

The Isomerization, Catalysed by Boron Trichloride, of 2-Methylbut-1-ene

Graeme S. Cameron and V. Raymond Stimson

Department of Physical Chemistry, University of New England,
Armidale, N.S.W. 2351.

Abstract

Boron trichloride (2% in carbon dioxide) catalyses the isomerization of 2-methylbut-1-ene to 2-methylbut-2-ene at 368–467° with

$$k_2 = 10^{9.71} \exp(-91460/8.314T) \text{ s}^{-1} \text{ ml mol}^{-1}$$

Gas-phase isomerization catalysed by Lewis acids is thus extended to olefins.

Hydrogen bromide and hydrogen chloride catalyse the isomerizations of olefins, cyclopropane and 1,1-dimethylcyclopropane in homogeneous molecular reactions.¹⁻⁴ We have recently shown that the Lewis acids boron trichloride⁵ and boron tribromide⁶ also effect the isomerization of cyclopropane in reactions whose transition states must involve the internal shift of a hydrogen atom, as none is available from the catalyst.

We now report the isomerization of 2-methylbut-1-ene to 2-methylbut-2-ene catalysed by boron trichloride in the gas phase.⁷

Experimental

2-Methylbut-1-ene was Phillips pure grade. The other materials and general procedures have been described previously.⁵

The vessel was coated with the decomposition products of propene at c. 480°, and 'washed' with propene between runs. The condition of the vessel was checked regularly by means of the boron-trichloride-catalysed isomerization of cyclopropane.⁵

Boron trichloride in carbon dioxide was 'blown into' a known pressure of 2-methylbut-1-ene. Twenty mixtures of boron trichloride in carbon dioxide, 1–3%, were used; these were mixed in a tap vessel fitted with a rolling glass ball. No pressure change greater than 0.5 mm took place during reaction. After reaction the catalyst mixture was removed on calcium hydroxide powder. The products were analysed gas chromatographically by means of a 10 ft by 1/8 in. Porapak Q column. 2-Methylbut-1-ene and 2-methylbut-2-ene were completely separated, with retention times 49 and 55 min respectively. Analysis was made by measurement of peak areas, and the procedure was calibrated by means of ten authentic mixtures.

¹ Stimson, V. R., and Watson, E. J., *J. Chem. Soc.*, 1960, 3920; 1961, 1392.

² Maccoll, A., and Ross, R. A., *J. Am. Chem. Soc.*, 1965, **87**, 4997.

³ Ross, R. A., and Stimson, V. R., *J. Chem. Soc.*, 1962, 1602.

⁴ Shapiro, J. S., and Swinbourne, E. S., *Can. J. Chem.*, 1968, **46**, 1341, 1351.

⁵ Johnson, R. L., and Stimson, V. R., *Aust. J. Chem.*, 1975, **28**, 447.

⁶ Stimson, V. R., and Taylor, E. C., *Aust. J. Chem.*, 1976, **29**, 2557.

⁷ Cameron, G. S., Thesis, University of New England, 1975.

Equilibrium and Uncatalysed Reaction

The reaction did not go to completion,¹ but reached equilibrium at *c.* 70% of 2-methylbut-2-ene. 3-Methylbut-1-ene only appeared in small amount after prolonged reaction, and evidently its production (*cf.*¹) is by way of 2-methylbut-2-ene. Uncatalysed isomerization took place slowly at temperatures above 460°, when corrections, never greater than 10%, were applied to the catalysed rates. Decomposition of the materials was negligible at the lower temperatures and very small at the higher temperatures.

Rates

In six experiments 2-methylbut-1-ene (90 ± 10 mm) and boron trichloride (2 ± 0.5 mm) in carbon dioxide reacted at 426.5° to 8.4, 10.2, 12.0, 15.8, 19.7, 25.7% reaction with $10^{-1}k_2$ 62, 68, 68, 64, 63, 57 s⁻¹ ml mol⁻¹, respectively. Thus the progress of the reaction followed the first-order form. At higher extents of reaction the value of k_2 fell significantly—up to 60% at 50% reaction, because of the back reaction. In general the reaction was taken to only *c.* 20%, when the consistency obtained did not warrant consideration of the back reaction. As reaction was maintained with the catalyst in such small proportion (*c.* 2%), it could not have been consumed in the reaction to any significant extent.

2-Methylbut-1-ene (10.6, 22.4, 39.4, 59.4, 80.8, 101.6, 128.6, 158.4, 187.2, 206.0 mm, variation: 19 times) and boron trichloride (2.0 ± 0.2 mm) reacted at 448° giving $10^{-1}k_2$ 122, 114, 112, 107, 101, 112, 106, 116, 119, 122 (mean: 113 ± 6) s⁻¹ ml mol⁻¹, respectively. Thus the reaction is first order in 2-methylbut-1-ene.

2-Methylbut-1-ene (83 ± 2 mm) and boron trichloride (1.05, 1.82, 2.62, 3.83, 4.61, 5.47, 6.13, 6.34, 7.25, 7.82 mm, variation: 7 times) reacted at 461° giving $10^{-1}k_2$ 178, 178, 171, 151, 163, 185, 179, 158, 153, 164 (mean: 168 ± 11) s⁻¹ ml mol⁻¹ respectively. Thus the reaction is first order in boron trichloride.

Propene (8.3, 55.2, 61.0 mm) was added to similar runs at 443.5° giving $10^{-1}k_2$ 102, 102, 110 (mean without propene: 102) s⁻¹ ml mol⁻¹, respectively. Thus propene did not affect the reaction.

Table 1. Variation of rate with temperature
mb1, 2-Methylbut-1-ene; btc, boron trichloride

Temp. (°C)	No. of runs	P_{mb1} (mm)	P_{btc} (mm)	$10^7 k_2$ (s ⁻¹ mm ⁻¹)	k_2 (s ⁻¹ ml mol ⁻¹)
467.4	4	62–80	1.2–2.5	420	1940
465.3	5	81–103	1.9–3.3	357	1640
461.5	10	80–86	1.0–7.8	367	1680
457.1	1	83	1.4	358	1630
452.0	3	54–73	1.3–1.8	294	1330
447.8	10	10–206	1.8–2.2	252	1130
443.5 ^A	3	33–104	1.6–8.0	233	1040
442.0 ^B	4	90–169	0.9–3.7	212	940
435.5	4	82–90	2.6–3.6	212	940
428.4	3	75–104	1.2–2.9	212	930
426.6 ^B	6	78–105	1.4–2.7	146	640
420.6	3	82–96	2.0–2.7	155	670
413.6	2	52–76	0.8–1.8	114	490
408.3	3	82–129	3.0–3.6	126	530
405.2	2	108–118	5.2–6.9	113	480
398.1 ^B	3	50–97	2.5–4.1	94	390
387.7 ^B	4	53–58	4.3–6.5	83	340
368.3 ^B	3	58–80	1.6–2.8	46	180

^A With added propene. ^B In packed vessel.

Results and Discussion

At 368–467° boron trichloride (*c.* 2% in carbon dioxide) catalysed the isomerization of 2-methylbut-1-ene to 2-methylbut-2-ene in a reaction that went to equilibrium at

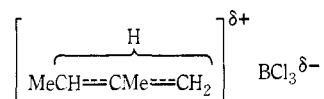
c. 70% of the latter. Individual runs followed the first-order form and the second-order rate constants were independent of initial pressures of the reactants for variations of 19 times for 2-methylbut-1-ene and 7 times for boron trichloride. Addition of propene and increase in surface of the reaction vessel did not affect the rate, and we believe the reaction to be molecular and homogeneous. The variation of rate is given in Table 1 and fits the Arrhenius equation

$$k_2 = 10^{9.71 \pm 0.3} \exp[(-91460 \pm 1000)/8.314T] \text{ s}^{-1} \text{ ml mol}^{-1}$$

At 450° the rate of this isomerization is one third that of cyclopropane.

The result shows that catalysis by boron trichloride, presumably acting as a Lewis acid, is not restricted to cyclopropane,⁵ but applies to olefins of which 2-methylbut-1-ene is a fairly reactive example. Preliminary experiments with the boron-trichloride-catalysed isomerization of the butenes showed that high catalyst concentrations, *c.* 100 mm, and high temperatures, >450°, were required, but the reactions were not kinetically simple; nevertheless neat hydrogen bromide² is effective at 280–380°.

As boron trichloride is electron-deficient and as it is a well known Lewis acid catalyst, it seems likely that the transition state is polar. As no hydrogen is available from the catalyst, the transfer of hydrogen must be internally 1 → 3. This type of shift is consistent with a polar transition state, e.g.



Manuscript received 18 October 1976