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The Ultraviolet Absorption Spectra of Cis- and Transdichloroethylenes

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The absorption spectra of cis- and of transdichloroethylene have been photographed from the visible to 750A. There are continua in the quartz region and at short wavelengths, but discrete bands in the general region of 1300 to 1700A. Two Rydberg series have been found in the cis-form predicting ionization potentials of 9.58 and 9.63 volts. A value in agreement with these figures is found by electron bombardment. No Rydberg series were found in the trans-form, although indications of an

ionization potential at about 11.3 volts were obtained by electron bombardment. In both forms the main progressions involve a C=C frequency of about 1400 cm⁻¹, although many prominent differences involving the lowest deformation frequency have been found. A discussion of the various absorption regions has been given, although definite proof of many points must come from other sources.

IN investigating the spectroscopic and photochemical properties of the double bond, it is evident that simple derivatives of ethylene would be advantageous substances with which to work. Olson and Maroney² have studied the thermal equilibrium and photochemical steady state for cis- and transdichloroethylenes. The results are in general agreement with a theory of cis-trans isomerization developed by Olson.³ The photochemical work seems to have been carried out in a region of continuous absorption. It was thought that a complete investigation of the spectra of these two compounds would be of value.

I. EXPERIMENTAL

The two isomers were obtained by fractional distillation of the Eastman product (b.p. 58–61°). This consisted largely of the cis- form, although enough of the trans-form was present for the purpose of the present experiments.

An eight-foot distilling column of the Vigreux type was used for the first separation of the trans-form and for further purification of the cis. The cis-form was distilled until successive fractions gave a constant index of refraction, which required four more distillations than were necessary to give a boiling point constant to 0.1°. Not enough of the transdichloroethylene was obtained to check its purity in this way, but since the first fraction had a smaller boiling range than the cis (0.3°), the same number of distillations was made using a microfractionating column.⁴ Just before

introducing the materials into the spectrograph small samples were again distilled through this small column, taking the first fraction of the trans- and the last fraction of the cis-dichloroethylene. The boiling points of the samples obtained in this way agreed with those in the literature,⁵ 60.1° for the cis- and 47.3° for the transdichloroethylene. The thermometer was calibrated by a Bureau of Standards thermometer and no stem correction was necessary.

A Hilger E-3 spectrograph with quartz train was used for wavelengths greater than 2100A. The hydrogen continuum was used as a source of radiation and a quartz absorption cell 20 cm in length was employed.

For shorter wavelengths a one-meter vacuum grating spectrograph with a dispersion of approximately 8.5A/mm in the first order, was used. The method of using this spectrograph and the light source have been described.⁶ Eastman III-0 plates sensitized with Nujol were used for most of the exposures, although Schumann plates were used occasionally, particularly for the extreme ultraviolet.

As wavelength standards the carbon lines at 1548.19 and 1371.28A together with the hydrogen line at 1215.68A in absorption were employed.

The spectrum from the visible to 750A was covered.

The method of measuring the ionization potentials by electron bombardment has been described.⁷

¹ Jesse Metcalf Fellow, 1934–35.

² A. R. Olson and W. Maroney, *J. Am. Chem. Soc.* **56**, 1320 (1934).

³ A. R. Olson, *Trans. Faraday Soc.* **27**, 69 (1931).

⁴ C. M. Cooper and E. V. Fasce, *Ind. Eng. Chem.* **20**, 420 (1928).

⁵ L. Ebert and R. Büll, *Zeits. f. physik. Chemie* **A152**, 451 (1931).

⁶ W. A. Noyes, Jr., A. B. F. Duncan and W. M. Manning, *J. Chem. Phys.* **2**, 717 (1934).

⁷ W. A. Noyes, Jr., *J. Chem. Phys.* **3**, 430 (1935).

II. RESULTS

The absorption spectra of the two isomers may be divided roughly into three regions.

(1) There is a region of continuous absorption first observed at low pressures at 1950Å for transdichloroethylene and at 1850Å for cis-dichloroethylene. This region spreads rapidly in both directions as the pressure is increased until at the highest pressures used (188 mm for the cis and 278 mm for the trans) with a path length of 20 cm complete absorption was observed below 2400Å. At higher temperatures absorption coefficients have been measured up to 2763Å.²

On three plates of the cis-form there seemed to be some very diffuse bands underlying the short wave end of this continuum.

(2) The region of discrete absorption extends from 1570Å to about 1350Å. The bands of the cis-form were shaded toward the violet, while those of the trans-form were shaded toward the red, although sharp band edges were discernible with difficulty except for the most intense bands. Bands of the cis-form were observed to 1340Å, while none below 1450Å was found for the trans-form. Overlaying the banded absorption of the cis-form was another continuum, first noticeable at low pressures at about 1470Å, but increasing in breadth and gradually merging with both the longer and shorter wave continua as the pressure increased.

(3) Below this discrete absorption was a third region of continuous absorption. In the cis-form this appeared to be a true continuum whose center of gravity lies about 78,000 cm⁻¹. In the trans-form there seems to be a series of wide, diffuse bands without structure which gradually merged as the pressure increased.

Table I gives the frequencies of the absorption bands of cisdichloroethylene, together with rough estimates of the intensities based on the appearance of the bands and the pressures at which they were first noticed. Only the discrete bands are included, since the diffuse bands are listed in Table III. The frequencies of the red edges are given. The bands marked *s* were sharper than the others and are probably accurate to about 5 cm⁻¹. The others were more difficult to measure with precision and are probably not reliable to better than 15 cm⁻¹.

TABLE I. Discrete bands of cisdichloroethylene (frequencies in wave numbers).

$\bar{\nu}$	INTEN- SITY	$\bar{\nu}$	INTEN- SITY	$\bar{\nu}$	INTEN- SITY
65016	0	68670	9	72408 (s)	7
65164 (s)	10	68872	5	72640 (s)	8
65260	1	69060	4	72957	7
65352	2	69266	3	73205	1
65737	3	69483	4	73328	5
65845 (s)	10	69796	4	73473	0
66020	4	69875	4	73547	3
66364	2	70060	6	73652	1
66550	5	70254	2	73816	4
66650 (s)	10	70717 (s)	9	74044	2
66742	1	70978 (s)	7	74240	3
66862	1	71220 (s)	8	74490	1
67030	5	71410	2	74590	1
67163	2	71527	4	74843	1
67266 (s)	10	71810	3	74954	1
67460	6	71902	3	75059	1
68060	7	72018	4	75437	0
68235	4	72122 (s)	9		
68471	6				

TABLE II. Discrete bands of transdichloroethylene (frequencies in wave numbers).

$\bar{\nu}$	INTEN- SITY	$\bar{\nu}$	INTEN- SITY	$\bar{\nu}$	INTEN- SITY
65096	6	66891 (s)	10	68322	5
65444 (s)	10	67111 (a)	3	68486 (b)	1
65813 (s)	10	67263 (s)	10	68538 (b)	2
66032	1	67466	2	68676	5
66174	7	67621	6	68892	2
66386 (s)	9	67835	4	69020	2
66541	7	67954	2	69249	2
66674 (b)	4	68137 (b)	2	69701	1
66752 (b)	5	68188 (b)	3		

(a) This band seemed to be double-headed but the long wave component could not be measured with precision. (b) These bands form pairs appearing as single double-headed bands both heads of which are given in the table.

Table II presents the absorption bands of transdichloroethylene. In this case the frequencies of the violet edges of the bands are given.

Tables III and IV give the diffuse bands for

TABLE III. Diffuse bands of cisdichloroethylene (frequencies are in wave numbers).

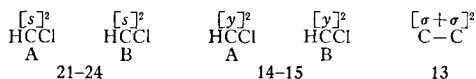
57747, 60562, 61169, 61967, 62605, 78100

TABLE IV. Diffuse bands of transdichloroethylene (frequencies are in wave numbers).

70080, 71000, 74270, 79180, 82000, 83761, 85560, 87010

the cis- and transdichloroethylenes, respectively. Since these bands do not possess heads the approximate centers of gravity are given. The 70,080 band of the trans-form is the most intense in the entire spectrum. No intensities are given

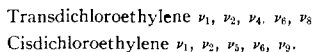
because they are hard to estimate. The cis-bands with the exception of the last, which is weaker, are about equal in intensity.



Below each type of electron is given a rough estimate of the expected ionization potential.

For each molecule three types of symmetry operation in addition to the identity are possible. The application of symmetry properties of polyatomic molecules to their spectra has been discussed by Mulliken⁹ and by Herzberg and Teller.¹⁰ It would be beyond the scope of the present article to discuss the selection rules in detail. Suffice to say that if the molecule absorbs either from the nonvibrating level or from a level involving symmetrical vibrations only, in the ground state, a rigid application of the selection rules would permit only symmetrical vibrations to be excited in the upper state.

The two molecules under consideration belong to different symmetry groups, the cis-isomer to group C_{2v} and the trans to group C_{2h} . Using the classification of the various modes of vibration given by Stuart,¹¹ the following would be totally symmetrical

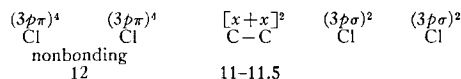


Of these frequencies one may be described as C=C stretching, one as C-Cl stretching, one as C-Cl bending, one as C-H stretching and one as C-H bending, although this way of describing the motions is rather qualitative.

For the trans-isomer six frequencies should be active in the infrared and six in the Raman spectrum. Actually more Raman lines have been found,¹² some of which may probably be classified as combination lines. For the cis-isomer all

III. DISCUSSION OF RESULTS

The electron configuration of the transdichloroethylene may be represented as follows⁸



twelve frequencies should be active in the Raman spectrum and ten should be active in the infrared. Ten Raman lines have been observed, some of which cannot be assigned to definite modes of vibration.¹²

The C=C frequency is 1587 for the cis- and 1577 cm^{-1} for the transdichloroethylene. Carbon-hydrogen stretching frequencies are of the order of 3000 cm^{-1} and carbon-hydrogen bending of the order of 1200 cm^{-1} . The carbon-chlorine frequencies are much lower.¹³

As judged by polarization measurements the lowest frequencies (349 for the trans and 175 for the cis) are symmetrical.¹² The Boltzmann factors for these two frequencies are 0.19 and 0.43, respectively.

It is not possible to classify all of the observed bands unambiguously, although certain regularities are apparent and a qualitative discussion of other important aspects of the spectra is possible.

The continuum observed at the longer wavelengths in both compounds is reminiscent of the continuum found in most compounds containing the carbon-chlorine bond¹⁴ and in all probability this bond is dissociated by absorption in this region of the spectrum. It is reasonable to ascribe the transitions to either the s or y electrons in the molecule. The diffuse bands on the short wave side of the continuum in the cis-form may indicate that more than one electron state is involved in this region of the spectrum. The frequency differences in these diffuse bands are not very accurate, but one lies in the general region of carbon-hydrogen stretching and the others in the general region of carbon-chlorine stretching, thus indicating that these modes of vibration may be excited without a primary dissociation of the

⁸ The authors wish to express their appreciation to Professor R. S. Mulliken for a private communication concerning the electron configurations of these compounds.

⁹ R. S. Mulliken, *Phys. Rev.* **43**, 279 (1933).

¹⁰ G. Herzberg and E. Teller, *Zeits. f. physik. Chemie* **B21**, 410 (1933).

¹¹ H. A. Stuart, *Molekülstruktur* (Julius Springer, Berlin, 1934), p. 336.

¹² Cf. B. Trumphy, *Zeits. f. Physik* **90**, 133 (1934); O. Paulsen, *Zeits. f. physik. Chemie* **B28**, 133 (1935).

¹³ Cf. W. D. Harkins and R. R. Haun, *J. Am. Chem. Soc.* **54**, 3920 (1932).

¹⁴ G. Herzberg and G. Scheibe, *Zeits. f. physik. Chemie* **B7**, 390 (1930).

TABLE V. *Rydberg series in cis-dichloroethylene.*

A. $\bar{\nu} = 77703 - R/(m-0.045)^2$		$m = 3, 4, 5, 6, \dots$	
Obs.	65164	70717	73205 74590
Calc.	65136	70688	73233 74609
Diff.	-28	-29	+28 +19
B. $\bar{\nu} = 78103 - R/(m-0.01)^2$		$m = 3, 4, 5, 6, \dots$	
Obs.	65845	71220	73652 75059
Calc.	65829	71210	73696 75045
Diff.	-16	-10	+44 -14

molecule. The appearance of the bands is, however, strongly suggestive of predissociation.

The discrete bands, at least in the cis- and probably also in the trans-form, seem to belong to several different upper electron states. This is indicated by the fact that two different Rydberg series are found among the bands of the cis-dichloroethylene. Table V shows the agreement between observed and calculated frequencies for the two series.

The convergence limits of these two series both lie in the short wave region of continuous absorption. The predicted ionization potentials are 9.58 and 9.63 volts, both of which lie well below the ionization potentials estimated by Mulliken⁸ for the transdichloroethylene. The fact that the two chlorine atoms are on the same side of the molecule, thus leading to a dipole moment considerably higher than for the trans-form would lead one to expect such an effect on the ionization potential.

Actual measurement of the ionization potential by the method previously described⁷ gave a value of 9.7 ± 0.3 electron volts, which is well within experimental error of the value predicted spectroscopically.

No Rydberg series could be found among the bands of transdichloroethylene, but an experimental determination of the ionization potential by the method of electron bombardment gave a value of 11.3 volts, which agrees reasonably well with the ionization potential predicted by Mulliken⁸ for the π electrons of the C=C bond.

The classification of the remaining bands of the cis-form among vibration levels is not possible without introducing arbitrary frequencies in such a manner that the meaning would be doubtful. Table VI shows some differences based on the bands in the B series of Table V.

Differences based on the A system of Table V are not as consistent as those for the B system,

TABLE VI. *Tentative progressions in the bands of cis-dichloroethylene.*

65845	71220	65845	70060 (185)	69875
1421	1420	175	194	
67266	72640	66020	70254	
1404	1404			
68670	74044	67266		
1390	1393	194		
70060	75437	67460		
1350				
71410		68670 (199)	68471	
		202		
		68872		
			71220	74044
			190	196
			71410	74240

although in each case frequencies between 1400 and 1500 and near 200 may be found.

There seems little doubt that the frequency about 1420 cm^{-1} is a modification of the C=C frequency which is 1587 cm^{-1} in the ground state. The frequency near 200 must be a modification of the deformation frequency 175 in the ground state. There seems to be little point in attempting a further classification of these bands, since it would be necessary to introduce too many arbitrary frequency differences. The electronic excitation in these bands is almost certainly connected with the C=C bonding electrons, either σ or π . Since the electric moment may change along any one of the three axes, there should be three upper electron states for a given electronic transition. Actually only two Rydberg series were found, although some evidence was found for a third. It seems impossible to state at present just what changes in vibration frequencies would be expected from one substate to another and this is one reason why a complete systematic classification of the bands is impossible.

The bands of transdichloroethylene may be classified into a vibrational scheme using one quantum number in the ground state and two in the upper. Here as in the cis-form it seems necessary to assume that the lowest deformation frequency is almost the same in the lower state as in the upper state. This makes unambiguous classification of the bands difficult, but intensity relationships furnish support for the tentative scheme given in Table VII.

The remaining bands of Table II are subheads of the double headed bands. While the significance is not clear it is noted that these double-headed bands all occur together in the B system

TABLE VII. *Tentative classification of the bands of transdichloroethylene.*

A SYSTEM					
65444	(348)	65096	65444	66891	68322
1447		1445	369	372	354
66891	(350)	66541	65813	67263	68676
1431		1413	361	358	344
68322	(368)	(67954)	66174	67621	69020
1382					
69701					
B SYSTEM					
66386	(354)	66032	66386	67835	
1449		1434	366	353	
67835	(369)	67466	66752	(68188)	
1414		1426	359	350	
69249	(357)	68892	67111	68538	

when both frequencies are involved in the upper state

The connection between the A and B systems is not obvious. It is true that by introducing one more mode of vibration a connection could be found, but it seems more probable that different electron states are involved. In the trans-form change of dipole moment will lead to only two different configurations since two will be identical. It is possible that such sub-electron states are involved, but a complete answer to the question here raised must await further theoretical developments.

The continuous absorption observed in both forms deserves some consideration. The most intense absorption in the trans-form is first noticeable at $70,080\text{ cm}^{-1}$ at low pressures and broadens approximately symmetrically with increasing pressure until the entire discrete absorption is obliterated by the continuum. There is a minor region of absorption at a frequency about 900 cm^{-1} higher. It may be worthy of note that there is a symmetrical frequency at 847 cm^{-1} observed in the Raman spectrum.¹² There is still a further region of continuous absorption beginning at $74,270$, or a little over 3000 cm^{-1} , higher than the previous band. These regions of absorption have some of the characteristics of predissociation bands. The one at $70,080$ corresponds to about $200,000$ calories per mole which, is some $50,000$ calories more than that necessary to dissociate the carbon-carbon double bond. It seems probable that this bond is dissociated in this continuum, the excess energy appearing either as excitation energy or kinetic energy or both.

The difference between the continuum at $70,080$ and the next higher region is very closely

the same as the difference between the frequencies of the bands tentatively taken as 0,0 bands for the A and B systems. Moreover the main progressions in both systems involve the carbon-carbon frequency, so that perturbation between the upper vibration levels of this state and the next higher electron state may be responsible for the predissociation.

In the cisdichloroethylene there are no regions of continuous absorption corresponding to those just mentioned for the trans-form. Continuous absorption starts about $78,100\text{ cm}^{-1}$ and broadens, particularly toward shorter wavelengths, as the pressure is increased. This continuum is weaker than those in the transdichloroethylene and falls just about at the convergence limit of the two Rydberg series.

Price¹⁵ has found a Rydberg series in ethylene predicting an ionization potential of 10.41 volts but makes no mention of a continuum at a corresponding frequency. He does mention that numerous faint bands were observed which were not classified. It is possible that the abundance of bands near the convergence limits of the two Rydberg series in the cis-form is partially responsible for the continuous appearance of the absorption. In general one would not expect to find a continuum corresponding to the removal of one electron from a complex molecule of this type. It seems more probable that the continuum is due to a transition to an upper electron state which is repulsive. Just what dissociation is involved may only be conjectured, although it is probably that of the carbon-carbon bond. The energy is, however, some $70,000$ calories per mole more than that necessary to produce such a dissociation. There is the further possibility that simultaneous removal of two chlorine atoms may occur.

The continuum which starts at $68,000\text{ cm}^{-1}$ in the region of discrete absorption may involve a weak transition to a repulsive upper state producing dissociation of the carbon-carbon bond.

In conclusion the authors wish to express their appreciation to Dr. A. B. F. Duncan for help during the experimental work and to Dr. E. B. Wilson, Jr. of Harvard for a conversation concerning the symmetry properties of the two molecules under discussion.

¹⁵ W. C. Price, *Phys. Rev.* **47**, 444 (1935).