The Review of Physical Chemistry of Japan Vol. 22 No. 1 (1952)

CIS-TRANS ISOMERIZATION OF MALEIC ACID TO FUMARIC ACID UNDER PRESSURE.

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Introduction.

Maleic and fumaric acids are cis-trans isomers. A number of investigators(1)–(5) have studied the mechanism of a catalyzed isomerization of maleic acid to fumaric acid and observed quantitatively that maleic acid was isomerized by heating the aqueous solution in the sealed tube above 130° C and by catalyzing with various acids and salts at 99.9° C under atmospheric pressure. Moreover, they experimented qualitatively that solid maleic acid was transmutated to solid fumaric acid by heating over the melting point and completely isomerized at 200° C in 1 ~ 2 hours. Other investigators(6),(7) have shown that maleic and fumaric acids reached equilibrium from each other in the aqueous solution in the light of ultraviolet.

The isomerization under pressures 15,000 ~ 20,000 Kg/cm² was tried at room temperature by Bridgman(8), and also by the authors, as crystal fumaric acid had 2.8 per cent smaller volume than crystal maleic acid at 20° C under atmospheric pressure, but in no case the form of smaller volume was produced by pressure.

Now the authors experimented the transmutation of maleic acid into fumaric acid in the solid or melting states under pressures 1 ~ 2,250 atm by heating at 100 ~ 175° C and discussed the effect of pressure on the isomerization.

Experimentals.

(1) Material.

Maleic acid was obtained by dissolving commercial maleic acid anhydride in water and by recrystallization.(4),(5) Its purity was tested by the titration (above 99.9 %) and the melting point (130.5° C).

(2) Procedure.

The experiment under atmospheric pressure was carried out as follows: soft glass test-tubes of about 10 cm in length and about 0.6 cm in inner diameter, each containing about 0.8 gr of maleic acid, were sealed and heated at the fixed temperature for a definite time in an oil-bath.

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(1) J. Pelouze, *Ann. Chem.*, **11**, 263 (1834)
(2) Zd. H. Skraup, *Monat. Chem.*, **12**, 107 (1891), *ibid.*, **14**, 501 (1893)
(3) S. Tanatar, *Ann. Chem.*, **273**, 31 (1893), *Ber.*, **27**, 1365 (1894)
(4) E. M. Ferry and L. Eichelberger, *J. Am. Chem. Soc.*, **47**, 1402 (1925)
(5) K. Nozaki and R. Ogg, *ibid.*, **63**, 2583 (1941)
(6) A. Smakura and A. Wassermann, *Z. Physik. Chem.*, **A155**, 353, 366 (1931)
(7) Bohhoeffer and Harteck, "*Grundlagen der Photochemie*", Dresden, Leipzig, p. 269 (1933)
(8) P. W. Bridgman, "*The Physics of High pressure,*" London, p. 378 (1949)

The experimental apparatus and procedure at high pressure are the same as in the reports of *This Journal.*(9),(10) About 0.8 gr of maleic acid in the pressure-proof vessel was preheated at about 120°C before the compressing procedure and controlled at the fixed temperature in a few minutes after the definite pressure was applied. A few per cent of maleic acid was isomerized to fumaric acid during the manipulation above described. The values are shown in Table 1, being within 0.1 per cent below 145° C. They were used as the initial concentration of the isomerization.

Table 1

Temp.°C \ Atm	Initial concentration in per cent				
	450	900	1350	1800	2250
155	0.3	0.4	0.4	0.2	<0.1
165	1.1	1.3	1.4	1.6	0.6
175	1.9	2.1	2.3	2.6	2.6

(3) **Determination of fumaric acid.**

The amount of maleic acid isomerized to fumaric acid was determined quantitatively as follows.(2)~(5) Fumaric acid slightly soluble is much less soluble in water than maleic acid. The solubilities(11) in 100 gr water of fumaric and maleic acids are 0.70 and 78.8 gr at 25° C respectively. A definite volume of a saturated aqueous solution of fumaric acid (0.035 M at 0° C)(5) was poured into an unknown sample of a mixture of maleic and fumaric acids, and maleic acid was completely dissolved after immersing in an ice-water bath for about 5 hours. The insoluble fumaric acid was filtered off with a suction on a small glass filter and carefully washed two or three times with a definite volume of a saturated aqueous solution of fumaric acid at 0° C. The filtrate was titrated with about 0.1 N standard alkali, using a phenolphtalein indicator. The quantity of fumaric acid added to the solution of the sample and its filtrate were corrected. More than 0.8 milligrammes of fumaric acid could be detected by this method.

Experimental Results.

The transition, under the conditions of temperatures 125 ~ 175° C, pressures 1 ~ 2,250 atm and reaction time 1/2 hour, is shown in Table 2 and Fig. 1. Every isotherm has an inflexion point which shifts to high temperature with increase in pressure. Maleic acid is isomerized in the liquid state fastly till the point and in the solid state slowly after the point. The diagram between the per cent of fumaric acid isomerized and the temperature is plotted in Fig. 2 from Table 2. The inflexion

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(9) R. Kiyama, *This Journal*, **19**, 1 (1945)

(10) R. Kiyama and T. Yanagimoto, *ibid.*, **21**, 32 (1951)

(11) Int. Crit. Table, vol. **4**, 25 (1928)

Table 2

Temp.° C \ Atm	Transition per cent in 1/2 hour					
	Atmos. Press.	450	900	1350	1800	2250
125	0.7	0.5	——	——	——	<0.1
135	9.2	10.2	4.9	2.3	1.1	0.5
145	18.0	21.5	23.3	10.1	4.1	1.7
155	26.2	30.4	35.3	37.3	14.6	5.3
165	35.3	39.5	45.1	51.2	55.8	21.1
175	45.7	49.7	55.8	61.7	67.7	67.1

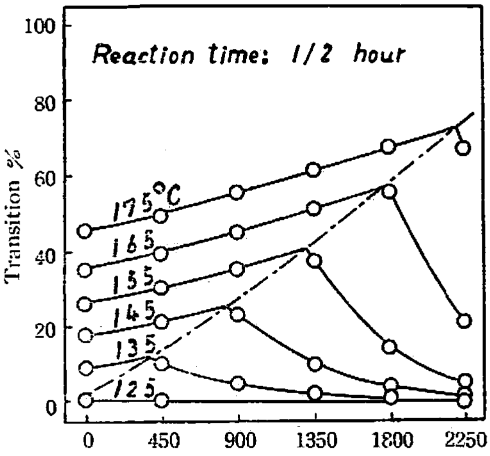

Fig. 1

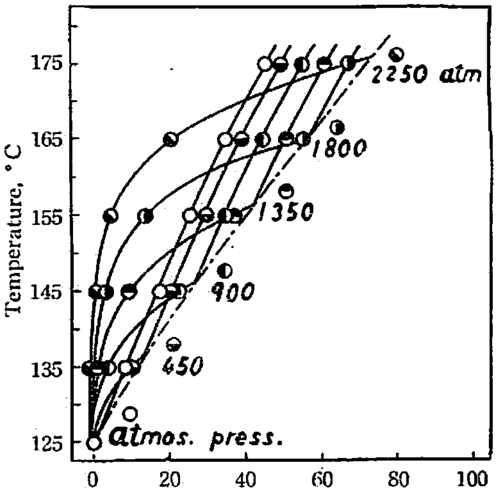

Fig. 2

point of every isobar shows the melting point of the mixture of various component ratio under pressure and shifts to high temperature with increase in pressure.

The transitions in the sealed tube at

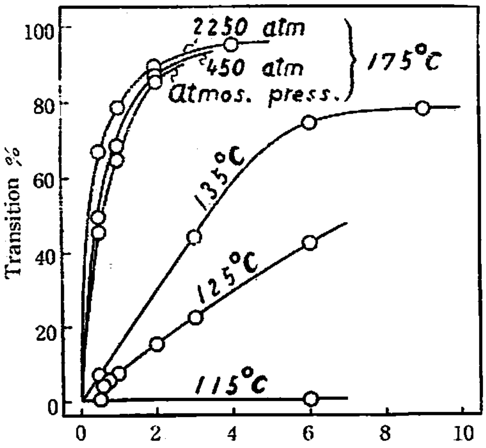

Fig. 3 Time (hour)

Table 3

Hour \ Atm	Transition % at 175° C		
	Atmos. Press.	450	2250
1/2	45.7	49.7	67.1
1	65.2	68.6	78.5
2	85.4	87.0	89.2
4	——	——	95.0

115~175°C, and under 450 and 2,250 atm at 175°C are shown in Fig. 3 and Table 3. The isomerization in the sealed tube was not found in 6 hours at 100°C and below 0.1 per cent at 110°C. The curve at 125°C has an inflexion point at the initial stage of isomerization. Maleic acid is still in the solid state till the point similarly as the solid state at 115°C and melts partially with fumaric acid after the point. Maleic acid melts completely in the course of isomerization as at 135 and 175°C and supersaturated fumaric acid is gradually depositted. The curve at 135°C reaches nearly equilibrium in 10 hours. The transition under pressure at 175°C results in little increase with pressure.

Discussions.

The main experimental results obtained above can be summerized as follows:

(1) Every isotherm has an inflexion point which shifts to high temperature with increase in pressure. Maleic acid is isomerized in the liquid state till the point and in the solid state after the point. (Fig. 1)

(2) The rate of transition increases with pressure till the inflexion point, but decreases after the point. (Fig. 1)

(3) The amount of transition at the fixed temperature for a few hours results in little increase with pressure. (Fig. 3)

The melting point of a material shifts to high temperature with increase in pressure. The values of a number of materials under pressure have been measured by Bridgman(12) and are found in Int. Crit. Table, vol. 4, p. 9, in which are given the two constants of the parabolic formula $t - t_0 = ap + bp^2$, in terms of which Tammann was able to reproduce his results. The rate of transition increases with pressure, so long as maleic acid melts, but it decreases in the solid state, as the melting point of maleic acid also shifts to high temperature with increase in pressure.

The effect of pressure of chemical equilibrium is given by the general expression,

$$\left(\frac{\partial G}{\partial P}\right)_T = V, \qquad (1)$$

where G is Gibbs's free energy, P pressure and V molecular volume.
And

$$R \ln K_p \Delta T = \Delta G \qquad (2)$$

where K_p is the equilibrium constant under a constant pressure and given by ([fumaric acid]/[maleic acid])*equil.* and ΔG is the difference of the free energy between fumaric and maleic acids. From equations (1) and (2),

$$\frac{d \ln K_p}{dP} = -\frac{\Delta V}{RT}, \qquad (3)$$ (13)(14)

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(12) P. W. Bridgman, "*The Physics of High Pressure,*" London, chap. 7 (1949)

(13) M. G. Evans and M. Polanyi, *Trans. Farad. Soc.*, **31**, 875 (1935), **32**, 1333 (1936), **33**, 448 (1938)

(14) M. G. Evans, *ibid.*, **34**, 49 (1938)

where ΔV is the difference of the molecular volume between fumaric and maleic acid and dependent on temperature and pressure. When it is postulated that ΔV results in little change with increases in temperature and pressure, the equation,

$$\ln\frac{K_p}{K_{p'}} = -\frac{\Delta V}{RT}(P - P'), \qquad (4)$$

is obtained from the integration of equation (3) and expresses the effect of pressure on the equilibrium. The molecular volumes of fumaric and maleic acids calculated from the densities(15) at 20°C under atmospheric pressure are 70.966 and 72.975 cc/mole respectively. The difference is -2.009 cc/mole. The isomerization at 175°C under atmospheric pressure calculated from equation (4) to the transition (95.0 %) for 4 hours under 2,250 atm, is 94.4 % in accordance with the experiment.

The authors are indebted to the Department of Education for the Grant to the Cooperative Research (The Fundamental Research on High Pressure Industries).

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Kyoto University.

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(15) C. D. Hodgman, "*Handbook of Chemistry and Physics*", Cleveland, Ohio, p. 683, 719 (1939)