Rate Oscillations in Cyclohexane Oxidation

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Introduction

In previous studies (Suresh et al., 1988, 1990) on cyclohexane oxidation, the authors described the features of the liquid-phase reaction carried out in a sparged and stirred tank reactor, oxygen, mixed with nitrogen, being used as the oxidizing agent. One feature of the work described was the use of a technique to measure the dissolved oxygen levels during oxidation. Experimental results show that dissolved oxygen levels achieve saturation values at the very beginning, but decrease with time as products build up, due to the autocatalytic nature of the reaction. On several occasions, the authors found dissolved oxygen levels to oscillate when the system approached the diffusional subregime, i.e., the condition of negligible oxygen levels in the liquid bulk. This paper reports briefly on these oscillations, attempts to characterize them and describes some experimental efforts to investigate possible causes.

Liquid phase hydrocarbon oxidations are characterized by quite complex kinetic mechanisms (Emanuel et al., 1967; Berezin et al., 1966) and often exhibit autocatalysis. The overall kinetics are thus nonlinear and incorporate a "feedback" mechanism through the autocatalytic steps. Some evidence of oscillatory phenomena and other exotic forms of behavior in these systems can be gleaned from the literature. Thus, Hobbs et al., (1972) in their work on the liquid phase oxidation of MEK found the system to exhibit certain "critical" conditions. The reaction came to a standstill as the temperature was lowered below a certain value, and could not be restarted until the temperature was increased much beyond this value. Hronec and Ilavsky (1982) reported aperiodic oscillations in the exit oxygen concentrations in the isothermal oxidation of a mixture of a p-xylene and p-toluic acid (catalyzed) and of *n*-Dodecane (uncatalyzed) in an air-sparged reactor. A number of papers (Jensen, 1983; Roelofs et al., 1983; Reimus et al., 1989, 1990) discussed oscillations in the air-oxidation of benzaldehyde under the catalytic influence of CO^{2+}/Br. The oscillations were initially observed as periodic changes in solution color and oxidation potential, but subsequently (Roelofs et al., 1983) were also observed in dissolved oxygen concentrations. The explanations offered invoke the shuttling of the cobalt species between the oxidation states of 2 and 3. In so far as the role of the catalyst is crucial to the explanation offered for the observed oscillations, the mechanism cannot explain oscillations observed in uncatalyzed hydrocarbon oxidations.

Oscillations in Cyclohexane Oxidation: Experimental Observations

Oscillatory phenomena in cyclohexane oxidation were referred to in our earlier papers (Suresh et al., 1988, 1990). Relevant experimental details have been described in Suresh et al., (1988a,b). Dissolved oxygen levels were determined by degassing a sample of the reactor liquid at intervals and analyzing the gases on a gas chromatograph fitted with an electron capture detector. A polarographic oxygen probe was used to monitor oxygen levels in the exhaust gases continuously. The oscillations were observed in semibatch oxidations in both the sparged reactor as well as the flat-interface reactor. The oscillations were quite variable in their frequency and amplitude, which depended on the conditions of the experiment. The discrete nature of the sampling for dissolved oxygen made it difficult to characterize these oscillations in detail, but a few general features could be observed. The oscillations occurred mainly in the region of low dissolved oxygen concentrations as the data for two runs at 430 K were performed under identical conditions, as shown in Figure 1. The oscillations were of the damped type, and ultimately dissolved oxygen levels decreased permanently to zero. The oscillations were more pronounced when the oxygen partial pressure was high; under these conditions their period and amplitude were larger. In the low partial pressure runs, they tended to die out quickly, and the system proceeded into the region of mass transfer enhancements as the values of Hatta number became high enough (Suresh et al., 1988c). The oscillations in the low partial pressure runs were usually observed only in the dissolved oxygen concentrations. The time lags in the gas sampling system were possibly damping out the rapid fluctuations in exit oxygen levels. The large period oscillations of the high partial pressure runs could however be seen in both exit oxygen as well as in dissolved oxygen, as shown in Figure 1.

The oscillations could be induced, after the dissolved oxygen had decreased to zero, by a step increase in the inlet oxygen level. The results of an experiment at 423 K are shown in Figure

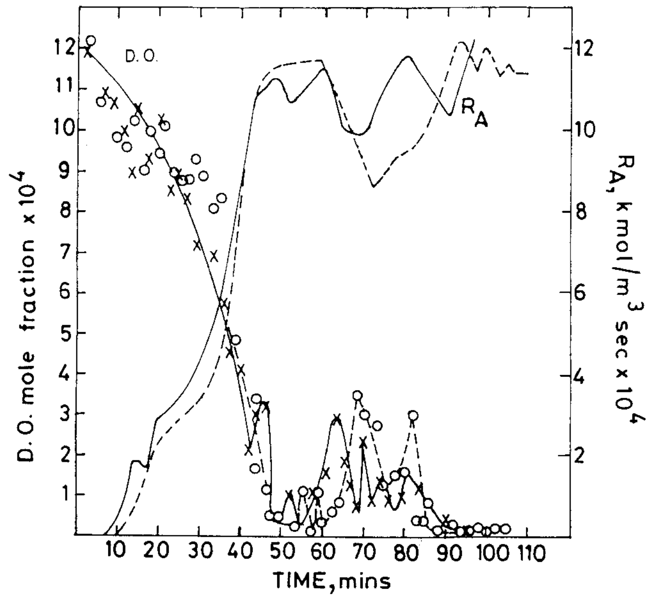

Figure 1. Oscillations in dissolved oxygen concentration in the sparged and stirred reactor in two runs.

Temperature = 430 K, inlet oxygen partial pressure = 0.84 bar, gas superficial velocity through the reactor = 0.018 m/s.

2, in which the oxygen level at the inlet was increased to 6.5% at a time when the dissolved oxygen levels in the bulk of the liquid were reduced to zero, in an experiment with an inlet oxygen level of 1.85%. The result was pronounced oscillations in the dissolved oxygen levels and the rate of absorption. Given the limitations of the monitoring equipment and methods, the oscillations in the absorption rate and dissolved oxygen concentration are seen to be approximately in phase in Figures 1 and 2.

Discussion

A kinetic model for the oxidation of cyclohexane was presented in Suresh et al. (1988b) and shown to be consistent with the experimental data over a range of temperatures and oxygen partial pressures. It can be shown, however, that this model cannot lead to oscillations in dissolved oxygen. This is also borne out by the simulations presented in Suresh et al. (1988b). The model does not contain a detailed description of the radical behavior in the absence of oxygen, since at the present time, there is no data on which such a description can be based.

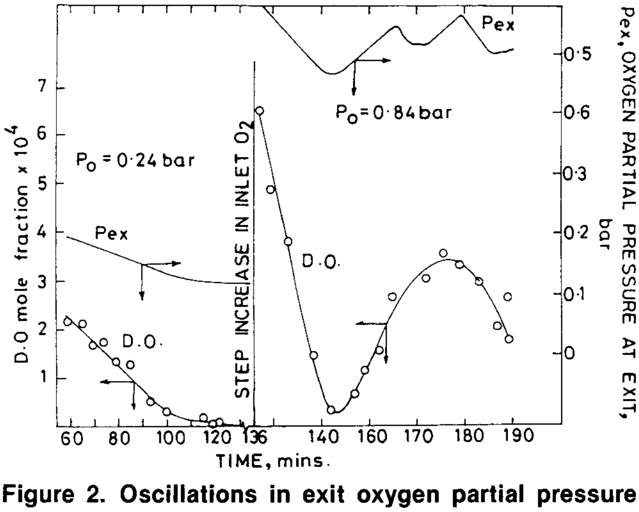

Figure 2. Oscillations in exit oxygen partial pressure and dissolved oxygen concentration induced by a step change in the inlet oxygen.

p_o is the partial pressure of oxygen at inlet.

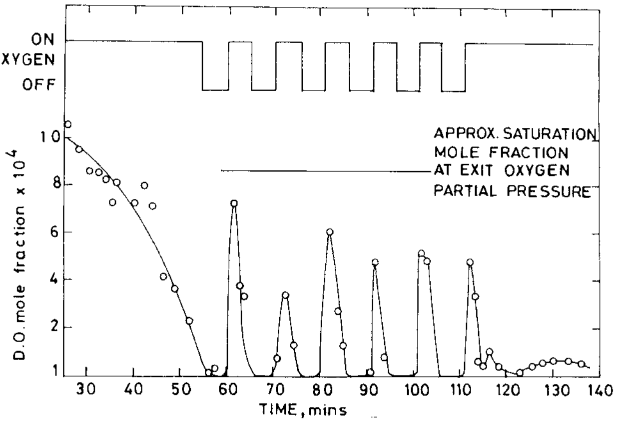

Figure 3. Dissolved oxygen concentration in the oxygen on-off experiment.

Conditions as in Figure 1.

The foregoing information has shown that oscillations are mostly observed under conditions of very low dissolved oxygen concentrations. The reaction which is normally zero order in oxygen would become first order in oxygen as oxygen concentration tends to zero, and hence one has to look to the kinetic mechanisms under oxygen starvation conditions for an explanation of the observed phenomena. One possible scenario is considered in the following paragraphs, and an attempt to verify the hypotheses experimentally is described.

Possibility of a Decrease in the Active Free Radical Concentration

The oxygen on-off experiment

It is known (Suresh et al., 1988b) that the uncatalyzed oxidation of cyclohexane takes some "induction time" to get under way, this being the time required for a concentration of free radicals to build up. The initiation of free radicals in neat cyclohexane requires the participation of oxygen. This induction period, although reduced significantly in the presence of reaction product or impurities that can aid in free radical production, is not totally eliminated even when the cyclohexane is dosed with 5-7% of cyclohexanone, as has been shown by the dosing studies of Suresh et al., (1988b). Since the conversion of cyclohexane at the time these oscillations were observed was of the same order, this opens up the possibility that the existing active free radicals die out quickly (or at least significantly decrease in concentration) when free oxygen is no longer available in the bulk liquid, leading to a decrease in the rate of consumption of oxygen.

To test this hypothesis, an experiment at 430 K was conducted, in which the oxygen into the reactor was alternately stopped and started at intervals of 5 minutes after the dissolved oxygen levels had decreased nearly to zero. The results are shown in Figures 3 and 4. The initial part of the experiment

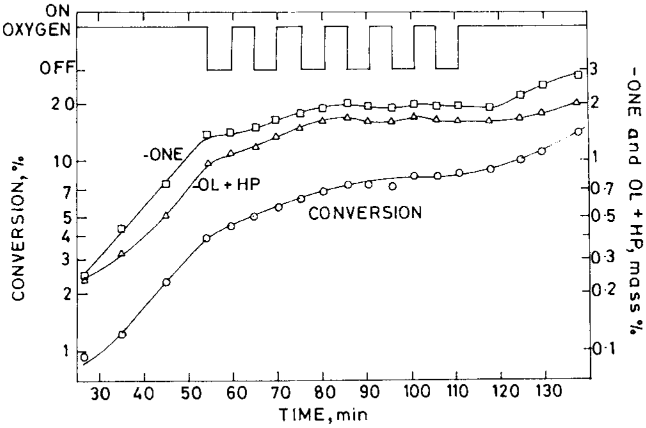

Figure 4. Development of cyclohexanone, cyclohexanol and hydroperoxide concentration in the oxygen on-off experiment.

was a repetition of the runs shown in Figure 1, and the rates of absorption and dissolved oxygen concentration agree quite well with those observed in the previous runs. A stoppage of oxygen for 5 minutes appears to be enough to reduce the active free radical concentration quite considerably, as shown by the fact that the oxygen levels increase almost to saturation on restarting the oxygen and then reduce quickly to zero. These results provide some support for the hypothesis that a reduction in the active free radical concentration is responsible for a reduction in rates when oxygen is totally consumed in the liquid bulk.

The results of chemical analysis from the above experiment are shown in Figure 4. It appears from these data that the conversion of cyclohexane does proceed, albeit slowly, in the periods during which the oxygen supply to the reactor is stopped. The concentrations of the intermediates (cyclohexanone, cyclohexanol and hydroperoxide) also show some variation during such periods. Although these results need further substantiation, they suggest that the process which results in a reduction of the concentration of the active free radicals involves the hydrocarbons in the system. It is thus possible that the radicals do not terminate, but are converted to less active forms by reaction with the hydrocarbons.

The following scenario can therefore be postulated. When dissolved oxygen availability in the liquid is high, the primary radicals obtained from cyclohexane or oxidation products (denoted by R'^* in our previous papers) are converted to their peroxy form ($R'O_2^*$) in a fast step. It is these peroxy radicals that take part in reactions with cyclohexane and its oxidation products, leading to the observed autocatalytic features as described in Suresh et al., (1988b). When oxygen is no longer available in abundance in the dissolved form, the R'^* radicals either terminate rapidly or react with the hydrocarbons in the medium to produce other radicals which are vastly less reactive. In either case reaction rates cannot be sustained at the existing level and dissolved oxygen levels build up in the liquid because of mass transfer from the gas phase. Once oxygen availability increases, the R'^* radicals preferentially react with the oxygen to form the peroxy radicals, and the reactions speed up due to the reactivity of the peroxy radicals. Confirmation of these hypotheses must come from a detailed study of the mechanism of the reaction under conditions of low oxygen availability and by the measurement of the concentrations of specific free radicals through techniques such as electron spin resonance.

Conclusions

This paper describes the oscillations observed in the dissolved oxygen concentrations in the dying stages of the slow reaction regime during cyclohexane oxidation in gas-liquid reactors, and with attempts to elucidate the mechanisms responsible for such behavior. Results of an experiment during which the oxygen supply was intermittently cut off show conclusively that there is a reduction in reactivity of the liquid under conditions of oxygen starvation. Such a decrease in reactivity possibly is brought about by the reactions of the active free radicals under conditions of low oxygen availability, which result in the active free radicals being replaced by less reactive species. Such a mechanism, if proven, would have interesting implications in the context of mass-transfer-limited reactions, since a bubble that is freshly formed under these circumstances sees liquid, the reactivity of which is less than would be expected from its conversion level. A part of the life of the surface element would therefore be used in building up a concentration of the active free radicals. The models of mass transfer (film, penetration) would need modification under such circumstances.

Acknowledgment

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