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THE PHOTOCHEMISTRY OF THE MATRIX-ISOLATED DICHLOROETHYLENES

JONATHAN A. WARREN, GEORGE R. SMITH and WILLIAM A. GUILLORY
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 (U.S.A.)

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Summary

The vacuum ultraviolet photolysis of the three isomers of dichloroethylene has been studied in argon, carbon monoxide, nitrogen and krypton matrices at 13 K. Selective excitation into various regions from 1200 to 2050 Å with resonance line sources and a medium pressure Hg lamp resulted in the formation of HCl and chloroacetylene as the major products detected by infrared spectroscopy. Isomerization among the three dichloroethylenes was also important, while the production of acetylene and dichloroacetylene made only minor contributions to the photochemistry. The chlorovinyl radical was not identified, though several unassigned absorptions were observed. The infrared absorptions of chloroacetylene and HCl produced by photolysis of *trans*-1,2-dichloroethylene were shifted from those produced from the other isomers, providing evidence for $\alpha\alpha$ elimination of HCl from the *trans* isomer. The effects of varying the matrix material from Ar to CO, N_2 or Kr show that all the processes, with the exception of the formation of acetylene and Cl_2, arise from triplet states. It is suggested that the $\alpha\alpha$ elimination process observed for the *trans* isomer is due to the participation of a $^3n\sigma^*$ state in the photochemistry of this isomer.

Introduction

In a recent publication [1] we discussed the vacuum ultraviolet photolysis of the difluoroethylenes. In the present paper the results of a parallel study of the dichloroethylenes are presented. The gas phase photochemistry of the dichloroethylenes has been studied several times [2 - 11]. Most recently, Ausubel and Wijnen (AW) [2 - 4] have used classical gas phase techniques to examine the photochemistry between 2000 and 2400 Å. In contrast, Berry [5], the only other author to study all three isomers, used HCl laser emission for product detection.

Over the past several years we have applied the matrix-isolation technique in an effort to gain a better understanding of primary photochemical and photophysical processes [1, 12 - 15]. In this study we make use of the known vacuum ultraviolet absorption spectra of the dichloroethylenes in conjunction with monochromatic light sources to characterize processes resulting from specific electronic excitations.

Experimental

The *cis*-1,2-dichloroethylene (CDCE, Eastman Kodak, 98% min.), *trans*-1,2-dichloroethylene (TDCE, Aldrich, 98% min.) and 1,1-dichloroethylene (DCE, Aldrich, 98% min.) were used without further purification except for pumping on the frozen samples at 77 K. The matrix gases Ar (Matheson Grade), CO (Scientific Gas Ultrapure), N_2 (Liquid Air Ultrahigh Purity), and Kr (Matheson Research Grade) were also used without purification. A matrix to parent ratio of 1000:1 was used in all of the experiments with a total of 10.7 μmol of parent species being deposited over a period of 1.5 h using continuous deposition. The cryogenic system used was an Air Products DE-202 Displex closed-cycle refrigerator.

Photolysis of the matrix-isolated species was accomplished by subjecting the samples on the cold CsI window to radiation from various resonance lamps filtered with an appropriate vacuum ultraviolet transmitting window. In this manner selective excitation into desired spectral regions is accomplished. The resonance line sources and the associated windows used in this study were H/LiF (1216 Å), O/LiF (1305 Å), Cl/LiF (1390 Å), Br/CaF_2 (1477, 1582, 1634 Å), N/CaF_2 (1493, 1743 Å) and C/quartz or CaF_2 (1561, 1657, 1931 Å). Details of the spectral characteristics of these flow lamps and their usage have been discussed elsewhere [12, 13]. In addition to these sources, a Hanovia medium pressure Hg arc lamp (1846, 1940, 2049 Å) was used with a quartz window and a nitrogen purge to prevent absorption of radiation by oxygen (the unpurged Hg lamp was a very inefficient photolysis source). Essentially all of the experiments involved *in situ* photolysis for a period of 3 h.

Identification of the photochemically produced species was made by analysis of the infrared spectra of the films taken with a Perkin–Elmer 180 spectrophotometer calibrated with water and NH_3 lines. Resolution was better than 2 cm^{-1} across the spectral range of interest.

Results

Photochemically, each of the dichloroethylenes decomposes in much the same manner. Each isomer produces the same products with the same relative yields. A typical spectrum of TDCE in Ar, before and after Hg photolysis, is shown in Fig. 1. It can be seen that conversion is very effective with the Hg source (about 86% of the parent species in this experiment has been photolyzed). When higher energy photolysis sources are used, conversion is less efficient but the relative yield of products remains constant.

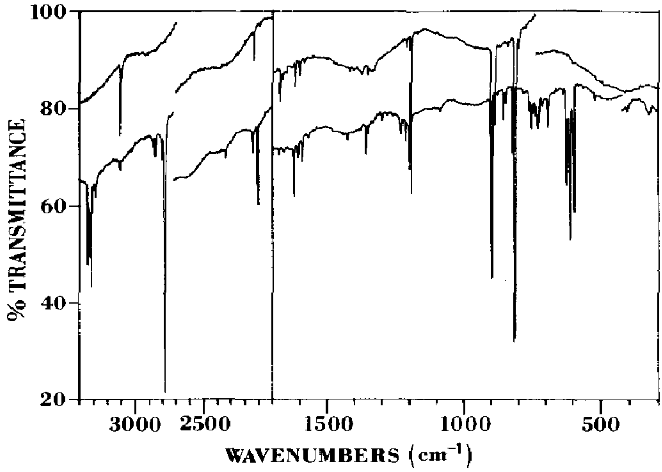

Fig. 1. Infrared spectrum of TDCE isolated in argon at 13 K: upper trace, before photolysis; lower trace, after 3 h photolysis with a N_2 purged Hg lamp.

TABLE 1

Summary of absorptions from photolysis experiments with TDCE in argon

Before photolysis (cm^{-1})	After photolysis (cm^{-1})	Assignments[a]
	3315 - 3341	CA
	3281 - 3303	A
3110	3110	TDCE
	3084	CDCE
	2848 - 2862	HCl
	2781	HCl
	2102 - 2113	CA
1677	1677	TDCE
	1593	CDCE
	1362	?
	1298	CDCE
	1234	?
1200	1200	TDCE
	1040	?
	985	DCA
896 - 909	896 - 909	TDCE
	842 - 852	CDCE
824 - 827	824 - 827	TDCE
	759 - 767	CA
	735 - 744	A
	718	CDCE
	699	CDCE
	608 - 631	CA
	570	CDCE
	408	?
	328	CA

[a] CA, chloroacetylene; A, acetylene; TDCE, *trans*-1,2-dichloroethylene; CDCE, *cis*-1,2-dichloroethylene; DCA, dichloroacetylene.

All of the absorptions of Fig. 1 are summarized and, where possible, assigned in Table 1. By far the predominant process is the formation of HCl and chloroacetylene (CA). Isomerization, though certainly prominent, appears to be somewhat less important, but its contribution is difficult to estimate as these products could undergo secondary photolysis. The formation of acetylene can be definitely identified as resulting from a minor process. Also, a very weak absorption is frequently observed at 985 cm^{-1} which is probably due to dichloroacetylene (this would be the only active fundamental of this molecule within the range of our instrument).

Weak product absorptions at 1362, 1234, 1040 and 408 cm^{-1} are as yet unidentified. These absorptions seem to be independent of each other, but appeared in many experiments. In controlled diffusion experiments, where the window was warmed to about 25 K and recooled, these unidentified absorptions disappeared, implying that they are due to reactive species. In addition, a relatively strong absorption at 1200 cm^{-1} was observed upon photolysis of DCE and CDCE. This absorption was not positively detected in TDCE experiments as this isomer possesses a strong fundamental at 1200 cm^{-1}. The major difference between this absorption and the other unidentified features is, besides its consistency, that it does not disappear upon warming. Thus, it probably corresponds to either a large radical or a stable species.

As mentioned above, the photolysis behavior of the three dichloroethylenes is essentially identical; however, there are two differences. The first concerns the isomerization. On the one hand, isomerization was observed between CDCE and TDCE in moderate yields while DCE produced both CDCE and TDCE in near equal amounts. Isomerization from a 1,2-isomer to DCE, on the other hand, was seen only occasionally when CDCE or TDCE was photolyzed for extended periods, and even then with low yields.

The other significant difference in the photolysis of the three isomers is apparent upon close examination of the absorptions of CA and HCl produced by the photolysis of TDCE in argon. Figure 2 shows the CA absorptions, expanded for clarity*. The transition at 326 cm^{-1} is not shown because of its low intensity. In each absorption region a distinct high frequency feature (marked with an arrow) appeared which was not observed in experiments with CDCE or DCE. Upon warming to 25 K and subsequent recooling these new shifted features significantly decreased in intensity while the other normal absorptions due to chloroacetylene increased in intensity. Identical behavior was observed in the HCl stretching region. In experiments with CDCE and DCE annealing produced no apparent change in the intensities of the CA and HCl absorptions. It appears, therefore, that these high frequency

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*Although not discussed in the main text, it is apparent from Fig. 2 that all the CA fundamentals are split at least into doublets. This behavior is observed in all three isomers. In the case of the 620 - 604 cm^{-1} pair, where the splitting is most pronounced, this is undoubtedly due to the matrix lifting the degeneracy of the CCH bend. For the other absorptions shown in Fig. 2 we must invoke "matrix effects". In any event, the spectra of CDCE and DCE are identical to Fig. 2 with the exception of the features marked with arrows.

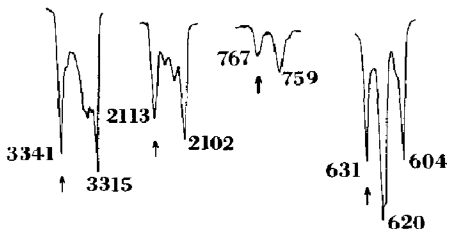

Fig. 2. Expansions of infrared absorptions of chloroacetylene produced by photolysis of TDCE in Ar. Arrows indicate high wavenumber shifts.

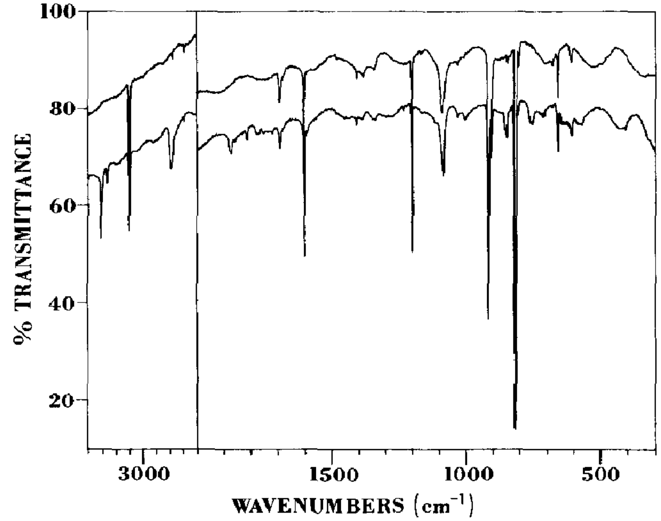

Fig. 3. Infrared spectrum of TDCE isolated in carbon monoxide at 13 K: upper trace, before photolysis; lower trace, after 3 h photolysis with a N_2 purged Hg lamp.

shifts are due to perturbations caused by CA and HCl molecules being isolated in a unique configuration relative to each other.

To aid in the characterization of the mechanisms involved, experiments were performed with CO as the matrix material. The infrared spectra of TDCE in a carbon monoxide matrix before and after Hg photolysis are shown in Fig. 3. Table 2 lists the observed absorptions and their assignments. Two major changes occurred in these experiments. First, new absorptions appeared at 1879, 1859, 1813, 1765, 1642 and 1090 cm^{-1} after photolysis. Upon warming, the features at 1879, 1859 and 1090 cm^{-1} disappeared while the remaining three increased in intensity. These absorptions are identified as due to ClCO [16] (1879), HCO [17] (1859, 1090) and Cl_2CO [18] (1813, 1765, 1642). Other absorptions of these molecules were either obscured or too weak to identify positively. The relative yields, and indeed the absolute yields, of these species are very similar to those seen in experiments performed in this laboratory involving the photolysis of HCl in CO. Thus, most of the production of these species in CO experiments could be due to secondary photolysis of product HCl. This is consistent with an observed decrease in

TABLE 2

Summary of absorptions from photolysis experiments with TDCE in carbon monoxide

Before photolysis (cm^{-1})	After photolysis (cm^{-1})	Assignments
	3310 - 3323	CA
	3261 - 3300	A
3099	3099	TDCE
	3084	CDCE
	2788	HCl
	2103	CA
	1879	ClCO
	1859	HCO
	1813	Cl_2CO
	1765	Cl_2CO
1681	1681	TDCE
	1642	Cl_2CO
	1592	CDCE
	1363	–
	1297	CDCE
	1234	–
1200	1200	TDCE
	1090	HCO
	1040	–
	985	DCA
918	918	TDCE
	849 - 854	CDCE
818 - 821	818 - 821	TDCE
	756 - 764	CA
	737	A
	715	CDCE
	707	CDCE
	610 - 623	CA
	570	CDCE
	408	–
	328	CA

ratios of HCl to CA observed in these experiments as compared with the ratios with an argon matrix. Unfortunately, however, this result does not allow us to draw any conclusions concerning the atomic *versus* molecular elimination modes of dichloroethylene photochemistry.

The other significant observation in the CO experiments involved the yield of photolytic products. The formation of all photolysis products was drastically reduced in experiments carried out in CO matrices. All processes appeared to be equally quenched with the possible exception of the formation of acetylene. The quenching of the process producing acetylene was inconsistent and may not be equally affected by the addition of CO. Also, the shifted absorptions of CA and HCl, from the photolysis of TDCE, were not observed in CO matrices.

Several experiments were carried out with an argon matrix doped with varying amounts of CO. From the resulting data of these experiments, the degree of quenching appeared to have an exponential dependence on the concentration of CO in the matrix.

To study further the effects of the matrix material, some experiments were performed in N_2 and Kr matrices. In N_2 conversion was less efficient than in Ar, but significantly greater than in CO. In Kr matrices, however, conversion was 100% complete; apparently, even the isomerization products were completely destroyed. In both N_2 and Kr matrices relative product yields were the same as in Ar (within the rather broad error limits owing to the comparison of intensities in different matrices), with the exception of the shifted CA and HCl absorptions. In both Kr and N_2 these features were relatively more intense, *i.e.* Kr seems to enhance the formation of the shifted features, while N_2 quenches their formation less than that of the normal products.

Discussion

Photochemistry

From the results of the present experiments the major primary photochemical processes of the matrix isolated dichloroethylenes are, in order of yield,

$$C_2H_2Cl_2 + h\nu \rightarrow C_2HCl + HCl \qquad (1a)$$

$$\rightarrow C_2HCl + H + Cl \qquad (1b)$$

$$\rightarrow C_2H_2Cl_2\ \text{(isomers)} \qquad (2)$$

$$\rightarrow C_2H_2 + Cl_2 \qquad (3a)$$

$$\rightarrow C_2H_2 + 2Cl \qquad (3b)$$

$$\rightarrow C_2Cl_2 + H_2 \qquad (4a)$$

$$\rightarrow C_2Cl_2 + 2H \qquad (4b)$$

Since we were unable to determine directly the relative importance of molecular *versus* atomic elimination, both possibilities have been included. No evidence for the production of the chlorovinyl radical, or any of the three possible carbenes, was observed. This is not unreasonable, however, as these rather large species, if they were formed at all, would have difficulty in diffusing out of the matrix site and would undoubtedly recombine to reform the parent species. This same diffusion argument allows us to suggest that the formation of HCl is primarily via reaction (1a). Hydrogen atoms are rather mobile in Ar matrices and if reaction (1b) were important we should see some evidence of a dichlorovinyl radical due to H atom migration from the site followed by recombination of Cl and CA. The conclusion that reaction (1a) is the major pathway is in agreement with AW [2 - 4] and Berry [5].

As mentioned previously, the data on the shifted CA and HCl produced from TDCE suggest that the shifted features are due to CA and HCl trapped in a unique configuration in the site. The planar dichloroethylenes have three possible elimination pathways: *cis*- or *trans*-$\alpha\beta$, and $\alpha\alpha$. For example, CDCE can eliminate HCl either *trans*-$\alpha\beta$ or $\alpha\alpha$. In contrast, DCE can eliminate via *cis*- or *trans*-$\alpha\beta$, but not by $\alpha\alpha$. Since the photolysis of these two isomers results in identical product spectra, we would assume that they eliminate by the common route: *trans*-$\alpha\beta$. However, consider that the spectrum produced by the photolysis of TDCE, which can eliminate *cis*-$\alpha\beta$ or $\alpha\alpha$, is again identical to that from CDCE and DCE, with the exception that a new set of shifted features has been added. Apparently, one of the TDCE elimination routes gives rise to a very similar (identical) product configuration to that produced by CDCE and DCE. Our experiments do not provide direct evidence for which route this is, but we intuitively prefer *cis*-$\alpha\beta$. Geometrically, there is no difficulty in envisioning *cis* elimination. In contrast, it seems that *trans* elimination from a truly planar molecule would be very unlikely to lead to bound HCl as H atoms could easily leave the site and result in formation of a dichlorovinyl radical. If indeed *trans* elimination does occur from planar DCE or CDCE, then it is necessary that the H atom migrate to the relatively immobile Cl atom and form a bond. In this case the result would be identical to *cis* elimination. More likely though (and almost certainly in the gas phase), both *cis* and *trans* elimination probably occur from a twisted parent molecule (the $^1\pi\pi^*$ state is non-planar at equilibrium) and result in identical products.

Given the above interpretation, the shifted features from TDCE must result from the only remaining pathway: $\alpha\alpha$ elimination. Since about 30% of the TDCE products appear to be due to the $\alpha\alpha$ process, this process must be nearly as probable as *cis*-$\alpha\beta$ elimination. Similarly, *trans*-$\alpha\beta$ elimination must be somewhat more probable than the $\alpha\alpha$ process as none of the $\alpha\alpha$ product is observed in the CDCE experiments (even with a × 20 expansion on the spectrometer). Of course, this implicitly assumes that a common dissociative state gives rise to both the shifted and normal features. Alternatively, the $\alpha\alpha$ elimination from TDCE could arise from a different state, as will be discussed in the next section.

Photophysics

The data pertinent to a discussion of the photophysics are summarized as follows.

(1) The product distribution in any given matrix is independent of the excitation source.

(2) With the exception of acetylene, product formation is enhanced in a heavier matrix.

(3) With the exception of acetylene, product formation is markedly reduced in the presence of CO.

(4) Product formation in N_2 is intermediate between Ar and CO matrices.

(5) Finally, and most significantly, TDCE undergoes a unique process to produce shifted CA and HCl. This process is enhanced more than the others in Kr, is quenched to a lesser extent in N_2 and is quenched totally in CO.

The results obtained in different matrices indicate that all processes, other than the formation of Cl_2 and A, occur through triplet states. We shall assume that Cl_2 and A are formed either from direct dissociation from the lowest $^1\pi\pi^*$ (V) state or by internal conversion (IC) to the continuum of the ground state, and shall not discuss it further. The quenching effects of CO could be due to two processes*: direct triplet quenching; or decreased contributions, relative to Ar, to external heavy atom enhanced spin orbit coupling (EHASOC). The greatly enhanced conversion efficiency in Kr shows that EHASOC is effective in this system. Strong support for direct quenching, however, is provided by the N_2 experiments. Although N_2 and CO would be expected to have very similar effects on spin orbit coupling, photolysis is more efficient in N_2 than in CO. If we assume direct quenching, this can be explained because the lowest triplet state of N_2 is about 1500 cm^{-1} higher than that of CO. Incidentally, this interpretation sets rather stringent requirements on the energetics of the quenching process**. Finally, in reference to intersystem crossing (ISC), we note that the ease of photolysis of the dichloroethylenes *versus* that of the difluoroethylenes [1] is consistent with a triplet mechanism which is enhanced by the increased spin orbit coupling due to the presence of the chlorine atoms.

The independence of the product distribution on excitation wavelength suggests that all higher electronically excited states quickly relax to the region of the V state maximum at about 2000 Å (or more correctly the region of Hg excitation) or slightly lower. Vibrational relaxation within the V state must be slower than that by ISC in order for CO to be an effective quenching agent (note that the onset of the CO triplet is about 3000 cm^{-1} below the maximum of the V state transition in TDCE and only about 1290 cm^{-1} below the lowest exciting line used in these experiments, Hg 2049 Å). The product distribution is not proof of relaxation in the singlet manifold, but further evidence again arises from the use of other matrices. The product distribution is also independent of excitation wavelength in solid CO. If cross-over to the dichloroethylene triplet manifold occurred from higher excited states, a higher (or at least different) quenching efficiency might be expected when excitation sources other than Hg are used. Similar conclusions might be drawn from the results in N_2 and Kr, but insufficient experiments were performed to be conclusive.

The state giving rise to normal CA and HCl is most likely the $^3\pi\pi^*$ (T) state, which has a non-planar equilibrium geometry. The fact that different HCl vibrational distributions are observed from TDCE and CDCE in the gas

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*There are other alternative explanations for a change in photolysis efficiency with matrix material. These include relative changes in the reflectivity or absorption characteristics of the matrix or matrix shifting of the electronic absorptions of the solute. These are not sufficient to explain the data of these experiments, however.

**Comparing the energy of the Hg excitation source and the triplet levels of CO and N_2 suggests that the entire process of excitation → ISC → quenching must be very nearly isoenergetic.

phase has been taken to indicate that dissociation occurs on a time scale competitive with, if not faster than, rotation in the V state [5]. If the $\alpha\alpha$ elimination products arise from a different electronic state, however, as we shall maintain, then it is necessary that ISC occur faster than rotation. As all singlet states above the V state are expected to have a planar configuration [19, 20], there is no difficulty in maintaining a planar geometry during the relaxation process when a higher energy exciting source is used.

That $\alpha\alpha$ elimination in TDCE occurs from a different state from that which gives rise to $\alpha\beta$ elimination is strongly suggested by the relative quenching and enhancement effects in the various matrices. Since the $\alpha\alpha$ elimination products are enhanced more in Kr, the state is more strongly spin orbit coupled to the initially excited state than is the T state. Since quenching of the process by CO is more efficient, the state is probably in closer resonance with the CO energy levels.

Considering that the electronic structure and spectrum of ethylene is not yet understood [21], we cannot hope to interpret quantitatively the photophysics involved in dichloroethylene photochemistry. Nevertheless, from a study of the available theoretical and experimental results we can suggest assignments for the states involved.

Within the limits of applicability of Koopmans' theorem, the photoelectron spectrum gives a picture of the ground state molecular orbitals of a molecule. The photoelectron spectra of the three dichloroethylenes have been investigated [22, 23] and an additional spectrum of TDCE has also been reported [24]. Klasson and Manne [25] considered the data of Lake and Thompson [22] and Jonathan *et al.* [23] in the light of the chlorine K_β emission spectra of the dichloroethylenes and made a partial reassignment. The discussion centers about the number of ionization potentials between 10.5 and 12.5 eV. Klasson and Manne [25] present a convincing argument for their conclusions, and have since received some experimental support [26]. We thus use their preferred values, as shown in Table 3. Note that there is insufficient experimental evidence for assignment of the symmetries of the n orbitals.

TABLE 3

Calculated energy levels of the dichloroethylene[a]

	CDCE (eV)	TDCE (eV)	DCE (eV)
E_1	9.9 ($b_1\pi$)	9.9 ($a_u\pi$)	10.0 ($b_1\pi$)
E_2	11.8 (n)	11.9 (n)	11.7
E_3	12.1 (n)	12.1 (n)	12.2
E_4	12.6 ($a_2\pi$)	12.6 ($b_g\pi$)	12.6

[a] Preferred values from Klasson and Manne [25].

Turning to the theoretical side, we find several MO treatments of the dichloroethylenes [19, 25, 27 - 32]. Although the differences among these calculations and between the calculations and the photoelectron data are large (it should be noted that most calculations do not make the needed corrections for correlation and reorganization energies to be directly comparable with the experimental ionization energies), there is general agreement that the highest occupied MO (HOMO) is a π orbital. The next lower orbitals are non-bonding, but there is no agreement on symmetry. Finally, at least for CDCE and TDCE, the fourth lowest filled orbital is another π orbital. As far as non-filled MOs are concerned, we have only one set of calculated data [19].

Kato *et al.* [19], Pellegatti *et al.* [28] and Favini and Simonetta [32] have explicitly calculated vertical $\pi\pi^*$ transition energies, and Kato *et al.* [19] have extended their calculations to include other transitions. As V ← N is the only valence transition reported in the UV spectra of the dichloroethylenes, we compare theory and experiment for this transition in Table 4.

TABLE 4

Observed and calculated $\pi\pi^*$ vertical excitation energies

CDCE (eV)	TDCE (eV)	DCE (eV)	Reference
6.13	6.21	6.44	19 (calc.)
6.40	6.39	6.71	28 (calc.)
6.27	6.38		32 (calc.)
6.52^a	6.26^b	6.42^c	(exp.)

^{a}Ref. 39. ^{b}Ref. 40. ^{c}Ref. 41.

Experimental evidence for other excited states is sparse. The calculations of Kato *et al.* [19] place the σ^* orbital below the π^*, and this is in agreement with their polarographic data on related compounds [33]. Their calculated transitions, in order of increasing energy, are $^1\pi\sigma^*$, $^1\pi\pi^*$, $^1n\sigma^*$. The $^1\pi\sigma^*$ transition is optically forbidden in DCE and TDCE, and is calculated to occur at about 2850 Å in CDCE, so this state is not likely to be important in the photochemistry in these experiments.

Of more interest to us is the predicted location of the $^1n\sigma^*$ state relative to that of the $^1\pi\pi^*$ state in CDCE and TDCE (it is predicted to be somewhat higher in DCE). There is diverse evidence for the presence of more than one singlet between the onset of the $^1\pi\pi^*$ absorption at about 2400 Å and the maximum at about 2000 Å. This includes marked asymmetry on the red side of the $\pi\pi^*$ transition [5] (in agreement with theory this asymmetry is slight in DCE), pre-resonance Raman effects in TDCE [34] and gas phase photochemical results†. Berry [5] has summarized more indirect evidence.

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†The observation that two excited states are required to explain the photochemistry in the gas phase (see [2 - 4]) does not require two singlet states, however, and even if two singlets are involved the $\pi\sigma^*$ could be the important one.

As to the associated triplets of the above states, there is direct experimental evidence only for the placement of the T state. Grabowski and Bylina [6] utilized a high pressure of O_2 to make direct $S_0 \rightarrow$ T absorption possible in TDCE and CDCE. They indicate the general range of absorption to be between 3000 and 4000 Å. Moore [35] investigated the H^+ and the He^+ impact spectra of DCE and located the vertical excitation energy of the T state at 3.9 eV. These results are in excellent agreement with the theoretical vertical transition energies of 3.81, 3.82 and 3.95 eV for TDCE, CDCE and DCE, respectively. There is no experimental evidence for the location of the $^3n\pi^*$ and $^3\pi\sigma^*$ states.

The locations of all the states discussed above are shown in Fig. 4. Also shown are the triplet levels of CO and N_2. These are adapted from gas phase data from Herzberg [36] by assuming that the shifting and broadening of the triplet levels on condensation is the same as for the singlet levels of CO [37]. It should be pointed out that we have only shown the $n\sigma^*$ states calculated in ref. 22. Since the ground state has two n orbitals within a few tenths of an electronvolt, there should be another pair of excited states for each molecule.

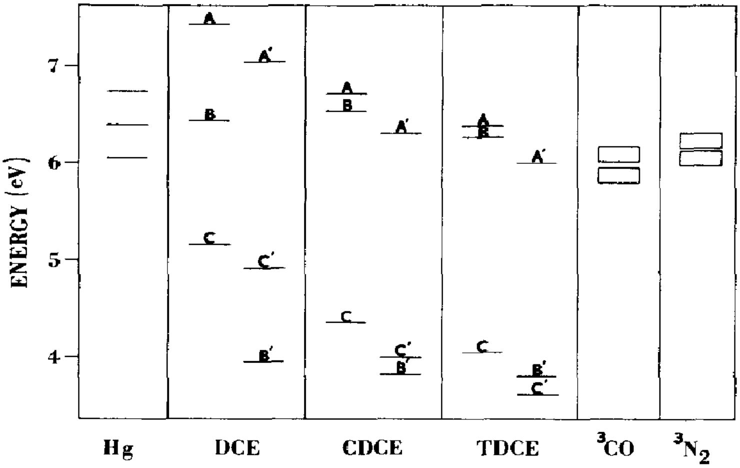

Fig. 4. Vertical transition energies in the dichloroethylene photochemical system. On the left are shown the three principal lines of the Hg arc spectrum, while on the far right are the first two transitions of the triplet spectra of CO and N_2. For the dichloroethylenes, A, B and C represent in each case the $n\sigma^*$, $\pi\pi^*$ and $\pi\sigma^*$ states and the primes denote the corresponding triplets. State symmetries are as follows: DCE, A($^1B_2$ or $^1A_1$), B($^1A_1$), C($^1A_2$); CDCE, A($^1A_1$ or $^1B_2$), B($^1B_2$), C($^1B_1$); TDCE, A(^1B_u or ^1A_g), B(^1B_u), C(^1B_g).

Except for the $n\sigma^*$ states, symmetry assignments are straightforward (if the ground state geometry is used for labeling the $^1\pi\pi^*$ state). In the case of the $n\sigma^*$ states, the state symmetry depends on which of the ground state orbitals is excited. Both cases are given in the figure caption.

Considering the assumptions needed to generate Fig. 4, the comparison with the results of the present experiments is amazingly good. In particular, we note that the $^3n\sigma^*$ state of TDCE is near resonant with the 0,0 band of the CO triplets. The maximum (for a planar geometry) of this transition falls below the lowest level of N_2. This is consistent with the behavior of the $\alpha\alpha$ elimination products formed from TDCE. Further, considering the selection rules for spin orbit coupling [38], TDCE is the only dichloroethylene for which mixing of the $^1n\sigma^*$ and $^3n\sigma^*$ is allowed to first order. (This is true regardless of the symmetry of the $n\sigma^*$ state, presuming the singlet and triplet to have the same symmetry. Spin orbit mixing of the $^1\pi\pi^*$ and $^3n\sigma^*$ is always forbidden because of orbital occupancy considerations.) This accounts for the fact that $\alpha\alpha$ elimination is enhanced more in Kr than are the other processes. There is also an implication here that the $^1n\sigma^*$ carries more of the oscillator strength of the "$^1\pi\pi^*$ band" than is usually assumed, as $\alpha\alpha$ elimination does appear to account for about 30% of the photochemistry of TDCE.

Conclusions

The UV photolysis of the three dichloroethylenes has been investigated in Ar, CO, N_2 and Kr matrices. It is found that TDCE produces CA and HCl in two distinct geometries. This has been attributed to an $\alpha\alpha$ elimination process in the molecule. It is suggested that $\alpha\alpha$ elimination arises from a $^3n\sigma^*$ state. Formation of normal CA and HCl and isomerization in all three isomers appears to arise from the $^3\pi\pi^*$ state, while traces of A and Cl_2 are apparently produced by dissociation in the singlet manifold.

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