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Reactions of Sulfur Dioxide with Oxidized Polyolefins*

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ABSTRACT

The reactions of gaseous sulfur dioxide with partially oxidized polypropylene and polyethylene have been investigated by iodometry and by Fourier Transform Infra-red (FTIR) spectroscopy. Comparison was also made with chemical changes observed in model liquid hydroperoxides which were analysed by FTIR, nmr and ultraviolet-visible spectroscopies. Reaction of macro- and model hydroperoxide groups with SO₂ proceeds by two consecutive reactions which occur in varying proportions depending upon the SO₂/hydroperoxide ratio. Because of this, the use of the SO₂ reaction products detected by infra-red (believed to be hydrosulfates) to quantify hydroperoxide is unreliable and gives little improvement in detection level over direct measurement of hydroperoxide by infra-red. Exposure to SO₂ and then gaseous ammonia produces some ammonium sulfate from hydroperoxide groups. The ammonium sulfate can be detected with high sensitivity by infra-red, but the stoichiometry of its generation is again variable.

INTRODUCTION

The oxidative degradation of polyolefins yields a complex mixture of products, as well as loss of physical properties.¹ Derivatization reactions, which will enhance the certainty of product identification and increase the precision of quantification, are needed to improve our knowledge of polymer oxidation mechanisms. Ideally, the derivation reactions should be quantitative with no side reactions, not limited by reagent penetration

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into solid polymer samples, and allow the characterization and quantification of important oxidation intermediates such as peroxidic and carbonyl species. Almost 20 years ago, the reaction of SO_2 with oxidized polymers was suggested to be an accurate, reliable way to quantify hydroperoxide ($-\text{OOH}$) groups in oxidized polyethylene (PE).² In this early study, it was claimed that an improvement in quantification by a factor of over 14 resulted when $-\text{OOH}$ groups were converted to sulfate groups and infra-red (ir) spectroscopy was used to measure both species. This method is still being used in investigations of polyolefin oxidation either directly by the ir method originally proposed³ or indirectly through the estimation of total sulfur products by x-ray fluorescence⁴ or electron spectroscopy (ESCA).⁵ This is despite the fact that the method has been suggested to be extremely unreliable for the quantification of oxidation in polypropylene (PP)⁴ and that the stoichiometry of the $\text{SO}_2/-\text{OOH}$ reaction has been reported to be variable.^{4,6,7} In addition, various species have been suggested as products from the reaction of SO_2 with polymeric and model, liquid-phase oxidation products, including sulfates, hydrosulfates, sulfuric acid and dialkyl peroxides.^{2,4,6,7,8}

In this paper we have re-investigated the reactions of SO_2 with $-\text{OOH}$ groups from the oxidation of PE and PP and with model liquid hydroperoxides. We have attempted to rationalize the apparently conflicting products previously reported and have explored the reliability of using SO_2 reactions to quantify $-\text{OOH}$ groups in polyolefins.

EXPERIMENTAL

Samples of polyethylene (DuPont, Sclair, 120 μm) and polypropylene (Hercules Profax, isotactic resin, 30 μm) films were exhaustively extracted with acetone (48 h, Soxhlet extraction). The dried films were then oxidized either by ultra-violet (uv) radiation (Atlas xenon arc WeatherOmeter), by oven ageing (60°C) or by γ irradiation (A.E.C.L. Gammacell 200, 1.1 Mrad h^{-1}).

Parallel studies of SO_2 reactions were also made on the model hydroperoxides, tert.-butyl hydroperoxide (99% pure by iodometry, purified by azeotropic distillation from the Aldrich technical product) and the trihydroperoxide produced from 1,3,5-trimethylcyclohexane (Aldrich) which can be regarded as a model of the adjacent PP- $-\text{OOH}$ groups.⁹ The oxidation of the cycloalkane was initiated by γ irradiation.

Oxidized films and liquid models were exposed to anhydrous, gaseous SO_2 (Matheson) at 22°C (films) or -10°C to 0°C (liquids). Most films and liquids were exposed to 100% SO_2 gas. In a few cases oxidized films were exposed to 1% SO_2 in nitrogen. At reaction temperatures below -10°C, large concentrations of free SO_2 remained in the liquid samples, even upon warming to room temperature. This resulted in intense, interfering ir bands at 1145 and $\sim 1340\text{ cm}^{-1}$ from the free SO_2 . The reactions of films of a phenoxy homopolymer [poly(2-hydroxypropyl ether of bisphenol A), Union Carbide Ucar] and propylene/6%-acrylic acid copolymer (Polysciences) toward SO_2 were also examined.

Before and after SO_2 treatment, the oxidized films were characterized by iodometry, ultraviolet-visible spectroscopy (Hewlett Packard 8450) and Fourier Transform Infra-red Spectroscopy (FTIR). A Perkin-Elmer 1500 FTIR spectrometer with a TGS detector was used for samples with $> 0.04\text{ mol kg}^{-1}$ —OOH groups, and a Nicolet 7199 spectrometer with a cooled MCT detector was used for samples with lower degrees of oxidation. To suppress troublesome interference ripples in the ir, all film spectra were recorded with an efficient polarizer in the ir beam, and with the samples inclined at the Brewster angle (56° for PP and PE) as proposed by Harrick.¹⁰ All ir absorbances were measured by peak heights from the best estimate of the base line for each peak. Chemical changes induced in samples were displayed by ir spectral subtraction, subtracting the ir spectrum of the starting material.

Hydroperoxide levels in PE and PP films were estimated from iodometric measurements in refluxing isopropanol.¹¹ Although repeated measurements on representative films showed that only a 5 min reflux was needed to give $> 95\%$ measurement of —OOH in photo- and thermally oxidized film, 60 min refluxes were found to be necessary for γ irradiated films. The liquid models and their products were also characterized by iodometry, as well as by FTIR and nuclear magnetic resonance spectroscopy (nmr, 60 MHz, Varian EM-360 at 22°C).

RESULTS

Polymer film reactions

Iodometry indicated that exposure of pre-oxidized PE and PP films to SO_2 caused virtually complete ($> 90\%$) loss of hydroperoxide groups. The effects of SO_2 exposure on pre-oxidized PE and PP film are shown by

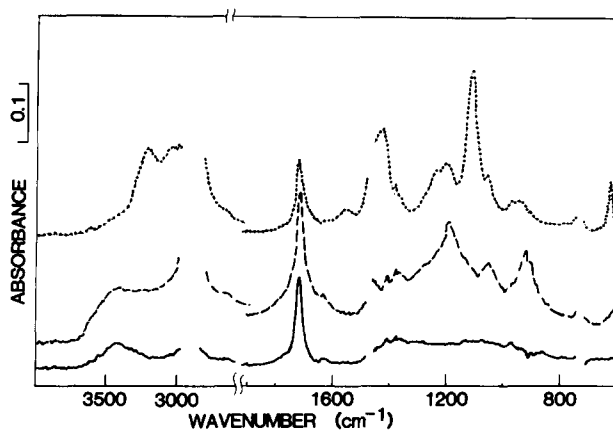


Fig. 1. Infra-red spectra of polyethylene film. All spectra obtained by subtraction of the spectrum for unoxidized PE. — After 20 Mrad γ irradiation in air. - - - - Oxidized film after SO_2 exposure. ····· Oxidized film after SO_2 then NH_3 exposure.

the ir spectral changes in Figs 1 and 2. These changes are representative of those found with PE and PP oxidized by all initiation processes. The PE changes are very similar to those originally reported by Mitchell and Perkins, but shown here more clearly by spectral subtraction.² The new absorptions plateau within ~ 2 h of exposure to 100% SO_2 for the PP films, although 24 h was routinely used and ~ 40 h was required for complete reaction with 1% SO_2 mixtures with nitrogen. No changes were

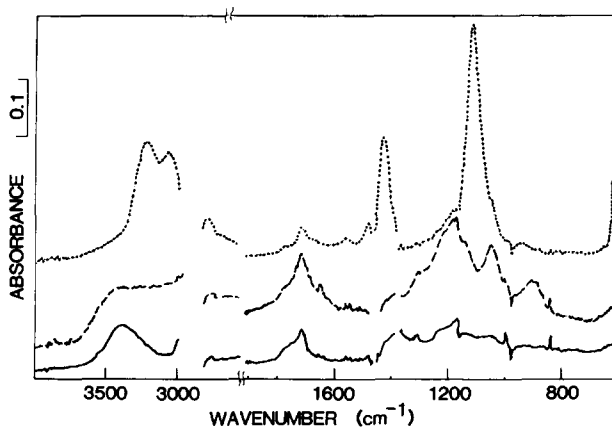


Fig. 2. Infra-red spectra of polypropylene film. All spectra obtained by subtraction of the spectrum for unoxidized PP. — After 8 Mrad γ irradiation in air. - - - - Oxidized film after SO_2 exposure. ····· Oxidized film after SO_2 then NH_3 exposure.

detected in the ir spectra of the phenoxy polymer or the propylene-acrylic acid copolymer upon prolonged exposure to 100% SO_2 , consistent with a lack of attack on alcohol $-\text{OH}$ or carboxylic acid groups.

Figures 1 and 2 show that similar absorptions result from the SO_2 exposure of oxidized PE and PP. The new bands are at ~ 900 , 1040 and 1195 cm^{-1} , although, in PE, the strong 1195 cm^{-1} absorption is ~ 3 times that of the initial $-\text{OH}$ absorption at 3400 cm^{-1} whereas, in PP, it is ~ 1.5 times that for the PP 3400 cm^{-1} absorption. Negligible free (non-bonded) alcohol $-\text{OH}$ or $-\text{OOH}$ were detected in our oxidized PP or PE samples. For example, the respective free $-\text{OH}$ absorbances at ~ 3600 and 3559 cm^{-1} were less than 1/10 of the 3400 cm^{-1} absorbance. However, the broad $-\text{OH}$ absorption at $\sim 3400\text{ cm}^{-1}$ may be a composite of hydrogen-bonded alcohol $-\text{OH}$ and $-\text{OOH}$ absorptions. Iodometric measurements showed that the dominant $-\text{OH}$ product ($>90\%$) is hydroperoxide in our γ -irradiated PP samples at levels of oxidation of up to 0.4 mol kg^{-1} whereas, in PE at the 0.05 mol kg^{-1} level, $\sim 80\%$ of the $-\text{OH}$ absorption can be attributed to $-\text{OOH}$ (extinction coefficient at 3400 cm^{-1} assumed to be $90(\text{mol kg}^{-1})\text{ cm}^{-1}$ for alcohol $-\text{OH}$ and hydroperoxide $-\text{OOH}$).¹² Based on the 1195 cm^{-1} absorption, the yield of this SO_2 product in PE is approximately 2–3 times the level from PP for equivalent hydroperoxide levels.

Exposure of the SO_2 -treated films (evacuated to remove residual free SO_2) to gaseous NH_3 for a few hours leads to a dramatic change in the ir spectra (Figs 1 and 2). The new band positions and relative intensities at 1420 , 620 cm^{-1} and the intense absorption at 1105 cm^{-1} are all consistent with the formation of ammonium sulfate (*cf.* Fig. 3). From a series of KBr discs with varying amounts of $(\text{NH}_4)_2\text{SO}_4$, extinction coefficients were estimated to be $1060(\text{mol litre}^{-1})\text{ cm}^{-1}$ at 1105 cm^{-1} and 440 at 620 cm^{-1} .

Representative quantitative data for polyolefin samples oxidized to various degrees by different initiation methods are shown in Table 1. Good correlation between $-\text{OOH}$ levels from iodometry and ir (3400 cm^{-1}) was obtained for all of the PP films. From a comparison of the initial $-\text{OOH}$ concentration from iodometry and $(\text{NH}_4)_2\text{SO}_4$ formed, after exposure to 100% SO_2 and the NH_3 , one mole of $-\text{OOH}$ yields approximately 0.7 mole of $(\text{NH}_4)_2\text{SO}_4$ in PE but only about 0.5 mole in PP.

Exposure of oxidized PE and PP films to SO_2 (or other acidic reagents such as CF_3COOH , SF_4 , anhydrides, BF_3) causes a distinct

TABLE 1
Analyses of SO₂-Treated Polyolefin Films^a

Oxidation history	3400 cm ⁻¹ absorbance	[—OOH] (mol kg ⁻¹)		1195 cm ⁻¹ absorbance ^b	1105 cm ⁻¹ absorbance ^c	[(NH ₄) ₂ SO ₄] (mol kg ⁻¹) ^c
		From I ₃ ⁻	From 3400 cm ⁻¹			
<i>Polypropylene</i>						
2 Mrad γ	0.012	0.035	0.040	0.017	0.09	0.024
10 Mrad γ	0.075	0.25	0.25	0.11	0.39	0.11
20 Mrad γ	0.11	0.41	0.37	0.14	0.72	0.20
50 h at 60°C ^d	0.04	0.15	0.13	0.075	0.22	0.06
160 h at 60°C ^d	0.20	0.61	0.67	0.32	1.10	0.32
135 h uv	0.0095	0.034	0.032	0.011	0.07	0.019
<i>Polyethylene</i>						
5 Mrad γ	0.020	0.013	0.014	0.060	0.17	0.010
20 Mrad γ	0.070	0.042	0.049	0.20	0.47	0.027

^a All samples treated with 100% SO₂. Infra-red absorbance relate to tilted films with optical paths of 36 μm (30 μm PP film) and 144 μm (120 μm PE film). Concentrations calculated from extinction coefficients of 90 (3400 cm⁻¹, —OOH) and 1060 (mol kg⁻¹) cm⁻¹ [1105 cm⁻¹, (NH₄)₂SO₄]. In SI units, 1 kGy 0.1 Mrad.

^b After SO₂ exposure.

^c After SO₂ exposure and then NH₃ exposure.

^d Samples γ irradiated (2 Mrad) prior to oven ageing at 60°C.

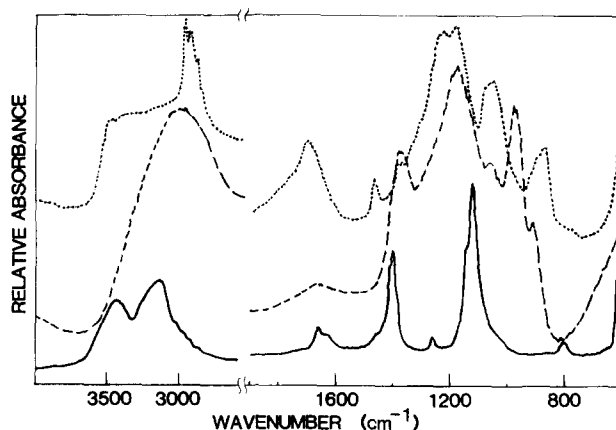


Fig. 3. Infrared spectra of sulfur compounds. — (NH₄)₂SO₄ in a KBr disc (0.01 wt %). - - - H₂SO₄ layer between thin Ge windows. ······ Peroxidized 1,3,5-trimethylcyclohexane after SO₂ treatment: involatile brown oil between NaCl windows.

yellow-brown discoloration. This discoloration has been employed by Richters¹³ to locate areas of preferential oxidation in commercial film. Ultraviolet-visible absorption spectra of all of our SO₂-treated films showed absorption maxima at ~225 and 290 nm, with a long tail extending into the visible region. The visible color of the SO₂-treated samples was a good semi-quantitative indicator of the hydroperoxide level in oxidized PE and PP films. NH₃ exposure caused the complete loss of the 290 and 225 nm absorptions, as well as a sharp decrease in the yellowness of films.

Model liquid reactions

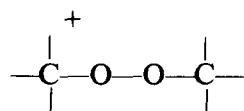
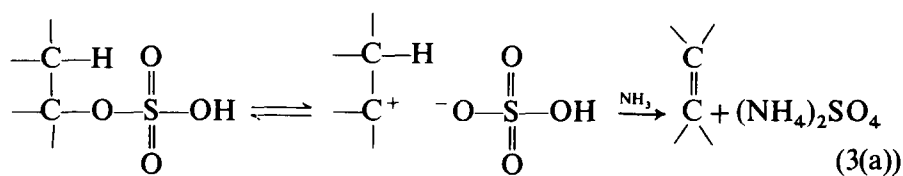
To gain further insight into the —OOH/SO₂ reactions in PP and PE, two model liquid hydroperoxide systems were studied: tert.-butyl hydroperoxide (BOOH) in CHCl₃ or CDCl₃ to model isolated —OOH groups and partially oxidized 1,3,5-trimethylcyclohexane (γ -irradiated to 14 Mrad with O₂ saturation, [—OOH] = 0.40 mol litre⁻¹ by iodometry). The latter, branched alkane is believed to be a good model for PP oxidation and produces a trihydroperoxide by an intramolecular, oxidative-chain propagation as expected in PP.^{1,9}

When SO₂ was passed into the trihydroperoxide solution at 20°C, a dense, yellow-brown oil quickly separated. This oil had a uv spectrum

with a maximum at ~ 290 nm and a long tail into the visible. The ir spectrum of this dense phase is shown in Fig. 3, and is very similar to that from SO_2 -treated, oxidized PP after subtraction of the PP spectrum (Fig. 2). Infra-red spectroscopy on the clear, colorless phase, followed by spectral subtraction to remove absorbances due to the (dominant) parent alkane, showed complete loss of the 1180, 1020 and 910 cm^{-1} absorptions of the trihydroperoxide and generation of new 880 and 812 cm^{-1} absorptions. Szymanski¹⁴ has tentatively assigned a 880 cm^{-1} absorption to the C—O—O—C link in dialkyl peroxides. Any reaction products in the clear colorless phase were too dilute to be detected by nmr spectroscopy which showed only the resonances of the starting alkane. However, the dense phase showed weak absorptions consistent with 1,3,5-trimethylbenzene (resonances at 6.7 and 2.23 ppm), as well as a strong resonance at 11.5 ppm. When NH_3 was passed into the dense oil, a white precipitate immediately formed and was identified as $(\text{NH}_4)_2\text{SO}_4$ by FTIR.

The reactions of SO_2 with 5% BOOH solutions were also followed by FTIR and nmr spectroscopy (in CHCl_3 and CDCl_3 solvents). Two distinct behaviors were found, depending on the SO_2/BOOH ratio used, although polarity effects complicated the interpretation of the nmr spectra. When an excess of SO_2 was added at $\sim 0^\circ\text{C}$ (SO_2 passed for ~ 6 min) no discoloration or phase separation occurred. However, the 1.28 ppm BOOH resonance had completely disappeared and was replaced by new resonances at 1.22 ppm and 12.3 ppm. The FTIR spectrum was very similar to that from the oxidized polyolefins after SO_2 exposure. When a deficiency of SO_2 was added to $\text{BOOH}/\text{CDCl}_3$ (SO_2 passed for ~ 20 s) or an equivalent of BOOH added to the excess SO_2/BOOH system, progressive phase separation occurred with the dense phase becoming yellow and then red/brown over many hours. The dense oil now showed a 10.5 ppm resonance whereas the supernatant had a FTIR spectrum identical to di-tert.-butyl peroxide and showed the 1.22 ppm nmr resonance together with weak 2.17 ppm and 1.28 ppm resonances (the latter from unreacted BOOH). The BOOH/SO_2 systems also showed many transient nmr resonances which seemed to depend both on reaction time, temperature and polarity of the medium (the latter especially in the 9–13 ppm region). Comparison with nmr spectra of known compounds obtained by adding these to the appropriate reaction mixtures indicated that 2.17 ppm was acetone, 1.22 ppm was di-tert.-butyl peroxide and 10.5–12.3 ppm was the $\text{HO—S(O)}_2\text{—O—}$ group (very medium sensitive).

dialkyl peroxides and H_2SO_4 as the dominant products. However, all of these authors' work employed a 5-fold excess of hydroperoxide so that only products from reaction (2) were observed. At very low SO_2 /hydroperoxide ratios and a higher temperature (75°C), catalytic decomposition of the hydroperoxide was found and attributed to a H_2SO_4 catalyzed reaction.⁶ However, our nmr experiments clearly showed the absence of methanol, methyl hydrosulfate and dimethyl sulfate (~ 3.5 , 4.08 and 4.00 ppm, respectively) which might be expected, based on the reported products from $\text{BOOH}-\text{H}_2\text{SO}_4$ reactions.^{6,18} Ammonium sulfate probably results from the reaction of ammonia via process (3).



For the oxidized polyolefins, the spectra shown in Figs 1 and 2 after SO_2 treatments can be qualitatively interpreted in terms of reactions (1) and (2). Under our reaction conditions, reaction of SO_2 with the oxidation sites in PE and PP will be controlled by the slow diffusion of SO_2 to these sites. In PE, where most ---OOH groups are randomly distributed along the backbones, but may be present as small clusters on adjacent segments, formation of the hydrosulfate by reaction appears to dominate, with only partial further reaction to give H_2SO_4 and a peroxide link. The ir spectrum shown in Fig. 1 for the $\text{SO}_2/\text{PE---OOH}$ product is consistent with the spectrum of inorganic hydrosulfates (peak maxima at 1170 , 1020 and 890 , no $\sim 1400\text{cm}^{-1}$).¹⁹ However, some H_2SO_4 may be present underlying the HOSO_3^- spectrum (*cf.* the broad H_2SO_4 spectrum in Fig. 3). In the case of oxidized PP, runs of adjacent tert. ---OOH groups are expected along segments, as well as much more extensive domains of local oxidation than found in PE (based on a faster oxidative propagation reaction and a slower radical termination).¹ As SO_2

molecules diffuse into these oxidized domains, they will be rapidly consumed by the excess —OOH groups. Consequently, reaction (1) in oxidized PP should be followed by extensive reaction (2). In Fig. 2, HO—SO₃— groups are visible (ir bands at 1170, 1020 and 890 cm⁻¹), but the HOSO₃—/initial —OOH ratio is much lower than observed in PE. The neighbouring —OOH groups expected along chain segments in oxidized PP should give rise to cyclic peroxides through reactions (1) and (2).^{7,17} Peroxide bands in the infra-red are generally weak and ill defined and so masked by the intense SO₄— and HOSO₃— bands.

Support for the sequential reactions (1) and (2) comes from the reactions of oxidized polyolefins with low SO₂ concentrations. When 1% SO₂/N₂ mixtures were used to treat both oxidized PE and oxidized PP, the absorbances at 1170, 1020 and 890 cm⁻¹ were reduced by ~40% as compared with 100% SO₂-treated samples. Similarly, the (NH₄)₂SO₄ absorptions, generated by the subsequent exposure to NH₃ of SO₂ pre-treated films, were reduced by this same percentage. The stoichiometry of (NH₄)₂SO₄ formation from —OOH in PP became ~0.33 (from ~0.5 in 100% SO₂) and from —OOH in PE became ~0.5 (from ~0.7 in 100% SO₂), presumably because of the increased importance of reaction (2) at the low SO₂ concentration.

Because of the dependence of the product mixture on the relative rates of reactions (1) and (2), on the spatial distribution of local —OOH groups and on the rate of SO₂ penetration into the oxidized domain in the polymer, the SO₂-hydroperoxide reactions may never be simple and truly stoichiometric even when 100% SO₂ is used. Thus, the 1195, 1050 and 900 cm⁻¹ absorptions are probably composites of hydrosulfate, sulfuric acid and peroxidic absorptions.

The conversion of H₂SO₄ and HOSO₃⁻ to ammonium sulfate by exposure to NH₃, possibly via reaction (3), does give a useful amplification of the weak, initial —OOH ir absorption (the ratio of the new absorbance at 1105 cm⁻¹ to the initial —OOH absorbance at 3400 cm⁻¹ is ~7 for PPOOH). However, it has the disadvantage of being a two-stage process. Furthermore, the yield of (NH₄)₂SO₄ from hydroperoxide is again dependent on the parameters controlling reactions (1) and (2) and should be used with caution to quantify —OOH levels. This same uncertainty will apply to the highly sensitive methods used by Briggs and Kendall⁵ and by Henman⁴ in which the products of SO₂-hydroperoxide reactions are not truly identified, but, instead, total sulfur quantified by ESCA (surfaces only) and by x-ray fluorescence,

respectively. Henman proposed a sensitivity by x-ray fluorescence of ± 5 ppm for S in SO_2 -treated films; this sensitivity is approached by the FTIR method after SO_2 and NH_3 exposure. Henman also observed stoichiometries of ~ 1.0 for PE hydroperoxide conversion to S products and ~ 0.5 for PP hydroperoxide.⁴ Husbands and Scott⁶ found variable SO_2 -hydroperoxide reaction kinetics dependent upon the reactant ratios.

Mitchell and Perkins² obtained ir absorbances similar to those from the oxidized PE/ SO_2 reaction shown in Fig. 1, but assigned them to dialkyl sulfates although it is difficult to propose a reasonable reaction leading to this product. In addition, sulfates should show major band intensities in the sequence $1195 > \sim 1400 > 1120 \simeq 966 > 800 \text{ cm}^{-1}$; only the 1195 and 920 bands in the spectra of our SO_2 -treated films (Figs 1 and 2) approximate to these absorptions. As mentioned above, from a comparison with ir spectra of known sulfur compounds and established hydroperoxide reactions, the product is identified as the hydrosulfate. The discrepancy with Mitchell and Perkins over the amplification of the $-\text{OOH}$ ir absorbance produced by SO_2 exposure ($\times 14$ in their work, $\times 1.5-3$ in our studies) comes from their use of only the very weak 3559 cm^{-1} absorbance of free $-\text{OOH}$ species, rather than taking into account product formation from SO_2 reaction with the total (free + H-bonded) $-\text{OOH}$ concentration. In addition, their estimates of detectable absorptions after SO_2 exposure (absorbance < 0.001) are highly optimistic because they ignore the problem of defining the true ir base line at high sensitivities.

CONCLUSIONS

The reaction of oxidized polyolefins with SO_2 proceeds via two consecutive reactions which lead to a mixture of products, including hydrosulfates and sulfuric acid, depending upon the availability of SO_2 and the local concentrations of $-\text{OOH}$ groups.

The method is unreliable for the quantification of $-\text{OOH}$ groups and gives only a small amplification in ir sensitivity when total hydroperoxide concentration is taken into account.

The sensitivity of the method can be enhanced by subsequent NH_3 reaction to give ammonium sulfate. However, the stoichiometry of the ammonium sulfate generation from $-\text{OOH}$ groups varies with the type of polyolefin and SO_2 availability and complex products are expected from the carbonium ion intermediate.

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