NOVEL PRODUCTS IN THE CO_2-LASER INDUCED REACTION OF TRICHLOROETHYLENE

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Previous reports on the thermal or CO_2-laser induced decomposition of trichloroethylene have identified only one condensible product, hexachlorobenzene (in addition to HCl and mono- and dichloroacetylene). We have found that trichloroethylene vapor exposed to cw irradiation on the P(24) line of the (001 – 100) band of the CO_2 laser at incident power levels from 8 – 17 W produces numerous products, of which the 13 major ones have been identified using IR, GC/MS, GC/FTIR, and NMR methods. All of these products have 4, 6, or 8 carbons, are highly unsaturated, and are completely chlorinated or contain a single hydrogen. C_4HCl_5 and C_6Cl_6 isomers (three of each) account for ≈ 55% to 85% of total products (based on peak areas in the total ion chromatograms in GC/MS runs), depending on reaction conditions. In addition to characterizing the products, we discuss the dependence of the product distribution on laser power, irradiation time, and cell geometry, and we outline a possible mechanism.

The decomposition of trichloroethylene (TCE) under CO_2-laser irradiation has been the subject of several investigations[1–4]. All used pulsed transversely excited, atmospheric pressure (TEA) lasers to initiate non-thermal reaction by multiphoton excitation; one commented briefly on the reaction induced by cw irradiation[2]. Multiphoton excitation produces primarily dichloroacetylene and smaller amounts of chloroacetylene. There has been considerable controversy as to whether the primary reaction step is HCl elimination or C–Cl bond breaking; this has apparently been settled on the side of HCl elimination[4], at fluences up to 100 J cm^{-2}. Prior results on the cw laser induced reaction reported only HCl, C_2Cl_2 , and hexachlorobenzene as products. This recalls the reaction of tetrachloroethylene to produce hexachlorobenzene when sensitized by CO_2-laser excited BCl_3 (ref.[5]). Hexachlorobenzene is also produced in theoretical yield by thermal pyrolysis of TCE between 385 and 445 °C (ref.[6]).

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While most studies of CO_2-laser induced reactions have used pulsed TEA lasers, studies using cw lasers have also been fruitful. The groups of Pola et al.[7] and Zitter et al.[8] have been particularly active in this area. As has been pointed out[9], this technique provides a means of studying thermal effects on reactions which minimizes surface effects. The present study was undertaken to obtain more definitive results on the cw laser induced reaction of TCE, and to compare those to the thermal and TEA laser cases. In contrast to all previous reports, we have found numerous condensible products. Depending on laser power, irradiation time, and cell geometry, we have found up to 13 "major" stable products, plus about twice that number of trace components. We detail the identification of the major products and outline a possible mechanism to account for their formation. We discuss how the product distribution is affected by experimental conditions.

EXPERIMENTAL

We used a Coherent Model 42 CO_2 laser. The beam was collimated from ≈ 5 mm diameter to ≈ 2 mm diameter by a pair of NaCl lenses. Laser power was monitored by a Coherent Model 301 power meter. Samples were irradiated on the (001 – 100) P(24) line at 940.56 cm^{-1}, which is absorbed by the ν_{10} ($-CCl_2$ asymmetric stretch) of TCE (ref.[4]). The wavelength was checked on an Optical Engineering CO_2 Spectrum Analyzer. The reaction cells were pyrex tubes with o-ring joints on the ends. NaCl windows were held on over viton o-rings by atmospheric pressure. The openings were 15 mm i.d., and the simplest cell was a cylinder of this diameter. Two other cells were used: a 15 mm cylinder with two sidearms, and a 100 ml round bottom flask with o-ring joints attached. In all cells, path length was 10.5 ± 0.2 cm. Cells were equipped with high vacuum glass stopcocks and were connected to a standard glass vacuum system for introduction of TCE. The background system pressure was ≈ 0.13 Pa. TCE pressure in the vacuum system was measured on a mercury manometer. Most runs were done with 8 – 9 kPa TCE (its vapor pressure at ambient temperature) or with ≈ 0.25 ml of TCE frozen into the bulb cell. This provided increasing pressure (up to about 27 kPa) as the cell warmed during irradiation. The TCE was MCB chromatoquality (99+%) and was degassed by repeated freeze-thaw cycles prior to use, and again daily if a sample was to be taken. Following irradiation, condensible products were collected by mechanical scraping and dissolving in methylene chloride.

Analysis of gaseous contents of the cell and preliminary analysis of condensible products (in KBr pellets) was done on a Beckman IR 20A or a Perkin–Elmer 1310 infrared spectrophotometer. Further analysis was done using a Hewlett–Packard 5988 GC/MS with a 30 m, 0.32 mm i.d., DB-5 column, a Digilab FTIR interfaced with a Hewlett–Packard GC (identical column), and a Varian VXR-300 NMR.

RESULTS

Based on previously published results, we expected to find C_2Cl_2 and hexachlorobenzene as major products. Initially, however, we saw no C_2Cl_2 and, while hexachlorobenzene could be tentatively identified by its IR peaks in a KBr pellet, there were other, unidentified products. When results from runs in the cylindrical cell and the 100 ml bulb were compared, it was clear that a much more complex mixture was obtained in the bulb. In order to obtain sufficient products for analysis, we froze ≈ 0.25 ml of TCE into the bulb, to provide a continuous source of vapor over an irradiation time extending up to several hours. In this way, we collected enough material to identify 13 products. Then we could analyze much smaller samples from single runs by matching GC retention times, in order to further investigate the reaction under various conditions.

A total ion chromatogram (TIC) from a GC/MS analysis of a single run in the bulb cell is shown in Fig 1. Mass spectra gave molecular formulae for all 13 major products. These were compounds which accounted for at least 1% of the peak area in the total ion chromatograms of bulb cell reactions run for 15 min or more at 20 – 22 W. (As Fig. 2 shows, the distribution changes slowly at longer times.) Four compounds were identified by matching with library spectra furnished with the GC/MS instrument. In the remaining cases, comparison to published spectroscopic data was used, with the exception of compound *VIII*, for which no data were found. Following is a brief discussion of the basis for identification of each compound. All IR spectra of compounds analyzed were obtained by GC/FTIR. This information is summarized, and the formulae are given, in Table I (refs[10–17]).

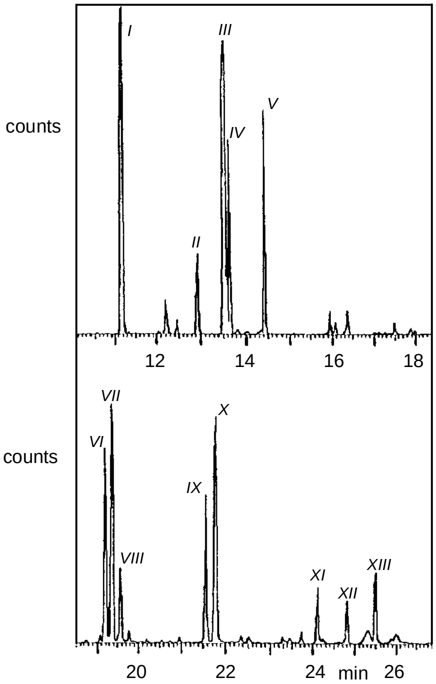


FIG. 1
The total ion chromatogram from a GC/MS run on the products of the reaction of trichloroethylene irradiated for 15 min at incident power of ≈ 16 W. Information for the 15-min points in Fig. 2 was taken from this run. Compounds are identified in Table I. The peak for compound *I* is approximately 124,000 counts

1,1,2,4-Tetrachlorobutenyne (I). Identification was made through mass spectral interpretation in combination with comparison of the IR spectrum to published IR data[10], in particular the −C≡C− stretch at 2 212 cm^{-1}.

(E)-1,1,2,3,4-Pentachloro-1,3-butadiene (II), *1,1,2,4,4-pentachloro-1,3-butadiene* (III), *and (Z)-1,1,2,3,4-pentachloro-1,3-butadiene* (IV). Compounds *II* and *IV* were identified on the basis of IR spectra and GC retention times (with the (*E*)-isomer being the faster eluting compound)[11]. In addition to matching the IR spectrum[11], 5.0 mg of compound *III* was isolated by preparative GC using a silicone stationary phase. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ in a 100 μl microcell. The C–H coupling constant was measured at 169.7 Hz, compared to the published value of 169 Hz (ref.[11]).

Hexachlorobutadiene (V). This was identified by a match found in the NIH Library[12] furnished with the GC/MS instrument. Identification was confirmed by the IR spectrum, as compared to Sadtler #3229 (ref.[13]).

TABLE I
Principal products from the reaction of trichloroethylene

Compound	Formula	Name(s)	Identification methods
I	C_4Cl_4	1,1,2,4-Tetrachlorobutenyne	IR (ref.[10]), MS
II	C_4HCl_5	(*E*)-1,1,2,3,4-Pentachloro-1,3-butadiene	IR, GC (ret. time) (both ref.[11])
III	C_4HCl_5	1,1,2,4,4-Pentachloro-1,3-butadiene	IR, ^{13}C and ^{1}H NMR (both ref.[11])
IV	C_4HCl_5	(*Z*)-1,1,2,3,4-Pentachloro-1,3-butadiene	IR, GC (ret. time) (both ref.[11])
V	C_4Cl_6	Hexachloro-1,3-butadiene	MS (NIH Library) (ref.[12]), IR (Sadtler #3229) (ref.[13])
VI	C_6HCl_5	Pentachlorobenzene	MS (NIH Library), IR (Sadtler #48116)
VII	C_6Cl_6	1,1,2,5,6,6-Hexachloro-1,5-hexadien-3-yne	IR (ref.[14]), MS
VIII	C_6HCl_7	1,1,2,3,5,6,6-Heptachloro-1,3,5-hexatriene	MS
IX	C_6Cl_6	Hexachlorofulvene [1,2,3,4-tetrachloro-5-(dichloromethylene)-1,3-cyclopentadiene]	MS (NIH Library), IR (ref.[15])
X	C_6Cl_6	Hexachlorobenzene	MS (NIH Library), IR (Sadtler #4545)
XI	C_8HCl_7	α,β,1,2,3,4,5-Heptachlorostyrene [pentachloro(1,1-dichloroethenyl)benzene]	MS, GC (ret. time) (ref.[16])
XII	C_8HCl_7	β,β,1,2,3,4,5-Heptachlorostyrene [pentachloro(1,1-dichloroethenyl)benzene]	MS, GC (ret. time) (ref.[16])
XIII	C_8Cl_8	Octachlorostyrene [pentachloro(trichloroethenyl)benzene]	MS (ref.[17]), GC (ret. time) (ref.[16])

Pentachlorobenzene (VI). This was identified as in the previous case. The Sadtler spectrum number is #48116.

1,1,2,5,6,6-Hexachloro-1,5-hexadien-3-yne (VII). Mass spectral interpretation and comparison of the IR spectrum to the published spectrum[14] were used to identify this compound.

1,1,2,3,5,6,6-Heptachloro-1,3,5-hexatriene (VIII). This structure is tentative, as no published data were found. The mass spectrum gave the molecular formula. The structure is plausible in terms of the reaction conditions in that it results from addition of HCl to compound *VII*.

Hexachlorofulvene (IX). This was identified by a mass spectral match in the NIH Library[12] and by the agreement of the IR spectrum with the published spectrum[15].

Hexachlorobenzene (X). Identification was made using the NIH Library match[12] and comparison of the IR spectrum to Sadtler spectrum #4545 (ref.[13]).

α,β,*1,2,3,4,5-Heptachlorostyrene* (XI) and β,β,*1,2,3,4,5-heptachlorostyrene* (XII). The identification of these compounds is somewhat less certain, due to the small amounts obtained, and the apparent absence of published IR and mass spectra. The identifications are proposed on the basis of the mass spectrum and the GC retention time relative to compound *XIII* (ref.[16]).

Octachlorostyrene (XIII). This identification is based on the comparison of the mass spectrum to published data[17]. Also the GC retention time relative to the compounds *XI* and *XII* is consistent with published results[16].

After identifying the products, we were able to investigate additional features of the reaction. The first was the effect of time on product distribution. This is shown in the bottom panel of Fig. 2 for samples irradiated in the bulb cell at 15 – 17 W incident power (20 – 22 W laser output). All these runs had a reservoir of liquid TCE in the cell, so the amount of products naturally increased with time. In addition, however, percentages of some compounds, notably *I* and *VII*, changed significantly with time. This variation is consistent with these being produced early and acting as precursors to other products. This panel is based on peak areas in the TIC. The top panel of Fig. 2 shows the yields of the three compounds for which calibration curves could be constructed using authentic samples. For these three components, the calibration plots of peak area vs mass were nearly identical over the range 0 – 2 mg ml^{-1}.

Table II shows results on the effects of irradiation power and cell geometry on the product distribution. The numerical values are percentages of the peak area in the total ion chromatogram. At less than about 8 W, no perceptible product formation occurs within an hour. Row 3 of Table II lists the distribution for a sample irradiated at 10 W for 90 min. For comparison, results from ten-minute and one-hour runs at high power, also in the bulb with a reservoir of TCE, are shown in the first two rows. Clearly the mixture is skewed far toward the lower molecular weight products compared to high-

TABLE II
Effect of power and cell geometry on product distribution

No.	Conditions	Compound											
		I	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*	*X*	*XI* and *XII*	*XIII*
1	20 – 22 W 10 min	15	2	25	3	7	7	15	3	5	14	1	3
2	20 – 22 W 1 h	12	4	17	6	8	10	11	4	7	13	4	4
3	10 W 90 min	26	3	40	5	2	3	9	2	2	7	–	–
4	Cylindrical cell, vapor only	–	–	–	–	–	13	t[a]	–	t[a]	64	t[a]	22
5	Bulb, vapor only 20 W, 30 min	11	2	33	4	7	3	18	6	2	8	1	4

[a] Trace.

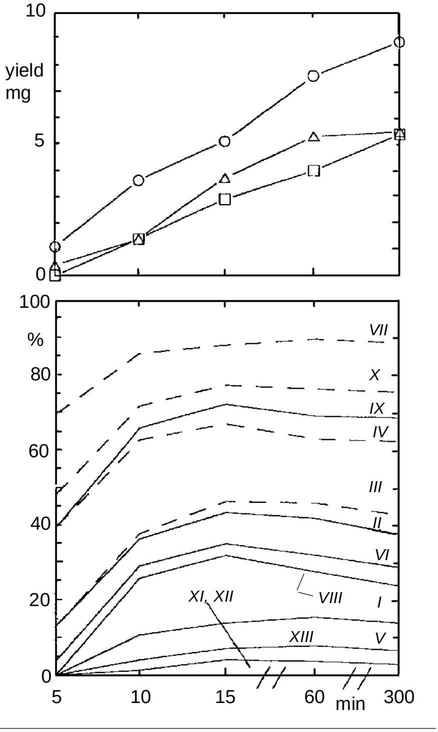


FIG. 2
Reaction products vs time for irradiation of TCE at 15 – 17 W incident power. The bottom panel is a distribution plot for the percentages of total peak area in the total ion chromatogram. The percentage due to each compound is given by the height of the interval of the section with that compound number. Compounds with different molecular formulae are separated by solid lines. Isomers are separated by dashed lines (except for compounds *XII* and *XIII*). The top panel gives absolute yields of the three compounds for which authentic samples were available. These values are accurate to within ≈ 15%: ❒ Hexachlorobutadiene, Δ pentachlorobenzene, ❍ hexachlorobenzene

power runs. This is as one would expect; lower power produces lower temperatures, so the reaction is not driven toward the heavier products.

The final factor influencing product distribution is cell geometry. After a series of 16 runs at 14 – 18 W for from 6 – 20 min with vapor only (8 – 9 kPa) in the cylindrical cell, the collected products had the distribution given in row 4 of Table II. Here there are only three major products, with hexachlorobenzene dominant. Since this was done with no reservoir of liquid, one must question whether that or the cell geometry is responsible for the difference. A run with vapor only in the bulb cell produced a mixture which was not substantially different in composition (although smaller in amount) from the mixture obtained with a reservoir, as seen by comparing row 5 with rows 1 and 2. Thus cell geometry is indeed the main factor in the different distribution of row 4.

The final aspect of the experimental investigation of this reaction was the isolation of C_2Cl_2, which we expected to be the *initial* product. A cell with two sidearms was constructed. The body of the cell was a 15 mm i.d. cylinder. The cell was filled with TCE vapor, which was then frozen into one sidearm. With the cell in the laser beam, this sidearm was warmed with water (≈ 40 °C). As soon as all the TCE vaporized, as indicated by a levelling off of transmitted power, the cell contents were frozen into the other sidearm with liquid nitrogen. C_2Cl_2 was detected by its IR peak[18] at 988 cm^{-1}. Maximum production of C_2Cl_2 was obtained after 4 – 6 such passes, after which the amount decreased. We isolated C_2Cl_2 by first separating it from HCl in order to prevent back reaction. This was done by holding the sidearm in an ethanol–liquid nitrogen bath (–120 °C) and pumping on it. Nearly complete separation from TCE was achieved by vessel-to-vessel transfer with the mixture in acetone–liquid nitrogen at –95 °C and the receiving vessel in liquid nitrogen. After two or three transfers, we could estimate the residual pressure of TCE at ≈ 27 Pa, based on its only remaining detectable IR peak. The published IR spectrum of C_2Cl_2 does not allow a quantitative interpretation of its IR peak. We did determine that ≈ 0.8 kPa of O_2 (from air) was required to react completely with a sample of C_2Cl_2 produced as described, which is consistent with a maximum C_2Cl_2 pressure of a few hundred Pascals. This reaction, which produces phosgene as the only IR detectable product[18], provided additional confirmation of the identification of C_2Cl_2. We later detected C_2Cl_2 in the gaseous contents of both the plain cylindrical and bulb cells, where it appears within the first 15 s of irradiation, and disappears within 5 min. Thus, C_2Cl_2 does appear as a product very early in the reaction scheme, as expected. The most likely reason that it is not detectable later is back reaction with HCl, which accumulates as the reaction proceeds.

DISCUSSION

Although it was not our purpose to determine a mechanism for this reaction, we can outline a very plausible scheme, which is based on the initial production of C_2Cl_2 and chain formation of four- and six-carbon radicals from this highly reactive species. Such a scheme accounts for our observations, but we recognize that there are probably multiple pathways to some products, even within this scheme, and there may be other contributing mechanisms.

Based on prior work[4] and on our detection of C_2Cl_2, we propose that the initiation of the reaction proceeds by elimination of HCl from TCE, followed by radical formation and oligomerization.

$$\mathrm{CHCl{=}CCl_2} \longrightarrow \mathrm{ClC{\equiv}CCl} + \mathrm{HCl}$$

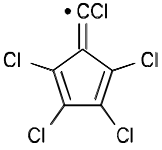
$$\mathrm{ClC{\equiv}CCl} \longrightarrow \mathrm{ClC{\equiv}C^{\bullet}} + \mathrm{Cl^{\bullet}}$$

$$\mathrm{ClC{\equiv}C^{\bullet}} + \mathrm{ClC{\equiv}CCl} \longrightarrow \underset{A}{\mathrm{ClC{\equiv}C{-}CCl{=}\overset{\bullet}{C}Cl}}$$

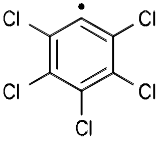
$$\mathrm{ClC{\equiv}C{-}CCl{=}\overset{\bullet}{C}Cl} + \mathrm{ClC{\equiv}CCl} \longrightarrow \underset{B}{\mathrm{ClC{\equiv}C{-}CCl{=}CCl{-}CCl{=}\overset{\bullet}{C}Cl}}$$

By picking up a free chlorine atom, or by abstracting one from another molecule, such as TCE, radical *A* can form compound *I*.

Radical *B* may cyclize to a five- or six-membered ring:



or



C *D*

These radicals may form products *IX* and *X*, respectively, by adding a chlorine atom. Radical *D* may likewise form compound *VI* by adding H, probably by abstraction from TCE.

Compounds *II*, *III*, *IV*, and *V* may be formed via radicals generated from TCE reacting with C_2Cl_2. For instance:

$$\mathrm{CCl_2{=}\overset{\bullet}{C}H} + \mathrm{ClC{\equiv}CCl} \longrightarrow \mathrm{Cl_2C{=}CH{-}CCl{=}\overset{\bullet}{C}Cl} \longrightarrow \mathit{III}\quad .$$

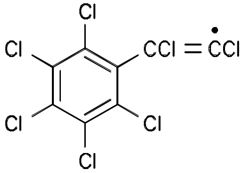
Likewise, the radical $\mathrm{CHCl{=}\dot{C}Cl}$ may react to form precursors to compounds *II* and *IV*, and $\mathrm{CCl_2{=}\dot{C}Cl}$ may react to form a precursor to compound *V*.

Compound *I* may form a radical by loss of Cl, which may then react with another molecule of C_2Cl_2, the resulting radical being a precursor to compound *VII*.

$$\mathrm{\dot{C}{\equiv}C{-}CCl{=}CCl_2} \quad + \quad \mathrm{ClC{\equiv}CCl} \longrightarrow \mathrm{\dot{C}Cl{=}CCl{-}C{\equiv}C{-}Cl{=}CCl_2} \longrightarrow \mathit{VII}$$

As mentioned above, compound *VIII* may be formed by addition of HCl to the triple bond of compound *VII*.

Radical *D* may react with another molecule of C_2Cl_2 to form an C-8 radical.



E

Radical *E* provides a path to the substituted styrene products, by direct addition of Cl (*XIII*) or H (*XI*), or by a rearrangement followed by addition of Cl (*XII*). As would be expected in this case, compound *XIII* is formed in larger amounts than the other two.

As an example of alternative pathways within this general scheme, compounds *II*, *III*, and *IV* may be formed by addition of HCl to compound *I* (or equivalently, to radical *A* followed by addition of Cl).

We believe that the central feature of this mechanism – the chaining of C-2 radicals – is most probably correct. It accounts for the observed products, and it accounts for the absence of products with more than 8 carbons, as the ready cyclization of the C-6 radical (*B*) to produce aromatic structures is preferred to lengthening the oligomers. It is probable that numerous rearrangements occur – for example compound *VII* being converted to compound *IX* or *X*. It is well established that even aromatic hydrocarbons undergo rearrangements at temperatures lower than those achieved here (vide infra) in thermal experiments[19], and previous work in our laboratory has demonstrated the cw CO_2-laser induced rearrangement of azulene to naphthalene[20].

We have not considered any laser-specific effects. Although such effects are known in cw laser induced chemistry, the conditions of our experiments – gas pressures on the order of 13 kPa and laser power well under 100 W – make them sufficiently unlikely that they may safely be neglected[9]. Thus, the mechanism is expected to be similar to that which operates in the thermally induced reaction.

However, there are two important distinctions between our experimental conditions and thermal reactions. The first is the temperature in the reaction zone. The calculation[9] of this value is highly uncertain, due to lack of thermal conductivity data for TCE (not to mention the product mixture). We did the calculation for two similar compounds. Using thermal conductivity data for CH_3CF_2Cl (ref.[9]), we estimate the temperature in the laser beam at the entrance window with the incident power on the cell of 15 – 17 W to be 1 000 – 1 100 K. Using ethylene as the comparison compound[21], the value is 1 200 – 1 300 K. It must be noted that these are local values; there are large gradients both axially and radially.

The other important difference between our experiment and thermal reactions is surface effects. As mentioned earlier, cw laser investigation provides a means of studying a reaction which minimizes surface effects. The only thermal study of TCE decomposition[6] was carried out in a long, thin (≈ 3 mm i.d.) pyrex tube coated with a coherent carbonaceous film, heated in an electric furnace to 385 – 445 °C. These conditions, which obviously favor surface reactions, produced essentially pure hexachlorobenzene as the final product.

In addressing the question of whether our results are consistent with those obtained in the thermal reaction, we note two points. First, the kinetics of the thermal reaction were found to be consistent with the initial step being HCl elimination[6], which is the most probable initiation step in our experiments. Second, the conditions of that reaction – i.e., a hot surface – would favor complete conversion to the thermodynamically most stable product, which we would expect to be hexachlorobenzene, whereas the conditions of our experiments – a hot laser beam region surrounded by a cool surface – enable us to preserve other less stable products which condense on that surface. Thus, we can conclude that our results are consistent with those reported for the thermal reaction, with no evidence for any difference in the basic mechanism.

With respect to the effects of cell geometry, we can surmise that, were we able to "stretch" our cylindrical cell out to a very long thin shape, in which the cell walls would be hot by virtue of proximity to the laser beam, we would then approximate the situation described for the thermal reaction, and would expect to produce hexachlorobenzene. As it is, this compound accounts for about 2/3 of the products formed in high-power reactions in the cylindrical cell, as seen in Table II, with two other aromatic compounds accounting for the remainder. This seems reasonable, if one views this as a case intermediate between the thermal reaction and the reaction in the bulb cell, where a much more complex mixture is obtained.

CONCLUSION

In previously reported work on decomposition reactions of neat TCE, the only reported products have been HCl, C_2Cl_2, C_2HCl, and C_6H_6. We have identified a variety of products in the cw laser induced reaction. Our results are consistent with previously reported results on the thermal reaction, with the different product distributions determined by experimental parameters. Since product distribution is sensitive to reaction conditions, it may be possible, by varying conditions, to isolate larger amounts of products in addition to those thus far characterized. In addition, the question of whether there are any laser specific effects in this reaction can be more definitively addressed by sensitizing the reaction, possibly with BCl_3 or SF_6. A purely thermal reaction would produce the same results regardless of the absorber. However, it has been reported in the cw laser induced decomposition of C_2Cl_4 that the reaction does have some specificity, as it is sensitized by BCl_3 but not by SF_6 or by BBr_3 (ref.[5]).

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REFERENCES

1. Reiser C., Lussie F. M., Jensen C. C., Steinfeld J. E.: J. Am. Chem. Soc. *101*, 350 (1979).
2. Katayama M., Mizugai Y.: Chem. Lett. *1979*, 965.
3. Choo K. Y., Kang T. J., Choi Q. W.: Chem. Phys. Lett. *102*, 321 (1983).
4. Caballero J. F., Wittig C.: J. Chem. Phys. *78*, 7169 (1983).
5. Bachman H. R., Rinck R., Noth H., Kompa K. L.: Chem. Phys. Lett. *45*, 169 (1977).
6. Goodall A. M., Howlett K. G.: J. Chem. Soc. *1954*, 2599.
7. Pola J., Horak M.: Collect. Czech. Chem. Commun. *58*, 121 (1993); and references therein.
8. Zitter R. N., Koster D. F., Cantoni A., Ringwelski A.: Chem Phys. *57*, 11 (1981); and references therein.
9. Zitter R. N., Koster D. F., Cantoni A., Pleil J.: Chem. Phys. *46*, 107 (1980).
10. Roedig A., Bonse G., Helm R., Kohlhaupt R.: Chem. Ber. *104*, 3378 (1971).
11. Carrega M.: Bull. Soc. Chim. Fr. *1968*, 4163.
12. *NBS/NIH/EPA/MSDC Database, Rev. 3.1.* Hewlett–Packard.
13. *Sadtler Standard Spectra*. Sadtler Research Laboratories, Philadelphia.
14. Roedig A., Keipert K.: Chem. Ber. *88*, 733 (1955).
15. McBee E. T., Wesseler E. P., Crain D. L., Hurnaus R., Hodgins T. J.: J. Org. Chem. *37*, 683 (1972).
16. Ramdahl T., Carlberg G. E., Kolsaker P.: Sci. Total Environ. *48*, 147 (1986).
17. Rivera J., Castener J., Ballester M.: An. Quim. *70*, 1194 (1974).
18. Klaboe P., Kloster-Jensen E.: Spectrochim. Acta A *26*, 1567 (1970).
19. Scott L. T.: Acc. Chem. Res. *15*, 52 (1982).
20. Scott L. T., Kirms M. A., Earl B. L.: J. Chem. Soc., Chem. Commun. *1983*, 1373.
21. Gray D. E., Ed: *American Institute of Physics Handbook*, 3rd ed., Sect. 4, p. 149. McGraw–Hill, New York 1972.