Oxidation of FA with Alkene or Alkyne Functionalities Studied with Chemiluminescence and Real-Time IR Spectroscopy

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ABSTRACT: The oxidation of well-defined FA derivatives has been studied with real-time IR (RTIR) and chemiluminescence (CL) techniques. Both methyl esters and model oils based on different FA have been studied to reveal the effect of functionality. The FA used were linoleic and crepenynic acid, the latter with an alkyne functionality. The purpose was to reveal how structural differences affect the oxidation and how this is monitored with CL and RTIR. Both model oils had longer oxidation induction times than the corresponding methyl esters, as seen by both IR and CL. Generally, the induction times measured with IR were shorter than those determined by CL, but the rate of oxidation did not seem to differ much between the model oils and the corresponding methyl esters. The results also imply that the higher functionality of the model oils gives a greater possibility of intramolecular addition reactions instead of chain scission during oxidation, making the model oils emit fewer low-M.W. volatiles than the methyl esters. There is also a difference between methyl crepenynate and methyl linoleate, in that the alkyne functionality seems to enhance the possibility of chain scission instead of addition reactions. The results presented imply that the CL signal can be used to monitor the oxidation and the formation of volatile compounds from a FA structure. By combining the CL measurements with RTIR data, information about the oxidation reactions can be obtained, giving a greater understanding of what reactions are occurring during oxidation and how they are related to each other.

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KEY WORDS: Alkyne, chemiluminescence, crepenynic acid, fatty acid, linoleic acid, model compound, oxidation, real-time IR.

Vegetable oils are a group of naturally occurring monomers that have long been used in coating applications, either as air-drying oils or as parts of resins (1), e.g., in alkyds. The development of synthetic resins has to a large extent lead to their replacement of vegetable oils in several applications, but they still have a number of uses in certain areas. Vegetable oils are a renewable resource that will be increasingly important in the future. A number of different vegetable oils previously unavailable may come on the market in the future, thanks to improved crop development techniques. FA containing various functional groups such as alkene, alkyne, epoxy, or hydroxyl groups exist in nature, but normally they exist in crops that are difficult to grow on a commercial basis (2,3). Crop development, either by gene modification (4) or by standard techniques, may change this situation, making these monomers available in larger quantities.

One topic in the coatings area that has received a significant amount of attention during the last decades is the problem of volatile organic content (VOC) in solvent-borne coatings. The introduction of powder coatings, water-borne systems, and radiation-curable systems are ways to overcome this problem. Another is to use reactive diluents to adjust the viscosity of paints. Vegetable oils, methyl esters, and derivatives thereof are interesting to use as reactive diluents, acting as nonvolatile solvents polymerized into the final film. FAME exhibit low viscosity, high dissolution capacity, low volatility, and nontoxicity, all of which are desirable properties for a reactive diluent. The main drawback is the normally low reactivity of the functional groups and the presence of side reactions during curing, but the potential use of these structures in coatings would significantly increase if the reactivity could be increased. The reactivity of a FA mixture may, however, be tailored by composition, and crop development techniques may be a useful tool for producing crops with an optimal FA pattern for use in coating applications. Very different structures, ranging from cationically curable epoxy-functional oils (5) to oxidatively drying systems can be used. Vegetable oils may also be used as stabilizers in coating systems. One example is epoxidized soybean oil used commercially as a hydrochloric acid quencher (6) in polyvinyl chloride plastisols. These new possibilities, together with environmental concerns, have sparked a renewed interest in FA derivatives as monomers. Significant research efforts involving traditional structures as well as new FA derivatives as monomers have been presented (7).

The mechanism for air-drying FA is a free radical process, involving abstraction of α-hydrogens, formation of hydroperoxides, addition reactions, and scission reactions. The exact schemes for all these reactions are, however, not fully revealed, since there are far too many reactions going on simultaneously to be able to monitor them one at a time (8). Most systems are mixtures of numerous different FA derivatives, resulting in several competing reactions. An improved understanding of these reactions and novel techniques to study the

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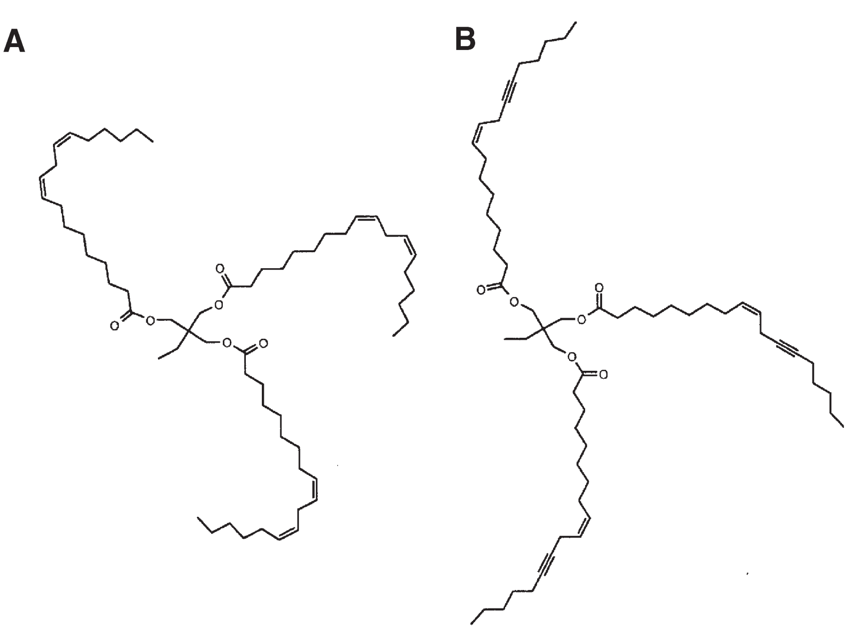

FIG. 1. Trimethylol propane (TMP)-trilinoleate (A) and TMP-tricrepenynate (B).

oxidation would aid the progress of the development of better coating systems.

This paper describes the synthesis and spectroscopic characterization of two pure model oils with alkene and alkyne functionalities. They have been synthesized from trimethylol propane (TMP), methyl linoleate, and methyl crepenynate, containing alkene and alkyne functionalities, respectively (Fig. 1). The study aims to reveal how structural differences as well as differences in functionality may affect FA oxidation and how this is detected by chemiluminescence (CL) and real-time IR (RTIR) techniques. The oxidation of the model oils is compared to the oxidation of the methyl esters to reveal how different functionalities affect oxidative stability and reactivity.

EXPERIMENTAL PROCEDURES

Materials. The crude vegetable oil (from *Crepis alpina*, containing crepenynic acid) was received from Lantmännen (Stockholm, Sweden). Methyl linoleate (99%) was purchased from Sigma-Aldrich (Stockholm, Sweden) and used as received. Methyl crepenynate was synthesized and purified according to procedures reported previously (9). TMP was obtained from Perstorp AB (Perstorp, Sweden). Silica gel used in the chromatography was SILICE 60 A from SDS (Peypin, France). All other chemicals used were purchased from either Sigma-Aldrich or Lancaster (Lancashire, United Kingdom) and used as received.

Instruments. ^{1}H NMR spectra were obtained on a 400 MHz Bruker Aspect NMR using $CDCl_3$ as solvent. IR spectra were recorded on a PerkinElmer Spectrum 2000 FTIR equipped with a heat-controlled single-reflection (ATR: attenuated total reflection) accessory (Golden Gate) from Specac Ltd. (Kent, England). CL data were obtained on a CL apparatus built by Färnert Digitalteknik (Stockholm, Sweden). The CL instrument is basically a temperature-controlled sample compartment of approximately 10 cm^3 located in a vacuum chamber. A controlled gas flow can be put through the sample compartment, either to obtain an inert atmosphere or an air atmosphere. A quartz lid allows emitted photons to be detected by a Hamamatsu H6180-01 integrated photon counting head.

Synthesis of TMP-tricrepenynate. Methyl crepenynate (0.88 g, 3.0 mmol) and TMP (0.14 g, 1.0 mmol) were added to a 25-mL flask together with 1 mL 0.1 M NaOH in MeOH. The mixture was left stirring at 80°C under argon flow for 24 h. The trisubstituted TMP was purified using flash chromatography on silica gel. Ethyl acetate, 1.25 and 2.5%, in hexane was used as eluent. Yield was 0.34 g (35%).

^{1}H NMR ($CDCl_3$): $\delta = 0.9$ (*t*, CH_3), 1.3–1.4 (*br*, aliphatic CH_2), 1.5 (*m*, $CH_2CH_2CH_2COO$), 1.6 (*m*, CH_2CH_2COO), 2.0 (*m*, $CH{=}CHCH_2CH_2$), 2.1 (*t*, $CH_2CH_2C{\equiv}C$), 2.3 (*t*, CH_2COO), 2.9 (*t*, $C{\equiv}CCH_2CH{=}CH$), 4.0 (*s*, $COOCH_2C$), 5.3–5.4 (*m*, $CH{=}CH$).

Synthesis of TMP-trilinoleate. Methyl linoleate (2.12 g, 7.25 mmol) and TMP (0.31 g, 2.31 mmol) were added to a 25-mL flask together with 1 mL 0.1 M NaOH in MeOH. The mixture was left stirring at 80°C under argon flow for 24 h. The product was purified using flash chromatography on silica gel. Ethyl acetate, 1.25 and 2.5% in hexane, was used as eluent. Yield was 1.19 g (54%).

^{1}H NMR ($CDCl_3$): $\delta = 0.9$ (*t*, CH_3), 1.3–1.4 (*br*, aliphatic CH_2), 1.6 (*m*, CH_2CH_2COO), 2.05 (*m*, $CH{=}CHCH_2CH_2$), 2.3 (*t*, CH_2COO), 2.78 (*t*, $CH{=}CHCH_2CH{=}CH$), 4.0 (*s*, $COOCH_2C$), 5.3–5.4 (*m*, $CH{=}CH$).

Procedures. (I) Chemiluminescence measurements. An airflow was purged through the sample compartment at a rate of

60 mL/min, and the oven temperature was set to 60°C. This temperature was chosen in order to get sufficient reaction rates, since oxidation rates at room temperature are too slow to get results within a reasonable time. After the apparatus reached 60°C, it was left for 30 min to equilibrate. A 10-µL sample was put in an aluminum cup, which was then placed into the sample compartment, and the measurement was started.

(ii) RTIR. The IR measurements were performed on a heat-controlled single-reflection ATR diamond crystal. The heat controller was set to 60°C and when this temperature was reached, a small portion of the sample, ~10 µL, was put on the ATR crystal and the measurement was started. A spectrum was recorded every 5 min using TimeBase® software from PerkinElmer.

RESULTS AND DISCUSSION

Synthesis. Model oils based on TMP propane were synthesized to have well-defined systems, since a TG normally consists of more than one type of FA. TMP was chosen because of its structural similarities with glycerol and the fact that it has only primary alcohols, making the transesterification easier. The synthesis and purification of the corresponding methyl esters have been reported previously (9). The low conversions in the transesterifications are due partly to difficulties during purification and partly to the fact that the syntheses are not optimized with respect to yield.

The NMR spectra of the model oils clearly show that the TMP is fully substituted, since peaks would have appeared at 3.56 ($-CH_2OH$) and 4.2 ($-CCH_2OCO-$) for the monosubstituted, and at 3.39 ($-CH_2OH$) and 4.03 ($-CCH_2OCO-$) for the disubstituted TMP. These peaks arise from the CH_2 group closest to the ester bond in the TMP and were determined by synthesizing mono-, di-, and trisubstituted model compounds from TMP and methyl stearate (Samuelsson, J., and M. Johansson, unpublished results).

Oxidation. The oxidation of FA structures generates a desired increase in M.W. and structure buildup in an air-drying system. However, oxidation reactions will eventually also degrade the film. The oxidation and degradation processes produce volatile low-M.W. compounds, generally aldehydes and carboxylic acids, which give air-drying alkyd paints and linseed oil-based coatings their characteristic smell (10,11). In coating applications it is desirable to maximize the oxidation reactions that lead to structure buildup and minimize oxidative degradation reactions. It is also desirable to increase the oxidation rate to obtain fast drying of the coating.

CL. The origin of the CL signal is disputed. Two main mechanisms are proposed to be responsible for the light emitted: the Russell mechanism (12) and β-scission. The Russell mechanism is a bimolecular reaction, in which it is proposed that two peroxy radicals combine into a tetroxide, which upon decomposition yields the excited carbonyls responsible for the CL. β-Scission, on the other hand, begins with the scission of a peroxide, yielding an alkoxy radical and a hydroxy radical. The alkoxy radical may induce scission of the carbon chain and give alkyl radicals and excited carbonyls. The carbonyls formed will eventually relax to a nonexcited state and some of them will emit photons. By using a sensitive photomultiplier to measure the amount of photons emitted from a sample, information about oxidation rate and stability can be obtained. Recent CL studies on the oxidation of polypropylene indicate that the β-scission is the cause of the CL signal rather than the decomposition of a tetroxide, as suggested in the Russell mechanism (13).

Several measurements were made to confirm that the data obtained from the CL measurements were reproducible. The oxidation of TMP-trilinoleate was performed using four different airflow rates: <10, 40, 60, and 120 mL/min. All four measurements showed the same induction time, and when plotting the data on one plot, all curves overlapped each other. This indicates that the oxidation rate is independent in this region of airflow rates, and that the IR data should be comparable to the CL data, although the IR measurements were done without a controlled airflow.

RTIR. IR spectroscopy is frequently used to obtain information about the oxidative behavior of FA derivatives (14,15). The abstraction of the α-hydrogen in a linoleate structure can be monitored by looking at the absorption band of the disappearing original unconjugated *cis*-unsaturations at ~3010 cm^{-1} (16), and also at the conjugated *trans*-double bond at ~990 cm^{-1} since the hydrogen abstraction will generate a rearrangement of the unsaturations. Addition of oxygen to the formed radical and subsequent hydrogen abstraction by the peroxy radical will result in a hydroperoxide with absorption at ~3400 cm^{-1}. A radical addition to the conjugated *trans*-structure would produce a nonconjugated double bond. The only unconjugated double bond with increasing absorption that can be seen in the IR spectra is unconjugated *trans*-unsaturations, appearing at ~970 cm^{-1}.

Since the IR measurements were performed without a controlled airflow, there is a greater uncertainty in the IR data than in the CL measurements. However, several IR measurements were done to ensure reproducibility.

Comparison of methyl linoleate and methyl crepenynate. The oxidation of a linoleate structure (Fig. 2A) starts with the abstraction of an α-hydrogen. The formed carbon-centered radical will cause the *cis*-unsaturations to rearrange into a conjugated *trans*-double bond. Since there is air present, subsequent addition of oxygen will result in a peroxy radical, which in turn will abstract a new α-hydrogen from another molecule to give a hydroperoxide. This hydroperoxide is relatively unstable and will, when decomposing, yield an alkoxy radical that, besides hydrogen abstraction and β-scission, will have the possibility of adding to unsaturations and forming oligomers. The addition of an alkoxy radical to the conjugated bonds competes with the β-scission reaction, but as long as there are accessible conjugated unsaturations, it seems that the alkoxy radicals in this system add to form oligomers rather than undergo β-scission.

In methyl crepenynate (Fig. 2B) the alkoxy radical formed seems to be less likely to add to the conjugated unsaturations

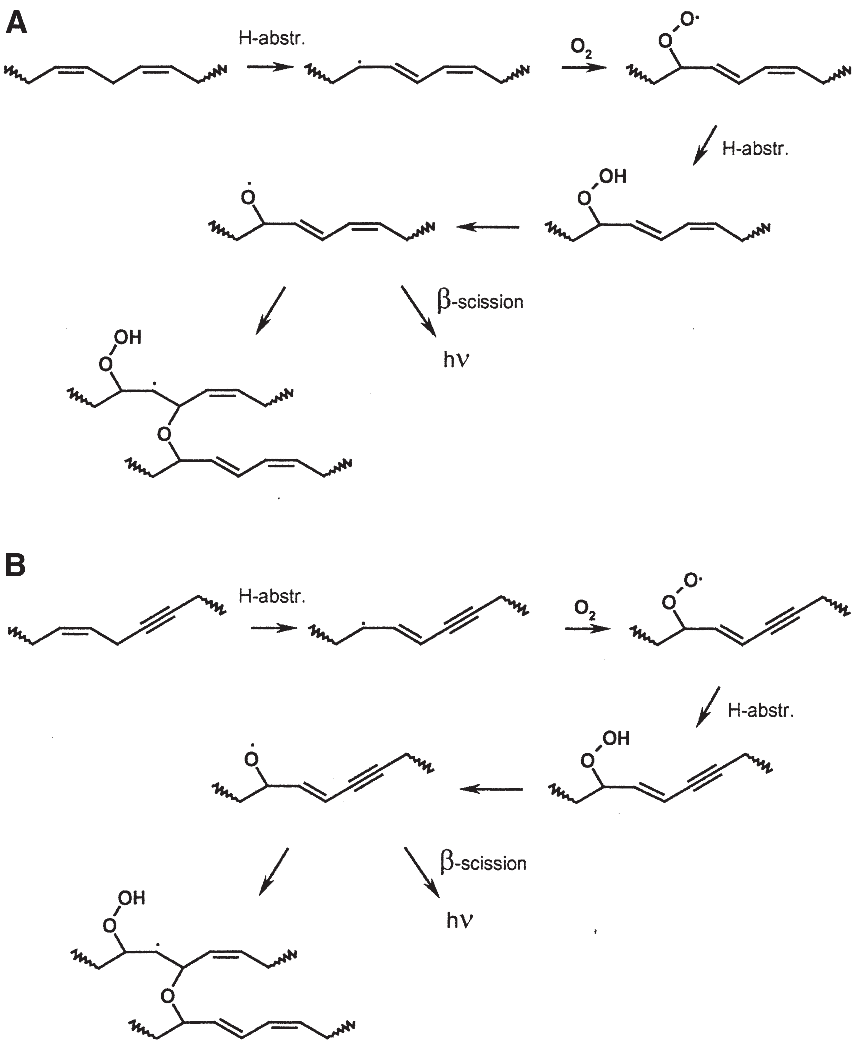

FIG. 2. Schematic oxidation of a linoleate (A) and a crepenynate structure (B).

at ~955 cm^{-1}, and a larger fraction will undergo β-scission instead, since crepenynate emits far more light in the CL measurements than linoleate (as discussed below and shown in Figs. 3 and 4). This indicates that the reactivity of the double bond toward radical addition is decreased when conjugated with a triple bond. It also shows a slightly shorter induction time than methyl linoleate as determined by CL. The induction time difference is smaller when measured with IR.

Comparison of methyl esters and model oils. Both TMP-trilinoleate and TMP-tricrepenynate exhibit longer induction times compared to the methyl esters. This behavior may be due to viscosity, since a higher viscosity is likely to decrease the mobility of the molecules in the film. The viscosity of the model oils is in approximately the same region as normal vegetable oils containing linoleic, linolenic, and oleic acids, which is about 10 times higher than the viscosity of the pure methyl esters. The pure methyl esters have viscosities between 3 and 7 mPa·s at 30°C (9).

The oxidation of the model oils follows the same reaction scheme as the methyl esters, but here there is also the possibility of intramolecular addition reactions. In the pure methyl ester, the formed alkoxy radicals will have a greater chance of undergoing β-scission, since there are no possibilities of intramolecular additions. The addition reactions would not result in any photons emitted, and this is suggested to be one of the reasons why the CL signal for the model oils appears later during oxidation than for the methyl esters.

There is a big difference in the consequences of β-scission of model oils compared with the methyl esters. When chain scission occurs in a small molecule such as a FA, two low-M.W. fragments are formed. When β-scission occurs in a larger molecule, a model oil, or a TG, only one volatile species would result, since the remaining part of the molecule still would be too large to be volatile.

In the oxidation of methyl linoleate, the CL signal appears after approximately 12 h, whereas the induction time for TMP-trilinoleate is about twice as long. However, the rate at which the unsaturations are rearranged into conjugated double

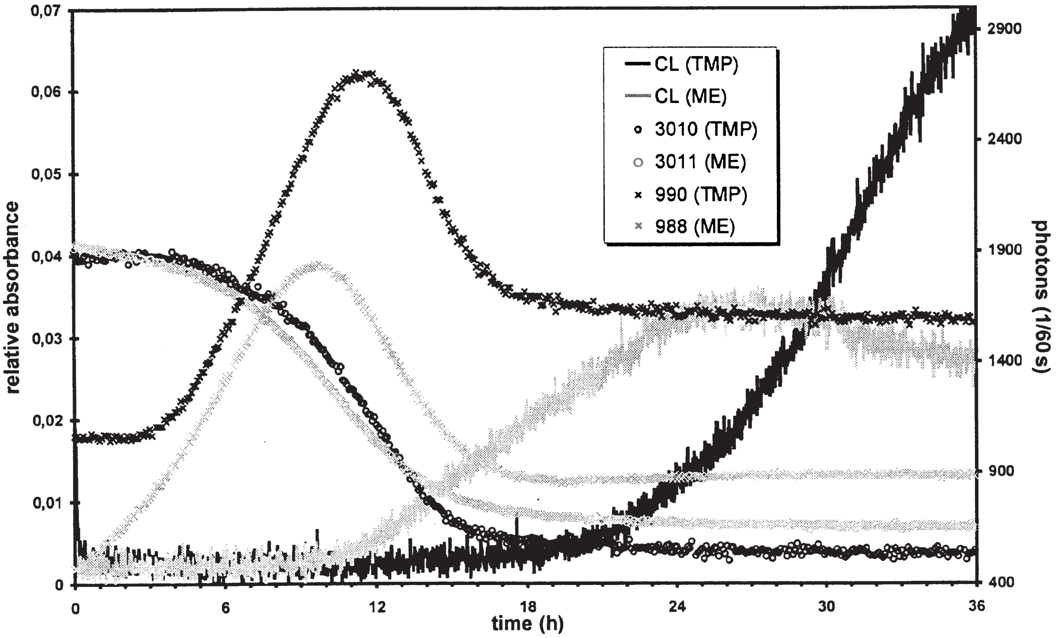

FIG. 3. IR absorbance profiles and chemiluminescence (CL) trace for methyl linoleate and TMP-trilinoleate. The values 3010, 3011, 990, and 988 represent wavelengths (cm^{-1}) at which absorbance was monitored. ME, methyl ester; for other abbreviation see Figure 1.

bonds is not very different for the model oils and the methyl esters, as seen in the absorbance profiles of the time-resolved IR spectra in Figure 3.

In TMP-trilinoleate, the CL signal appears when all the unconjugated *cis*-unsaturations at ~3010 cm^{-1} are consumed and converted into conjugated double bonds at ~970 cm^{-1}. Also, as they are formed, the *trans*-conjugated unsaturations are disappearing due to addition reactions with radicals present in the system. The CL signal does not increase until most of the conjugated *trans*-double bonds have been consumed. This indicates a

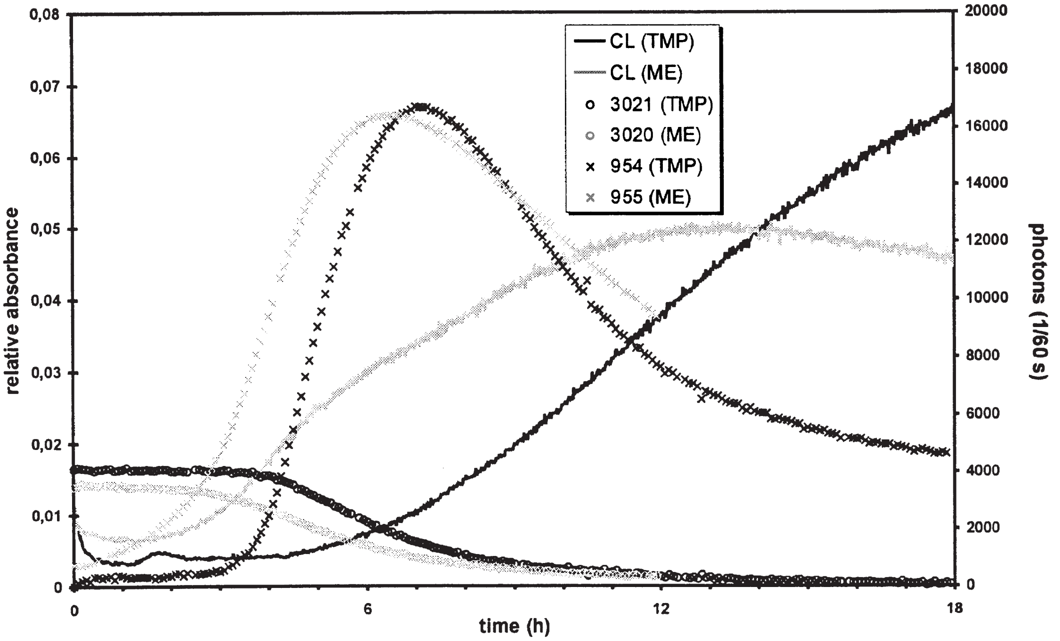

FIG. 4. IR absorbance profiles and CL trace for methyl crepenynate and TMP-tricrepenynate. The values 3020, 3021, 954, and 955 represent wavelengths (cm^{-1}) at which absorbance was monitored. For abbreviations see Figures 1 and 3.

large rate difference between addition of oxygen-centered radicals to conjugated double bonds and β-scission. This is a somewhat different behavior compared with that of methyl linoleate, where the CL signal appears when the concentration of conjugated *trans*-double bonds reaches its maximum. This supports the theory that the increased possibility of intramolecular reactions in the model oils suppresses chain scission reactions.

In both methyl crepenynate and TMP-tricrepenynate, the induction time seen with CL is much shorter than the induction times for methyl linoleate and TMP-trilinoleate. The two systems look almost the same: The CL signal appears at the same time as the disappearance of unconjugated *cis*-unsaturations with absorbance at ~3020 cm^{-1} (Fig. 4). This implies that only a small fraction of the alkoxy radicals adds to the double bonds instead of undergoing β-scission. If addition reactions were prevailing, the β-scission would be suppressed and the CL signal would be delayed and weaker, as in the case with TMP-trilinoleate.

Comparing the residual specimens of the methyl esters and the model oils after the CL measurements also supports the theory that higher functionality not only increases the possibility of intramolecular reactions but also suppresses chain scission reactions. The model oils become highly viscous liquids or solid films, whereas the samples of the methyl esters almost disappear due to formation of volatile compounds.

If a vegetable oil or a methyl ester is to be used as a reactive diluent, it is obviously desirable to have a high level of addition compared to β-scission, since the scission in FA chains yields low-M.W. volatile compounds. By changing the FA composition of a vegetable oil, it may be possible to control the amount of volatiles formed during oxidation. The results presented imply that the CL signal can be used to monitor the oxidation and the formation of volatile compounds in a FA structure. By combining the CL measurements with RTIR data, information about the oxidation reactions can be obtained, giving a greater understanding of what reactions are occurring during oxidation and how they are related to each other.

The results also imply that a crepenynate structure, although it oxidizes quickly, is less suitable than a linoleate structure as a component in an air-drying coating system. Since the chain scission reactions prevailing in the oxidation of crepenynate do not contribute to the desired structure buildup, the oxidation will mainly yield low-M.W. volatiles and will not contribute to film drying.

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