

Mechanism of Polyethylene Oxidation

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Synopsis

Acetic and formic acids and acetone are products of the oxidation of propylene and ethylene polymers and copolymers. The two- and three-carbon products can be accounted for as the result of intramolecular attack by radicals, leading to β -oxidation. A high proportion of scissions in polypropylene involves multiple intramolecular attack.

This paper reports some observations pertinent to the mechanism of oxidation of polyethylene and polypropylene. A number of previous investigations have dealt with other aspects of the oxidation process, including effects of temperature, crystallinity, and other external conditions.¹⁻¹⁸

Oxidation of low molecular weight hydrocarbons, which might be considered suitable models for polyethylene and polypropylene^{19,20} leads to complex mixtures of products. Sandler and Beech²¹ reported at least 29 peaks in the chromatogram of the product mixture from the oxidation of pentane. Boord²² lists fourteen products of the oxidation of hexane, and others have been identified. Well over forty peaks have been observed in the chromatogram of oxidation products of a C₃₂ hydrocarbon in these laboratories. On the other hand, known volatile products of polyethylene oxidation are limited in number. Burgess²³ reported as probable products of photooxidation acetone, acetaldehyde, "oxides of carbon," and water. Beachell and Nemphos⁶ observed formaldehyde and, at temperatures where cracking might be important, methane and ethylene in the vapor phase. Others have reported carbon monoxide and carbon dioxide to be products.

We have examined gas chromatograms of product mixtures from oxidation of a number of ethylene and propylene polymers and copolymers and found simple mixtures of volatile products, in keeping with earlier observations.

The only compounds identified additional to those reported previously are formic and acetic acids, which are produced in fairly high yields, shown in Figure 1. The observed acid yields depended on temperature and crystallinity of the samples.

The yields of the two acids are approximately equal, independently of the amount of branching of the parent hydrocarbon. Liquid-liquid chromatograms illustrating this are shown in Figure 2.

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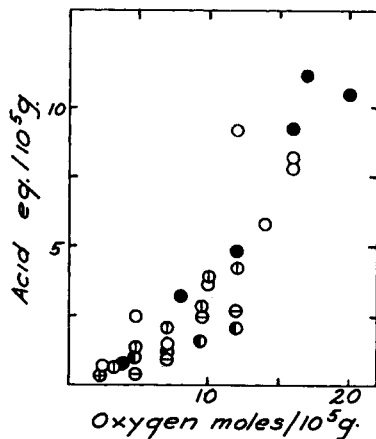


Fig. 1. Acid yields from ethylene and propylene polymers: (⊕) DYNK, oxidation at 150°C.; (⊖) Fiber B, oxidation at 150°C.; (○) EPR oxidation at 140, 150°C.; (●) atactic polypropylene, oxidation at 120°C.; (◐) Profax, oxidation at 150°C.;

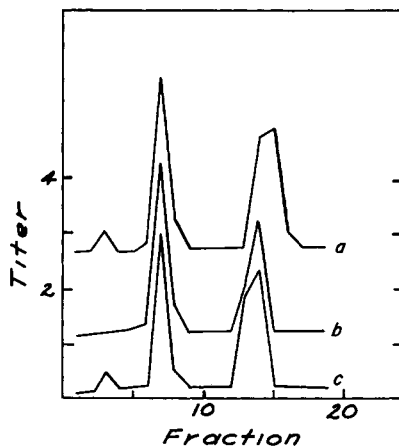


Fig. 2. Fractionation of acid mixtures from ethylene and propylene polymers: (a) polypropylene (atactic); (b) EPR (50/50); (c) polyethylene (DYNK). Peak at fraction 7-8 acetic acid, at 13-14 formic acid.

The high molecular weight of the polymer is the reason for the small number of products observed; products of a single chain scission are not sufficiently volatile to escape from the sample and so are not observed. The products isolated are formed as a result of two breaks in the hydrocarbon chain. If random attack were responsible for their formation, it would be expected that products having four or more carbon atoms would be found as well as those having one to three. If formed at all, compounds with four or more carbon atoms in the chain are much less abundant than those with one or two carbons (Fig. 3). It seems probable then that a special process not requiring two separate attacks on the hydrocarbon

chain is responsible for formation of the observed products; the nonvolatility of the polymer makes the products obvious. With low molecular weight models the creation of new endgroups is not as obvious.

Besides acetic and formic acids (and the corresponding aldehydes) the principal product is acetone. This is found in higher yield from polypropylene but is still readily detected as a product of oxidation of polymethylene, as seen in Figure 3.

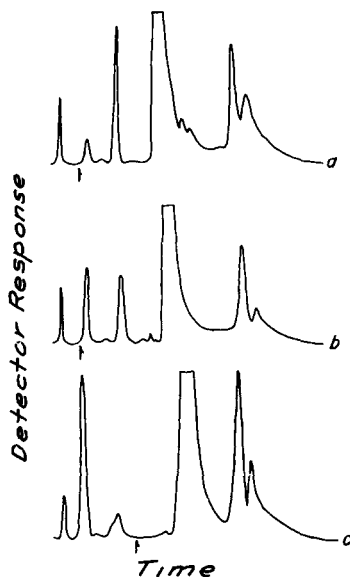
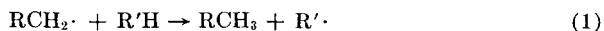
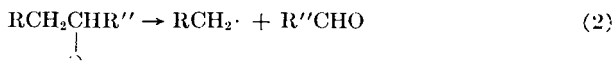


Fig. 3. Gas chromatograms of volatile products: (a) polypropylene; (b) EPR; (c) polymethylene. Temperature 50°C. to tick then at 3.3°C./min. to 165°C. Major peaks air, acetaldehyde, acetone, water, acetic acid, formic acid. The acetone peak from polymethylene contains another (unidentified) constituent.

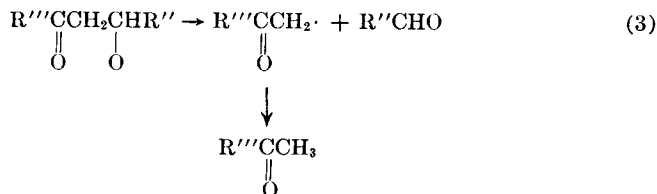
It is therefore necessary to account for two things: the creation of methyl groups from a polymethylene chain and the appearance of one-, two-, and three-carbon fragments. These can be accounted for in terms of mechanisms already established from work with low molecular weight compounds. Methyl groups are formed by reaction of methylene radicals with the hydrocarbon as indicated by George and Walsh:²⁴



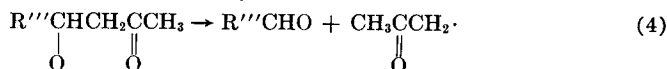
the methylene radical arising by decomposition of a secondary alkoxy radical:



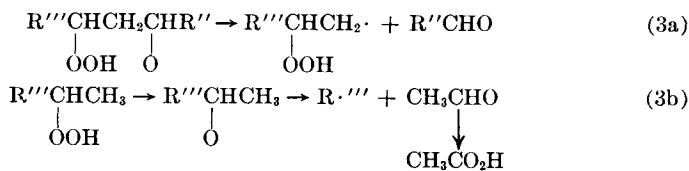
But in our case, R contains a carbonyl function ($R''CO$) so that the reaction is



In the case of acetone this is followed by

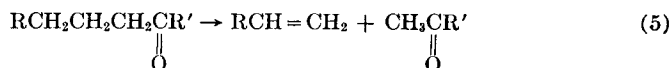


which finally becomes acetone. To form acetic acid, R''' in eq. (3) must be OH, or else the carbonyl group is formed in a second step:



In order for either of these sequences of reactions to occur, two carbon atoms β to each other must be oxidized. To form acetone, a five-carbon chain with three oxidized carbon atoms must exist.

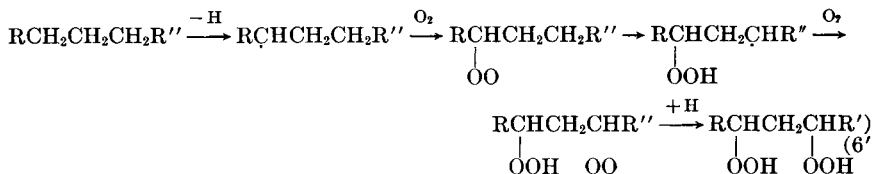
(It may be noted here that the formation of acetone in thermal oxidation and in photooxidation proceeds by two different mechanisms. Burgess²³ attributes creation of a methyl group during photooxidation to a decomposition



in which a terminal double bond is created as well. The infrared spectrum of polyethylene after oxidation is consistent with this process in photooxidation but not in thermal oxidation. There is no increase in unsaturation during thermal oxidation,¹ whereas vinyl unsaturation increases during photooxidation,¹ paralleling the increase in carbonyl groups.²³)

In order for two or more nearby, but not adjacent, carbon atoms to be oxidized after a single initial attack by a free radical, intramolecular reaction must occur. Evidence for intramolecular reaction already exists for low molecular weight analogs of polypropylene and polyethylene. Rust²⁵ has shown that compounds containing suitably located tertiary carbon atoms can be oxidized to give high yields of products of multiple attack. Highest yields are obtained when two tertiary atoms are separated by a single atom (β attack), next highest when two atoms intervene (γ attack). Poor yields of products of multiple attack were obtained when the tertiary atoms were adjacent or were separated by more than two carbon atoms in a row.

Barusch and co-workers²⁶ showed that 1,3-diketones are important products of oxidation of straight chain hydrocarbons. The mechanism they suggest also accounts for Rust's results. It requires that oxidation proceed down the chain, skipping every other carbon atom:



Applying this mechanism to polymethylene (and to polypropylene) we see that it predicts the formation of the intermediates required for methylene radicals and to acetyl endgroups.

Although reaction (6) is written as though the stable peroxide is the first product, in line with Rust's results, scission may not necessarily involve a stable intermediate. Alkoxy radicals required for scission according to eqs. (3) and (4) can be formed by decomposition of the hydroperoxide:



or



They can also be formed by interaction of two peroxy radicals



This reaction has been demonstrated only for tertiary radicals²⁷ and may not occur in the oxidation of polyethylene. Secondary peroxy radicals are considered to interact without scission:



as has been demonstrated for ethylbenzene.²⁸

Estimates of the relative frequency of inter- and intramolecular radical attack have not yet been obtained for polyethylene, partly because of difficulty with crosslinking, but an idea can be obtained from some results with a crystalline polypropylene. Results are given in Table I. Molecular weights were estimated from solution viscosities in tetralin at 135°C. with the use of the equation of Moraglio.²⁹ Acids were determined by titration with 0.02*N* NaOH and terminal acetyl groups by the iodoform reaction.³⁰

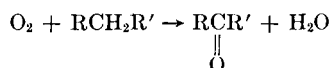
From the data of Table I scission efficiency is ~ 0.10 , total acid yield ~ 0.02 , and total methyl ketone ~ 0.007 . From Figure 3 the acetyl group analysis is estimated to represent about 90% acetone and 10% acetaldehyde. Since scission yield should be calculated from number-average molecular weight rather than viscosity-average molecular weight, there is an uncertainty of a factor of about two in this figure. Comparison of the data of Table I with the other values plotted in Figure 1 indicates that the acid yields may also be somewhat underestimated. We can conclude that not less than 15% and (considering the data in Figure 1) possibly as

TABLE I
 Oxidation of Polypropylene (Profax)

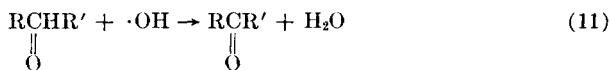
Oxygen, moles/10 ⁴ g.	[η], dl./g.	Scissions (calc.), moles/10 ⁴ g.	Acid, meq./10 ⁵ g.	"Methyl ketone," moles/10 ⁵ g.
0	1.55	—	—	
1.2	0.44	0.26	0.47	
2.4	0.24	0.59	0.62	
3.6	0.35	0.34	—	
4.8	0.29	0.46	1.09	
6.0	0.23	0.65	—	
7.2	0.27	0.50	1.11	
8.4	0.17	1.00	—	
9.6	0.17	1.00	2.60	
10.8	0.17	1.00	—	
12.0	0.21	0.74	2.04	
2.0				0.21
4.0				0.19
6.0				0.31
8.0				0.46
10.0				0.55
12.0				0.62

much as 50% of the main chain breaks involve intramolecular attack; the ratio of second stage to first stage attack is of the order of 1:3.

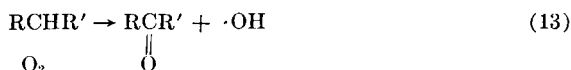
The last major volatile product of polyethylene oxidation is water, which is produced in highest yield. All the water required to balance scission reactions is insufficient to account for the amount found. This is additional evidence that reactions occur of the overall form



Water probably arises from more than one reaction. A number have been written speculatively, but there is no experimental basis for a choice. The most probable is a series of elementary reactions.



and possibly



The reaction scheme as outlined does not specifically account for the high yield of formic acid. Further study will be necessary to determine if the ratio of acid yields is fortuitous or a consequence of the reaction mechanism.

Experimental

Olefin polymers were all commercial materials except experimental samples of atactic polypropylene (National Lead Company) and of EPR (U. S. Rubber Company). Other samples included polypropylene Profax 6511 (Hercules), polyethylenes DYNK (Bakelite), and Fiber B (Carbide and Carbon). Samples were extracted with acetone at room temperature before oxidation.

Fibers were wound on glass forms, other polymers deposited on glass from solution. Oxidation was in a gas-circulating apparatus described previously.³¹ Oxygen at 1 atm. was used. The temperature was 120–150°C., the higher temperature being used for crystalline polymers.

Liquid-liquid chromatograms of acids were made essentially by the procedure of Bulen, Varner, and Burrell.³² The stationary phase was 0.5*N* sulfuric acid on silicic acid; the moving phase 5% tert-amyl alcohol in chloroform. Samples of approximately 0.1 meq. were fractionated.

Gas chromatography was carried out with an F&M Model 202B gas chromatograph. The liquid phase was cyanoethylated glycerol. It was supported on five times its weight of acid-washed Chromosorb W (Johns-Manville). Column were coiled from 10 ft. lengths of 1/4 in. o.d. copper tubing. Helium flow was 30 ml./min., inlet gas pressure 30 lb./in.², outlet pressure atmospheric. Programming was as indicated.

Acetaldehyde and acetone were identified by retention time and preparation of 2,4-dinitrophenylhydrazones. Acids were identified by retention time as well as by liquid chromatography. Water was identified by retention time.

References

1. Cross, L. H., and R. B. Richards, and H. A. Willis, *Discussions Faraday Soc.*, **9**, 235 (1950).
2. Myers, C. S., *Ind. Eng. Chem.*, **44**, 1095 (1952).
3. Biggs, B. S., in *Polymer Degradation Mechanisms*, NBS Circ. 525, Nov. 16, 1953 p. 137.
4. Rugg, F. M., J. J. Smith, and R. C. Bacon, *J. Polymer Sci.*, **13**, 535 (1954).
5. Wilson, J. E., *Ind. Eng. Chem.*, **47**, 2201 (1955).
6. Beachell, H. C., and S. P. Nemphos, *J. Polymer Sci.*, **21**, 113 (1956).
7. Hawkins, W. L., W. Matreyek, and F. H. Winslow, *J. Polymer Sci.*, **41**, 1 (1959).
8. Bobalek, E. G., J. N. Henderson, T. T. Serafini, and J. R. Shelton, *J. Appl. Polymer Sci.*, **2**, 210 (1959).
9. Baum, B., *J. Appl. Polymer Sci.*, **2**, 281 (1959).
10. Burnett, J. D., *Ind. Chim. Belge (Suppl.)*, **24**, 319 (1959).
11. Van Schooten, J., *J. Appl. Polymer Sci.*, **4**, 122 (1960).
12. Luongo, J. P., *J. Polymer Sci.*, **42**, 139 (1960).
13. Grafmuller, F., and E. Huseman, *Makromol. Chem.*, **40**, 161, 172 (1960).
14. Alter, H., *Ind. Eng. Chem.*, **52**, 121 (1960).
15. Meltzer, T. H., J. J. Kelley, and R. N. Goldney, *J. Appl. Polymer Sci.*, **3**, 84 (1960).
16. Beachell, H. G., and G. W. Taret, *J. Polymer Sci.*, **45**, 451 (1960).
17. Winslow, F. H., W. L. Hawkins, and W. Matreyek, *Am. Chem. Soc. Div. Polymer Chem. Preprints*, **2**, 186 (1961).

18. Notley, N. T., *Trans. Faraday Soc.*, **58**, 66 (1962).
19. Roedel, M. J., *J. Am. Chem. Soc.*, **75**, 6110 (1953); A. H. Willbourn, *J. Polymer Sci.*, **34**, 569 (1959); D. A. Boyle, W. Simpson, and J. D. Waldron, *Polymer*, **2**, 323, 325 (1961).
20. Smith, D. C., *Ind. Eng. Chem.*, **48**, 1161 (1956).
21. Sandler, S., and J. A. Beech, *Can. J. Chem.*, **38**, 1455 (1960).
22. Boord, C. E., "Mechanism of the Oxidation of Hydrocarbons," Final Report Contract AF18(600)-787, AFOSR-TR58-82, April 1958, p. 93.
23. Burgess, A. R., in *Polymer Degradation Mechanisms*, NBS Circ. 525, Nov. 16, 1953, p. 149.
24. George, P., and A. D. Walsh, *Trans. Faraday Soc.*, **42**, 94 (1946).
25. Rust, F. F., *J. Am. Chem. Soc.*, **79**, 4000 (1957).
26. Barusch, M. R., H. W. Crandall, J. Q. Payne, and J. R. Thomas, *Ind. Eng. Chem.*, **43**, 2764 (1951).
27. Blanchard, H. S., *J. Am. Chem. Soc.*, **81**, 4548 (1959); T. G. Traylor and P. D. Bartlett, *Tetrahedron Letters*, **1960**, 30.
28. Russell, G. A., *J. Am. Chem. Soc.*, **79**, 3871 (1957).
29. Moraglio, G., *Chim. Ind. (Milan)*, **41**, 879 (1959).
30. Dal Nogare, S., T. O. Norris, and J. Mitchell, Jr., *Anal. Chem.*, **23**, 1473 (1951).
31. Bevilacqua, E. M., *J. Am. Chem. Soc.*, **79**, 2915 (1957).
32. Bulen, W. A., J. E. Varner, and R. C. Burrell, *Anal. Chem.*, **24**, 187 (1952).

Résumé

L'acide acétique, l'acide formique et l'acétone sont des produits de l'oxydation des polymères et des copolymères de propylène et d'éthylène. Les produits à deux et trois carbones peuvent être expliqués comme étant le résultat de l'attaque intramoléculaire par des radicaux, conduisant à l'oxydation en β . Un nombre élevé de scissions dans le polypropylène implique de nombreuses attaques intramoléculaires.

Zusammenfassung

Eisigsäure, Ameisensäure und Aceton treten bei der Oxydation von Propylen- und Äthylenpolymeren und -copolymeren als Produkte auf. Die C_2 - und C_3 -Produkte entstehen durch einen intramolekularen Angriff von Radikalen, der zur β -Oxydation führt. In Polypropylen geht ein Grossteil der Spaltungen auf mehrfachen intramolekularen Angriff zurück.

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