served experimentally. Another possibility might involve a thermal pumping of the $^3(n,\pi^*)$ carbonyl to the $^1(n,\pi^*)$ state and subsequent reaction from this state[40] but certainly in the case of the acetone/TME this possibility may be rejected as the observed activation energies are only one half as large as the minimum figure of 2000 cm^{-1} reported for the separation of the $^3(n,\pi^*)$ and $^1(n,\pi^*)$ states of acetone. The same considerations, no doubt, apply to acetaldehyde although no explicit measurements of the $^1(n,\pi^*)$–$^3(n,\pi^*)$ separation has been reported for this molecule.

Summation

A study of the photochemistry of two carbonyl–olefin systems, acetone-d_6/tetramethylethylene and acetaldehyde-d_4/*cis*-2-butene, reveals three types of reactions derivable from the $^3(n,\pi^*)$ state of the carbonyl: (1) a transfer of triplet excitation energy as manifest in the cis–trans isomerization of the olefin, (2) an exchange of substituted methylenic groups between carbonyl and olefin and (3) the formation of the ground state oxetane complex of the two. The similarity in activation energies, the demonstration of the lack of diffusion control, and the quenching by oxygen and 1,3-pentadiene of all three processes point to a triplet oxetane as a common intermediate. This is further supported by a theoretical calculation[25] showing a more favorable energy path for oxetane formation *via* a 4-center as opposed to 2-center photocycloaddition.

Molecular orbital correlation along a 4-center coordinate, Q, linking the symmetrical oxetane with the separated carbonyl and olefin in both the initial and methylene exchanged forms reveals a region of metastability having a minimum at the configuration of the symmetrical oxetane. The proposed triplet oxetane mechanism requires methylene exchange and ground state oxetane formation to have sufficient energy to surmount the barriers bounding the region of metastability. The radiationless transfer of triplet excitation energy, however, does not require that the barrier be surmounted. Its energy of activation suggests that it occurs in a region near the top of the barrier but at intermolecular distances less than the sum of van der Waals radii of the carbonyl and olefin where strong exchange repulsion interaction can effect the transfer.

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The Reaction of Trifluoromethyl Radicals with Hexafluoroacetone Imine

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By photolyzing hexafluoroacetone the addition reaction between CF_3 radicals and hexafluoroacetone imine has been studied. The reaction is rapid, with an A factor of 5.2×10^{10} cm^3 mol^{-1} sec^{-1} and an activation energy of 3900 cal mol^{-1}. Hydrogen atom abstraction occurs much less readily, with $A = 1.6 \times 10^9$ cm^3 mol^{-1} sec^{-1} and $E = 4500$ cal mol^{-1}.

We have recently investigated the photochemistry of hexafluoroacetone imine at 2537 Å.[1,2] CF_3CN was the only major volatile product, while CF_3H was a minor product, and C_2F_6 could not be positively identified.[2] It was anticipated that the photochemical cleavage of the imine would generate CF_3 radicals, but the absence of C_2F_6 indicated that this may not be so. However, due to the very low quantum yields found for the photodecomposition,[2] the stationary concentration of the CF_3 radicals could be extremely low, and if they further reacted facilely with the imine source, detectable amounts of C_2F_6 may not have been produced. To examine this possibility we have used hexafluoroacetone (HFA) as a photolytic source of CF_3 radicals to investigate their reaction with hexafluoroacetone imine. The experiments were carried out at

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(1) S. Toby and G. O. Pritchard, *J. Phys. Chem.*, **75**, 1326 (1971).

(2) F. S. Toby, S. Toby, and G. O. Pritchard, Abstracts 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Phys 034.

3130 Å, at which wavelength the imine does not absorb.[1,2]

The photolysis of HFA at 3130 Å has been extensively investigated, and it is well established that $R_{C_2F_6} = R_{CO}$,

$$(CF_3)_2CO + h\nu \longrightarrow 2CF_3 + CO \qquad (1)$$

$$2CF_3 \longrightarrow C_2F_6 \qquad (2)$$

in the temperature range of interest.[3] In preliminary experiments at 150°, using 20 Torr of HFA in the presence of 20 Torr of added imine, C_2F_6 formation was almost completely suppressed; it was found that $R_{C_2F_6} \simeq 0.01R_{CO}$. A small quantity of CF_3H was also produced. This indicates that CF_3 radicals must enter into a very rapid addition reaction with the imine

$$CF_3 + (CF_3)_2C{=}NH \longrightarrow (CF_3)_2\dot{C}{-}N(CF_3)H \text{ and/or } (CF_3)_3C{-}\dot{N}H \ (r_3) \qquad (3)$$

The rapid addition of CF_3 radicals to the —N=N— double bond in hexafluoroazomethane is well documented.[3]

$$CF_3 + CF_3N{=}NCF_3 \longrightarrow (CF_3)_2N{-}\dot{N}CF_3 \qquad (4)$$

CF_3H can only arise *via* the abstraction reaction

$$CF_3 + (CF_3)_2C{=}NH \longrightarrow CF_3H + (CF_3)_2C{=}\dot{N} \ (r_5) \qquad (5)$$

Table I: Photolysis of HFA in the Presence of Hexafluoroacetone Imine

Temp, °C	Time, min	Initial pressure, cm: HFA	Initial pressure, cm: Imine	Products, mol × 10⁶: CO	Products, mol × 10⁶: C_2F_6	Products, mol × 10⁶: CF_3H	Ratio C_2F_6/CO
154	10	2.0	0.0	7.85	7.83		1.00
154	10	2.0	0.0	11.2	11.4		1.02
155	10	2.0	2.0	8.90	0.11	0.13	0.01
154	10	2.0	1.0	6.88	0.14	0.06	0.02
137	10	5.0	1.0	7.36	0.55	0.11	0.08
137	20	5.0	1.0	23.7	2.30	0.29	0.10
132	5	5.0	1.0	3.86	0.30	0.05	0.08
112	12.5	5.4	1.2	10.8	1.10	0.12	0.10
111	16.5	5.0	1.0	13.6	1.52	0.20	0.11
75	25	5.0	1.0	14.3	2.14	0.10	0.15
75	25	5.0	1.0	14.4	1.97	0.15	0.14
75[a]	10	5.0	0.9	13.0	3.63	0.14	0.28
75[a]	10	5.0	1.0	14.1	2.91	0.12	0.21
27	50	5.0	1.0	13.1	4.71	0.12	0.36
27	55	5.0	1.0	17.2	6.18	0.11	0.36
27.5[a]	60	5.0	1.0	48.2	21.5	0.15	0.45
27.5[a]	30	5.0	1.0	24.8	9.66	0.10	0.39
0.5[a]	60	5.0	1.2	25.6	10.2	0.21	0.40
0.5[a]	20	5.0	1.0	10.8	5.08	~0.1	0.47
−30[a]	30	5.0	1.2	12.8	8.40	None	0.66

[a] Reaction volume 188.2 ml. A double-walled vessel was used and temperatures were maintained *via* circulating fluids through the outer chamber. The other reactor was 152.6 ml. Both vessels were approximately 5-cm diameter × 10-cm long cylindrical quartz cells.

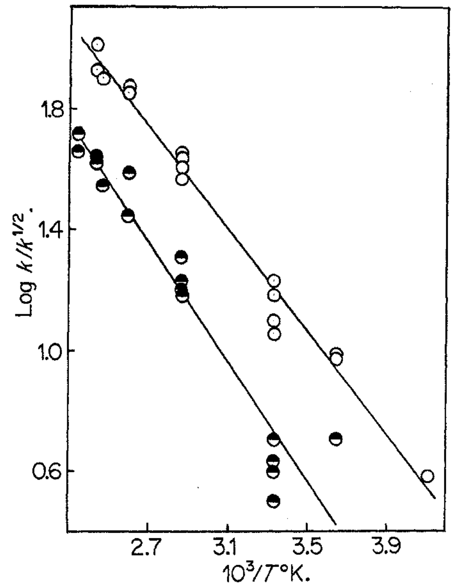

Figure 1. Arrhenius plots for $k_3/k_2^{1/2}$ and $k_5/k_2^{1/2}$, units $cm^{3/2}$ $mol^{-1/2}$ $sec^{-1/2}$: $k_2/k_3^{1/2}$ plot, ○; $k_5/k_2^{1/2}$ plot, ◒. The ordinate has been increased by 1.5 log units for $k_5/k_2^{1/2}$ plot.

The complete data are recorded in Table I; conditions were chosen so that the competition between reactions 2 and 3 could be most effectively studied.

Our basic kinetic assumptions are that reaction 3 is rate determining, and that the radicals produced (r_3) react rapidly with a further CF_3 radical

$$r_3 + CF_3 \longrightarrow (CF_3)_3C{-}N(CF_3)H \qquad (6)$$

to give the final addition product. Thus the rate of formation of the addition product is equal to $(R_{CO} - R_{C_2F_6})$,[4] and the rate constant for the addition reaction is given by[5]

$$k_3/k_2^{1/2} = (R_{CO} - R_{C_2F_6})/R_{C_2F_6}^{1/2}[\text{imine}] \qquad (7)$$

The original data[6] on reaction 4 were treated in this manner, and a steady-state treatment leads to an identical result.[3] An Arrhenius plot of expression 7 is given in Figure 1, which yields $k_3/k_2^{1/2} = 1.1 \times 10^4 \exp(-3900/RT)$ $cm^{3/2}$ $mol^{-1/2}$ $sec^{-1/2}$ by the method of least squares. The estimated error is ±100 cal. The imine concentration used was an averaged value based on the initial concentration less $^1/_2\{[CO] - [C_2F_6]\}$. The correction varied between 1 and 10% for all experiments, except for two higher conversion runs at 27.5 and 137°, respectively, where it amounted to about

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(3) S.-L. Chong and S. Toby, *J. Phys. Chem.*, **74**, 2801 (1970), and references contained therein.

(4) This expression ignores CF_3H formation in the radical balance; however its significance is negligible relative to this difference, at all temperatures. Only data up to 137° are considered, where $R_{C_2F_6} \simeq 0.1R_{CO}$.

(5) Alternatively, assuming the rapid removal of r_3 and r_5 by CF_3 radicals, expression 7 is simply derived from a steady-state treatment, when $k_3 \gg k_5$.

(6) G. O. Pritchard, H. O. Pritchard, H. I. Schiff, and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **52**, 849 (1956).

15%. The ketone conversion was generally about 3%. Adopting[7] $k_2 = 2.3 \times 10^{13}$ cm^3 mol^{-1} sec^{-1}, we obtain $k_3 = 5.2 \times 10^{10} \exp(-3900/RT)$ cm^3 mol^{-1} sec^{-1}, which may be compared[8] to $k_4 = 3.9 \times 10^{10} \exp(-3900/RT)$ cm^3 mol^{-1} sec^{-1}. The similarity in the Arrhenius parameters suggests that reaction 3 occurs predominantly by addition to the N atom.[8]

Because of the rapid addition reaction, the competition between abstraction and combination (reactions 5 and 2) is not easily studied. However, for the small yields of CF_3H obtained, we may write

$$k_5/k_2^{1/2} = R_{CF_3H}/R_{C_2F_6}^{1/2}[\text{imine}] \quad (8)$$

The Arrhenius plot for expression 8 is shown graphically in Figure 1, from which a value of $k_5 = 1.6 \times 10^9 \exp(-4500/RT)$ cm^3 mol^{-1} sec^{-1} is obtained. The low activation energy is compatible with similar studies involving >N–H groups,[9] but the A factor appears to be somewhat lower than that for comparable systems. However the agreement between k_3/k_5 obtained in this work and that obtained in the direct photolysis of the imine[2] lends credence to our value.

The data are consistent with the production of CF_3 radicals in the direct photolysis of the imine. At low stationary CF_3 radical concentrations C_2F_6 production would not occur due to the highly efficient addition reaction. The formation of CF_3H in the direct photolysis may be attributed, in part, to H-atom abstraction by CF_3 radicals as well as to an intramolecular elimination from the photoexcited imine. The primary processes are discussed in detail elsewhere.[2]

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[7] P. B. Ayscough, *J. Chem. Phys.*, **24**, 944 (1956).

[8] The data at 154° give log $k_2/k_3^{1/2}$ values of 2.07 and 2.25, respectively, which lie close to the line in Figure 1. However, they are omitted due to the low C_2F_6 yields and some interference by about equivalent amounts of CO_2 in the analysis. A trace (~0.025%) of CO_2 was present in the HFA, but its formation in the reactor at 154° could occur to a slight extent. See ref 3.

[9] P. Gray, A. A. Herod, and A. Jones, *Chem. Rev.*, **71**, 247 (1971).

Photoreactions in Aqueous Solutions of Thymine, pH 12

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Aqueous solutions of thymine at pH 12 have been studied by flash photolysis. Under these conditions we see a transient species due to the hydrated electron which arises from excitation of OH^-. This electron absorption is quenched by N_2O, by O_2 at a rate of 1.6×10^{10} M^{-1} sec^{-1} and by the thymine anion at a rate of 3.0×10^9 M^{-1} sec^{-1}. In addition two species which we attribute to absorption by thymine alone are observed. One of these is short-lived and quenched by O_2; it is also quenched by ground-state thymine at a rate of 7.3×10^8 M^{-1} sec^{-1} and is almost certainly the triplet state. The spectrum of this species is red-shifted 60 nm compared to that of the neutral triplet seen at pH 7. The other species produced in thymine alone has a lifetime of at least 1 msec and may in fact be a stable product. This species is not quenched by O_2. Its nature is unclear.

Introduction

When neutral aqueous solutions of thymine are irradiated with ultraviolet (uv) light, permanent photodimers identical with those which cause biological inactivation of DNA are produced.[2] These dimers have been shown to result from the bimolecular reaction of a thymine ground state and an excited triplet state. The triplet state has been detected by flash photolysis techniques and has been characterized by its spectrum. Rate constants for reactions with ground-state thymine and O_2 have been determined.[3]

Our interest in the excited states of thymine led us to examine species produced in solutions of thymine above the pK for ring ionization which occurs about pH 9.9.[4] Changes in properties of the excited states at high pH are not unexpected since one tautomeric

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[1] Research Fellow, National Cancer Institute of Canada.

[2] G. J. Fisher and H. E. Johns, *Photochem. Photobiol.*, **11**, 429 (1970).

[3] D. W. Whillans and H. E. Johns, *J. Amer. Chem. Soc.*, **93**, 1358 (1971).

[4] D. Shugar and J. J. Fox, *Biophys. Biochem. Acta*, **9**, 199 (1952).