The Paramagnetic Isomerisation of Maleic Acid into Fumaric Acid in Aqueous Solution.

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R. Kuhn,(1) who demonstrated the cis-trans-isomerisation of some ethylene compounds (dimethyl ester of maleic acid and *cis*-stilbene) catalysed by paramagnetic metals, suggested as regards the mechanism of the reaction, that the absence of rotation imposed by the double bond would be overcome by the interaction between magnetically uncompensated electrons of the reacting molecule and the catalyst. Later it was shown by the present authors,(2) that the isomerisation of dimethyl ester of maleic acid can be catalysed by molecular oxygen, whose molecule is paramagnetic in spite of its even number of electrons, so that this result can be accounted for by the same mechanism. The similar view seems to be possible also in the catalysed conversion of maleic acid into fumaric acid by hydrogen ions in aqueous solution.(3)

Now in the following experiments, we attempted to ascertain the possible catalytic influence of the molecular oxygen, some paramagnetic metals and ions, on the isomerisation of maleic acid into fumaric acid in aqueous solution. It is already known that the para-ortho-hydrogen conversion in solution can be accerelated by the presence of paramagnetic molecules and ions.(4)

I.

In the first part of the following experiments, we have simply compared the amounts of the fumaric acid produced after a relapse of certain time in the reaction mixture, in the presence of paramagnetic substances with various magnetic moments. The experiments with oxygen have been always coupled with the similar experiments with nitrogen, whose molecule is diamagnetic. Thus we may be justified to conclude that the relative catalytic effects of the substances are determinable, taking into con-

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(1) K. Freudenberg, "Stereochemie," 913, Leipzig (1933).

(2) B. Tamamushi and H. Akiyama, *Z. Elektrochem.*, **43** (1937), 156.

(3) C. Horrex, *Trans. Faraday Soc.*, **33** (1937), 570.

(4) L. Farkas and H. Sachsse, *Z. physik. Chem.*, B, **23** (1933), 1, 19.

sideration the role of the thermal or solvent effect, which may take place in every case under those conditions, which controlled our measurements.

The method of analysis of the reaction product which was adopted in the present work is due to Freundlich and Schikorr,⁽⁵⁾ who studied the nature of the isomerisation of maleic acid to fumaric acid in aqueous solution in the presence of colloidal sulphur. The analysis, which is based upon the difference of solubilities of maleic acid and fumaric acid, proceeds in the following way.

Twenty c.c. of the solution to be analysed is pipetted into a 100 c.c. beaker and gently dried up on the water bath. To the residue is added 2–3 c.c. of water, which is just enough to dissolve the maleic acid in the mixture. As soon as we are sure that this process is completed, we filter the liquid with a small funnel into a small dry beaker, and then we take 1 c.c. of the filtrate for the titration with standard baryta solution, using phenolphthalein as an indicator. Thus we find out the amount of the maleic acid in the solution. The rest of the filtrate and the acids which remain in the pipette, funnel and filter paper are then transferred to the first beaker. The liquid is then boiled and titrated in the similar way as above, without newly charging the burette, so that the last reading of the baryta solution gives the total amount of the acids in the given solution. We have thus only to take the difference of the total amount of acids and the amount of the maleic acid, in order to find out the amount of the fumaric acid produced.

Since the error in the reading of burette greatly affects the result, we have constructed a special precision burette for the present purpose, which enabled us to read 0.005 c.c. accurately.

Now the amount of maleic acid which will be dissolved in the above procedure is so large, that its own volume will change the volume of the water taken, and this must be taken in account in the calculation.

If x equivalents of maleic acid are dissolved in q c.c. of water and one equivalent occupies the volume v c.c., then the volume of the solution after dissolving maleic acid will be $(q + vx)$ c.c. Assuming that 1 c.c. of the solution uses a c.c. of the normal solution, i.e. $a\frac{f}{1000}$ acid-equivalents, we have for $(q + vx)$ c.c. solution $(q + vx)\frac{af}{1000}$ acid-equivalents, where f denotes the factor of the normal solution. So that we get the equation:

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(5) H. Freundlich and G. Schikorr, *Kolloid-Beihefte*, **22** (1926), 1.

$$(q+vx)\frac{af}{1000}=x\,,$$

from which we obtain x.

The equivalent volume v was in our case determined by special experiments with the following results: $v=39.1$ c.c. at 10°C. and $v=40.0$ c.c. at 14°C.

The control experiments were made with a known mixture of the two acids, which contained namely 0.058 g. of fumaric acid and 1.102 g. of maleic acid and consequently just 5.00% of fumaric acid. The results obtained are given in Table 1.

Table 1.

No. of Exp.	Fumaric Acid (%)		Error (%)
	theor.	exp.	
1	5.00	4.62	7.6
2	5.00	4.85	3.0
3	5.00	5.07	1.4
4	5.00	4.67	6.2
			Mean 4.6

The accuracy of the analysis can therefore be estimated to about 5 percent in the mean.

A small quartz or Pyrex flask with reflex condenser, into which 30–50 c.c. half molar solution of maleic acid had been introduced, was put in a boiling water bath thermostat, temperature of which was regulated electrically within ± 0.2°, during the reaction time. The upper part of the flask was covered with an aluminium foil to protect the solution from light, which is well known to have an influence on the rate of the isomerisation.

In the case of measurements with oxygen or nitrogen, the gas was bubbled through the solution under a constant pressure during the reaction to ensure the solution to be saturated with the gas. By the method of Kautzky and Thiele⁽⁶⁾ we prepared the nitrogen used in the experiment, which was completely free from oxygen.

In the following series of experiments with paramagnetic ions, a small amount of sulphates of divalent metals or nitrates of trivalent metals was added to the solution, the concentration of the salt being 5 millimolar per litre in each case, so that any secondary chemical change in the solution could be excluded.

The platinum black and the palladium black were prepared by the method of Mond, Ramsay, and Shields,⁽⁷⁾ which exhibited high catalytic

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(6) H. Kautzky and H. Thiele, *Z. anorg. allgem. Chem.*, **152** (1926), 342.

(7) L. Mond, W. Ramsay, and J. Shields, *Phil. Trans.*, **186** A (1895), 661.

activity in burning hydrogen. The chemicals used were the purest ones of either Merck or Kahlbaum.

The results obtained are summarized in the following tables, in which the values of magnetic moments or of magnetic susceptibilities of the catalysts are too noted. The adopted values of the fumaric acid produced in Table 3 and 4 are the mean of two or three measurements, since they fluctuate considerably within the error of the analysis.

Table 2. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

No. of Exp.	Fumaric Acid produced (%) in presence of	
	O_2	N_2
1	8.7	5.1
2	9.1	5.7
3	9.0	6.1

Table 3. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Ion (5 millimol/l.)	Fumaric Acid produced (%)	Magnetic Moment(8) in Bohr Magneton Number
Zn^{2+}	6.5	0
Cu^{2+}	7.7	3.53
Mn^{2+}	8.6	5.92
Fe^{2+}	8.9	6.54
Co^{2+}	11.1	6.56
Ni^{2+}	11.3	5.56
Pr^{3+}	9.5	3.62
Nd^{3+}	10.1	3.68
Er^{3+}	11.1	9.70

Table 4. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Catalyst (0.03 g. in 30 c.c. solution)	Fumaric Acid produced (%)	Specific Mass Susceptibility $\chi \cdot 10^6$
Pt-black	8.8	1.1
Pd-black	10.7	5.8

As we see in Table 2, the amount of the fumaric acid produced in the presence of oxygen evidently exceeds that produced in the presence of nitrogen. The isomerisation must have been accerelated by the non-homogeneous magnetic field of the O_2-molecules in the process of collision. A more or less considerable isomerisation is also observed in the presence of the paramagnetic ions or metals, where a certain parallelism being displayed between the fumaric acid produced and the magnetic moment of the catalyst. We dare not, however, formulate quantitatively the relation between them, in order to make use of it in further discus-

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(8) J. H. van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford (1932).

sions, for our experiments have not yet so far advanced as to determine the velocity constant of the reaction in each case, whereas an interesting quantitative treatment has been performed in the case of the para-ortho-hydrogen conversion in solution catalysed by paramagnetic ions.(9)

The concentration of the paramagnetic ions seems to have in general no remarkable effect on the rate of the isomerisation, as is shown in Table 5, although a slight increase of the reaction product with the ion-concentration is noticed in the case of Nd^{3+}. The effect of the anion has been examined with the salts of the same cation in the same molar concentration and it was found to be negative, as is given in Table 6.

Table 5. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Salt	Concentration of Salt (millimol/l.)	Fumaric Acid produced (%)
$NiSO_4$	5	11.3
	10	11.4
	20	11.4
$Nd(NO_3)_3$	5	9.7
	10	10.7
	20	12.7

Table 6. Conc. of Maleic Acid = 0.5 mol/l. Temp. = 99.5°C. Reaction Time = 10 hours.

Salt (5 millimol/l.)	Fumaric Acid produced (%)
$NiCl_2$	11.9
$NiSO_4$	11.9
$Ni(NO_3)_2$	12.5

It is of interest to compare these results with those, which have been obtained by Farkas and Sachsse in the para-ortho-hydrogen conversion.

The effect of water itself as a solvent on the isomerisation of maleic acid in solution, which will be brought about by the nuclear moment of the protons of water molecules and which may probably take place as in the case of the para-ortho-hydrogen conversion,(10) can not, however, be brought out so long as the reaction is not studied in other solvents.

II.

The next step in our studies was to get some informations about the nature of the reaction under consideration, and for this purpose we have made kinetic measurements, which however concern only the reaction in the presence of paramagnetic oxygen molecules on the one hand, and on the other the reaction in the presence of diamagnetic nitrogen molecules.

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(9) Farkas and Sachsse, *Z. physik. Chem.*, B, **23** (1933), 19; H. Sachsse, *Z. Elektrochem.*, **40** (1934), 531.

(10) Farkas and Sachsse, *Z. physik. Chem.*, B, **23** (1933), 14.

The rate of the reaction was determined in both cases at different temperatures, namely at 80°, 90° and 100°C., while the reaction vessel was put in an electrically regulated oil thermostat with the temperature variation within ± 0.1°.

The reaction mixture was taken from time to time to be analysed in the manner as described above. The results are tabulated in Table 7 and 8, where *k* denotes the unimolecular velocity constant. Although this constant shows some irregular variations, the correctness of the assumption of unimolecularity can be accepted on the ground of the experiment with varied initial concentrations of the reacting substance, the results of which being shown in Table 9.

Table 7. Conc. of Maleic Acid = 0.5 mol/l. Saturated with O_2.

Temp. (°C.)	Time (hours)	Fumaric Acid produced (%)	$k \cdot 10^6$ (sec.$^{-1}$)
80	15	3.2	0.60
	25	5.4	0.62
	40	9.9	0.72
			Mean 0.65
90	10	5.3	1.52
	23	7.8	0.98
	35	11.9	1.00
			Mean 1.17
100	10	9.0	2.62
	17	11.0	1.90
	20	11.8	1.73
			Mean 2.04

Table 8. Conc. of Maleic Acid = 0.5 mol/l. Saturated with N_2.

Temp. (°C.)	Time (hours)	Fumaric Acid produced (%)	$k \cdot 10^6$ (sec.$^{-1}$)
80	15	2.1	0.39
	25	3.7	0.42
	40	6.1	0.44
			Mean 0.42
90	10	3.4	0.97
	23	5.4	0.68
	35	7.0	0.58
			Mean 0.74
100	10	6.1	1.75
	14	7.1	1.47
	23	8.1	1.01
			Mean 1.41

Table 9. Maleic Acid Solution, saturated with O_2. Reaction Time = 15 hours.

Initial Conc. of Solution (mol/l.)	Fumaric Acid produced in millimol/l. after			$k \cdot 10^6$ (sec.$^{-1}$)
	5 hours	10 hours	15 hours	
0.25	0.0013	0.0023	0.0030	2.53
0.5	0.0031	0.0045	0.0070	2.75
1.0	0.0069	0.0092	0.0113	2.87
2.0	0.0126	0.0176	0.0206	2.73

Of the values of the fumaric acid which was produced in the above experiments at lower temperatures than 100°, due corrections were made according to the circumstance, that in the reaction mixture, which was used for the analysis, the reaction would proceed, during the process of evaporation, further than the proper stage of the reaction. These corrections are not more than one percent, which was proved by special experiments and also by calculations from the data obtained at 100°.

From the data in Table 7 and 8, it is again obvious that the isomerisation proceeds remarkably quicker in the presence of oxygen than in the presence of nitrogen. The variation of the velocity constant with temperature follows the equation of Arrhenius:

$$\ln k = \ln Z - \frac{E}{RT},$$

as is illustrated in Fig. 1. We obtain thus for the reaction with oxygen the equation:

$$\ln k = 6.75 - \frac{14600}{RT},$$

and for the reaction with nitrogen:

$$\ln k = 7.96 - \frac{15800}{RT},$$

where k being measured in sec.$^{-1}$

The energy of activation is thus lowered in the presence of oxygen, and this accounts for the catalytic action of molecular oxygen. The comparatively low values of ln Z are due to the slowness of the reaction in question.

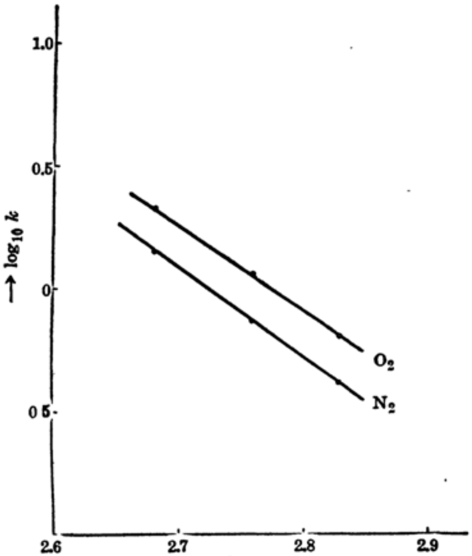

Fig. 1.

It would be rather accidental that the energy of activation obtained above in the reaction with nitrogen i.e. 15.8 Cal. per mol is coincident with that, which was found by Höjendahl(11) for the isomerisation of maleic acid into fumaric acid in fused state, while Kistiakowsky and Nelles(12) found 26.5 Cal. per mol for the isomerisation of dimethyl maleic acid to dimethyl fumaric acid in gaseous state.

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(11) K. Höjendahl, *J. Phys. Chem.*, **28** (1924), 758.

(12) G. B. Kistiakowsky and Nelles, *Z. physik. Chem.*, Bodenstein-Festband (1931), 369.

We hope that we can enter into further discussions on this subject, when we shall make reports of the studies of kinetics, which are now under way in our laboratory, concerning the isomerisation of dimethyl ester of maleic acid in gaseous phase in presence and in absence of molecular oxygen.

Summary.

It has been demonstrated that the isomerisation of maleic acid into fumaric acid in aqueous solution is accerelated by the presence of molecular oxygen, platinum black, palladium black, and various paramagnetic ions, where the isomerisation being probably effectuated by the non-homogeneous magnetic fields of the catalysts in the collision.

The isomerisation of maleic acid to fumaric acid in aqueous solution has been kinetically studied both in the presence of paramagnetic oxygen molecules and in the presence of diamagnetic nitrogen molecules, and the energy of activation of the reaction has been calculated. The lower energy of activation in the reaction with oxygen accounts for the catalytic action of the oxygen molecules.

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