Isomerization of *cis*-But-2-ene Induced by Adsorbed Nitrogen Dioxide

By MAKOTO HATTORI, YUJI WADA, AKIRA MORIKAWA,* and KIYOSHI OTSUKA
(*Department of Chemical Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo* 152, *Japan*)

Summary Double bond migration and geometrical isomerization of *cis*-but-2-ene or the latter only were catalysed by nitrogen dioxide adsorbed on various adsorbents.

WE have found that nitrogen dioxide adsorbed on solids catalyses the isomerization of olefins at rather low temperatures, demonstrating its potential chemical reactivity in the adsorbed state. Compared with nitric oxide, there is little

TABLE. Effect of adsorbed nitrogen dioxide on the catalytic isomerization of *cis*-but-2-ene.

Adsorbent	NO$_2$ adsorbed/10^{13} molecules cm^{-2}	Rate of reaction[a] $R/10^{10}$ molecules cm^{-2} s^{-1}		Temperature/°C
		R_{c-t}	R_{dbm}	
Porous Vycor glass (Corning 7930)	0	0·065	0·11	25
	0·44	2·14	0·026	25
Silica gel-60	0	0·002	0·002	25
	1·66	0·316	b	25
Ca X zeolite	0	0·013	0·012	100
	2·09	1·47	2·23	100
	4·19	4·44	4·06	100
	5·36	5·74	5·74	100
Na X zeolite	4·54	0·043	0·072	100
γ-Alumina	0	15·1	2·16	25
	39·0	2·12	0·00	25

[a] Initial rates of the *cis–trans* (R_{c-t}) and double bond migration (R_{dbm}) isomerization, calculated from the yield of but-1-ene and *trans*-but-2-ene, respectively, for pressures in the range 40—85 Torr. [b] Not observed.

information available on the behaviour of nitrogen dioxide on solid catalysts.

Nitrogen dioxide adsorbed on the various adsorbents in the Table was as good a catalyst for the isomerization of *cis*-but-2-ene as sulphur dioxide.[1] However, in contrast to sulphur dioxide, depending on the adsorbent, it enhances either only *cis–trans* isomerization, as does sulphur dioxide, or both double bond migration and *cis–trans* isomerization. The latter occurred for metal-ion exchanged X-type zeolites, and the enhancements in the rates of the reactions were very high for the calcium zeolite. The reaction rates were proportional to the amount of adsorbed nitrogen dioxide, and their apparent activation energies were identical (10·5 kcal mol^{-1}). These results, together with the fact that both types of isomerization occur, suggest that the reaction mechanism may involve a carbenium ion intermediate. The rather low enhancement for the sodium zeolite may be attributed to the fewer hydroxy-groups than on the calcium zeolite, which are assumed to be activated by the adsorption of nitrogen dioxide.

Nitrogen dioxide adsorbed, *e.g.*, on porous Vycor glass enhances only the *cis–trans* isomerization, and it shows a poisoning effect on double bond migration. As the reaction proceeded, an e.s.r. signal attributable to a nitroxide radical[2] appeared and increased in intensity. These results suggest that the isomerization may occur through a radical intermediate, such as an adduct of nitrogen dioxide and the butene, and not through the carbenium ion intermediate assumed to be formed on Brönsted acid sites in the reaction between adsorbed nitrogen dioxide and surface hydroxy-groups. This is compatible with the mechanism proposed for the gas-phase reaction[3] even though the reaction temperature in the present work was much lower.

For γ-alumina, nitrogen dioxide acted as a poison for both isomerizations, but some *cis–trans* isomerization, nevertheless did take place; this isomerization may be attributable to an intramolecular process[4] in addition to the processes occurring on the Brönsted and Lewis acid sites, although the mechanism of the poisoning is not yet certain.

(*Received*, 26*th July* 1977; *Com.* 770.)

[1] K. Otsuka and A. Morikawa, *J. Catalysis*, 1977, **46**, 71.
[2] L. Jonkman, H. Muller, C. Kiers, and J. Kommandeur, *J. Phys. Chem.*, 1970, **74**, 1650.
[3] J. L. Sprung, H. Akimoto, and J. N. Pitts, Jr., *J.Amer. Chem. Soc.*, 1971, **93**, 4358.
[4] M. P. Rosynek, W. D. Smith, and J. W. Hightower, *J. Catalysis*, 1971, **23**, 204.