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Photochemical Reaction of Nitrosyl Chloride with Polyethylene

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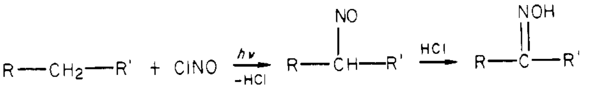
ABSTRACT: Irradiation of NOCl with low molecular weight alkanes yields oximes after rearrangement of the intermediate nitroso group. Upon irradiation of NOCl with high-density polyethylene, the oxime was not observed, but *gem*-chloronitroso and nitrato functionalities were found. The *gem*-chloronitroso group was proposed to arise from reaction of NOCl with the oxime, while the nitrate was proposed to originate from reaction of NO with the intermediate nitroso functionality. Possible mechanistic pathways to these products are discussed.

Introduction

Polymeric materials have found application in many areas as structural or decorative devices. Often the bulk properties of the polymer match the requirements for a given application, while the surface region is lacking in some critical property such as wettability. An example of a polymer having such characteristics is PE (polyethylene), which has interesting bulk properties useful in many ways, yet has surface characteristics which generally yield poor adhesion. This problem has been addressed often and successfully by techniques such as oxidative surface modification and by grafting. Our interest in modifying PE has recently been in the area of photochemically induced reactions.

In his pioneering work, Lynn[1] found that photoreaction of NOCl (nitrosyl chloride) with low molecular weight alkanes yields oximes. The pathway for this reaction apparently proceeds through the nitroso group, which then rearranges to the oxime:



$$R{-}CH_2{-}R' + ClNO \xrightarrow[-HCl]{h\nu} R{-}\overset{NO}{\overset{|}{C}H}{-}R' \xrightarrow{HCl} R{-}\overset{NOH}{\overset{\|}{C}}{-}R' \quad (1)$$

Müller[2] later developed the reaction quite extensively, eventually revealing an efficient synthesis of cyclohexanone oxime from cyclohexane.

As a part of our continuing interest in photochemical modifications of polymers,[3] this reaction appeared to be a route to the formation of carbon-nitrogen bonds on PE (polyethylene),[4] particularly HDPE (high-density PE). Our initial results indicated that the reaction pathway differed from that observed with low molecular weight alkanes, which prompted the detailed study described in this report.

While our work was in progress, two other groups reported on their work involving the photoreaction of NOCl with PE. Pozzi et al.[5a] attempted to use the reaction to form oximes on the polymer followed by a hydrolysis procedure to transform the oxime group to a carbonyl functionality to yield a photodegradable polymer. Degtyareva et al.[5b] reported an infrared spectrophotometric investigation of the products of the photoreaction of NOCl with PE and observed the presence of the oxime along with a *gem*-chloronitroso functionality and chlorinated hydrocarbon. Our results differed from these reports, and the differences are detailed in the Discussion.

Experimental Section

The HDPE film utilized had a thickness of approximately 0.038 mm (1.5 mil) and was specially prepared from Phillips Marlex 6006. This material is reported to be a linear polyethylene with a moderately broad molecular weight distribution. The measured density was 0.955 g cm^{-3} at 25 °C, and the crystallinity was calculated to be 71%. For experiments conducted with LDPE (low-density PE) a commercial film of thickness 0.032 mm (1.25 mil) was employed. All gases, Cl_2, HCl, NO, NO_2, and NOCl, were received from Matheson, fractionally distilled three times, and stored over phosphorus pentoxide.

Photolyses were performed in a cylindrical cell, 4.3 cm o.d. × 31 cm, constructed of Pyrex, in which the PE film was supported on a cylindrical Pyrex insert, 2.8 cm o.d. and 19 cm in length. All work with the gases was conducted on a standard vacuum assembly with illumination by a Kodak Safelight. All irradiations were carried out in a Rayonet Type RS preparative photochemical reactor from Southern New England Ultraviolet Co. equipped with four 12.5-W RUL 3500A lamps.

Infrared spectra were determined with a Beckman IR5A spectrophotometer and a Digilab FTS-20 Fourier transform infrared spectrometer. Mass spectra were accomplished with a Hitachi Perkin-Elmer RMU-6E mass spectrometer.

Results

A series of photolyses was carried out by using different gases with HDPE. The residual gases were analyzed by mass spectroscopy, and the films were analyzed by infrared

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spectrophotometry. The infrared assignments given below are discussed later in more detail.

NOCl + HDPE. NOCl was admitted to the photolysis cell containing HDPE to a pressure of 380 mmHg and irradiated for 3.0 h. The residual gases were removed, and only a portion was condensable with liquid nitrogen. This material was primarily N_2O, while the noncondensable fraction was molecular nitrogen. Immediately after photolysis the film had a blue color. IR analysis revealed new absorptions at 1629 ($CHONO_2$), 1581 (CClNO), 1275 ($CHONO_2$), 863 ($CHONO_2$), 668 (CHCl and/or CClNO), 612 cm^{-1} (CHCl and/or CClNO). Weak absorptions at 1640 (CH=CH) and 910 cm^{-1} (CH=CH) were no longer present after photolysis.

Exposure of the film to air for 2 weeks resulted in the disappearance of the absorption at 1581 cm^{-1} (CClNO) and of the blue color and, additionally, gave the appearance of a new absorption at 1561 cm^{-1} ($CClNO_2$).

The previous experiment was repeated with the exception that this system was not vigorously dried. Similar results were obtained as previously described, with the addition of a new absorption at 1718 cm^{-1} (C=O).

The initial experiment was repeated again with the exception that after the photolysis and removal of the residual gases, NO was admitted to the photolysis cell to a pressure of 380 mmHg. After 24 h in the dark, the film revealed new IR absorptions at 1658 ($CClONO_2$) and 824 cm^{-1} ($CClONO_2$), with decreased absorption at 1581 cm^{-1} (CClNO).

NOCl + HCl + HDPE. NOCl and HCl were admitted to the photolysis cell containing HDPE. Three different photolyses were performed with NOCl and HCl pressures of 355 and 115 mmHg, 369 and 369 mmHg, and 132 and 358 mmHg, respectively. Each system was irradiated 3.0 h. No strong effect of added HCl was detected, as the ratio of the absorbance at 1629 cm^{-1} ($CHONO_2$) to the absorbance at 1581 cm^{-1} was within 5% of 1.48, the value obtained upon photolysis in the absence of added HCl.

Cl_2 + HDPE. Cl_2 was admitted to the photolysis cell containing HDPE to a pressure of 380 mmHg and then irradiated for 5.0 h. After photolysis, new absorptions were seen in the IR spectrum at 668 (CHCl) and 612 cm^{-1} (CHCl).

NO + HDPE. NO was admitted to the photolysis cell containing HDPE to a pressure of 380 mmHg and then irradiated for 21 h. After photolysis, new absorptions were observed in the IR spectrum at 1629 ($CHONO_2$), 1567 ($CHNO_2$), 1275 ($CHONO_2$), and 863 cm^{-1} ($CHONO_2$).

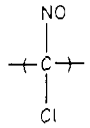
NO_2 + HDPE. NO_2 was admitted to the photolysis cell containing HDPE to a pressure of 380 mmHg and then irradiated for 21 h. After photolysis, a new absorption at 1567 cm^{-1} ($CHNO_2$) was observed in the IR spectrum.

Discussion

On the basis of extensive past work on lower molecular weight alkanes and cycloalkanes and due to previous work on polyethylene, the presence of oximes was expected upon photolysis of NOCl with HDPE. However, the C=N stretch of ketoximes[6] should absorb in the IR spectral range 1652–1682 cm^{-1} and the O–H stretch[7] should occur at approximately 3500 cm^{-1}; yet no changes in the IR spectrum of the film were observed in these regions. These results led to the conclusion that the oxime failed to form or survive the photolysis.

Infrared Assignments. Several changes in the infrared spectrum of HDPE were observed upon photolysis with NOCl, with new absorptions at 1629, 1581, 1275, 863, 668, and 612 cm^{-1} while weak absorptions at 1640 and 910 cm^{-1} disappeared. The absorptions at 1640 and 910 cm^{-1} were due to residual unsaturation in HDPE,[8] and their disappearance may be attributed to addition of NOCl to these double bonds.[9]

An impurity[10] sometimes found in the photolysis of NOCl with low molecular weight alkanes is the *gem*-chloronitroso derivative (I). Several studies on the IR spectra of these compounds have been reported,[11] and the range 1564–1587 cm^{-1} has been attributed to the N=O stretch of the *gem*-chloronitroso group. This range correlates well with the new absorption at 1581 cm^{-1} found in photolyzed HDPE.



$$\overset{NO}{\underset{Cl}{-\!\!\!+\!C\!+\!\!\!-}}$$

I

Monomeric nitroso compounds have a distinctive blue color due to absorption at 630–790 nm in the visible region,[12] and the HDPE film appeared blue after irradiation with NOCl, which provided further support for the assignment of the new absorption at 1581 cm^{-1} to the *gem*-chloronitroso species.

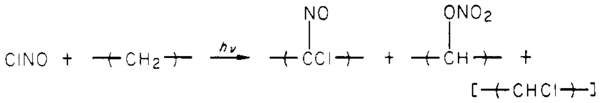
Aliphatic nitroso compounds are known to oxidize in air to the corresponding nitro derivative.[12,13] The photolyzed film was air oxidized by exposure to the atmosphere, and the blue color disappeared along with the IR absorption at 1581 cm^{-1}. Coupled with these disappearances, a new absorption at 1561 cm^{-1} appeared. Brown[14] has studied the IR spectrum of 2-chloro-2-nitropropane and assigned an absorption at 1565 cm^{-1} to the asymmetric stretch and also assigned an absorption at 1342 cm^{-1} to the symmetric stretch of the nitro group. The correlation between the 1561-cm^{-1} absorption in the oxidized HDPE photoproduct and Brown's assignment provides further support for the assignment of the 1561-cm^{-1} absorption to the *gem*-chloronitro functionality. By analogy to Brown's results, the symmetric stretch of the *gem*-chloronitro group should occur at about 1342 cm^{-1}, but delineation of an absorption in this region assignable to the nitro group was not possible due to the presence of the methylene deformation of HDPE.[8]

To provide further support for the assignment of the 1561-cm^{-1} absorption to the *gem*-chloronitro group, HDPE was photolyzed with NO_2 to incorporate the alkyl nitro functionality.[15] The IR spectrum of the photoproduct yielded a new absorption at 1567 cm^{-1}, which was attributed to the asymmetric stretch of the nitroalkane, analogous to the results of Blacet, Hall, and Leighton.[16] Again the symmetric stretch of the nitro group was not observable due to the methylene deformation of HDPE.[8]

The absorptions that appeared at 668 and 612 cm^{-1} upon irradiation of NOCl with HDPE occurred in the C–Cl stretching region, and this was confirmed by irradiation of Cl_2 with HDPE, which resulted in similar absorptions. After Lüttke,[17] it was tempting to assign the 668-cm^{-1} absorption to the C–Cl stretch in the *gem*-chloronitroso functionality and the 612-cm^{-1} absorption to the C–Cl stretch in the chlorinated alkane group. However, Quenum et al.[18] have reported an extensive study of the IR spectra of PE chlorinated to different extents. They assigned a band between 610 and 615 cm^{-1} to the C–Cl stretch of CHCl units in a poly(vinyl chloride) syndiotactic sequence. Additionally, they assigned a band at 660 cm^{-1} to CHCl units surrounded by PE units. Thus, while the absorptions at 668 and 612 cm^{-1} are almost certainly due to C–Cl stretching modes, specific assignments to the *gem*-chloronitroso group were not possible.

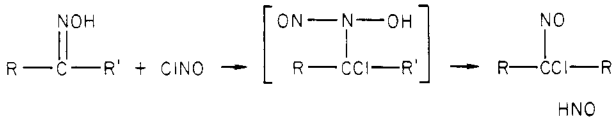
Of the changes in the IR spectrum of HDPE upon photolysis with NOCl, only the absorptions at 1629, 1275, and 863 cm^{-1} remained unassigned. These absorptions were characteristic of alkyl nitrates and were assigned based on the work of Carrington.[19] The absorption at 1629 cm^{-1} was assigned to the asymmetric stretch, while the 1275-cm^{-1} absorption was assigned to the symmetric stretch. The absorption of 863 cm^{-1} was assigned to the O–NO_2 stretch. The presence of the nitrate group was unexpected, but a proposed mechanism of formation is given below.

Reaction Pathway. From the infrared assignments previously discussed, the products of the photolysis of NOCl with HDPE were as shown below, with the chlorinated methylene group shown bracketed due to the ambiguous IR assignment.



$$\mathrm{ClNO} + -(\mathrm{CH_2})- \xrightarrow{h\nu} -(\overset{\mathrm{NO}}{\overset{|}{\mathrm{C}}}\mathrm{Cl})- + -(\overset{\mathrm{ONO_2}}{\overset{|}{\mathrm{C}}}\mathrm{H})- + [-(\mathrm{CHCl})-] \quad (2)$$

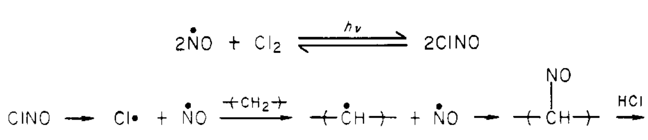
As described previously, the *gem*-chloronitroso functionality was known to be formed in small amounts during photolysis of low molecular weight compounds.[10] Kissinger and Ungrade[20] investigated the reaction of NOCl with different oximes and found the product to be the *gem*-chloronitroso derivative. While they proposed two alternative mechanisms, both required the presence of an *N*-nitrosohydroxylamine intermediate.



$$\mathrm{R}-\overset{\mathrm{NOH}}{\overset{\|}{\mathrm{C}}}-\mathrm{R'} + \mathrm{ClNO} \rightarrow \left[\begin{matrix}\mathrm{ON}-\mathrm{N}-\mathrm{OH}\\ |\\ \mathrm{R}-\mathrm{CCl}-\mathrm{R'}\end{matrix}\right] \rightarrow \mathrm{R}-\overset{\mathrm{NO}}{\overset{|}{\mathrm{C}}}\mathrm{Cl}-\mathrm{R'} + \mathrm{HNO} \quad (3)$$

Furthermore, Müller and Metzger[21] demonstrated that *N*-nitrosohydroxylamines were unstable and decomposed to nitroso compounds. If the stoichiometry of the reaction were correct, formation of nitroxyl (HNO) would be required. However, nitroxyl dimerizes and decomposes spontaneously to water and nitrous oxide.[22] This pathway was possibly occurring in the present studies, as nitrous oxide was observed in the residual gases from the photoreaction.

Coupling these observations with the basic reactions of NOCl, we propose the following reaction sequence:



$$2\dot{\mathrm{N}}\mathrm{O} + \mathrm{Cl_2} \overset{h\nu}{\rightleftharpoons} 2\mathrm{ClNO}$$

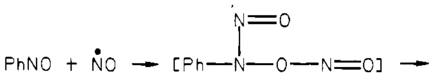
$$\mathrm{ClNO} \rightarrow \mathrm{Cl}\bullet + \dot{\mathrm{N}}\mathrm{O} \xrightarrow{-(\mathrm{CH_2})-} -(\dot{\mathrm{C}}\mathrm{H})- + \dot{\mathrm{N}}\mathrm{O} \rightarrow -(\overset{\mathrm{NO}}{\overset{|}{\mathrm{C}}}\mathrm{H})- \xrightarrow{\mathrm{HCl}}$$

$$-(\overset{\mathrm{NOH}}{\overset{\|}{\mathrm{C}}})- \xrightarrow{\mathrm{ClNO}} -(\overset{\mathrm{NO}}{\overset{|}{\mathrm{C}}}\mathrm{Cl})- + \mathrm{HNO} \rightarrow \mathrm{H_2O} + \mathrm{N_2O} \quad (4)$$

Apparently, the presence of excess NOCl consumed the formed oxime and forced the reaction to the *gem*-chloronitroso derivative.

The mechanistic pathway previously described contained an intermediate alkylnitroso derivative. The presence of the nitroso group allowed a proposed pathway for the formation of the nitrate functionality seen in the photolysis of NOCl with HDPE. Donaruma and Carmody[23] reacted nitrosocyclohexane with NO and obtained cyclohexyl nitrate. Since photolysis of NOCl yielded NO and due to the postulated presence of the nitroso derivative shown in eq 4, the reaction observed previously by Donaruma may have been occurring with HDPE.

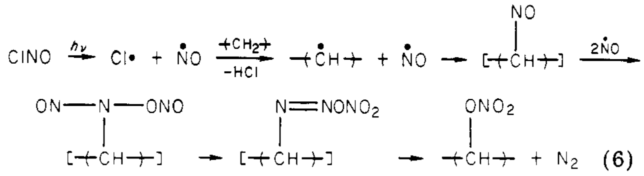
Bamberger[24] reacted NO with nitrosobenzene to yield benzenediazonium nitrate and postulated a nitritonitrosoamine intermediate:



$$\mathrm{PhNO} + \dot{\mathrm{N}}\mathrm{O} \rightarrow [\mathrm{Ph}-\overset{\mathrm{N=O}}{\overset{|}{\mathrm{N}}}-\mathrm{O}-\mathrm{N=O}] \rightarrow \mathrm{Ph}-\mathrm{N=N}-\mathrm{O}-\mathrm{NO_2} \quad (5)$$

Brown[25] studied the reaction of alkyl free radicals with NO but was unable to isolate either the nitritonitrosoamine intermediate or the alkyldiazonium nitrate. He did extend Bamberger's mechanism by proposing that the alkyldiazonium nitrate decomposed spontaneously. Such alkyldiazonium nitrates have apparently never been isolated and are thought to be stable only when conjugated.[26]

If such a mechanism occurred in the photolysis of NOCl with HDPE, it would rationalize the formation of the observed nitrate photoproduct as shown below:



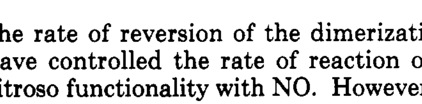
$$\mathrm{ClNO} \xrightarrow{h\nu} \mathrm{Cl}\bullet + \dot{\mathrm{N}}\mathrm{O} \xrightarrow[-\mathrm{HCl}]{-(\mathrm{CH_2})-} -(\dot{\mathrm{C}}\mathrm{H})- + \dot{\mathrm{N}}\mathrm{O} \rightarrow [-(\overset{\mathrm{NO}}{\overset{|}{\mathrm{C}}}\mathrm{H})-] \xrightarrow{2\dot{\mathrm{N}}\mathrm{O}}$$

$$[-(\overset{\mathrm{ON-N-ONO}}{\overset{|}{\mathrm{C}}}\mathrm{H})-] \rightarrow [-(\overset{\mathrm{N=NONO_2}}{\overset{|}{\mathrm{C}}}\mathrm{H})-] \rightarrow -(\overset{\mathrm{ONO_2}}{\overset{|}{\mathrm{C}}}\mathrm{H})- + \mathrm{N_2} \quad (6)$$

This pathway required the evolution of molecular nitrogen, and a considerable portion of the residual gas after the photoreaction of NOCl with HDPE was noncondensable with liquid nitrogen. This fraction was determined to be molecular nitrogen by mass spectrometry.

If this pathway had occurred, it remained to be explained why the alkylnitroso functionality yielded the alkyl nitrate while the *gem*-chloronitroso groups failed to react similarly. If reaction of NO with the nitroso functionality was considered to be an electrophilic free radical reaction, the presence of the chloro substituent may have tended to retard the reaction. To investigate this possibility, a sample of HDPE was photolyzed with NOCl. After the reaction and removal of the residual gases, NO was admitted to the photolysis cell and allowed to react for an extended time in the dark. The IR spectrum revealed a decreased absorption at 1581 cm^{-1}, previously assigned as the *gem*-chloronitroso functionality, coupled with new absorptions at 1658 and 824 cm^{-1}. These new absorptions were assigned by correlation as the nitrate group and presumed to be the *gem*-chloronitrato functionality after Burrell.[27] Therefore, both the nitroso and the *gem*-chloronitroso groups react with NO to form the nitrate functionality but the reaction rate of the alkylnitroso functionality is much greater than that of the chloronitroso derivative. Thus, under our standard photolysis conditions, the rate of reaction of the *gem*-chloronitroso compound was so slow that only the alkyl nitrate was observed.

An alternate rationalization to the lack of formation of the *gem*-chloronitrato functionality under standard photolysis conditions was that the *gem*-chloronitroso groups dimerized to *N,N'*-azo dioxide structures.[12]



$$2\mathrm{R_2CClNO} \rightleftharpoons \begin{matrix}\mathrm{R_2ClC} & & \mathrm{O}\\ & \mathrm{N=N} & \\ \mathrm{O} & & \mathrm{CClR_2}\end{matrix} \quad (7)$$

Thus, the rate of reversion of the dimerization process could have controlled the rate of reaction of the *gem*-chloronitroso functionality with NO. However, the probability of this pathway was not considered to be great because the extent of dimerization of nitroso compounds containing electron-withdrawing groups in the α position is diminished[28] and no evidence of dimer formation was observed. Nitroso dimers exist as cis and trans isomers, with the trans isomer being more stable.[29] The presence

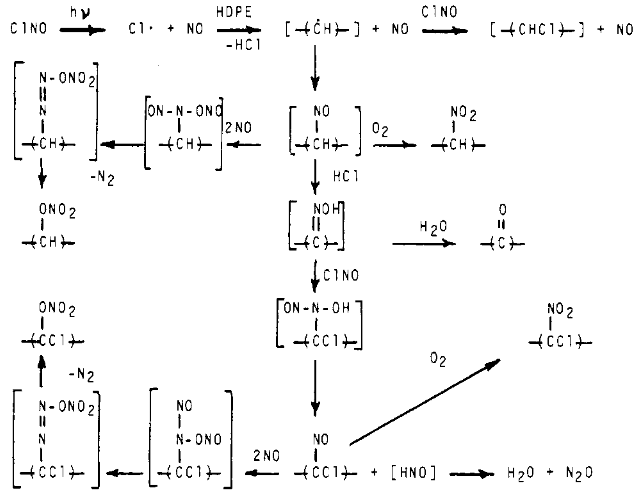


Figure 1. Summary of reaction pathway for photolysis of NOCl with HDPE.

Table I
Infrared Spectral Assignments for Modified Polyethylene

absorp, cm^{-1}	assignment
1718	C=O str
1658	asym str of NO_2 in $CClONO_2$
1629	asym str of NO_2 in $CHONO_2$
1581	N=O str of CClNO
1567	asym str of NO_2 in $CHNO_2$
1561	asym str of NO_2 in $CClNO_2$
1275	sym str of NO_2 in $CHONO_2$
863	O—NO_2 str of $CHONO_2$
824	O—NO_2 str of $CClONO_2$
668, 612	C—Cl str of CHCl and/or CClNO

or absence of the cis isomer, although not expected, could not be confirmed due to the presence of the methylene deformation of HDPE.[8,12] Absorption due to the trans dimer was expected at 1210–1222 cm^{-1} for primary compounds,[11,30] 1191–1214 cm^{-1} for secondary compounds,[14,30] and 1204–1279 cm^{-1} for tertiary compounds.[11,14,30] Dimeric trans tertiary nitroso compounds could have been present yet unobserved due to the strong nitrate absorption at 1275 cm^{-1}, but the level of such materials was presumed to be very low in HDPE. Absorption due to primary and secondary trans dimer should have been distinguishable from the nitrate absorption, yet none was detected.

From the data given, a fairly complete picture of the photoreaction of NOCl with HDPE was constructed and is presented in Figure 1. Postulated intermediates in Figure 1 are shown in brackets. Additionally, a summary of all IR assignments is given in Table I.

Reaction Constraints. One of the original goals of this work was formation of carbon–nitrogen bonds on polyethylene. As previously discussed, the photolysis of NOCl with HDPE does yield some C-N bonds in the form of *gem*-chloronitroso compounds, yet the formation of the alkyl nitrate detracts from the efficiency of the reaction. This efficiency might have been affected in the reaction sequence given in Figure 1 by control of the reactions of the alkylnitroso intermediate. If this group could be influenced to rearrange to the oxime rather than react with NO, the reaction could be driven to the *gem*-chloronitroso functionality.

Gowenlock and Lüttke[12] discussed the rearrangement of nitroso compounds to oximes and suggested that nitroso compounds may be stable to rearrangement unless catalyzed. Indeed, Donaruma[31] studied the isomerization of nitrosocyclohexane to cyclohexanone oxime and concluded that the material was stable even to 80 °C in a nonpolar solvent. However, isomerization did proceed in the presence of acid or base or in a polar solvent.

To determine the effect of the HDPE medium on the product distribution, NO was photolyzed with HDPE for an extended time, as NO absorbs very weakly at the wavelengths employed. The only changes in the IR spectrum observed were due to alkyl nitrate and nitroalkanes. The absence of any observable oxime indicated that HCl was required for rearrangement of the alkylnitroso to the oxime. The nitrate probably arose from reaction of NO with the alkylnitroso compound as previously described. The nitroalkane probably occurred from NO_2 formed by disproportionation of NO and NO_3, which failed to undergo cage recombination during rupture of the diazonium nitrate.

Since HCl was found to be required for rearrangement of the nitroso group to the oxime, several photolyses were conducted with different ratios of NOCl and added HCl. However, no significant changes in the product distribution were observed in the IR spectra. While HCl was apparently required to catalyze the reaction as shown from the photolysis with NO, some process other than HCl catalysis apparently controlled the isomerization of the nitroso group, and that process may have been the constraint of the HDPE matrix.

Prior Work. Two other groups previously photolyzed NOCl with PE. First, Pozzi et al.[5a] attempted to use the reaction to form the oxime. They wished to then hydrolyze the oxime to the carbonyl, forming a photodegradable modified PE. Their experimental arrangement appeared to be similar to that of the present work, with irradiation through Pyrex of a mixture of NOCl and HCl in the presence of the polymer. These workers did not give definitive analytical data but may have obtained a mixture of nitrate, nitro, and nitroso functionalities, which were probably sites for the eventual photodegradation that they observed.

Degtyareva et al.[5b] studied the kinetics and mechanism of the photochemical reaction of NOCl with PE. These workers apparently used incandescent light for irradiation, but this should not affect the primary dissociation pathway of NOCl upon comparison to our use of ultraviolet light. They did observe the blue color indicative of the presence of nitroso groups, and this color diminished with time. We attributed the loss of blue color to oxidation of the nitroso group while Degtyareva apparently attributed the loss to rearrangement to the oxime.

Degtyareva did give infrared spectral results on the modified PE prepared by irradiating NOCl. They observed changes in the infrared spectrum, with new absorptions at 1560, 1630, and 1720 cm^{-1}. The bands at 1560 and 1720 cm^{-1} were assigned to the nitroso functionality while the band at 1630 cm^{-1} was assigned to the oxime. On the based of the assignments given in the present work, the absorption at 1560 cm^{-1} may have been due to the *gem*-chloronitro group, while the 1630-cm^{-1} band may have been due to the nitrate functionality.

The band at 1720 cm^{-1} observed by Degtyareva et al. was not seen in the present work. To investigate this absorption more closely, we repeated the photoreaction of NOCl with HDPE except that the system was not rigorously dried. In this photoproduct, a new absorption at 1718 cm^{-1} was found. This species was assigned as the carbonyl group,[32] thought to occur from hydrolysis of the oxime.

Substrate Comparison. The HDPE was a highly crystalline material that was composed of linear chains. Since it was considered that the HDPE matrix was controlling the product distribution to some degree, the photolyses with NOCl were repeated with low-density polyethylene that was highly branched. The same functional groups were introduced but the relative yields were different from that observed with HDPE. Qualitative comparisons of the absorption due to the *gem*-chloronitroso as compared to the nitrate indicated that low-density PE yielded a greater amount of nitrate than did HDPE. This difference was attributed to the greater number of tertiary sites in low-density PE, which would tend to react first by the free radical mechanism to yield the nitroso functionality. The tertiary nitroso group would then be unable to tautomerize to the oxime and thus only be capable of eventually forming the nitrate group.

An important point not yet addressed was the strong difference between the clean formation of oxime observed with low molecular weight alkanes as compared to the results with HDPE. A portion of the answer may have been the concentrations of reactants employed as the photooximation reactions for low molecular weight materials employed high concentrations of HCl and relatively low concentrations of NOCl. Thus, when the nitroso compound was formed, the HCl catalyst allowed rapid formation of the oxime. Further, the large concentration of HCl then formed the salt of the oxime, which precipitated from the hydrocarbon solution, removing the oxime from the reaction zone[33] and thereby avoiding the formation of more than trace amounts of the *gem*-chloronitroso functionality.

Finally, upon comparison of the results of the photolysis of NOCl with low molecular weight alkanes against the results with HDPE, one of the differences remained unexplained. While the failure of the oxime to survive the reaction was understandable due to the inability to remove the oxime from the NOCl in the reaction zone, the lack of control of the rearrangement of the nitroso to the oxime was obscure. This rearrangement apparently required HCl catalysis, yet the product ratio was apparently unperturbed by added HCl or by changes in the HCl/NOCl ratio. Thus, apparently some of the formed nitroso groups were prevented or constrained from rearrangement to the oxime, and that constraint may have been the moderately rigid HDPE matrix.

Conclusion

The results of this study on the photolysis of NOCl with HDPE indicated the following points:

1. While the reaction proceeds smoothly in solution with low molecular weight alkanes to yield the oxime, the major products of the reaction with HDPE were the nitrato and *gem*-chloronitroso functionalities. The *gem*-chloronitroso group probably arose from the oxime, while the nitrate functionality probably originated from reaction of NO with the intermediate nitroso functionality.

2. A fraction of the formed nitroso groups were apparently constrained from rearranging to the oxime, and these nitroso groups eventually reacted further with NO to yield the nitrate group. The constraint may have been the HDPE matrix.

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