Finally, the effect of structure upon the rate of hydrogen abstraction needs brief discussion. Although a slight trend in $(k_2/k_1)_{\text{exp}}$ (see ref. 3) has been observed for the ten methylated dibenzfulvenes, we doubt whether this trend measures correctly the rate of hydrogen abstraction. The abstraction was definitely observed for vinyl-mesitylene (see Fig. 1) and the value of 2.4 was obtained for $k_{3'}/k_1$, *i.e.*, for the relative rate constant of abstraction per active hydrogen (9 hydrogens are active in vinyl-mesitylene). A considerable abstraction was observed in the reaction involving indene (Fig. 1), and the respective $k_{3'}/k_1$ was found to be 47. The $k_{3'}/k_1$ for toluene[1] seems to be about 1, and thus the value found for vinyl-mesitylene is at least of the expected order of magnitude. The much higher value found for indene arises from two effects: the active hydrogens are secondary and this leads to a ten-fold increase in their reactivity,[3] and the radical formed is conjugated both with a benzene ring and a C=C double bond. This again increases the reactivity, *e.g.*, $k_{3'}/k_1$ for pentadiene-1,4 (secondary hydrogens, radical conjugated to two C=C double bonds) is 20.[13]

In conclusion we acknowledge the support of this investigation by the National Science Foundation. We also wish to thank Dr. Hawkins, Dr. Katz, Dr. Kice and Dr. Overberger for supplying us with the necessary compounds.

SYRACUSE, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

The Photochemical Decomposition of Hydrogen Peroxide in Aqueous Solutions of Allyl Alcohol at 2537 Å.[1]

BY DAVID H. VOLMAN AND JUNE C. CHEN

RECEIVED JANUARY 26, 1959

The photochemical decomposition of hydrogen peroxide at 2537 Å. has been studied in aqueous solutions with and without added allyl alcohol. At high intensities and low peroxide concentration, the quantum yield for hydrogen peroxide decomposition was independent of intensity and concentration and was found to be 0.94 ± 0.06 in the absence of allyl alcohol and 0.54 ± 0.05 in the presence of allyl alcohol at 27°. These results are consistent with a kinetic interpretation in which the limiting quantum yield in the absence of allyl alcohol should be twice the quantum yield of the primary decomposition of hydrogen peroxide into OH radicals and the limiting yield in the presence of allyl alcohol should be just equal to the quantum yield of the primary decomposition. Evidence for the formation of tetrahydroxyhexane was obtained. This is expected if the mechanism is the addition of hydroxyl radical to allyl alcohol and then association of the diol free-radicals.

Introduction

Independent studies of the vapor phase[2] and aqueous solution[3] photodecomposition of hydrogen peroxide at 2537 Å. have shown that at relatively high intensities and low peroxide concentrations the chain reaction may be suppressed. Under these conditions, the decomposition may be explained by the consecutive reactions

$$H_2O_2 + h\nu \longrightarrow 2OH \qquad k_1I_a \quad (1)$$

$$OH + H_2O_2 \longrightarrow HO_2 + H_2O \qquad k_2 \quad (2)$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad k_3 \quad (3)$$

The limiting quantum yield at 25° has been variously reported as 1.7 ± 0.4 in the gas phase[2] and 1.4 ± 0.1,[3] 0.98 ± 0.05,[4] 1.9 ± 0.1[5] and 1.00 ± 0.02[6] in solution. The values reported by Lea[3] and by Dainton and Rowbottom[5] were both obtained with unfiltered light from quartz low pressure mercury resonance lamps. Since no precautions were used to eliminate the 1849 Å. resonance radiation generally emitted from such lamps, the values reported are open to serious question. The results of Hunt and Taube[4] and of Baxendale and Wilson[6] are in remarkably good agreement with each other and may be taken as reliable within the stated limits of error.

The complete mechanism for the chain decomposition of H_2O_2 is generally considered to include also the reaction

$$HO_2 + H_2O_2 \longrightarrow H_2O + OH + O_2 \qquad k_4 \quad (4)$$

The quantum yield for peroxide decomposition is then

$$\Phi = 2k_1 + 2k_4(k_1/k_3I_a)^{1/2}(H_2O_2) \qquad (5)$$

Under the limiting conditions referred to, the quantum yield of peroxide decomposition is $2k_1$. Thus one-half the limiting quantum yield is k_1 or the primary quantum yield for peroxide decomposition into OH radicals. This quantity is susceptible to direct experimental determination, and specific methods for the determination of hydroxyl radicals have been used to evaluate k_1.[6,7]

Free-radical trapping by the use of olefinic compounds is a more general method applicable to a wide variety of free-radicals. The nature of the problems involved in water solutions at wave lengths as low as 2537 Å. have been discussed earlier.[8] We wish to report here the use of allyl alcohol, water soluble and transparent at 2537 Å., as a scavenger for free-radicals formed in the photolysis of hydrogen peroxide. Allyl alcohol

---

[1] Sponsored by the Office of Ordnance Research, U. S. Army, and by the Research Corporation.

[2] D. H. Volman, *J. Chem. Phys.*, **17**, 947 (1949).

[3] D. E. Lea, *Trans. Faraday Soc.*, **45**, 81 (1949).

[4] J. P. Hunt and H. Taube, THIS JOURNAL, **74**, 5999 (1952).

[5] F. S. Dainton and J. Rowbottom, *Trans. Faraday Soc.*, **49**, 1160 (1953).

[6] J. H. Baxendale and J. A. Wilson, *ibid.*, **53**, 344 (1957).

[7] J. L. Weeks and M. S. Matheson, THIS JOURNAL, **78**, 1276 (1956).

[8] D. H. Volman, J. C. Chen and L. W. Swanson, *ibid.*, **81**, 756 (1959).

proved to be an efficient trap and water soluble products were formed, an important one being tetrahydroxyhexane.

Experimental

Kinetic Runs; Apparatus.—The reaction vessel was a cylindrical quartz tube, 16 mm. in diameter and 30 cm. long. Stirring was accomplished by a motor driven Pyrex rod which ran the length of the reaction vessel. Experiments with allyl alcohol were conducted in a similar reaction vessel except that the reaction vessel was sealed off under vacuum to eliminate dissolved oxygen, and the solutions were not stirred. The reaction tube was placed within a quartz water jacket through which water at 27° circulated. The entire assembly was contained within a helical mercury resonance arc housed in "Vycor." Since such arcs emit chiefly 2537 and 1849 Å. mercury resonance radiation, the effective transmitted light may be taken as 2537 Å. since "Vycor" is opaque to 1849 Å. light. It is well known that reaction vessels for kinetic studies of hydrogen peroxide must be carefully treated if reproducible results are to be obtained and that cleaning solutions containing chromic acid may be particularly unsatisfactory. In this work, hot concentrated nitric acid was used. Baxendale and Wilson[6] have used a mixture of concentrated sulfuric acid and potassium permanganate. We take this opportunity to emphasize that this may be hazardous since manganese heptoxide, explosive in the presence of oxidizable material, may be formed, and we have had a rather serious explosion using this mixture.[9]

Actinometry.—Both monochloroacetic acid and uranyl oxalate were used as actinometer solutions. The procedure was to substitute for the hydrogen peroxide solution a solution of either monochloroacetic acid or uranyl oxalate which had the same optical density as the peroxide solution. Absorption coefficients were measured by use of a spectrophotometer. In calculating the concentration of the actinometer solution, it was assumed that Beer's law held for both hydrogen peroxide solution and the actinometer solution. Monochloroacetic acid was used in experiments at low optical densities. The quantum yield used for the uranyl sulfate actinometer was that reported by Leighton and Forbes[10] of 0.600. For monochloracetic acid the value given by Smith, Leighton and Leighton[11] of 0.34 at 27° was used. The principle of using equivalent optical densities in actinometry recently has been discussed thoroughly by Claesson.[12]

Materials.—Triply distilled water was used in all experiments. The peroxide was a 90% solution in water from Buffalo Electrochemicals Company and was used as received. Allyl alcohol, obtained from Paragon Testing Laboratories, was subjected to fractional distillation; $n^{20}\text{D}$ 1.4132, lit.[13] $n^{20}\text{D}$ 1.4135.

Analysis.—For concentrations of hydrogen peroxide less than 0.004 *M*, peroxide was determined iodometrically. This method also could be used in the presence of allyl alcohol provided the concentration of the latter did not exceed 0.2 *M*. Above 0.004 *M*, peroxide was determined by titration with potassium permanganate in the absence of allyl alcohol. Either in the presence or absence of allyl alcohol, titration of peroxide with ceric solution was possible, and this method was used for the higher range of peroxide concentration. For experiments with allyl alcohol, unsaturation was determined by the bromate–bromide method.[14] This method gave a total of peroxide and unsaturation but since peroxide was determined independently, unsaturation could be calculated.

Products of the Reaction with Allyl Alcohol; Irradiation.—Sixty-ml. portions of aqueous solutions, 3 *M* allyl alcohol and 3 *M* hydrogen peroxide, were irradiated at 2537 Å. The reaction mixtures were concentrated below 50° under reduced pressure and a viscous product was obtained, Table I.

TABLE I

IRRADIATION OF ALLYL ALCOHOL 3 *M*–HYDROGEN PEROXIDE 3 *M*

T, °C.	Time, hr.	Final concn., *M* H_2O_2	Final concn., *M* Alc.	Viscous product analysis Wt., g.	Viscous product analysis C, %	Viscous product analysis H, %	Viscous product analysis O, %
2	9.3	0.50	0.51	10.7	51.4	8.4	40.2
27	16.0	.003	.32		52.1	8.9	39.0
50	3.3	.70	.17	11.6	47.8	8.9	43.3

For the reaction at 27°, the product had 4.23 × 10^{-5} meq./g. unsaturation, a negligible amount. The unreacted allyl alcohol was obtained, therefore, by determination of total unsaturation in the reaction mixture.

The products obtained from the reaction at 50° were fractionally distilled under reduced pressure and the fractions taken were subjected to elemental analysis: Fraction 1, 3.0 ml., b.p. 70–130° (2 mm.), C, 47.7; H, 8.1. Fraction 2, 1.2 ml., b.p. 130–150° (2 mm.), C, 49.4; H, 8.6. Fraction 3, 1.6 ml., b.p. 150–160° (2 mm.), C, 52.0; H, 8.6. Calcd. for $C_6H_{14}O_4$: C, 48.0; H, 9.3.

Glycerol by Paper Chromatography and Periodate Oxidation.—The viscous products were subjected to paper chromatography according to the method of Bergner and Sperlich.[15] A 15% aqueous solution of the products was spotted on Whatman No. 1 paper. The chromatograms were developed in water saturated butanol by the ascending technique. When the solvent front reached the top of the paper, the sheet was dried at room temperature, sprayed with a 5% solution of silver nitrate in 25% ammonia solution and heated at 100–105° for 15–25 minutes. Excess reagent was removed by immersing the paper in a 5% sodium thiosulfate solution. By comparison with known samples, three components were identified as glycerol, 1,2-propanediol and 1,3-propanediol. Glycerol was estimated by visual comparison with a known sample. 0.67 and 0.87 mmole/g. of 2 and 50° reaction product were found.

Glycerol also was determined by titrating formic acid produced in periodate oxidation.[16] The results obtained, 0.64 and 0.90 mmole/g. of 2 and 50° reaction product, were in good agreement with the chromatographic analysis.

Diols by Gas Chromatography.—A 60% ethanolic solution of the viscous products was subjected to gas chromatography on 33% Reoplex 400 on Sil-O-Cel insulation brick at 187° with a helium flow rate of 37 ml./min. Most of the product was retained in the column. However, 1,2-propanediol and 1,3-propanediol were expelled and were determined quantitatively by comparison with known samples. The 2° reaction product yielded 0.46 and 0.15 mmole/g. 1,2-propanediol and 1,3-propanediol. The 50° reaction product yielded 0.26 and 0.24 mmole/g. of 1,2-propanediol and 1,3-propanediol.

Adjacent Hydroxyl by Periodate Oxidation.—The viscous products and the distilled fractions were subjected to periodate oxidation according to the method of Pohle and Mehlenbacher.[17] Five g. of periodic acid was dissolved in 200 ml. of water and 800 ml. of acetic acid. A sample containing approximately 0.0005 to 0.001 mole of adjacent hydroxyl groups was added to 100 ml. of the oxidizing agent and allowed to stand for 0.5 hr. at room temperature. Twenty ml. of a 20% KI solution was added, and the liberated iodine was titrated with 0.1 *N* sodium thiosulfate, Table II.

TABLE II

HYDROXYL GROUP ON ADJACENT CARBON ATOMS

	Adjacent hydroxy groups, meq./g.
2° reaction product	3.51
50° reaction product	4.80
50°, fraction 1	3.81
50°, fraction 2	4.48
50°, fraction 3	3.32

---

(9) Dr. Baxendale, private communication, has subsequently furnished us with explicit directions used in his laboratory to make the procedure safe. Nevertheless, we wish to call attention to the potential danger.

(10) W. G. Leighton and G. S. Forbes, THIS JOURNAL, **52**, 3139 (1930).

(11) R. N. Smith, P. A. Leighton and W. G. Leighton, *ibid.*, **61**, 2299 (1939).

(12) I. M. Claesson, *Arkiv Kemi*, **10**, 1 (1956).

(13) 1. M. Heilbron and H. M. Bunbury, *Dictionary of Org. Compounds*, **1**, 47 (1943).

(14) S. Winstein and H. J. Lucas, THIS JOURNAL, **59**, 1461 (1937).

(15) K. E. Bergner and H. Sperlich, *Anoles bromatol (Madrid)*, **5**, 241 (1953).

(16) J. C. M. Griffin, *J. Assoc. Off. Agr. Chem.*, **37**, 874 (1954).

(17) W. D. Pohle and U. C. Mehlenbacher, *Oil and Soap*, **22**, 115 (1945).

Acetylation.—The viscous products were acetylated according to the method of Bailey and Sorenson.[18] A solution of 5.2 g. of the viscous product in 15 ml. of acetic anhydride and 5 ml. of acetic acid was added dropwise with stirring to 50 g. of refluxing acetic anhydride. The mixture was refluxed 15 hr. and evaporated *in vacuo* at room temperture to give 7 g. of crude product, 64% yield based on tetrahydroxyhexanes. The crude product was fractionally distilled under reduced pressure. Each fraction was subjected to gas chromatography, subjected to elemental analysis, and the saponification equivalent determined: 1.0 g., b.p. 110° (2 mm.), C, 52.2; H, 7.0; sapon. eq., 74.4. 0.4 g., b.p. 142° (2 mm.), C, 53.2; H, 7.1; sapon. eq., 77.0. 1.3 g., b.p. 175° (2 mm.), C, 53.8; H, 7.4; sapon. eq., 79.3. Calcd. for $C_6H_{10}(OCOCH_3)_4$; C, 52.8; H, 6.9; sapon. eq., 79.5.

The acetates were subjected to gas chromatography on 33% silicone oil on Sil-O-Cel insulation brick at 240° with a helium flow rate of 50 ml./min. There were three peaks, one of which corresponded to that of an authentic sample of the tetraacetate of 2,3-(hydroxymethyl)-1,4-butanediol. The infrared spectra of the acetates of the 50° reaction product were essentially identical to that of the synthesized sample.

Synthesis of 2,3-Di-(hydroxymethyl)-1,4-butanediol and its Tetraacetate.—The tetrahydroxy compound and its acetate were synthesized by the method of Bailey and Sorenson.[18] The melting points were 114° and 67–68°, respectively, in agreement with Bailey and Sorenson. In addition, the boiling point of the alcohol determined by a micromethod was found to be 288°, corrected.

Results

The Limiting Quantum Yield.—Quantum yields obtained under conditions of high intensity and low concentration are shown in Table III.

TABLE III

THE LIMITING QUANTUM YIELD AT 2537 Å. AND 17°

H_2O_2, mmole	I_a (quanta/l./sec.) × 10^{-18}	$\Phi_{H_2O_2}$
2.18	8.60	0.92
2.18	8.85	.87
2.21	8.50	.95
2.21	8.67	.97
4.33	16.8	.84
4.33	16.9	.85
17.7	50.2	.96
17.7	50.4	1.02
35.6	70.5	1.03
35.6	71.7	1.01

From Table III, the average value and mean deviation obtained is 0.94 ± 0.06. This value is in good agreement with those obtained by Hunt and Taube[4] and by Baxendale and Wilson.[6] The highest intensities used in this work are about 150-fold greater than the highest used by Hunt and Taube and about 10-fold greater than the highest used by Baxendale and Wilson.

Quantum Yield in Allyl Alcohol.—The rate of decomposition decreased rapidly as allyl alcohol was added, falling to a minimum rate which was independent of subsequent allyl alcohol addition. Quantum yields obtained for a constant light intensity of 50.0 × 10^{18} quanta l.$^{-1}$ sec.$^{-1}$ and hydrogen peroxide concentration of 0.0175 are given in Table IV.

Limiting quantum yields for peroxide decomposition in 0.1 *M* allyl alcohol were determined using 0.002 *M* hydrogen peroxide with an intensity of 8.0 × 10^{18} quanta l.$^{-1}$ sec.$^{-1}$ and 0.0175 *M* hydrogen peroxide with an intensity of 50.2 × 10^{18} quanta l.$^{-1}$ sec.$^{-1}$. No significant differences between the two sets were observed. Nine determinations yielded a value of 0.54 ± 0.05.

TABLE IV

EFFECT OF ALLYL ALCOHOL ON THE QUANTUM YIELD OF HYDROGEN PEROXIDE DECOMPOSITION

Allyl alcohol, *M* × 10^2	$\Phi_{H_2O_2}$
0	1.00
0.037	0.59
.073	.62
.37	.48
2.2	.53
3.7	.53
7.3	.57
18.4	.58

Discussion

Effect of Temperature.—Hunt and Taube consider the primary process in terms of the scheme

$$H_2O_2 + h\nu \longrightarrow H_2O_2^* \qquad (6)$$

$$H_2O_2^* \longrightarrow H_2O_2,\ k_d \qquad (7)$$

$$H_2O_2^* \longrightarrow \text{dissociation},\ k_r \qquad (8)$$

$H_2O_2^*$ may represent either an activated molecule or OH radicals in a solvent cage. Reaction 7 represents deactivation of the excited species or recombination of radicals in the solvent cage. Reaction 8 represents escape from the cage or diffusion of OH radicals into bulk. R. M. Noyes[19] in a detailed consideration of reactive fragments produced in pairs separates reactions such as (7) into a "primary recombination" and into a "secondary recombination" portion. Primary recombination is considered to occur in a period of the order of a vibration, 10^{-13} sec., while secondary recombination occurs within about 10^{-9} sec. and is still limited to the original radical pair. Primary recombination is so rapid that diffusion into bulk cannot compete with it. Diffusion into bulk, however, can compete with secondary recombination.

For the reaction under limiting conditions where

$$\Phi = 2k_r(H_2O_2^*)/I_a \qquad (9)$$

a steady-state approximation for (H_2O_2) yields

$$\Phi/(2 - \Phi) = k_r/k_d \qquad (10)$$

In addition to the results given in Table III, we have obtained a limiting quantum yield of 0.74 at 2° and 1.10 at 50° . Hunt and Taube[4] have obtained 0.76 at 0° and Baxendale and Wilson[6] have obtained 0.80 at 4°. In Fig. 1, the logarithm of the ratio of k_r/k_d calculated from eq. 10 is plotted against the reciprocal of the absolute temperature. Values from the other two studies are also shown. The straight line obtained tends to justify the kinetic treatment and indicates that k_r/k_d follows an exponential of the Arrhenius form. $E_r - E_d$ is found to be 2.7 kcal. This compares well with 2.9 kcal. obtained by Hunt and Taube[4] from the experiments at 0 and 25°, and a value of 3.1 kcal. which we have calculated from the data of Baxendale and Wilson[6] at 4 and 25°.

Determination of k_1.—If it is assumed that OH radicals add to allyl alcohol and the following steps involve only polymerization and chain ter-

---

(18) W. J. Bailey and W. R. Sorenson, THIS JOURNAL, **78**, 2287 (1956).

(19) R. M. Noyes, *ibid.*, **77**, 2042 (1951).

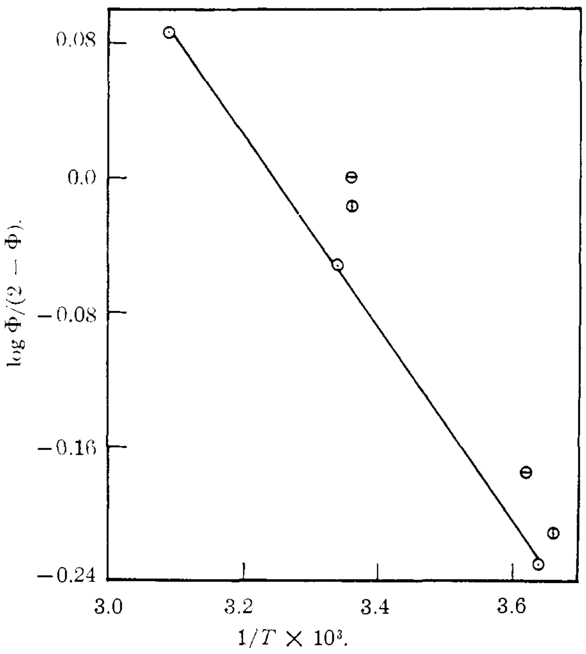

Fig. 1.—Effect of temperature on quantum yield: ⊖, Baxendale and Wilson; ○, Hunt and Taube.

mination by radical–radical reaction, the limiting quantum yield for hydrogen peroxide decomposition in allyl alcohol is just k_1. From our results $k_1 = 0.54 \pm 0.05$ is obtained. The expected value from half the limiting value in the absence of allyl alcohol would be 0.47 ± 0.03. These results are thus consistent and in good agreement with those of Weeks and Matheson,[7] 0.49 ± 0.06, and those of Baxendale and Wilson,[6] 0.50.

It may be observed that the small amounts of propanediol found is evidence that some hydrogen atom abstraction occurs. Although it would be expected that allyl alcohol would be the principal hydrogen atom donor, abstraction from hydrogen peroxide would tend to yield a high value for k_1.

Products of the Reaction with Allyl Alcohol.—The photochemical reaction of allyl alcohol and hydrogen peroxide has been reported to yield glycerol as probably the only product.[20] The means of identification was solely by boiling point determination. In our work under comparable conditions glycerol accounts for only a few per cent. of the total product. This discrepancy may be explained by observing that the boiling point of glycerol and that of 2,3-di-(hydroxymethyl)-1,4-butanediol are practically identical. Using two micro melting point tubes, one containing glycerol and the other containing the tetrol, at the same time in a single bath, we found that the tetrol boils at about 2° below the glycerol.

Studies of the electron resonance spectrum of ultraviolet irradiated solutions of hydrogen peroxide in allyl alcohol in the glassy state at 77°K. have been interpreted as showing that the principal reaction is the abstraction of an α-hydrogen from allyl alcohol by an hydroxyl radical.[21] No evidence for significant amounts of this reaction has been obtained in our work. Either the e.r.s. spectrum needs reinterpretation, or the experimental conditions are such as to make hydrogen atom abstraction more likely in the glassy state at 77°K.

The evidence we have obtained for the formation of appreciable amounts of tetrahydroxyhexane appears to be conclusive. Since small amounts of both 1,2- and 1,3-propanediol are formed, hydroxyl addition to the double bond of allyl alcohol probably occurs at both β- and γ-positions; H atom abstraction by these free radicals would give rise to both glycols while hydroxyl addition would give glycerol, which also is found. Association of the free-radicals could give rise to three isomeric tetrahydroxy hexanes. Evidence that all three are in fact formed is found in the three gas chromatography peaks obtained with the acetylated product, of which at least one has been identified as the 2,3-di-(hydroxymethyl)-1,4-butanediol by comparison with a synthesized sample. Evidence that at least one other tetrol is formed is obtainable from the adjacent hydroxyl determination. The 2,3-di-(hydroxymethyl)-1,4-butanediol has no adjacent hydroxyl groups while, of the others, 2-hydroxymethyl-2,4,5-pentanetriol has one pair and 1,2,5,6-hexanetetrol has two pairs. Based on fraction 2 of the 50° reaction, which appears to be the purest tetrahydroxyhexane sample, the hydroxyl groups which exist as adjacent pairs are found to be 22% of the total. This value is not unreasonable if one takes the ratio of the two propanediols formed as an indication of the fraction of β- and γ-hydroxyl addition.

$$\mathrm{OH} + \mathrm{CH_2CHCHOH} \longrightarrow \mathrm{CH_2OH}\underset{\cdot\cdot}{\mathrm{C}}\mathrm{HCHOH} \quad (11)$$

$$\mathrm{OH} + \mathrm{CH_2CHCHOH} \longrightarrow \underset{\cdot}{\mathrm{C}}\mathrm{H_2CHOHCHOH} \quad (12)$$

DAVIS, CALIFORNIA

---

[20] N. A. Milas, P. F. Kurz and W. P. Anslow, Jr., THIS JOURNAL, **59**, 543 (1937).

[21] J. F. Gibson, D. J. E. Ingram, M. C. R. Symons and M. G. Townsend, *Trans. Faraday Soc.*, **53**, 914 (1957).