

200. *Liquid-phase Reactions at High Pressures. Part X.** *The Rates of Some Isomerisations and Rearrangements.*

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The rates of five isomerisations and rearrangements in solution have been measured at pressures up to 5000 atmospheres. One of the reactions is slowed by high pressures and the other four are accelerated, but to widely varying degrees. The differences in the response to pressure can be explained on the basis of the ionic solvation theory of the pressure effect, except in the case of the cyclisation of citraldehyde. The acceleration of this reaction probably indicates that the configuration necessary for ring-formation is favoured by high pressures.

THE investigation of the effect of high pressures on the rates of reactions in liquids and solutions has been extended to some isomerisations and molecular rearrangements. Rate determinations have been made up to 5000 atm. and usually at several temperatures, for (i) the isomerisation of maleic acid to fumaric acid, catalysed in aqueous solution by potassium thiocyanate, (ii) the isomerisation of diethyl maleate to diethyl fumarate in acetone, catalysed by diethylamine, (iii) the rearrangement of *N*-chloroacetanilide to *o*- and *p*-chloroacetanilide, catalysed by hydrochloric acid, in aqueous solution, (iv) the rearrangement of α -phenylallyl alcohol to cinnamyl alcohol in aqueous dioxan, catalysed by hydrochloric acid, and (v) the cyclisation of citraldehyde to *p*-menth-1-ene-3:8-diol, catalysed by hydrochloric acid in aqueous ethanol.

EXPERIMENTAL

Apparatus.—The high-pressure equipment has been described in earlier papers.¹ The cylindrical steel vessel is immersed in an oil-bath at a constant temperature ($\pm 0.05^\circ$), and is closed at the top by a steel screw plug. The lower end of the cylinder is connected by steel capillary tubing to a piston intensifier. The apparatus contains medicinal paraffin and the pressure is transmitted to the reactants through a mercury seal at the bottom of the Pyrex glass reaction tube of 3 to 4 ml. capacity.

Procedure.—Solutions of reactant and catalyst of concentrations chosen to give a time of half-change between four and seven hours were mixed and put in the reaction tube. This was enclosed in the pressure vessel and pressure was generated through the intensifier by means of an oil hand-pump. The pressure on the low-pressure side of the intensifier was measured on a Bourdon tube gauge (calibrated against a free-piston gauge) and the pressure in the reaction vessel was calculated from the known effective ratio of the intensifier. Throughout the runs (250 to 500 min.) the pressure was kept constant ($\pm 1\%$).

Materials.—Potassium thiocyanate, hydrochloric acid, acetone, and dioxan of "AnalaR" grade, and absolute ethanol were used. Diethylamine (b. p. $55.5^\circ/755$ mm.) and α -citraldehyde (b. p. $118^\circ/20$ mm., n_D^{17} 1.4895) were redistilled. Maleic acid (m. p. 131°) was prepared by dissolving redistilled maleic anhydride (b. p. $84^\circ/15$ mm.) in water, recrystallising twice, and drying *in vacuo*. Diethyl maleate (b. p. $120^\circ/25$ mm., $n_D^{17.5}$ 1.4409) and diethyl fumarate (b. p. $106^\circ/25$ mm., $n_D^{17.5}$ 1.4420) were prepared from ethanol and the acids.² α -Phenylallyl alcohol (b. p. $106^\circ/16$ mm., $n_D^{17.5}$ 1.5442) was prepared from acraldehyde and phenylmagnesium bromide.³ *N*-Chloroacetanilide was made from acetanilide and sodium hypochlorite⁴ and was 99.5% pure (titration of iodine liberated from potassium iodide). Solutions of the reactants were stored in the dark.

Analytical Methods.—*Reaction* (i). Maleic acid solution (2 ml.) and potassium thiocyanate solution (1 ml.) were pipetted into the reaction tube, and Terry and Eichelberger's analytical method⁵ was used. Fumaric acid was precipitated at 0° , and the unchanged maleic acid titrated with sodium hydroxide (phenolphthalein).

* Part IX, *J.*, 1955, 2295.

¹ (a) P'eng, Sapiro, Linstead, and Newitt, *J.*, 1938, 784; (b) Weale, *J.*, 1954, 2959.

² Wachholtz, *Z. phys. Chem.*, 1927, 125, 1.

³ Braude, Jones, and Stern, *J.*, 1946, 396.

⁴ Barnes and Porter, *J. Amer. Chem. Soc.*, 1930, 52, 1721.

⁵ Terry and Eichelberger, *ibid.*, 1925, 47, 1402.

Reaction (ii). Nozaki's modification⁶ of Kistiakowsky and Smith's⁷ method was employed. After removal of solvent and catalyst, 0.40 ml. of the partially isomerised ester was added to 0.60 ml. of liquid paraffin and the consolute temperature determined. The composition was then obtained ($\pm 0.5\%$) from the linear relation between consolute temperature and composition found experimentally (100% maleate, 105.1°; 100% fumarate, 30.0°).

Reaction (iii). *N*-Chloroacetanilide was determined by titration with thiosulphate of the iodine liberated from 2 ml. of reaction mixture by 20 ml. of 0.1*N*-potassium iodide containing acetic acid.

Reaction (iv). As in the method of Braude *et al.*,³ the change in absorption at 251 μ was measured with a Unicam ultraviolet spectrophotometer. Considerable care was necessary with the acetone solutions as this solvent absorbs appreciably at 251 μ .

Reaction (v). The rate of the cyclisation of citraldehyde, which is accompanied by disappearance of the aldehyde group and one of the two double bonds, was measured in water by Price and Dickman.⁸ Aqueous ethanol, in which citraldehyde is more soluble, was used in the high-pressure experiments because of the small volume of the reaction tube. The reaction was followed by quantitative bromination. To 1 ml. of the reacting solution was added a measured excess of freshly standardised bromine water, and the mixture kept for 2 min. Excess of potassium iodide solution was then added and the iodine titrated with thiosulphate. Three such determinations were performed in succession, and the bromine water was immediately re-standardised.

Experiments without Catalyst.—Subsidiary experiments showed that none of the reactions proceeded at a measurable rate under pressure without a catalyst. Diethyl maleate containing diethylamine, but without solvent, underwent 100% isomerisation in less than 1 hr.

Results.—With the possible exception of the isomerisation of maleic acid, previous workers have established that at normal pressure the reactions are of the first order with respect to the substance undergoing rearrangement.^{3, 6, 8, 9, 10, 11} It has also been shown that the observed reaction constants, k' , contain the catalyst activity (in two cases the square of the activity) as a factor. To have systematically confirmed these findings at high pressures would have been prohibitively time-consuming, but the rate constants for each reaction, calculated according to the normal-pressure kinetics from runs of varying duration, were satisfactorily consistent.

Each of the observed constants, k' , should therefore be divided by the appropriate power of the catalyst activity at the pressure and temperature of the measurement, to convert it into the true first-order constant, k . If this is not done the effect of pressure on the rate may be obscured by changes in the activity of the catalyst at high pressures. Except for aqueous dioxan solutions the actual catalyst concentrations can be calculated from existing data for the compressions of the solvents. An expression for the activity coefficients of hydrochloric acid in water at high pressures is given by Harned and Owen¹² so that the complete correction can be made for the *N*-chloroacetanilide rearrangement. Although only the concentration correction has been applied to the other reactions, the effect of pressure on the activity coefficients of the catalysts will usually be of a lower order of magnitude than the effect of pressure on k , and inability to allow for it will not change the general conclusions.

The absolute values of k for these reactions would be different if accurate activity coefficients were available. From data at 1 atm.¹³ it is estimated that the approximate activity coefficients of the catalysts in the solvents employed for the cyclisation of citraldehyde at 25°, the isomerisation of maleic acid at 79.8°, and the allylic rearrangement in aqueous dioxan at 30° and 50° (for which solvent there are no compression data) are respectively 0.66, 0.7, 0.4, and 0.35. The values of k in Table 1 for these reactions would therefore be greater by factors of about 1.5, 1.4, 2.5, and 2.9 if the complete correction could be made.

For calculation of the catalyst concentration in water and in acetone Bridgman's compression data¹⁴ were used, those for acetone being smoothed by use of Huddleston's relationship.¹⁵

⁶ Nozaki, *J. Amer. Chem. Soc.*, 1941, **63**, 2681.

⁷ Kistiakowsky and Smith, *ibid.*, 1934, **56**, 638.

⁸ Price and Dickman, *Ind. Eng. Chem.*, 1948, **40**, 257.

⁹ Nozaki and Ogg, *J. Amer. Chem. Soc.*, 1941, **63**, 2583.

¹⁰ Harned and Seltz, *ibid.*, 1922, **44**, 1475.

¹¹ Percival and La Mer, *ibid.*, 1936, **58**, 2413.

¹² Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Edn., Reinhold, New York, 1950, p. 378.

¹³ Ref. 12, pp. 548—563.

¹⁴ Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1912, **48**, 309; 1913, **49**, 1.

¹⁵ Huddleston, *Trans Faraday Soc.*, 1937, **33**, 97. Cf. (a) Newitt and Weale, *J.*, 1951, 3092; (b) Bett, Weale, and Newitt, *Brit. J. Appl. Phys.*, 1954, **5**, 243.

Moesveld's values¹⁶ for aqueous ethanol were also extrapolated by this method, and the compressions of aqueous acetone were calculated from those of the pure components, as they are nearly additive at the composition used.^{15a}

The method of converting the observed first order constant, k' (sec.⁻¹), to the corrected constant, k , is indicated for each reaction in Table 1. Concentrations are in moles litre⁻¹, C is

TABLE 1. *Rate constants of the isomerisations and rearrangements.*

(i) Isomerisation of maleic acid in water catalysed by potassium thiocyanate.

$$k = k'/C, C_0 = 0.0893, [\text{maleic acid}] = 1.3-1.5.$$

Temp.	P	$10^4 k$	k_p/k_1
79.8°	1	2.82	1.0
"	1000	3.40	1.2
"	3000	5.02	1.78
"	4900	6.98	2.48

(Second-order rate constant, $10^4 k_2 = 3.77, 4.52, 6.40, 9.13$).

(ii) Isomerisation of diethyl maleate in acetone catalysed by diethylamine.

$$k = k'/C^2, C_0 = 0.0216, [\text{diethyl maleate}] = 1.105.$$

25°	1	84.5	1.0
"	1500	270	3.2
"	3000	628	7.43
30	1	110	1.0
"	3000	895	8.13
35	1	141	1.0
"	500	180	1.28
"	1000	325	2.31
"	2000	623	4.43
"	3000	1170	8.30

(iii) Rearrangement of *N*-chloroacetanilide in water catalysed by hydrochloric acid.

$$k = k'/a_{H^+} a_{Cl^-} = k'/a_{HCl}^2, C_0 = 0.1, [N\text{-chloroacetanilide}] = 0.005.$$

25°	1	27.3	1.0
"	1500	18.0	0.66
"	2000	15.6	0.57
"	3000	13.9	0.51
"	5000	11.9	0.44
35	1	88.2	1.0
"	2000	49.2	0.56
"	3000	40.0	0.45
"	5000	30.7	0.35

(iv) Rearrangement of α -phenylallyl alcohol: (a) in aqueous acetone (45.7 wt. % Me₂CO) catalysed by hydrochloric acid.

$$k = k'/C, C_0 = 0.05, \text{Concn. of alcohol, } 0.0782\% \text{ (w/v)}.$$

Temp.	P	$10^4 k$	k_p/k_1
30.0°	1	1.03	1.0
"	2000	1.51	1.47
"	4000	1.64	1.59
85.6	1	2.32	1.0
"	1000	2.92	1.26
"	2000	3.57	1.54
"	4000	3.88	1.67
40.0	1	4.05	1.0
"	1000	5.05	1.25
"	2000	5.97	1.47
"	4000	6.75	1.67
45.4	1	8.38	—

(b) in aqueous dioxan (60% v/v). (Constants not corrected for catalyst concentrations or activity coefficients.)

$$C_0 = 0.08, \text{Concn. of alcohol, } 0.0979\% \text{ (w/v)}.$$

30.0	1	0.0498	—
"	1000	0.0545	1.09
36.3	1	0.0942	—
"	1000	0.108	1.14
43.1	1	0.225	—
50.0	1	0.462	—
"	1000	0.570	1.23

(v) Cyclisation of citraldehyde in aqueous ethanol (44.1 wt. % EtOH) catalysed by hydrochloric acid.

$$k = k'/c, C_0 = 0.1, [\text{citraldehyde}] \simeq 0.025.$$

25.2°	1	0.912	1.0
"	1000	2.28	2.5
"	2000	4.43	4.9
"	3000	6.73	7.4
"	4000	7.88	8.6
"	5000	8.57	9.4
30.0	1	1.22	1.0
"	1000	3.17	2.6
"	2000	5.70	4.7
"	3000	8.58	7.0
"	4000	10.3	8.4
"	5000	10.6	8.7
35.4	1	1.85	1.0
"	1000	4.55	2.5
"	2000	7.65	4.1
"	3000	11.3	6.1
"	4000	13.1	7.1

the catalyst concentration at the appropriate pressure and temperature, while C_0 is that at 1 atm. and 20°; the reactant concentrations also refer to this temperature and pressure. P is the pressure in atmospheres (1 atm. = 1.0133 bars = 1.0322 kg./cm.²), and k_p/k_1 is the ratio of the rate at P to that at ordinary pressure.

The isomerisation of maleic acid was measured only at 79.8° because the pressure effect was small and there was a tendency for fumaric acid to precipitate during runs at lower temperatures. The Arrhenius parameters of the other reactions, obtained from the graphs of

¹⁶ Moesveld, *Z. phys. Chem.*, 1923, **105**, 450.

TABLE 2. *The Arrhenius parameters of the rearrangements.*

<i>P</i>	<i>E</i> (kcal. mole ⁻¹)	log ₁₀ <i>A</i>	<i>P</i>	<i>E</i> (kcal. mole ⁻¹)	log ₁₀ <i>A</i>	<i>P</i>	<i>E</i> (kcal. mole ⁻¹)	log ₁₀ <i>A</i>
(ii) Diethyl maleate (in acetone)			(iv) α-Phenylallyl alcohol (in aqueous acetone)			(v) Citraldehyde (in aqueous ethanol)		
1	9.3	4.75	1	26.3	15.0	1	12.5	5.1
3000	10.7	6.7	1000	23.7 *	13.2	1000	11.9	5.1
(iii) <i>N</i> -Chloroacetanilide (in water)			2000	26.4	15.2	2000	9.6	3.7
1	21.3 *	13.1	4000	26.7	15.4	3000	8.9	3.2
2000	21.0 *	12.6	(iv) α-Phenylallyl alcohol (in aqueous dioxan) †			4000	8.8	3.4
3000	19.3 *	11.3	1	22.5	10.8	* From rates at only two temperatures. † Calc. from <i>k'</i> .		
5000	17.3 *	9.7	1000	22.9	11.2			

log₁₀ *k* against 1/*T*, are given in Table 2. Only in the case of *N*-chloroacetanilide are the values of *A* corrected for the activity coefficient of the catalyst.

Where comparison can be made the results at 1 atm. agree satisfactorily with previously recorded values. The maleic acid reaction (see p. 958) is represented slightly better by first-order than second-order constants, but both are shown in Table 1 and are in agreement, at 1 atm., with Nozaki and Ogg's values⁹ of 2.77×10^{-4} and 3.87×10^{-4} (sec.⁻¹) respectively. The value of k_p/k_1 is little influenced by the choice of first- or second-order constants. The rate constants and the activation energy of the rearrangement of *N*-chloroacetanilide at 1 atm. agree with the values 2.65×10^{-3} , 8.68×10^{-3} (sec.⁻¹), and 21.57 calculated from Harned and Seltz's results¹⁰ (see also Percival and La Mer,¹¹) at the same temperatures and catalyst concentration. The results for the allylic rearrangement in aqueous dioxan accord reasonably well with those of Braude *et al.*³ for a somewhat higher catalyst concentration, and the activation energy of the isomerisation of diethyl maleate in acetone is similar to the value of 9.94 kcal. measured in ether by Nozaki.⁶ Because of the difference in solvent and catalyst concentration the results for the cyclisation of citraldehyde cannot be compared with those of Price and Dickman.⁸

DISCUSSION

The dependence of the rates of reactions in liquids on pressure has been related to the volume change, ΔV^* , which accompanies formation of the transition state by the equation¹⁷ $\partial \log k / \partial P = -\Delta V^* / RT$. ΔV^* can be obtained from the slopes of the log k_p/k_1 -*P* isotherms (Figure). As Table 3 shows, ΔV^* is positive for the *N*-chloroacetanilide reaction,

TABLE 3. *Volume changes for transition-state formation, ΔV^* (c.c./mole).*

	Temp.	<i>P</i> (atm.)					
		1	1000	2000	3000	4000	5000
(i) Maleic acid	79.8°						-5.44, -5.18*
(ii) Diethyl maleate	25	-22.9	-16.0	-14.5	-12.7		
	35	-25.4	-18.7	-15.8	-14.6		
(iii) <i>N</i> -Chloroacetanilide	25	7.2	6.7	5.2	3.0	2.0	1.0
	35	8.1	7.7	6.4	4.4	3.3	2.6
(iv) α-Phenylallyl alcohol (aq. acetone) ...	30	-5.0	-5.0	-2.9	-1.6	-1.0	
	35.6	-6.1	-5.1	-2.9	-1.6	-1.0	
	40	-6.2	-5.2	-3.0	-1.6	-1.0	
(iv) α-Phenylallyl alcohol (aq. dioxan) ...	30		-3.24 †				
(v) Citraldehyde	25.2	-24.5	-20.1	-13.8	-5.6	-2.5	-1.3
	30	-25.8	-17.1	-12.4	-8.4	-1.6	-0.4
	35.4	-26.2	-16.3	-11.8	-6.9	-0.6	—

* From 1 to 5000 atm., first- and second-order respectively.

† From 1 to 1000 atm., from uncorrected constants.

which is retarded by pressure, and is negative for the other reactions but varies considerably from one to another. For the isomerisations of maleic acid, and of diethyl maleate in ether, ΔV^* is independent of pressure.

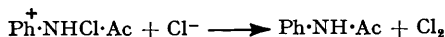
Buchanan and Hamann¹⁸ have recently presented new evidence that, if ionic charges appear or disappear during the rate-determining step, the sign of ΔV^* (respectively

¹⁷ Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875; 1936, **32**, 1333.

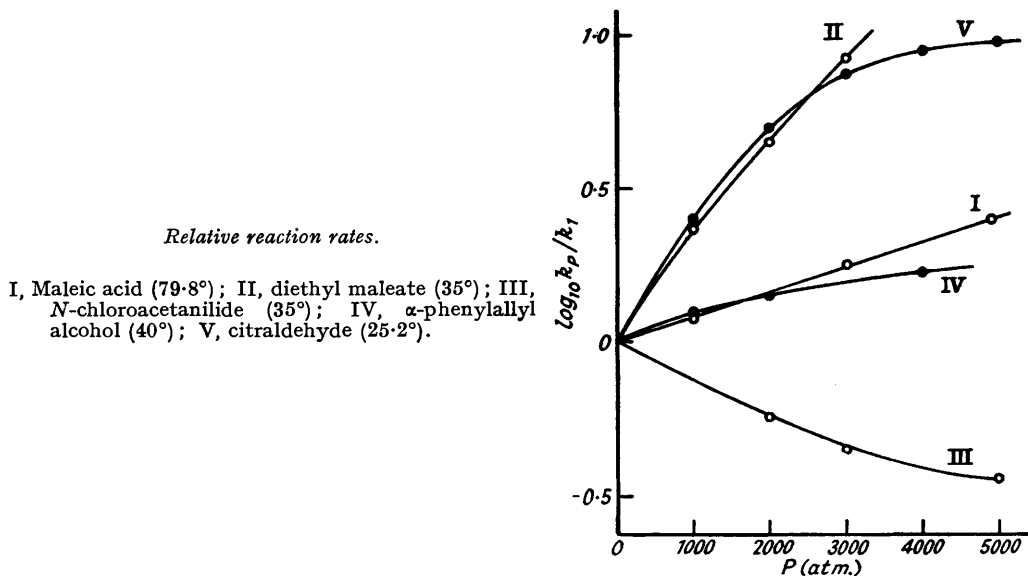
¹⁸ Buchanan and Hamann, *ibid.*, 1953, **49**, 1425.

negative or positive) is determined by this characteristic. In such reactions ΔV^* is largely accounted for by the electrostriction or liberation of neighbouring molecules, and at high pressures there is a reduction of the free energy of ionic solvation which is part of the free energy of activation. A quantitative estimate of the effect is possible for some reactions, if the appropriate ionic equilibria have been measured at high pressures, and there should exist a general correlation between pressure-response and electrical charge-type.

Although the rearrangement of *N*-chloroacetanilide does not result in a net gain or loss of ionic charge, the rate-determining stage (HCl catalyst) is

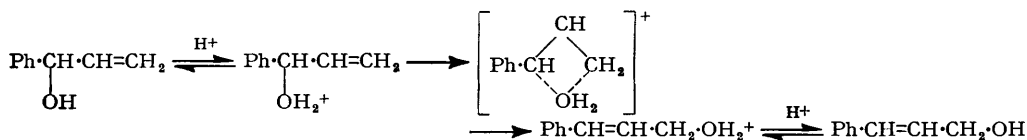


which is followed by chlorination of the acetanilide.¹⁹ In this stage two charges disappear and the liberation of electrostricted solvent molecules will cause ΔV^* to be positive. The



retarding effect of pressure, found experimentally, is thus predictable from the charge-type. It is comparable with the retardation of the decomposition of allylbenzylmethylphenylammonium bromide,²⁰ and of the formation of urea from ammonium cyanate.²¹

In contrast, the rearrangement of α -phenylallyl alcohol does not, according to the oxotropic mechanism of Braude *et al.*,³ involve the appearance or disappearance of charges. The reaction follows the course:



The only changes in solvation will be due to differences in ionic size, so that pressure may be expected not to disturb any of the stages of the reaction appreciably. A correspondingly small effect on the rate is observed, and in aqueous dioxan this is at least partially attributable to the increase of catalyst concentration caused by the volume compression of the solvent, for which no correction was made.

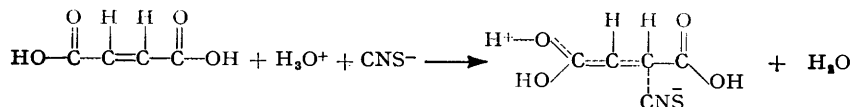
Nozaki and Ogg,⁹ in the mechanism they advanced for the potassium thiocyanate-catalysed isomerisation of maleic acid, postulated the addition of a proton to a carbonyl

¹⁹ Hughes and Ingold, *Quart. Rev.*, 1952, **6**, 34.

²⁰ Perrin, *Trans. Faraday Soc.*, 1938, **34**, 144.

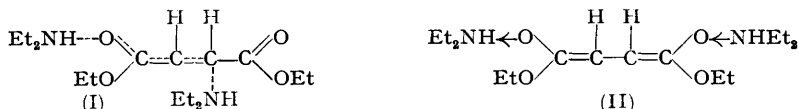
²¹ David and Hamann, *ibid.*, 1954, **50**, 1188.

oxygen atom of the acid molecule, and the approach of a CNS^- anion to the more remote of the olefinic carbon atoms.



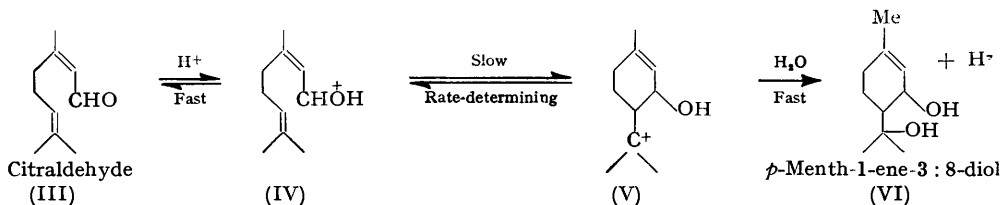
By this process the double bond is sufficiently shifted for isomerisation to occur. The protons are derived from the ionisation of other acid molecules and for this reason the isomerisation should be of indeterminate order, between $1\frac{1}{2}$ and 2, with respect to the maleic acid concentration. As the ionic charges do not change in the transition state, pressure will be expected to accelerate the reaction chiefly by increasing the proton concentration, through further ionisation of the weak acid. The moderate acceleration observed is of the magnitude to be expected from the effect of pressure on the ionic equilibrium of fumaric acid which was measured by Brander.²²

The other *cis-trans*-isomerisation (of diethyl maleate) was established to be of second



order with respect to the diethylamine catalyst by Nozaki,⁶ who confirmed the absence of catalysis by tertiary amines. Nozaki formulates the transition state as (I) in which association of an amine-nitrogen atom with an olefinic carbon atom, and of an amine-hydrogen atom with a carbonyl-oxygen atom, produces an electron shift sufficient to permit isomerisation. The alternative structure (II) appears preferable, but in each the association of amine and ester involves the appearance of whole or partial ionic charges.²³ In accordance with this theory the acceleration by pressure is considerably greater than for the thiocyanate-catalysed isomerisation of the acid, and is of the order of magnitude found for Menschutkin reactions.²⁰

The effects of pressure on the four reactions discussed above are all reconcilable with the ionic solvation theory, but this is apparently not the case for the cyclisation of citraldehyde. The mechanism advanced by Price and Dickman⁸ is as shown, the rate-



determining step being the isomerisation (IV) \rightleftharpoons (V). There is no disappearance of ionic charge, so that according to the solvation theory pressure should have little effect on the rate, as in the case of α -phenylallyl alcohol. The measurements, however, show a strong accelerating effect, which diminishes fairly rapidly with increasing pressure. The explanation is probably to be found in the special nature of the reaction, and it is possible that at high pressures the entropy of activation associated with the ring-closure is reduced. Unfortunately no conclusions on this point can be drawn from the Arrhenius parameter A since the reacting species from which the transition state is formed is the ion (IV), of unknown concentration, and not the neutral molecule (III).

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²² Brander, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, 1932, **6**, (8) 1.

²³ Davies and Evans, *Trans. Faraday Soc.*, 1955, **51**, 1506.