

**SPECIFICITY AND NON-SPECIFICITY IN THE SENSITIZED
CO₂-LASER-INDUCED REACTION OF TETRACHLOROETHENE**Boyd L. EARL^{1,*} and Richard L. TITUS²

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Previous workers have investigated the reaction of tetrachloroethene using thermal initiation and CO₂-laser initiation *via* sensitizing species. In both instances, the principal product was found to be hexachlorobenzene. One group reported evidence of laser specificity in this reaction, in that BCl₃ acted as a sensitizer to produce hexachlorobenzene as the principal product, but SF₆ and BBr₃ did not. We have found that specificity is highly dependent on reaction conditions. We reproduced the previous results using similar experimental conditions, but under different conditions, we found that the specificity is lost, with all three sensitizers which we used (BCl₃, SF₆, and SiF₄) sensitizing the reaction to produce mainly hexachlorobenzene. There were some differences among the sensitizers, as, for example, the fact that SF₆ produced the most nearly pure hexachlorobenzene product.

Keywords: Laser chemistry; Sensitizers; Specificity; Tetrachloroethene; Chloroalkenes; Chlorinated compounds.

Previous workers have investigated the reaction of tetrachloroethene initiated by simple heating and by CO₂-laser initiation *via* sensitizing species which absorb the laser radiation¹. At around 700 °C, the principal product in the thermal reaction is hexachlorobenzene. Likewise, the cw-laser-induced reaction has been found to yield primarily hexachlorobenzene. A particular point of interest is that Bachman *et al.*¹ reported specificity in this reaction: to wit that BCl₃ sensitized the reaction producing primarily hexachlorobenzene, whereas SF₆ and BBr₃ did not. (BCl₃ was the first species in which multiphoton absorption of CO₂-laser radiation sufficient to create electronic excitation and dissociation was reported², and it has been used as a medium of absorption to induce reaction in several other chemical systems⁴⁻⁷.) As part of a larger investigation of the cw-CO₂-laser-induced reactions of chlorinated ethenes³, we undertook to investigate this specificity more systematically. We report here on the reaction of C₂Cl₄ sensitized by absorption of cw-CO₂-laser radiation using three sensitizers: BCl₃, SF₆,

and SiF_4 . The significant result of our investigations is that, while specificity does obtain under conditions similar to those of ref.¹, different reaction conditions result in loss of specificity, with only relatively minor differences among the results from the three sensitizers; specificity is highly dependent on reaction conditions.

EXPERIMENTAL

Details of the reaction apparatus and analytical methods and instrumentation were given previously³. Briefly, we used a Coherent Radiation model 42 CO_2 -laser capable of producing ≈ 20 W in the continuous-wave mode, and a set of lenses which focused the beam to ≈ 2 mm diameter. We used an Optical Engineering model 16-A spectrum analyzer to determine the laser lines, and a Coherent model 201 power meter to measure the laser power. We used two glass reaction vessels: a 10.5 cm long \times 15 mm cylinder, and a 100 ml bulb fitted with glass O-ring joints with the same path length. The cell windows were common one-inch diameter NaCl infrared windows. (The vessel used in ref.¹ was a 6 cm \times 25 mm cylinder.) As in ref.¹, we used C_2Cl_4 vapor at its ambient vapor pressure, with some increase in the vapor pressure in one set of experiments associated with cell heating (*vide infra*). We discarded gaseous products and collected condensible products by rinsing out the cell with dichloromethane. These products were analyzed primarily by GC/MS, with some additional analysis using GC/FTIR and NMR. We had identified all of the major products previously³, so only GC retention time was necessary to identify them in this case. Products which occur in smaller but significant amounts, which we had not encountered previously, are discussed in Results and Discussion.

The principal differences between our usual procedure and that of ref.¹ were in the laser power and the sensitizer pressure. While the procedure in ref.¹ could be characterized as "high-pressure, low-power", ours, by comparison, would be "low-pressure, high-power". In the case of BCl_3 , on which ref.¹ concentrated, they used 20–26 kPa BCl_3 , and a laser output power of ≈ 6 W. They did not specify the diameter of the laser beam. We used ≈ 2.6 kPa BCl_3 , and laser output sufficient to produce ≈ 15 W incident on the cell after passing through the focusing lenses.

Under low-pressure, high-power conditions, we ran three types of experiments with each sensitizer– C_2Cl_4 mixture: gas only in the cylindrical cell; gas only in the bulb cell; and ≈ 0.25 ml C_2Cl_4 frozen into the bulb cell, with gaseous sensitizer admitted afterward. Sensitizer pressures in these runs were chosen such that, with 15 W incident on the cell, the power absorbed through the cell was 10 ± 1 W. Thus, although the pressures of the sensitizers were different, the absorbed power and the pressure of C_2Cl_4 were identical in all runs. In the first two protocols, the pressure of C_2Cl_4 was its ambient vapor pressure, ≈ 2.1 kPa. In the last protocol, the C_2Cl_4 pressure would initially be the same, but would increase somewhat as the cell warmed up. However, the bottom of the cell did not exceed ≈ 40 °C, which would increase the vapor pressure to 5.3 kPa. With BCl_3 , we irradiated using the R(32) line of the 10.6 μm (001–100) band at 983.29 cm^{-1} (chosen to be in a region in which another compound which we studied is transparent). SF_6 was irradiated using R(24) of the 10.6 μm band at 978.49 cm^{-1} , or P(14) of the same band at 949.49 cm^{-1} , and SiF_4 was irradiated on P(32) of the 9.6 μm (001–020) band at $1\,033.48\text{ cm}^{-1}$. C_2Cl_4 is transparent to all these lines.

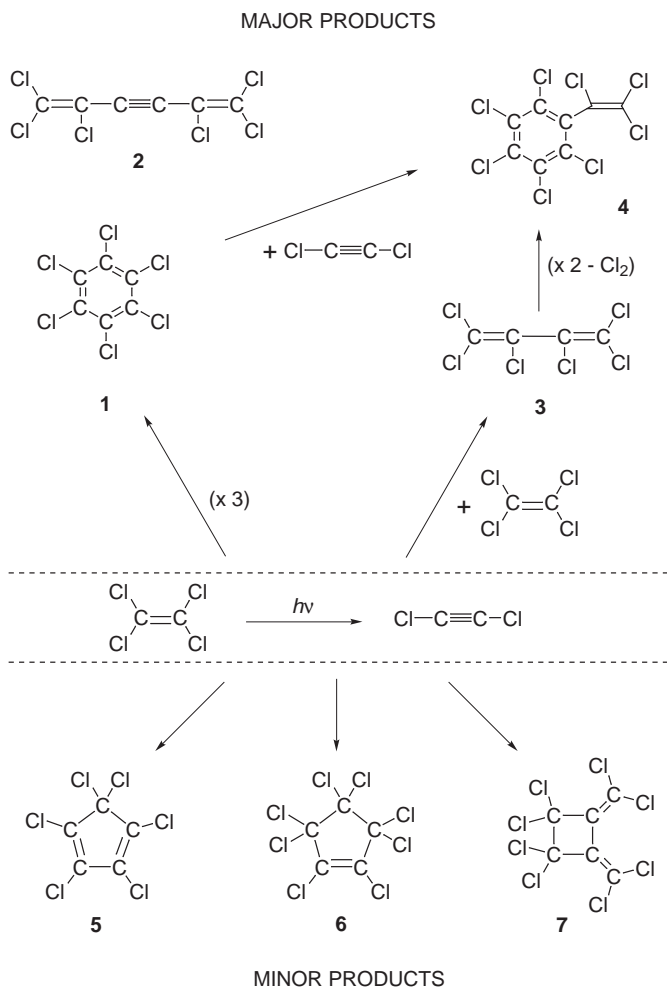
To confirm the results of ref.¹ under high-pressure, low-power conditions, we irradiated BCl₃ using the P(24) line of the 10.6 μm (001–100) band at 940.56 cm⁻¹. The procedure used in ref.¹ was to begin irradiating the cell with only BCl₃ present, then admit C₂Cl₄ from a sidearm. To achieve comparable conditions, we froze a small sample of C₂Cl₄ into the bulb cell with liquid nitrogen, then froze in sufficient BCl₃ from the vacuum line to produce a pressure of ≈20 kPa in the cell. When the cell was placed into the laser beam, the much more volatile BCl₃ vaporized first, resulting in total extinction of the laser beam within one minute. Then the C₂Cl₄ melted and produced vapor at a pressure determined by its temperature in the cell. This effectively created the same situation as in ref.¹. In experiments on SF₆ and SiF₄ under these conditions, we used the 10.6 μm R(24) line and the 9.6 μm P(32) line as above, respectively. We also ran a control with SF₆ using the same line as for BCl₃, 10.6 μm P(24), which it absorbs very intensely.

RESULTS AND DISCUSSION

Scheme 1 shows the products found in this study. In our previous work³ and in other prior work⁸, it has been shown that the initial step in the CO₂-laser-induced reaction of trichloroethene is the formation of dichloroethyne. Given the similarity in the products formed in this case, this is presented as the likely initiating step in the reaction scheme. The four major products, hexachlorobenzene (**1**), hexachlorohexa-1,5-dien-3-yne (**2**, a highly unsaturated linear isomer of **1**), hexachlorobuta-1,3-diene (**3**), and octachlorostyrene (**4**), were all identified in our previous study. Three products which appeared in minor, but significant amounts in some of these experiments, which we did not find in the previous study were hexachlorocyclopentadiene (**5**), octachlorocyclopentene (**6**), which was also identified as a product in ref.¹, and perchloro-1,2-dimethylidenecyclobutane (**7**). Compounds **5** and **6** were identified by GC/MS analysis, based on the NIH mass spectral library⁹. Although this database and spectral matching program proved very accurate in our previous study, these identifications should not be regarded as completely certain, since they are not confirmed by an independent method. For compound **7**, a good match was found with the published IR spectrum¹⁰, but since we have no other basis for this, it should be regarded as tentative. The very small amounts of these three compounds precluded additional analysis. However, our main point in this study, which is the dependence of claimed specificity on reaction conditions, is completely unaffected by any uncertainty which may exist as to the exact identification of these minor products.

Table I summarizes the results of reactions run under low-pressure, high-power conditions. Products are shown in order of decreasing peak size in the total ion chromatogram from GC/MS analysis. The most striking feature of these results is the similarity of the results from the three sensitizers.

Hexachlorobenzene (**1**) was the primary product in every experimental run. On the basis of the total ion chromatograms, the estimated fraction of the total condensable products accounted for by **1** ranged from approximately 40 to >95%. In only a single run did **1** account for less than one-half of the products. The other product which appears most frequently in the table is octachlorostyrene (**4**) which appears in all BCl_3 and SiF_4 runs. Compound **2** appears in all BCl_3 runs.



SCHEME 1

Products in the sensitized CO_2 -laser-induced reaction of tetrachloroethene

Although it was not our purpose to quantitate the yield of these reactions, we could estimate the relative yields in different runs from the intensities of the total ion chromatograms, since all samples were treated identically. This provided an estimate of the relative efficiency of the sensitizers. Based on this estimate, BCl₃ and SiF₄ were roughly equally efficient in sensitizing the reaction, while SF₆ was less efficient by a factor of approximately 5. While this is a significant difference in the efficiencies of the sensitizers, it clearly does not qualify as specificity, in the absolute sense used in ref.¹. Those authors do not state the limits of their conclusion that SF₆ and BBr₃ do not produce reaction, but one must assume, based on

TABLE I

Product distributions in the sensitized CO₂-laser-induced reaction of tetrachloroethene as a function of sensitizer and experimental conditions in "low-pressure, high-power" runs (laser power 15 W, sensitizer pressure as given). Relative error in these results is estimated as ±20% (ref.³)

Sensitizer (pressure) Laser line	Cylindrical cell gas only	Bulb cell gas only	Bulb cell with C ₂ Cl ₄ reservoir
BCl ₃ (2.4 kPa)	1 (60%)	1 (60%)	1 (30%)
R(32) 10.6 μm band	2	4	2 (30%)
	4	2	3
			4
			5
SiF ₄ (0.93 kPa)	1 (80%)	1 (70%)	1 (60%)
P(32) 9.6 μm band	4	4	3
			5
			6
			4
SF ₆ (8.8 kPa)	1 (>95%)	1 (>95%)	1 (60%)
R(24) 10.6 μm band			7
SF ₆ (1.3 kPa)	1 (>95%)	1 (>95%)	1 (80%)
P(14) 10.6 μm band			7
SF ₆ (1.3 kPa)	1 (>95%)		
P(24) 10.6 μm band			

the IR spectrum of the products from BCl_3 , that any reaction produced by the other sensitizers must have been no more than a few percent of that produced by BCl_3 in order for the products to be undetectable.

SF_6 was used at three different laser frequencies, and was, within our ability to estimate, equally efficient at all frequencies. As indicated above, the SF_6 pressure was adjusted to provide the same power absorbed in all cases. This result indicates clearly that the ability of a sensitizer to produce reaction is not strongly dependent on laser frequency within the set of frequencies which are absorbed with sufficient intensity by the sensitizer.

As shown in Table I, product distributions in the gas-only reactions were essentially identical in the two different cells. In the cases of SiF_4 and SF_6 , hexachlorobenzene accounted for at least 90% of the products. However, significantly more complex product mixtures resulted from the reactions run in the bulb with a reservoir of liquid C_2Cl_4 . Two additional products occurred in significant amounts in the case of BCl_3 (**3** and **5**), one occurred in the case of SF_6 (**7**, a somewhat bizarre cyclobutane derivative), and three occurred in the case of SiF_4 : hexachlorobutadiene (**3**), and compounds **5** and **6**, the perchloro forms of cyclopentadiene and cyclopentene.

In comparing these results to those under conditions comparable to the conditions of ref.¹, which will be described below, it must be kept in mind that the results in the gas-only runs are quite distinct from those with a reservoir of liquid. The gas-only results are appropriate to compare to ref.¹, while the latter runs were included only to provide complete data for comparison with prior and projected work in our laboratory. In the gas-only runs, **1** accounts for 60% or more of the total products in all cases, and with SF_6 is the only significant product. The only other products which occur in these runs are **2** and **4**. By contrast, the product mixtures with a liquid reservoir are considerably more complicated, and include the three minor products (**5**, **6**, and **7**) which were not seen in our previous work.

How can one account for the increased complexity of the product mixtures produced with a reservoir of C_2Cl_4 ? As indicated above, during the experimental run, the cell warms appreciably, which raises the temperature of the C_2Cl_4 resting in the bottom of the cell. An additional feature is that the supply of C_2Cl_4 , rather than being depleted as the reaction proceeds, is continuously replenished. Since the formation of hexachlorobenzene must occur *via* some multistep mechanism, one might expect that, in gas-only experiments, less thermodynamically stable products which may be formed at some point are ultimately converted to the more stable hexachlorobenzene. By contrast, with a reservoir of C_2Cl_4 , and an elevated vapor pressure,

there is an ample supply to continue producing some of these intermediate products throughout the course of the reaction.

Our results do not provide a basis for elucidating the reaction mechanism or mechanisms which may be operating in this system. In our previous work³ we described a scheme based primarily on free-radical reactions which would account for all the products. On the other hand, concerted reactions may also be invoked to account for many of the observed products. For example, **4** may be arrived at *via* (i) **1** reacting with either dichloroacetylene or a radical formed from tetrachloroethene, or (ii) Diels–Alder dimerization of **3** followed by elimination of Cl₂. There is no reason to suppose that only a single pathway exists to a given product. Additionally, the presence of even small amounts of **5** and **6**, which have an odd number of carbon atoms, in the product mixtures from some of the experimental runs with the reservoir of liquid tetrachloroethene, is strong evidence of some additional process beyond those discussed above.

High-pressure, low-power runs were carried out with all three sensitizers as described above, in a manner which produced very similar conditions to those of ref.¹. Sensitizer pressure was ≈20 kPa in every case, and the laser power was 6 W. Table II shows the results of these runs, which essentially confirm the main conclusion of ref.¹. (The row Total TIC relative intensity is the sum of the integrated peak areas in the total ion chromatogram for

TABLE II

Product yields in the sensitized CO₂-laser-induced reaction of tetrachloroethene with different sensitizers under “high-pressure, low-power” conditions¹ (laser power 6 W, sensitizer pressure ≈20 kPa). Relative error in these results is estimated as ±20% (ref.³)

Parameter	BCl ₃	SiF ₄	SF ₆ P(24) 10.6 μm	SF ₆ R(24) 10.6 μm
Total TIC relative intensity	550	14	9	no detectable reaction
Products (relative intensity)	1 (350)	1 (12)	1 (4)	< 5 total product intensity
	2 (90)	2 (2)	7 (4)	
	4 (50)		2 (1)	
	C ₁₀ Cl ₈ (24)			
	6 (19)			
	5 (12)			

all products which are at least 1% of the total.) Although the specificity of BCl_3 under these conditions is not absolute, the other two sensitizers produce only 2–3% of the amount of products produced by BCl_3 . Our results are different from those of ref.¹ in that the product mixture is more complex. They reported only a single condensable product in addition to hexachlorobenzene: compound **6**, which they stated was a “minor” product. In our case, hexachlorobenzene accounts for 60% of the products, and, with the addition of compounds **3** and **4**, for 90% of the products. The other products which are more than 1% of the total are compounds **5** and **6**, and a compound which has not been identified, with the molecular formula C_{10}Cl_8 , which comprised 4% of the total. This is the only occurrence of this product in this or prior work in our laboratory.

In the first runs under high-pressure, low-power conditions, we irradiated BCl_3 and SF_6 with the same line as was used in ref.¹, P(24) of the 10.6 μm band. We ran two additional control experiments with SF_6 . The first of these was to irradiate with the R(24) line of the 10.6 μm band, which produced reaction under low-pressure, high-power conditions. This was done to confirm that lack of reaction under the high-pressure, low-power conditions was a result of those conditions, and was not an effect of laser frequency. The second was to do one run with SF_6 under low-pressure, high-power conditions using the P(24) line of the 10.6 μm band, the result of which is shown in the last row of Table I. This was to confirm that irradiation with this line, which produced very little reaction under high-pressure, low-power conditions, produced the expected amount of products under low-pressure, high-power conditions. The final conclusion of these control experiments is that both lines yield reaction, with the same product, under low-pressure, high-power conditions, but little or no reaction under the high-pressure, low-power conditions. There is no doubt that the extent of reaction is indeed a function of these reaction conditions, and not of laser frequency.

Since our experimental conditions were not identical to those of ref.¹, the relatively minor differences in the results are not surprising. Comparison of our results is made somewhat difficult by the lack of specific information. Reference¹ does not state the diameter of the laser beam, which exerts a significant effect on the temperature in the beam¹¹. They do not state which laser line was used to irradiate BBr_3 . They do not state the uncertainty limits on their conclusion that SF_6 and BBr_3 produce no reaction. However, the principal conclusion remains robust: under these high-pressure, low-power conditions, BCl_3 acts very differently from the other sensitizers. By con-

trast, under our other conditions, only relatively minor differences obtain among the three sensitizers.

Reference¹ posited no hypothesis for the observed specificity. Although the present investigation is experimental, we have some suggestions for explaining the differences between their results and ours. (Although one would not suppose that lack of specificity would require an explanation, the fact that specificity obtains under some conditions and not others needs to be explained.)

Two differences are obvious between our protocols and those of ref.¹. At high sensitizer pressures, the laser energy is absorbed within a very small path length very near the entrance window of the cell. This produces a very high local temperature¹¹ (which probably cannot even be estimated) very near the solid surface of the cell window.

By contrast, our protocols involve absorption of 2/3 of the laser power over a 10.5 cm path. Thus, while the temperatures within the beam are "high" (they can be reasonably estimated as being within the range $\approx 1\ 000$ – $1\ 500$ K in the region near the entrance window^{3,11}), they are almost certainly much lower than in the other method. Lack of thermal conductivity data on the reaction mixture precludes a more precise determination. In addition, as has been noted, experiments conducted according to our protocols minimize surface effects in gas-phase reactions¹¹.

A potentially fruitful line of thought for explaining the different results with BCl₃ may lie in its ability to convert vibrational excitation to electronic energy, as evidenced by its visible luminescence. This was not exhibited by the other sensitizers which we used. In addition, with BCl₃, it occurred only under the higher pressure conditions. Our laser power was not sufficient to induce luminescence with the lower pressures of BCl₃ used in our standard experimental protocols. Laser-specific effects are well known in pulsed laser experiments, which deposit sufficient energy to produce electronic excitation and bond-breaking. Thus different results in experiments in which BCl₃ exhibits electronic excitation versus those in which it does not are not surprising.

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