production of formaldehyde will have to be considered in any mechanistic interpretation of the kinetic studies. These experiments are continuing and will be reported in detail at a later date.

REFERENCES

1. Margolis, L. Y., *Advan. Catalysis* **14**, 429–501 (1963).
2. Voge, H. H., and Adams, C. R., *Advan. Catalysis* **17**, 158–221 (1966).
3. Hayes, K. E., *Can. J. Chem.* **37**, 583 (1959).
4. Feigl, F., "Spot Tests in Organic Chemistry," p. 349. Am. Elsevier, New York, 1960.
5. Walker, J. F., *in* "American Chemical Society Monograph, Formaldehyde, No. 159." Reinhold, New York, 1964.

R. W. Macdonald
K. E. Hayes

Chemistry Department
Dalhousie University
Halifax, Nova Scotia, Canada

Received February 18, 1969
Revised June 16, 1969

Reaction of Buta-1,3-diene over a Carbon-Supported Cobalt Oxide Catalyst

The homogeneous gas phase dimerization of buta-1,3-diene is a well-known reaction and has been extensively studied. At short contact times in glass vessels at 300°C the main product is the Diels-Alder adduct 4-vinylcyclohexene (*1*) while under prolonged exposure to temperatures of 500°C and above a profusion of secondary reactions occurs leading to the formation of aromatic and unsaturated alicyclic compounds (*2*). Relatively little attention appears to have been given, however, to the solid catalyzed reactions of gaseous butadiene at elevated temperatures and we wish to report here some results obtained using a charcoal supported cobalt oxide catalyst. Materials of this type have recently been used as mono-olefin dimerization catalysts (*3–6*) and dienes have been shown to interact with them at low temperatures (*3*). No studies of this interaction at high temperatures have previously been reported.

EXPERIMENTAL METHODS

The charcoal used in the catalyst preparation was a BDH granular coconut shell charcoal with an ash content of 4.26% reduced to 0.92% by leaching with 48% hydrofluoric acid (*3*). Catalysts were prepared somewhat after the manner of Schultz *et al.* (*3*) by washing the charcoal with concentrated (0.880) ammonium hydroxide solution, drying under vacuum, impregnating with an aqueous solution of cobalt nitrate hexahydrate (BDH AnalaR), drying again, and then heating in a stream of dry nitrogen at 400°C for 30 min. Decomposition of cobalt nitrate to the oxide began at about 130°C. Catalysts were prepared in this way having a cobalt oxide concentration of 5 and 15%.

Reactions were carried out by passing gaseous butadiene (Matheson Research Grade) at atmospheric pressure and at a measured rate through a fixed bed containing 8 g of catalyst maintained at 300°C in a glass reactor supported in a furnace. The effluent gases were passed through a water condenser and then into a system of gas burettes which enabled measurements to be made of their rate of flow. Liquid products were analyzed using a Pye 105 gas chromatograph fitted with a 10-m squalane column maintained at 136°C. Satisfactory gas analyses were obtained with a 2-m tetraisobutene column maintained at 0°C in a Perkin-Elmer F.11 instrument.

RESULTS

On admitting butadiene to the catalyst the flow of effluent gas almost ceased indicating that considerable adsorption of diene onto the catalyst surface was taking place. Thereafter the effluent gas flow rate gradually increased until after some 40 min the inlet and outlet flow rates became identical. The initial strong adsorption of diene was followed some 25 min later by the production of a condensible water-white liquid. This liquid product was found to be composed, in the case of the 15% cobalt oxide containing catalyst, almost entirely of aromatic compounds; the 5% cobalt oxide catalyst gave a liquid product which contained a high concentration of alicyclic compounds (Table 1). In a typical run with either catalyst the total liquid yield based on the butadiene feed was about 23% (w/w).

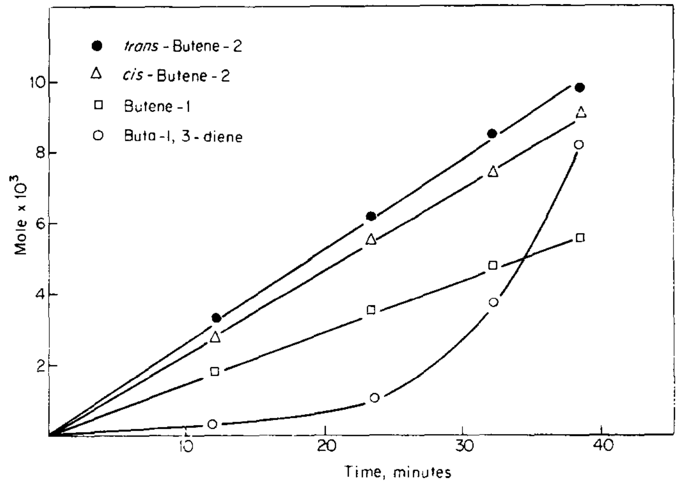


FIG. 1. Gaseous products from reaction of buta-1,3-diene over 15% cobalt oxide on charcoal at 300°C and GHSV 150 hr^{-1}.

TABLE 1

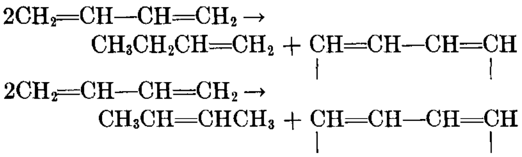
LIQUID PRODUCTS FROM REACTION OF BUTA-1,3-DIENE OVER CHARCOAL SUPPORTED COBALT OXIDE CATALYSTS AT 300°C AND GHSV 150 hr^{-1}

Component	Catalyst: Cobalt oxide 15%	5%
Benzene	3.09	1.22
Methylcyclohexadienes	1.38	8.10
Toluene	6.44	2.63
Dimethylcyclohexenes and methylmethylenecyclohexenes	4.30	17.23
4-Vinylcyclohexene	4.63	18.67
Ethylbenzene	36.55	28.65
p-Xylene	10.80	4.23
m-Xylene	1.39	1.83
o-Xylene	31.30	15.55
Styrene	—	1.60

Samples of the effluent gas were collected at intervals and analyzed. These analyses showed that in the early stages of a run the effluent was composed mainly of butenes (Fig. 1). The concentration in the effluent of butadiene remained relatively low up to the point where liquid products began to be evolved whereupon a steep rise in the diene concentration–time curve was observed.

DISCUSSION

A reaction mechanism which is consistent with these observations is as follows. In the initial stages of the reaction butadiene is adsorbed on the catalyst surface and undergoes a disproportionation to form the butenes and a hydrocarbon residue:

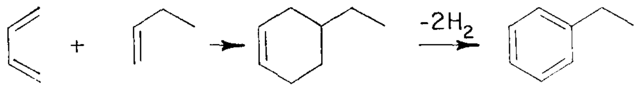


$$\mathrm{2CH_2{=}CH{-}CH{=}CH_2 \rightarrow CH_3CH_2CH{=}CH_2 + \underset{|}{CH}{=}CH{-}CH{=}\underset{|}{CH}}$$

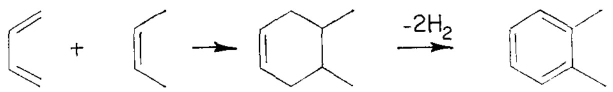
$$\mathrm{2CH_2{=}CH{-}CH{=}CH_2 \rightarrow CH_3CH{=}CHCH_3 + \underset{|}{CH}{=}CH{-}CH{=}\underset{|}{CH}}$$

Much of the so formed olefinic material is desorbed and appears in the effluent gas stream but a considerable proportion remains on the catalyst surface where it is available for reaction with further diene molecules from the feed. (That these secondary reactions are in fact solid catalyzed is shown by the observation that when butene-1 or *cis*-butene-2 was included in the feed a decreased amount of liquid product was formed.) These reactions take the form of Diels-Alder type combinations and lead to the formation of adducts which are the precursors of the aromatic compounds found in the liquid products. For example:

(a) ethyl benzene:



(b) *o*-xylene:



The preponderance of these precursors in the liquid product from the reaction over the 5% cobalt oxide containing catalyst suggests that the cobalt is acting predominantly as a dehydrogenation center in this system. As is the case with the high temperature homogeneous reaction (*2*) it seems likely that the minor liquid products are formed by a series of isomerizations and decompositions involving the major products.

References

1. Kistiakowsky, G. B., and Ransom, W. W., *J. Chem. Phys.* 7, 725 (1939).

2. Gil-Av, E., Shabtai, J., and Steckel, F., *J. Chem. Eng. Data* 6, 98 (1960).

3. Schultz, R. G., Schuck, J. M., and Wildi, B. S., *J. Catalysis* 6, 385 (1966).

4. Schultz, R. G., Engelbrecht, R. M., Moore, R. N., and Wildi, L. T., *J. Catalysis* 6, 419 (1966).

5. Schultz, R. G., *J. Catalysis* 7, 286 (1967).

6. Belgian Patent No. 694433.

J. G. Yates
K. W. Wheatley

Department of Chemical Engineering
University College London
London, W.C.1., England

Received May 21, 1969

Enhancement of Metal-Ion Catalysis by Ligands: The Resonance Effect in Catalysis by Iron(II)

The ligands attached to a metal ion affect its ability to catalyze the decarboxylation of dimethyloxaloacetic acid (*1*). When it was observed that, like the enzyme protein in biological systems, 1,10-phenanthroline is a coordinating agent that enhances catalysis (*2*), we became interested in determining the physical basis of enhancement. Our method was to examine catalysts consisting of 1:1 complexes of metals and various sub-