

Study on Quantitative Analyses of Hydroperoxides and Alcohols by NMR Shift Reagent

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ABSTRACT

Recently, much literature concerning the effects of NMR shift reagents upon compounds with Lewis's basic functional groups have been reported. These literatures have shown the effects of NMR shift reagents upon hydroxyl, amino, carbonyl, ether, ester carbonyl, cyano, and epoxy compounds but not hydroperoxyl compounds. Chemical and paramagnetic shifts of protons in *t*-butyl and cumene hydroperoxides, *t*-butyl and 2-phenyl-2-propyl alcohols, and autoxidized methyl linoleate with incremental additions of an NMR shift reagent were determined. These experimental results indicated that each alcohol and hydroperoxide could be determined separately and quantitatively even in their mixtures. Moreover, this method can be recommended to obtain information about the structures of hydroperoxides, as well as alcohols.

INTRODUCTION

NMR is an extremely useful technique for the structural determinations of many types of organic compounds (1-11). Analyses of compounds with Lewis's basic functional groups by NMR shift reagents, such as Tris- β -diketone salts of Lanthanide, are interesting techniques to determine coupling constants and environments of groups. When an NMR shift reagent forms a complex with an electronegative functional group, an NMR shift is induced. Complex formations were divided into two types. One is due to an irreversible contact to induce a contact shift. Another is due to a reversible contact to induce a pseudocontact shift. An NMR shift by an NMR shift reagent is known to be induced by the change in the magnetic environment of protons due to forming a complex of an NMR shift reagent with an electronegative functional group in the fast reversible reaction. Therefore, NMR shifts of protons increase with incremental additions of shift reagents. Moreover, NMR shifts are much greater, as protons are nearer to an electronegative functional group. Consequently, NMR signals of protons can be shifted separately at different positions by distance from a coordination site.

Generally, NMR shift reagents are paramagnetic ionic types, such as Eu(III) and Pr(II). If NMR shift reagents can be applied to hydroperoxides, a clue in the determination of a hydroperoxide structure would result. Experimental results indicated that the NMR shift reagent induced the effective NMR shifts of hydroperoxides' protons. In this case, the two types of pseudocontacts upon two oxygen atoms in hydroperoxides occurred individually but not simultaneously. As this result, each NMR signal of protons in hydroperoxides was separated further into two peaks, respectively.

This separation of NMR signals for the same protons was characteristic in hydroperoxides with the two oxygen atoms as an electronegative functional group but not in alcohols. Ratios of two contact types in hydroperoxides changed with differences on structures in hydroperoxides and concentrations of an NMR shift reagent. Moreover, there were great differences between NMR shift intensities of protons in alcohols and hydroperoxides. At these points, alcohols and hydroperoxides could be quantified separately even in mixtures. Still, the results of IR spectra indicated that the coordination numbers of hydroperoxides to a shift reagent were considerably lower than their corresponding alcohols. The information concerning coordination numbers of alcohols and hydroperoxides to a shift reagent was obtained by determinations of IR spectra.

EXPERIMENTAL PROCEDURES

Sievers's reagent (2,2-dimethyl-6,6,7,7,8,8,8-hepta-fluoro-3,5-octanedione Europium $[C_{10}H_{10}F_7O_2]_3Eu$) (pre-sented hereafter as $Eu[fod]_3$) was used as a shift reagent. It was used in the anhydrous condition after drying for 1 week under 10^{-3} mmHg pressure on P_2O_5 . *t*-Butyl, 2-phenyl-2-propyl alcohols and cumene. *t*-butyl hydroperoxides were purified by evaporating operations. *Cis*-9, *cis*-12 methyl octadecadienoate (methyl linoleate, 99% gas liquid chromatography [GLC]) was autoxidized under the following conditions: oil thickness, 1.03mm, and reaction temperature, 36.5 ± 0.5 C, in an incubator. Commercial di-*t*-butyl peroxide and dicumene peroxide were used.

Alcohols, hydroperoxides, and peroxides were of high purities, as shown by GLC, NMR, and IR spectrophotometric analyses and determinations of peroxide values (12), melting points, and refractive indexes. Samples (2.50×10^{-4} mole) were put into NMR tubes with 5.0 mm diameter; and then purified carbon tetrachloride (0.40 ml), $Eu(fod)_3$ (0.00 - 2.50×10^{-4} mole), and a small amount of tetramethylsilane-carbon tetrachloride solution were added, respectively. NMR spectra were run at 25 C on a Japan Electron Optics Lab. Co., model JNM-C-60HL high resolution spectrometer at 60 MHz. Coordination numbers were determined at 25 C with a grating IR spectrophotometer: Japan Spectroscopic Co., model DS-402G. A liter of carbon tetrachloride was prepared so as to contain 0.01 mole of an alcohol or a hydroperoxide. At this condition, only an absorption band due to a monomeric hydroxyl or a hydroperoxyl group was observed. Then, to these solutions were added various concentrations of $Eu(fod)_3$ (0.00 - 1.00 mole/mole of a substrate). These samples were determined using an IR spectrophotometer equipped with a 9.97 mm NaCl cell. The presumptions of coordination numbers of alcohols and hydroperoxides to NMR shift reagents by an

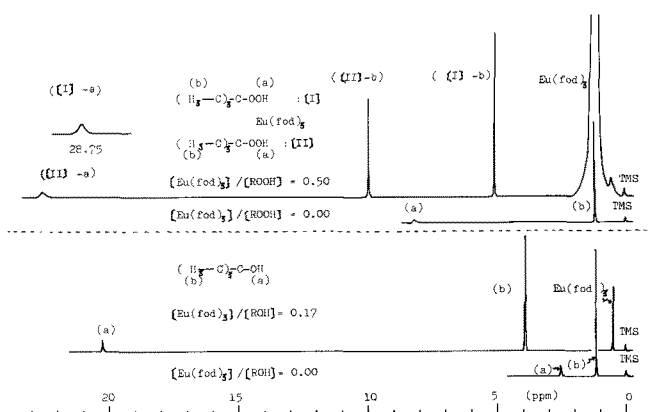


FIG. 1. NMR spectra of *t*-butyl alcohol and *t*-butyl hydroperoxide at the absence or the presence of $Eu(fod)_3$. TMS = 10 μ liter of 10% carbon tetrachloride solution, ROH = ROOH = 2.50×10^{-4} mole.

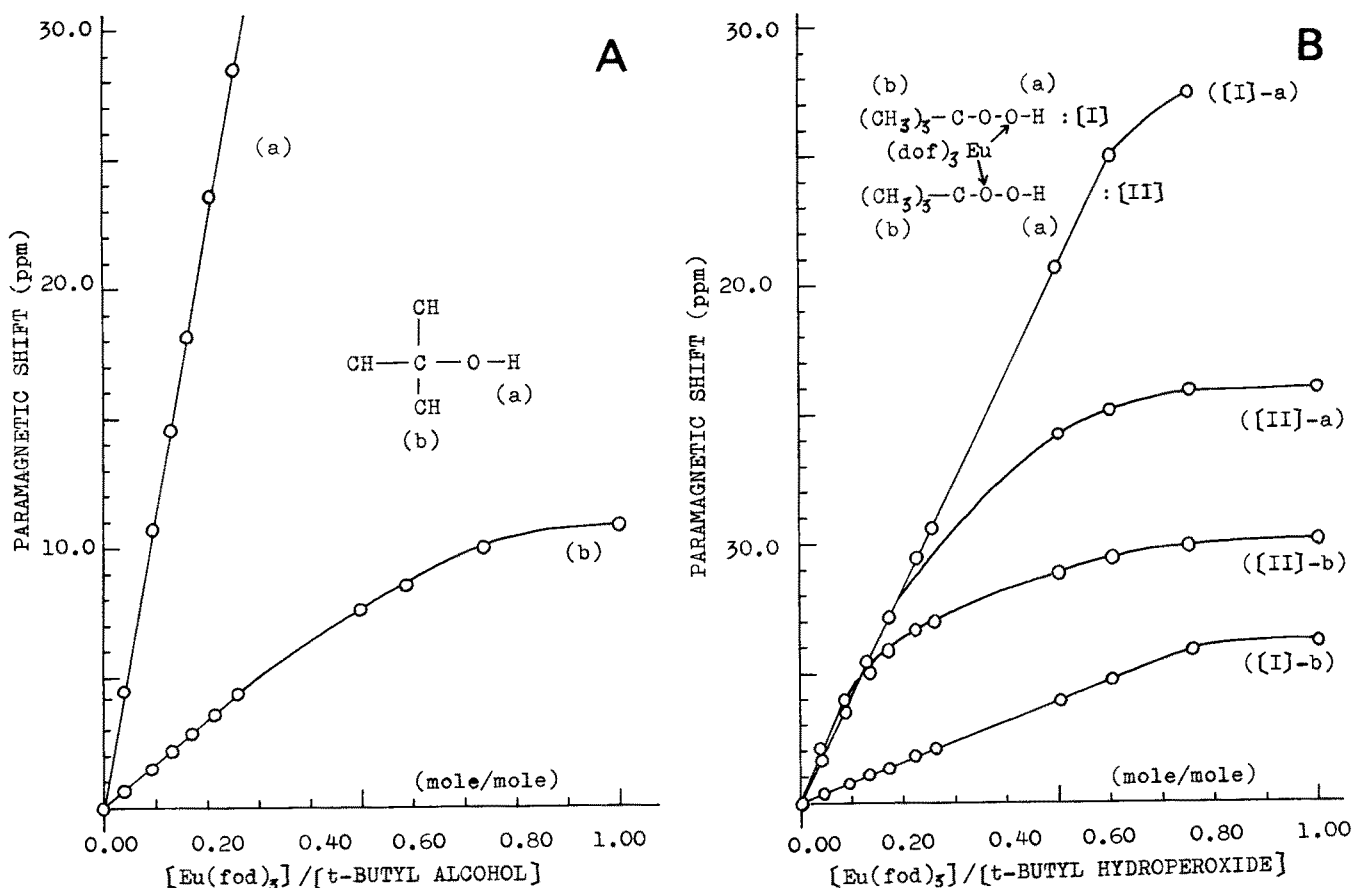
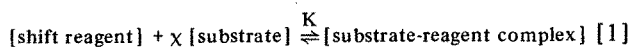


FIG. 2. Paramagnetic shift plots obtained from incremental additions of $Eu(fod)_3$ to t-butyl alcohol (A) and t-butyl hydroperoxide (B).

IR spectrophotometer have not been reported previously (13).

RESULTS AND DISCUSSIONS

NMR spectra of t-butyl alcohol and its hydroperoxide with and without $Eu(fod)_3$ are shown in Figure 1. In this study, all NMR signals of protons in used alcohols and hydroperoxides were seen to shift toward a low magnetic field, as shown in Figure 1. Also their shifts obviously were induced in the fast reversible reaction with a pseudocontact (equation 1, shown below), because NMR signals from protons belonging to an uncomplexed site were not observed at the determined concentration range of $Eu(fod)_3$:



This reversible reaction generally is known to be so rapid on the NMR time scale that the spectra present time averaged proton resonances and signals belonging to complexed or uncomplexed sites cannot be detected separately. The strength of a chemical shift (δ_{Eu}) is gained directly by the determination of an NMR spectrum. A paramagnetic shift (δ_{EuO}) is obtained from the following correlative equation with a chemical shift:

$$\delta_{EuO} = \delta_{Eu} - \delta_o [2]$$

where δ_o represents the chemical shift of the same protons in the absence of $Eu(fod)_3$.

The paramagnetic shifts of protons in t-butyl alcohol and t-butyl hydroperoxide, 2-phenyl-2-propyl alcohol and cumene hydroperoxide, and pure and autoxidized methyl linoleate with incremental additions of $Eu(fod)_3$ are shown in Figures 2, 3, and 4, respectively.

Each proton signal in the alcohols studied was shifted downfield in response to the distance from the reaction site producing the pseudocontact of $Eu(fod)_3$ with the oxygen atom of a hydroxyl group.

The methylene protons in long chain alcohols present one overlapped signal in normal NMR spectra, but individual analyses of methylene protons at the fifth carbon from a hydroxyl group has been possible using a shift reagent. On the contrary, NMR signals from protons in hydroperoxides in the presence of $Eu(fod)_3$ were remarkably different from those of alcohols as shown in Figure 1. The NMR spectra of hydroperoxides in the presence of $Eu(fod)_3$ were peculiar at the points discussed below. (A) The NMR signals from protons in hydroperoxides in the presence of $Eu(fod)_3$ were more complex than expected from their substrates. For instance, the NMR spectrum of t-butyl hydroperoxide, as shown in Figure 1, showed four separate singlet signals in the presence of $Eu(fod)_3$, although the NMR spectrum in the absence of $Eu(fod)_3$ showed one singlet signal for each methyl and hydroperoxyl proton. Mixtures of t-butyl alcohol and t-butyl hydroperoxide yielded three signals for methyl or hydroxyl and hydroperoxyl groups. (B) Integral ratios of the hydroperoxides' proton signals varied with the concentration of $Eu(fod)_3$; these variations of integral ratios in discrete NMR signals were linear with the concentration of $Eu(fod)_3$ (Fig. 5). The totals of each separated signals, both increasing and decreasing intensity, were constant and independent of the concentration of $Eu(fod)_3$. These coincided with the theoretical ratios of hydroperoxides' protons. For instance, the integral ratios of the peaks I-a, II-a, I-b, II-b in the spectrum of t-butyl hydroperoxide, as shown in Figure 1, varied linearly with the concentration of $Eu(fod)_3$. I-a and I-b values tended to decrease with the incremental additions of $Eu(fod)_3$, those from II-a and II-b exhibited the opposite relationship.

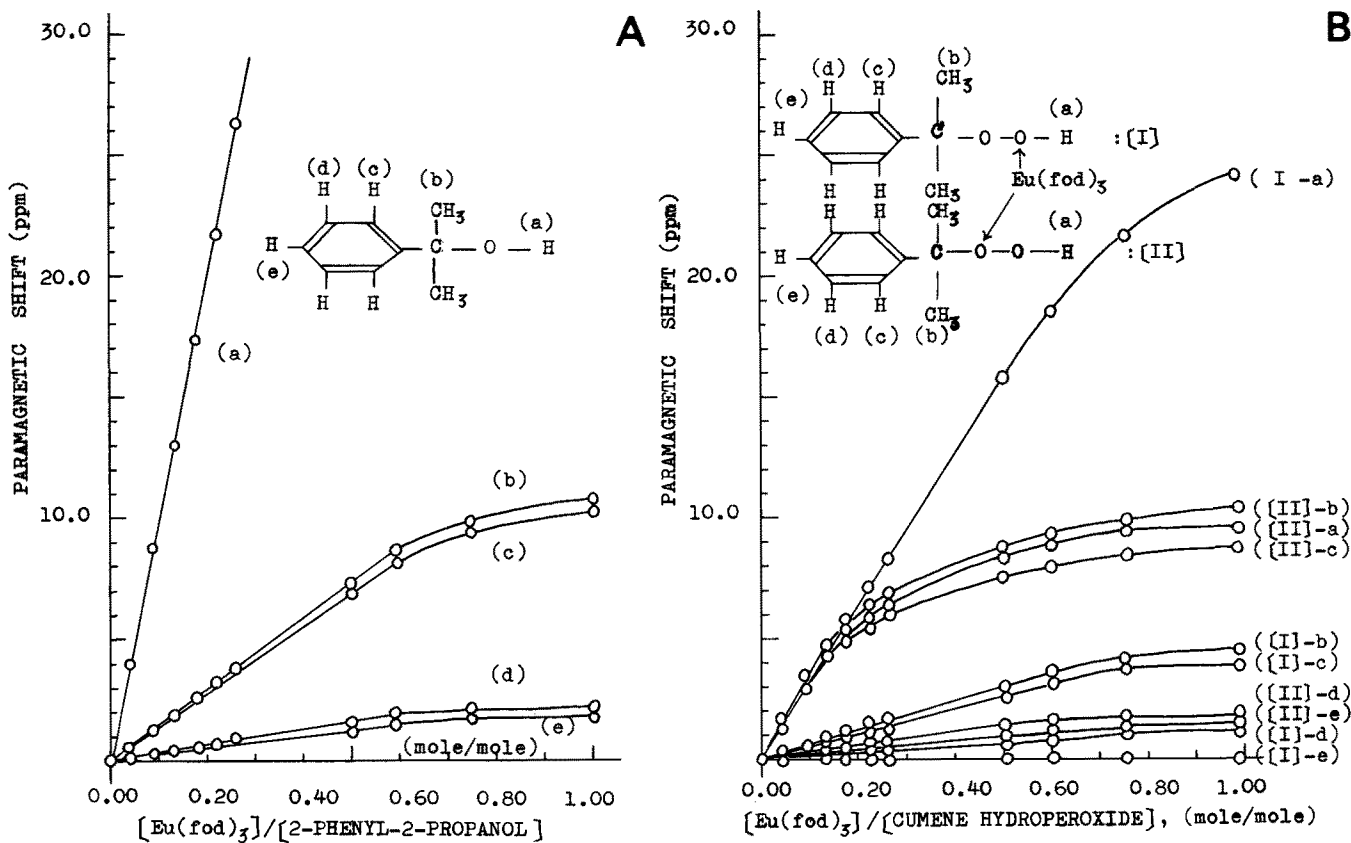


FIG. 3. Paramagnetic shift plots obtained from incremental additions of $\text{Eu}(\text{fod})_3$ to 2-phenyl-2-propyl alcohol (A) and cumene hydroperoxide (B).

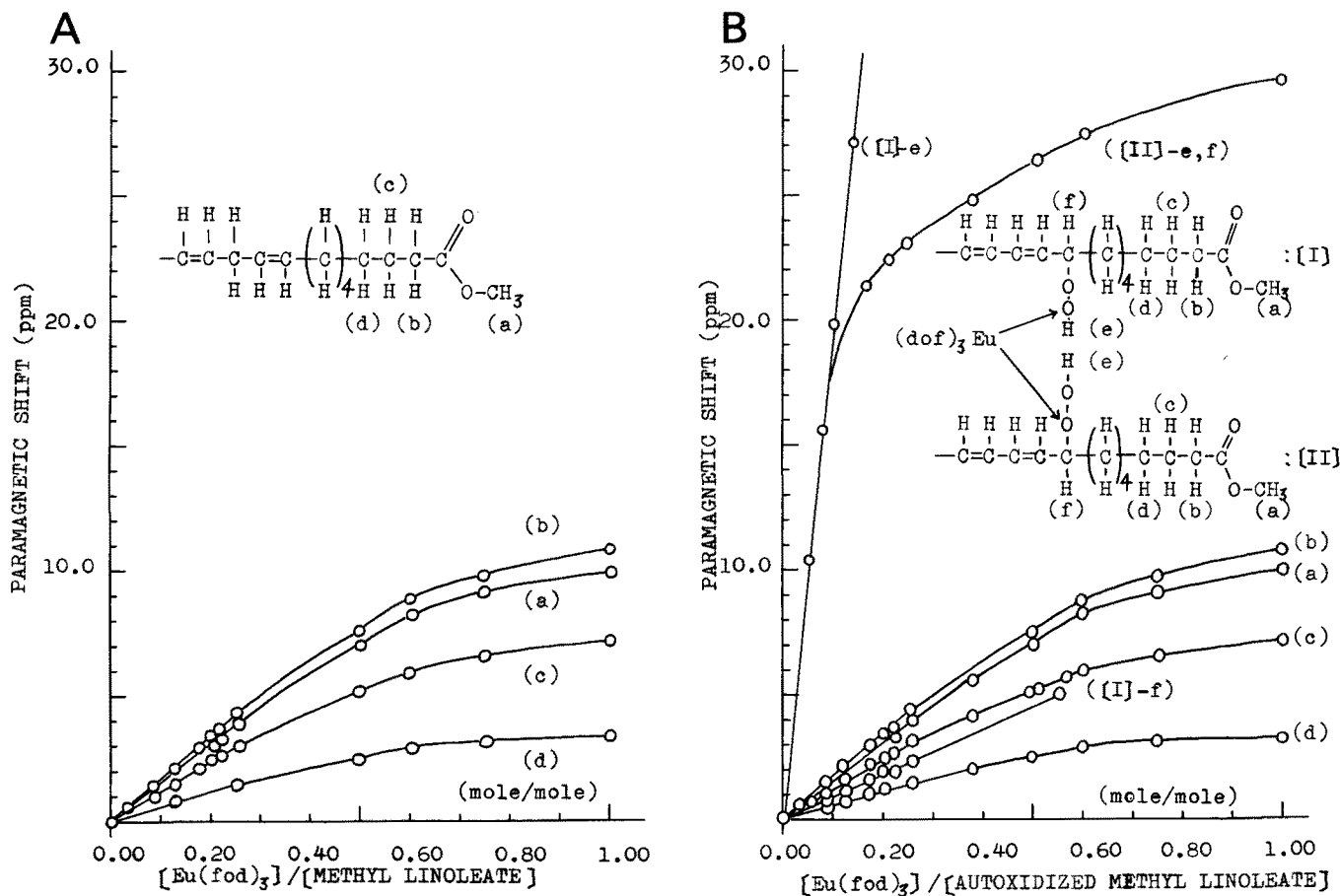
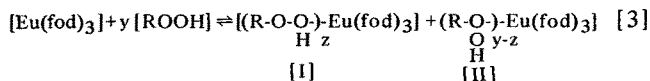
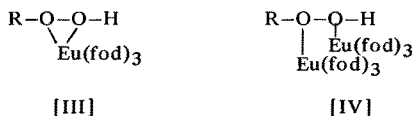


FIG. 4. Paramagnetic shift plots obtained from incremental additions of $\text{Eu}(\text{fod})_3$ to methyl linoleate (A) and autoxidized methyl linoleate (B).

These sums of I-a and II-a, and I-b and II-b signal areas were constant and independent of the concentration of $\text{Eu}(\text{fod})_3$. The ratio of these coincided with the ratio of hydroperoxyl to methyl protons. From the results obtained, it was concluded that the two types of pseudocontacts on two oxygen atoms in hydroperoxides occurred individually but not simultaneously (equation 3) and so the two types of different NMR shifts were induced.



ROOH in equation 3 presents a hydroperoxide. In addition to the formation of I and II, the formation of III or IV can be considered.



The formation of III or IV was denied by the reasons discussed below. (C) Their formation cannot explain the evidences of (A) and (B) as mentioned above. (D) Their formation does not explain the fact that NMR shift intensities of the two separated signals for each proton were considerably different. (E) If the formation of III or IV occurs, I and II can be produced naturally; then three or four signals for each proton should be observed. However, in practice, only two signals were observed. (F) The formation of IV may be difficult at the point of steric hindrance. The NMR signals of the protons in dicumene and di-*t*-butyl peroxides were not shifted with $\text{Eu}(\text{fod})_3$. This likely may have been due to their steric hindrance. Therefore, the experimental results may be explained by the formations of complexes with structures I and II.

The ratios of two contact types in hydroperoxides were obtained from calculations of quantitative ratios of the two discrete signals for each proton in the NMR spectra based upon the formation of complexes I and II (Fig. 5). For instance, the ratio of two contact types at one concentration of $\text{Eu}(\text{fod})_3$ in *t*-butyl hydroperoxide was presented by the integral ratio of I-a to II-a or I-b to II-b as shown in Figure 1. The ratio of I-a to II-a always was equal to the ratio of I-b to II-b. The contacts of $\text{Eu}(\text{fod})_3$ on the two oxygen atoms in hydroperoxides cannot be made at a constant ratio but varied with the concentration of $\text{Eu}(\text{fod})_3$; however the complex formation of II was preferred at high concentrations of $\text{Eu}(\text{fod})_3$. The preferential formation of complex I at low concentrations of $\text{Eu}(\text{fod})_3$ may be understood by consideration that $\text{Eu}(\text{fod})_3$ was compelled to have a higher coordination number, because the concentrations of hydroperoxides were relatively greater, this might be relieved, and so the complex formation of II is increased. Eventually, the fact that the complex formation of II was preferred as the effect of steric hindrance decreased is likely, based upon the differences of electron densities (14,15) between the two oxygen atoms in hydroperoxides. The effect of steric hindrance was indicated by the fact that the degree of the complex formation of II in autoxidized methyl linoleate was always much more than that of *t*-butyl and cumene hydroperoxides at the same concentration of $\text{Eu}(\text{fod})_3$. At concentrations greater than 0.55 mole of $\text{Eu}(\text{fod})_3$ /mole of substrate, the formation of essentially only II was recognized.

The suggestion of the formation of the complexes with structures I and II in hydroperoxides was supported by the results of IR spectra determined in the presence of $\text{Eu}(\text{fod})_3$. The change of the stretching vibrational band due to a monomeric hydroxyl or a monomeric hydroper-

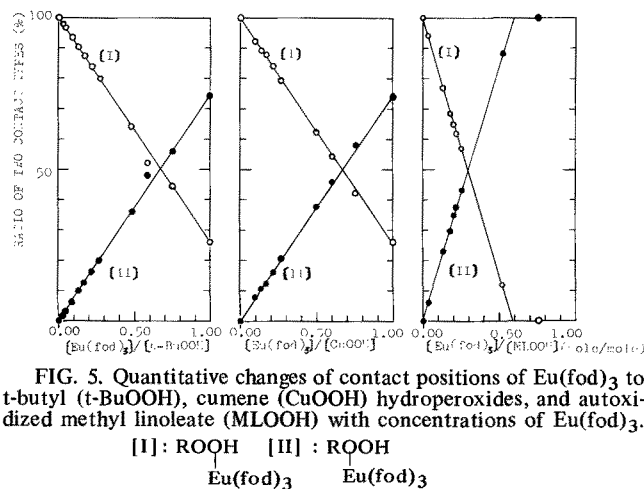
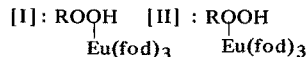


FIG. 5. Quantitative changes of contact positions of $\text{Eu}(\text{fod})_3$ to *t*-butyl (*t*-BuOOH), cumene (CuOOH) hydroperoxides, and autoxidized methyl linoleate (MLOOH) with concentrations of $\text{Eu}(\text{fod})_3$.



oxyl group was compared with each of their blanks of $\text{Eu}(\text{fod})_3$ (13). The absorption bands at 3610-3640 cm^{-1} due to monomeric noncomplexed hydroxyl groups disappeared gradually with the incremental additions of $\text{Eu}(\text{fod})_3$, and new absorption bands based upon complexed substrates appeared at 50-90 cm^{-1} lower frequencies. The stretching vibrational bands at 3540-3560 cm^{-1} , due to monomeric hydroperoxyl groups, disappeared with the incremental additions of $\text{Eu}(\text{fod})_3$ and, in place of these, two new absorption bands, appeared at 110-150 and 180-190 cm^{-1} lower frequency (Table I). The ratios of the absorbancy index between these two new absorption bands varied with the concentration of $\text{Eu}(\text{fod})_3$ as predicted by the NMR spectra. Deviations ($\Delta\nu$) between absorption bands due to complexes and noncomplexes were almost parallel with intensities of paramagnetic shifts of protons in the NMR spectra of complexes for identical coordination numbers. Other experimental results in various alcohols showed that $\Delta\nu$ and the paramagnetic shifts of their protons in their NMR spectra for identical coordination numbers were much greater in the order of primary < secondary < tertiary alcohols. Paramagnetic shifts in NMR spectra of protons in alcohols with identical coordination numbers

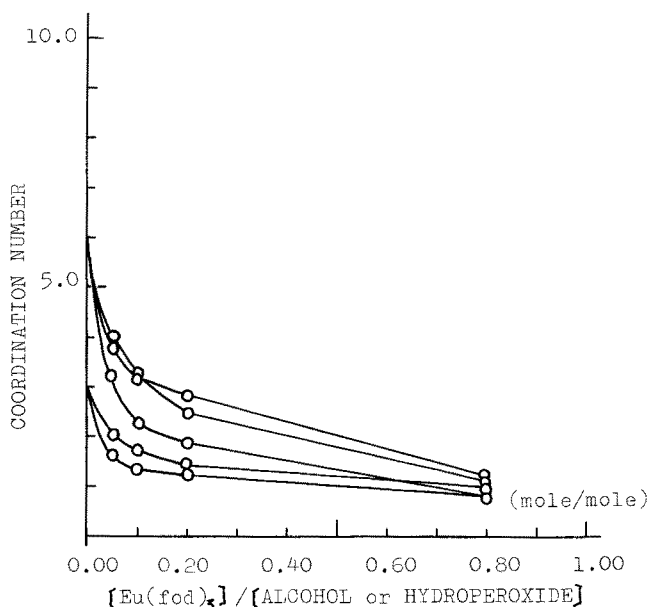


FIG. 6. Relations between $\text{Eu}(\text{fod})_3$ concentrations and coordination numbers by IR spectrophotometer. Autoxidized methyl linoleate, 6; *t*-butyl alcohol, 6; 2-phenyl-2-propyl alcohol, 6; cumene hydroperoxide, 3; and *t*-butyl hydroperoxide, 3; (listed from top to bottom).

TABLE I
Characteristic Tables Measured with NMR and IR Spectrometers^a

Sample	NMR spectra								
	Sao	Ga	Gac	Sbo	Gb	Gbc	Sco	Gc	Gcc
t-BuOH	2.56	109.5	142.4	1.18	16.8	22.5			
2- -2-PrOH	2.53	100.8	134.4	1.44	15.1	20.1	7.32	14.5	19.3
Cumene-OOH	7.67	33.9	90.4	1.54	39.2	104.5	7.37	32.7	87.2
t-BuOOH	8.27	25.2	67.2		5.7	15.2		6.0	16.0
		43.7	116.5	1.20	43.9	117.1			
		28.4	75.7		8.4	22.4			
Autoxidized methyl linoleate	8.45	124.0	165.3	4.20	175.0	233.0			
		199.0	265.0		8.8	11.7			

Sample	NMR spectra						IR spectra			
	Sdo	Gd	Gdc	Seo	Gec		ν_o	ν_s	Δf	DN
t-BuOH							3620	3540	-80	6
2- -2-PrOH	7.22	3.0	4.0	7.14	2.9	3.9	3600	3530	-70	6
Cumene-OOH	7.34	2.1	5.6	7.16	1.6	4.3	3550	3400	-150	3
		1.2	3.2		0.0	0.0		3360	-190	
t-BuOOH							3560	3430	-130	3
								3370	-190	
Autoxidized methyl linoleate							3540	3430	-110	6
								3360	-180	

^aSao-Sco: situations in the absence of $\text{Eu}(\text{fod})_3$, a-e: as shown in Figure 1, 2,3,4. Ga-Ge: G-values. Gac-Gec: corrected G-values to 8 holds coordination numbers. ν_o : absorption bands of hydroxyl or hydroperoxyl groups due to nonassociating substrates. ν_s : absorption bands due to complexes with $\text{Eu}(\text{fod})_3 \cdot \Delta\nu = \nu_o - \nu_s$. CN = coordination numbers.

increased as the position of methyl groups came nearer to their functional groups, and they were decreased by the presence of a double bond or a phenyl group at the β -position. These effects indicate that the pseudocontacts on electron rich oxygens are tight and compact.

The coordination numbers of alcohols and hydroperoxides at various concentrations of $\text{Eu}(\text{fod})_3$ were calculated individually from the disappearance of their absorption bands due to nonassociating noncomplexed substrates (Fig. 6).

It is natural that the coordination numbers of alcohols and hydroperoxides to $\text{Eu}(\text{fod})_3$ were reduced with incremental additions of $\text{Eu}(\text{fod})_3$, because the coordination numbers that $\text{Eu}(\text{fod})_3$ can hold are dependent upon the relative concentrations of $\text{Eu}(\text{fod})_3$ to substrates. This explains why NMR shifts produced by $\text{Eu}(\text{fod})_3$ did not become parallel with high concentration of $\text{Eu}(\text{fod})_3$ /mole of substrate. From this point of view real coordination numbers are likely obtained at much lower molar concentration of $\text{Eu}(\text{fod})_3$ /mole of substrate. Therefore, when extrapolated to an infinite dilute concentration of $\text{Eu}(\text{fod})_3$ /mole of substrate, the data obtained may be regarded as the real coordination number (Table I).

Coordination numbers of substrates to $\text{Eu}(\text{fod})_3$ were eight in primary and secondary alcohols, six in tertiary alcohols, three in cumene and t-butyl hydroperoxides, and six in autoxidized methyl linoleate. These data show that the coordination numbers of hydroperoxides are considerably lower than the corresponding alcohols. The effects of $\text{Eu}(\text{fod})_3$ upon the paramagnetic NMR shifts of alcohols or hydroperoxides are shown in Table I. The intensity of the paramagnetic shift of the hydroperoxyl proton in autoxidized methyl linoleate was greater than in t-butyl and cumene hydroperoxides. This phenomenon may be explained in terms of coordination numbers and content ratios between the formation of complexes I and II. Coordination numbers of t-butyl and cumene hydroperoxides were ca. half in the case of autoxidized methyl linoleate. Moreover t-butyl and cumene hydroperoxides required ca. 2.3 times in mole of $\text{Eu}(\text{fod})_3$ /mole substrate to gain an identical content of the I or II formation. Therefore, intensities of the paramagnetic shifts of protons observed

experimentally in t-butyl and cumene hydroperoxides are 1/4.6 in the case in autoxidized methyl linoleate. The slight difference between shifts of protons in cumene and t-butyl hydroperoxides is due to the effects of electron densities as recognized in alcohols. The induced NMR shifts are dependent upon how tight the bonds of substrates with $\text{Eu}(\text{fod})_3$ are. The effects of electron densities are as expected by consideration of the $\Delta\nu$ values in Table I. Calculations of NMR shifts induced by $\text{Eu}(\text{fod})_3$ /identical contact units of substrates (the same coordination numbers and the same contents of the contacts) show that the real paramagnetic shifts of protons in hydroperoxides are greater than in alcohols.

McConnell, Robertson and LaMar (16,17) have reported that pseudocontact shifts with paramagnetic reagents depended upon the distance (r_i) between the i-th proton from a functional group and a metal ion, and the angle (ϕ_i) between the i-th proton and the principal axis (equation 4):

$$\Delta H_i/H_p = K (3\cos^2\phi_i - 1)/r_i^3, \quad [4]$$

where K is a constant for any given molecule at a known temperature. Induced paramagnetic shifts of protons in each of alcohols and hydroperoxides seemed to follow r and ϕ factors in the McConnell and Robertson formula. The determination of paramagnetic shift intensities of protons in each of alcohols and hydroperoxides showed that induced NMR shifts became greater as the protons in complex came nearer to a functional group. However, the comparison of induced NMR shifts with $\text{Eu}(\text{fod})_3$ between different substrates cannot always be done as coordination numbers (18) to $\text{Eu}(\text{fod})_3$. Electron densities (14,15) of functional groups and quantitative ratios of the formation of complexes I and II in hydroperoxides are different between substrates. Therefore, the McConnell and Robertson formula should be adopted for substrates under the same condition factors discussed above or in the same molecule.

NMR signals for hydroperoxyl and hydroxyl protons were either not observed or were not quantitative in the absence of $\text{Eu}(\text{fod})_3$. This was alleviated with the use of $\text{Eu}(\text{fod})_3$. The associations of hydroperoxides or alcohols are lessened by fast reversible reactions in states of

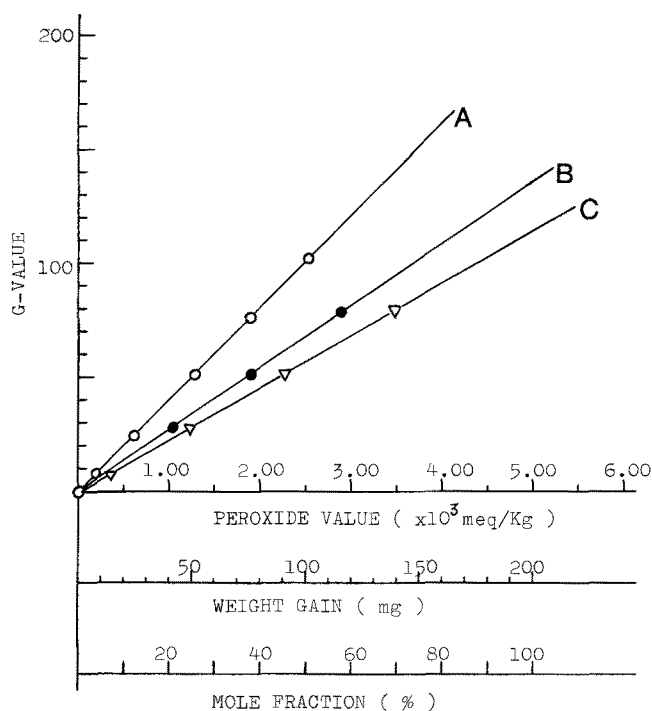


FIG. 7. Relations between G-values and (A) weight gains (mg), (B) mole fractions (%), and (C) peroxide values (KI-method) in the autoxidized methyl linoleate.

equilibrium. The experimentally observed induced NMR shifts were obviously different between alcohols and hydroperoxides. Moreover, the induced NMR shifts of protons in autoxidized methyl linoleate with contacts of hydroperoxyl groups to $\text{Eu}(\text{fod})_3$ were greater than with contacts of ester carbonyl groups. Autoxidized methyl linoleates at various oxidation steps were mixtures of non- and autoxidized substrates, but extrapolations of paramagnetic shifts for hydroperoxide concentrations in mixtures agree with the paramagnetic shifts for the sum of two moles of hydroperoxides and one mole of nonoxidized parts. This fact can be supported by the evidence that paramagnetic shifts with the contacts on ester-carbonyl groups remained constant in pure and autoxidized methyl linoleate. Therefore it was concluded that induced NMR shifts of protons in pure compounds are the same as in mixtures, if the quantities of functional groups present are considered. In autoxidized methyl linoleate NMR signals for the (E) and (F) protons in Figure 4 were superimposed. Contents of hydroperoxides may be determined directly by the ratios of their areas at the concentrations of $\text{Eu}(\text{fod})_3$, such that more complexes of I or II were formed. Good correlations of their areas with peroxide values were gained at 0.00-0.10 mole of $\text{Eu}(\text{fod})_3$ /mole of substrate in *t*-butyl and cumene hydroperoxides and at over 0.55 mole of $\text{Eu}(\text{fod})_3$ /mole of substrate in autoxidized methyl linoleate. Correlations between G-values (paramagnetic shifts [ppm]/mole of $\text{Eu}(\text{fod})_3$ /mole of substrate) of hydroperoxyl protons for the II type complex and peroxide values, G-values and wt gains during autoxidations (19-21), and G-values and mole fractions of hydroperoxides in autoxidized methyl linoleate are shown in Figure 7.

Therefore, other quantitative analyses of hydroperoxides in the presence of $\text{Eu}(\text{fod})_3$ can be made indirectly by the determinations of their G-values or induced shift intensities at a certain concentration of $\text{Eu}(\text{fod})_3$. It goes without saying that the quantitative analyses of alcohols can be done by the same techniques.

Alcohols produced during autoxidations of methyl linoleate were unfortunately not detected with the NMR spectrometer. It was, however, confirmed in mixtures of

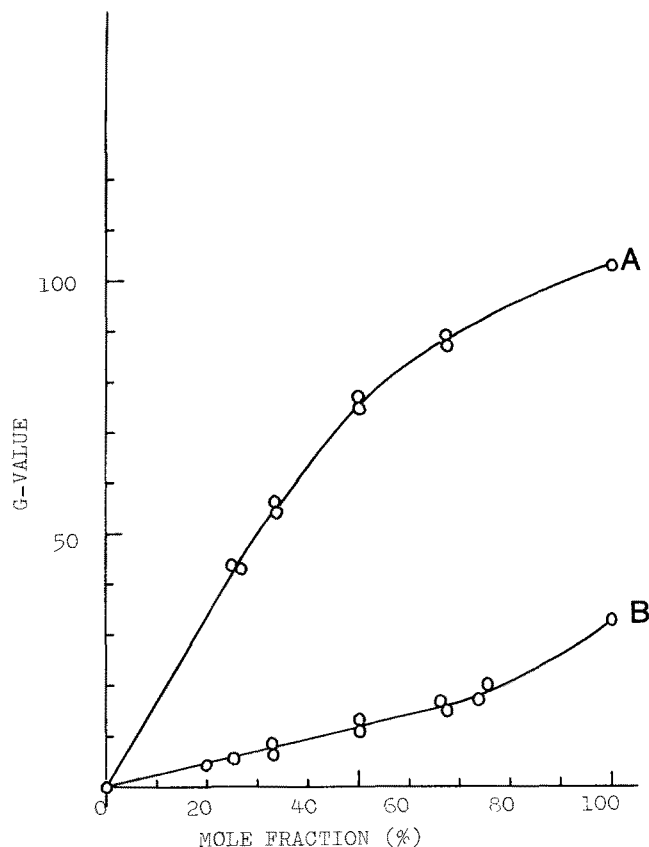


FIG. 8. Relations between G-values and mole fractions in mixtures of 2-phenyl-2-propyl alcohol A and cumene hydroperoxide B.

cumene hydroperoxide and 2-phenyl-2-propyl alcohol that the contents of alcohols and hydroperoxides could be quantified separably even in their mixtures. The correlations between G-values (for the II complex in the hydroperoxide) and mole fractions of their mixtures are shown in Figure 8.

Contents of hydroperoxides and alcohols can be quantified separably even in their mixtures by using these correlations if their G-values or NMR shift intensities at a certain concentration of $\text{Eu}(\text{fod})_3$ are obtained.

As mentioned above, an estimation of the quantities of alcohols and hydroperoxides in the presence of $\text{Eu}(\text{fod})_3$ can be made directly by the comparison of their areas in NMR spectra and indirectly by the determinations of their G-value or NMR shift intensities at a certain concentration of $\text{Eu}(\text{fod})_3$. Also the differences in their structures induced different chemical and paramagnetic shifts of their protons. These differences in induced NMR shifts may be corrected by considerations of their coordination numbers, electron densities of functional groups, and types of complex formations. This method of using an NMR shift reagent not only is effective to quantify contents of alcohols and hydroperoxides, but also offers much information to assist in determining their structures. Moreover, the highly sensitive detection of alcohols may be possible if NMR shift reagents can be applied to trimethyl silylated alcohols.

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