

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

## KINETICS OF A THERMAL CIS-TRANS ISOMERIZATION. II

By M. NELLES<sup>1</sup> AND G. B. KISTIAKOWSKY

RECEIVED DECEMBER 23, 1931

PUBLISHED JUNE 6, 1932

Isomerization reactions involving a rotation around a carbon double bond have frequently been studied from a chemical point of view. In recent years kinetic studies of the process have been undertaken and some progress in this direction has been made. Most of this work however has been concerned with the photochemical and catalyzed reactions and therefore it need not concern us here.

Höjendahl<sup>2</sup> has studied the thermal isomerization of the maleic into fumaric acid in liquid state. He found a unimolecular reaction with an activation energy of some 15,000 cal. It is somewhat doubtful whether Höjendahl was not dealing with a reaction due to ionic catalysis in view of the low activation energy observed.

Ebert and Büll<sup>3</sup> have announced that measurements on the rate of isomerization of gaseous *cis* and *trans* dichloroethylenes are in progress. They reported that in thermal equilibrium at 300° the mixture contains about 65% *cis* and 35% *trans* compound.

The homogenous isomerization of the dimethyl ester of maleic acid in gaseous state has been recently described by the present authors.<sup>4</sup> The results presented there tend to show that the reaction is of the unimolecular type, although in the pressure range investigated (500 to 45 mm.) the activation rate is insufficient to maintain a unimolecular reaction rate. From the temperature dependence of the rate in the range 270–380°, the activation energy was calculated to be 26,500 cal.

The only secondary reaction which in any way complicated the measurements was a slow decomposition of the fumaric ester formed in the main reaction. The decomposition reaction is accompanied by pressure change, one molecule of carbon dioxide and one molecule of a substance (probably  $\text{CH}_3\text{—CH=CH—COOCH}_3$ ), which condenses on cooling to room temperature, being formed.

Further experiments seemed necessary to establish more conclusively some of the results obtained. The present paper deals with the reaction rate at pressures above atmospheric, with the influence of inert gases on the rate and with an attempt to determine the position of thermal equilibrium.

<sup>1</sup> Charles A. Coffin Fellow.

<sup>2</sup> Höjendahl, *J. Phys. Chem.*, **28**, 758 (1924).

<sup>3</sup> Ebert and Büll, *Z. physik. Chem.*, **152**, 451 (1931).

<sup>4</sup> Kistiakowsky and Nelles, *ibid.*, Bodenstein Festband, 369 (1931); in the following pages referred to as the first paper.

### Experimental Details

The preparation of the materials and the analysis of the reaction mixtures by the freezing point method have been described in the first paper.

A static method was used in the high pressure experiments. Two quartz tubes (capacity 185 and 55 cc.) with heavy walls served as reaction vessels. The following procedure was adopted after several other methods proved unsatisfactory in that they gave unreproducible results. One end of the quartz tube was drawn to a capillary (B in Fig. 1) and the other sealed, through a graded seal, to a T joint. One end of this was connected through a mercury cut-off to the mercury pump and the other ended in a ground joint to which fitted a small tube containing a weighed amount of the ester. The system was evacuated, the ester cooled by carbon dioxide-ether mixture and the quartz vessel degassed at 500-600°. The mercury cut-off was closed, the cooling mixture transferred to the quartz vessel and the ester allowed to distil at room temperature. The quartz vessel was sealed off and placed in a molten lead-tin bath (Fig. 1) for a suitable length of time. It was then quickly cooled by a blast from a carbon dioxide tank. The capillary end of the vessel was attached to a mercury manometer by a cement joint. The manometer was evacuated and the capillary broken by a magnetic plunger while the esters were cooled by carbon dioxide-ether mixture. From the manometer readings and the volume of the system the pressure of carbon dioxide at the end of the heating period could be readily calculated. The liquid products were then analyzed by the freezing point method.

The effect of inert gases on the reaction rate was also studied in a static system which is shown in Fig. 2. The ester was introduced through B into C and the former sealed off. The system was then evacuated through A while the ester was cooled by solid carbon dioxide. The inert gas was admitted through a three-way stopcock placed between A and the pump. The system was sealed off at A and the ester vaporized by applying a smoky flame. Finally C was covered with a small electric furnace heated to the temperature of the main furnace. On completion of a run C was cooled and immersed in a carbon dioxide cooling mixture. A rubber tubing attached to the pumps was slipped over A and the tip of this broken with a pair of pliers. The inert gas was slowly pumped out while the ester condensed in C. Appropriate manometer readings were taken to determine the pressure of the inert gas, the total pressure and its change in the course of a run. All gases studied were taken from commercial cylinders. Nitrogen and hydrogen were passed through a purifying train containing a heated tube with copper gauze, wash-bottles with sodium hydroxide solution and sulfuric acid and a tube with phosphorus pentoxide. Propane was purified by passing it through wash-bottles containing fuming sulfuric acid, dilute sulfuric acid, alkaline potassium permanganate and concentrated potassium hydroxide solution. After drying over phosphorus pentoxide it was fractionated several times in vacuum. Carbon dioxide was subjected only to a repeated fractional sublimation in vacuum. With the last two

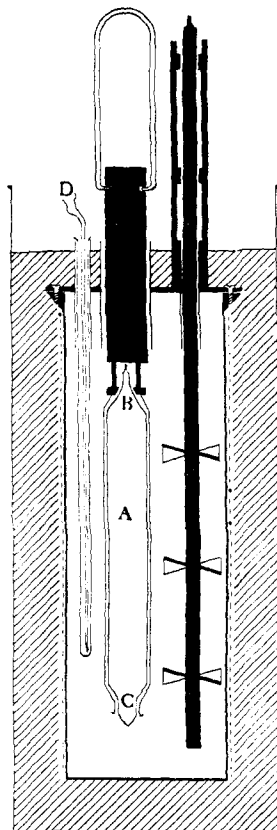


Fig. 1.—The thermostat for high pressure experiments.

gases it was found that a very thorough purification was required, quite erratic results being obtained otherwise.

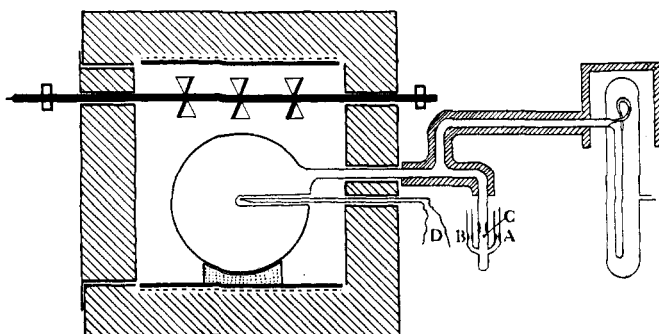


Fig. 2.—The apparatus for low pressure experiments.

### Experimental Results and Discussion

Table I presents the results of the final series of experiments on the rate at high pressures.

No.	T, °K.	Time, minutes	TABLE I		Fumaric ester, %		K min. <sup>-1</sup> × 10 <sup>4</sup>	
			p, mm.	Δp, mm.	By analysis	Corrected		
1	573	122	732	34.5	11.2	15.9	2.67	
2	573	108	731	40.0	8.5	14.0	2.63	
3	573	121	731	32.4	10.8	15.2	2.58	
							Av.	2.62
4	573	60	2140	30.0	12.0	13.4	4.52	
5	573	60	2139	31.2	11.8	13.4	4.52	
6	573	62	2142	27.8	13.2	14.5	4.75	
							Av.	4.57
7	573	30	4070	32.4	7.8	8.6	5.65	
8	573	45	4060	44.0	9.4	10.5	4.65	
9	573	45	4060	46.2	3.6	10.7	4.74	
							Av.	5.01

In column 5 is given the amount in mm. of carbon dioxide formed at the temperature of the experiment. It was set equal to the amount of fumaric ester decomposed and added to the fumaric ester found by analysis in calculating the rate constants. The rest of the table is self-explanatory. It will be noticed from these data that with increasing pressure the rate tends to become unimolecular. This is particularly well shown by Fig. 3, in which the new data as well as those obtained previously (I) have been plotted. The velocity constant at 45 mm. pressure has not been included in Fig. 3 in order not to reduce the scale of the drawing too much. This constant does not fall on the straight line drawn, being about 30% too high. The measurements at this pressure, however, were rather unsatis-

factory due to large percentage decompositions of fumaric ester and little weight should be attributed to this discrepancy. The rest of the points in Fig. 3 fall very near a straight line calculated from the equation

$$K_{573^\circ} = \frac{7.7 \times 10^{-4}}{1 + \frac{1400}{P_{\text{mm}}}} \text{ min.}^{-1} \quad (1)$$

showing that the reaction is indeed of unimolecular type.

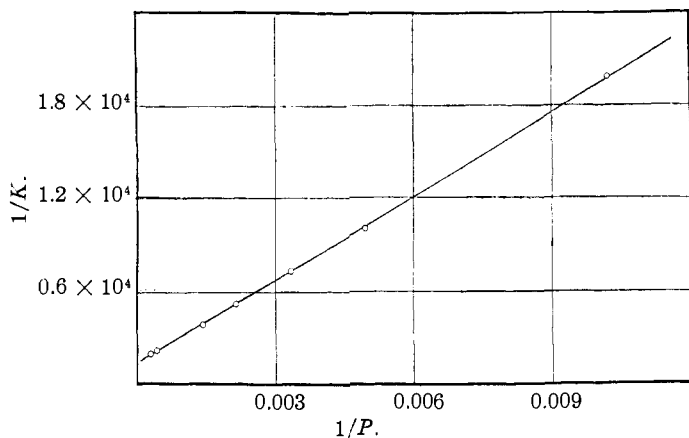


Fig. 3.—A plot of inverse velocity constants against inverse pressure.

In Table II are presented experiments dealing with the action of inert gases.

TABLE II  
EXPERIMENTS WITH INERT GASES

No.	T, °K.	Time, minutes	Pressure, mm.	Total pressure	Δ pressure	Fumaric ester, % By analysis	Corrected	K × 10 <sup>4</sup>
No added gas								
19	593	56	110		1	3.0	3.9	6.71
18	593	126	108		1	6.7	7.7	6.38
20	593	177	112		1	11.1	12.0	7.20
21	594	234	108		2	14.9	16.9	7.91
								7.05 at 593°
Hydrogen 250 mm.								
118	591	93	110	360	1.5	5.2	6.6	6.65
119	588	63	110	360	1.0	3.0	3.9	6.35
120	588	84	110	360	1.4	4.4	5.7	7.00
								6.65 at 588°
Hydrogen 500 mm.								
121	588	66	114	614	1.0	4.4	5.3	8.80
122	591	63	120	620	1.1	4.0	4.9	7.72
123	589	92	112	612	1.2	5.5	6.6	7.76
								8.1 at 590°

TABLE II (Concluded)

No.	T, °K.	Time, minutes	Pressure, mm.	Total pressure	$\Delta$ pressure	Fumaric ester, % By analysis Corrected		K $\times 10^4$
Nitrogen 250 mm.								
111	595	71	110	360	1.2	4.0	5.1	7.14
113	594	37	109	359	0.6	2.4	2.9	7.84
114	599	79	113	363	1.4	4.7	6.0	6.60
<hr/>								
7.22 at 594°								
Nitrogen 500 mm.								
115	592	47	112	616	0.9	1.7	2.5	5.66
116	593	82	111	611	1.6	3.5	5.0	6.27
117	593	39	112	612	0.8	1.4	2.1	5.50
<hr/>								
5.81 at 593°								
Propane 500 mm.								
170	591	60	164	664	2.5	8.1	9.6	16.9
171	592	58	113	613	2.5	6.1	8.3	15.2
172	591	62	126	626	1.4	6.7	7.8	13.5
<hr/>								
15.2 at 591°								
Carbon Dioxide 500 mm.								
127	591	61	112	612	6.8	10.7		18.6
128	591	29	107	607	5.3	16.4		22.5
<hr/>								
20.5 at 591°								

Hydrogen and nitrogen are both found to be without influence on the reaction. Propane has a feeble accelerating action, equal to about one-tenth of the effect of the esters themselves. The effect of carbon dioxide is more pronounced. It is obscured somewhat by a rapid decomposition of the esters induced apparently by carbon dioxide. Because of this the isomerization rate constants have been calculated here neglecting the decomposition reaction. They represent therefore the minimum values of the acceleration produced. Inasmuch as it is not known whether fumaric ester alone or maleic ester also decomposes in presence of carbon dioxide, a more accurate calculation is impossible.

Some experiments have been carried out to determine the position of thermal equilibrium. The decomposition of fumaric ester precludes the study of equilibrium by the usual methods. The procedure adopted was to heat known mixtures of the esters for a short time and to determine the change in the freezing point. It was found that at 280° the freezing point remained unchanged in a 1 : 1 mixture. It was lowered in mixtures richer in fumaric ester and raised in mixtures richer in maleic ester. On studying the temperature dependence of this apparent equilibrium over the range 255–320°, the following expression was found to represent it approximately

$$\ln K = \frac{6000}{RT} - 5.5$$

Such a large entropy change in a reaction of the present type seemed to be quite unlikely and suggested that the equilibrium was fictitious. Further experimentation showed indeed that the liquid formed on heating fumaric ester was not maleic ester. The lowering of the freezing point is due therefore chiefly to decomposition reactions. Although this finding precludes an accurate determination of the equilibrium, still the conclusion can be reached that in the true state of equilibrium more than 50% of fumaric ester is present. This is to be compared with the observation of Ebert and Büll that, of the two dichloroethylenes, the *cis* modification is the more stable one.

It has been pointed out in the first paper that the isomerization process is unusually slow as compared with other unimolecular reactions. The measured rate of activating collisions, equal to the reaction rate at low pressures, is of the order of  $10^{28} e^{-24,500/RT} c^2$  ( $c$ , concentration in moles per liter). The rate of collisions with energy in excess of 26,500 cal. contained in two square terms is about  $7 \cdot 10^{31} e^{-24,500/RT} c^2$ . Experiments at higher pressures indicate that the limiting velocity constant at infinite pressure is

$$K_{\infty} = 1.3 \times 10^5 e^{-26,500/RT} \text{ sec.}^{-1}$$

Usually the temperature independent factor is at least of the order of  $10^{10}$ . The other unimolecular reactions which have activation rate not exceeding the rate of collisions with energy contained in two square terms are the decompositions of nitrous oxide<sup>5</sup> and of nitryl chloride.<sup>6</sup> As both these molecules consist of only very few atoms, a much greater rate could hardly be expected. The decompositions of larger molecules, studied thus far, all require the assumption of internal energy exchange between several degrees of freedom. It has been noticed, however,<sup>7,8</sup> that most frequently not all degrees of freedom, available from the point of view of specific heats, participate in the reaction. The barriers which partially prevent energy exchange within the molecules must be particularly effective in the isomerization process, as shown by the present measurements. This should be attributed to the character of mechanical motion responsible for the reaction: a rotation of heavy atomic groups around the double bond instead of the longitudinal vibrations active in decomposition processes. From this point of view it is comprehensible also that only heavy molecules like carbon dioxide and propane are able to participate in the activation process of the isomerization, while in decomposition reactions of organic molecules hydrogen seems to participate more readily than any other molecule.

<sup>5</sup> Volmer, *Z. physik. Chem.*, **9B**, 141; **10B**, 414 (1930).

<sup>6</sup> Schumacher and Sprenger, *ibid.*, **12B**, 112 (1931).

<sup>7</sup> Rice, *ibid.*, **7B**, 226 (1930).

<sup>8</sup> Ramsperger and Leermakers, *THIS JOURNAL*, **53**, 2061 (1931).

In view of the slowness of the activation rate, it could be assumed that energy is transferred in collisions directly to the oscillatory motion around the double bond. When energy in excess of 26,500 cal. has been accumulated, free rotation results. On the next inelastic collision accompanied by energy loss a maleic or fumaric ester molecule is formed depending on the orientation of the two rotating halves of the molecule in the instant of collision. The relative yields of the two are determined by the average times spent by the rotating molecule in the *cis* and the *trans* configuration. There are no grounds to assume that the times spent in either form differ considerably and therefore about a 50% yield of fumaric ester should be expected. On the basis of this mechanical model the gradual falling off of the reaction rate, as compared with activation rate, with increasing pressure is due to the fact that some molecules lose their energy before carrying out a 90° rotation. A considerable difficulty appears, however, if this assumption is made. It will be noticed from equation (1) that half of all activated molecules lose their energy, before free rotation has been established, at 1400-mm. pressure. The collision frequency at this pressure is about  $10^{11}$  sec.<sup>-1</sup>. Activation occurs on less than one in a thousand possible collisions and, since the statistical energy distribution must be maintained, the same is true of deactivation. Therefore the average time between activation and deactivation is of the order of  $10^{-8}$  sec. This is a considerably longer time interval than the likely period of a rotation. Thus the possibility must be considered that some time elapses between the instant of the activating collision and the setting in of free rotation. This would occur if the energy was first transferred to some other mode of motion within the molecule and only later supplied to the rotation around the double bond. A proposal of this kind, while eliminating one difficulty, is not entirely satisfactory in that it obscures the cause of the exceptional slowness of energy exchange between ester molecules and also the lack of energy exchange with any but heavy inert gas molecules. Experiments on other esters of maleic acid, now in progress in this Laboratory, will perhaps settle this problem.

The position of equilibrium with dichloroethylenes as determined by Ebert and Büll<sup>3</sup> shows that dipole interaction in these molecules is quite small. In dimethyl esters of maleic acid the interaction should be even weaker on account of larger distance between the dipoles. It is thus apparent that the activation energy observed (26,500 cal.) represents almost exclusively the straining of the double bond on a 90° rotation of the two atomic groups composing the molecule.

### Summary

1. The rate of homogenous isomerization of gaseous dimethyl maleic ester into dimethyl fumaric ester has been studied at pressures up to 5

atm. and also in the presence of hydrogen, nitrogen, propane and carbon dioxide.

2. The variation of the velocity constant with pressure can be represented by the equation

$$K_{573^\circ} = \frac{7.7 \times 10^{-4}}{1 + (1400/P)} \text{ min.}^{-1}$$

from which the limiting value at infinite pressure is obtained to  $K_\infty = 1.3 \times 10^5 e^{-26500/RT}$  sec.<sup>-1</sup>.

3. Hydrogen and nitrogen have no effect on the reaction velocity, while propane and carbon dioxide accelerate it.

4. In the thermal equilibrium the ratio of fumaric to maleic ester is greater than unity.

5. The slowness of the activation process in the reaction is discussed and is linked to the nature of the mechanical motion responsible for the reaction.

CAMBRIDGE, MASSACHUSETTS

---

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN]

## THE PREPARATION AND PROPERTIES OF TITANIUM TETRABROMIDE AND TITANIUM TRIBROMIDE HEXAHYDRATE<sup>1</sup>

BY JOHN C. OLSEN AND EMMETT P. RYAN

RECEIVED DECEMBER 26, 1931

PUBLISHED JUNE 6, 1932

Very few of the salts of titanium have been prepared in pure form and their properties studied. Considerable work has been done at the Polytechnic Institute on titanium compounds. As a part of this research titanium tetrabromide and titanium tribromide hexahydrate have been prepared and studied.

Duppa<sup>2</sup> prepared the tetrabromide and describes it as an amber-yellow substance, attracting moisture with the greatest avidity and being converted into titanous and hydrobromic acids, boiling at 230° and melting at 39°. Thorpe<sup>3</sup> describes it as a dark yellow or orange crystalline mass melting at about 40° and boiling at 229° uncorrected. Its density is reported as 2.6 by Duppa and 3.37<sub>4</sub><sup>5</sup> by Klemm, Tilk and Müllenheim.<sup>4</sup>

**Preparation of Titanium Tetrabromide.**—The tetrabromide was prepared in three ways.

<sup>1</sup> From the thesis submitted in partial fulfilment of the requirements for the degree of Master of Science by Emmett P. Ryan. This paper was read at the Buffalo Meeting of the American Chemical Society, August 30–September 4, 1931.

<sup>2</sup> Duppa, *Proc. Roy. Soc. (London)*, **8**, 42 (1857).

<sup>3</sup> Thorpe, *J. Chem. Soc.*, **47**, 126 (1885).

<sup>4</sup> Klemm, Tilk and Müllenheim, *Z. anorg. allgem. Chem.*, **176**, 1–22 (1928).