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NOTES

The Oxidative Dehydrodimerization and Aromatization of Isobutene

Recent studies have revealed that the catalytic oxidation of propylene to hexadiene and to benzene may be carried out over several metal oxides (*1–4*). The reaction has been suggested to proceed through consecutive steps involving oxidative removal of hydrogen to produce allylic intermediates, which then react to produce hexadiene and acrolein. Further oxidative attack on hexadiene gives cyclohexadiene and benzene. Thallium oxide has been found to be selective towards hexadiene (*1*), and the salts of indium, bismuth, tin and cadmium catalyze the oxidation to benzene (*2–4*). The present note reports the analogous oxidation of isobutene to 2,5-dimethyl-1,5-hexadiene and *p*-xylene over indium oxide, one of the more selective catalysts for the oxidative aromatization of propylene.

Experiments were completed in a standard flow apparatus, products being analyzed by gas chromatography (*2*). Preliminary experiments revealed the presence of methacrolein, carbon dioxide, 2,5-dimethyl-1,5-hexadiene, *p*-xylene, toluene and benzene among the products, these

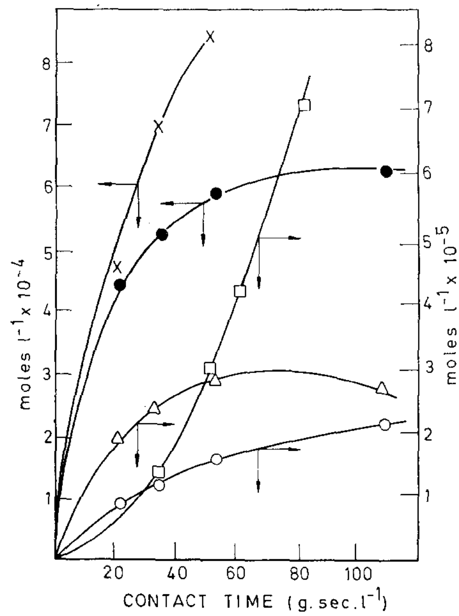


FIG. 1. Product–time curves for the oxidation of isobutene. $T = 520°C$. [isobutene] = 5.0×10^{-3} moles/liter; [oxygen] = 8.9×10^{-3} moles/liter; (●) 2,5-dimethyl-1,5-hexadiene; (△) *p*-xylene; (○) benzene; (×) carbon dioxide; (□) toluene.

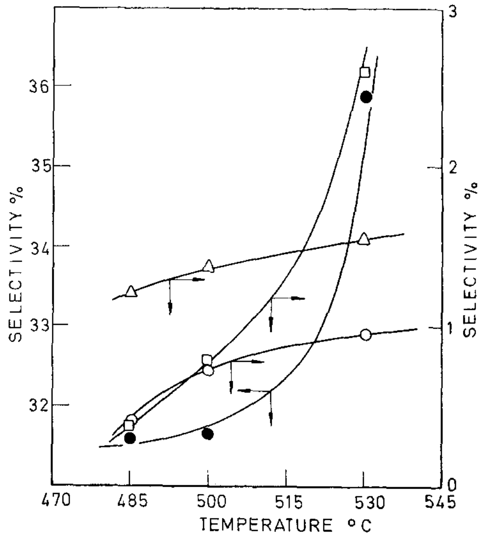


FIG. 2. The effect of temperature on the selectivity of oxidation to products. Selectivity = (moles product/moles reactant reacted) × (no. of C atoms in product/no. of C atoms in reactant) × 100%. Contact time = 109 g sec/liter. [isobutene] = 5.0×10^{-3} moles/liter; [oxygen] = 8.9×10^{-3} moles/liter; (●) 2,5-dimethyl-1,5-hexadiene; (△) *p*-xylene; (□) toluene; (○) benzene.

identifications being checked mass-spectrometrically. Only traces of *o*- and *m*-xylene could be observed. Measurements were made of the kinetics of production of dimerized and cyclized products during the initial stages of the reaction, and of the dependence of yields and selectivities upon reaction parameters at longer contact times. Typical product–time curves are shown in Fig. 1.

The reaction was found to be very dependent upon temperature, with the selectivity of oxidation to the diene being about ten times as large as that to the aromatic products (Fig. 2). The yield of total aromatics was found to increase linearly with contact time, and studies of the oxidation of reaction products showed that toluene and benzene originated from the overoxidation of dimethylhexadiene and *p*-xylene, with approximately equal percentages of both products undergoing demethylation.

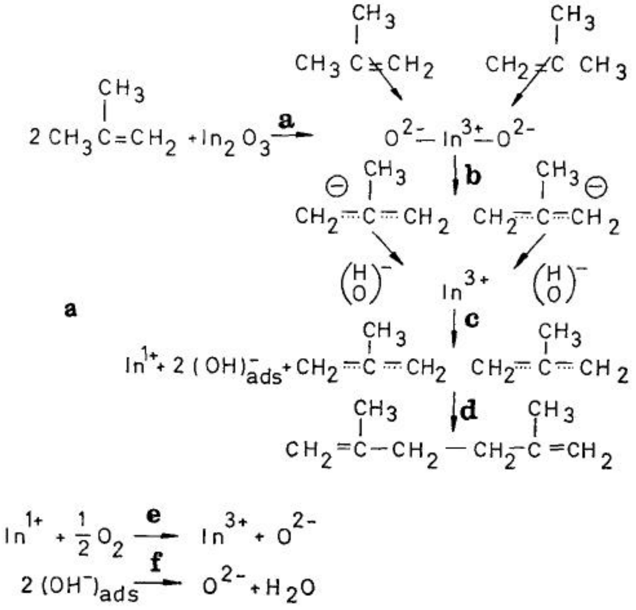
The kinetics of the production of dimethylhexadiene and of *p*-xylene were measured over the initial stages of reaction where insignificant amounts of toluene and benzene were produced. Diffusion was found not to affect the values obtained and homogeneous reactions were negligible in the temperature range of the measurements. The rate equations obtained are given below: activation energies were measured over the range 460–495°C. The addition of *p*-xylene and dimethylhexadiene to the feed had a small inhibitory effect due entirely to the diene. This was negligible for the concentrations of product present during the initial rate measurements.

$$485^\circ\text{C} \qquad \frac{d(\text{diene})}{dt} = 0.30[\text{isobutene}][\text{oxygen}]^{0.8} \qquad E_A = 30 \text{ kcal/mole}$$

$$485^\circ\text{C} \qquad \frac{d(p\text{-xylene})}{dt} = 0.69[\text{isobutene}][\text{oxygen}]^{0.95} \qquad E_A = 31 \text{ kcal/mole}$$

It is interesting to note that these initial rates of production of diene and of xylene are of the same order, the high selectivity to the diene only becoming apparent at longer contact times (Fig. 2).

The kinetic expressions obtained were compared with predictions based on the application of Langmuir–Hinshelwood ar-



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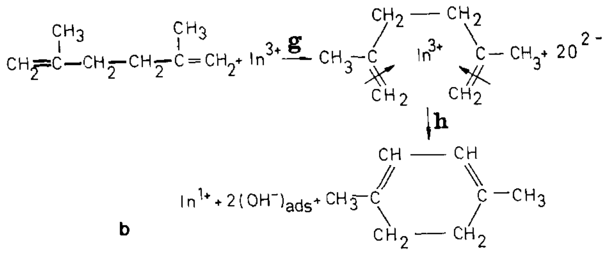

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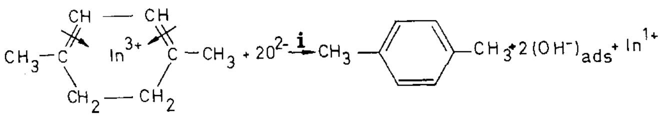

guments to different theoretical models. Over the range of experimental results available, most satisfactory agreement was obtained with a model based on the reaction of two adsorbed isobutene molecules with dissociatively adsorbed oxygen, where isobutene and diene compete for the same sites, but oxygen is adsorbed at different sites. However, a model based on the reaction of gaseous isobutene with dissociatively adsorbed oxygen was acceptable, though it gave a less good fit with experimental results. No satisfactory fit was obtained with any other model.

The results can be satisfactorily explained by a mechanism analogous to that proposed for the oxidation of propylene, in which the dimerization of allylic intermediates is responsible for the formation of dimethylhexadiene:

Neither isobutene or 2,5-dimethyl-1,5-hexadiene is strongly adsorbed on the catalyst, and the further oxidation of dimethylhexadiene to aromatics is less favored than in the case of propylene. It might be possible to increase the yield of aromatics by modifying the catalyst. Alternatively, a two-stage process involving indium oxide as an oxidative dimerization catalyst and chromia as a cyclization catalyst should lead to higher yields of aromatics (*5*).

References

1. Trimm, D. L., and Doerr, L. A., *J. Catal.* **23,** 49 (1971).
2. Trimm, D. L., and Doerr, L. A., *J. Catal.* **26,** 1 (1972).
3. Seiyama, T., Egashira, M., Sakamoto, T., and Asu, I., *J. Catal.* **24,** 76 (1972).
4. Ohdan, K., Ogawa, T., Unemura, S., and Yamada, K., *Kogyo Kagaku Zasshi* **73,** 842 (1970).
5. Swift, H. E., and Bozik, J. E., *J. Catal.* **22,** 427 (1971).

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