[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Thermal and Photochemical Equilibria of the Cis–Trans Isomers of Dichloro- and Dibromoethylene

BY A. R. OLSON AND WILLIAM MARONEY

The photochemical conversion of one geometrical isomer of the *cis–trans* type into the other has been studied from the theoretical standpoint by Olson[1] and by Mulliken.[2] An experimental study of this problem using aqueous solutions of various organic acids was published recently by Olson and Hudson,[3] who also gave references to many earlier experiments in this field. The present study was undertaken using a gaseous system in order to eliminate the disturbing effect of a solvent and thus to approach more nearly the conditions postulated in the theoretical study.

Cis and *trans* dichloroethylenes were chosen for this investigation, for they can easily be prepared in the pure form, they are fairly stable with respect to thermal decomposition, mixtures of the two forms can easily be analyzed, and they have moderately large extinction coefficients in a region of the spectrum which is easily obtainable in the laboratory.

Olson and Hudson[3] showed that the probability, p, that a molecule activated by monochromatic light will return to the *trans* state on deactivation, to the probability, $1-p$, that it will return to the *cis* state, is given by the expression

$$p/1 - p = C_t/C_c \times \epsilon_t/\epsilon_c \qquad (1)$$

where ϵ_t and ϵ_c are the extinction coefficients, and C_t and C_c are the mole percentages of the *trans* and *cis* isomers, respectively. Since in most of our experiments we have used the unfiltered light from a mercury arc, we will follow their procedure in defining a mean ratio of the extinction coefficients as

$$\frac{\Sigma_K\ (\text{percentage absorbed})_K \cdot (\text{relative intensity})_K\ (\epsilon_t/\epsilon_c)_K}{\Sigma_K\ (\text{percentage absorbed})_K \cdot (\text{relative intensity})_K} \qquad (2)$$

where the summation extends over all the arc lines which are involved.

Preparation of Materials

The *cis* isomer was prepared from commercial dichloroethylene by repeated fractional distillation. The *trans* isomer was prepared by reducing tetrachloroethane with zinc and ethyl alcohol, separating from the alcohol by washing with water, and then fractionally distilling. The distillations were repeated until products with unchanged dielectric constants were obtained. This required four or five fractionations, more than was required to yield products with constant boiling points.

Experimental

The reaction vessels were spherical quartz flasks, each having a small Pyrex side tube attached to it with a graded seal. This side tube was connected to a mercury diffusion pump, and also to a segment of tubing drawn out into a capillary which could be broken *in vacuo* when the sample was to be removed. The mixture of the liquid isomers to be investigated was placed in the side tube, frozen out with liquid air, and after the remaining gases had been pumped off by the diffusion pump, the pump connection was sealed. The reaction vessel was then placed in a thermostat and exposed to the unfiltered light from a quartz mercury arc for a period varying from five minutes to one hour, depending upon the temperature. The pressure in the reaction vessel varied from 0.8 to 3.5 atmospheres at the temperature of exposure. After illumination, the reaction product was distilled by means of liquid air into an evacuated vessel which contained a small fixed condenser, consisting of three concentric silver cylinders. The analysis of the reaction product contained in the silver condenser was carried out by utilizing the difference in the dielectric constants of the two isomers. A crystal controlled oscillator was set up similar to the one described by Olson and Hirst.[4] The reading of the variable precision condenser in the external circuit of the oscillator at the point of resonance was determined with mixtures of the isomers of known percentage composition (made by weighing out the pure isomers) in the silver condenser. A graph was made of the readings of the precision condenser plotted against the percentage composition. By finding the reading of the precision condenser when the silver condenser contained the reaction product, the percentage composition could be determined to 0.1% from the graph. The results are summarized in Table II, Column 3.

The values used for the relative intensity in equation (2) were taken from the work of McAlister.[5] The present work was carried out at nearly the same arc voltage used by that author (150 volts), except the measurement at 150°, which was made using 123 volts. No correction

---

[1] A. R. Olson, *Trans. Faraday Soc.*, **27**, 69 (1931).

[2] R. S. Mulliken, *Phys. Rev.*, **41**, 751 (1932).

[3] A. R. Olson and F. L. Hudson, THIS JOURNAL, **55**, 1410 (1933).

[4] A. R. Olson and L. L. Hirst, THIS JOURNAL, **51**, 2378 (1929).

[5] E. D. McAlister, "Smithsonian Misc. Coll.," Vol. 87, No. 17 (1933).

in the intensity distribution of the arc due to this voltage change has been made, nor has any allowance been made for the reflection and absorption losses from the quartz surfaces, since these corrections are smaller than our experimental error.

The extinction coefficients were measured by the method employed by Gibson and Bayliss.[6] The absorption cells were filled at a definite pressure as determined by a sulfuric acid manometer. When a high concentration of the isomer was needed, the absorption cell was connected to a 500-cc. flask, the whole system was filled with the vapor of the isomer at a definite pressure, and then was frozen out in the absorption cell, which was sealed off from the flask. The concentration of the isomer in the absorption cell could be determined from the ratio of the volume of the cell to the total volume.

TABLE I

EXTINCTION COEFFICIENTS OF DICHLOROETHYLENE ISOMERS

Wave length, Å.	100°	150°	200°	250°
		Cis		
2302	31.7	61.2	81.3	97.3
2325	18.6	36.4	49.2	78.9
2345	9.4	17.0	25.1	43.9
2378	6.3	10.8	16.1	24.9
2399	4.5	6.9	10.0	15.9
2446	1.3	2.2	3.9	5.9
2462	0.57	1.3	2.3	3.8
2482	.47	0.83	1.6	2.6
2536	.080	.24	0.74	1.3
2576	.032	.094	.28	0.70
2609		.060	.18	.37
2643		.038	.083	.21
2675			.053	.14
		Trans		
2302	81.9	118	160	229
2325	46.6	78.7	99.3	126
2345	21.8	38.6	56.2	80.7
2378	11.8	19.5	28.6	46.8
2399	7.4	13.0	21.1	31.0
2446	2.8	5.0	7.7	12.9
2462	2.2	3.3	5.2	9.7
2482	0.84	2.2	4.1	6.9
2536	.17	0.54	1.26	3.3
2576	.060	.21	0.56	1.6
2609	.031	.11	.34	1.1
2643	.020	.053	.17	0.53
2700			.058	.26
2753			.038	.15

The values of the extinction coefficient listed in Table I were calculated from the equation

$$I/I_0 = 10^{-\epsilon c d}$$

where c is the concentration in moles per liter and d is the length of the absorbing path. The logarithms of these coefficients were plotted against wave length, and a smooth curve drawn. The extinction coefficients used in the calculations were taken from this plot.

The percentages absorbed were calculated from the relation

$$(\text{Per cent. absorbed})_K = 100\ (1 - I/I_0) \qquad (3)$$
$$= 100\ \left\{1 - 10^{-(\epsilon_t\ \%\ trans\ +\ \epsilon_c\ \%\ cis)d}\right\}$$

where the composition of the mixture which occurs in the exponent refers to the photostationary state. The length of the absorbing path, d, was taken to be slightly greater than the diameter of the spherical reaction vessels employed.

From the preceding data, we have calculated by equation (2) the mean ϵ_t/ϵ_c ratios which occur in Table II, Column 5, and then by equation (1) the $p/1-p$ values listed in the last column.

TABLE II

Temp., °C.	Measurements	*Cis* at photostationary state, %	C_t/C_c	Mean ϵ_t/ϵ_c	$p/1-p$
100	30	67.3 ± 2.0	0.486	1.96	0.95
150	10	64.9 ± 0.6	.541	2.15	1.16
200	18	63.3 ± 0.6	.580	2.28	1.32
250	20	62.7 ± 0.7	.595	2.33	1.39
300	17	61.8 ± 0.7	.618	2.36[a]	1.46
250 (CCl_4 filter)	29	63.9 ± 1.0	.565	2.22	1.25

[a] This value was obtained by graphical extrapolation of the four preceding values.

The carbon tetrachloride filter employed in the measurement at 250° was a cell with quartz ends. The light passed through about 2 mm. of the carbon tetrachloride. The transmission of the filter was measured by the photographic method used in determining the extinction coefficients.

Wave length, Å.	2536	2576	2609	2643	2700 (and above)
Transmission, %	<1	8	14	82	87

In calculating the probability ratios for the experiment with this filter, the relative intensities of the mercury lines were multiplied by the percentage transmission of the filter at the given wave length.

The change in the $p/1-p$ ratios with the temperature is in agreement with Olson's prediction, as is also the change of this ratio with the wave length of light used. Unfortunately thermal isomerization and decomposition prevent the

---

[6] G. E. Gibson and N. S. Bayliss, *Phys. Rev.*, **44**, 188 (1933).

work from being extended to higher temperatures where this ratio should decrease to unity. It was pointed out by Olson that if we regard the carbon atoms in an unsaturated compound in the normal state as two tetrahedra joined along a common edge, and in the excited state as two tetrahedra joined at one corner, rotation about this common corner will not suffice to explain the *cis–trans* reaction. However, if we couple such a rotation with the inversion of one of the carbon atoms, then we have a mechanism which will account for the facts.[7]

Heat of Transition

The thermal equilibrium between the two dichloroethylene isomers has been measured using the same method employed in determining the photostationary states. The time required for attaining thermal equilibrium was found to be much longer than that required for reaching the photostationary state.

Temperature, °C.	300	350
Measurements	19	11
Cis at equilibrium, %	60.8 ± 0.7	59.4 ± 0.3

Using the relation

$$N_1/N_2 = e^{-\Delta H/RT}$$

where N_1/N_2 is the ratio of *trans* to *cis* at equilibrium, the heat of transition at 300° is found to be 500 cal./mole, and at 350°, 470 cal./mole. These values are in fair agreement with 600 cal./mole, calculated from the equilibrium measurement at 300° of Ebert and Büll.[8] The fact that ΔH is the same within experimental error for the two temperatures is consistent with the heat capacity measurements of Olson and Brittain,[9] who have found ΔC_v for this reaction to be zero within the limits of their experimental error.

The values of the dielectric constants listed below were determined in a manner similar to that employed in analyzing the equilibrium mixtures, by plotting the readings of the precision condenser against the dielectric constants, employing for standard liquids carefully purified samples of benzene, aniline and ethylene dichloride. The dielectric condenser employed in these measurements had an air capacity of about 43 micromicrofarads.

	Dielectric constants, ν = 1090 kilocycles 0.0°C.	25°C.
Cis	10.16	9.30
Trans	2.42	2.35

Dibromoethylene

Tetrabromoethane was reduced with zinc and ethyl alcohol to obtain dibromoethylene. The equilibrium mixture of the isomers was separated into the *cis* and *trans* forms by fractionation with ethyl alcohol. The separated isomers were washed with water, dried with calcium chloride and distilled under reduced pressure. The pure isomers prepared in this manner have been kept for several months without any measurable isomerization.

The dielectric constants were measured by the method used for the dichloroethylene isomers.

	Dielectric constants, ν = 1090 kilocycles 0°C.	25°C.
Cis	7.72	7.08
Trans	2.97	2.88

In the table below are summarized the measurements which have been made on the equilibria of the two isomers.

TABLE III

	Temp., °C.	Measurements	*Cis* at equilibrium, %	Heat of transition cal./mole
Thermal equilibrium	150	6	60 ± 2	340
Thermal equilibrium	20–25[a]	5	63 ± 2	310
Photostationary state	150	8	57 ± 2	

[a] Catalyzed by hydrogen bromide.

The general illumination of the quartz mercury arc operating at 155 volts was used in measuring the photostationary state. A Pyrex reaction vessel was used, which absorbs most of the radiation below 3100 Å.

Summary

The dielectric constants of *cis* and *trans* dichloro- and dibromoethylene have been determined at 0 and 25°. The thermal equilibria between the isomers of these two compounds have been obtained at several different temperatures, and from them the heats of transition have been calculated. The extinction coefficients of *cis* and *trans* dichloroethylene have been measured over a range of temperature and light frequencies.

The photostationary states for the dichloroethylene isomers have been measured for a temperature range of 100–300°. The ratio of the probability that an excited molecule will return to the *trans* state to the probability that it will return to the *cis* state on deactivation has been calculated, and has been shown to agree with that predicted by theory.

BERKELEY, CALIFORNIA RECEIVED APRIL 13, 1934

---

[7] See Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[8] E. Ebert and R. Büll, *Z. physik. Chem.*, **A152**, 451 (1931).

[9] A. R. Olson and F. W. Brittain, THIS JOURNAL, **55**, 4063 (1933).