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Catalysis in Liquid-Phase Autoxidation

I. Effect of Polymeric Surfaces

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The catalytic effect of polyethylene, polypropylene, and poly(tetrafluoroethylene) surfaces on the rate of oxidation of tetralin has been studied. Rate measurements were made in the liquid phase using chlorobenzene as a solvent over the range of 65 to 115°C at atmospheric pressure with the polymers in the form of 60/80 mesh powders. All of the polymers were active catalysts for the autoxidation of tetralin. Polyethylene and polypropylene exhibited higher activity than poly(tetrafluoroethylene). The specific activity of polypropylene was approximately 10-fold higher than poly(tetrafluoroethylene) at 90°C. Studies with poly(tetrafluoroethylene) indicated that both the initial reaction rate and length of the induction period were temperature dependent. An Arrhenius plot of the initial rate yielded an apparent activation energy of 17.0 kcal/mole, and an Arrhenius plot of the reciprocal of the induction period yielded a temperature dependency equivalent to 16.7 kcal/mole. A comparison with the literature indicated that at 65°C the polymeric surfaces tested are approximately equivalent in activity to many active metal oxide surfaces.

I. INTRODUCTION

It is well known that dissolved metals homogeneously catalyze the liquid-phase autoxidation of compounds such as hydrocarbons (*1*, *2*). Other studies have shown that insoluble metal oxides heterogeneously catalyze the rate of reaction of hydrocarbons with oxygen in the liquid phase (*3–5*). Because of this known activity, attempts have been made to render metal surfaces quiescent for autoxidative hydrocarbon reactions leading to deposit formation by coating these surfaces with polymetric materials. Studies, however, indicate that rather than suppressing autoxidative hydrocarbon deposit formation, polymer coatings increased their rate of formation, suggesting that polymeric surfaces function as a catalyst for autoxidative reactions (*6*). Similarly, Emanuel has reported that coating the wall of a reactor with poly(tetrafluoroethylene) accelerated the rate of liquid-phase autoxidation of propene compared with results obtained in a steel or glass reactor (*7*). To further elucidate these effects, we carried out a study of the catalytic influence of various polymeric surfaces on the liquid-phase autoxidation of a typical hydrocarbon. Tetralin was chosen as a model compound for this study. Because of the importance of specific reaction rate, i.e., rate per unit area of catalyst, in studies of this nature (*8–10*), the specific activity of polypropylene and poly(tetrafluoroethylene) are also compared.

II. EXPERIMENTAL

A. Apparatus and Procedure

A conventional liquid-phase autoxidation apparatus was used (*11*). The reactor was a 25-ml Pyrex long-necked flask with a side arm. The reactor was immersed in a temperature bath controlled to ±0.5°C and attached to a vibrator. Mass transfer limitations were minimized by vibrating the reactor at a speed of 800 cycle/min. Experiments demonstrated that the rate of oxidation was independent of vibration speed at this level. In each run 2.0 ml of tetralin, 2.0 ml of chlorobenzene, and 0.30 g of catalyst were charged to the reactor, hooked into the reaction system and the reactants were degassed by freezing with liquid N_2, evacuation, thawing, refreezing, and re-evacuation. The reactor was then filled with O_2 and immersed in the temperature controlled bath. Oxygen uptake measurements were made at a constant pressure of 1 atm. Aliquot samples for analysis during the run were removed via a syringe through a septum cap attached to a side arm on the reactor. Tetralin conversion was measured using an F&M model 500 temperature programmed gas chromatograph with a 2-ft column containing 10% QF-1 (fluoronated silicone oil) on 45/60 mesh chromosorb W. The column was programmed from 50 to 175°C at 7.9°C/min. The tetralin hydroperoxide content was determined chemically by the method of Wagner *et al.* (*12*). Oxygen uptake, tetralin conversion, and tetralin hydroperoxide content data all confirmed that the initial oxidation product is tetralin hydroperoxide.

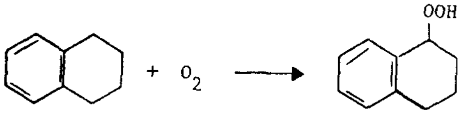
B. Reagents

Tetralin (Matheson, Coleman and Bell, practical grade) was purified by washing with concentrated sulfuric acid until the washings were colorless, followed by washing with distilled water to remove residual acidity and drying with anhydrous $MgSO_4$ (*13*). The resulting tetralin was then repeatedly distilled in a spinning band column until a fraction was obtained which showed no impurities by glpc analyses. Glpc-pure chlorobenzene (Matheson, Coleman and Bell) was employed.

The polymer catalysts were all prepared as 60/80 mesh powders by cooling with liquid N_2, grinding in a Waring blender, sieving, and washing with a solvent. Methylene chloride was used with poly (tetrafluoroethylene) and acetone with polyethylene and polypropylene. All inspections were obtained on the prepared powder. The poly(tetrafluoroethylene) was obtained from E. I. duPont de Nemours & Company, Wilmington, Delaware. Powdered catalysts were prepared from both molded samples and from Teflon 7 granular resin which was pressed at 24,000 psi prior to starting the normal preparative procedure. Tests indicated that the resultant 60/80 mesh poly(tetrafluoroethylene) powders were essentially equivalent in activity. The polypropylene was obtained from the Enjay Chemical Company, Linden, N. J., in an extruded form. The polyethylene was obtained from Ace Scientific Co., Linden, N. J., in an extruded form.

III. Results

Polymer surfaces tested for their catalytic activity, included poly(tetrafluoroethylene), polyethylene, and polypropylene. All were tested as 60/80 mesh powders prepared as described in the experimental section. Detailed inspections of these powders are shown in Table 1. It can be seen that metal impurity levels are quite low. Rate measurements were made over the range of 65 to 115°C at atmospheric pressure using chlorobenzene as a solvent. Quantitative analyses confirmed that the initial oxidation product is tetralin hydroperoxide.



(1)

Data for the oxidation of tetralin at 90°C in the presence of both polypropylene and poly(tetrafluoroethylene) are shown in Fig. 1. Data obtained at 65°C in the presence of polyethylene and poly(tetrafluoroethylene) and for the uncatalyzed oxidation of tetralin are shown in Fig. 2. As shown in Fig. 2, the presence of the various polymeric surfaces markedly changed the rate of oxidation of tetralin, as manifested both by a dramatic reduction in the induction period and by the actual rate of oxygen consumption. For the poly (tetrafluoroethylene)-catalyzed reaction the maximum rate measured occurred initially after the induction period, whereas when polypropylene was employed the rate

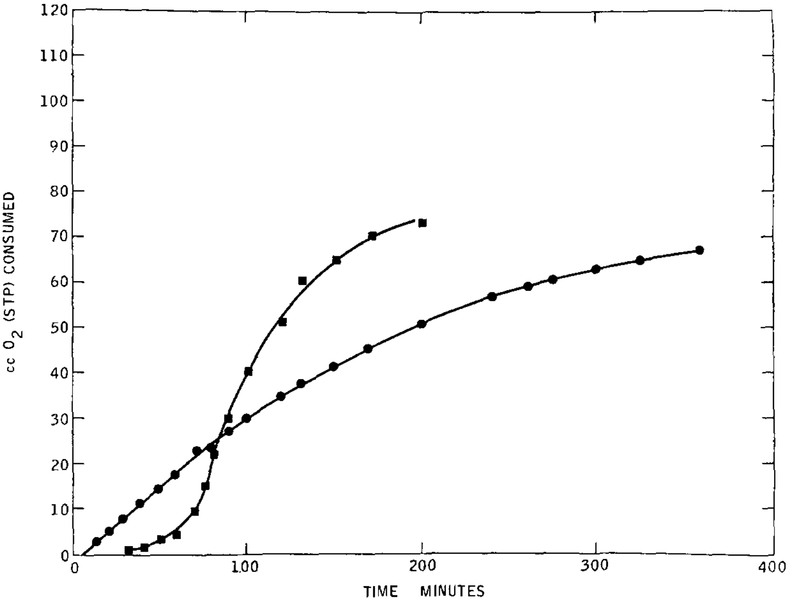


Fig. 1. Oxidation of tetralin at 90°C: ■, polypropylene catalyst; ●, poly(tetrafluoroethylene) catalyst. A 2-ml sample of tetralin was employed.

continued to increase with time before it finally began to level off.

In general, the rate of oxidation tended to decrease during the later part of the runs. Part of this decrease undoubtedly reflects the effect of decreased tetralin concentration on the rate; however, catalyst deactivation may also contribute to this.

Data on the effect of temperature on the initial rate of oxidation of tetralin in the presence of poly(tetrafluoroethylene) over the range of 65–115°C are shown in Fig. 3. The apparent activation energy derived from this Arrhenius plot is 17.0

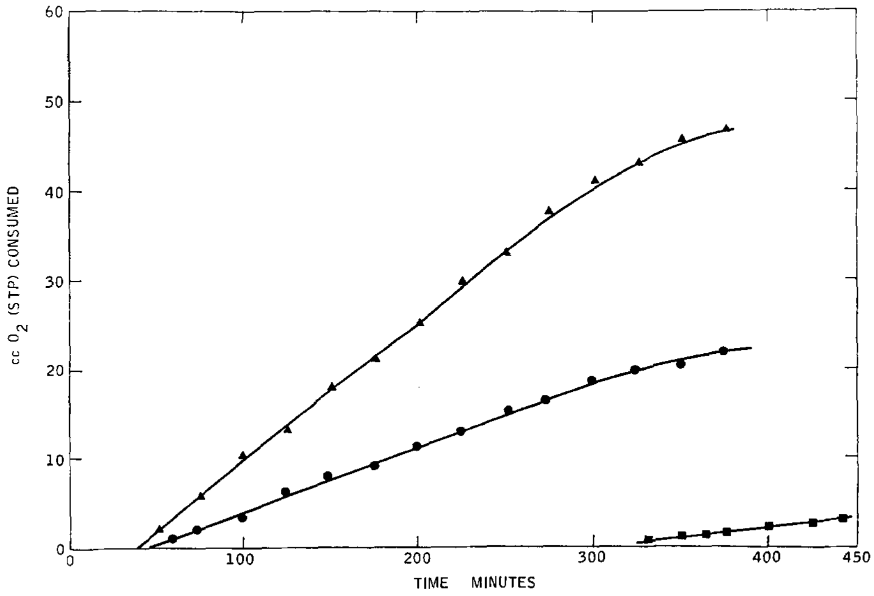


Fig. 2. Oxidation of tetralin at 65°C: ▲, polyethylene catalyst; ●, poly(tetrafluoroethylene) catalyst; ■, no catalyst. A 2-ml sample of tetralin was employed.

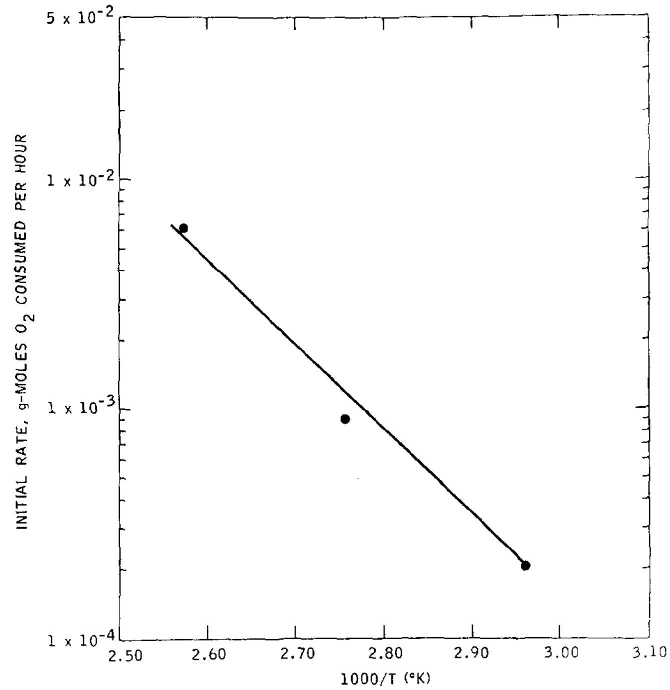


FIG. 3. The effect of temperature on the initial rate of oxidation of tetralin in the presence of poly(tetrafluoroethylene) catalyst. A 2-ml sample of tetralin was employed.

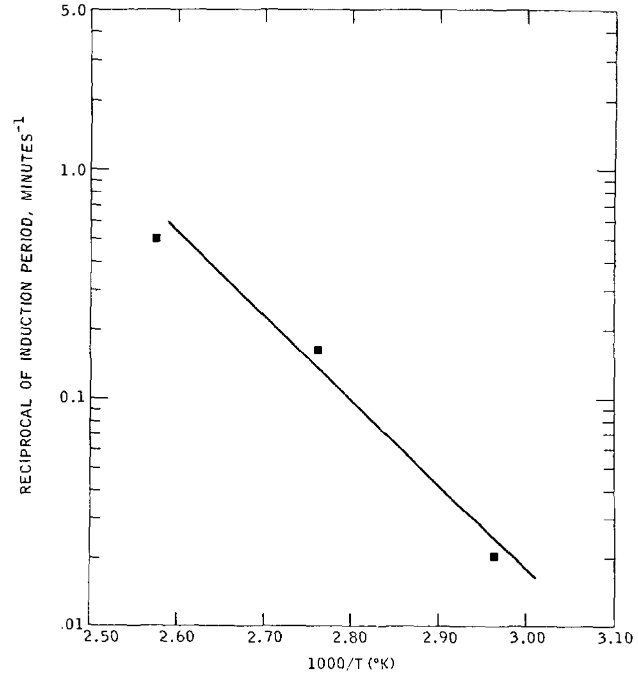


FIG. 4. Arrhenius plot of the reciprocal of the induction period as a function of temperature for tetralin oxidation in the presence of a poly(tetrafluoroethylene) catalyst.

TABLE 1
SUMMARY OF POLYMER CATALYST ACTIVITY AND INSPECTIONS

	Poly (tetrafluoroethylene)	Polyethylene	Polypropylene
Initial activity (g-moles of O_2/hr g of polymer per ml of tetralin)			
115°C	10.4×10^{-3}[a]	—	—
90°C	14.9×10^{-4}[a]	—	44.7×10^{-4}[b]
65°C	3.38×10^{-4}[a]	7.59×10^{-4}[a]	—
BET Surface area (m^2/g)	0.69	—	0.21
Specific activity (g-moles of O_2/hr per ml of tetralin per m^2 of polymer)			
115°C	1.51×10^{-2}[a]	—	—
90°C	2.16×10^{-3}[a]	—	21.3×10^{-3}[b]
65°C	4.90×10^{-4}[a]	—	—
Ash Content (wt %)	0.010 @ 800°C	0.080 @ 550°C	0.082 @ 550°C
Metal components of ash by emission spectra:			
Major	—	Si	Ca
Minor	—	Mg, Fe	Al
Trace	Si, Mg, Fe, Cu, Ag, Na, Zn, Ti, Ni, Ca, Al	Na, Cu, Al, Ca, Cr	Ti, Fe, Si, Mg

[a] Rate of oxidation immediately following induction period. Other conditions: 2 ml tetralin in 2 ml of chlorobenzene with 0.30 g of catalyst.

[b] Maximum rate which occurred during first minutes after induction period.

kcal/mole. The induction period for the poly(tetrafluoroethylene) catalyzed oxidation of tetralin decreased as the reaction temperature increased. In Fig. 4, an Arrhenius plot is shown of the reciprocal of the induction period observed with the poly(tetrafluoroethylene) catalyzed oxidation of tetralin. Each induction period shown is the average of at least three separate experimental determinations. The apparent activation energy derived from this plot is 16.7 kcal/mole. In Table 1 the specific activity, i.e., the rate per unit area, is tabulated for the various polymers employed. These values were obtained by dividing the initial rate of oxidation per gram of catalyst by the total surface area of the polymer powder per gram of polymer. As shown, the specific activity of polypropylene is higher than that of poly(tetrafluoroethylene) at 90°C by a factor of approximately 10.

IV. DISCUSSION

The autoxidation of tetralin has been studied extensively including uncatalyzed studies (*14–16*), homogeneously catalyzed studies (*17–21*), and heterogeneously catalyzed studies with metal oxides (*13*, *22*). For the heterogeneous metal oxide catalyzed oxidation of tetralin, apparent activation energies ranging from 9 to 10 kcal/mole were reported (*13*), compared with 17.0 kcal/mole found for poly(tetrafluoroethylene) in the present study. The activation energy for the thermal initiation reaction was measured during the oxidation of tetralin in the presence of an inhibitor and was reported to be 23.0 kcal/mole (*16*). Apparent activation energies from this range down to 13 kcal/mole have been reported for the homogeneously catalyzed oxidation (*20*, *21*). Mukherjee (*13*) presents extensive data at 65°C for the heterogeneous catalyzed oxidation of both pure tetralin and tetralin in chlorobenzene. A very striking and complex effect of the amount of catalyst on the rate of oxidation is also reported, i.e., a critical catalyst concentration above which the rate is inhibited which is dependent on the concentration of tetralin in chlorobenzene (*13*). A comparison at 65°C and otherwise identical conditions (3.7 moles/liter tetralin in chlorobenzene, 6.7 ml of tetralin/g of catalyst) indicates that the most active catalyst in this work [Fig. 2 in Ref. (*13*)], i.e., Mn_2O_3, is approximated 10 times more active than poly(tetrafluoroethylene) and 5 times more active than polyethylene. The other metal oxide catalysts were less active than Mn_2O_3 at 65°C by a factor of from 3 to 6 [Fig. 1 in Ref. (*13*), comparison of catalysts at a tetralin to catalyst ratio of 6.7 ml/g]. Thus polymer catalysts are comparable to these less active metal oxide catalysts, e.g., PbS, NiO, at 65°C.

Because of the higher apparent activation energy of poly(tetrafluoroethylene) as compared to the metal oxides studied (i.e., 17 versus 9 kcal/mole), a comparison at temperatures higher than 65°C would be more favorable to this polymer. In view of this, it is difficult to see how the activity of these polymeric materials could result from the trace levels of metallic impurities present (Table 1). In addition, it should be pointed out that no surface areas are reported for the metal oxide catalysts, so that specific activities cannot be compared.

A number of studies have indicated that hydrocarbons will adsorb on low surface energy solids such as poly(tetrafluoroethylene) and polypropylene. Included in these adsorption studies are ethane on polypropylene (*23*); ethane, *n*-butane, and *n*-octane on poly(tetrafluorethylene) (*24*); and *n*-hexane and benzene on poly(tetrafluorethylene) (*25*). A consideration of isosteric heats of adsorption as a function of surface coverage led Graham (*23*, *24*) to conclude that both polypropylene and poly(tetrafluoroethylene) surfaces are highly heterogeneous. Such a conclusion is certainly consistent with the ability of such surfaces to catalyze the autoxidation of tetralin. Graham (*23*) has also pointed out that poly(tetrafluoroethylene) is a lower surface energy solid than polypropylene. The observed higher specific activity of polypropylene relative to poly(tetrafluoroethylene) could reflect this difference in surface energy between these solids.

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REFERENCES

1. DENISOV, E. T., AND EMANUEL, N. M., *Russ. Chem. Rev.* **29,** 645 (1960).

2. URI, N., *in* "Autoxidation and Antioxidants" (W. O. Lundberg, ed.), Vol. 1. Wiley, New York, 1961.

3. BURGER, J., MEYER, C., AND BALACEANU, J. C., *Compt. Rend.* **252,** 2235 (1961).

4. IOFFE, I. I., KLIMOVA, N. V., AND MOKROUSOVA, I. Y., *Dokl. Akad. Nauk. SSSR* **169,** 389 (1966).

5. KLIMOVA, N. V., AND IOFFE, I. I., *Kinetika i Kataliz* **8,** 565 (1967).

6. TAYLOR, W. F., *J. Appl. Chem. (London),* **19,** 222 (1969).

7. EMANUEL, N. M., *World Petrol. Congr. Preprints, 7th, Mexico City, 1967.*

8. YATES, D. J. C., TAYLOR, W. F., AND SINFELT, J. H., *J. Am. Chem. Soc.* **86,** 2996 (1964).

9. SINFELT, J. H., TAYLOR, W. F., AND YATES, D. J. C., *J. Phys. Chem.* **69,** 95 (1965).

10. TAYLOR, W. F., *J. Catalysis* **9,** 99 (1967).

11. BOLLAND, J. L., *Proc. Roy. Soc. (London) Ser.* **A186,** 220 (1946).

12. WAGNER, C. D., SMITH, R. H., AND PETERS, E. D., *Anal. Chem.* **19,** 976 (1947).

13. MUKHERJEE, A., AND GRAYDON, W. F., *J. Phys. Chem.* **71,** 4232 (1967).

14. GEORGE, P., AND ROBERTSON, A., *Proc. Roy. Soc. (London) Ser.* **A185,** 309 (1946).

15. ROBERTSON, A., AND WATERS, W. A., *J. Chem. Soc.* **1948,** 1574.

16. CARLSON, D. J., AND ROBB, J. C., *Trans. Faraday Soc.* **62,** 3403 (1966).

17. KAMIYA, Y., BEATON, S., LAFORTUNE, A., AND

INGOLD, K. U., *Can. J. Chem.* **41,** 2020 (1963).

18. KAMIYA, Y., BEATON, S., LAFORTUNE, A., AND INGOLD, K. U., *Can. J. Chem.* **41,** 2034 (1963).

19. KAMIYA, Y., AND INGOLD, K. U., *Can. J. Chem.* **42,** 1027 (1964).

20. KAMIYA, Y., AND INGOLD, K. U., *Can. J. Chem.* **42,** 2424 (1964).

21. WOODWARD, A. E., AND MESROBIAN, J., *Am. Chem. Soc.* **75,** 6189 (1953).

22. GEORGE, P., *Trans. Faraday Soc.* **42,** 210 (1946).

23. GRAHAM, D. P., *J. Phys. Chem.* **68,** 2788 (1964).

24. GRAHAM, D. P., *J. Phys. Chem.* **69,** 4387 (1965).

25. KISELEV, A. V., AND SERKOBOV, M. V., *Kolloidn. Zh.* **25,** 543 (1963).