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NOTES

Mechanism of Heterogeneous Liquid-Phase Oxidation of Cyclohexene, Cumene, and Tetralin[1]

For the heterogeneous liquid phase oxidation of cyclohexene, tetralin, and cumene catalyzed by transition metal oxides it has been established that there is a critical weight of the catalyst above which the rate of oxidation drops suddenly (*1–5*). A general mechanism explaining the simultaneous formation and destruction of hydroperioxide in the oxidation of cyclohexene has recently been proposed by Graydon and co-workers (*3, 6*), and used by Agarwal and Srivastava (*7*) to explain the kinetics of cumene oxidation. However, in the region where inhibition was effective, very few experimental data have been presented. The proposed mechanism is given below.

Initiation:

$$\mathrm{ROOH} + M \overset{k_1}{\rightleftharpoons} \mathrm{ROOH}\ldots M \qquad (1)$$

$$\mathrm{ROOH}\ldots M \xrightarrow{k_2} \mathrm{RO}^{\cdot} + {}^{\cdot}\mathrm{OH}\ldots M \qquad (2)$$

$$\mathrm{ROOH} + {}^{\cdot}\mathrm{OH}\ldots M \xrightarrow{k_3} \mathrm{RO}^{\cdot}_2 + \mathrm{H_2O} + M \qquad (3)$$

$$\mathrm{RO}^{\cdot} + \mathrm{RH} \xrightarrow{k_4} \mathrm{ROH} + \mathrm{R}^{\cdot} \qquad (4)$$

Propagation:

$$\mathrm{R}^{\cdot} + \mathrm{O_2} \xrightarrow{k_5} \mathrm{ROO}^{\cdot} \qquad (5)$$

$$\mathrm{ROO}^{\cdot} + \mathrm{RH} \xrightarrow{k_6} \mathrm{ROOH} + \mathrm{R}^{\cdot} \qquad (6)$$

Termination:

$$\mathrm{ROO}^{\cdot} + \mathrm{ROO}^{\cdot} \xrightarrow{k_7} \text{inactive products} + \mathrm{O_2} \qquad (7)$$

$$\mathrm{ROO}^{\cdot} + M \overset{k_8}{\rightleftharpoons} \mathrm{ROO}^{\cdot}\ldots M \qquad (8)$$

$$\mathrm{ROO}^{\cdot}\ldots M + \mathrm{ROO}^{\cdot} \xrightarrow{k_9} \text{inactive products} \qquad (9)$$

In the present work MnO_2-catalyzed oxidation of cyclohexene, tetralin, and cumene has been studied in the inhibition region at 60, 65, and 80°C, respectively. The details of the oxidation apparatus, operating procedure, and analyses have been described previously (*4*). Monochlorobenzene was used as inert solvent for the dilution experiments.

RESULTS AND DISCUSSION

To simplify matters the symbols RH and ROOH are used in general for hydrocarbons and their hydroperoxides, respectively.

In order to study the effect of hydrocarbon concentration in the region where inhibition was effective, it was necessary to establish the oxidation rate as a function of the catalyst ratio for all the three systems. Figure 1 shows the plots of oxidation rates as functions of catalyst ratios for pure samples of cyclohexene, cumene, and tetralin. The oxidation rates increased steadily with the MnO_2–catalyst ratio until the latter reached a critical value, after which the rate dropped suddenly. The rate

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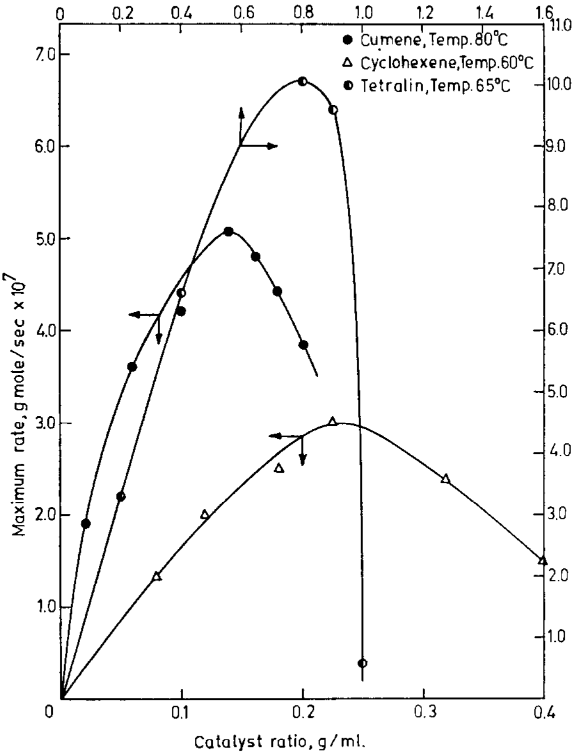

FIG. 1. Rate of oxidation as a function of MnO_2–catalyst ratio.

expressions derived by Neuberg *et al.* (*6*) and Agarwal and Srivastava (*7*) clearly account for the observations before the break point.

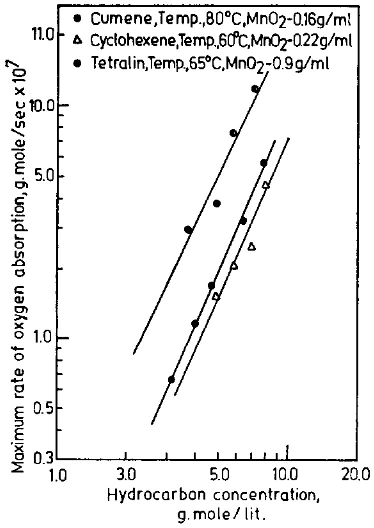

FIG. 2. Rate dependence with respect to hydrocarbon concentration in inhibition region.

It is assumed that at the limiting rate of oxidation the rate of formation of hydroperoxide becomes equal to its rate of decomposition (*6*, *7*). The limiting rate of oxidation is given by

$$-\frac{d[O_2]}{dt} = \frac{\alpha k_6^2[RH]^2}{2k_7 + K_8k_9[M]}, \tag{10}$$

where α is the fraction of hydroperoxide yielding free radicals.

The influence of cyclohexene, cumene, and tetralin concentrations on the rate of oxidation was studied with the mixtures of the corresponding hydrocarbon with monochlorobenzene at a catalyst ratio chosen from the inhibition range (Fig. 1). In Fig. 2 maximum rates of oxygen absorption are plotted against hydrocarbon concentrations. The orders were 1.7, 2.1, and 2.3 for cyclohexene, tetralin, and cumene, respectively. In the case of cumene, where the detailed study on hydrocarbon dependence in the inhibition region was performed, it was observed that in all cases the resulting order was approximately 2. It can therefore be concluded that the limiting rate of oxidation was proportional to the square of the hydrocarbon concentration, in accordance with the rate expression of Eq. (10).

From the present results we conclude that the oxidations of cyclohexene, cumene, and tetralin in the presence of transition metal oxides proceed via a degenerate chain-branching mechanism. The similarity in the kinetic behavior of the three systems may be due to formation of resonance-stabilized radical species ($\dot{R}$) in each of these cases. Therefore, a single mechanism satisfactorily explains all the kinetic data observed for these systems.

REFERENCES

1. Mukherjee, A., and Graydon, W. F., *J. Phys. Chem.* **71**, 4232 (1967).
2. Varma, G. R., and Graydon, W. F., *J. Catal.* **28**, 236 (1972).
3. Neuburg, H. J., Basset, J. M., and Graydon, W. F., *J. Catal.* **25**, 425 (1972).
4. Srivastava, R. K., and Srivastava, R. D., *J. Catal.* **39**, 317 (1975).
5. Tobolsky, A. V., Metz, D. J., and Mersobian, R. B., *J. Amer. Chem. Soc.* **72**, 1942 (1950).
6. Neuburg, H. J., Phillips, M. J., and Graydon, W. F., *J. Catal.* **38**, 33 (1975).
7. Agarwal, A. K., and Srivastava, R. D., *J. Catal.* **45**, 86 (1976).

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