NOTES
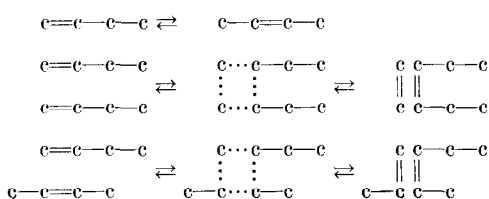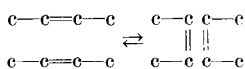
Tracer Studies of Olefin Disproportionation

INTRODUCTION

In the past few years, olefin disproportionation by molybdena-alumina catalysts has been investigated. Banks and Bailey (1, 2) showed near equilibrium disproportionation conversions at temperatures of about 200–400°F. Propylene, for example, disproportionated to ethylene and n-butenes at conversions as high as 40% with efficiencies of 95%.

Bradshaw, Howman, and Turner (3) studied conversion of n-butenes into olefins of higher and lower carbon number. All the results obtained supported the theory that reaction occurs via a "quasi-cyclobutane" intermediate formed by alignment of the double bonds of two reacting olefins. Applied to the n-butenes, with allowance for the isomerization of butene-1 to butene-2, the reaction of butene-1 is pictured as follows:

The reaction of two molecules of butene-2 would produce no new olefin species

Further studies on the disproportionation of propylene, under conditions such that the rate of reaction was controlled by a surface mechanism, indicate that the surface mechanism is a dual-site mechanism (5).

More recently, Mol et al. (6) have shown that the disproportionation of propylene-2-C^{14} formed only radioactive butene with no activity detected in the ethylene produced.

In the present work, radioactive propylene-1-C^{14} was used as a tracer to study the mechanism of the disproportionation of propylene over a cobalt oxide-molybdena-alumina catalyst. Specifically, the purpose of the investigation was to determine if delocalization of the double bond in propylene occurred to any extent upon adsorption on the catalyst surface as has been suggested by infrared studies (4).

METHODS

A commercial catalyst (7) of 3.5% Co and 10.0% MoO$_3$ on alumina in the form of 1/8-in. pellets was used. Nonradioactive C. P. Grade propylene was used while the propylene-1-C^{14} was obtained from the New England Nuclear Corp. and contained 0.2 mCi per liter (STP).

The reactor consisted of a thin catalyst bed supported in a heated section of 3/8-in. diameter stainless-steel tubing.

Following catalyst activation for 6 hr at 1000°F, the reactor was cooled to the desired reaction temperature (300 or 350°F) and then nonradioactive propylene was fed at a rate of 1 ml/sec (WHSV = 1.1) and at atmospheric pressure. The flow of nonradioactive propylene was continued until a steady-state was obtained (in about 20 min), and thereafter radioactive propylene was fed. After changing the feed from propylene to radioactive propylene there was a time lag allowed before sampling for flushing of the nonradioactive propylene.

Previous studies using composition pulses established that this time lag before sampling should be about 5 min.

All samples were analyzed on a gas chromatograph, and in the radioactive cases, a proportional counter was attached to the outlet of the chromatograph to determine the distribution of radioactivity in the various chromatograph fractions.

RESULTS

The results of the study are given in Table 1. These results show that radioactivity is observed in both ethylene and 2-butene. Approximately equal amounts of radioactivity are found in the approximately equal molar quantities of ethylene and butene at both 300 and 350°F.

TABLE 1
CONVERSION AND TRACER DISTRIBUTION FOR PROPYLENE-1-C^{14} DISPROPORTIONATION[a]

Test	Temp. (°F)	Product	Mole (%)	Radio-activity, % of total
1	300	Ethylene	20.5	18.0
		Propylene	68.2	72.8
		2-Butene	11.0	9.2
2	300	Ethylene	22.9	19.2
		Propylene	65.2	71.7
		2-Butene	11.6	9.1
3	350	Ethylene	20.4	19.2
		Propylene	60.9	66.4
		2-Butene	16.5	14.4
4	350	Ethylene	21.5	18.8
		Propylene	61.5	66.3
		2-Butene	15.1	14.9

[a] Pressure = 1 atm; WHSV = 1.1.

DISCUSSION

The results observed here for the disproportionation of propylene-1-C^{14} are quite different from those observed for propylene-2-C^{14} by Mol et al. (6). However, these two different results are not necessarily at variance. In fact, postulation of either double-bond delocalization or isomerization of radioactive propylene on the catalyst to give propylene-2 would predict that C^{14} should appear only in butene product. However, the results for 1-C^{14} show clearly that the double bond in the olefin can be quite mobile. Clark has reported results similar to those given here for similar operating temperatures, but reports that the apparent double bond isomerization is suppressed at lower temperatures (8). The negligible isomerization of the 2-butene here would suggest that an explanation of this double-bond mobility as simple isomerization is probably an oversimplification, although such a reaction step could be used to correctly predict possible products.

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F. L. WOODY
M. J. LEWIS
G. B. WILLS

Department of Chemical Engineering
Virginia Polytechnic Institute
Blacksburg, Virginia 24061