20 min. After the reaction was complete a fine black powder containing metallic lead settled at the bottom of the flask, leaving no lithium floating. Filtration in a dry box gave a light yellow solution. The ether was removed by vacuum, leaving a solid. The solid was washed quickly with petroleum ether, and 4.8 g. of pale white vinyllithium (90% yield) was collected on a filter. This solid was violently pyrophoric in air, evolved ethylene on hydrolysis, and was shown to contain vinyl groups by infrared absorption peaks at 6.4 μ. The analytical sample was dried under vacuum for 0.5 hr. at room temperature.

*Anal.* Calcd. for $C_2H_3Li$: C, 70.69; H, 8.90. Found: C, 70.77, 70.85; H, 8.93, 8.99.

*Preparation and isolation of vinyllithium from the reaction of tetravinyltin and lithium.* The procedure used in the metal exchange reaction between tetravinyllead and lithium was repeated with 1.68 g. of lithium (200% excess), 0.008 g. of benzophenone, 4.54 g. of tetravinyltin (0.02 mole), and 10 ml. of dry diethyl ether solvent. The suspension turned black in 2 hr. The mixture was stirred overnight and then worked up as described above. The black solid was found to contain metallic tin. The product was isolated as a pure white solid which was violently pyrophoric, giving a brilliant red flash on contact with air. The product evolved ethylene on hydrolysis. The yield of vinyllithium was 1.15 g. or 42.5%.

This experiment was checked in repeated runs which showed that yields as high as 55% of pure product can be obtained in reaction periods as short as 4 hr. when high purity tetravinyltin and clean lithium are used.

*Anal.* Calcd. for $C_2H_3Li$: C, 70.69; H, 8.90. Found: C, 70.46; H, 9.20.

*Conversion of tributyltin chloride to tributylvinyltin with isolated vinyllithium.* Vinyllithium (4.8 g. or 0.141 mole) was dissolved in 110 ml. of dry diethyl ether in a flask fitted with a condenser, stirrer, and dropping funnel, resulting in the formation of a clear solution. By means of a dropping funnel, 45.9 g. of freshly distilled tributyltin chloride (0.141 mole, $n_D^{28}$ 1.4880) was added at a sufficient rate to maintain a gentle reflux. On addition of the tributyltin chloride to the solution, a vigorously exothermic reaction occurred with deposition of a white solid. The addition was complete in 20 min. The cooled reaction mixture was hydrolyzed by addition of water followed by 10% hydrochloric acid. The ether layer was washed with water and dried overnight over anhydrous sodium sulfate. The ether was removed through a 9-inch column filled with fine helices, and the product was distilled through a regular Claisen head. The yield was 38.0 g. or 85% of colorless liquid, b.p. 60–63° at 0.2 mm., $n_D^{26.5}$ 1.4770. The literature value for tributylvinyltin is $n_D^{25}$ 1.4761.[12] The presence of the vinyl group was confirmed by absorption in the infrared at 6.31 μ. The elemental analysis as well as the refractive index indicates about 8% tributyltin chloride contaminant in the tributylvinyltin. A small (2.7 g.) final fraction of unchanged tributyltin chloride was collected at 70–73° at 0.2 mm., $n_D^{26.5}$ 1.4838.

The purification of the product and identification as tributylvinyltin was done as follows: The tributyltin chloride in the crude tributylvinyltin was converted to the nonvolatile bistributyltin oxide by treatment with aqueous sodium hydroxide. Ten grams of the crude product was treated in this fashion and after fractionation there was recovered 7.76 g. of pure tributylvinyltin, b.p. 73–74° at 0.1 mm., $n_D^{26.5}$ 1.4763.

*Anal.* Calcd. for $C_{14}H_{30}Sn$: C, 53.03; H, 9.54. Found: C, 53.10, 53.18; H, 9.61, 9.75.

*Acknowledgment.* The authors are indebted to J. B. Honeycutt for valuable suggestions relating to this work, to D. Mitchell for checking the lithium-tetravinyltin reaction, and to R. P. Curry, R. A. Ashby, and W. J. Easley for analytical data.

Baton Rouge, La.

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(12) S. D. Rosenberg, A. J. Gibbons, and H. E. Ramsden, *J. Am. Chem. Soc.*, 79, 2137 (1957).

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[Contribution from the Petro-Tex Department, Food Machinery and Chemical Corp. Central Laboratory]

# Metal-Salt–Catalyzed Oxidation of Methacrolein

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The kinetics and products of the metal-salt–catalyzed oxidation of methacrolein and other unsaturated aldehydes in acetic acid were investigated. Methacrolein goes to peroxide, methacrylic acid, and, on extended oxidation, soluble polymer. At high aldehyde concentrations the oxidation rate was dependent on the first power of the oxygen pressure and to a fractional power of catalyst concentration. Unsaturated aldehydes were oxidized more slowly then the corresponding saturated aldehydes. Results are explained by a conventional oxidation mechanism in which the rate is determined by the reaction of unsaturated acyl radical with oxygen. The influence of termination due to the presence of monomer was considered.

The autoxidation of aldehydes to carboxylic acid occurs readily in solution at room temperature and has been shown by a large number of investigators to be catalyzed by metal ions and peroxides and to proceed by a free radical chain mechanism.[1] The nature of the peroxide intermediates and the reaction kinetics for the oxidation of saturated aldehydes, especially acetaldehyde,[2] has been widely studied but no attention has yet been given to unsaturated aldehydes which present unique experimental difficulties.

The oxidation of acrolein in acetic acid has been cursorily described[3] as occurring readily but, contrary to what is reported in the patent literature,[4] as yielding little or no monomeric acid. Church and Lynn[5] were unable to detect any re-

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(1) J. P. McNesby and C. A. Heller, *Chem. Revs.*, 54, 325 (1954).

(2) C. E. H. Bawn, T. P. Hobin, and L. Raphael, *Proc. Royal Soc. (London)*, A237, 313–324 (1956).

(3) S. A. Ballard, *et al.*, *World Petrol. Congr., Proc., 4th Congr. Rome*, 1955, Section IV C, Preprint 2.

action on oxidizing methacrolein catalytically in various solvents at atmospheric pressure but reported good yields of methacrylic acid using oxygen under pressure. Work in our laboratories had shown that the autoxidation of methacrolein[5,6] or acrolein[4] under any of the reported conditions yields little or no free acid.

The present paper reports a study of the products and the kinetics of the autoxidation of methacrolein in acetic acid. The effect of conjugation on reactivity was evaluated by investigating the oxidation rates of some saturated and unsaturated aldehydes under comparable conditions.

## EXPERIMENTAL

*Materials.* Methacrolein from a single batch supplied by Union Carbide Corp. was distilled through a glass helices packed column. The distillate obtained at 68° had a purity of 99%, the major contaminant being acrolein. It was used immediately to prepare solutions of the desired concentrations. The solutions were used within 5 min. and gave rates which could be duplicated within better than 3%. Methacrolein which had been stored at Dry Ice temperature after distillation appeared to have the same analysis but gave slower oxidation rates. For example, stored methacrolein used to prepare a $2.0M$ solution in acetic acid, with $4 \times 10^{-2}M$ cobalt acetate, gave a rate at 20° only one fifth of that normally obtained.

Other aldehydes were purified and used in the same manner. Cobaltic acetate was prepared by oxidizing cobaltous acetate with acetaldehyde[7] and dried over phosphorus pentoxide. Matheson extra dry oxygen was used and was found to be free of ozone on testing with neutral potassium iodide.

*Procedure.* The freshly prepared aldehyde solutions were added by a 100-ml. pipet to a 150-ml. magnetically stirred, water jacketed flask which had been flushed with oxygen. The reaction temperature was controlled to within ±0.3° by either removing the heat of reaction or warming with circulating water. Oxygen was measured with a gas displacement buret except in experiments where a flow of excess oxygen was employed to remove product gases and wet test meters were used. Since samples of only 0.002 ml. were required for product analysis by gas chromatography, oxygen consumption and product formation could usually be followed in a single run. When chemical analysis was required duplicate runs were made. All glass surfaces contacted by reaction solution were carefully cleaned after each experiment to prevent metal ion contamination.

Zero reaction time was taken to coincide with the initiation of stirring at 1600 r.p.m. The oxidation was found to be independent of agitation[8] above stirring speeds of 1000 r.p.m. By removing and analyzing gas samples from above the reaction solution, oxygen absorption measurements could be corrected for the build up in gaseous products which occurred when no exit gas was employed. Corrected oxygen concentrations were also necessary in determining rate dependency. The use of a constant exit gas minimized this complication but required corrections for aldehyde lost.

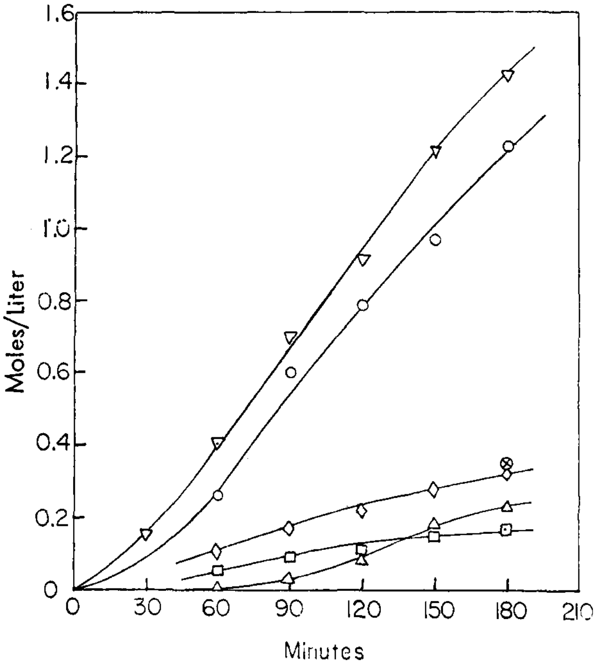

Fig. 1. The oxidation of $2.0M$ methacrolein at 20° with $0.04M$ cobaltic acetate: ▽, oxygen consumed; ○, methacrolein consumed; ◇, carbon monoxide; △, carbon dioxide; □, methacrylic acid; ⊗, polymer

The oxidation rates were determined from a plot of oxygen consumed against time as shown in Fig. 1. The early production of carbon monoxide, especially for cobaltic acetate catalyzed reactions, made observation of the induction period difficult. The rate was taken as the linear portion of the curve up to about 20% reacted. The empirical rate equation was obtained from the effect on the rate of changes in initial aldehyde or catalyst concentrations and oxygen pressure under identical experimental conditions.

*Analysis of products.* The liquid reaction products analyzed by gas chromatography were methacrolein, acrolein, acetic acid, and methacrylic acid. Satisfactory resolution was obtained at 130° on a 4 m. commercial column packed with 25% diisodecyl phthalate on Celite (Perkin-Elmer "A") using a helium flow rate of 50 ml./min. at 25 p.s.i. Using micropipets to inject constant volume samples, peak areas were calibrated against prepared standard solutions. Polymeric products failed to emerge from the chromatographic column but polymer concentration could be estimated from the shrinkage in expected total area.

Peracid was determined iodometrically using a 5% potassium iodide solution in $1.0N$ sulfuric acid after the method of D'Ans and Frey[9] for peracetic acid. Total peroxides were determined after the method of Kagan and Lubarsky[10] in which the peroxide and a 10% aqueous potassium iodide solution were reacted in acetic acid. Equivalent peroxide values were obtained under anhydrous conditions by adding powdered potassium iodide to acetic acid.

Oxygen, carbon dioxide, and carbon monoxide concentrations were determined by gas chromatography using parallel columns of silica gel and of activated carbon. This method

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(4) (a) H. P. Staudinger and K. Tuerck (to Distillers Co., Ltd.), U. S. Patents 2,341,339 (1944); Reissue 23,001 (1948); 2,377,584 (1945). (b) H. P. Staudinger, K. Tuerck, C. Brighton (to Distillers Co., Ltd.), U. S. Patent 2,381,561 (1945). (c) H. P. Staudinger, *et al.* (to Distillers Co., Ltd.), U. S. 2,386,365 (1945). (d) K. Tuerck (to Distillers Co., Ltd.), U. S. Patent 2,397,891 (1946).

(5) J. M. Church and L. Lynn, *Ind. Eng. Chem.*, 42, 768-776 (1950).

(6) W. Bauer (to Rohm & Haas), U. S. Patent 2,153,406 (1939).

(7) W. O. Walker, U. S. Patent 1,976,757.

(8) M. F. R. Mulcahy and I. C. Watt, *Proc. Roy. Soc.* (*London*), A216, 10, 30 (1953).

(9) J. D'Ans and W. Frey, *Z. anorg. Chem.*, 84, 145 (1914).

(10) M. Y. Kagan and G. D. Lubarsky, *Acta Physicochim.*, 2, 665 (1935).

was capable of detecting hydrocarbons containing up to three carbon atoms but only traces of methane was found.

*Polymeric product.* When an oxidation was interrupted by rapid cooling and the addition of hydroquinone, a solution was obtained which did not precipitate solid on dilution with water or ether. Removal of solvent and volatile products at room temperature under high vacuum gave an oily residue which was soluble in acetic acid and benzene. A typical residue, from a manganese catalyzed oxidation interrupted when 35% of the methacrolein had reacted, gave an analysis of 0.6 m.eq./g. of peroxide and had an apparent neutral equivalent of 132 on back titrating a basic solution. Its infrared spectra was best interpreted as representing an ester or lactone and showed no peracid and almost no carboxyl group present.

When precautions were not taken to prevent polymerization on completion of the reaction, dilution with water gave a white precipitate. This polymer had an analysis corresponding to up to 80% of the free carboxyl groups expected for polymethacrylic acid but it was soluble in acetone and showed broad absorption in the 9 to 11 μ region.

## RESULTS AND DISCUSSION

The oxidation of methacrolein in acetic acid at 40° catalyzed by a variety of metal salts and oxides gave only small amounts of free methacrylic acid. The major product was a soluble acidic polymer. Analysis of oxidation mixtures by titriometric methods shows high apparent methacrylic acid yields when this is not recognized (Table I). To a slight extent this error is reflected in the gas chromatogram area analysis also since polymer is not represented.

TABLE I

ACTIVITIES OF VARIOUS CATALYSTS AND APPARENT YIELDS OF METHACRYLIC ACID[a]

| Catalyst | Rate[b] $\times 10^5$ | Ald. react., %[c] | Yields,[d] % Gas C.[e] | Tit. |
|---|---|---|---|---|
| $Co(OAc)_3$ | 26.5 | 66 | 35 | 79 |
| Co-Acetylacetonate | 25.8 | 70 | 13 | 67 |
| $Co(OAc)_2$ | 17.9 | 76 | 5 | 61 |
| $Mn(OAc)_2$ | 11.7 | 41 | 28 | — |
| Cu-Methacrylate | 10.0 | 10[f] | 7 | 13 |
| $V_2O_5$ | 11.8 | 82 | 9 | 55 |
| $HVO_3$ | 11.0 | 54 | 10 | 81 |
| $SeO_2$ | 2.4 | 43[f] | 13 | — |

[a] 0.04*M* catalyst, 2.0*M* methacrolein, 40°, oxygen off gas of 18 ml./l., min. [b] Oxidation rate in moles $O_2$/l., sec. [c] Reaction time four hours. [d] On aldehyde reacted. [e] By % total peak area. [f] Reaction time five hours.

Table I shows the efficiencies of various catalysts. While only small differences in behavior were observed for the soluble catalysts, cobaltous acetate gave a faster rate than manganous acetate which is contrary to what has been reported for the oxidation of acetaldehyde.[2] In the absence of catalysts under scrupulously clean conditions, no oxidation was observed even in experiments conducted for as long as six hours at 20°. Cobaltic acetate and cobaltic acetylacetonate, in which the anion is already in its highest oxidation state, gave the fastest rates observed and were able to do so even in the presence of added quantities of hydroquinone sufficient to normally inhibit oxidation completely.

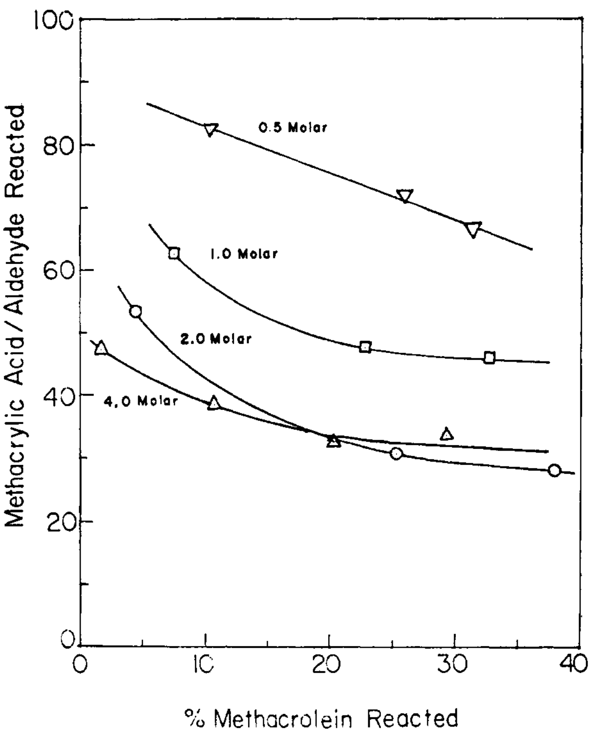

Fig. 2. Influence of methacrolein concentration and per cent methacrolein reacted on yields of methacrylic acid. The temperature is 40° and the catalyst is manganous acetate

Examination of the initial real yields of methacrylic acid indicated that the polymerization of the product was far more important than polymerization of the starting aldehyde. As shown in Fig. 2 at sufficiently low concentrations, methacrolein appeared to go initially almost quantitatively to free acid. On increasing the extent of oxidation yields decreased strongly. The failure of methacrolein polymerization to influence strongly early yields is interesting since in the absence of oxygen methacrolein formed a polymer which precipitated from the acetic acid solutions used at only a few per cent reacted. Since the formation of a precipitate was never observed during an oxidation, significant polymerization of methacrolein could have occurred only if extremely rapid oxidation of the polymer formed was possible or if a copolymer of completely different solubility was formed.

The manganous and cobaltic ion catalyzed oxidations were studied over a range of catalyst concentrations of $5 \times 10^{-3}$ to $40 \times 10^{-3}M$ and aldehyde concentrations of 0.5 to 4.0*M*. The oxidation rate was found to have very low dependency on catalyst concentration and at methacrolein concentrations above 0.5*M*, to be independent of aldehyde concentration. With cobaltic acetate the production of acetic acid and carbon monoxide was favored, the former increasing with increasing catalyst concentration. Variation of oxygen pressure from 600 to 870 mm. indicated a first order rate dependency on oxygen. First order dependency was also found for the analogous saturated aldehyde, isobutyraldehyde, under the concentration conditions of this study. Data is summarized in Tables II and III. The resulting empirical rate equation was shown to be

$$\frac{d[O_2]}{dt} = k\ (\text{Catalyst})^{0.26}(O_2)$$

The rate of disappearance of methacrolein was also investigated and appeared to approach first order with respect to time and initial concentration up to 2.0*M*.

TABLE II

COBALTIC ACETATE CATALYZED OXIDATION OF 2.0*M* METHACROLEIN AT 20°

| Influence of catalyst concentration on rate[a] and products[b] | | | | |
|---|---|---|---|---|
| Cat., $M \times 10^{-3}$ | 5 | 10 | 20 | 40 |
| Rate[c] $\times 10^5$ | 12.1 | 13.9 | 15.0 | 18.7 |
| Acetic acid | 25 | 37 | 40 | 54 |
| Acrolein | 8 | 9 | 11 | 5 |
| Methacrylic acid | 17 | 13 | 13 | 12 |
| Effect of pressure on rate[d] | | | | |
| Mm. | 695 | 765 | 791 | 864 |
| Rate $\times 10^5$ | 19.1 | 21.0 | 24.6 | 29.4 |

[a] Experiments with off gas. [b] % based on aldehyde consumed at approximately 60% reacted. [c] Moles $O_2$/l., sec. [d] $4 \times 10^{-2}M$ catalyst.

TABLE III

MANGANESE ACETATE CATALYZED OXIDATION OF METHACROLEIN[a]

| Effect of temperature[b] | | | | | |
|---|---|---|---|---|---|
| °C. | 14 | 15 | 20 | 30 | 40 |
| Rate $\times 10^6$ | 0.9 | 0.9 | 3.6 | 5.0 | 11.7 |
| Influence of catalyst and methacrolein concentration[c] | | | | | |
| Aldehyde, *M* | 0.5 | 1.0 | 2.0 | 2.0 | 4.0 |
| Cat., $M \times 10^{-2}$ | 1.0 | 2.0 | 4.0 | 1.0 | 8.0 |
| Rate $\times 10^5$ | 3.7 | 9.5 | 11.7 | 9.2 | 13.6 |

[a] Off gas used. [b] $4.0 \times 10^{-2}M$ catalyst, 0.2*M* methacrolein. [c] 40°.

While activation energies for oxygen dependent reactions have frequently been reported, doubt has been cast on their validity,[1] because of the change of oxygen solubility with temperature. However, assuming that the change in oxygen solubilities in acetic acid below 40° was small enough to be neglected, an activation energy for the manganese catalyzed oxidation of approximately 8.5 Kcal. was estimated. The disappearance of methacrolein had almost the same energy of activation, 8.7 Kcal. As rates at the lower temperatures were extremely slow, it was impractical to allow the oxidation to proceed far enough to obtain meaningful analyses for all products. However, it did appear that at 15° and approximately 5% conversion, over 60% of the methacrolein reacted existed as peroxide. The production of carbon dioxide and carbon monoxide was also discouraged by low temperatures. This was especially true for manganese catalyzed reactions where only traces of these gases remained at 20°. Cobaltic ion continued to favor the production of carbon monoxide at this temperature as shown in Fig. 2.

The first stable product of the autoxidation of acetaldehyde and benzaldehyde is the corresponding peracid. Peracetic acid has been shown to react with acetaldehyde to form an equilibrium mixture with an intermediate peroxide[2,10] while perbenzoic acid reacts directly with benzaldehyde to give two molecules of benzoic acid. Peracid and total peroxide analyses in the manner described by Bawn[2] indicate that methacrolein forms an intermediate peroxide but it was not possible to check the reliability of the analytical methods in distinguishing peracid and the extremely low values found introduced considerable error. For the manganese catalyzed oxidation of 2.0*M* methacrolein at 20° the peracid and total peroxide values ($M \times 10^{-3}$) at various times were: 2 hr., 4.6, 55; 3 hr., 4.6, 28; 4 hr., 4.6, 18.6; 5 hr., 9.6, 23.2. The close to mole for mole correspondence between aldehyde reacted and oxygen cannot supply evidence for a peroxidic intermediate since the stoichiometry is complicated by side reactions such as decarbonylation.

Accepting the initiation step of Bawn and the propagation steps of Backstrom[11] for the oxidation of aldehydes gives the following where $Co^{+3}$ may be replaced by $Mn^{+2}$ and A is $CH_2{=}C(CH_3)CO$

$$\begin{aligned}
&\text{Initiation;} && (1a)\ AH + CO^{+3} \xrightarrow{k_{1a}} A\cdot + Co^{+2}\\
& && (1b)\ AOOH + Co^{+3} \xrightarrow{k_{1b}} AOO\cdot + Co^{+2}\\
&\text{Propagation;} && (2)\ A\cdot + O_2 \xrightarrow{k_2} AO_2\cdot\\
& && (3)\ AO_2\cdot + AH \xrightarrow{k_3} AO_2H + A\cdot\\
&\text{Termination;} && (4)\ A\cdot + A\cdot \xrightarrow{k_4}\\
& && (5)\ A\cdot + AO_2\cdot \xrightarrow{k_5}\\
& && (6)\ AO_2\cdot + AO_2\cdot \xrightarrow{k_6}\\
& && (7)\ AO_2\cdot \text{ or } A\cdot + M \xrightarrow{k_7}
\end{aligned}$$

Reaction 1a is the most acceptable initiaton step since the oxidation shows no induction period and immediate production of carbon monoxide is observed when $Co^{+3}$ is the added catalyst. However reaction 1b could become the important mode of initiation following rapid peracid formation due to reaction 1a. In addition to the usual chain terminating radical interactions 4, 5 and 6, the addition of the propagation radicals to unsaturated methacrolein or methacrylic acid 7 must be considered in the present case. The only single termination

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[11] H. L. J. Backstrom, *Z. physik. Chem.*, **B25**, 115 (1934).

step leading to a rate expression showing the dependency on oxygen found by experiment and a low order dependency on initiation was reaction 4. This gives

$$\frac{d[O_2]}{dt} = \frac{k_2}{(2k_4)^{1/2}} R_i^{1/2}(O_2)$$

If the assumption of long chains is made, the initiation of methacrylic acid polymerization by reaction 7 may occur without changing the rate equations. It is more likely that radicals from peroxide decomposition initiate polymerization. The importance of chain transfer from oxidizing methacrolein to a monomer or growing polymer chain can be judged better by comparing the rates of unsaturated aldehydes with their saturated analogs.

The rates of the manganous acetate catalyzed oxidation of acrolein, methacrolein, and crotonaldehyde and those of the analogous saturated aldehydes is shown in Table IV. In each case unsaturation slows the oxidation rate, the magnitude of this effect being greater the more readily the corresponding saturated aldehyde is oxidized. Methacrolein and acrolein oxidize at about the same rate indicating that an *alpha* methyl group has little effect while a seven-fold increase in rate is observed for crotonaldehyde showing an accelerating influence for *beta* substitution. The effect of structure from these examples is in the same direction and approximately of the same magnitude as reported for olefin oxidations[12] a case in which however the rate is related to the ease of removal of *alpha* hydrogen in propagation step 3.

For saturated aldehydes, reactivity is enhanced by increasing the chain length and degree of branching. For RCHO, the rate changes with R as follows: isopropyl > *n*-propyl > ethyl > methyl. Here again the order of decreasing carbon hydrogen bond dissociation energies is followed if it is assumed that the effect of changing R is the same on RCO-H as on $RCH_2$-H where values have been reported.[13]

TABLE IV

INFLUENCE OF STRUCTURE IN THE OXIDATION OF ALDEHYDES[a]

| Aldehyde | Rate[b] × $10^5$ | Yields,[c] % Reacted | Acid | Peroxide |
|---|---|---|---|---|
| Acetaldehyde | 2.0 | 15 | 79 | 9 |
| Propionaldehyde | 2.7 | 45 | 94 | 4 |
| Butyraldehyde | 25.0 | 47 | 61 | 5 |
| *i*-Butyraldehyde | 31.0 | 45 | 71 | 4 |
| Acrolein | 1.0 | 13 | 29 | 33 |
| Methacrolein | 0.8 | 5 | 47 | 13 |
| Crotonaldehyde | 5.3 | 23 | 25 | 9 |

[a] 2.0*M* aldehyde, 0.04*M* manganese acetate in acetic acid at 20°. [b] Moles $O_2$/l., sec. [c] Based on aldehyde reacted.

For oxygen dependent oxidations the effect of alkyl substitution must be related to hydrogen abstraction during initiation rather than during propagation as cited for olefins. However, the difference in reactivity between saturated and unsaturated aldehydes should arise from $k_2$ which depends on the activity of the radical A· and should be smaller for the allylic radicals derived from unsaturated aldehydes. Thus, if the rate equation describes the reaction correctly and is not oversimplified, slower rates for unsaturated aldehydes should be considered normal.

Termination by radical addition to monomer would also operate to give slower rates for unsaturated aldehydes but the small magnitude of the rate differences observed makes it seem unlikely that this effect is also important.

PRINCETON, N. J.

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(12) J. L. Bolland, *Quart. Revs.*, **3**, 1 (1949).

(13) E. W. R. Steacie, *Atomic and Free Radical Reactions*, Vol. I, Reinhold Publishing Corp., New York, N. Y., 1954, p. 98.