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Oxidation by Solids. I. Oxidation of Selected Alcohols by Manganese Dioxide

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It has been found that the rates of oxidation of a variety of phenylcarbinols by manganese dioxide in benzene can be readily followed by noting the rate at which the by-product water distills into a Dean-Stark trap. The aldehydes and ketones produced are obtained in high yields and close to the theoretical volume of water is collected. The effects of changes in structure of the alcohols on their rates of oxidation are consistent with the proposal that the reaction proceeds *via* free radical intermediates. Aliphatic alcohols underwent oxidation much more slowly and in much lower yields than did the phenylcarbinols.

The limited number of studies on the effect of changes in structure of organic compounds on their rates of oxidation[2] stand in marked contrast to the large number of applications of oxidation in preparative organic chemistry.[2] Since relationships between structure and reactivity are less well established for free radical than for ionic reactions[3] the investigation of such relationships for homolytic oxidations are of increased interest.[2] The results of a study of the effects of changes in structure of selected alcohols on their rates of oxidation by solid manganese dioxide are reported here.

In the standard procedure developed for the experiments of Table I, a magnetically stirred suspension of manganese dioxide in benzene and the alcohol was heated under reflux in an apparatus equipped with a Dean-Stark trap until evolution of water ceased. A plot of the volume of water collected against time gave a smooth curve of constantly decreasing slope. Since these curves were found to be closely reproducible and of the same general shape the time required for a 50% yield of water to collect was a valid measure of the relative rate.

It is evident (Table I) that a wide variety of phenylcarbinols are rapidly oxidized in high yields and that close to theoretical yields of water are obtained. The advantages, for preparative purposes, of this distillation method of oxidation with manganese dioxide are readily apparent.[4,5]

The data in the first two sections of the table show that a change in the electron-attracting ability of a *para* substituent has a much smaller effect on the rate than would be expected if carbonium ions, as recently suggested,[4] are the important intermediates. Except for the methoxyl compounds the rate gradually increases with increasing electron-attracting ability of the substituent while a sharp decrease in rate would be expected for a carbonium ion reaction[6,7]; *p*-nitrobenzyl alcohol in particular reacts very sluggishly, if at all, *via* the carbonium ion intermediate.[7] It was also found that the addition of acid slightly decreased the rate of oxidation of benzyl alcohol although it would be expected to facilitate greatly the formation of carbonium ions.

The relatively minor effects on the rate of varying the *para* substituents are, however, consistent with the proposal that free radical intermediates such as C_6H_5—$\dot{C}$HOH are involved. It is not unusual for free radical reactions to be accelerated by both electron-attracting and electron-releasing groups as was found here.[8,9] The methoxyl compounds may, however, be exceptions to the trends established for the other *para* substituted compounds because of differing adsorption on the solid manganese dioxide.[10] The addition of diphenylamine decreased the rate of oxidation of benzyl alcohol as expected for a free radical reaction.

Results in the third section of the table together with selected data from other sections show that the rate of oxidation of C_6H_5CHOHR alcohols increases with change in —R in the order: —CH(CH_3)C_6H_5, —CH(CH_3)$_2$, —$CH_2C_6H_5$, —CH_3, —H, —C_6H_5, —CH=CHC_6H_5 and —$\overset{\overset{O}{\|}}{C}C_6H_5$. The over-all increase is about sevenfold. Substituting a methyl group for hydrogen [compare —CH_3 with —H, —CH(CH_3)$_2$ with —CH_3 and —CH(CH_3)C_6H_5 with —CH_2(C_6H_5)] causes a consistent decrease in rate possibly because the methyl group interferes sterically with adsorption on the manganese dioxide[10]; in fact the order of the four groups preceding —H in the above series may well be the order of decreasing steric hindrance. Although the adsorption characteristics of the three groups following

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[1] From the Ph.D. thesis of John F. Van de Castle, June 1960.

[2] W. A. Waters, *Organic Chemistry*, H. Gilman, Ed., Wiley, New York, 1953, Vol. IV, pp. 1121, 1130, 1131.

[3] E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Holt, New York, 1959, p. 693.

[4] R. M. Evans, *Quarterly Reviews*, **13**, 61 (1959). Both this and ref. 5 contain valuable reviews of related work.

[5] R. J. Gritter and T. J. Wallace, *J. Org. Chem.*, **24**, 1051 (1959).

[6] E. F. Pratt and P. W. Erickson, *J. Am. Chem. Soc.*, **78**, 76 (1956).

[7] E. F. Pratt, R. K. Preston, and J. D. Draper, *J. Am. Chem. Soc.*, **72**, 1367 (1950).

[8] Ref. 3, p. 694.

[9] J. Hine, *Physical Organic Chemistry*, McGraw-Hill, New York, 1956, p. 381.

[10] M. Harfenist, A. Bavley, and W. A. Lazier, *J. Org. Chem.*, **19**, 1608 (1954).

TABLE I

OXIDATION OF SELECTED ALCOHOLS

Alcohol	$t_{50\%}$, min.	H_2O, %	Product, %
p-$RC_6H_4CH_2OH$ ALCOHOLS			
p-$CH_3OC_6H_4CH_2OH$	44	104	79
p-$(CH_3)_2CHC_6H_4CH_2OH$	52	91	82
$C_6H_5CH_2OH$	47	101	68
p-$ClC_6H_4CH_2OH$	46	91	77
p-$O_2NC_6H_4CH_2OH$	37	98	81
(*p*-$RC_6H_4)_2CHOH$ ALCOHOLS			
(*p*-$CH_3OC_6H_4)_2CHOH$	30	96	93
(*p*-$CH_3C_6H_4)_2CHOH$	36	97	88
$(C_6H_5)_2CHOH$	33	94	92
(*p*-$ClC_6H_4)_2CHOH$	25	97	96
(*p*-$O_2NC_6H_4)_2CHOH$	17	100	94
C_6H_5CHOHR ALCOHOLS			
$C_6H_5CHOHCH(CH_3)C_6H_5$	150	99	95
$C_6H_5CHOHCH(CH_3)_2$	88	102	77
$C_6H_5CHOHCH_2C_6H_5$	62	97	83
$C_6H_5CHOHCH_3$	56	98	72
$C_6H_5CHOHCOC_6H_5$	22	95	84
OTHER PHENYLCARBINOLS			
$C_{10}H_6CHOHCH_2$[a]	121	96	71
$C_6H_4CHOHC_6H_4O$[b]	31	96	90
$C_6H_4CHOHC_6H_4$[c]	6	114	84
OLEFINIC ALCOHOLS			
$CH_3CH{=}CHCH_2OH$	75	101	28[d]
$C_6H_5CH{=}CHCH_2OH$	37	98	82
$C_6H_5CH{=}CHCHOHC_6H_5$	25	95	90
SECONDARY ALIPHATIC ALCOHOLS[e]			
$CH_3(CH_2)_5CHOHCH_3$	850	68	42[f]
$CH_2CH_2CH_2CH_2CHOH$	1073	78	12
$CH_2CH_2CH_2CH_2CH_2CHOH$	980	71	17
$CH_2CH_2CH_2CH_2CH_2CH_2CHOH$	560	88	49[g]
PRIMARY ALIPHATIC ALCOHOLS[e]			
$CH_3(CH_2)_6CH_2OH$	1200	65	7
$C_6H_5CH_2CH_2CH_2OH$	800	74	8
$C_6H_5CH_2CH_2OH$	495	82	2

[a] Acenaphthenol. [b] Xanthydrol. [c] Fluorenol. [d] Doubtlessly much more was formed, but was volatilized with the benzene. [e] Yields calculated from vapor phase chromatography and refractive index measurements (see Experimental). [f] Twice as much manganese dioxide gave a 65% yield. [g] Twice as much manganese dioxide gave a 67% yield.

—H could also influence their position in the above series it seems probable that their relative positions are chiefly determined by their increasingly large tendency to stabilize free radical intermediates of the general formula $C_6H_5\dot{C}OHR$.[11] The almost threefold increase in rate as —R is changed from $—CH_2C_6H_5$ to $—\overset{\overset{O}{\|}}{C}C_6H_5$, for example, is a reasonable result of the radical stabilizing ability of an adjacent carbonyl group.[12]

The extremely rapid oxidation of fluorenol (fourth section of the table) as compared to benzhydrol is also consistent with a free radical mechanism since fluorenol and fluorene are autoxidized, presumably *via* free radicals, to the ketone much more readily than are benzhydrol and diphenylmethane.[13]

Results of attempts to oxidize aliphatic alcohols are given in the last two sections of Table I. Yields are much lower than for the phenylcarbinols although fair yields of ketone were obtained from two of the secondary alcohols.[14] Since even when little aldehyde or ketone was obtained fair yields of water were collected it appears that some water-producing side reaction occurs to a major extent when the desired reaction proceeds very slowly. Studies on the source of the excess water are in progress. There is no evidence that excess water is produced to any serious extent when, as in the experiments in the first five sections of the table, the desired oxidation proceeds readily. It would be predicted, on the basis of free radical intermediates, that primary aliphatic alcohols would oxidize slower than secondary which in turn would oxidize slower than phenylcarbinols as was found here.[11]

Manganese dioxide has been employed previously for oxidizing selectively only one of the hydroxyl groups of polyalcohols.[15] The shape of the rate curve obtained when polyalcohols are oxidized by the distillation method reported here should be valuable both for establishing which selectve oxidations are practical and for determining at what point to stop the reaction for maximum selectivity. The data in Table I should be useful for predicting the probable success of attempts at selective oxidation.

The following reaction route is proposed as the simplest consistent with available data. It is an adaptation of general suggestions concerning the

$$R_2CHOH + O{=}\overset{IV}{Mn}{=}O \longrightarrow R_2\dot{C}OH + HO{-}\overset{III}{Mn}{=}O \longrightarrow$$

$$R_2\dot{C}O + HO{-}\overset{II}{Mn}{-}OH \longrightarrow R_2C{=}O + H_2O + \overset{II}{Mn}{=}O$$

oxidation of organic compounds by covalent inorganic oxides.[16] The second step is included to suggest how $R_2C{=}O$ may be formed from $R_2\dot{C}OH$, but is not meant to imply $R_2\dot{C}O$ need exist independently. The manganese dioxide employed is difficult to define precisely,[5] but the previous finding[4] that its oxygen content decreases by the amount demanded by the equation was confirmed

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[11] Ref. 3, p. 707.

[12] Ref. 3, pp. 697, 718.

[13] E. F. Pratt and L. E. Trapasso, *J. Am. Chem. Soc.*, **82**, 6405 (1960).

[14] M. Z. Barakat, M. F. Abdel-Wahab, and M. M. El-Sadr, *J. Chem. Soc.*, 4685 (1956).

[15] F. Sondheimer, C. Amendolla, and E. Rosenkranz, *J. Am. Chem. Soc.*, **75**, 5932 (1953).

[16] W. A. Waters, *Trans. Faraday Soc.*, **42**, 184 (1946).

in the present study. The nearly quantitative yield of water formed further supports this finding.

EXPERIMENTAL

Starting materials. The manganese dioxide was prepared by a modified Attenburrow procedure.[17] Manganese sulfate monohydrate (Mallinckrodt analytical reagent) was employed in place of the tetrahydrate and the solutions of it and of sodium hydroxide were added over 1 hr. at 80–90° to the permanganate solution. Stirring was continued for another hour at 90°, the hot suspension was filtered, and the manganese dioxide was washed free of permanganate with large amounts of hot water. Washing with tap water was continued until the filtrate was neutral to litmus. The powder was dried 4 hr. at 125°, well ground and reheated at 125° for 24 hr. and finally ground further to pass a 60-mesh screen and dried again for 24 hr. at 125°.

All other constituents of the reaction mixture were purified by standard crystallization or distillation procedures until the physical constants agreed closely with the literature values.

Experiments of Table I. A 500-ml. volumetric flask was filled to the mark with benzene; a volume in milliliters corresponding to the weight in grams of the alcohol was withdrawn along with an additional 25 ml. for rinsing and the remainder added to a 1-l. spherical flask with three standard taper necks. One neck was fitted with a Dean-Stark water trap[18] surmounted by a West condenser. A calibrated thermometer was placed in the second neck in a well which extended into the liquid, but which left room for a 1.5 in. Teflon covered magnetic stirring bar. The magnetic stirring motor[19] was found to operate satisfactorily through a hemispherical mantle by which heat was supplied at a rate just below that which would flood the condenser. The same voltages were applied to the stirrer and the mantle for all experiments. All pertinent precautions and refinements of previous related studies by the distillation method[18] were employed; in particular it should be noted that the water is removed very rapidly and accurate rates are obtained as long as the time for 50% reaction is not less than about 15 min.[6] Approximately 1 ml. of water was placed in the trap which was then filled with benzene. Heat was applied and refluxing allowed to continue for about 30 min. to remove a film of water from the interior of the flask, condenser, and trap. It was found that the water evolved from the reaction did not adhere to the inner walls of the condenser and trap if these were scrubbed well with soap and water, thoroughly rinsed and used directly without prior drying in an oven. Four tenths of a mole (34.77 g.) of manganese dioxide was added and refluxing continued for 5.0 hr. during which about 0.9 ml. of water collected; very little water was evolved after the first hour. After the suspension had been allowed to cool a few degrees 0.1 mole of the alcohol was rinsed in with the 25 ml. of benzene which had been reserved. Heating was resumed and zero time taken when the first drop of liquid fell from the condenser. Frequent readings of water volume, time, and temperature were taken over the 10 to 90% portion of the reaction and the rate curves plotted. Most of the curves approximated those for a reaction which is first order with respect to the alcohol, but the significance of this in this heterogeneous system is not readily apparent. After readings were suspended refluxing was ordinarily allowed to continue overnight to give the total yield of water listed in Table I.

The temperature of the refluxing suspension increased gradually as the reaction progressed. With one exception (fluorenol) the increase for the 10 to 90% portion of the reaction was not over 0.4°. Among most of the experiments the temperature was 81.1 ± 0.3° and among practically all it was 81.0 ± 0.6°. It was found by carrying out numerous duplicate experiments that the time required for the production of a 50% yield of water was readily checked within about 4%. For example two standard experiments on benzyl alcohol gave $t_{50\%}$ values of 47 and 48 min. It was necessary to prepare a second batch of manganese dioxide for the experiments in the last part of Table I. A check on benzyl alcohol with this batch gave a $t_{50\%}$ value of 47 min. Additional check runs showed that the activity of the manganese dioxide did not change significantly over a period of several weeks.

Isolation of products. The products from the experiments listed in the first five sections of Table I were isolated by standard distillation and crystallization procedures. Except for crotonaldehyde, which although distilled through a 4 ft. Todd Column packed with glass helices still contained traces of benzene according to the results of vapor phase chromatography, the refractive indices or melting points agreed satisfactorily with the literature values.

It was found to be impractical to separate completely the mixtures of alcohols and ketones obtained from the experiments in the last two sections of Table I. The carbonyl content of the distillation fractions was therefore calculated from the results of both vapor phase chromatography and refractive index measurements to give the tabulated yields. Results from the two methods of calculation ordinarily agreed satisfactorily.

Supplementary experiments. The amount of manganese dioxide was varied in a group of four experiments otherwise identical with the standard experiment for benzyl alcohol (Table I). When 0.2, 0.4, 0.6, and 0.8 mole of the dioxide were used the total yields of water were 54, 101, 102, and 122% and the $t_{50\%}$ values were 142, 47, 52, and 63 min. The inordinately long $t_{50\%}$ time obtained with the 0.2 mole of dioxide is of limited significance since the total yield of water was only slightly over 50%. Decreased stirring efficiency may have been responsible for the slightly slower reaction with the two highest amounts of dioxide.

With the two aliphatic secondary alcohols, on the other hand (footnotes *f* and *g* of Table I), the $t_{50\%}$ values fell from 850 and 560 min. to 144 and 116 min., respectively, as the amount of dioxide was increased from 0.4 to 0.8 mole. The total yields of water were 128 and 129%.

The effects of adding 0.002 mole of *p*-toluenesulfonic acid monohydrate, diphenylamine, potassium hydroxide, or cupric bromide[20] were determined in a group of four experiments otherwise identical with the standard experiment with benzyl alcohol (Table I). The $t_{50\%}$ values were 51, 63, 36, and 44 minutes, respectively. The total yield of water was about 100% in each case.

It was found, in agreement with a previous report,[5] that substitution of a nitrogen atmosphere had no detectable effect on the rate of reaction in an experiment otherwise identical with the standard experiment for benzyl alcohol and that the amounts of gas evolved during reaction were so small as to be of only minor, if any, significance.

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[18] E. F. Pratt and J. D. Draper, *J. Am. Chem. Soc.*, **71**, 2846 (1949).

[19] Arthur H. Thomas Co., Cat. No. 9235-S.

[20] M. S. Kharasch and G. Sosnovsky, *Tetrahedron*, **3**, 97 (1958).