72-420-427

THE GAS PHASE RADIOLYSIS AND VACUUM ULTRAVIOLET PHOTOLYSIS
OF HETEROCYCLIC ORGANIC COMPOUNDS

Progress Report

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February 1, 1974 - February 1, 1975

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Some of the general principles concerning the gas phase high energy chemistry of complex organic molecules derived from our studies of the molecules in Table 1 are presented in the accompanying PROPOSAL. Here we deal with some of the specifics of our recent efforts. This PROGRESS REPORT is organized into five sections as indicated below. The initials in parentheses after each section indicate the individuals who have contributed to each area.

- A. Tetrahydrofuran Radiolysis. (A.A.S.)
- B. Heterocyclic Amine Radiolysis. (D.S.)
- C. Heterocyclic Sulfide Vacuum Ultraviolet Photolysis. (I.C.)
- D. Photoionization Mass Spectrometer Construction. (J.D.)
- E. Ionization Efficiency and Extinction Coefficient Determination. (D.S.)

Table 1

Heterocyclic Molecules Being Investigated

I. Oxygen Heterocycles

propylene oxide

oxetane

tetrahydrofuran (THF)

1,4-dioxane

ethylene oxide

tetrahydropyran (THP)

1,3-dioxane

II. Sulphur Heterocycles

ethylene sulfide

thietane sulfone

tetramethylene sulfoxide

thietane

tetrahydrothiophene (THT)

sulfolane

pentamethylene sulfide

III. Nitrogen Heterocycles

ethyleneimine

azetidine

pyrrolidine

N-methylpyrrolidine

pyrazoline

piperidine

IV. Mixed Heterocycles

1,4-thioxane

morpholine

A. Tetrahydrofuran γ -Radiolysis

In the γ -radiolysis of THF, Table 1, there are pronounced density effects which are apparent in the pressure range 0-50 torr. These effects are readily observed in Figure 1 which graphically presents the ion-pair yields (M/N) for the most important products as a function of pressure. The most striking aspect of the data is that all of the yields decline as the pressure is increased. The yield reduction is in the 50-60 percent range and is quite different from that observed in the xenon photolysis of THF where the total quantum yields for all C_2 and C_3 products actually increase with increasing pressure. The observed decrease in yields with increasing density in γ -radiolyses is certainly consistent with the decrease in the fragmentation yields of other organics observed when gaseous and liquid phase γ -radiolyses are compared.^{1,2} Our present thinking concerning these systems makes us reluctant to postulate the quenching of excited states, although this could easily account for these observations and emission from highly excited neutral heterocyclic dimer molecules has been observed.³ We feel that the effects evident in Figure 1 are the results of decreased fragmentation of the parent ion as the pressure is increased. We suspect this because, aside from the yields of three products which are of minor importance in the xenon photolysis namely acetylene, allene and propane, the relative product yields observed at 50 torr in both the xenon photolysis, where no ions are present, and in the γ -radiolysis are almost identical (Table 2). Therefore we have concluded that at 50 torr, most of the observed products arise from reactions 1 and 2 which are also the major reactions in the xenon photolysis of THF.

The three products which are unimportant in the xenon photolysis probably arise from the ion-molecule reactions:

1. A.A. Scala Progress Report No. AT(11-1)-3569-1.
2. G.R. Freeman; Proc. Fourth International Congress on Radiation Research., Evian, France, 1970, in "Advances in Radiation Research", Eds. J.F. Duplan and A. Chapiro, Gordon and Breach, London, 1973, pp 351-60.
3. F.H. Hirayama, C.W. Lawson and S. Lipsky, J. Phys. Chem., 74, 2411.

Table 1

Gas Phase γ -RadiolysisTetrahydrofuran^a

Pressure (torr)	0.5	1.0	1.6	2.0	2.0	5.0	5.2	5.2	50	50
Additive (%)					DI(5)	NO(5)	NO(5)	O ₂ (10)		
Product										
CH ₄	.33	.32	.19	.22					.40	.35
C ₂ H ₂	.33	.23	.21	.18	.16	.18	.11	.076	.11	.15
C ₂ H ₄	1.03	.72	.64	.55	.47	.43	.38	.21	.32	.37
C ₂ H ₆	.069	.047	.045	.032	.032	.00	.00	.00	.015	.020
C ₃ H ₆	.57	.43	.39	.42	.40	.31	.30	.13	.23	.25
C ₃ H ₈	.16	.12	.073	.027	.025	.012	.010	.063	.061	.043
C ₃ H ₄	.12	.077	.030	.027	.019	.052	.041	.017	.037	.047
C-C ₃ H ₈	.12	.095	.095	.085	.068	.084	.059	.044	.073	.077
1-C ₄ H ₈			.061	.048	.038			.074	.013	.010

a. Dose 20 Mrad. Yields are ion pair yields (W=25eV assumed)

Figure 1

Figure 1: The pressure dependence of the ion pair yields (M/N) of ethylene, ; propylene, ; cyclopropane, ; acetylene, . The pressure dependence of the quantum yield of ethylene and acetylene in the xenon photolysis, .

Table 2

Relative Product Yields from the Photolysis and Gamma
Radiolysis of 50 Torr Tetrahydrofuran

	γ Radiolysis	Xenon Photolysis
$C_2 H_2$	37.5	1.5
$C_2 H_4$	100	100
$C_2 H_6$	4.5	10.0
$C_3 H_6$	71.5	71.2
$C_3 H_8$	20.0	2.4
$C_3 H_4$	11.8	1.1
$C \equiv C_3 H_6$	23.0	30.8
$1 \equiv C_4 H_8$	3.4	13.3

If we use the 70eV mass spectrol cracking pattern of THF to estimate the importance of these reactions, we can calculate a maximum ion pair yield for acetylene, allene and propane from these reactions. The calculated yields are 0.06, 0.19 and 0.37 respectively, while the observed reduction in these yields are 0.13, 0.42 and 0.19 respectively. Although using the 70 eV cracking pattern to estimate ion abundances in γ -radiolyses is only an approximation this calculation would seem to indicate that acetylene and allene are also formed from more highly excited neutral molecules than those produced in the xenon photolysis. For example in the xenon photolysis at 50 torr essentially all of these products which were present at 2 torr have been quenched. The insensitivity of these product yields to the presence of nitric oxide is consistent with these suggested modes of formation.

It is worthy of note that although part of the propane is scavenged by nitric oxide, indicating a free radical precursor, about 50 percent is insensitive to nitric oxide and therefore formed by reaction 5.

Reduced ionic fragmentation leads to increased importance of the parent ion reactions. The major reaction of THF^+ is proton transfer. This reaction has been observed in the

solid phase radiolysis of α -methyltetrahydrofuran at 77°K.⁴ The radical (I) would then lead to high molecular weight products which would not be observed in our analytical scheme. At low pressure the fragment ions produce the quenchable products by the following ion-molecule reactions.

If we assume a very simple kinetic scheme in which we have unimolecular decomposition of the parent ion competing with bimolecular collisional stabilization;

4. F.S. Dainton and G.A. Salmon, Proc. Royal Soc., A 285, 319 (1965)

then we arrive at equation 1 for the pressure dependence of an ionic product.

$$\frac{1}{(\text{Product})} = \frac{1}{(\text{Product})_0} \left(1 + \frac{k_s}{k_d} M\right) \quad (1)$$

Using this kinetic approach we have plotted in Figure 2 the reciprocal of the ethylene and total C_3H_6 ion pair yields as a function of pressure. Within experimental error both lines have identical slopes. This suggests that the ion whose decomposition is being quenched is the precursor of both reaction products ethylene and C_3H_6 . The parent ion is the only ion whose decomposition could lead to both of these products. The actual values for k_s/k_d for ethylene and C_3H_6 production are 1.05 and 1.80 respectively. This difference is the result of each line having a different intercept. This could arise because the yield of ethylene from neutral molecule decomposition is higher than the corresponding yield of C_3H_6 .

The very low total ion pair yields observed at high pressure, $\Sigma M/N \approx 0.9$, and the realization that there are probably three to four neutral excited molecules produced per ion pair may eventually force us to conclude that quenching of neutral excited states is also occurring. It may in fact be the quenching of such states which is the cause of slow increase in reciprocal ion pair yields above 5 torr. It seems at the moment that the only way to avoid this conclusion would be to observe large yields of high molecular weight products. These have not been observed.

The great similarity of xenon photolysis and γ -radiolysis is evident when we consider not only product yields, Table 2, but also the pressure sensitivity of relative product yields. This comparison is shown in Figure 3 for total $\text{C}_3\text{H}_6/\text{C}_2\text{H}_4$ and $\text{C}-\text{C}_3\text{H}_6/1-\text{C}_3\text{H}_6$. The very similar behaviors of both photolysis and γ -radiolysis we believe supports our contention that in both systems a quasi equilibrium is established and excited molecules and ions are able to sample the potential surfaces and choose the thermodynamically more favorable paths. There is a major difference between these two systems however, and that is shown in Figure 1. In the xenon photolysis quantum yields actually increase with increasing pressure while in the γ -radiolysis they decrease. We have already attributed the decrease in ion pair yields in the γ -radiolysis to quenching of fragmentation reactions of the parent ion which is absent in the xenon photolysis.

Figure 2.

Figure 2. The pressure dependence of the reciprocal of the ion pair yields $(M/N)^{-1}$ of ethylene, ; total C_3H_6 ,

Figure 3. The pressure dependence of $t\text{-C}_3\text{H}_6/\text{C}_2\text{H}_4$ in the γ -radiolysis, and xenon photolysis, of tetrahydrofuran. The pressure dependence of $c\text{-C}_3\text{H}_6/\text{C}_3\text{H}_6$ in the γ -radiolysis, and xenon photolysis, of tetrahydrofuran.

B. Heterocyclic Amine Radiolysis

The ion-pair yields for the major products from the γ -radiolysis of the heterocyclic amines, ethylenimine, (EI), azetidine, (AZ), pyrrolidine, (PY), and piperidine, (PI), are presented in Table 1. In Figure 1 is presented the pressure dependence of the ion pair yields of ethylene and propylene for the γ -radiolysis of EI, PY, and PI. It should be noted that propylene is not a product in the EI radiolysis. These data are not available as yet for AZ. In Figure 2 is presented the pressure dependence of the ratio total C_3H_6/C_2H_4 for the γ -radiolysis of both pyrrolidine and piperidine. The pressure dependence of this ratio in the xenon photolysis of these compounds is also presented in Figure 2.

The radiolysis of heterocyclic amines is quite similar to the radiolysis of cyclic ethers. The drop in the ion pair yields of the major products with increasing pressure can be ascribed to the quenching of ion-molecule reactions at higher pressures. The insensitivity of neutral reactions to increasing pressure is clearly demonstrated in Figure 2, by the xenon photolysis data. Reactions 1 and 2 which are the major fragmentation

reactions of the PY^+ ion in the 70 eV mass spectrum of pyrrolidine are the most likely candidates for those reactions which are being quenched.^{1,2} If we use the ratio Reaction 2/Reaction 1 as determined in the mass spectrometer (0.52) the observed ratio of 0.15 in the low pressure γ -radiolysis would suggest that the decomposition of neutral excited states produced in the γ -radiolysis yield significantly more ethylene than propylene. This is also true of the neutral decomposition of excited states produced in the xenon photolysis of pyrrolidine (Figure 2).

1. E.J. Gallegos, R.W. Kiser, J. Phys. Chem., 66, 136 (1962).
2. A.M. Duffield, H. Budzikiewicz, D.H. Williams, and C. Djerassi, J. Am. Chem. Soc., 87, 810 (1965).

Table I

The Gas Phase γ -Radiolyses of Heterocyclic Amines^a

	Ethylenimine					Azetidine		Pyrrolidine			Piperidine		
Pressure (torr)	3.0	5.0	9.0	15.0	3.0	2.0	2.0	2.0	5.0	11.0	1.7	5.0	14.0
Additive (%)			SF ₆ (15)		O ₂ (20)		H ₂ S (20)		NO (20)				
Product													
CH ₄	.81	.10	.89	.74	.043	.28	.31	.094	.024	.084	.072	.11	.094
C ₂ H ₂	.11	.22	.12	.12	.10	.012	.019	.12	.054	.031	.17		.062
C ₂ H ₄	.98	.73	.66	.53	1.47	2.80	2.31	1.03	.40	.23	1.18	.57	.23
C ₂ H ₆	.056	.17	.027	.052	.00	.12	.35	.015			.021	.048	.050
C ₃ H ₆		.01				.056	.057	.15	.048	.039	.12	.084	.069
C ₃ H ₈		.01				.27	<u>2.95</u>						
C ₃ H ₄								.048	.012	.010	.018	.005	.012
C-C ₃ H ₆								.016					
1-C ₄ H ₈								.017			.066	.050	.038

a. Dose 10 M rads; yields are ion pair yields

Figure 1

Figure 1. The pressure dependence of the ion pair yields of ethylene and propylene from the γ -radiolysis of ethylenimine, (EI), pyrrolidine, (PY), and piperidine (PI).

Figure 2

Figure 2. The pressure dependence of the $C_3H_6 : C_2H_4$ ratio in the γ -radiolysis and xenon-photolysis of pyrrolidine, (PY), and piperidine, (PI).

In the γ -radiolysis of piperidine (PI) the decrease in the yields of the major products ethylene and propylene with increasing pressure (Figure 1), can also be attributed to quenching of decomposition of the parent ion PI^+ . The major unimolecular reactions of the parent ion in the mass spectrometer are:

In addition to these reactions the parent ion itself accounts for another twenty percent of the ions in the mass spectrometer². In this respect the γ -radiolyses of pyrrolidine and piperidine are quite similar. The major difference observed is the increase in the ratio total C_3H_6/C_2H_4 with pressure. This is further evidence that ionic reactions are being quenched. The increasing ratio total C_3H_6/C_2H_4 with increasing pressure may be attributed to the greater importance of C_3H_6 in the decomposition of neutral excited states of piperidine. At low pressures the product distributions and the C_3H_6/C_2H_4 are determined by the relative contributions of ionic and neutral molecule decompositions. In the case of pyrrolidine the importance of C_3H_6 from neutrals is relatively small and when the ions are quenched no significant increase in the ratio C_3H_6/C_2H_4 is observed. However in the case of piperidine the C_3H_6 must be relatively much more important in neutral molecule decomposition. Therefore as the ions are quenched the greater importance of the C_3H_6 from neutral molecule decomposition becomes evident and an increase in the total C_3H_6/C_2H_4 is observed. Generally speaking more propylene is usually observed in the γ -radiolysis of these compounds; However the increase in the C_3H_6/C_2H_4 in the case of piperidine is an indication that the neutral excited molecules produced in the γ -radiolysis have a greater tendency to decompose by reaction 6 as compared to reaction 5 than do the excited molecules produced at the xenon photolysis. This is also true for pyrrolidine except that there the total C_3H_6/C_2H_4 ratio does not change significantly

That the quenching of fragmentation of the parent ion at these pressures is certainly possible is further indicated by the detection of metastable ions in the mass spectrum of both pyrrolidine and piperidine.²

As with pyrrolidine and piperidine in the γ -radiolysis of ethylenimine, (EI), the ethylene yield shows a decrease with increasing pressure, (Figure 1). The methane yield all of which arises from methyl radicals is constant over the pressure range studied and therefore must be produced mainly from the neutral reaction 7 rather than the ionic reaction 8, even though reaction 8 occurs in the mass spectrometer with an ion

pair yield of 0.22. Since the only other significant ions produced in the mass spectrometer are $C_2H_4N^+$, (.28); CH_2N^+ , (.22); $C_2H_5N^+$, (.18), it is difficult to see how quenching of any of these ions could lead to a reduction in the ion pair yield of ethylene.¹ At the present time we are therefore unable to explain the reduction in the ethylene yield as the pressure is increased. This peculiarity of ethylenimine may be related to the unusually high ring strain present in this molecule.

No pressure studies have been made for azetidine photolysis. The major product in fact almost the only product is ethylene. Ethylene is also the major product in the xenon photolysis of azetidine being produced by reaction 9. Ethylene could also be produced from the fragmentation of the parent ion, AZ^+ as shown in reactions 10 and 11,

followed by the proton transfer

reaction 12. In the mass spectrometer the parent ion and the CH_2N^+ ion account for ion

pair yields of 0.14, and 0.30, respectively. We expect therefore to find that a sizeable fraction of the ethylene yield will be quenched as the pressure is increased.

The only other aspect of azetidine radiolysis worthy of comment at this time is the large increase in the propane yield observed when H_2S is added to the radiolysis. At present we suggest that since proton transfer to azetidine is likely (reaction 12) the protonated azetidine reacts with H_2S to produce propane as shown in reaction 13, which is expected to be exothermic by 45 kcal/mole.

If we assume the same sort of simplified kinetic scheme for the quenching of heterocyclic amine ions as we used for the quenching of tetrahydrofuran ions namely,

then we can evaluate k_s/k_d from equation (1) in section A and a plot of $(M/N)^{-1}$ against pressure. This plot has been presented in Figure 3. Using the slopes of the lines for piperidine, pyrrolidine and ethylenimine we obtain the values for k_s/k_d of .094, .097, and .058 respectively. We believe these values reflect the similar stability of the five and six membered rings and the greater instability of the three membered ring of ethylenimine.

Figure 3

Figure 3. The pressure dependence of the reciprocal of the ethylene ion pair yield $(M(C_2H_4)/N)^{-1}$ from the γ -radiolysis of ethylenimine, (EI), pyrrolidine, (PY) and piperidine (PI).

C. Heterocyclic Sulfide Vacuum Ultraviolet Photolyses

Unlike electronically excited oxetane which decomposes exclusively by reaction 1, highly excited thietane molecules decompose by two competing reactions.

Reaction 3 accounts for something on the order of 40 percent of the decomposition of neutral

electronically excited thietane molecules produced by the absorption of either 147 or 123.6 nm photons. The pressure dependence of the ratio $\text{C}-\text{C}_3\text{H}_6/\text{C}_3\text{H}_6$ which is presented in Table 1 make it clear that the C_3H_6 species produced in reaction 3 is the trimethylene diradical. Based upon a comparison of our previous study of cyclobutanone photolysis, which decomposes by reactions 4 and 5, the elimination of a sulfur atom from thietane, (reaction 3), is

more probable than the elimination of carbon monoxide from cyclobutanone by about a factor of four. This is somewhat surprising especially in view of the fact that the reaction analogous to reaction 3 does not occur when oxetane is photolyzed. In this respect thietane is more similar, in its reactivity, to cyclobutanone than to oxetane.

The pressure dependence of the ratio $\text{C}-\text{C}_3\text{H}_6/\text{C}_3\text{H}_6$ at 147 and 123.6 nm is consistent with the higher energy of the latter line and in fact indicates that the average energy deposited in thietane molecules in γ -radiolysis is even higher than it is in the krypton photolysis. The total C_3H_6 yield is also consistent with this interpretation since C_3H_6 is a product of highly excited molecules and its importance in the product distribution is greater in the γ -radiolysis.^{1,2}

In the krypton photolysis as well as in the γ -radiolysis ions make a significant contribution to the overall reaction mechanism. In fact at the krypton resonance line, ions account for 44 percent, of the excited molecules. In the krypton photolysis the only ion possible is the parent ion $\text{C}_4\text{H}_8\text{S}^+$. The study of this molecule in the photoionization mass spectrometer will certainly provide the answer to question of how the parent ions react. At present we suspect that proton transfer may be the major reaction of the parent ion. This reaction is similar to the proton transfer reaction which occurs in THF^3 .

1. D.R. Dice and R.P. Steer, J. Phys. Chem., 77, 434 (1973).

2. H.A. Wiebe and J. Heicklen, J. Am. Chem. Soc., 92, 7031 (1970).

3. F.S. Dainton and G.A. Salmon, Proc. Royal Soc., A285, 319 (1965).

Table 1

Photolysis and γ -Radiolysis of Thietane

Product	147 nm				123.6 nm				γ -Radiolysis		
	1	5	10	20	1	5	10	20	1	5	10
CH_4	2.3	4.6	4.0	2.8	6.7	5.1	3.5	1.2	5.1	3.4	2.3
C_2H_6	6.5	5.5	6.3	3.6	18.2	7.1	6.7	3.1	12.7	13.5	12.7
C_2H_4	93.5	94.5	93.7	96.4	81.8	92.9	93.3	96.9	87.3	86.5	87.3
C_2H_2	0.70	1.1	2.6	0.76	1.7	0.82	0.84	0.45	2.0	2.0	1.9
C_3H_8	43.7	40.0	34.7	26.6	50.9	36.1	33.3	19.4	41.2	42.1	36.8
C_3H_6	1.3	3.3	3.0	1.9	3.2	2.6	1.9	1.7	2.0	2.4	1.1
C_3H_4	4.0	6.1	4.5	4.7	6.0	4.3	4.4	2.6	2.1	2.5	2.2
$\text{c-C}_3\text{H}_6$	9.9	31.7	39.0	35.6	17.5	21.2	22.3	18.2	29.0	22.9	19.7
$\text{c-C}_3\text{H}_6 / 1\text{-C}_3\text{H}_6$	0.23	0.79	1.12	1.34	0.34	0.59	0.67	0.94	0.70	0.54	0.54

We have written it with the ring opened since thietane is considerably more strained than THF. Reaction 6 will probably be slower than the corresponding reaction in the HF system because of the expected lower proton affinity of the sulfur compound.

In the γ -radiolysis at low pressure we may use the low pressure mass spectral cracking pattern to estimate the ions present and their relative importance. Here again the parent ion is quite important (25%). The only other ion of any significance is the CH_2S^+ ion (50%).⁴ The reactions of the CH_2S^+ ion are uncertain. The production of this ion also results in a molecule of neutral ethylene and consequently does not change end product distributions very greatly.

Further speculation concerning the ionic mechanism is unwarranted at this time. However the similarity of the product distributions in the xenon and krypton photolysis and in the γ -radiolysis is worthy of note. Since the contribution of ionic reactions is likely to be quite different at each of these energies, particularly in the xenon photolysis where no ions are present, we suspect that ions are not producing observable products, either because they are undergoing reactions such as reaction 6, which produce high molecular weight products, or they undergo neutralization prior to reaction and decompose as highly excited neutrals rather than ions.

When the ring size is increased to five atoms the sulfur (THT) and oxygen (THF) heterocycles behave quite similarly.⁵ The two major decomposition reactions of tetrahydrothiophene (THT) are given below and are analogous to the reactions observed in the THF system. In addition to reactions 7 and 8 we have also observed the molecular

elimination of H_2S as shown in reaction 9. The analogous reaction could not account

for more than one percent of the decomposition of THF. In THT decomposition it represents approximately 8% of the total reaction mechanism.

Despite the fact that 52 percent of the excited molecules ionize at the krypton resonance line and only 10 percent ionize at the xenon resonance line, the product distributions observed are quite similar. Again we are faced with either of two possible explanations. The parent ion either undergoes the proton transfer reaction and gives only

4. E.J. Gallegos and R.W. Kiser, J. Phys. Chem., 66, 136 (1962).

5. S. Braslavsky and J. Heicklen, Can. J. Chem., 49, 1317 (1971).

Table 2

Photolysis and γ -Radiolysis of Tetrahydrothiophene

Product	147 nm				123.6 nm				γ -Radiolysis			
	Pressure(torr)	1	5	10	15	1	2	5	10	1	5	10
CH ₄		3.5	2.2	1.6	1.2	12.4	10.4	9.7	7.2	20.9	50.0	21.6
C ₂ H ₂		4.6	5.7	4.4	2.2	8.1	7.1	6.7	5.0	15.3	17.0	8.8
C ₂ H ₄		95.4	94.3	95.6	97.8	91.9	92.9	93.3	95.0	84.7	83.0	19.2
C ₂ H ₆		0.86	0.83	0.60	1.2	0.82	0.85	1.1	1.8	3.6	3.8	3.0
C ₃ H ₆		5.8	6.4	6.6	6.7	4.4	4.7	6.9	6.8	14.0	12.3	14.1
C ₃ H ₈		0.54	0.73	0.78	0.31	0.46	0.52	0.42	0.82	2.0	1.0	1.3
C ₃ H ₄		1.4	1.2	1.1	0.42	2.7	2.9	2.4	2.5	2.5	2.0	2.2
c-C ₃ H ₆		1.6	1.9	2.0	2.3	0.8	1.1	1.1	2.8	0.77	0.87	0.86
1,3-C ₄ H ₆		5.4	7.0	7.3	9.1	7.1	7.3	7.8	9.5	7.4	5.2	4.3

high molecular weight products or it undergoes neutralization and then reacts as a highly excited neutral. The same situation applies in the γ -radiolysis except for a different reason. Using the mass spectral cracking pattern to estimate the importance of ions in the low pressure γ -radiolysis we can estimate that the major ions present and their percent abundance will be: $\text{CH}_3\text{CH}_2\text{S}^+$, 35%; $\text{C}_4\text{H}_8\text{S}^+$, 18%; CH_3S^+ , 10%; CHS^+ , 10%; $\text{C}_2\text{H}_5\text{S}^+$, 9%.⁴ Each of the ionic decomposition processes which leads to these fragment ions also produces a neutral product, all of which are identical to the products observed from neutral decomposition. Again this tends to obscure the ionic reactions.

We have only a limited amount of data on the vacuum ultraviolet photolysis of sulfolane. However it is already clear that while little or no elimination of a sulfur atom occurs in THT its 1,1 dioxido eliminates SO_2 very readily Table 3.

The analogous reaction of cyclopentanone is also essentially the only reaction of highly excited cyclopentanone. In both cases the C_4H_8 produced is the tetramethylene diradical

which undergoes either cleavage, cyclization or isomerization reactions.

A comparison of the products from the xenon photolysis of cyclopentanone and sulfolane is presented below. This comparison indicates that the tetramethylene diradical produced from

Product	Cyclopentanone	Sulfolane
C_2H_4	100	100
C_3H_6	1.1	0.87
$1\text{-C}_4\text{H}_8$	1.2	4.2
$\text{c-C}_4\text{H}_8$	1.0	3.7

the photolysis of sulfolane contains less energy than that produced from cyclopentanone. This is likely related to the two additional vibrational degrees of freedom in the SO_2 molecule as compared to carbon monoxide.

D. Photoionization Mass Spectrometer Construction.

All of the components for construction of our photoionization mass spectrometer have been acquired and despite some long delivery times we expect to have it in operation by March 1. The major task in building this instrument has been in the construction of the vacuum chambers. These are now complete; the system has been assembled and all that remains to be done is the check-out of the vacuum system. It would not have been possible to accomplish this so inexpensively and so well without the fine work of our machinist and mechanical designer Charles A. Keisling. A photograph of the instrument in its present state of completion is attached.

Our first attempt with this system will be a study of trimethyl amine. Hellner and Sieck¹ have already investigated this system and evaluated the rate constant for the reaction. We will use this reaction to evaluate the kinetic parameters of our instrument.

Once this is accomplished we will investigate the reactions of THF, THT and pyrrolidine parent ions produced by 123nm photoionization of these compounds.

1. L. Hellner and L.W. Sieck, Inter. J. Chem. Kinetics, 5, 177 (1973).

E. Ionization Efficiency and Extinction Coefficient Determination

Using saturation ion current measurements as described in our last report, No. AT(11-1)-3569-3, we have continued to determine ionization efficiencies (η) and extinction coefficients (Σ), for most of the molecules with which we have been concerned. These are being determined routinely as we continue to investigate these molecules. These constants are useful in our photochemical studies and are not readily available in the literature. The constants determined are presented in Table I. As we accumulate this kind of data we are beginning to develop an understanding of the factors which affect ionization efficiencies. We believe that the photoionization of these molecules is mainly autoionization and consequently structure and mass have pronounced effects in determining the availability of alternate reaction channels. The greater the number of reaction channels alternate to ionization and the faster these reactions the lower will be the ionization efficiency. Our ideas on this problem are not yet firm enough to clearly suggest an approach to this problem. However as we accumulate this information and analyze it different approaches are suggested and pursued.

A preprint of our paper which enables ionization efficiencies and saturation currents to be used as an actinometer at 147 nm is attached. We believe this to be a significant contribution since it enable quantum yields to be measured routinely and easily.

Ionization Efficiencies and Extinction Coefficients
of Complex Molecules

Molecule	Xe ^a		Kr ^b		Ar ^c	
	η^d	Σ^e	η	Σ	η	Σ
Cyclobutanone	(9.1) ^f		0.24	767	0.22	1320
Cyclopentanone	(9.3)	370	0.28	1190	0.23	2800
Cyclohexanone	(9.1)		0.24	3120	0.24	4760
Tetrahydrofuran	(9.5)	270	0.12			
Trimethylamine	0.39	250				
Triethylamine	0.47	235				
Dipropylamine	0.10	1088				
Diisopropylamine	0.16					
Dimethyl-t-lritylamine	0.38					
Bio-dimethylamine methane	0.49					
Aziridine	(9.3)	205	0.19		0.36	
Azetidine	(9.1)					
Pyrrolidine	0.05	316	0.18		0.28	
Piperidine	0.07				0.36	
Thietane	(8.9)	531	0.44			
Tetrahydrothiophene	.10	501	0.52			