Catalysis by Adsorbed Sulphur Dioxide of the *cis-trans*-Isomerization of But-2-enes at Room Temperature

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Summary Sulphur dioxide condensed on various adsorbents catalyses the *cis–trans*-isomerization of but-2-enes without enhancement of the rate of double bond migration.

NaX ZEOLITE, Na-mordenite, KL zeolite, porous Vycor glass (Corning 7930), and Silica gel-60 (Merck) with SO_2 condensed at 24·5 °C catalyse the *cis–trans*-isomerization of but-2-enes at the same temperature, without inducing the formation of any but-1-ene. Without SO_2, these adsorbents do not catalyse either reaction. NaY zeolite, Al_2O_3, HY zeolite (47% Na exchanged from NaY), and silica gel-No. 12. (Davison) catalysed both reactions appreciably at 24·5 °C in the absence of SO_2. Addition of SO_2 to these four adsorbents greatly enhanced the rate of *cis–trans*-isomerization, but reduced the rate of double bond migration. The initial rates of both reactions with and without SO_2 are in the Table. On all the adsorbents examined, SO_2 catalyses *cis–trans*-isomerization and poisons double bond migration to but-1-ene.

Geometrical isomerization of *cis*- and *trans*-but-2-ene accompanying polysulphone formation in liquid SO_2 has been reported.[1,2] In the present work, no polymerization

TABLE. Initial rates of *cis–trans*-isomerization, R_{c-t}, and double bond migration, R_{DBM}, on various adsorbents at 24·5 °C.

Adsorbent[a]	$R_{c-t} \times 10^6$/(mol min^{-1} g^{-1}) Without SO_2[b]	With SO_2[c]	$R_{DBM} \times 10^6$/(mol min^{-1} g^{-1}) Without SO_2[b]	With SO_2[c]
NaX zeolite	d	4·21	d	d
Porous Vycor glass	d	0·91	d	d
SiO_2-60	d	2·57	d	d
Na-mordenite ..	d	0·43	d	d
KL zeolite ..	0·02	10·2	0·04	0·04
NaY zeolite ..	0·34	41·5	4·91	0·08
HY zeolite ..	7·23	31·9	3·72	2·89
γ-Al_2O_3	9·40	23·7	3·46	d
SiO_2-No. 12 ..	3·14	11·1	2·44	1·08

[a] 0·2—0·5 g; pretreated with oxygen and evacuated, at 500 °C. [b] Initiated with $9·0 \times 10^{-4}$ mol of pure *cis*-but-2-ene in a circulating system of 225 ml dead volume. [c] SO_2 ($5·4 \times 10^{-4}$ mol) was added initially, and the reaction was started by introducing $9·0 \times 10^{-4}$ mol of *cis*-but-2-ene. The coverage of condensed SO_2 was in the range 0·02 (SiO_2-60) to 0·4 (NaX). [d] Rate $< 0·01 \times 10^{-6}$ mol min^{-1} g^{-1}.

was observed on NaY, NaX, and porous Vycor glass during the isomerization at 24·5 and 0 °C, confirmed by the absence of a pressure drop in the reactants. This may suggest that the isomerization on the solid surface does not correlate with polysulphone formation, or that the ceiling temperature[1,2] of the polymerization lies far below that determined in liquid SO_2.

Above the ceiling temperature for polymerization in liquid SO_2, no isomerization takes place in the absence of illumination or of an initiator such as benzoyl peroxide.[1] It is surprising that condensed SO_2 induces *cis–trans*-isomerization even on catalytically inactive adsorbents such as silica gel, NaX, or porous Vycor glass, at room temperature. This implies that the formation of a molecular complex[3] between the physically adsorbed SO_2 and but-2-ene might play a significant role in the reaction.

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[3] D. Booth, F. S. Dainton, and K. J. Ivin, *Trans. Faraday Soc.*, 1959, **55**, 1293.