Kinetics of Thermal Cis-Trans Isomerization. III

BY G. B. KISTIAKOWSKY AND WALTER R. SMITH

In two previous papers[1,2] investigations on the thermal isomerization of dimethyl maleate, in the gaseous state, have been described. In the temperature range 270 to 380° the reaction is homogeneous and of the quasi-unimolecular type, the first order constants beginning to drop off at about three atmospheres. The limiting value at infinite pressure is described as $k = 6.8 \times 10^5 \, e^{-26,500/RT}$ sec.$^{-1}$. The experimental rate was found to be so slow that even the assumption of only two square terms in the energy yielded calculated rates some 10^4 larger than the experimental values.

To account for this qualitatively it was suggested that in the isomerization process, in which a rotation around a carbon–carbon double bond is involved, longitudinal vibrations effective in decomposition reactions are incapable of exchanging energy with the oscillator responsible for the reaction.

The present paper describes the investigations on three other ethylenic compounds, namely, the thermal isomerization of gaseous diethyl maleate, dimethyl citraconate and isostilbene.

Experimental Details

Preparation of Materials

Diethyl Maleate.—This compound was prepared by the direct esterification of pure maleic acid with ethyl alcohol as described by Wachholtz.[3] The middle fraction in the final distillation with a boiling point of 120° at 25 mm. was employed in the investigation. It had a refractive index, n_D^{20} 1.4407. The diethyl fumarate was similarly prepared and had a refractive index n_D^{20} 1.4410.

Dimethyl Citraconate.—This ester of methylmaleic acid was prepared by saturating a cold alcoholic solution of pure citraconic acid with hydrogen chloride essentially as described by Perkin.[4] The middle fraction distillate, which was employed in the investigation, had a boiling point of 95° at 12 mm. Its refractive index was n_D^{20} 1.4478.

Dimethyl Mesaconate.—Mesaconic acid (methylfumaric acid) was prepared from pure citraconic acid by the catalytic action of bromine in sunlight on an ether–chloroform solution of citraconic acid as described by Fittig.[5] The acid was recrystallized from ether. The final product had a melting point of 199°. The dimethyl ester was pre-

pared by the same method described above for the citraconic ester. The middle fraction with a boiling point of 86° at 11 mm. and a refractive index n_D^{20} 1.4557 was employed in the investigation.

Stilbene and Isostilbene (Diphenylethylene).—These substances, which were of the highest purity, were especially prepared for this investigation[6] by the catalytic hydrogenation of tolane in the presence of colloidal palladium. The isostilbene had a boiling point of 145° at 10 mm. The stilbene possessed a melting point of 124°.

Methods of Analysis

In view of the fact that diethyl maleate and fumarate and dimethyl citraconate and mesaconate are all liquids at room temperature, the maleate freezing around −10.5°, while even in dry ice–ether mixtures the citraconate forms a glass, it was obvious that the freezing point method employed in the earlier work would not be a convenient one here.

Considerable time was spent in an attempt to utilize the difference in dielectric constants of *cis* and *trans* compounds as a general method of analysis of their liquid mixtures. Using a high frequency heterodyne method and a micro condenser of about 0.5-cc. volume it was found possible to determine the composition of the mixtures to about 5% accuracy. This being inadequate for the purpose of this research the method was finally abandoned. A method utilizing the different miscibility of the esters with mineral oil (Nujol) was finally devised.[7] It was found that when both *cis* and *trans* modifications of the esters are liquids the *trans* form is much more soluble in mineral oil than the *cis* modification. For example, when 0.6 cc. of oil and 0.4 cc. of diethyl maleate were mixed the two became completely miscible at around 101.5° while the fumarate was miscible to 5°. In the case of the citraconic and mesaconic esters the former was completely miscible at 125°, while the latter was miscible at 25°. Mixtures of the two geometric modifications become more miscible in the 0.6 cc. of oil as they become richer in the *trans* form. This was then employed as a means of analyzing the reaction mixtures. Known mixtures of the *cis* and *trans* forms of the esters were made up by weighing out the desired quantity of each modification. These mixtures were then employed in calibrating a single junction copper-constantan thermocouple. Calibrations were obtained for both the maleic–fumaric esters and also the citraconic-mesaconic esters in the following manner.

Four-tenths cc. of ester mixture and 0.6 cc. of mineral oil, at 25°, were placed in a small glass tube. This was then suspended in a bath consisting of a 600-cc. beaker of mineral oil. A pencil of light from a small lamp was focused through the bath onto the tube. The bath was

(1) Kistiakowsky and Nelles, Z. physik. Chem., Bodenstein Festband, **152**, 369 (1931).

(2) Nelles and Kistiakowsky, THIS JOURNAL, **54**, 2208 (1932).

(3) F. Wachholtz, Z. physik. Chem., **125**, 4 (1927).

(4) Perkin, Ber., **14**, 2541 (1881).

(5) Fittig, Ann., **304**, 149 (1899).

(6) The stilbene and isostilbene were prepared by: Dr. Asmus and Dr. Meyer, successors to Dr. H. Cohen and Co., Berlin-Charlottenburg 2, Bismarkstrasse 7, Germany.

(7) We are much indebted to Professor Arthur B. Lamb for the original suggestion.

heated to around 90° until the oil and esters became perfectly miscible. During the heating the mixture was stirred with a small rod carrying the single junction thermocouple. When the mixture became perfectly miscible it was allowed to cool slowly. Suddenly a cloudiness occurred just at the consolute temperature. This point was easily and accurately discernible because of the Tyndall effect produced in the beam of light. The temperature at this point was measured with the aid of a Leeds and Northrup Type K potentiometer and an H S type galvanometer, to an accuracy corresponding to 0.3% variation in the composition of the ester mixture.

Since stilbene is a crystalline solid melting at 124° and isostilbene is a clear liquid even at 0° the analysis by means of melting point was most convenient here. A series of known mixtures of stilbene and isostilbene was prepared and the temperature at which the last crystal disappeared, on gradually warming the mixtures, was noted. The temperature was followed by means of the copper–constantan couple and the potentiometer assembly referred to above. The results are presented in Fig. 1.

Experimental Procedure

The apparatus employed was the static low pressure system described in an earlier paper.[2] A few minor changes were made. The volume of heated tubing outside the furnace was diminished so that it never amounted to more than 1–2% of the total. A de Khotinsky bimetallic regulator in conjunction with a telegraphic relay controlled the temperature, which never varied more than 0.5° even during the longest runs.

The technique of starting the reaction by "flaming" the ester into the evacuated system and also of stopping were the same as those described in the earlier work. If any isostilbene isomerized during the "flaming" in, which usually took some thirty seconds, it was less than 0.5%.

Experimental Results and Discussion

Diethyl Maleate.—It is unfortunate that the experiments on this ester had to be abandoned because of excessive decomposition. At 300° this amounted to about 15% the first sixty minutes, while at 350° it decomposed about 70% in the first sixty minutes. The decomposition appeared to be homogeneous since treating the walls of the vessel with potassium chloride and substituting packed flasks had no effect on the rate of decomposition. The condensate was a dirty brown liquid and contained considerable amounts of a white solid. Analysis of the gaseous product showed it to consist of some 70% carbon monoxide and 10% carbon dioxide in addition to unidentified hydrocarbons. It

was obviously useless to attempt any investigation on isomerization under these conditions.

Dimethyl Citraconate.—Homogeneous decomposition occurred here to a considerable extent and attempts to correct the results for it were unsuccessful. Thus the data obtained are suitable only for semi-quantitative interpretation. To conserve space they are not reproduced here. The irregularities in the data were due to decomposition in the gas phase and not to changes in the liquid products during analysis by the miscibility method. This was demonstrated by permitting the liquid reaction products to stay at 100° in the oil-bath for some hours. No change in the consolute temperature could be detected. It was possible by means of accurate pipets to prepare the mixture of 0.6 cc. of oil and 0.4 cc. of reaction products to a reproducibility within 0.3%.
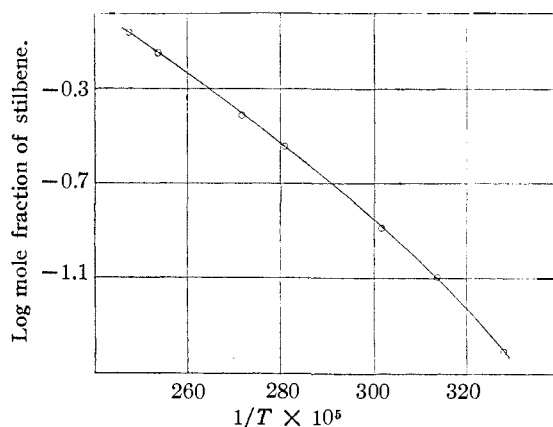

Fig. 1.—Calibration curve for stilbene–isostilbene mixture.

Over 100 runs were made at temperatures varying from 280 to 360° and at pressures from 500 to 30 mm. It was possible to establish that the isomerization is homogeneous and proceeds at a rate quite comparable to that of methylmaleic ester. The plot of log k against inverse temperature gives a curve, the activation energy increasing with temperature and reaching about 25,000 calories for the highest temperatures studied. Here the decomposition is relatively least important and the true activation energy should not be far from this value. The velocity constants show considerable dependence on pressure over the entire interval studied. It is thus possible to say that all conclusions reached in the case of dimethyl maleate apply, at least approximately, to this reaction.

Isostilbene.—This compound proved to be very stable. In some of the runs at lower tem-

peratures a slight drop in pressure was noted, but it never exceeded 1-2% of the total pressure. This however did not affect the reproducibility of the results. The reaction products condensed at once on applying solid carbon dioxide–ether mixture.

The liquid product was as clear and colorless as at the beginning of the run. The white crystals present in the product were identical in appearance with pure stilbene and possessed a melting point of 124° and gave an unchanged melting point on mixing with pure stilbene.

Rate measurements described below indicated the presence of the reverse reaction and a study of the position of thermal equilibrium was made. The results are reproduced in Table I. The values obtained by approaching equilibrium

TABLE I

T, °K.	Time, sec.	Initial Mol. fract. isostilbene	Mol. fract. stilbene	Final mol. fract. stilbene
593	996	0.00	1.00	0.957
593	1980	.00	1.00	.940
593	3660	.00	1.00	.940
593	5502	1.00	0.00	.828
593	12018	1.00	.00	.830
593	4116	0.171	.829	.932
593	3732	.064	.936	.932
		Probable equilibrium		.936
			K =	.0684
614	648	0.00	1.00	0.937
614	1638	.00	1.00	.924
614	1404	1.00	0.00	.817
614	3762	1.00	.00	.822
614	1752	0.178	.822	.917
614	1938	.053	.947	.923
		Probable equilibrium		.923
			K =	.083

from the stilbene (*trans*) side lie between 92–94% stilbene over the range 320–341° and are quite reproducible. When approaching the equilibrium from the isostilbene (*cis*) side the value lies between 82–83% over the same temperature range. Starting with mixtures around 83% stilbene or more the equilibrium value obtained with pure stilbene is approached. It is evident that the value obtained on heating the *trans* modification, which coincides with that obtained on heating mixtures, is the true equilibrium. Undoubtedly the lower value, 82–84%, obtained on heating the *cis* modification is due to some slight side reaction which occurs on prolonged heating of isostilbene, but not on heating the *trans* form. In view of the constant pressure

during reaction the process must be a rearrangement giving a liquid product which lowers the freezing point of the mixtures and thus registers in our analyses as isostilbene.

While the presence of measurable equilibrium is established by these experiments, the nature of the analytical method used does not allow a determination accurate enough to calculate the heat of reaction from the temperature coefficient of the equilibrium constant. It is preferable instead to set the entropy change in the isomerization equal to zero, an assumption not seriously in error. The heat of reaction thus obtained is $\Delta H = 3000$ calories, a value which will give a temperature coefficient of the equilibrium constant undetectable by our analytical method.

Measurements of the rate showed that the first order constants fall off during the progress of the reaction. This is due to the combined effect of the reverse reaction and the rearrangement postulated above. As the kinetics of the latter are unknown, the simple procedure was adopted of calculating the first order constants as if equilibrium existed at 83% stilbene at all temperatures. This procedure may be criticized as arbitrary. However, in almost all cases the corrections are small and independent of temperature and do not affect any of the conclusions reached below.

Table II presents the data accumulated for the determination of the activation energy. The constants in column 5 have been calculated from the simple first order equation. In column 6 the constants have been calculated by the equation

$$k = \frac{1}{t(1 + \alpha)} \log \frac{100}{100 - x(1 - \alpha)}$$

where α is the equilibrium constant at 83% stilbene and has the value 0.205. From Fig. 2 an activation energy of 42,800 calories is obtained. Table II shows the effect of pressure on the rate. The runs marked with an asterisk were carried out in a packed flask where the surface had been increased six times with Pyrex tubing. It had been observed that the first run or two in a new flask always gave slightly higher values than the subsequent reproducible runs. The slightly higher values in the packed flask are probably due to this. It may be concluded that the isomerization, as studied here, is essentially a homogeneous process. Table II shows that the rate constants were independent of pressure down to 5 mm. over nearly a 100-fold range.

The results of these experiments can be represented by the equation

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

If it is assumed that at the lowest pressures studied, 5 mm., the reaction rates may have fallen off 10%, an amount still within experimental error, it is possible to obtain a value for the minimum number of oscillators participating in energy transfer within the molecule. Using the method given by Kassel[8] with an assumed diameter for stilbene of 6×10^{-8} cm., at least 12 oscillators are found to be concerned in the energy transfer within the molecule.

TABLE II

T, °K.	p mm.	Time, sec.	Stilbene, %	k sec.⁻¹ × 10⁴	k_corr. sec.⁻¹ × 10⁴
553	148	1830	11.9	0.70	0.71
553	130	3816	20.7	.61	.62
553	135	7260	29.1	.63	.68
553	135	12006	51.5	.60	.67
			Av.	.63	.67
574	102	888	21.4	2.7	2.8
574.5	112	960	23.4	2.8	2.9
574	119	1140	24.1	2.4	2.5
574	113	3624	58.3	2.4	2.8
575	115	3660	59.8	2.5	2.9
			Av.	2.6	2.8
594	135	630	42.8	8.9	9.6
593	137	1206	62.5	8.1	9.6
593	137	1806	74.9	7.7	10.7
			Av.	8.2	9.9
615	143	258	54.5	30.5	34.6
614	144	624	75.3	22.4	31.7
			Av.	26.5	33.1

TABLE III

T, °K.	p mm.	Time, sec.	Stilbene, %	k sec.⁻¹ × 10⁴	k_corr. sec.⁻¹ × 10⁴
575	4.1	3060	58.4	2.9	3.3
574	4.9	2460	47.8	2.6	2.9
574	4.8	2880	54.6	2.7	3.1
			Av.	2.7	3.1
574	11.8	1008	22.6	2.5	2.6
574.5	11.8	1824	37.7	2.6	2.8
574	11.8	4386	63.1	2.3	2.7
			Av.	2.5	2.7
574	102	888	21.4	2.7	2.8
574.5	112	900	23.4	2.8	2.9
574	119	1140	24.1	2.6	2.5
574	113	3624	58.3	2.6	2.8
575	115	3660	59.8	2.5	2.9
			Av.	2.7	2.8

(8) L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," p. 210. The Chemical Catalog Co., Inc., New York.

574.6	141	1782	35.2	2.4	2.6
574	155	1800	36.0	2.5	2.6
			Av.	2.5	2.6
574	197	948	22.3	2.7	2.7
574	189	1542	30.7	2.4	2.5
575	205	1896	37.1	2.5	2.6
			Av.	2.5	2.6
575.5	370	1176	27.5	2.7	2.8
574.5	381	1998	40.5	2.6	2.8
575.0	310	3702	56.5	2.2	2.6
			Av.	2.5	2.7
*575	104	690	19.3	3.1	3.2
*575	101	2382	49.2	2.9	3.1
*575	104	2016	43.3	2.8	3.0
*575	105	3588	58.9	2.5	2.9
			Av.	2.8	3.1

* Runs in packed flask 6 × surface.

These results are in striking contrast with those obtained for dimethyl maleate where the limiting constant was given by[9]

$$k = 6.8 \times 10^5 e^{-26,500/RT}$$

and where not more than one oscillator participated in the activation process.

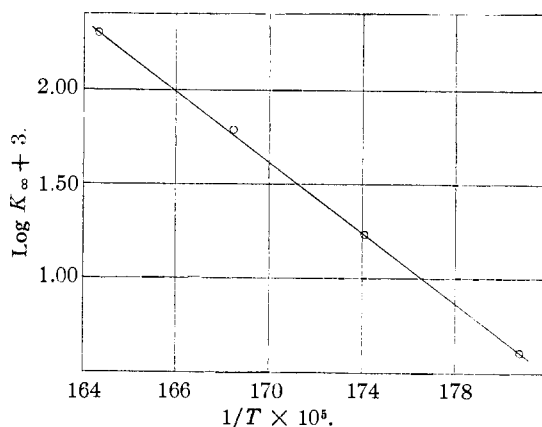Fig. 2.—Plot of log K_∞ vs. $1/T$.

While it is perhaps quite premature to make any rigid statements concerning the difference between the mechanism of these two isomerizations, an interpretation may lie in the following tentative remarks.

The large difference in activation energy for isomerization of the esters and of isostilbene may not necessarily indicate that the actual process of isomerization in both cases is not identical. Isomerization in both cases may be the same

(9) In the paper by Kistiakowsky and Nelles, THIS JOURNAL, 54, 2208 (1932), a numerical error is present and all constants in Table I should be multiplied by 5.29 to obtain correct values.

setting in of free rotation around the ethylenic carbons and subsequent deactivation, the large difference in activation energy being due to: (1) in the case of isostilbene the strength of the double bond may be greater due to the presence of the phenyl groups; (2) according to Tolman the measured energy of activation represents the difference in energy of average and activated molecules. This may be very different for stilbene and ester molecules since according to Raman spectra the two possess quite different oscillation frequencies. That this could account for large differences in activation energy will be demonstrated by Rice and Gershinowitz.[10]

The greater similarities of vibrational frequencies of the ethylenic carbon bond and the double bonds of the attached phenyl groups may account for the efficient energy transfer in isostilbene as contrasted with the esters.

Studies now in progress on esters of *cis* and *trans* cinnamic acid as well as derivatives of stilbene should yield data which will enable us to give a more comprehensive picture of the above facts.

Summary

1. Thermal isomerization of dimethyl citraconate has been investigated. Although the data obtained do not allow quantitative conclusions, evidence is obtained that this reaction is very similar to the earlier described isomerization of dimethyl maleate.

2. Isomerization of isostilbene to stilbene has also been studied. This unimolecular reaction has an activation energy of 43,000 calories and shows no falling off with pressure down to 4 mm. At least 12 oscillators must participate in the isomerization process.

3. Equilibrium in the gaseous system stilbene $\longrightarrow$ isostilbene has been observed. Equilibrium constants near 600 Å. are of the order of 0.07, from which an approximate heat of reaction of 3000 calories is calculated.

(10) O. K. Rice and H. Gershinowitz, in press.

The Heat of Adsorption of Carbon Monoxide on Copper[1]

BY RALPH A. BEEBE AND EDWIN LINCOLN WILDNER

In support of the theory that the atoms in the surface of an adsorbent possess varying degrees of activity, attention has been called to the measurements of heats of adsorption made by Bull, Hall and Garner[2] for oxygen on charcoal and by Beebe[3] for carbon monoxide on copper. In both researches it was reported that the differential heats of adsorption decreased progressively as successive small increments of gas were added to the adsorbing surface. The higher initial heats were explained by assuming that the first small portions of gas were adsorbed on atoms of charcoal, or of copper, of relatively high activity as compared to the other atoms in the surfaces.

Recently, several cases have been reported in which the differential heats of adsorption were found to be independent of the amount of gas already adsorbed on metallic surfaces.[4] More-

over defects have been discovered[5] in much of the earlier calorimetric work which may lead to serious errors in the results, especially for the initial stages of adsorption where the residual gas pressures are low. As a result some doubt has been cast on the reliability of the measurements for carbon monoxide on copper. One of us has reported elsewhere[5c] a careful search for possible sources of error in this case. With the information gained by this study, a new calorimeter has been designed and the measurements have been repeated for the initial stages of the adsorption.

Experimental

Description of the Method.—For reasons to be discussed later, the method was a modification of that developed by Bull, Hall and Garner[2] in its final form. The glass vacuum chamber used by these authors was simplified as shown in Fig. 1. While measurements were being taken, this chamber was maintained at constant temperature by an ice–water mixture. By vacuum jacketing the reference junction, it was possible to obtain time–temperature

(1) This article is based upon experimental work done by E. L. Wildner in partial fulfilment of the requirements for the degree of Master of Arts at Amherst College.

(2) Bull, Hall and Garner, *J. Chem. Soc.*, 837 (1931).

(3) Beebe, *J. Phys. Chem.*, **30**, 1538 (1926).

(4) (a) Ward, *Proc. Roy. Soc.* (London)., **A133**, 506 (1931); (b) Garner and Kingman, *Trans. Faraday Soc.*, **27**, 322 (1931); (c) Maxted and Hassid, *ibid.*, **29**, 698 (1933).

(5) (a) Maxted and Hassid, *J. Chem. Soc.*, 3313 (1931); (b) Schwab and Brenneke, *Z. physik. Chem.*, **16B**, 19 (1932); (c) Beebe, *Trans. Faraday Soc.*, **28**, 761 (1932).