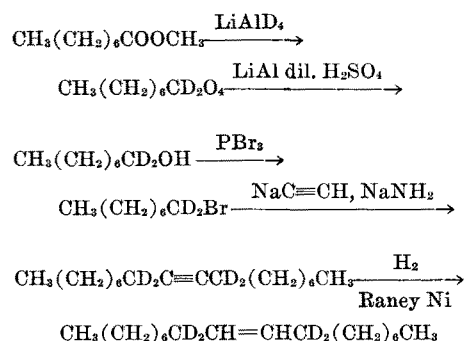


# The Synthesis and Autoxidation of 8,8,11,11-Tetradeutero- Cis-9-Octadecene<sup>1,2</sup>

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IN a previous paper Khan, Brown, and Deatherage (1) have reported on the autoxidation of methyl 9,10-dideuterooleate in studying the role of olefinic hydrogen and deuterium in the formation of water during the autoxidation of fats. Since Deatherage and Mattill (2) have shown that *cis*-9-octadecene and methyl oleate are autoxidized in a similar way, a study of the autoxidation of 8,8,11,11-tetradeutero-*cis*-9-octadecene might give useful information on the role of the hydrogen atoms  $\alpha$  to the double bond in the formation of water. This is of particular interest since it has often been inferred that water is formed from the decomposition of the hydroperoxide,  $-\text{CH}=\text{CHCHOOH}-$ . By using the methyl deuteriooleate and comparing its autoxidation with methyl oleate and methyl stearolate, the importance of the olefinic position as suggested by Gunstone and Hilditch (3) and of the alpha position as shown by Farmer (4, 5) has been confirmed. In this same study Khan *et al.* (1) found evidence for the early formation of water during the course of the autoxidation reactions.

The synthesis of 8,8,11,11-tetradeutero-*cis*-9-octadecene was carried out as follows:



The above syntheses were perfected in the preparation of *cis*-9-octadecene, which was made in the same manner except that lithium aluminum hydride was used instead of lithium aluminum deuteride.

The autoxidation studies of these two octadecenes were carried out in a manner similar to that reported by Deatherage and Mattill (2) and Khan *et al.* (1).

## Preparation of Materials

*n*-Octyl alcohol. This was prepared from methyl caprylate by the method of Nystrom and Brown (6), using lithium aluminum hydride. The yields based on the hydride were 80-90%.

*n*-Octyl bromide. 20 g. (0.154 mole) of *n*-octyl alcohol was placed in one 3-neck 500-ml. flask equipped with dropping funnel, stirrer, and condenser with HBr trap. 38.0 g. (0.1 mole) of phosphorus tribromide was gradually added with stirring. By use of

an oil bath at 120°C. reflux was maintained for eight hours. After cooling, the flask contents were transferred to a separatory funnel and washed with concentrated sulfuric acid three times. The combined washings were extracted with 100 ml. petroleum ether and the resulting extract added to the crude bromide. This ether mixture was washed with water, then sodium bicarbonate solution, and then water to neutrality. After drying the ether solution with anhydrous sodium sulfate, the ether was removed and the bromide distilled at 99°C. and 32 mm. Hg. Yields of *n*-octyl bromide of 85-95% were obtained. Distillation residues were retained for reworking with subsequent runs.

*9*-Octadecene. 40 g. (0.2 mole) of *n*-octyl bromide was placed in a Parr bomb, which was then closed and cooled in dry ice. Next 3.9 g. (0.1 mole) of sodium amide and 4.8 g. (0.1 mole) of monosodium acetylide were weighed into small bottles, stoppered, and then cooled in dry ice. The sodium amide and monosodium acetylide had previously been made in larger quantities by the method of Greenlee (7). When the bomb and contents had cooled below  $-40^\circ$ , the bomb was opened and 75 ml. of liquid ammonia, the sodium amide, and the monosodium acetylide were quickly added. The bomb was immediately closed and sealed. The temperature of the bomb and contents gradually increased and exceeded room temperature. Within an hour the temperature began to drop, and the bomb was then gently agitated for 36-48 hours. Next the bomb was cooled in dry ice and opened. Approximately 50 ml. of water was cautiously added dropwise over a period of 30-50 min. This mixture was transferred to a 1-l. separatory funnel with 300 ml. of petroleum ether. The aqueous phase was separated and extracted with petroleum ether. The ether extracts were combined and washed four to six times with 1 N. hydrochloric acid and then with water until neutral. After drying the extract with anhydrous sodium sulfate and removing the solvent, the residue was fractionally distilled. Four to seven grams of impure 1-decene distilled at 50-65° and 32 mm. Hg. The next fraction was 13-17 g. of 9-octadecene coming over at 142-145° at 2 mm. Hg. The 9-octadecene had the following characteristics:  $d_{20}^{20}$ , 0.795;  $n_{20}^{20}$ , 1.4475; I. N. (iodine number) 98.

The 1-decene from several runs was accumulated and treated as above with sodium amide and *n*-octyl bromide in equivalent amounts to give more 9-octadecene.

The 9-octadecene can be prepared by carrying the reaction in one or two stages at atmospheric pressure and using a dry ice condenser for ammonia reflux as the work of Henne and Greenlee (8) suggests. This procedure is long, and the yields are lower. In fact, the best yields were obtained when the temperature of the bomb increased to about 70° and was maintained there for a few hours.

*cis*-9-Octadecene. Five g. of 9-octadecene was dissolved in 35 ml. cyclohexane and placed in a semi-

<sup>1</sup> Supported in part by a grant-in-aid from the Graduate School.  
<sup>2</sup> Journal article No. J 32-50 of the Ohio Agricultural Experiment Station, published with the permission of the assistant director.  
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micro hydrogenator as described by Joshel (9). 0.5 g.  $W_1$  Raney nickel was added and hydrogenation carried to the absorption of 1 mole of  $H_2$ . The hydrogenation was very selective, and hydrogen absorption stopped when 1.00 mole of  $H_2$  was taken up. Even when platinum oxide catalyst (10) was used to hydrogenate the octadecene to completion, there was a sharp drop in rate of hydrogen uptake after 1 mole of  $H_2$  was used. Four hydrogenations were carried out and the products combined after removal of the catalyst. The solvent was removed, and then 200 ml. of ethyl ether was added. This solution was allowed to crystallize at  $-40^\circ$  to  $-50^\circ$  when two crops of crystals were removed (approximately 2 g.). After removing the solvent from the residual solution, the octadecene was distilled at  $138-148^\circ$  at 2 mm. Hg. Yield: 12-17 g. *cis*-9-octadecene;  $d^{21}$ , 0.795;  $n^{21}$ , 1.4431; I. N. 99-100; C, H found 84.97% and 14.04%.

When this preparation of octadecene was subjected to autoxidation, there was very little  $O_2$  absorbed and no typical autoxidation took place. Even after redistillation the octadecene would not autoxidize. A trace of nitrogen was detected, and so the octadecene was purified as follows: 12 g. octadecene was dissolved in 30 ml. carbon tetrachloride, and bromine in carbon tetrachloride was added dropwise until the color of bromine remained; care was taken to keep the temperature at approximately  $0^\circ$ . Excess bromine was discharged with one drop of octadecene, and the resulting solution was extracted 15-20 times with concentrated sulfuric acid until the acid layer remained colorless. The 9,10-dibromoöctadecane solution was washed with water, 5% sodium bicarbonate solution, and again with water to neutrality. The solvent was removed and 40 g. anhydrous *n*-amyl alcohol and 8 g. zinc dust were added. This mixture was refluxed 12 hours, and then the zinc was removed by filtration from the hot solution. The solution was extracted with 1 N. HCl twice and with water until neutral. The alcohol was removed and the residue fractionally distilled yielding 6 grams of *cis*-9-octadecene of I. N. 99.

That the hydrogenation and subsequent bromination-debromination procedure yielded the *cis* configuration is indicated by the infra-red absorption spectrum, Figure 1. The repurified octadecene was used in the autoxidation studies.

*1,1-Dideutero-n-octyl alcohol.* The procedure described above for *n*-octyl alcohol was used except that lithium aluminum deuteride was used instead of the hydride. The deuteride was purchased from the Metal Hydrides Inc., Beverly, Mass., and was claimed to be 98.5% pure.

*1,1-Dideutero-n-octyl bromide.* This was prepared from 1,1-dideutero-*n*-octyl alcohol by the same procedure described above for *n*-octyl bromide.

*8,8,11,11-Tetradeutero-9-octadecene.* This compound was prepared from 1,1-dideutero-*n*-octyl bromide by the method given above for 9-octadecene. When distilling the products of the bomb reaction a solid material appeared in the distilling column when the octadecene distilled over. Further redistillations failed to remove this solid so it was removed by low temperature crystallization. The final product distilled at  $145^\circ$  at 2 mm. Hg. The infra-red absorption spectrum for this compound is shown in Figure

1 and a doublet indicating the deuterium can be seen at 4.64 and 4.84 microns.

*8,8,11,11-Tetradeutero-cis-9-octadecene.* The selective reduction of 8,8,11,11-tetradeutero-9-octadecene using  $W_1$  Raney nickel was carried out as with *cis*-9-octadecene. The bromination, sulfuric acid extraction, and debromination purification procedure was also carried out since the product without this purification failed to autoxidize in a typical manner. The final product had the following characteristics: B. P.  $139-140^\circ$  at 2 mm. Hg.;  $d^{21}$ , 0.795;  $n^{21}$ , 1.4431; I. N., 99; deuterium content 9.95 atoms % of hydrogen and deuterium (theory, 11.1). The infra-red absorption spectrum is shown in Figure 1 and shows the doublet at 4.64 and 4.84 microns, characteristic of  $-CD_2-$ .

### Methods

The autoxidations were carried out at  $75^\circ$  in the manner reported by Deatherage and Mattill (2). The analytical procedures were the same as by Khan, Deatherage, and Brown (1).

### Results and Discussion

It was quite unexpected that the original preparation of *cis*-9-octadecene did not autoxidize in view of its apparent purity from various physical and chemical characteristics. After 240 hours at  $75^\circ$  very little oxygen had been absorbed by seven grams of the hydrocarbon. A sample of the substrate was removed, and no more than a trace of peroxide was found. 100 mg. of linoleic acid was then added. Oxygen absorption started and then subsided, and after 60 additional hours the run was discontinued. 120 mg. of water was found in the first dry ice trap. The residue had a peroxide number of only 5, and the iodine number had decreased from 99 to 90. A negative Kreis test was observed, and no peroxide was found in the volatile matter.

The octadecene apparently contained some impurity which prevented autoxidation. The hydrocarbon was recrystallized from diethyl ether and after distilling again a seven-gram portion was placed in the autoxidation vessel with 32 mg. of linoleic acid. During 160 hours of exposure to  $O_2$  a small amount of oxygen was absorbed, yet the typical yellow to brown color of dehydrite (2) which is so characteristic of this type of study did not appear. The reaction was stopped. Only a trace of peroxide was found in the volatile material and residue. The iodine number had decreased from 100 to 93.5. The Kreis test was negative, and 50 mg. of water was found in the traps and somewhat less non-aqueous volatile matter. Hence something seemed to interfere with the reaction.

Since some of the synthetic work was done in liquid ammonia, it was considered that perhaps some nitrogenous compound might be the offending impurity. Analyses indicated a few hundredths per cent of N which did not decrease on repurification so the bromination, extraction with concentrated sulfuric acid, and debromination procedure was applied. This yielded *cis*-9-octadecene, which autoxidized in a typical manner.

Similar trouble occurred with the 8,8,11,11-tetradeutero-*cis*-9-octadecene. After 132 hours no typical autoxidation had taken place as peroxides were present only in trace amounts; the Kreis test was negative, and there was no typical odor of rancidity. The 45 mg. of water contained 7.38 atoms % of deuterium.

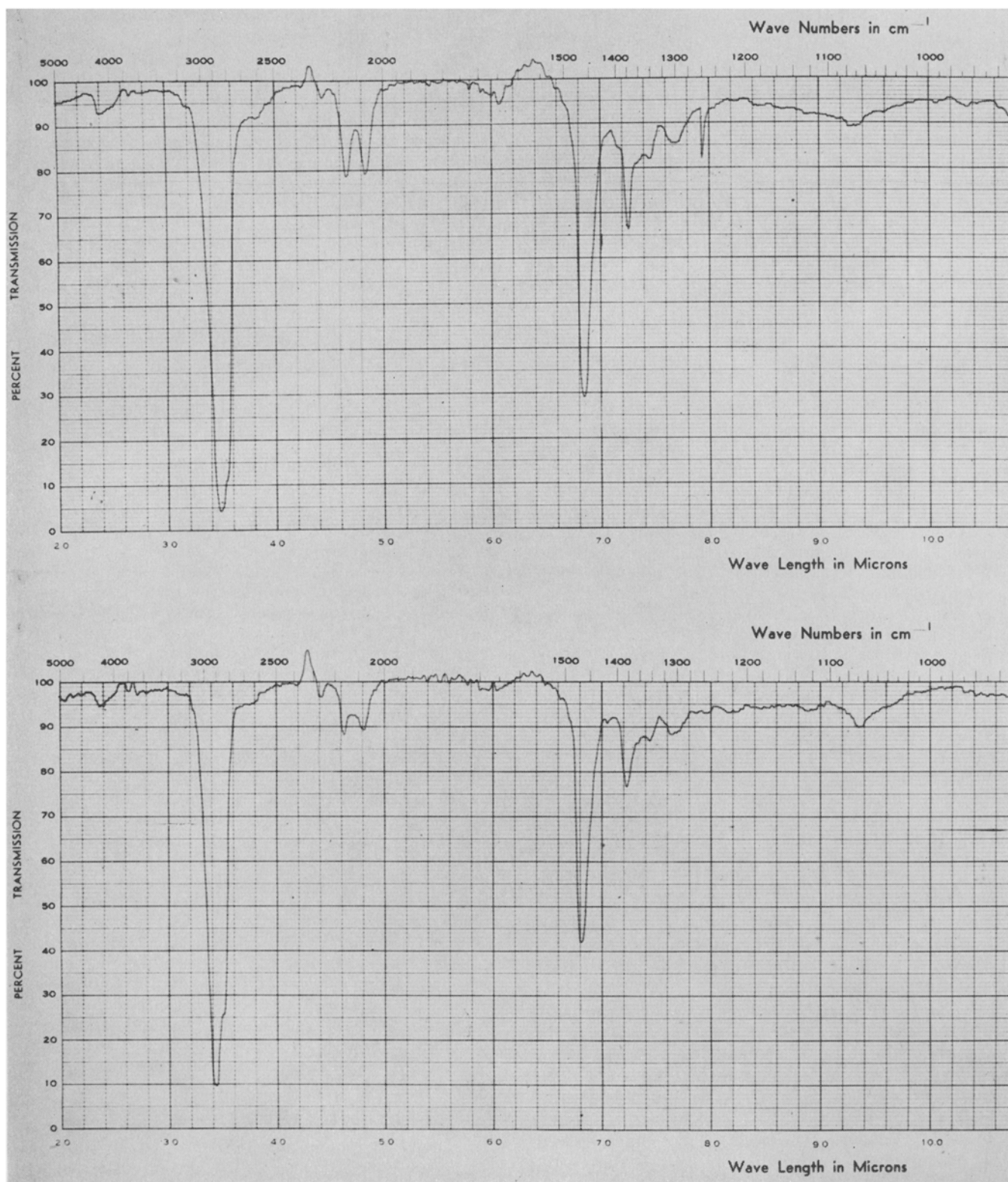


Fig. 1. Infra-red absorption spectra for 8,8,11,11-tetradeutero-*cis*-9-octadecene (above) and 8,8,11,11-tetradeutero-9-octadecine (below).

Consequently this hydrocarbon too was repurified by the bromination, extraction, debromination procedure. The physical and chemical constants and the deuterium analyses indicated that the repurified material was not altered by this treatment.

To the repurified octadecene 0.4 mole % of linoleic acid was added; the autoxidation proceeded in a typi-

cal manner with the results closely resembling those reported by Deatherage and Mattill (2). See Table I and Figure 2.

The repurified tetradeuterooctadecene with the same amount of linoleic acid added had an induction period approximately five times as long as octadecene, but it oxidized in a similar manner except for the rate which

TABLE I

Chemical Characterization of the Autoxidation of *Cis*-9-Octadecene and 8,8,11,11-Tetra deuterio-*Cis*-9-Octadecene

	$-\text{CH}_2\text{CH}=\text{CHCH}_2-$	$-\text{CD}_2\text{CH}=\text{CHCD}_2-$
Induction period, hours.....	12	64
Total time of autoxidation, hours.....	133.5	260.8
O <sub>2</sub> consumed, moles/mole of double bond destroyed.....	2.03	1.48
—COOH— in residue, millimoles/g.....	0.819	1.61*
—COOC— in residue, millimoles/g.....	1.34	0.189
—CH=CH— in residue, millimoles/g.....	1.35	2.84
—OH in residue, millimoles/g.....	1.01	0.400
Peroxide in residue, millimoles/g.....	0.570	0.215
H <sub>2</sub> O, moles/mole of substrate.....	0.49	0.19
H <sub>2</sub> O, moles/mole of double bond destroyed.....	0.74	0.65
CO <sub>2</sub> , moles/mole of substrate.....	0.0167	0.071
CO <sub>2</sub> , moles/mole of double bond destroyed.....	0.023	0.28
Non-aqueous volatile products, mg./millimole of substrate.....	33.2	25.5
		16.4*
Non-aqueous volatile products, mg./millimole O <sub>2</sub> consumed.....	25.5	58.4
		38.4*
Non-aqueous volatile products, mg./millimole double bond destroyed.....	50.5	86.0
		65.0*
Peroxide —O— in non-aqueous volatile products in first dry ice trap, millimole/g.....	3.92	2.70
		4.13*
Total volatile non-aqueous peroxide, moles/mole O <sub>2</sub> consumed.....	0.120	0.094
Total volatile non-aqueous peroxide, moles/mole of double bond destroyed.....	0.239	0.140
		0.162*
Deuterium content of original substrate, atoms per cent of hydrogen and deuterium.....	.....	9.95
Deuterium content of autoxidation residue, atoms per cent of hydrogen and deuterium.....	.....	9.94
Deuterium content of water from autoxidation, atoms per cent of hydrogen and deuterium.....	.....	4.57

\* Corr.

was only one-fifth that of the undeuterated hydrocarbon. (Table I and Figure 2). The reaction gave the typical color on dehydrite, and both volatile matter and residue contained large amounts of peroxide and gave intense Kreis reactions, particularly the volatile matter. There was some unoxidized deuteriooctadecene

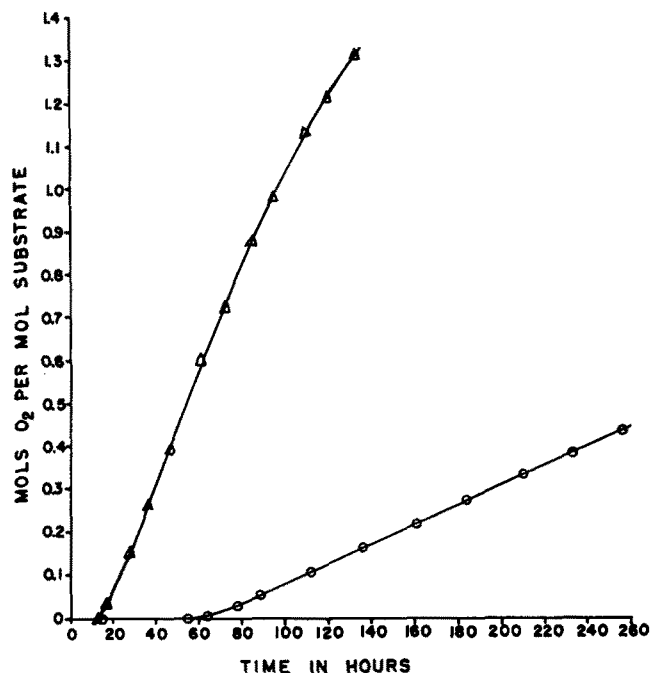


FIG. 2. O<sub>2</sub> absorption at 75°C. by *cis*-9-octadecene (Δ) 8,8,11,11-tetra deuterio-*cis*-9-octadecene (○).

that came over to the dry ice traps. This could be estimated from weight changes in the system. In Table I where "corr." follows the entry, the corrected value was computed, allowing for unchanged substrate volatilized and collected in the traps. A similar correction for the octadecene is relatively insignificant.

Whereas Figure 2 brings out the differences in the O<sub>2</sub> absorption by the two substrates, Table I compares the chemical characteristics of the autoxidation products.

The data concerning *cis*-9-octadecene agree quite closely with the work of Deatherage and Mattill (2), but it is quite evident that the autoxidation of the 8,8,11,11-tetra deuterio-*cis*-9-octadecene differs in some respects even though both compounds autoxidized to give the typical rancid odors, the Kreis test, and similar peroxidic materials. The moles of O<sub>2</sub> consumed per mole of double bond destroyed was less for the deuterium compound, and so also was the residual acid and ester when allowance is made for the unoxidized substrate. The amount of residual peroxide and hydroxyl values are comparable when the same allowances are taken into account.

The amount of carbon dioxide seemed insignificant for the octadecene but was found in somewhat greater amounts for the deuteriooctadecene.

For the deuteriooctadecene significantly more non-aqueous volatile matter was found even when corrected for volatilized substrate which collected in the traps. The meaning of this is not clear, but perhaps it could mean less polymerization because of the slow rate of autoxidation and/or more cleavage of the C-C bond.

It appears that there is some similarity in the non-aqueous volatile matter from the two substrates; this is particularly true of the peroxide oxygen content. However it is worthy of note that in the deuteriooctadecene the number of moles of peroxide oxygen is less when expressed in terms of total oxygen absorbed or double bonds destroyed.

When the water formed is expressed in terms of the double bond destroyed, there was no difference between the two hydrocarbons. But the water formed per mole of O<sub>2</sub> absorbed is somewhat higher for the deuteriooctadecene. If it is remembered that the autoxidation rate was much less for the deuteriohydrocarbon and that even when a typical autoxidation did not occur some water was found, water formation does not appear to result from the decomposition of a hydroperoxide as such. Further evidence of this is the small amount of deuterium found in the water from the autoxidation of the deuteriooctadecene and the unchanged deuterium concentration in the autoxidation residue. Indeed, if it is admitted that this compound autoxidized in a typical fashion (and the available evidence indicates such), one should expect the decomposition of the —CH=CHCDOOD— to yield water high in deuterium. Less deuterium was found in the water from the autoxidation of the compound where the deuterium atoms were *a* to the double bond than where the deuterium atoms were on the double bonded carbon atoms (1). In view of the evidence one is led to the suggestion that water results from more or less random attack on the carbon chain by peroxides, peroxidic radicals, or other forms of active oxygen through some yet unknown mechanism. This, of course, is in line with the complexity of the autoxidation phenomena.

The slow rate of autoxidation of the tetradeuteriooctadecene compared to the octadecene is to be expected if the autocatalytic step concerns the formation of the hydroperoxide at the  $\alpha$  position; and the results reported here support this point of view. Many organic reactions involving comparable C-H and C-D linkages show three to eight times the reaction rates for the C-H compound as for the C-D compound. Christopher L. Wilson (11) has explained such differences on the basis of slight increases in the activation energies for the deuterio compounds.

In a sense the work reported here and that by Khan *et al.* (1) have given negative evidence on the mechanism of water formation and cleavage of the C-C bond since these results indicate reactions involving the decompositions of hydroperoxides to give water and carbonyl groups do not go to any great extent. However the observations made in these studies on the volatile peroxides, which confirm and expand the findings of Deatherage and Mattill (2), raise the question: Do these peroxidic compounds come directly from the hydroperoxides by cleavage of the adjacent C-C bond in some unknown manner? The peculiar character of these volatile peroxides and of their active oxygen and the fact that 10 to 12% of the total O<sub>2</sub> consumed is found as volatile peroxide oxygen indicate that further study on the characterization of these materials might yield information on some of the obscure reactions involved in the rancidification of fats. Further work in this direction is contemplated.

### Summary

8,8,11,11-Tetradeuterio-*cis*-9-octadecene and *cis*-9-octadecene have been synthesized and their autoxidation studied at 75°. The autoxidation of both

compounds proceeded in a similar manner except that the rate of reaction for the deuteriooctadecene was one-fifth that of the octadecene. This apparently indicates that the important sustaining reaction in autoxidation is oxidative attack at the  $\alpha$  methylenic position. That only a very small amount of deuterium was found in the water from the autoxidation of the deuteriooctadecene indicates that water does not come by direct decomposition of the  $\alpha$  hydroperoxide.

### Acknowledgments

The authors are particularly indebted to Christopher L. Wilson of the Department of Chemistry for the infra-red studies and for other valuable suggestions concerning the deuterio compounds encountered in this work. M. S. Newman and K. W. Greenlee of the Department of Chemistry have made helpful suggestions on some of the syntheses.

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[Received August 3, 1950]