DEVELOPMENT OF ADVANCED TECHNOLOGIES
FOR PHOTOCHEMICAL TRITIUM RECOVERY

Bi-Quarterly Progress Report
For the Period
July 1, 1981 through December 31, 1981

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MASTER

February 3, 1982

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ABSTRACT

Intensive research on infrared photolysis of chloroform began, and laser development and process studies for the tritium recovery continued during this reporting period.

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I. INTRODUCTION

During the past reporting period important progress was made in characterizing the photochemical processes used in tritium recovery by isotopically-selective infrared laser multiple-photon dissociation (MPD) of chloroform. Experimental assessment of 12 μ lasers for tritium separation continued, the apparatus for performing T/D laser enrichment measurements was constructed, and progress was made in the overall process analysis.

II. SYNTHESIS OF MONOTRITIATED WORKING MOLECULES

The CTF_3 , CTCl_3 , and CTBr_3 synthesis procedures outlined in earlier reports¹ are totally satisfactory for the program. No new research was done to improve them.

The impurity found in all the CTCl_3 samples synthesized last period,¹ that was characterized by the infrared absorption peak near 794 cm^{-1} , is CCl_4 . This carbon tetrachloride contribution is mainly due to a contamination in early samples of CDCl_3 ; fresh chloroform-d samples have no such impurity. However, the CCl_4 infrared peak appears to increase with the age of the tritiated sample, presumably due to radiolysis, so a minute part of this impurity may be due to the exchange process itself.

Though the $\sim 10\text{Ci}$ samples of CTF_3 and CTCl_3 stored in $\sim 50\text{ cc}$ stainless steel containers appear to be stable over the period of several weeks, decay due to radiolysis is evident during 6 month - 1 year storage. Specifically, after 11 month storage, most of the CTF_3 in Run 29 disappeared; instead, a copious quantity of SiF_4 was observed. About half the $\text{CTCl}_3/\text{CDCl}_3$ reacted after 6 months (Run 43). In addition to the large quantities of CCl_4 (790 cm^{-1}) that formed, some HCl appeared. The previously small peak in the infrared spectrum at 1850 cm^{-1} grew much larger, due to another radiolysis product.

In runs 54-57 (see previous reports), more CTCl_3 was produced.

III. MOLECULAR PHOTOCHEMISTRY

CDCl₃ IR Photolysis

Past studies of chloroform pyrolysis do not give a definitive prediction of the nascent dissociation pathways of pulsed infrared laser multiple-photon excited molecules. Several investigations²⁻⁵ suggest that molecular elimination occurs as in Eq. (1) for CTCl₃/CDCl₃ mixtures:

Still, the results of other studies^{6,7} imply that atomic elimination dominates as in Eq. (4):

Using the most recently measured value of the enthalpy of dichlorocarbene,⁸ the overall ΔH for reaction (1) is ~ 56 Kcal/mole, while it is ~ 70 Kcal/mole for reaction (4). Since molecular dissociation should have a small barrier, ~ 3 Kcal/mole, while the atomic dissociation route essentially no barrier, the activation energy of the first route is lower by only ~ 10 Kcal/mole. Since the pre-exponential factor for atomic elimination is relatively larger, the rates of the two processes should be competitive in MPD of CTCl₃.

Though T/D recovery will be successful with either elimination route dominant, it is clearly quite important to learn the details of the reaction dynamics. For example, in some cases the addition of molecular scavengers of radicals may be essential [reaction (5)]. Examination of the MPD reaction dynamics in chloroform began this reporting

period. Some observations and interpretations cited here are more accurate than those reported earlier in Ref. 9.

CDCl_3 was photolyzed using up to 1.5 J of R(48), 10.91 μ from a TEA CO_2 laser under a variety of experimental conditions. Analysis was performed by gas chromatography using an n-octane/porasil C column, which separated the various reactants and products quite well. Still, appreciable experimental effort was required to characterize and improve the collection efficiency of the apparatus (which is essential in experiments involving tritium), and to investigate the saturated and non-linear response of the overall detection system.

Typically, four carbon-bearing photoproducts were observed in the MPD of neat CDCl_3 . Tetrachloroethylene was usually the major product at lower pressures, ≤ 200 mtorr. Carbon tetrachloride was always observed in quantities in excess of the impurity levels that were found to be present in early samples of CDCl_3 . The yield of trichloroethylene varied markedly from run-to-run; wall reactions were shown to be responsible for forming this product.

The identification of the fourth photoproduct was somewhat difficult. In a previous report,⁹ a column which more poorly separated the products was employed, and this last photoproduct was identified as 1,1-dichloroethylene. Mass spectrometric and infrared spectroscopic measurements of the separated product now prove that it is instead dichloroacetylene (C_2Cl_2). In one instance, phosgene (COCl_2) was also observed, presumably due to an oxygen impurity. Though C_2Cl_2 is reported to be quite unstable in air in large quantities, ~ 50 torr-cc were stored in vacuo for several months with no signs of decomposition, before being pumped away.

At lower CDCl_3 pressures, ≤ 200 mtorr, C_2Cl_2 was a minor MPD product; however, with ≥ 1 torr CDCl_3 , and fluences of $\geq 1 \text{ J/cm}^2$, thermal runaway occurred with nearly complete conversion to roughly equal quantities of C_2Cl_2 and (presumably) DCI . In the low pressure experiments C_2Cl_2 may be formed as a

secondary process by 10.9 μ photolysis of cold or hot C₂Cl₄. Fortunately, C₂Cl₄ does not absorb at 12 μ , the wavelength used in T/D recovery.

A series of runs was performed in which the number of 1.4J P(48), 10.91 μ pulses focused (50 cm f.l. KCl lens) into a photolysis cell (100 mtorr CDCl₃) was varied. With fewer than $\sim$ 200 pulses irradiating the cell, only the four mentioned carbon-bearing photoproducts were detected, and the conversion fraction was linear with the number of pulses. With more than 200 pulses, two other heavy, unidentified products formed due to secondary photolysis.

The laser removed 20% of the CDCl₃ reactant after 225 pulses, measured directly by the depletion in CDCl₃. However, only 45% of this depletion can be traced to the four products based on carbon balance, assuming all five molecules have equal thermal conductivity responses. The discrepancy may be due to either of these response factors, possible polymer formation, wall reactions, or nonlinear gas chromatograph response. This last contribution was examined further; it may well account for $\sim$ 50% of the discrepancy. Assuming a critical fluence above which reaction occurs with unity probability, and below which there is no reaction, the critical fluence for CDCl₃ is very roughly 20 J/cm² for P(48) (916.6 cm⁻¹). Note that the ν_4 peak in CD³⁵Cl₃ is at 913.3 cm⁻¹ and the laser line used is actually on the blue side of the peak. Also $X_{44} = -10.6$ cm⁻¹,¹⁰ so that the peak of the MPD spectrum may be closer to 900 cm⁻¹, which could not be obtained with our CO₂ laser.

During the course of this set of experiments, occasionally a run was performed under conditions identical to a previous run. In these cases, the trichloroethylene product was invariably smaller, while the tetrachloroethylene was larger in the later run, though the fraction of removed CDCl₃ remained the same. Evidently the trichloroethylene formed more easily in the earlier runs with unseasoned walls. It was also found that the reaction product mixture left in the photolysis cell for 16 hours before analysis was identical to that analyzed immediately.

The fluence dependence of the C_2Cl_4 product pulse, normalized to the initial $CDCl_3$ concentration, is shown in Fig. 1 (100 mtorr $CDCl_3$, 50 cm f.l. lens, P(48), 10.9 μ). Above the threshold at ~ 0.1 J the C_2Cl_4 yield is linear with fluence.

The yield of the four carbon-bearing products is shown as a function of the $CDCl_3$ pressure for 0.74 J, P(48) pulses in Fig. 2. At pressures below ~ 200 mtorr, the primary dissociation process is collision-free and C_2Cl_4 is the only important product; whereas at higher pressures, thermal effects appear and larger amounts of other products, especially C_2Cl_2 , are formed.

The addition of 46 torr argon buffer to 100 mtorr $CDCl_3$ [0.75 J, P(48)] did not affect the depletion of $CDCl_3$, but had a dramatic impact on the product distribution. The C_2Cl_4 yield was unchanged; the C_2DCl_3 peak totally disappeared even with the addition of a few torr argon; the C_2Cl_2 product decreased to essentially zero with 46 torr argon, while the CCl_4 increased. Evidently the buffer did not affect the primary MPD process, but only the subsequent chemistry. Heterogeneous production of trichloroethylene is inhibited because of the longer diffusion time to the wall. The appearance of large amounts of CCl_4 suggests that the molecular dissociate route, reactions (1)-(3), is not the sole decomposition pathway.

Added hydrogen affected the product distribution in a quite different manner. Tetrachloroethylene monotonically decreased with added H_2 , to $\sim 1/10$ its unbuffered yield with 60 torr added (100 mtorr $CDCl_3$, 0.75 J, 10.9 μ). At these high pressures C_2DCl_3 also decreased to zero, but the yield of C_2Cl_2 increased to twice its unbuffered yield with 2 torr H_2 , and decreased to only its unbuffered quantity with 60 torr H_2 .

In high temperature pyrolysis studies of $CDCl_3$, H_2 can play a major role in the chemistry after unimolecular decomposition. In the molecular route, reaction (6) is the analog of reaction (1):

The enthalpy change of reaction (7) is ~ -23 Kcal/mole; most likely it has a very small energy barrier and proceeds rapidly at ambient temperature. Note however, that CHCl_2 absorbs at 900 cm^{-1} ,¹¹ which is near the laser frequency. Added D_2 , would produce CDCl_2 , which absorbs near 974 and 815 cm^{-1} .¹¹

For atomic elimination, the following steps would occur:

No dichloromethane was observed with added H_2 ; however, reaction (9) is expected to be very slow at ambient temperature, based on the analogous reaction of CCl_3 ($\log A = 12.32$, $E_{\text{act}} = 14.3$ Kcal/mole).

The main affect of added hydrogen in CDCl_3 MPD, as exemplified by the drastic decrease in C_2Cl_4 yield, is in vibrational relaxation of hot CDCl_3 ; thus unimolecular decomposition of chloroform is strongly inhibited with added H_2 . Perhaps, C_2Cl_2 is formed as a result of collisions of hot CDCl_3 molecules which are not sufficiently energetic to unimolecularly dissociate.

Preliminary experiments of MPD on dilute mixtures of CDCl_3 in CHCl_3 (1:10/ CDCl_3 : CHCl_3 , 200 mtorr) were performed. The product distribution was the same as with neat CDCl_3 , with the exception of the appearance of a new unidentified peak; this may be due to an impurity in the gas handling system and is under investigation.

Ammonia Laser Development

The mirrorless, superradiant one-pass NH_3 laser was further investigated during this reporting period, by focusing the R(30), 9.22μ CO_2 laser into a cell much longer than the 115 cm long cell used earlier.¹ Effective 2 m focal length optics, focused the pump ~ 2 m inside the 292 cm long cell which contained various mixtures of NH_3/N_2 . Measurement of the wavelength-unresolved 12μ output showed that a maximum of 500 mJ per pulse could be obtained at ambient temperature employing 1 torr $\text{NH}_3/40$ torr N_2 mixtures. Using a CCl_4 cold gas filter to selectively absorb the lines near 750 cm^{-1} , it was shown that all but at most 60 mJ of the output was in the $828\pm 30\text{ cm}^{-1}$ spectral bandwidth.

More detailed wavelength examination of the one-pass NH_3 laser began late in the reporting period. With the ammonia laser mixture set for maximum 12μ output, $\leq 5\%$ of the entire output was at 828 cm^{-1} , corresponding to the sP(7,K) transitions which are directly coupled to the sR(5,K) pumping lines. Most of the observed energy is due to the inversion of lower rotational levels populated by collisions with the N_2 buffer (which needs to be added to increase NH_3 absorption of the pump line). About $\sim 55\%$ of the 12μ output has photon energy in the range $814\text{--}817\text{ cm}^{-1}$, due to the aP(6,K) transitions; $\sim 30\%$ is in the $833\text{--}835\text{ cm}^{-1}$ range, aP(5,K); and $\sim 25\%$ is near 854 cm^{-1} due to aP(4,K). With less added N_2 , the overall output decreases, but the fraction of output power from the directly laser-pumped rotational states increases. Details will be presented in the next report.

Tritium Enrichment Measurements

The vacuum system was upgraded to the extent required to begin initial tritium enrichment experiments in the coming reporting period. An ionization chamber was installed at the effluent port of the gas chromatograph to monitor the tritium concentration of the reactant and various product peaks. This device is sensitive enough to conduct experiments on only a few torr•cc of 10-100 ppm $\text{CTCl}_3/\text{CDCl}_3$. Such dilute mixtures of tritiated chloroform were prepared.

IV. PROCESS DEVELOPMENT

A process to photochemically remove tritium from heavy water was described in Fig. 2 of the previous progress report.¹ Order-of-magnitude cost estimates for this process have been made, based on the specifications, assumptions, and parameters shown in Tables 1, 2, and 3 (some of which are revised since the last report, Ref. 1, Tables 3-5). The estimated costs of each unit and of the complete system are given in Table 4. The total capital cost (excluding laser cost) of \$650,000 corresponds to a cost of \$0.08/Ci tritium removed, for plant amortization over one year. From Table 3, the electrical load is about 154 kW; this is equal to a cost of \$0.01/Ci tritium removed (80% capacity factor, \$0.05/kWh). Therefore the order-of-magnitude total cost of tritium removal is about \$0.09/Ci.

Experimental data on the $D_2O/DTO/CDCl_3$ system are needed to permit a detailed design of the exchange unit; the necessary experiments will soon be performed by a summer student.

The stripper concept must also be better defined. With a good understanding of these units, the crucial parameters and tradeoffs can be identified and balanced in a final process design. The collaborative effort with the Savannah River Laboratory will help with process development, and will ensure that all Savannah River Plant requirements are met.

TABLE 1. Initial specifications - Cleanup of Savannah River Plant Heavy Water Reactor.

Reactor volume:	500 tonne D_2O
Tritium concentration:	20 Ci/liter
Desired Tritium level:	2 Ci/liter (10% of initial concentration)
Time allowed to reach desired level:	1 year

TABLE 2. Assumptions used in calculation of mass balance data shown in Table 3.

o	Chloroform flow in exchange unit is 130% of theoretical minimum.
o	Photoproduct stripper efficiency is 100%
o	Optical selectivity: $S = 650$ for laser-induced reaction
o	Enrichment factor: $\beta = 1000$ for laser-induced reaction

TABLE 3. Process parameters for the cleanup of Savannah River Plant Heavy Water Reactor.

Heavy water flow through exchanger	7.1 liter/min
Chloroform flow through exchanger	41.6 liter/min
Protoproduct formation rate:	
TCI	0.6 cc/min
DCI	5.0 cc/min
C_xCl_y	7.9 cc/min
Make-up chloroform flow	12.5 cc/min
Electric power to laser (1.25% efficiency)	111 kW
Pumping power (reactor at 100 torr, rest of process at 1 atm)	43 kW

TABLE 4. Approximate Capital Costs of Tritium Cleanup System for Savannah River Plant.

Exchange Unit	\$38,000
Reaction Tube	\$21,000
Compressor	\$58,000
Photoproduct Stripper	<u>\$19,000</u>
Cost of major units	\$136,000

Applying Lang factor of 4.8 (Peters and Timmerhaus, Plant Design and Economics for Chemical Engineers, 3rd edition, p 181) gives total capital cost estimate of \$650,000 (excluding laser cost).

V. PROGRAM PERSONNEL

Frank Magnotta joined the Laboratory and the tritium recovery program during this reporting period, and recently received his Q-clearance. Also, Frederick Aldridge transferred to this effort from another program in O-Group.

Irving Herman visited the Savannah River Laboratory and discussed with staff members the special tritium recovery needs of the Savannah River Plant. As a result of this visit, Robin Young of SRL will join the tritium recovery program to investigate the process engineering aspects of the process along with Jon Maienschein of the LLNL Tritium Facility.

VI. CONCLUDING REMARKS

In the coming reporting period, the performance of the laboratory-scale ammonia laser will be optimized, and initial T/D enrichment measurements will be made. Work on short pulse, high power 12μ laser sources, laser photochemistry and process development will continue.

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FIG. 1. The fluence dependence of C_2Cl_4 product with P(48), 10.9μ focused by a 50 f.l. lens on 100 mtorr $CDCl_3$. Normalization assumes equal detector response for $CDCl_3$ and C_2Cl_4 , an irradiation volume equal to 2×10^{-3} of the cell volume, and includes a factor of 2 accounting for the carbon balance.

FIG. 2. The yield of the 4 carbon-bearing photoproducts in CDCl₃ MPD with 0.74 J, P(48), 10.91 μ focused on the sample by a 50 cm focal length lens. Identical normalization was used for all products.

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