TABLE I

These calculations were made assuming the mole fraction of heavy water to be a linear function of the specific gravity.[3] The formula used was: $\Delta s = 0.1074 N_{D_2O}$ where $\Delta s = d^{25}_{25} - 1$. The value $d^{25}_{25} = 1.1074^4$ for pure D_2O was used.

		Original water	Water from combustion	Water from Ca(OH)₂
Run A	d^{25}_{25}	1.0515	1.0438	1.0478
	n_{D_2O}	0.4795	0.4078	0.4451
	% D_2O	50.58	43.35	47.13
Run B	d^{25}_{25}	1.0507	1.0464	1.0486
	n_{D_2O}	0.4721	0.4320	0.4525
	% D_2O	49.84	45.80	47.87
Run C	d^{25}_{25}	1.0222	1.0202	1.0202
	n_{D_2O}	0.2067	0.1881	0.1881
	% D_2O	22.45	20.47	20.47
Run D	d^{25}_{25}	1.0000	0.9998	
Run E	d^{25}_{25}	1.0511	1.0407	1.0545
	n_{D_2O}	0.4758	0.3790	0.5075
	% D_2O	50.21	40.41	53.38
Run F	d^{25}_{25}	1.0000	1.0001	0.9999
Run G	d^{25}_{25}	1.0469	1.0409	1.0495
	n_{D_2O}	0.4367	0.3808	0.4609
	% D_2O	46.28	40.59	48.72
Run H	d^{25}_{25}	1.0462	1.0407	1.0468
	n_{D_2O}	0.4302	0.4790	0.4358
	% D_2O	45.62	40.41	46.19
Run I	d^{25}_{25}	1.0242	1.0220	1.0254
	n_{D_2O}	0.2253	0.2048	0.2365
	% D_2O	24.24	22.25	25.60
Run J	d^{25}_{25}	1.0844	1.0827	1.0855
	n_{D_2O}	0.7858	0.7700	0.7961
	% D_2O	80.30	78.81	81.27

(3) Lewis and Luten, THIS JOURNAL, **55**, 5061 (1933).
(4) Tronstad, *et al.*, *Nature*, **136**, 515 (1935).

over wire form copper oxide heated to a dull red heat in two tubes 15 × 1 cm. Organic material was thereby oxidized. The air was then cooled and the bulk of the water vapor removed by passing through two bulbs immersed in cold brine. The last traces of water vapor were removed by passing successively through five bulbs immersed in an alcohol–solid carbon dioxide mixture, then through three bulbs immersed in liquid air, and finally through a tube filled to a height of 7 cm. with phosphorus pentoxide. A continuous all-glass system was used beginning with the five tubes immersed in the alcohol–carbon dioxide mixture. All ground glass joints shown were used without lubrication. Hence pressures slightly above atmospheric were maintained in the system.

The products of combustion were passed through the condenser (E) and the water was trapped in the bulbs (F) immersed in an alcohol–carbon dioxide mixture. The water so obtained was triply distilled in an enclosed all-glass system and its density determined by means of a pycnometer of one-half ml. capacity.

The results are given in Table I. Runs A, B and C, were made before the system was assembled in its final form. They indicate the care that is needed to remove the last traces of moisture. Runs D and F were made with redistilled conductivity water to check the possible effect of other impurities. If such impurities exist they do not affect the density beyond the fourth decimal place. The results of runs E, G, H, I, and J show definitely that a separation of the isotopes has been effected.

Summary

A partial separation of the isotopes of hydrogen has been achieved by the action of water, containing various percentages of deuterium, on calcium carbide.


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

cis-trans-Isomerization with Boron Fluoride

### BY CHARLES C. PRICE AND MORRIS MEISTER

In a previous communication[1] it was suggested that the catalytic effect of boron fluoride or aluminum chloride in causing olefins to condense with aromatic compounds or to polymerize involved activation of the carbon–carbon double bond by association with the catalyst.
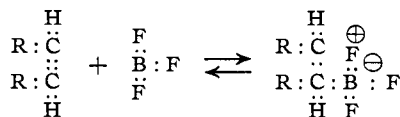
A consequence of such association should be establishment of equilibrium between *cis-trans* isomers. This has now been confirmed ex-

(1) Price and Ciskowski, THIS JOURNAL, **60**, 2499 (1938).
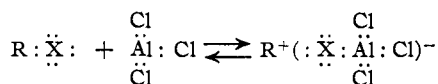
perimentally for the case of the isomeric stilbenes.
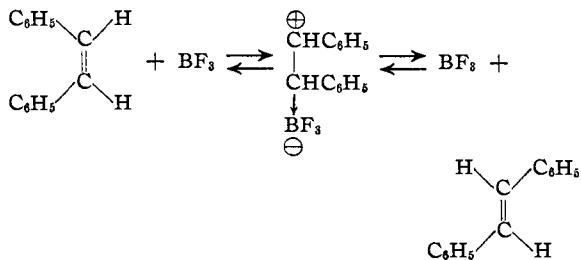
The conversion may be accomplished in the course of a day or so at room temperature using the boron fluoride–ether complex or in fifteen

minutes by bubbling boron fluoride through the cis-isomer in carbon tetrachloride solution. In either case a maximum of 92–93% of the cis-stilbene had been isomerized.
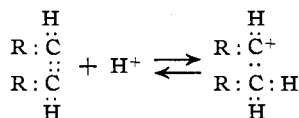
Attempts to isomerize ethyl maleate at room temperature using either boron fluoride or its ether complex failed, even in the presence of dry hydrogen bromide, less than 1% of the ester having changed in a week. Dry hydrogen bromide in the presence of air in the dark was also not effective in isomerizing this ester in carbon tetrachloride solution.
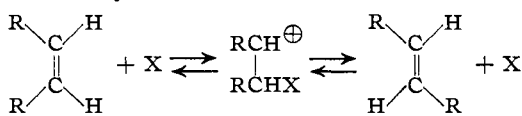
Discussion

Recently Gilbert, Turkevich and Wallis[2] pointed out that the suggestion of Kuhn[3] that catalytic cis–trans-isomerism was due to paramagnetism of the catalyst molecule was not in accord with their experiments on the effectiveness of various compounds in producing this change in ethyl maleate. It is of particular interest to note that their most effective catalysts[4] are compounds which are capable of acting as catalysts in the Friedel–Crafts type of reaction, a reaction which also involves the ability of the catalyst to associate with another pair of electrons.[5]

$$R : \ddot{X} : + \; \overset{Cl}{\underset{Cl}{\overset{|}{\underset{|}{Al}}}} : Cl \rightleftarrows R^{+}(: \ddot{X} : \overset{Cl}{\underset{Cl}{\overset{|}{\underset{|}{Al}}}} : Cl)^{-}$$

The catalysis of strong acids in the isomerization of olefins, the condensation of olefins with aromatic compounds, and the polymerization of olefins may be accounted for in a similar manner, a proton being the electron-deficient (electrophilic) catalyst in this case.

$$\underset{H}{\overset{H}{\underset{R : \overset{..}{C}}{\overset{R : \overset{..}{C}}{}}}} + H^{+} \rightleftarrows \underset{H}{\overset{H}{\underset{R : \overset{..}{C} : H}{\overset{R : \overset{..}{C}^{+}}{}}}}$$

These three reactions for an olefin may then be summarized as follows, allowing X to represent the catalyst.

The fact that ethyl maleate is not as readily isomerized by these catalysts as cis-stilbene is probably due, in part, to the fact that the catalysts readily associate with an unshared pair of electrons from the oxygen atoms in preference to a pair from the carbon–carbon double bond; in fact many such ester–boron fluoride complexes are stable enough to isolate. Further experiments on the effect of various groups attached to the double bond on the ease of its isomerization are under way.

Experimental

The cis-stilbene was prepared from tolane[6] by hydrogenation using a palladium catalyst according to the directions of Bourguel.[7] The yield was 75%, b. p. 140.5–141° (13 mm.).

The isomerizations were all carried out in the dark. cis-Stilbene (0.5 g.) was dissolved in 4 cc. of boron fluoride-ether complex (b. p. 125°) and after standing for the prescribed time the ether solution of stilbene was washed thoroughly with aqueous sodium carbonate to remove boron fluoride, dried and evaporated. Alcohol (3 cc.) was added to the residue and the trans-stilbene, after being washed twice on the filter with 1-cc. portions of alcohol, was weighed. Since 0.044 g. of stilbene was soluble in 5 cc. of alcohol, this factor was added to the actual weight in each case. The results, summarized below, indicate that the reaction is autocatalytic.

Time, hours	12	24	30	36	72
% Conversion	<10	38.1	74.8	92.3	92.2

Isomerization in carbon tetrachloride was much more rapid. Boron fluoride was bubbled through a solution of 0.5 g. of cis-stilbene in 2 cc. of carbon tetrachloride. In fifteen minutes a copious precipitate of trans-stilbene separated. At the end of the prescribed time, the carbon tetrachloride was removed by evaporation and the procedure above followed. The results are summarized below.
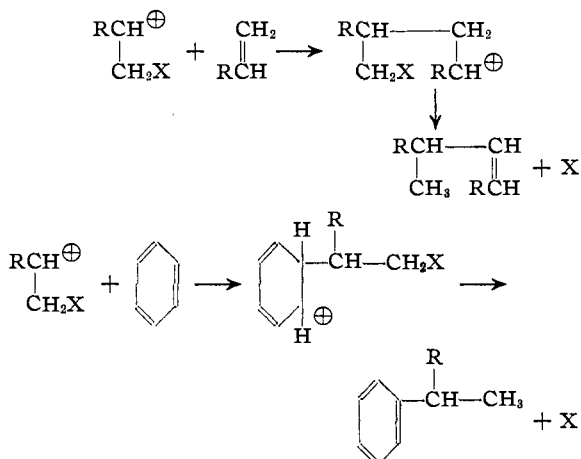
(2) Gilbert, Turkevich and Wallis, J. Org. Chem., 3, 611 (1939).

(3) Freudenberg "Stereochemie," Franz Deuticke Verlag, Leipzig, 1933, p. 917.

(4) Sodium, of course, must be excepted since, in this case, the reaction probably involves the intermediate addition of a sodium atom.

(5) Wertyporoch and Firla, Ann., 500, 287 (1933); Ulich and Heyne, Z. Elektrochem., 41, 509 (1935); Dilthey, Ber., 71, 1350 (1938).

(6) Schlenk and Bergmann, Ann., 463, 76 (1928).

(7) Bourguel, Bull. soc. chim., [4] 45, 1067 (1929).

Time, minutes	16	18	19
% Conversion	81.0	93.1	93.1

Ethyl maleate was treated in a similar manner with boron fluoride in carbon tetrachloride, with boron fluoride–ether complex alone and with dry hydrogen bromide added, and with hydrogen bromide in carbon tetrachloride. In every case less than 1% of the ester was isomerized. The analyses were carried out as before.[8]

Summary

It has been found that boron fluoride readily converts cis-stilbene to the trans-isomer.

(8) Price and Thorpe, THIS JOURNAL, **60**, 2839 (1938).

Many compounds have in common the ability to catalyze the Friedel–Crafts type of reaction, the polymerization of olefins, the condensation of olefins with aromatic compounds and the cis–trans-isomerization of olefins. It is suggested that the common factor in these reactions is the electron-deficient nature of the catalyst and that such catalysts may associate with the electrons of the carbon–carbon double bond to give an active intermediate common to each reaction.

URBANA, ILLINOIS   RECEIVED MARCH 31, 1939

NOTES

Note on the Leakage of Helium through Pyrex Glass at Room Temperature. III

BY G. P. BAXTER

Some years ago an experiment was begun to measure the rate of leakage of helium through Pyrex glass at room temperature.[1] A sealed globe (1044 ml.) filled with helium originally under slightly less than average atmospheric pressure in this locality, 75 cm., was occasionally compared in weight with a very similar sealed globe, containing argon under a pressure somewhat above atmospheric, 79 mm. Over a period of three and one-half years the rate of loss was about 1% per year.

Recently, after over eleven years, when a reweighing of the globe was undertaken, a small crack was discovered in the argon globe. Since the argon was originally at a pressure above atmospheric, mechanical loss of argon would diminish, not increase, the loss in weight of the helium globe. In spite of the crack the helium globe was found to have lost a total of 17.8 mg., in a little over eleven years (4128 days), or over 10% of the original helium or 109 cm.[3] The over-all rate for the total period is 0.053 mm.[3] per day per cm.[2] of Pyrex glass of average thickness 1.34 mm. This is a slightly lower rate than that calculated from the first year's experience, 0.059 mm.[3] per day per cm.[2] but the greater part of this difference is accounted for by the diminishing helium content of the globe.[2]

(1) Baxter, Starkweather and Ellestad, Science, **68**, 516 (1928); Baxter and Starkweather, ibid., **73**, 618 (1931).
(2) Original weight of helium = 0.171 g. Erroneously given in ref. 1 as 0.168 g.

In the following table are given the leakage constants (years^{-1}) assuming the rate to be proportional to the pressure, for periods from one year to over eleven years, the actual losses in weight, and the losses calculated from the average leakage constant for the first three periods.[3] From the leakage constant and loss in weight for the total period it seems probable that the argon counterpoise was losing in weight owing to the crack, although in the recent weighing, which was continued over several weeks, the helium globe was still diminishing in weight by comparison.

Years	K, years^{-1}	Actual loss in wt., mg.	Calcd. loss in wt., mg.
1	0.0102	1.73	1.78
1.5	.0106	2.71	2.66
3.5	.0106	6.23	6.15
Av.	.0105		
11.3	.0097	17.8	19.1

(3) For a discussion of the mechanism of the leakage of helium through glass, see Urry, THIS JOURNAL, **54**, 3887 (1932). Urry's experimental data are not inconsistent with the above.

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Isotopes of Potassium in Phosphate Rocks and Soils

BY A. KEITH BREWER

Taylor and Urey[1] have shown recently that in the base exchange of potassium in zeolites "the heavier isotope is taken up more readily and is more difficult to replace." Since base exchange regularly occurs in nature, isotope abundance

(1) I. W. Taylor and H. C. Urey, J. Chem. Phys., **6**, 429 (1938).