

# Catalyzed Oxidation of Cyclohexane in the Liquid Phase

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As a class of reactions, the liquid phase oxidation of hydrocarbons is a major source of organic chemicals in industry. The oxidation of cyclohexane is an important member of this class of reactions, and the products of this reaction—cyclohexanol, cyclohexanone, and adipic acid—supply much of the raw material for the manufacture of Nylon-6 and Nylon-6,6. While the reaction mechanisms in cyclohexane oxidation have been well researched (see for example, Berezin et al., 1966), not much quantitative information on the kinetics is available in the published literature. Another aspect that has remained obscure, in spite of some noteworthy papers (Steeman et al., 1961; Alagy et al., 1974) is the relative importance of mass transfer and kinetic rates in this gas-liquid reaction. Given the complex kinetics of the reaction, both rate and selectivity of the intermediates would depend on the relative rates of mass transfer and kinetics.

The present authors (Suresh et al., 1988 a, c) have described studies on the uncatalyzed oxidation of cyclohexane using an  $O_2$ - $N_2$  mixture, considering separately the aspects of physical mass transfer, homogeneous kinetics and mass transfer with chemical reaction. A simple kinetic model derived from the free-radical mechanism of the reaction was shown (Suresh et al. 1988b) to be consistent with the rate data from homogeneous reaction as well as from a heterogeneous reactor under conditions of kinetic control. Mass-transfer rate enhancements were observed under certain experimental conditions and correlated with a suitably defined Hatta parameter. A phenomenological model for mass transfer from bubble swarms with reaction in the liquid phase was developed and shown to describe the observed trends, including conditions of mass transfer rate enhancements.

The present paper describes an extension of the ideas put forth in the previous papers to the gas-liquid oxidation of cyclohexane using soluble cobalt naphthenate as catalyst. Salts of cobalt have been the catalysts of choice in cyclohexane oxidation, and have been reported to reduce or even eliminate the induction period as well as hasten the decomposition of the cyclohexyl hydroperoxide intermediate (Berezin et al., 1966). This paper reports experimental data obtained in two types of reactors, a batch microautoclave where homogeneous reaction is ensured and a sparged and stirred reactor which features mass transfer from gas bubble into the liquid and chemical reaction in the liquid. The applicability of the kinetic model proposed earlier (Suresh et al., 1988b) is here examined for catalyzed oxidation. In the gas-liquid reactor, the various regimes that the autocatalytic system moves through have been recognized using measurement of dissolved oxygen levels during the oxidation. Observed mass-transfer rate enhancements have been compared with those in uncatalyzed oxidation. The catalyzed oxidation also shows a striking reversal in the rate vs. time behavior and a possible reason for this is discussed.

## Experimental

The batch microautoclaves and the stirred tank reactor system used in this study were the same as the ones used in the uncatalyzed study, and have been described in detail elsewhere (Suresh, et al., 1988a and b, Suresh, 1986). The micro-autoclaves were 35 cm<sup>3</sup> in volume and 25 cm<sup>3</sup> of liquid was used in the experiments. Oxygen was predissolved at high pressure at room temperature, and the micro-autoclave sealed off. The

reaction was started by raising the temperature of the liquid sharply by immersing the reactor in a fluidized bed maintained at the reaction temperature. Mixing was provided by a stainless steel ball inside, moved backwards and forwards by a magnet. Reaction was stopped by quenching the reactor in a room temperature water bath. The catalyst (cobalt naphthenate, supplied by Colours and Chemicals Pty. Ltd., Melbourne) was used in concentrations of 1.5 ppm (as cobalt), and was predissolved in the cyclohexane. Oxygen conversions were determined by collecting and measuring the volume of unconsumed oxygen after the reaction.

The stirred tank reactor (STR) system consisted basically of a 13-cm-dia. stirred tank (equipped with a single orifice sparger and a 6-blade turbine stirrer) and associated equipment for saturating the gases entering the reactor and for condensing and recycling the cyclohexane vapors from the leaving gases. Adequate consideration was given to the safety aspects in the design of this system (Suresh et al., 1988a). The system was batch with respect to the liquid and once-through with respect to the gases. A concentrated solution of cobalt naphthenate in cyclohexane was made and the required amount of this was pumped into the reactor using a liquid chromatography pump just before commencement of the reaction, so that the concentration of cobalt in the reactant liquid was 1.5 ppm. Oxygen levels in the exhaust gases were continuously monitored by a polarographic oxygen probe (Titron Ltd., Melbourne) and occasionally checked by sampling the gases into a Hewlett-Packard gas-chromatograph equipped with an Electron Capture Detector. Dissolved oxygen levels in the liquid were determined from time to time by desorbing the dissolved gases from a liquid sample and analyzing them for oxygen in the same chromatograph. Oxidate samples for product analysis were taken from time to time and stored in a refrigerator. Gas chromatography was used for chemical analysis of the oxidate (Suresh, 1986).

## Results and Discussion

### Oxygen conversion kinetics from batch micro-autoclaves

Reaction studies in the batch micro-autoclaves were conducted at two temperatures, 423 and 433 K. The oxygen conversions (moles of oxygen absorbed per mole of initial cyclohexane) from these results at different reaction times are shown in Figure 1. It was seen in similar kinetic studies on uncatalyzed oxidation (Suresh, Sridhar, and Potter, 1988b), that in the range of small (1–5%) conversion, the relationship between the logarithm of the oxygen conversion the batch time was linear. The present results, which also exhibit a similar behavior, show therefore that the catalyzed oxidation is an autocatalytic reaction as is the uncatalyzed oxidation. The slopes of the straight lines in Figure 1 are much higher than the slopes of the lines for the uncatalyzed case at equal temperatures, showing that the catalyst causes an acceleration in the overall rate. In fact, comparing the results of the catalyzed experiments at 423 and 433 K with those of the uncatalyzed experiments at 433 and 443 K, respectively (also shown in the figure), it is seen that the increase in rate produced by the catalyst is almost equivalent to that due to a rise in temperature of 10 K.

### Catalysed Oxidation

Figures 2 and 3 show the results of oxidation at 424 K with 1.5 ppm of cobalt naphthenate. Although qualitative similarities

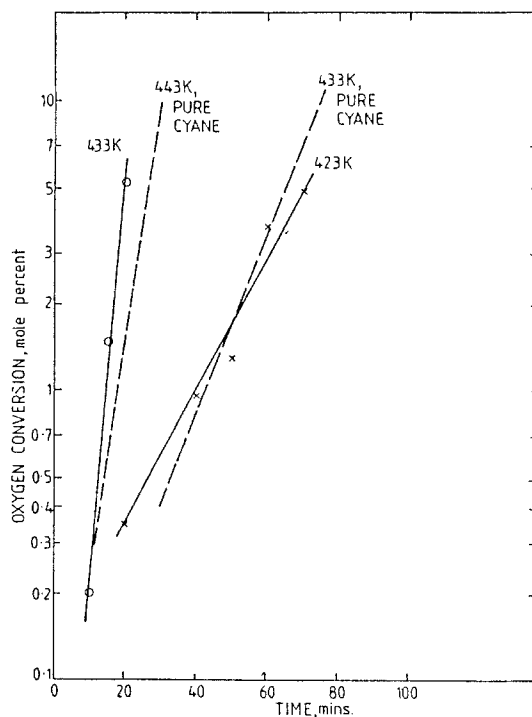


Figure 1. Effect of cobalt naphthenate on oxygen conversion kinetics.

with the results of uncatalyzed oxidation (Suresh et al., 1988b) can be recognized, the variation of absorption rate with time exhibits some rather striking features. Based on this curve, the entire experiment can be divided into three regions: the initial period of slow reaction during which a measurable concentration of dissolved oxygen is present, the period of mass transfer enhancements, and the period of decreasing rates. The characteristics of these regions will now be considered in some detail.

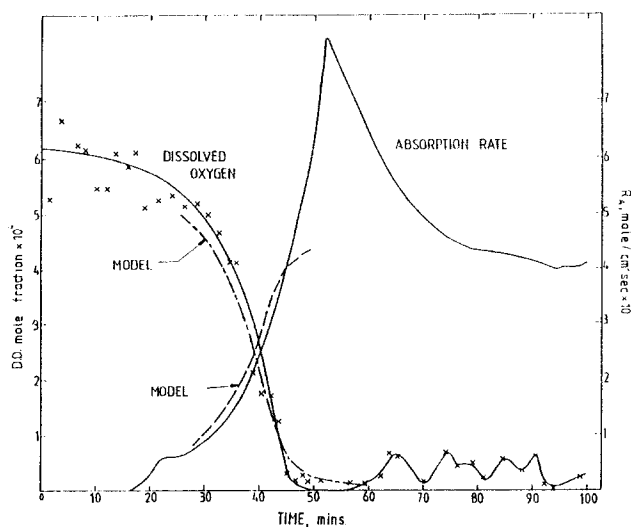


Figure 2. Variation of dissolved oxygen concentration and oxygen absorption rate in catalyzed oxidation in the STR.

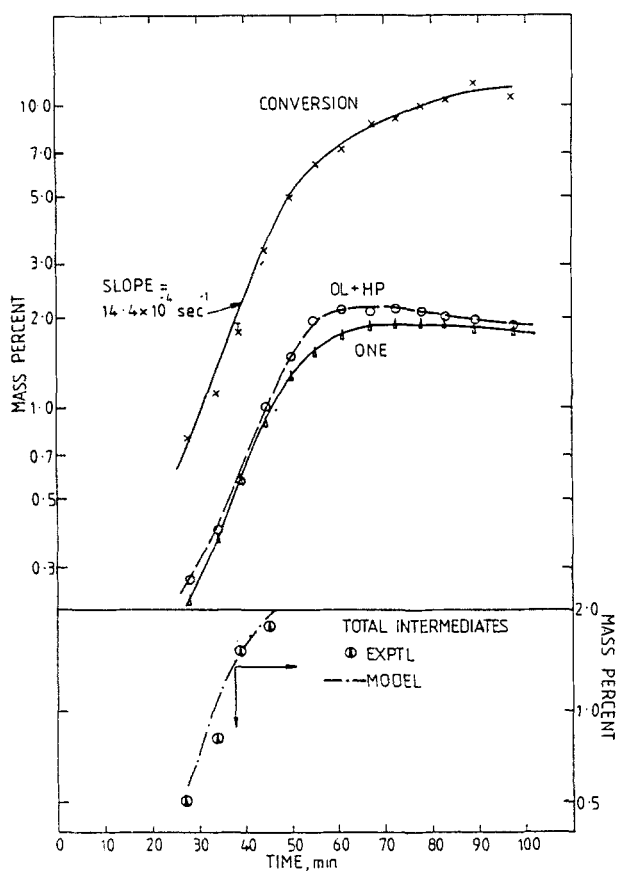


Figure 3. Product concentration development in catalyzed oxidation.

### The slow reaction regime

The slow reaction regime exhibits all the features seen in the uncatalyzed oxidation. After a brief induction period (the induction period is not totally eliminated at the concentration of the catalyst used), the absorption rate increases and the dissolved oxygen concentration decreases, showing the autocatalytic nature of the reaction. The physical mass transfer coefficient can be estimated from the dissolved oxygen concentrations and the exit oxygen flowrates in this region as described in Suresh, et al. (1988a). A value of  $3.11 \times 10^{-4}$  m/s was thus obtained for  $k_L$ , and this is in good agreement with the earlier values obtained at 423 K (Suresh, et al., 1988a). The conversion time of Figure 3 also shows that the variation of  $\ln X$  with batch time is linear in this region.

The similarities between the present results and those from the uncatalyzed oxidation suggest a similarity of underlying mechanisms. The kinetic model derived in Suresh et al. (1988b) should therefore be applicable in this case also. The kinetic model in that study led to the following equations for the kinetic rates of cyclohexane and oxygen conversion, respectively:

$$r_c = \frac{k_o k_3 c_p c_L}{(k_{o1} + k_{o2} c_p + k_3 c_L)} \quad (1)$$

and

$$r_o = \frac{k_3 c_L c_p (k_{o1} + k_3 c_L)}{(k_{o1} + k_{o2} c_p + k_3 c_L)} \quad (2)$$

The linearity of the  $\ln X - t$  data have already shown that the cyclohexane conversion rates are predicted well by Eq. 1 under conditions of high  $c_L [k_3 c_L \gg (k_{o1} + k_{o2} c_p)]$ , i.e., the cyclohexane conversion rate is first order with respect to total products and zero order with respect to oxygen at low conversions and high  $c_L$ . The linear portion of the  $\ln x - t$  plot yields a value of  $14.4 \times 10^{-4} \text{ s}^{-1}$  for  $k_{o1}$ , at 423 K. This value is quite close to the value obtained at 433 K for uncatalyzed oxidation by Suresh et al. (1988b) ( $12 - 13 \times 10^{-4} \text{ s}^{-1}$ ). Figure 2 also shows the results of reactor simulation in the slow reaction regime using the above kinetic model. Reaction was assumed to be in the liquid bulk, and both gas and liquid phases were assumed to be well mixed. (The reactor model equations have been set out in Appendix B of Suresh et al., 1988b). With rate constants of  $k_{o1} = 14.4 \times 10^{-4} \text{ s}^{-1}$ ,  $k_{o2} = 6 \times 10^{-3} \text{ m}^3/\text{kmol} \cdot \text{s}$  and  $k_3 = 18 \text{ m}^3/\text{kmol} \cdot \text{s}$ , the model is seen to fit the experimental data on absorption rate and dissolved oxygen quite well. Again, these rate constants at 423 K for the catalyzed oxidation compare with what would be expected at 430–432 K for the uncatalyzed oxidation (Suresh, et al., 1988b). The present results therefore show that the increase in the kinetic rates produced by 1.5 ppm of the catalyst is akin to that produced by an increase in temperature of about 8–10 K. The results confirm the applicability of the kinetic model to catalyzed oxidation.

Because of the high value of the constant,  $k_3$ , the fall of dissolved oxygen is quite steep, indicating zero order behavior down to quite small oxygen concentrations.

### Mass transfer enhancements

After the dissolved oxygen concentration decreases to negligible values, the absorption rate continues to increase, producing mass transfer enhancement. Suresh et al. (1988c) showed that all their experimental data on enhancement factors for uncatalyzed oxidation could be brought together by plotting them as a function of the parameter

$$\sqrt{M} = \frac{\sqrt{2D(k_{o1} c_p + k_{o2} c_p^2/c^*)}}{k_L} \quad (3)$$

Figure 4 shows the enhancement factors for the present case, calculated from measured absorption rates during the period when  $c_L$  was zero but rates were increasing (Figure 2). For comparison, a line that represents experimental data for uncatalyzed oxidation in the temperature range 423–433 K (Suresh et al., 1988c) is also shown in Figure 2. With the rate constants calculated above, Figure 4 shows the comparison between present data and that for uncatalyzed oxidation to be good. This further confirms the similarity of overall kinetic features.

### Period of decreasing rates

Following the period of mass-transfer enhancement, the rate of absorption registers a sharp maximum and begins to decrease, finally stabilizing at a value of about  $4 \times 10^{-4} \text{ kmol/m}^3 \cdot \text{s}$ . Simultaneously, small levels of dissolved oxygen concentrations could be detected in the liquid, the dissolved oxygen concentration showing a tendency to oscillate. The final absorption rate achieved, as seen by a comparison with the rate to which the model simulations in the slow reaction regime asymptotes, is only slightly less than the physical mass-transfer rate calculated from the  $k_{L,a}$  in the slow reaction regime and the exit partial

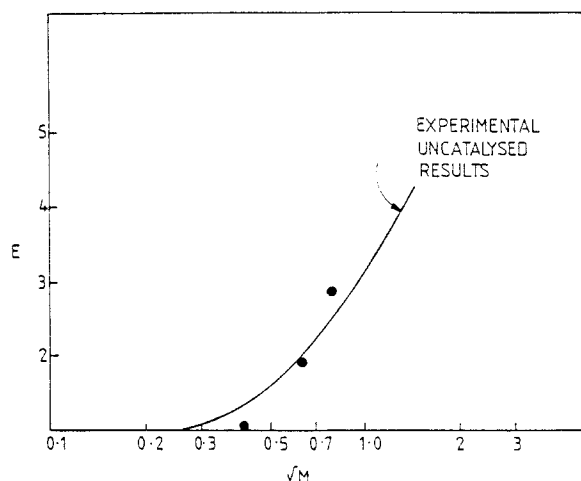


Figure 4. Enhancement factors in catalyzed oxidation.

pressure of oxygen. The small difference can probably be attributed to the small levels of dissolved oxygen in the liquid which decrease the driving force for mass transfer. Both this absorption rate, as well as the oscillations in dissolved oxygen (which, in the uncatalyzed reactions, were typically observed towards the end of the slow reaction regime) suggest that the system reverts back to a diffusional regime after producing enhancements.

This striking behavior seems to indicate a decrease in the kinetic rates at advanced stages of the reaction. Berezin et al. (1966), commenting on studies using cobalt naphthenate catalyst, state that part of the catalyst precipitates out as cobalt adipate due to the formation of adipic acid during the oxidation, and ceases to be effective as a catalyst. Since, at the conversions at which the maximum in the rate curve is observed (about 6%), the secondary stages of the reaction which produce adipic acid are likely to be quite active, it is possible that the catalyst is precipitated out gradually by the adipic acid formed. The catalyst would thus become unavailable at such conversions. This could possibly explain the decrease in kinetic rates.

### Product concentration development

In the method of chemical analysis followed (Suresh et al., 1988b) any hydroperoxide was first quantitatively converted to the alcohol and the total alcohol estimated. Figure 3 shows the development of the concentrations of the intermediates, cyclohexanol (+ cyclohexyl hydroperoxide) and cyclohexanone, with time. Quite in contrast to the results of uncatalyzed oxidation, the concentration of cyclohexanol is seen to be equal to, or higher than that of cyclohexanone, at all conversions. This then suggests that, although the kinetic mechanisms can be considered to be unchanged as far as overall kinetics are concerned, the paths by which individual intermediates form and disappear could well be modified by the presence of the catalyst. Since the presence of the catalyst is known to result in lower levels of

hydroperoxide, such differences in the fine detail of the kinetic mechanism should be expected. The observed differences are also consistent with those reported by Berezin et al., (1966).

The bottom part of Figure 3 compares the experimentally observed total concentration of the intermediates in the slow reaction regime with the predictions of the model, using the rate constants obtained above. It is interesting that, in spite of the differences in the distributions of individual intermediates in the oxidate, their total concentration is predicted extremely well by the model. This shows that, if it is the total concentration of intermediates that one is interested in, the kinetic model can still be used with confidence.

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### Notation

- $a$  = gas-liquid interfacial area,  $m^2/m^3$
- $c_L$  = concentration of dissolved oxygen in bulk liquid,  $kmol/m^3$
- $c_p$  = concentration of total products in the liquid,  $kmol/m^3$
- $c^*$  = concentration of dissolved oxygen at the gas-liquid interface, corresponding to equilibrium at the exit oxygen partial pressure,  $kmol/m^3$
- $D$  = diffusivity of oxygen in cyclohexane,  $m^2/s$
- $E$  = enhancement factor
- $HP$  = cyclohexyl hydroperoxide
- $k_{o1}$  = first rate constant,  $s^{-1}$
- $k_{o2}$  = second rate constant,  $m^3/kmol \cdot s$
- $k_3$  = third rate constant,  $m^3/kmol \cdot s$
- $k_L$  = physical mass-transfer coefficient,  $m/s$
- $M$  = diffusion-reaction parameter defined by Eq. 3
- $OL$  = cyclohexanol
- $ONE$  = cyclohexanone
- $P_o$  = oxygen partial pressure at reactor outlet, under conditions of no absorption, bar
- $R_A$  = rate of oxygen absorption,  $kmol/m^3 \cdot s$
- $r_c$  = kinetic rate of cyclohexane conversion,  $kmol/m^3 \cdot s$
- $r_o$  = kinetic rate of oxygen conversion,  $kmol/m^3 \cdot s$
- $X$  = cyclohexane conversion

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