

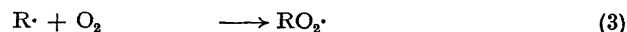
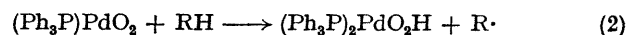
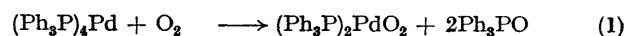
Mechanism of Initiation of Cumene Autoxidation by Palladium(0) Complexes

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Summary Chain initiation in the liquid-phase autoxidation of cumene at 35° catalysed by the palladium(0) complex $(\text{Ph}_3\text{P})_4\text{Pd}$, occurs *via* hydroperoxide decomposition and not *via* an "oxygen activation" mechanism.

HOMOGENEOUS catalysis of hydrocarbon autoxidation by several oxygen complexes of Group VIII metals (Ir, Rh, Pt, Pd) has been reported.¹⁻⁷ Recent investigations^{3,6} have shown that these reactions have the characteristics of radical-chain processes initiated by metal-catalysed hydroperoxide decomposition. However, Stern reported¹ that $(\text{Ph}_3\text{P})_4\text{Pd}$ catalysed the liquid-phase autoxidation of cumene at 35° *via* an oxygen activation mechanism [equations (1)–(4)].



It seemed likely to us that initiation had occurred *via* decomposition of traces of hydroperoxide, although the cumene was described as peroxide-free. To distinguish between these two mechanisms we have made a kinetic study of this reaction. Our results show unequivocally that chain initiation occurred *via* decomposition of the hydroperoxide still present in the cumene. These conclusions are based on the following evidence.

(1) The normal procedure for obtaining hydroperoxide-free samples of cumene (washing with conc. H_2SO_4 and distilling under nitrogen) was shown to be insufficient. Cumene purified by this method exhibited induction periods of less than 10 min under autoxidation conditions (1 atm of oxygen). Subsequent purification by passing the cumene down a column of basic alumina, immediately prior to use, gave samples with induction periods of 1–3 h. Addition of *t*-butyl hydroperoxide (0.01 mol%) to these samples resulted in almost instantaneous oxygen absorption. These results suggest that in the experiment reported by Stern the cumene used still contained traces of hydroperoxide.

(2) If the cumene autoxidation is initiated by radicals formed from hydroperoxide decomposition, there should be a direct relationship between the rates of cumene autoxidation and hydroperoxide decomposition, namely the rate of initiation of the former reaction (R_i) should be equal to the rate of radical production (R_r) in the latter.

$(\text{Ph}_3\text{P})_4\text{Pd}$ was found to catalyse the decomposition of *t*-butyl hydroperoxide in chlorobenzene at 35°.† The rate of oxygen evolution was directly proportional to the catalyst concentration. The rate of radical production (R_r) was measured by the inhibition method,⁸ using Ionol (2,6-di-*t*-butyl-4-methylphenol). That the decomposition involves a normal type of radical-induced hydroperoxide decomposition, like that with, *e.g.*, Co salts, was confirmed by the

chain length of the reaction $[(d\text{O}_2/dt)/R_r]$, which was found to be 10, in agreement with other studies.^{9,10}

For 8×10^{-4} M catalyst concentration and 0.4M-Bu^tOOH we obtained $R_r = 3.5 \times 10^{-9}$ mol ml⁻¹ s⁻¹. This rate was (within experimental error) equal to the rate of initiation, $R_i = 4.5 \times 10^{-9}$ mol ml⁻¹ s⁻¹ of cumene autoxidation at the same catalyst concentration, temperature, and at hydroperoxide concentrations between 0.005 and 0.05M. The values of R_i were calculated from the initial rate of oxygen absorption $\{d\text{O}_2/dt = k_p [\text{cumene}] \sqrt{(R_i/2k_t)}\}$ using the known values¹¹ of k_p and k_t , as well as from the length of the inhibition period ($t_{\text{inh.}}$) brought about by the addition of Ionol to the autoxidizing system ($R_i = 2[\text{Ionol}]/t_{\text{inh.}}$).

In the cumene autoxidation as well as in the hydroperoxide decomposition the rate decreased steadily with time, presumably owing to catalyst deactivation *via* irreversible oxidation of the metal (to Pd^{II}) and/or the phosphine ligands (to the oxide).

The liquid-phase autoxidation of styrene at 35°, in the presence of $(\text{Ph}_3\text{P})_4\text{Pd}$, was also examined because of the possibility of the oxygen complex $(\text{Ph}_3\text{P})_2\text{PdO}_2$ catalysing the autoxidation of olefins by the addition mechanism.¹² However, as with cumene, long induction periods were observed in the absence of added *t*-butyl hydroperoxide.

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† Stern¹ reported that there was no decomposition of cumene hydroperoxide, which was, presumably, concluded from the yield of hydroperoxide. However, for his catalyst concentration (1.7×10^{-4} M) we calculate from our results a chain length of *ca.* 70 in the autoxidation of cumene. Hence we would expect < 2% hydroperoxide decomposition.

¹ E. W. Stern, *Chem. Comm.*, 1970, 736.

² J. P. Collman, M. Kubota, and J. W. Hosking, *J. Amer. Chem. Soc.*, 1967, **89**, 4809.

³ V. P. Kurkov, J. Z. Pasky, and J. B. Lavigne, *J. Amer. Chem. Soc.*, 1968, **90**, 4743.

⁴ J. Blum, H. Rosenman, and E. D. Bergmann, *Tetrahedron Letters*, 1967, 3667.

⁵ A. J. Birch and G. R. S. Subba Rao, *Tetrahedron Letters*, 1968, 2917.

⁶ L. W. Fine, M. Grayson, and V. H. Suggs, *J. Organometallic Chem.*, 1970, 219.

⁷ K. Takao, Y. Fujiwara, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Japan*, 1970, 1153.

⁸ N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, "Liquid Phase Oxidation of Hydrocarbons," English translation, Plenum Press, New York 1967, p. 51.

⁹ R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *J. Org. Chem.*, 1968, **33**, 1421.

¹⁰ R. Hiatt, J. Clipsham, and T. Visser, *Canad. J. Chem.*, 1964, **42**, 2754.

¹¹ D. G. Hendry, *J. Amer. Chem. Soc.*, 1967, **89**, 5433.

¹² Y. Kamiya, *Tetrahedron Letters*, 1968, 4965.