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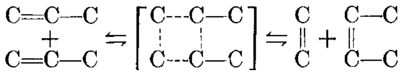
NOTES

The Mechanism of Olefin Disproportionation

Some years ago Banks and Bailey (*1*) made the first report of the catalytic disproportionation of olefins, a reaction in which linear olefins are converted to homologues of lower and higher carbon number. Thus, propylene is disproportionated into ethylene and butene-2. Since the initial discovery several workers have proposed a possible mechanism for this sort of reaction. A linear as well as a radical mechanism (*2*) has been suggested, both of which are not in correspondence with the results of our experiments with ^{14}C-labeled propylene (*3, 4*). In experiments with propylene-2-^{14}C all the radioactivity in the products was found in the butenes and none in the ethylene giving evidence for a four-membered ring intermediate, confirming the suggestion of Bradshaw *et al.* (*5*).



$$\begin{array}{c} C{=}C{-}C \\ + \\ C{=}C{-}C \end{array} \rightleftharpoons \left[\begin{array}{c} C{-}{-}C{-}{-}C \\ \vdots \quad \vdots \\ C{-}{-}C{-}C \end{array}\right] \rightleftharpoons \begin{array}{c} C \\ \| \\ C \end{array} + \begin{array}{c} C{-}C \\ \| \\ C{-}C \end{array}$$

Although it is quite clear now that a cyclic intermediate plays a part during the disproportionation of olefins, the very nature of the intermediate complex is still not exactly known. The cyclobutadiene (*4*) as well as the cyclobutane structure (*6*) was suggested, though the former was proved by Crain (*7*) to be less probable, at least in the case of ethylene cleavage of 2,3-dimethyl-butene-2. A theoretical approach for a similar reaction has been presented by Mango and Schachtschneider (*8*).

To obtain information concerning the mobility of ring hydrogen atoms during the disproportionation reaction, experiments were carried out using 2-deuteropropylene as starting material. In case of hydrogen abstraction, followed by recombination and forming of products, a certain amount of deuterated ethylene will be obtained. When the hydrogen atoms are immobile the ethylene formed will contain no deuterium. Further information was obtained from experiments with 1,2-dimethyl-cyclobutane (DMCB).

EXPERIMENTAL METHODS

The 2-deuteropropylene was prepared by reduction of purified acetone with LiAlD$_4$ and subsequent dehydration (*9, 10*). The 2-*D*-propylene was identified by its mass spectrum and its nuclear magnetic resonance spectrum indicating a purity of 99% 2-*D*-propylene. It should be remarked that as a consequence of the possibility of isomerization during the dehydration process the formation of 1-*D*-propylene may occur. It is this compound that may give rise to misleading results, owing to the formation of deuterated ethylene also in the case of immobility of ring hydrogen atoms.

DMCB was prepared from *trans*-1,2-bis(aminomethyl)-cyclobutane (kindly provided by the Centraal Laboratorium, Staatsmijnen/DSM, Geleen, The Netherlands). Hofmann degradation and pyrolysis of the quarternary ammonium salt yields 1,2-dimethylene-cyclobutane which gives DMCB upon catalytic reduction with hydrogen (*11*). The product was purified by preparative gas chromatography and identified by its refractive index and infrared and nuclear magnetic resonance spectra, showing a *cis/trans* mixture.

The catalyst for the disproportionation reaction, Re$_2$O$_7$/Al$_2$O$_3$, was prepared by impregnating alumina with an aqueous solution of ammonium perrhenate and drying at 200°C. This yielded a catalyst containing a calculated amount of Re_2O_7 of 19%.

The experiments were carried out in a stainless steel micro catalytic reactor mounted in an electric furnace and equipped with conventional temperature-, pressure-, and flow-control devices. The pulse technique was applied for these experiments. The products were collected in a liquid nitrogen trap before entering into the gas chromatograph giving a better separation of the several components. Helium was used as carrier for the whole system. One g of the catalyst was placed in the reactor and activated *in situ,* for 1 hr in a stream of dry air at 580°C and for 1 hr in dry helium. The reactor was cooled to the reaction temperature maintaining the helium flow. After stabilization of the system the feed was injected by means of a hypodermic syringe. The pressure in the system was kept at 2 atm. Gas chromatographic separation of the products was performed on a 4-m × ¼-in. column of 15% propylene carbonate on alumina at room temperature.

RESULTS AND DISCUSSION

Experiments with 2-deuteropropylene. The disproportionation reaction with 2-deuteropropylene was run at 85°C and with a carrier gas velocity of 120 ml of He/min. The separated products were identified by mass spectrometry. Analysis of the butenes, mainly *trans-* and *cis-*butene-2 and traces of 1-butene, showed a parent peak of 58 mass units indicating the presence of two deuterium atoms. The propylene contained one deuterium atom and the ethylene was nearly free of deuterium. Two experiments gave the values for D-containing ethylenes, shown in Table 1. Values were calculated from 5 mass spectra with an average error of ±0.5% (abs). From Table 1, it can be concluded that no hydrogen exchange takes place. The small quantities of C_2H_3D and $C_2H_2D_2$ can be considered as being the result of disproportionation of 1-*D*-propylene in the starting material. Our results are in correspondence with those of Olsthoorn (*12*) who subjected a mixture of C_2H_4 and C_2D_4 to disproportionation conditions, yielding besides the starting material only $C_2H_2D_2$. This indicates that a cyclobutane structure plays a part in the reaction mechanism, at least a much less unsaturated ring as was formerly suggested.

TABLE 1

Expt. no.	2-*D*-propylene converted (%)	Analysis of C_2-hydrocarbons (%)		
		$C_2H_2D_2$	C_2H_3D	C_2H_4
1	40	0.3	1.3	98.4
2	23	0.6	1.1	98.3

Experiments with 1,2-dimethyl-cyclobutane. With respect to the foregoing conclusion it is noteworthy that experiments with DMCB showed that this compound is stable, when subjected to conditions at which propylene gives high conversions. Only at high temperature (>300°C) olefins are formed as a result of thermal cracking (*13*).

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HNO as an Intermediate in the Catalytic Reduction of Nitric Oxide

The catalytic reduction of nitric oxide with hydrogen has been reported by several workers (*1–5*). Most of these investigations have been carried out at or above room temperature, the reduction products being reported as water, ammonia, nitrogen, or hydroxylamine. More recently, Kokes (*5*) has studied the reduction of nitric oxide with hydrogen on an alumina supported platinum catalyst over a wide range of temperatures. In these studies, it has been found that at low temperatures nitrous oxide is the main product with only traces of ammonia formed; however, ammonia formation increases with increasing temperature. At temperatures above 400°K only ammonia and water are found in the reduction products. It is assumed that hydrogen is activated on the platinum sites and migrates from particle to particle until encountering a nitric oxide molecule to form HNO, a well characterized species in the gas phase (*6*), the dimer of which has been found to be stable below 183°K (*7*). This initial HNO formation is followed by one of the subsequent steps.

$$(HNO)_2 \rightarrow N_2O + H_2O \qquad (1)$$

$$HNO + 2H_2 \rightarrow NH_3 + H_2O \qquad (2)$$

The high nitrous oxide yields at low temperatures might possibly be attributed to the stability of the dimer of HNO below 183°K. If this be true, the reaction products obtained from the reaction of hydrogen atoms with nitric oxide at low temperatures should be similar to those obtained for the catalytic system studied by Kokes. Preliminary studies (*8*) carried out on the addition of hydrogen atoms generated in the gas phase to nitric oxide physically adsorbed on silica gel at 77°K have shown this to be a particularly reactive system. This reaction has now been studied in more detail.

Method

The reaction vessel used has been extensively described elsewhere (*9*). The adsorbent, Cab-O-Sil M2 obtained from the Cabot Corporation, Boston, Massachusetts, was spread over the bottom of the flask to form a layer roughly 2 mm thick. A chromel-alumel thermocouple was inserted in the adsorbent to enable adjustment to the desired surface temperature during the adsorption and desorption process. In the following discussion, it will be assumed that θ is the volume of nitric oxide adsorbed at 77°K divided by the B.E.T. monolayer volume obtained from nitrogen adsorption. All gases were C. P. grade or better and were purified by standard gas purification techniques. Prior to each run, the Cab-O-Sil was outgassed at 400°C for 3 hr. In a typical run, the desired volume of nitric oxide was measured out and adsorbed on the surface at 77°K. Following adsorption, the liquid nitrogen dewar was adjusted so that the entire reaction vessel was immersed in liquid nitrogen. The reaction was then started by admitting hydrogen and letting it come into contact with a heated tungsten filament. The hydrogen atomizes on the hot filament and