The Oxidation of α-Methylstyrene in the Presence of Benzaldehyde

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The oxidation of α-methylstyrene in the presence of benzaldehyde was studied at 40°C, with and without added metal salt catalysts, from the viewpoint of the products obtained. The products were α-methylstyrene oxide, acetophenone, formaldehyde, α-methylstyrene polyperoxide, perbenzoic acid, and benzoic acid; few side reactions between these products were observed under the reaction conditions employed here. Emphasis was laid on the effect of metal salt catalysts and of the initial composition of the oxidants on the cleavage products from α-methylstyrene. Manganese and copper salts were found to have little effect, while cobalt salt showed a characteristic effect on the formation of the cleavage products. In the presence of cobalt salt, the formation of acetophenone was accelerated. The increase in the formation of α-methylstyrene oxide in this system compared with the oxidation of α-methylstryene alone may well be attributed to the polar reaction of α-methylstyrene with perbenzoic acid formed from benzaldehyde. The consumption of perbenzoic acid in various systems was also examined. The increase in the initial concentration of benzaldehyde increased the yield of α-methylstyrene oxide and decreased that of acetophenone.

It has been well known that the oxidation of the olefinic compounds in the presence of aldehydes gives epoxide[1,2] and ester[3]. Moreover, peroxy acids, the oxidation products of aldehydes, have received considerable attention in recent years as epoxidizing reagents. In this paper, the oxidation

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1) E. Raymond, *J. Chim. Phys.*, **28**, 480 (1931).
2) D. Swern, T. W. Findley and J. T. Scanlan, *J. Am. Chem. Soc.*, **66**, 1925 (1944); **72**, 4315 (1950); D. Swern, *Chem. Revs.*, **45**, 1 (1949).

3) L. Schulz and W. Treibs, *Ber.*, **77**, 377 (1944); **80**, 214, 217 (1947).

of α-methylstyrene in the presence of benzaldehyde will be investigated from the viewpoint of the products, especially the cleavage products from α-methylstyrene.

The oxidation of benzaldehyde has been studied in detail since Bäckström[4] first concluded that this reaction is a radical chain reaction. The basic mechanism is similar to that of hydrocarbons[5,6] in the initial stages, when peroxy acid is formed in the reaction mixture. As the oxidation advances, the peroxy acid formed undergoes an acid-base catalyzed reaction with aldehyde to give carboxylic acid, which acts as a catalyst.[7] This side reaction complicates the kinetic scheme of the reaction. On the other hand, the oxidation of α-methylstyrene is rather unusual[8,9]; namely, it undergoes two simultaneous reactions, a copolymerization of α-methylstyrene with oxygen to form polyperoxide, and a cleavage reaction to form α-methylstyrene oxide, acetophenone, and formaldehyde. This characteristic feature results from the presence of a reactive and polymerizable double bond in α-methylstyrene.

Experimental

Benzaldehyde was distilled under reduced nitrogen pressure, collected in a darkened storage vessel, and kept under oxygen-free nitrogen. The other materials, procedures, and analytical methods were the same as have been described in a previous paper.[9] Perbenzoic acid was prepared by Braun's method[10] as modified by Kolthoff et al.[11]

As will be described later, two kinds of peroxides are formed in this system; one is α-methylstyrene polyperoxide, and the other is perbenzoic acid. Polyperoxide of a high molecular weight can be separated by precipitation with methanol.[9] However, little of the precipitate could be obtained, apparently because of its low molecular weight. In order to estimate these two peroxides separately, three kinds of iodometric titrations were employed: Wagner's method[12]; Wibaut's method,[13] where peroxide is treated with KI in 80% acetic acid at room temperature, and Hiatt's method,[14] where 0.8 g of solid NaI and up to 1 mmol of peroxide are added to 15 ml of a solution of 20% acetic acid - 80% isopropyl alcohol, after

which the mixture is refluxed for 15 min. In Wagner's method, a known amount of benzoic acid is added to the sample to liberate the iodine; then, after the titration of peroxide by a thiosulfate solution, benzoic acid is determined by aqueous sodium hydroxide. However, this method suffers from some loss of precision, probably because of the consumption of benzoic acid by the reaction with epoxide during the course of the reflux procedure. The direct titration of the untreated sample of the reaction mixture with aqueous sodium hydroxide was interfered with by peroxide.

Results and Discussion

The products from α-methylstyrene were α-methylstyrene oxide, acetophenone, formaldehyde (equimolar to acetophenone[9]), and α-methylstyrene polyperoxide, while those from benzaldehyde were perbenzoic acid and benzoic acid. In addition to these products, the side reaction products must be taken into consideration. The reaction of α-methylstyrene oxide with benzoic acid was studied separately, but its rate was found to be very small under the reaction conditions employed. Kato and Mashio[15] reported the transformation of α-methylstyrene oxide to acetophenone and α-phenylpropionaldehyde at 100°C by splitting off the methylene unit and by rearrangement respectively. The decomposition of α-methylstyrene oxide was examined under the reaction conditions employed here, but no decomposition of the epoxide was observed at all. No phenyl acetate formed by the Baeyer-Villiger reaction between acetophenone and perbenzoic acid[16] was detected.

The typical example of the oxidation of α-methylstyrene in the presence of benzaldehyde is shown in Fig. 1. As the figure shows the three iodometric methods did not give identical titers. Hiatt, Gould, and Mayo[14] reported, in their study of the decomposition of hydroperoxides in oxidizing olefins, that styrene polyperoxide did not give a titer in Wibaut's method, whereas it interfered in Hiatt's method. Assuming that α-methylstyrene polyperoxide does not give a titer in Wibaut's method, the value determined by Wibaut's method should give that of perbenzoic acid. As is shown in Fig. 1, the peroxide value determined by Wibaut's method was 0.175 mol/l when the reaction was carried out for 60 min. At that point, α-methylstyrene polyperoxide produced was calculated to be 0.33 mol/l from the knowledge of α-methylstyrene reacted and of the cleavage products formed. Accordingly, the total value of the peroxides was estimated to be 0.505 mol/l, while Wagner's and Hiatt's methods gave 0.433 and 0.540 mol/l respectively. Roughly speaking, the line 9 in Fig. 1 may be considered to denote the value of benzoic

4) H. L. J. Bäckström, *J. Am. Chem. Soc.*, **49**, 1460 (1927).
5) J. L. Bolland, *Quart. Revs.*, **3**, 1 (1949).
6) L. Bateman, *ibid.*, **8**, 147 (1954).
7) W. A. Waters, *J. Chem. Soc.*, **1951**, 872.
8) F. R. Mayo and A. A. Miller, *J. Am. Chem. Soc.*, **80**, 2480 (1958).
9) E. Niki and Y. Kamiya, This Bulletin, **39**, 1095 (1966).
10) G. Braun, "Organic Syntheses," Coll. Vol. 1, 431 (1946).
11) I. M. Kolthoff, T. Lee and M. A. Mairs, *J. Polymer Sci.*, **2**, 199 (1947).
12) C. D. Wagner, R. H. Smith and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976 (1947).
13) J. P. Wibaut, H. B. van Leeuwen and B. Van der Wal, *Rec. trav. chim.*, **73**, 1033 (1954).
14) R. Hiatt, C. W. Gould and F. R. Mayo, *J. Org. Chem.*, **29**, 3461 (1964).

15) S. Kato and F. Mashio, Presented at the Meeting of the Society of Organic Synthetic Chemistry of Japan, October, 1965.
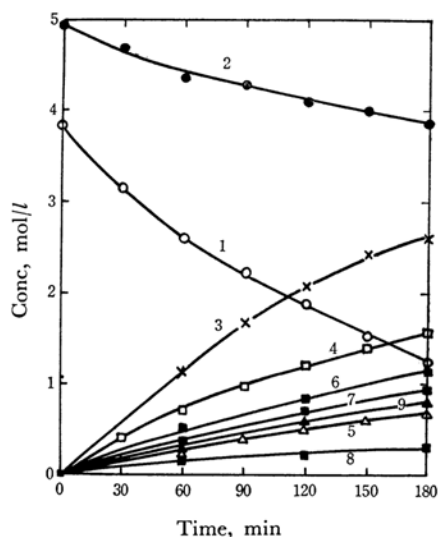16) S. L. Friess, *J. Am. Chem. Soc.*, **71**, 14 (1949); **73**, 3968 (1951).

Fig. 1. Oxidation of α-methylstyrene in the presence of benzaldehyde at 40°C.
Co naphthenate, 1.1×10^{-3} mol/l
1: α-Methylstyrene
2: Benzaldehyde
3: Oxygen absorbed
4: Acetophenone
5: α-Methylstyrene oxide
6: Peroxide by Hiatt's method
7: Peroxide by Wagner's method
8: Peroxide by Wibaut's method
9: (Benzaldehyde reacted)−
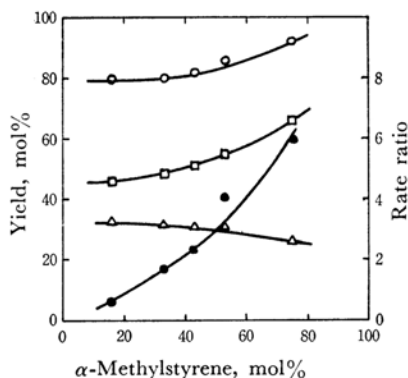   (peroxide by Wibaut's method)

Fig. 2. The effect of initial monomer composition.
40°C, Co naphthenate=1.1×10^{-3} mol/l
Oxygen pressure=760 mmHg
□: Acetophenone
△: α-Methylstyrene oxide
○: Cleavage products
●: (Rate of α-methylstyrene)/(rate of
                    benzaldehyde)

acid produced. The yield of the cleavage products remained almost constant after the initial stages of the oxidation.

The cleavage products formed from α-methyl-styrene were studied as a function of the metal salts and of the initial composition of the oxidants. The

results are shown in Table 1 and Fig. 2. The most significant difference from the oxidation of α-methylstyrene alone is that up to 35% of α-methylstyrene oxide is formed independent of the presence or absence of the metal salt catalysts, and 75—90% of α-methylstyrene is converted to the cleavage products, whereas the yield of the cleavage products reached only about 50% in its neat oxidation.[9]

TABLE 1. THE EFFECT OF METAL SALTS
ON THE PRODUCTS AT $40°C$[a]

Catalyst		Product: Yield in mol%[b]		
Metal[c]	mol/l	Aceto-phenone	α-Methyl-styrene oxide	Cleavage product
None		41	34	75
Mn	1.0×10^{-4}	42	34	75
Mn	1.0×10^{-3}	41	36	77
Cu	1.0×10^{-4}	34	28	62
Cu	1.0×10^{-3}	40	30	70
Co	3.5×10^{-5}	41	34	75
Co	1.3×10^{-4}	54	31	85
Co	3.0×10^{-4}	59	28	87
Co	7.1×10^{-4}	55	33	88
Co	1.1×10^{-3}	58	26	84
Co	4.7×10^{-3}	59	30	89
Co	1.0×10^{-2}	56	29	85

a) Initial α-methylstyrene concn.=43 mol%
    Oxygen pressure=760 mmHg
b) Based on α-methylstyrene reacted.
c) Metals were used as naphthenate.

The fact that quite a lot of epoxide is formed in the presence of benzaldehyde may well be attributed to the following polar reaction[17] or α-methylstyrene with perbenzoic acid produced from benzaldehyde:
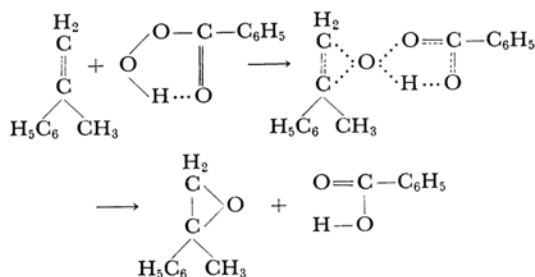
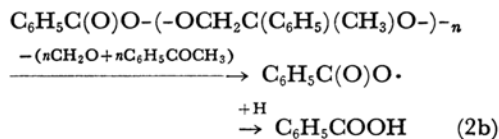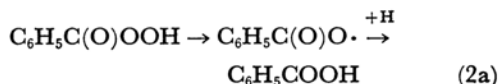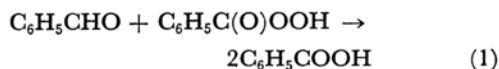
The effect of the initial composition on the products affirms this consideration. As is shown in Fig. 2, an increase in the initial molar ratio of α-methylstyrene decreases the yield of α-methyl-styrene oxide and increases that of acetophenone. The rates of the oxidation of α-methylstyrene and benzaldehyde were measured by following the disappearance of the two oxidants. In Fig. 2 the ratio of the average oxidation rate of α-methyl-styrene to that of benzaldehyde is also plotted

17) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, **1955**, 1525.

against the initial concentration of α-methylstyrene. The dependence of the products on the initial composition must stem from this variation in the rate ratio of the two oxidants, implying that, in a mixture containing much benzaldehyde, the system may be richer in benzoylperoxy radicals than in a mixture containing much α-methylstyrene. Therefore, the lower the initial concentration of α-methylstyrene the more perbenzoic acid produced, increasing the yield of α-methylstyrene oxide and decreasing that of acetophenone.

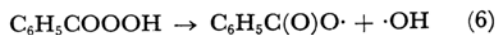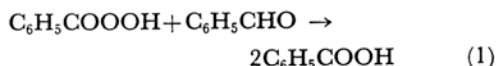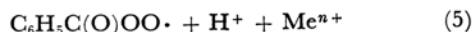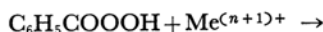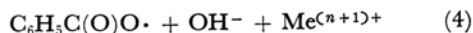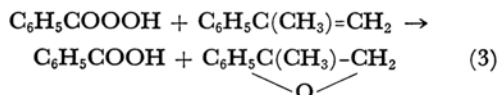In its individual oxidation, benzaldehyde is much more readily oxidized than α-methylstyrene.[18] Nevertheless, the oxidation of aldehydes is inhibited in the presence of olefinic compounds (Fig. 1).[19] This may be attributed to the difference in reactivity toward peroxy radicals between aldehydes and olefinic compounds. The double bond of α-methylstyrene is so reactive that α-methylstyrene is a strong radical scavenger, approximately 3—9 times as reactive as benzaldehyde toward α-methylstyrylperoxy and benzoylperoxy radicals.[18] Thus the formation of perbenzoic acid is suppressed in the presence of α-methylstyrene, and the formation of acetophenone is thereby more favored than that of α-methylstyrene oxide.

The reaction between α-methylstyrene and perbenzoic acid produces benzoic acid in an amount equivalent to that of α-methylstyrene oxide. Benzoic acid may also be produced by the reaction of perbenzoic acid with benzaldehyde, and by hydrogen atom abstraction by the benzoyloxy radical which is produced by the decomposition of perbenzoic acid and/or by the decomposition of the polymeric radical. However, since most of perbenzoic acid may be consumed by the reaction

$$C_6H_5CHO + C_6H_5C(O)OOH \rightarrow$$
$$2C_6H_5COOH \qquad (1)$$

$$C_6H_5C(O)OOH \rightarrow C_6H_5C(O)O\cdot \xrightarrow{+H}$$
$$C_6H_5COOH \qquad (2a)$$

$$C_6H_5C(O)O-(-OCH_2C(C_6H_5)(CH_3)O-)-_n$$
$$\xrightarrow{-(nCH_2O + nC_6H_5COCH_3)} C_6H_5C(O)O\cdot$$
$$\xrightarrow{+H} C_6H_5COOH \qquad (2b)$$

with α-methylstyrene (as will be discussed later), benzoic acid is expected to be formed in about the same or a little greater amount than the epoxide (lines 5 and 9 in Fig. 1).

Several reactions of perbenzoic acid are possible in this system:

$$C_6H_5COOOH + C_6H_5C(CH_3)=CH_2 \rightarrow$$
$$C_6H_5COOH + C_6H_5C(CH_3)-CH_2 \qquad (3)$$
$$\diagdown O \diagup$$

18) E. Niki and Y. Kamiya, unpublished data.
19) G. Wittig, Ann., 558, 207, 218 (1947).

$$C_6H_5COOOH + Me^{n+} \rightarrow$$
$$C_6H_5C(O)O\cdot + OH^- + Me^{(n+1)+} \qquad (4)$$

$$C_6H_5COOOH + Me^{(n+1)+} \rightarrow$$
$$C_6H_5C(O)OO\cdot + H^+ + Me^{n+} \qquad (5)$$

$$C_6H_5COOOH + C_6H_5CHO \rightarrow$$
$$2C_6H_5COOH \qquad (1)$$

$$C_6H_5COOOH \rightarrow C_6H_5C(O)O\cdot + \cdot OH \qquad (6)$$

The rates of the consumption of perbenzoic acid in various systems were studied; i. e., the reaction of perbenzoic acid with (a) α-methylstyrene and (b) benzaldehyde, (c) cobalt-, (d) manganese-, and (e) copper-catalyzed decompositions, and (f) the uncatalyzed thermal decomposition of perbenzoic acid. The rates, being extremely rapid, were hard to evaluate precisely. The results are tabulated in Table 2.

TABLE 2. THE DECOMPOSITION OF PERBENZOIC ACID IN VARIOUS SYSTEMS AT $40°C$, INITIAL CONCENTRATION OF PERBENZOIC ACID: 0.072 mol/l

	Solvent	Catalyst		Half-life of perbenzoic acid, min
		Metal	mol/l	
(a)	α-Methylstyrene	None		<1
(b)	Benzaldehyde	None		9
(c)	Benzene	Co	1.0×10^{-3}	4
(d)	Benzene	Mn	1.0×10^{-3}	1
(e)	Benzene	Cu	1.0×10^{-3}	>35
(f)	Benzene	None		—

The uncatalyzed decomposition of perbenzoic acid in benzene was very slow. Bawn and Jolley[20] reported, in their comprehensive study of the cobalt salt-catalyzed oxidation of benzaldehyde at $25°C$, that the cobalt-catalyzed decomposition of perbenzoic acid was approximately ten times greater than the reaction of the peroxy acid with benzaldehyde, while the uncatalyzed thermal decomposition was so small that it could be neglected. Tokumaru, Shimamura and Fukuyama[21] studied the decomposition of perbenzoic acid in solution. According to their data, the half life of perbenzoic acid in a benzene solvent may be calculated to be about 450 min, even at $79°C$.

The metal salts in this system showed effects similar to those in the oxidation of α-methylstyrene alone[9]; i. e., manganese and copper naphthenates had little effect, while cobalt naphthenate had a characteristic effect on the oxidation products. The finding, shown in Table 1, that the yield of α-methylstyrene oxide is about the same in the absence or in the presence of the metal salts suggests

20) C. E. H. Bawn and J. E. Jolley, Proc. Roy. Soc., A237, 297 (1956).
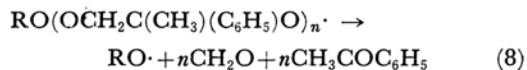21) K. Tokumaru, O. Shimamura and M. Fukuyama, This Bulletin, 35, 1673, 1678, 1955 (1962); 36, 72, 76, 333 (1963).

that the polar reaction of perbenzoic acid with α-methylstyrene is predominant over the metal salt-catalyzed decomposition of perbenzoic acid. However, it is unlikely that the metal-catalyzed decomposition is negligible compared with the reaction of peroxy acid with α-methylstyrene. As has been discussed previously,[22,9] manganese and copper salts terminate chains by trapping the peroxy radical, and these metals are deactivated. This deactivation must be, in part, the reason why manganese and copper salts have little effect on the products. Cobalt naphthenate, unlike manganese and copper, did not show an inhibiting effect on the oxidation of α-methylstyrene except at an extremely high concentration, suggesting that no deactivation occurred.[9] The same phenomena were again observed in this system; cobalt salt accelerated the oxidation significantly, while manganese and copper salts retarded the oxidation, especially at high concentrations. After all, perbenzoic acid may be consumed mostly by the reaction with α-methylstyrene, and only to a lesser extent by the cobalt-catalyzed decomposition.

Cobalt salt may participate in the initiation (Eq. (7)) and in the decomposition of perbenzoic acid

$$C_6H_5CHO + Co^{3+} \rightarrow$$
$$C_6H_5C(O)\cdot + H^+ + Co^{2+} \quad (7)$$
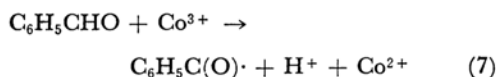
(Eq. (4)), as has been discussed by Bawn and Jolley.[20] The cobaltous ion introduced into the initial reaction mixture is immediately converted to the cobaltic state by reaction with a minute trace of perbenzoic acid. Reaction 4 serves to reconvert the cobaltous ion to the higher-valency state. At a very small concentration of cobalt salt (3.5×10^{-5} mol/l), the products were exactly the same as in the uncatalyzed oxidation, but an increase in the concentration of cobalt salt decreased the yield of α-methylstyrene oxide a bit and increased that of acetophenone considerably. The metal salt-catalyzed decomposition of perbenzoic acid naturally lowers the yield of the epoxide. In the meantime, cobalt naphthenate was found to be valid for the formation of α-methylstyrene oxide by a radical mechanism.[9] If so, it can compensate for the decrease in the yield of α-methylstyrene oxide caused by suppressing the polar reaction mentioned before (Eq. (3)), and so the net decrease may be rather small. The increase in the yield of acetophenone may also support this consideration. Acetophenone and formaldehyde are presumably formed largely by the decomposition of a polymeric radical, ending in an alkoxy unit. This depolymerization is expected to be rapid and complete.[8]

$$RO(OCH_2C(CH_3)(C_6H_5)O)_n\cdot \rightarrow$$
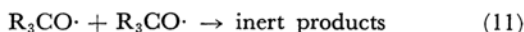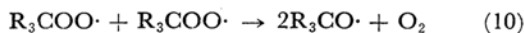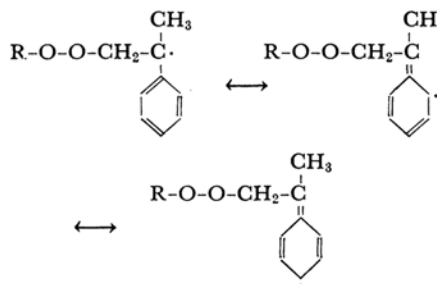$$RO\cdot + nCH_2O + nCH_3COC_6H_5 \quad (8)$$

The formation of α-methylstyrene oxide by a radical mechanism is presumed to be due to the decomposition of a free radical of an unspecified length, ending in a monomer unit[9]; this process also produces an alkoxy radical in an amount equivalent to the epoxide.

$$ROOCH_2C(CH_3)(C_6H_5)\cdot \rightarrow$$
$$RO\cdot + CH_2\text{-}C(CH_3)C_6H_5 \quad (9)$$
$$\diagdown O \diagup$$
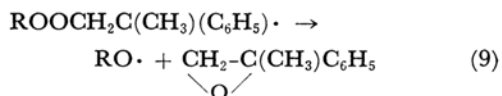
Therefore, the formation of α-methylstyrene oxide by a radical mechanism should bring about an increase in the yield of acetophenone.

Another good source of acetophenone may be the alkoxy radical produced in the termination reaction. The addition of the peroxy radical to the double bond of α-methylstyrene will take place in the β-position, since the resulting β-substituted radical is more stabilized by resonance. Consequently, the α-methylstyrylperoxy radical is tertiary; its termination reaction may proceed via the alkoxy radical.[23-26] Some portion of the alkoxy

$$R_3COO\cdot + R_3COO\cdot \rightarrow 2R_3CO\cdot + O_2 \quad (10)$$
$$R_3CO\cdot + R_3CO\cdot \rightarrow \text{inert products} \quad (11)$$

radicals thus formed may undergo the bimolecular recombination reaction[27] to form α-methylstyrene polyperoxide. However, the absence of the methanol-insoluble polyperoxide and the investigations by Traylor et al.[24-26] show that the resulting polymeric α-methylstyrylperoxy radical, ending in an alkoxy unit, may undergo a rapid depolymerization reaction[8] to form acetophenone and formaldehyde (Eq. (8)).

22) Y. Kamiya and K. U. Ingold, *Can. J. Chem.*, **42**, 1027, 2424 (1964).

23) H. S. Blanchard, *J. Am. Chem. Soc.*, **81**, 4548 (1959).
24) P. D. Bartlett and T. G. Traylor, *ibid.*, **85**, 2407 (1963).
25) A. Factor, C. A. Russell and T. G. Traylor, *ibid.*, **87**, 3692 (1965).
26) T. G. Traylor and C. A. Russell, *ibid.*, **87**, 3698 (1965).
27) R. Hiatt and T. G. Traylor, *ibid.*, **87**, 3766 (1965).