

Determination of Carboxyl Groups in the Presence of Carbonyl Groups in Oxidized Polyolefins by Using Sulfur Tetrafluoride

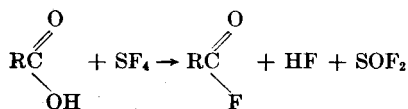
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Introduction

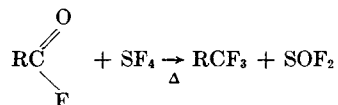
Infrared absorption spectrometry has been widely used to determine the oxidation products, and the rate of formation of these products during the thermal or photo oxidation of polyethylene.¹⁻³ Acids, ketones, and aldehydes, the end products reported from these oxidations, have similar spectra in the 5.5-6.0 μ region. It is only in this carbonyl stretching region that the products have suitable absorptivity to give quantitative data. The absorption band of the acid (5.84 μ), ketone (5.81 μ), and aldehyde (5.77 μ) groups present in oxidized polyethylene are so overlapped as to give only a broad band on standard laboratory spectrometers. Interpretation of these data, based on the increase in total carbonyl rather than on a single chemical moiety could lead to incorrect conclusions because of the large differences in the absorptivity of the various oxidation products. Acid absorptivity has been reported⁴ to be 2.4 times greater than that of ketones and 3.1 times greater than that of aldehydes.

Rugg, Smith, and Bacon,⁴ using a grating spectrometer for increased resolution, have demonstrated that the carbonyl groups formed by heat oxidation are mainly ketonic, while in highly photooxidized polyethylene the amounts of aldehyde, ketone, and acid are approximately equal. This procedure is adequate for qualitative but not suitable for accurate quantitative data. Cooper and Prober⁵ have used alcoholic sodium hydroxide to convert the acid groups to sodium carboxylate (6.4 μ) to analyze polyethylene oxidized with corona discharge in the presence of oxygen and ozone. This procedure requires five days and has been found to extract the low molecular weight acids from the film.

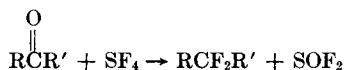
It has recently been reported that sulfur tetrafluoride, a gas at room temperature and pressure, readily reacts with carboxyl groups at room temperature or below to form the acid fluoride.⁶



More strenuous conditions, 130–150°C., convert the acid to the α,α,α trifluoromethyl derivative.



Aldehydes and ketones also are reported⁶ to react with sulfur tetrafluoride to give the difluoro derivatives.



The conditions for these reactions are more strenuous than the formation of the acid fluoride but not as strenuous as the complete conversion of the acid to the trifluoromethyl derivative. Esters, acid salts, and anhydrides are also converted to the trifluoromethyl derivative but require an even more elevated temperature.

Experimental

Melt-pressed or extruded films of photooxidized polyethylene (1–6 mils) were scanned between 5 and 7 μ . The thickness of the film was selected so that the absorbance of the total carbonyl band at 5.8 μ was not greater than 1.0.

These films were then placed in a 500-ml., thick-walled, wide-mouthed polyethylene bottle equipped with polyethylene fittings so that SF_4 could be flushed through the system and discharged through a 10% sodium hydroxide solution. Stainless steel bombs or Hastelloy C-lined bombs with brass fittings can be used rather than polyethylene if desired. Glass equipment should not be used for these reactions as sulfur tetrafluoride reacts with glass in the presence of trace amounts of moisture. The apparatus should be assembled in a well ventilated hood.

Sulfur tetrafluoride was then flushed slowly through the system until most of the air in the polyethylene bottle had been replaced with sulfur tetrafluoride. The valves were then closed and the reaction between film and gas allowed to proceed for 24 hr. If a shorter reaction time is desired, the bottle can be immersed in 80°C. water. At 80°C., 8 hr. was sufficient to complete the reaction. The minimum time was not established at either temperature.

Dry air or nitrogen was then flushed through the system to remove the sulfur tetrafluoride from the bottle and the film. The purging gas was bubbled through the caustic solution to remove the sulfur tetrafluoride. Sulfur tetrafluoride is a reactive gas which exhibits a high order of toxicity. Contact of the gas with skin must be avoided, since hydrogen fluoride is formed on contact with moisture. Burns should be treated as those obtained from hydrogen fluoride.⁷

The films are then removed from the bottle and stored in a desiccator over anhydrous calcium chloride until infrared scans can be run. The acid

fluoride is quite stable to atmospheric conditions, but hydrolysis can be accomplished with steam.

The films are then scanned between 5 and 7 μ with a standard infrared spectrometer, such as a Perkin-Elmer 21, equipped with a sodium chloride prism. It is essential that the scan be slow, as the absorbance at 5.45 μ is extremely sharp. Absorbances at 5.45 μ (acid fluoride) and 5.8 μ (ketones and aldehydes) were measured. The carboxyl content of the film can then be measured as a function of the absorbance at 5.45 μ or the disappearance of the absorbance at 5.8 μ . The molar absorptivity ϵ ($\epsilon = MA/bc$ in which M is molecular weight, A is absorbance, b is sample path length in centimeters, and c is concentration in grams/liter) of the acid fluoride at 5.45 μ prepared from ethylene/methacrylic acid copolymers was found to be 610 $\text{cm.}^{-1} \text{ mole}^{-1}$. The molar absorptivity of the acid at 5.8 μ was found to be 530 $\text{cm.}^{-1} \text{ mole}^{-1}$.

Discussion

Absorbances at 5.8 μ of the ketone carbonyl, as measured in a control film of poly(ethylene/carbon monoxide), and aldehyde carbonyl, as measured in a control film of polymethacrolein, were unaffected by the sulfur tetrafluoride under these conditions. Polymethacrolein developed a brown color, but no decrease in absorbance at 5.8 μ was observed and no new absorption peaks could be found in the 2–15 μ region of the infrared spectrum.

The acid carbonyl in the poly(ethylene/methacrylic acid) as measured by the absorbance at 5.8 μ was quantitatively converted to the acid fluoride as measured by the absorbance at 5.45 μ . The acid fluorides formed from photooxidized, low density polyethylene films can be hydrolyzed to give an absorbance at 5.8 μ equal to the absorbance of the film before the

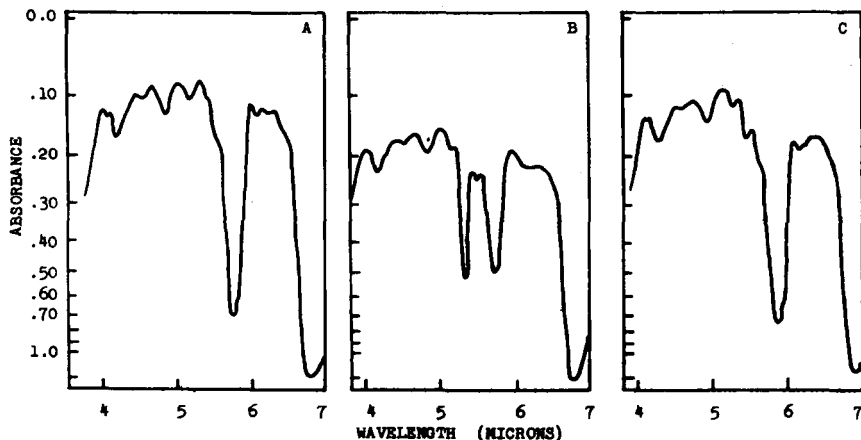


Fig. 1. Infrared spectra of photooxidized polyethylene film treated with sulfur tetrafluoride: (A) photooxidized 6-mil polyethylene film; (B) polyethylene film after treatment with sulfur tetrafluoride; (C) polyethylene film treated with sulfur tetrafluoride and hydrolyzed for 8 hr. with steam.

reaction with sulfur tetrafluoride (Fig. 1). This demonstrates that the sulfur tetrafluoride is not oxidizing any reaction intermediates, since the large molar absorptivity of the acid groups would result in a considerable increase in absorbance.

This technique seems to be applicable to all polyolefins and related polymers provided that the polymer does not have interfering absorbance bands in the 5.45 μ region. Oxidized linear polyethylene and polypropylene have been demonstrated to form acid fluorides with sulfur tetrafluoride.

A similar reaction can be carried out using thionyl chloride vapor to convert the acid groups to acid chlorides. An elevated temperature is required for complete conversion, and the acid chloride absorbs at 5.6 μ . This absorption peak will often appear as a shoulder on an oxidized sample containing a high concentration of ketonic carbonyls.

References

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Synopsis

A simple analytical technique has been developed to determine the amount of carboxyl groups present in degraded polyethylene film. This procedure is based upon the relative reactivities of the various carbonyl groups present, in oxidized polyethylene film, to sulfur tetrafluoride gas. The quantity of the carboxyl groups in the film is then measured as a function of the absorption at 5.45 μ .

Résumé

Une technique d'analyse simple a été développée, pour la détermination de la quantité de groupes carboxyles présents dans un film de polyéthylène. Ce procédé est basé sur les réactivités relatives des divers groupes carbonyles présents dans le film de polyéthylène oxydé, vis-à-vis du tétrafluorure de soufre à l'état gazeux. La quantité des groupes carboxyles dans le film est alors mesurée en fonction de l'absorption à 5.45 microns.

Zusammenfassung

Auf der Grundlage der relativen Reaktivität der in oxydierten Polyäthylenfilmen enthaltenen verschiedenen Carbonylgruppen gegen Schwefeltetrafluoridgas wurde eine einfache Analysenmethode zur Bestimmung der in abgebauten Polyäthylenfilmen enthaltenen Carboxylgruppen ausgearbeitet. Die Anzahl der im Film enthaltenen Carboxylgruppen wird durch darauffolgende Messung der Absorption bei 5,45 μ bestimmt.

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