A Note on the Catalytic Isomerization of Dimethyl Maleate to Dimethyl Fumarate.

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(Received July 13, 1942.)

The catalytic effect of a paramagnetic substance on the cis-trans isomerization of ethylene compounds has been first discussed by R. Kuhn,(1) who at the same time qualitatively demonstrated that some paramagnetic metals (alkali metals, platinum, palladium, etc.) and gases (especially NO_2) are really effective in accelerating the isomerization of dimethyl maleate and cis-stilbene. Further quantitative studies on such catalytic effect have been carried out in our laboratory both in gaseous and liquid states of the reacting substance (dimethyl maleate and cis-dichlorethylene).(2) In the course of these studies, we made some complementary experiments on the isomerization of dimethyl maleate to dimethyl fumarate in the presence of some paramagnetic and other catalysts, the results of which may also be worth while to be reported.

Experiment 1. Dimethyl maleate was distilled in a small Claisen flask under the pressure of 7 mm. and 760 mm. Hg, in contact with a catalyst—copper wire, platinum wire, platinum black, metallic sodium—the catalyst being placed in the vapour phase. No conversion, which would be detected by the subliming fumarate, was observed in each case.

Experiment 2. The maleic ester was heated to 200°C. in a small Terex flask for about 3 hours with the same catalysts as used in the experiment 1, which now being placed in the liquid phase. There happened no remarkable conversion with copper or platinum wire, while it took place to a striking degree with platinum black (30%-fumarate) and with metallic sodium (80%-fumarate). The analysis of the reaction product was done by determining its crystallization temperature, the previously obtained standard relation between the crystallization temperature and the composition of mixtures of the cis and trans compounds being here applied.

Experiment 3. The maleic ester was kept in an Erlenmeyer flask with a stopper at 110–120°C. for 30–40 minutes in contact with a gas mixture of oxygen and nitrogen oxide prepared by the action of nitric acid on copper. The liquid became soon pale blue, while the isomerization proceeded so far as to give 40% dimethyl fumarate, large crystals of the fumarate subliming on the wall of the flask.

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(1) R. Kuhn, "Stereochemie," herausgeg. von K. Freudenberg, Leipzig (1933), p. 913.

(2) B. Tamamushi, H. Akiyama and K. Ishii, *Z. Elektrochem.*, **43** (1937), 156; **45** (1939), 72; **47** (1941), 340; this Bulletin, **12** (1937), 382; **17** (1942), 321.

Experiment 4. The maleic ester was maintained at the temperature of 150°C. in a quartz flask, once without catalyst and then with metallic phthalocyanines (copper-, magnesium- and iron phthalocyanines)—0.01 g. catalyst in 3 c.c. of the reacting substance—for 3, 5, 7 hours; the product was then analysed. The results obtained are as follows:

Time (hrs.)	3	5	7
Without catalyst	0.85	1.5	2.7%-fumarate
With copper phthalocyanine	1.1	1.8	2.8
With magnesium phthalocyanine	0.95	1.5	2.7
With iron phthalocyanine	1.4	2.2	3.1

Iron phthalocyanine is, therefore, proved to be more or less effective in accelerating the isomerization, whereas copper and magnesium phthalocyanines are practically ineffective.(3) The similar results were obtained in the experiment at 170°C.

Experiment 5. The maleic ester was heated to boiling under the normal pressure and the vapour was made to flow over a catalyst—platinum black, iron or copper phthalocyanine—in a Terex reaction tube maintained at 300°C. in an electric furnace at the flow rate of 1 c.c. of the liquid per 30 minutes. The product was condensed in an ampoule and analysed. The following results were obtained:

	Fumarate formed (%)
Without catalyst	1.9
With platinum black (0.5 g.)	4.9
With iron phthalocyanine (1 g.)	8.0
With copper phthalocyanine (1 g.)	4.2

Experiment 6. The maleic ester was vapourized into a reaction flask of Terex glass under the pressure of about 40 mm. Hg. at the temperaure of 300°C. in contact with platinum black. After the reaction time of 3–7 hours, the product was taken out in an ampoule by condensation and analysed. The fumarate content was found to be 3–17%, while the reaction without catalyst under the same conditions gave 1.7–3% of the fumarate. The platinum black was found to be also effective in accelerating the reverse reaction, namely, the isomerization of dimethyl fumarate to dimethyl maleate. It is to be noticed that the cis-trans isomerization of dichlorethylene in gaseous state is also remarkably catalysed in the presence of platinum black.(4)

Materials used in the Experiments. Dimethyl maleate: prepared by the method of Walden.(5) B.p. 83–84° (11 mm.), n_D^{20} 1.4445.

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(3) The magnetic susceptibilities of metallic phthalocyanines have not yet been extensively determined. After the measurement of Klemm and Senff, however, iron and manganese phthalocyanines have greater susceptibilities than other metallic phthalocyanines. *J. prakt. Chem.*, **154** (1939), 73.

(4) B. Tamamushi, *this Bulletin*, **17** (1942), 321.

(5) P. Walden, *Z. physik. Chem.*, **20** (1896), 377.

Platinum black: prepared by the method of Ramsay, Mond and Shields.(6) Copper-, magnesium-, and iron phthalocyanines: prepared and kindly afforded by Mr. H. Akiyama of Nippon Yushi Company, to whom my sincere thanks are due. The samples were purified by sublimation in a high vacuum.

I express my warm thanks for Messrs. K. Ishii, K. Fuse and S. Tohmatsu for their help in the experiment.

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