH could be formed. From pulse radiolysis work,⁷ the \cdot CONH₂ radical has a $\lambda_{max} \sim 320$ nm and the HCONH was found to have a maximum below 245 nm. In the acetone-photosensitized decomposition of formamide, CONH₂ is the main radical observed in flash photolysis and by esr spectroscopy.⁹ The products observed²¹ in the steady-state photolysis of CH₃COCH₃ and HCONH₂ include (CONH₂)₂ and (CH₃)₂C(OH)(CONH₂), in good agreement with our conclusions.

With dimethylformamide, the main hydrogen abstraction by triplet CH_3COCH_3 appears to be at the N-CH₃ group, to produce $HCON\dot{C}H_2(CH_3)$. This radical was found⁷ to have two peaks at 380 and 248 nm, with extinction coefficients of 1600 and 6900 M^{-1} cm⁻¹, respectively.

It could be argued that the transient species observed are not produced by hydrogen abstraction by triplet excited acetone, but by methyl radicals. This is not considered to be the case since (a) the rate²² of H-atom abstraction by CH₃ radicals is approximately four to five orders of magnitude lower than that of recombination of CH₃, and at the relatively high intensities produced in flash photolysis most of the CH₃ radicals would form¹² C₂H₆; (b) the CH₃C(OH)CH₃ radical is observed in the photolysis of acetone-amide mixtures.

$$CH_{3}COCH_{3}^{3} + CH_{3}CONH_{2} \longrightarrow CH_{2}CONH_{2} + CH_{3}C(OH)CH_{3}$$
(6)

$$\longrightarrow CH_2CO\dot{N}H + CH_3\dot{C}(OH)CH_3$$
(7)

$$\xrightarrow{\text{CH}_{2}\text{COCH}_{3}^{3} + \text{CH}_{3}\text{CON}(\text{CH}_{3})_{2} + \text{CH}_{3}\dot{\text{C}}(\text{OH})\text{CH}_{3} } (8)$$

$$\longrightarrow CH_{3}CONCH_{2}(CH_{3}) + CH_{3}C(OH)CH_{3}$$
(9)

The transient absorption spectra of the four amide radicals in reactions 6–9 have been observed⁷ by pulse radiolysis, and their decay rates and extinction coefficients have been determined. The $\dot{C}H_2CONH_2$ radical has an absorption maximum at 400 nm and $\epsilon_{400} = 1050 \ M^{-1} \ cm^{-1}$, and the CH₃CONH radical $\lambda_{max} < 235 \ nm$ and $\epsilon_{235} = 2000 \ M^{-1} \ cm^{-1}$. The CH₃-CON $\dot{C}H_2(CH_3)$ radical has $\lambda_{max} 350$ and 245 nm with $\epsilon_{350} = 2000 \ M^{-1} \ cm^{-1}$ and $\epsilon_{245} = 7000 \ M^{-1} \ cm^{-1}$; the $\dot{C}H_2CON(CH_3)_2$ radical absorbs $\lambda_{max} 490 \ nm$ and $\epsilon_{490} = 1000 \ M^{-1} \ cm^{-1}$. Quenching of singlet excited acetone is not considered likely. Energy transfer from triplet acetone to the amides cannot be ruled out, since the triplet energy level of the amide group is not known. However, this possibility could be discarded since direct optical excitation of these amides did not produce any transients

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(of course the ϕ_{ISC} might be low) and, again, CH₃C-(OH)CH₃ radicals are formed.

Conclusions

These results can best be interpreted on the basis of hydrogen-atom abstraction from the amides by triplet excited acetone. It is interesting to note that the site of abstraction by triplet excited acetone, as observed by flash photolysis (this work) and by esr spectroscopy,⁹ is the same as that which has been found⁷ for OH radicals produced under pulse radiolysis conditions. Hydroxyl radicals are known to be electrophilic in their reaction with compounds. Furthermore, it would appear that, qualitatively, the rate of abstraction from different amides by triplet acetone follows the same order as the rate' of abstraction by OH radicals. Should these relationships be found to hold with other sensitizers and H-atom donors, it would be possible to predict the site of abstraction by triplet excited molecules based on the wealth of information available for OH radicals.

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Ultraviolet Photochemistry of Acetatopentaamminecobalt(III)

in Aqueous Solution¹

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The 254-nm photolysis of $Co(NH_3)_5O_2CCH_3^{2+}$ in aqueous solution generates Co^{2+} , CO_2 , C_2H_5 , and CH_4 with $\phi_{Co^{2+}} \simeq \phi_{CO_2} \simeq (2\phi_{C_2H_5} + \phi_{CH_4}) = 0.19$. The stoichiometry and absence of any photoaquation products indicate that irradiation of the charge-transfer band of the complex results in electron transfer from the acetato ligand to the metal center. Isotopic substitution, radical scavenging, and light intensity studies demonstrate that CH_3 radicals are released into solution. At 366 nm, on the other hand, irradiation of the ligand-field band with slight charge-transfer overlap yields $(NH_3)_4Co(OH_2)O_2CCH_3^{2+}$ with very small amounts of Co^{2+} . There is no evidence of primary acetate aquation or the oxidation of an ammonia ligand.

Introduction

Irradiation of pentaammine complexes of Co(III) [of the general form $Co(NH_3)_5X^{2+}$] in their intense ligand-to-metal charge-transfer absorption band results in a number of possible processes, the most predominant of which is photoreduction with the formation of Co^{2+} and an oxidized ligand free radical from the one-electron transfer. Only in a limited number of cases has the radical been identified and characterized, either by direct flash photolytic observation or through the variation of final products in the presence of radical scavengers.² Penkett and Adamson³ observed Br₂⁻ and I_2^- from the flash photolysis of $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5I^{2+}$, respectively, and concluded that Br and I atoms were generated in the primary process. On the other hand, the flash photolysis of $Co(NH_3)_5Cl^{2+}$ gave no transient unless free Cl- was present; under those conditions a transient species was detected that could not be identified as Cl_2^- but rather as NH_2Cl^- or $NH_3Cl.^4$ Product yields and scavenger studies are consistent with the formation of the N₃ radical from Co- $(NH_3)_5N_3^{2+.5}$ Kinetic and flash results show that a radical is implied in the photochemistry of oxalato-

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