

395. Isomeric Change in Certain Stilbenes.

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The stilbenes CHPh:CHPh, CCIPh:CHPh and CCIPh:CCIPh can each be obtained in their two geometrically isomeric forms, and the rates of change of the less stable of each pair into the equilibrium mixture of both have been measured in the liquid state at temperatures in the region of 200°. The results show that the heats of activation for the change, which must depend on the nature of the double bonds, are almost the same in all three compounds. This is unexpected, since the chlorine atoms in the last two are unreactive; hence there must be an interaction between the C—Cl and C=C links which would be expected to show itself in the behaviour of the double bond. Another unexpected result is that, although the rate of change of *isostilbene* into stilbene is extremely sensitive to the presence of traces of acid, yet with the two chlorinated compounds there is no acid catalysis whatever. Possible reasons for these phenomena are discussed. Observations on the catalysis of these changes by other agents are described.

THE experiments now described deal with the rate of change in the liquid state of the less stable geometrical isomers of stilbene (CHPh:CHPh) and monochlorostilbene (CCIPh:CHPh) into the equilibrium mixture in which the more stable (*trans*) form largely predominates, and of the similar change with dichlorostilbene (CCIPh:CCIPh) where the equilibrium mixture contains 75% of the *cis*-compound. The object of the work was to establish the behaviour of these stilbenes in thermal isomeric change and towards catalysts, in order to contrast it with other cases of geometrical isomers, and to explore the effect on the double bond of the substitution of chlorine for hydrogen; the reciprocal effect, that of the double bond on the chlorine atom, is shown in these compounds by the unreactivity of the chlorine atoms. The only earlier observations of this kind are isolated statements as to the stability of *isostilbene*, the liquid *cis*-compound (Wislicenus, *Zentr.*, 1901, I, 463; Straus, *Annalen*, 1905, **342**, 262), and the careful measurements of the rate of the gaseous reaction *isostilbene* → stilbene at a series of temperatures by Kistiakowsky and Smith (*J. Amer. Chem. Soc.*, 1934, **56**, 638); the latter are discussed below. The effect of certain catalysts on the same reaction has been described and discussed by Kuhn (Solvay Report, 1931, p. 364).

Stilbene.

isoStilbene can be obtained in quantity by the method of Taylor and Crawford (J., 1934, 1130), and since it is a liquid at room temperature whereas stilbene melts at 124°, the composition of stilbene-*isostilbene* mixtures over a wide range of concentration can be determined from their binary m. p. curve. Kistiakowsky and Smith (*loc. cit.*) have published this curve, but there must be some error, because their curve does not pass through the m. p. of pure stilbene; hence it has been redetermined. Preliminary experiments with various samples of *isostilbene* showed that the rate of change into stilbene is extremely sensitive to the presence of traces of acids; only by the most thorough washing of the ethereal solutions of the *isostilbene* with aqueous sodium carbonate can samples be

obtained which give consistent results. This purified *isostilbene* is more stable than some of the observations recorded suggest; below 200° the rate of change into stilbene is very small, and at 214° only 7.9% has been transformed after 20 hours. This fact makes it difficult to measure the rate of change in the liquid state with high accuracy, because at these temperatures both stilbene and *isostilbene* decompose slowly and become brown, and the rate of decomposition increases rapidly with temperature. In order to minimise this decomposition, all the experiments described below, both with *isostilbene* and with the substituted stilbenes, were carried out in an atmosphere of nitrogen. The removal of air from the sealed tube containing the substance is of interest from another point of view. Kuhn (*loc. cit.*) has discussed the possibility that the efficiency of certain substances such as bromine atoms, sodium atoms, and nitrogen peroxide as catalysts for this isomeric change is bound up with the fact that these substances are paramagnetic and for this reason are able to interact with the four electrons of the double bond. The oxygen molecule is paramagnetic and thus there is the possibility that it is a catalyst and that the rates of change measured in tubes containing air are not the true thermal rates. Tamamushi and Akiyama (*Bull. Chem. Soc. Japan*, 1937, **12**, 382) claim to have found a slight increase in the rate of change of maleic into fumaric acid in the presence of oxygen, though Urushibara and Simamura (*ibid.*, p. 507) found no such effect with methyl maleate or *isostilbene*. Our experiments with *isostilbene*, in which we have measured the rate of change both in an atmosphere of nitrogen and in one of oxygen, show that the rate is somewhat higher in the latter; but there is also more strongly marked decomposition, and when these tubes are opened, the contents are distinctly acidic, the acid presumably being formed by oxidation. Since, as is shown below, the change is catalysed even by acids as weak as benzoic acid, there seems little doubt that true catalysis by oxygen is not observably present, but that the increase in rate is due to the acid.

The binary m. p. curve for mixtures of stilbene and *isostilbene* has been redetermined by Mr. W. C. J. Coughtrey. In every case stilbene was caused to separate from the liquid mixture by immersion in a freezing mixture; the large crystals formed on slow cooling can easily lead to too high a value for the clearing point. The mixture was illuminated with a screened beam of light in which the crystals showed clearly by reflexion; the clearing points were first observed to the nearest degree and then redetermined with very slow heating. When $\log 1/T$ is plotted against $\log (\% \text{ stilbene})$, a curve is obtained which is straight over the greater part of the range, and this curve was used in subsequent analyses.

Stilbene, %	100	92.4	78.3	57.8	40.0	28.4	15.1	7.0	4.3
Clearing point	124.0°	120.2°	113.5°	102.0°	88.0°	77.0°	58.7°	37.0°	27.2°

The b. p. of *isostilbene* was found to be 134°/10 mm., in agreement with the earlier result, and not 145°/10 mm. as reported by Kistiakowsky and Smith (*loc. cit.*).

Lengths of washed and steamed glass tubing were closed at one end, and the substance to be examined (about 0.1—0.5 g.) introduced either by a small pipette or, if a solid, as a pellet; the tube was then connected with a Hyvac pump and a supply of nitrogen which had been washed through two long towers of alkaline pyrogallol and dried. The tube was repeatedly exhausted and filled with the nitrogen and then sealed off. With oxygen in the tube there was much greater inconsistency between separate experiments than with nitrogen; typical results are given in the following table, which also contains results in nitrogen at the same temperature, 214°. The time is expressed in minutes.

In oxygen.				In nitrogen.	
Time.	Stilbene, %.	Time.	Stilbene, %.	Time.	Stilbene, %.
403	4.3	304	3.4	400	2.8
560	5.6	460	4.3	600	4.1
740	7.0	540	5.0	800	5.4
1084	9.8	700	6.2	1000	6.7
1398	12.8	914	7.9		

The Position of Equilibrium.—To obtain the velocity constants of the rate of thermal change, the position of equilibrium at the temperatures used must be known. Kistiakowsky and Smith have pointed out that the variation of the equilibrium constant with tempera-

ture is too small to be measured, and have determined its position in the gas phase at 280—342°; starting with pure stilbene, they found the equilibrium mixture to contain 6—8% of *isostilbene*, but approaching the equilibrium from the other side, they found 17—18%; the discrepancy they explained as due to the formation of a liquid rearrangement product in the latter case, which lowered the clearing point. Our preliminary experiments showed that it was hopeless to try to find the true equilibrium in the liquid state at 200—220° by maintaining a sample at this temperature for a long time because of the inevitable decomposition even in nitrogen; hence we have used the catalytic effect of benzoic acid to accelerate attainment of equilibrium, the clearing point curves for mixtures of stilbene, *isostilbene*, and known quantities of that acid having been determined (see below). At 200° from either isomer the same equilibrium mixture was obtained and it consisted of 96% of stilbene and 4% of *isostilbene*. This value was used in the subsequent calculations.

The Rate of Thermal Change in Nitrogen.—Since one of the most important quantities to be measured is the heat of activation of the isomeric change, the temperatures at which the rate is measured should be as wide apart as possible. It was found, however, that much above 220° *isostilbene* decomposed too rapidly, turning brown and giving inconsistent results, while below 210° the slowness of the change meant long periods of heating and again decomposition. Hence we have only measured the rate of change with any accuracy at 214° and 223°, and this narrow range seriously limits the accuracy in the heat of activation. The values of the velocity constants lead to a heat of activation for the isomeric change of 36,700 cal. per g.-mol., and the constant can be expressed at these temperatures by the equation $k = 2.7 \times 10^{10} \times e^{-36,700/RT}$. The equation of Kistiakowsky and Smith for the rate of the gaseous reaction in the interval 280—342° is

$$k = 6 \times 10^{12} \times e^{-42,800/RT}$$

and the difference between these equations is not so large as appears at first sight; there is also an uncertainty in that they used an equilibrium concentration of 84% stilbene as an arbitrary correction for the formation of the liquid by-product in the gas phase. It is clear that to a first approximation the reaction is of the same type in the liquid and in the gaseous phase.

The percentages of stilbene found from the various experiments were plotted against time, and from the best curve drawn through these points the stilbene content at intervals of 200 minutes was taken. Velocity constants were calculated from these values by the equation $k = [1/t(1 + E)] \log_e 100/[100 - (1 + E)x]$, where x is the % of stilbene and E the equilibrium constant between stilbene and *isostilbene*. The results are shown in the following table, where t is given in mins. and k in terms of natural logarithms and sec.⁻¹.

Temp. 214°.			Temp. 223°.		
Time.	Stilbene, %.	$k \times 10^6$.	Time.	Stilbene, %.	$k \times 10^6$.
400	2.8	1.18	400	5.65	2.43
600	4.1	1.15	600	8.1	2.35
800	5.4	1.15	800	10.25	2.27
1000	6.7	1.15	1000	12.0	2.15
2000	11.9	1.07	1200	13.7	2.05
3000	15.6	0.92			
3400	16.8	0.90			

The values of k fall with time, a result to be expected from the decomposition, since after 1000—1200 mins., the contents of the tubes were no longer colourless, and decomposition products will lower the clearing points. For the heat of activation the velocity constant at 214° and at 223° was taken as the mean up to 800 mins., *i.e.*, 1.16×10^{-6} and 2.32×10^{-6} .

Catalysis of the Rate of Change.—Addition of traces of basic compounds (piperidine, aniline, quinoline) to samples of *isostilbene* heated to 190° for various periods did not bring about any appreciable formation of stilbene. This result is in striking contrast to the effect of bases on the esters of maleic acid, which, as Clemo and Graham have shown (J., 1930, 213), are converted in a few seconds at room temperature into the esters of

fumaric acid by the addition of a trace of a primary or secondary base. This catalysis is clearly a function of the carboxyl groups attached to the doubly bound carbon atoms. The rate of isomeric change is, however, very sensitive to the presence of acidic substances, and it is sufficient to pass the nitrogen used in filling the tubes over a little hydrochloric acid in order to convert *isostilbene* into *stilbene* in 4 hours at 190°. In the method of preparation used, the *isostilbene* is extracted with ether from a solution containing excess of hydrochloric acid, and if this extract is not washed repeatedly with aqueous sodium carbonate, the rate of isomeric change is much higher although the amount of hydrochloric acid is too small to be determined by the ordinary methods. A series of measurements was made with such samples, but since the catalyst concentration is unknown, the results will not be given. Measurements of the rate at three different temperatures by Mr. W. C. J. Coughtrey with one sample indicate that the heat of activation has fallen to about 23,000 cal. per g.-mol. Addition of benzoic acid in quantities of the order of 5–15% of the *isostilbene* also brings about a marked increase in the rate of change.

It was hoped to measure the rate in presence of known amounts of benzoic acid, and for this purpose clearing point curves were constructed for ternary mixtures containing a constant fraction of the acid and varying amounts of the two isomers; the data are given below:

Clearing points of mixtures of stilbene, isostilbene, and benzoic acid.

15% Benzoic acid.				10% Benzoic acid.			
Stilbene, %.	Clearing point.	Stilbene, %.	Clearing point.	Stilbene, %.	Clearing point.	Stilbene, %.	Clearing point.
0	53.4°	50	88.5°	5	41°	50	90.5°
10	51.4	60	95	10	41	60	96
15	49	70	100.5	15	49	70	102.5
20	58	85	108.5	20	57.5	85	110
30	71	100	115	30	72.5	100	117
40	80.5			40	82.5		

It was found, however, that in the presence of benzoic acid the isomeric change in the region of 200° is accompanied by a side reaction in which small quantities of a colourless, insoluble compound are formed, and that in spite of the very small amount, the presence of this interferes with the clearing points to such an extent that accurate measurement of the velocity constant is impossible. The by-product could only be obtained in very small quantity; it melts at 247° and contains oxygen. If, instead of pure *isostilbene*, the starting material in the tube was a mixture of *stilbene* and *isostilbene*, it was possible after freezing out the solid phase to observe the temperature at which the last crystals of *stilbene* disappeared, disregarding the trace of by-product, and thus obtain an approximate analysis. The values of the velocity constants, however, fell rapidly with time because of the inaccuracy of the estimation and are useless for calculating the heat of activation of the reaction catalysed by benzoic acid. At 195° the velocity constant with 10% of the acid is of the order of 6×10^{-6} (log₁₀; sec.⁻¹) and with 15% of the acid 9×10^{-6} ; hence it seems probable that the rate is proportional to the concentration of benzoic acid, and it is certain that the acid is a catalyst, the rates being 5–8 times as large as that of the uncatalysed reaction at a temperature 20° higher.

Monochlorostilbene.

The more stable isomer of monochlorostilbene was obtained by Sudborough (*Ber.*, 1892, **25**, 2237; *J.*, 1897, **71**, 220) by the action of chlorides of phosphorus on deoxybenzoin and is called by him the β -isomer. Zinin (*Annalen*, 1869, **149**, 375) has described an oily monochlorostilbene which Sudborough has suggested is essentially the geometrically isomeric form. Repetition of the earlier preparations gave products which were difficult to purify, but it was found that they could be prepared easily from the two diastereoisomeric *stilbene* dichlorides. The α -dichloride (m. p. 191.5°) with $\frac{1}{2}$ equiv. of alcoholic potash gives an oil which does not solidify at – 20° and at lower temperatures becomes a glass; analysis shows this to be a monochlorostilbene, and following Sudborough it is called here the α -isomer. It resembles *isostilbene* in being rapidly converted into the more stable isomer when it is exposed to sunlight in the presence of a trace of bromine or iodine. Since it

could not be obtained crystalline, there is no certainty that our preparation is completely free from the more stable isomer; in any event the complete homogeneity of the compound is not of importance for the present purpose since a sufficient quantity was prepared so that the same sample was used in all the measurements described. That it is free from the β -compound is probable because the rate of thermal isomeric change is very small at all the temperatures used in the preparation and also because, unlike *isostilbene*, its isomeric change is not catalysed by acid.

The monochlorostilbenes do not decompose so readily as the stilbenes in the range 200—240°, and the position of equilibrium between them at these temperatures was found by keeping samples of both in sealed tubes until the clearing point was constant; the equilibrium mixture contains 2% of the α -isomer. The configurations of the isomers are unknown but presumably correspond to those of the stilbenes, the more stable β -isomer being the *trans*- and the less stable α -isomer the *cis*-compound. The rate of isomeric change of the α -compound into the equilibrium mixture was measured at 226° and 246° in an atmosphere of nitrogen. The results give for the heat of activation a value of 37,000 cal. and the velocity constant can be expressed by the equation

$$k = 1.4 \times 10^{11} \times e^{-37,000/RT}$$

The most striking result with this compound and with the dichlorostilbenes is that the sensitivity of the rate of isomeric change to acids, so marked with *isostilbene*, seems to be entirely absent. This fact is not so easy to establish with mono- as with di-chlorostilbene because the low m. p.'s of the isomers in the former case give a binary m. p. curve which lies awkwardly low, but a series of experiments was carried out at 226° in which the nitrogen was bubbled through concentrated hydrochloric acid before admission to the tubes; the points obtained lay on the same curve as those for the change in pure nitrogen.

Preparation.—Chlorine was passed into a solution of 40 g. of stilbene in 400 c.c. of chloroform cooled in ice and kept in the dark, since light decreased the amount of α -dichloride formed. After 2 hours, 16 g. of the α -dichloride were collected and recrystallised from toluene, and from the filtrate 22 g. of the β -dichloride were obtained and recrystallised from light petroleum. 10 G. of the latter compound in 100 c.c. of quinoline were heated to 180—190° (oil-bath) for 1 hour; the mixture was cooled and poured into excess of dilute hydrochloric acid; extraction with ether gave a brown oil which solidified on cooling. This is the β -compound; it was recrystallised from light petroleum in which it is very soluble, or better from aqueous alcohol; it formed colourless plates, m. p. 52° (cf. Pfeiffer, *Ber.*, 1912, 45, 1817). 10 G. of α -stilbene dichloride were refluxed for 1 hour in 150 c.c. of alcohol with 2.4 g. of potassium hydroxide. The solution was then no longer alkaline, and was cooled and filtered; 1 g. of the dichloride was recovered. Excess of water was added, and ether extraction gave 7.2 g. of the oily α -isomer, which was distilled under reduced pressure; b. p. 160—162°/12 mm. (Found: Cl, 16.7. Calc. for $C_{14}H_{11}Cl$: Cl, 16.6%). Attempts to obtain the less stable isomer in quantity by illuminating β -monochlorostilbene in a quartz vessel with a quartz mercury-vapour lamp were not successful.

Since the m. p. of the β -isomer is 52°, all the clearing points of mixtures of the two isomers were low, and with less than 30% of the solid isomer were below 12°. Mixtures with less than 50% of the solid isomer would not crystallise on cooling unless scratched, and consequently in some of the subsequent velocity experiments the sealed tube had to be opened; this meant that only one point on the time-composition curve could be obtained from such a tube. Attempts to overcome the difficulty by converting the mixture into a ternary one with inert substances such as anthracene or dibenzyl were unsuccessful, because the solubility of the third substance in the two isomers is so similar that the difference in clearing points is too small to be of use.

Clearing points of mixtures of α - and β -monochlorostilbene.

β -Isomer, %	100	70.5	53.3	35.9	30.8
Clearing point	52°	42°	32°	18°	13°

In the rate measurements the method and calculation were the same as those described above. The results with the α -compound as starting material were:

Temp. 226°.			Temp. 246°.		
Time (mins.).	β -Isomer, %.	$k \times 10^5$ (\log_e ; sec. ⁻¹).	Time (mins.).	β -Isomer, %.	$k \times 10^5$ (\log_e ; sec. ⁻¹).
240	14.5	1.09	100	24.3	4.62
480	25.5	0.97	200	43	4.74
720	34.5	0.99	300	54	4.41
960	43.5	1.01	400	63.5	4.34
1200	51	1.01	500	70	4.22

Mean values taken : 226°, $k = 1.01 \times 10^{-5}$; 246°, $k = 4.46 \times 10^{-5}$.

With hydrogen chloride introduced with the nitrogen only one point could be obtained from each tube because the tube had to be opened for a solid phase to separate; the results of one experiment were as follows :

Time (mins.)	570	660	1140	1260
β -Isomer, %	34	35	54	59

The mean value of the velocity constant from these unsmoothed values is 1.1×10^{-5} as compared with 1.01×10^{-5} found at the same temperature with no hydrogen chloride.

Dichlorostilbene.

The geometrically isomeric dichlorostilbenes are known and their configurations have been established by the measurements of electric moment by Bergmann (J., 1936, 402). The α -compound (m. p. 143°) has zero moment and is the *trans*-compound; the β -compound has a moment of 2.69 D. and is therefore the *cis*-isomer. An equilibrium between the two isomers was observed by Blank (*Annalen*, 1888, 248, 17), who found that interconversion to an equilibrium mixture took place when either isomer was distilled at 320°, but only very slowly below 200°, and by Eiloart (*Amer. Chem. J.*, 1871, 12, 231); both workers determined the position of equilibrium by extracting the mixture with cold alcohol, in which the α -compound is sparingly soluble, and found it to contain about 68% of the β -compound. In our experiments the dichlorostilbenes were as stable to heat as the monochloro-compounds, and the equilibrium mixture could be obtained by heating either isomer until a constant clearing point was reached; the composition follows from the clearing point curve which has been determined. The mean result was that in the region 220—230° the equilibrium mixture contains 75% of the *cis*- β -isomer, so that here there is a complete reversal of the stabilities in the stilbenes and monochlorostilbenes, where the *trans*-isomer forms nearly all of the equilibrium mixture. A similar behaviour is known in the dichloroethylenes and the chloroiodoethylenes, where at equilibrium there is 80% and 82.5% of the *cis*-isomer respectively (Chavanne, *Bull. Soc. chim. Belg.*, 1912, 26, 287; Stuart, *Physikal. Z.*, 1931, 32, 793; Van de Walle and Henne, *Acad. Roy. Belg.*, 1925, 11, 360); it is due to the attractive (London) forces between the two halogen atoms which overcome the normal steric repulsive forces between the phenyl groups. The rates of change of the two isomers into the equilibrium mixture were measured by methods similar to those described above. In the temperature range 175—200° the heat of activation was found to be 34,000 cal. per g.-mol., and the velocity constant can be expressed as $k = 9.9 \times 10^{10} \times e^{-34,100/RT}$.

As with monochlorostilbene, no indication whatever of catalysis of the isomeric change by the addition of acids could be observed. This surprising result was confirmed by experiments in which hydrogen chloride was introduced into the tube as a gas and also in mixtures containing 25% by weight of benzoic acid, the rate being followed by means of the ternary clearing point curve with benzoic acid. The velocity constants obtained, together with those in the absence of any acid, are shown below and stand in marked contrast to the results with *isostilbene*.

Velocity constants (\log_e ; sec.⁻¹) for the change α -dichlorostilbene \rightarrow equilibrium mixture.

	175°.	196°.
Pure compound	$2.9_9 \times 10^{-6}$	$1.6_0 \times 10^{-5}$
With trace of HCl	—	1.5_3 „
With 25% benzoic acid	2.7_1 „	1.5_6 „

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The two dichlorostilbenes were prepared by the pyrogenic decomposition of benzylidene chloride (Löb, *Z. Elektrochem.*, 1901, **7**, 903; 1903, **9**, 906) and also by treating tolan tetrachloride with zinc (Blank, *loc. cit.*); both methods gave a mixture of isomers which was separated with cold alcohol. The α -compound, recrystallised from alcohol, melted at 143°; the β -compound does not show a sharp m. p., and after repeated recrystallisation from light petroleum, ethyl or methyl alcohol, melted over the range 61—64°; this is in agreement with Stelling (*Z. physikal. Chem.*, 1934, *B*, **24**, 407). The clearing point curves used in the velocity experiments were constructed from the following data.

Binary mixtures of α - and β -dichlorostilbene.

α -Compound, %	0	2.5	5.6	7.6	10.0	15.1	20.0	24.2
Clearing point	64°	63.5°	71°	75°	78.5°	85°	93°	97.5°
α -Compound, %	25	39.4	50.9	57.3	66.9	79.7	92.9	
Clearing point	97°	110°	118°	122.5°	129°	135°	141°	

Ternary mixtures: α - and β -dichlorostilbenes + 25% of their weight of benzoic acid.

β -Compound, %	5.02	9.92	14.98	20.07	24.84	29.94
Clearing point	130°	128°	125.5°	123°	120.5°	118.5°

The velocity constants were obtained from smoothed curves derived from several experiments and calculated as above; for the rate of change of the α -isomer into the equilibrium mixture the following results were obtained:

Temp. 175°.			Temp. 196°.		
Time (mins.)	β -Isomer, %	$k \times 10^6$ (log _e ; sec. ⁻¹)	Time (mins.)	β -Isomer, %	$k \times 10^6$ (log _e ; sec. ⁻¹)
100	1.8	3.03	50	4.6	1.57
200	3.5	2.98	100	9.0	1.58
300	5.25	3.02	150	13.2	1.62
400	6.8	2.97	200	17.3	1.64
500	8.45	2.97	250	21.0	1.64

The rate of change of the β -compound into the equilibrium mixture was also measured, but because the β -compound forms the greater part of that mixture, the change in composition is smaller and slower, and it was more difficult to obtain satisfactory results. The values observed were in the range 4.6—6.1 $\times 10^{-6}$ at 196°, whereas that predicted from the rate of change of the α -compound and the equilibrium constant is 4.8 $\times 10^{-6}$.

In the presence of 25% of benzoic acid the velocity constants for the change of the α -compound tend to fall with time, and the values given above are taken from the initial stages of the change. This effect may be due to the same phenomenon which was observed with *isostilbene*. The data obtained were:

Temp. 175°.			Temp. 196°.		
Time (mins.)	β -Isomer, %	$k \times 10^6$	Time (mins.)	β -Isomer, %	$k \times 10^6$
100	1.9	3.30	100	9.4	1.67
200	3.0	2.55	150	13.0	1.59
300	4.0	2.28	200	16.4	1.54
400	5.0	2.15	250	18.7	1.43
			300	22.2	1.46
			350	25.0	1.45

In the experiments with hydrogen chloride, this was introduced with the nitrogen as described above, and the tube sealed. The depression of the clearing point of the pure α -dichlorostilbene before heating was 1.5°, and the assumption was made that the clearing points of all the mixtures would be lowered by this amount; this cannot be far from the truth, since the heat of fusion of the isomers will be almost the same. The rate of change so measured gave the following results at 196°:

Time (mins.)	50	100	150	200	300
β -Isomer, %	4.9	8.8	12.5	15.9	21.6
$k \times 10^6$ (log _e ; sec. ⁻¹)	1.68	1.56	1.53	1.53	1.41

Many unsuccessful attempts were made to obtain both isomeric forms of ethylstilbene and of diethylstilbene.

DISCUSSION.

The two most interesting points that emerge from these experiments are that the heat of activation of the isomeric change is very little affected by the replacement of hydrogen attached to the doubly bound carbon atoms by chlorine, and that this replacement, even of only one hydrogen atom, causes the acid catalysis of the change to disappear. The heats of activation are summarised below.

	Heat of activation, cal./g.-mol.
<i>iso</i> Stilbene	36,700
Monochlorostilbene	37,000
Dichlorostilbene	34,100

At first sight it would be expected that the replacement would produce a large reduction in the heat of activation. The chlorine atoms in the chlorinated compounds are unreactive; for instance, Limpricht and Schwanert (*Ber.*, 1871, **4**, 379) found that dichlorostilbene is unchanged by heating with silver acetate to 200°. The accepted explanation of this vinyl chloride type of unreactivity is that, because the chlorine atom has unshared electrons, in addition to the structure that is normally written (I), another structure (II) is possible in which carbon and chlorine are united by a four-electron bond and carbon and carbon by a two-electron bond; two structures being possible, the actual state is intermediate between them and the actual formula is a hybrid of (I) and (II). There is definite



evidence in support of this view in the lengths of the carbon-chlorine links; in normal compounds such as methyl chloride and chloroform it is 1.77 Å., but in chloroethylene it has shortened to 1.69 Å., and in chlorobenzene, which presents a similar problem, to 1.70 Å. (for references see Brockway and Taylor, *Ann. Reports*, 1937, **34**, 205 *et seq.*). This shortening is a measure of the extent to which double-bond character is entering into the carbon-chlorine link. Such an effect, however, should have the converse consequence in the carbon-carbon double bond; instead of being a true double bond, it should have an element of single bond in it. This change in its nature would be expected to manifest itself in the heats of activation measured in these experiments; the torsional rigidity might be reduced and hence less energy be needed to overcome the resistance to change of configuration. The unexpected result that there is no reduction in the heat of activation is probably due to the following considerations: Pauling and Brockway (*J. Amer. Chem. Soc.*, 1937, **59**, 235) have calculated from a theoretical basis the bond character of a certain number of bonds intermediate between true double and single bonds and have plotted their results against the lengths of the bonds accurately determined from X-ray and electron-diffraction measurements. The curves so obtained are concave towards the axis on which the lengths are plotted; in other words, if a single bond alters to a state in which it has 25% of double-bond character, its length is changed much more than is the length of a double bond which is altered so that it has 25% of single-bond character. If the length of the bond is taken as a rough measure of its general characteristics, this would predict that, in the above example, the resonance between the various states will produce a much greater change in the nature of the single carbon-chlorine link than in that of the double carbon-carbon link. This conclusion is in agreement with our results, *viz.*, an unreactive chlorine atom, but an unaltered heat of activation of the double bond. There are, unfortunately, no accurate measurements of the length of the double bond in ethylene and the chloroethylenes, but it is perhaps significant that Brockway, Beach, and Pauling (*ibid.*, 1935, **57**, 2693) could interpret satisfactorily their electron diffraction results with a model in which the length of this bond is unaffected by the introduction of chlorine atoms. Other evidence pointing in the same direction is the recent calculation of the force constant of the C:C link in ethylene and tetrachloroethylene from the Raman spectra of these compounds. Duchesne (*Nature*, 1938, **142**, 256) finds that the substitution of four chlorine atoms in the place of hydrogen has no appreciable effect on the value of this constant.

It will be noticed from the equations for the velocity constants given above that introduction of one chlorine atom increases the value of the temperature-independent factor in the equation, but that there is no further increase with a second chlorine atom. This factor is, however, so complicated in its origin that discussion of this result is pointless.

The disappearance of acid catalysis when one chlorine atom is introduced is also entirely unexpected and more difficult to explain. In the parallel case of catalysis by hydrogen chloride of isomeric change in the system $>C:N$ it has been shown (Taylor and Roberts, J., 1933, 1439) that the catalyst is the undissociated molecule of acid, and in the present case the conditions under which the reaction proceeds also point to the undissociated molecule; hence there seems to be a direct interaction between the molecule of hydrogen chloride and the four electrons of the carbon-carbon link in *isostilbene*, which brings about a decrease in the torsional rigidity of that bond and hence increases the rate of change. This view is supported by the estimates of the heat of activation in the presence of acids. The disappearance of the catalysis with the chlorinated compounds must then mean that this interaction does not take place, and for this there might be three reasons; it might be a true steric effect, it might be because the double bond is of an entirely different nature in the chlorinated compounds, or it might be because the hydrogen chloride is interacting preferentially with something other than the double bond. Our failure to obtain other suitably substituted stilbenes in the required less stable isomeric form makes it difficult to decide between these alternatives with any certainty. The first two are, however, unlikely. With the oximes, acid catalysis is found both in aldoximes and ketoximes, and the introduction of quite large groups in place of hydrogen in the system $RCH:NX$ does not suppress acid catalysis. Secondly, the values for the heats of activation show that the double bond in *isostilbene* is not widely different in nature from those in the chlorinated compounds, so that the second alternative is improbable. This leaves the third, and it may well be that the catalysis disappears because the molecule of catalyst interacts, not with the electrons of the double bond, but preferentially with the unshared electrons of the chlorine atom or atoms.

Note on the Effect of Hydrogen Bromide on α -Dichlorostilbene in Air and Light.—Kharasch (J. Amer. Chem. Soc., 1937, 59, 1155) in his studies of the effect of a small amount of oxygen on the addition reactions of hydrogen bromide has observed that *isostilbene* is converted into stilbene at room temperature by hydrogen bromide if oxygen or air is present and if the mixture is exposed to light. He finds that addition of anti-oxidants stops the isomeric change and that there is no similar effect with hydrogen chloride; he suggests that the mechanism is oxidation of the hydrogen bromide to bromine which, as is well known, is a very efficient catalyst, even in the smallest quantity, for this isomeric change when it is dissociated into atoms by light. The ineffectiveness of hydrogen chloride he attributes to the greater difficulty of oxidising this compound to chlorine. It seemed of interest to repeat these observations with α -dichlorostilbene, since with this compound there is no acid catalysis under any conditions, so that the possibility of confusion is reduced. A series of qualitative experiments was carried out which confirmed Kharasch's findings in this new case. Kharasch's view of the mechanism seems satisfactory.