TABLE III

2,4-DINITROPHENYLHYDRAZONES[a]

Aldehyde	M.p. of DNP, °C.	Nitrogen, % Calcd.	Nitrogen, % Found
5-Methoxypentanal	79–79.5	18.91	19.10
6-Hydroxyhexanal	104–105	18.91	19.09
6-Methoxyhexanal	74–74.5	18.06	18.36
8-Hydroxyoctanal	91–93	17.28	17.33
8-Methoxyoctanal	73–74	16.56	16.48
9-Methoxynonanal	73–74	15.90	15.98
10-Hydroxydecanal	80[b] 101–103	15.90	16.33
10-Methoxydecanal	77	15.29	15.25

[a] These derivatives were prepared by standard procedures as given by Shriner and Fuson[25] and A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., Inc., New York, N. Y., 1948, p. 342. [b] Double m.p. sintered at 80° and melted 101–108°.

"75% dioxane" was prepared by mixing three volumes of dried and purified[26] dioxane with one volume of distilled water. The samples measured were generally the same as those submitted for analysis or were purified as described under their preparation. Equilibrium conditions in solutions of the hydroxy aldehydes were obtained within one to three days. Initial absorption was usually considerably lower than that at equilibrium. The existence of equilibrium was verified by rechecks on different solutions or by returning to the original temperature after measurements at another temperature. The equilibria were quite mobile once established, about one-half hour at a given temperature generally being sufficient for the attainment of stable readings. The precision of the results may vary somewhat, since a few of the measurements were made at high transmittancies where the spectrophotometer is less accurate.[27] Data on the methoxy aldehydes are given in Table I.

Acknowledgments.—One of us (W. H. S.) is indebted to the Allied Chemical and Dye Corporation for financial aid in the form of a fellowship, 1950-1951. Microanalysis for carbon, hydrogen, nitrogen were performed by Misses C. Brauer and J. Sorensen.

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[26] L. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., New York, N. Y., 1941, p. 369.

[27] G. H. Ayres, *Anal. Chem.*, **21**, 652 (1949).

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Rates of Chromic Acid Oxidation of Some Cyclanols[1,2]

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RECEIVED MAY 19, 1952

The rates of chromic acid oxidation of isopropyl alcohol and four cyclanols follow the order $C_8H_{15}OH > C_7H_{13}OH > C_4H_7OH > C_5H_9OH > C_6H_4OH > C_3H_7OH$.

It is well known that the rates and equilibria of reactions involving alicyclic compounds often vary profoundly with ring size. Several factors appear to be involved. Some of these have been embraced in the concept of I-strain by Brown and coworkers.[3] Thus a quadricovalent cyclopropane derivative will be less strained due to the bond angles imposed by the ring structure than a tricovalent (*e.g.*, ion, radical or ketone) or pentacovalent (transition state in an S_N2 displacement) species. Transformation from the first to either of the latter two is therefore relatively difficult; the reverse transformation is relatively easy. A similar argument applies to cyclobutane derivatives where the differences in strain are smaller. However, complications can be introduced, for example, by the fact that the cations from some cyclobutyl and cyclopropylmethyl derivatives may be identical.[4] For the 5- and 7-membered rings torsional forces due to hydrogen–hydrogen repulsions[3,5] appear to account for the greater ease of the quadricovalent-to-tricovalent transformation of a carbon atom compared with the 6-membered ring; in the latter hydrogen–hydrogen repulsions are at a minimum because of the possibility of a completely "staggered" configuration.

In order to obtain additional quantitative information on the reactivities of alicyclic derivatives we have measured the rates of chromic acid oxidation of isopropyl alcohol and the series cyclobutanol through cycloöctanol. As a result of the elegant investigations of Westheimer and co-workers[6] the mechanisms of oxidation of secondary alcohols are fairly well understood. The slow step in the reaction involves participation by the alcohol, acid chromate ion and one or two protons as kinetically distinguishable species in water. Furthermore, removal of the hydrogen on the carbinol carbon is part of this step, as evidenced by the fact that 2-deutero-2-propanol reacts only about one-sixth as fast as ordinary 2-propanol.[6b] The mechanisms may be represented as

$$R_2CHOH + HCrO_4^- + H^+ \underset{}{\overset{\text{fast}}{\rightleftarrows}} R_2CHOCrO_3H + H_2O \overset{H^+}{\rightleftarrows} [R_2CHOCrO_3H_2]^+ \quad (1)$$

$$R_2CHOCrO_3H + H_2O \xrightarrow[k_1]{\text{slow}} H_3O^+ + R_2C{=}O + HCrO_3^- \quad (2)$$

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[1] Taken in part from the Master's Thesis of W. J. Becker, III, June, 1951.

[2] The authors gratefully acknowledge the assistance provided by a Frederick Gardner Cottrell grant of the Research Corporation.

[3] H. C. Brown and M. Gerstein, THIS JOURNAL, **72**, 2926 (1950); H. C. Brown, R. S. Fletcher and R. B. Johannsen, *ibid.*, **73**, 212 (1951). The latter paper contains a summary of pertinent data for 5-, 6- and 7-membered ring compounds. See also H. C. Brown and M. Borkowski, *ibid.*, **74**, 1897 (1952).

[4] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509, 3542 (1951).

[5] K. S. Pitzer, *Science*, **101**, 672 (1945); J. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2483 (1947); C. W. Beckett, K. S. Pitzer and R. Spitzer, *ibid.*, **69**, 2488 (1947).

[6] (a) F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); (b) F. Westheimer and N. Nicolaides, THIS JOURNAL, **71**, 25 (1949); (c) F. Holloway, M. Cohen and F. H. Westheimer, *ibid.*, **73**, 65 (1951).

$$[R_2CHOCrO_3H_2]^+ + H_2O \xrightarrow[k_2]{\text{slow}} HO^+ + R_2C{=}O + H_2CrO_3 \quad (3)$$

It is seen from these equations that the over-all rate for a given alcohol will depend on the position of equilibrium (1) and the rate of reaction (2) or (3). The position of the equilibria can be assumed to be independent of the alcohol. This is reasonable because the positions of esterification equilibria for carboxylic acids vary only slightly with the structure of the alcohol component.[7] Hence, with the equilibrium constant as an essentially invariant factor in the rate expressions, the rate constants observed for a series of alcohols will reflect the rates of ester decomposition.

Results and Discussion

The rate constants k_1 and k_2 for the reactions involving one and two protons, respectively, at 40° at an ionic strength of 0.40 are listed in Table I.

TABLE I

RATES OF CHROMIC ACID OXIDATION OF SECONDARY ALCOHOLS IN WATER AT 40° WITH IONIC STRENGTH 0.40

Alcohol	k_1, (mole/l.)$^{-2}$ min.$^{-1}$	k_2, (mole/l.)$^{-3}$ min.$^{-1}$
2-Propanol	0.053	1.94[a]
Cycloöctanol	.47	13.5
Cycloheptanol	.61	12.4
Cyclohexanol	.16	3.24
Cyclopentanol	.13	4.90
Cyclobutanol	(.20)[b]	(5.07)[b]

[a] If only reaction (3) is assumed as a slow step k = 2.15 (mole/l.)$^{-3}$ min.$^{-1}$, in good agreement with k = 2.06 (mole/l.)$^{-3}$ min.$^{-1}$ at 0.27 M H^+ reported in reference 6a. [b] See text.

The oxidation of cyclobutanol by chromic acid is known[8] to yield significant amounts of cyclopropanecarboxaldehyde. It seems probable that its formation results from rearrangement of cyclobutanol to cyclopropylcarbinol[9] followed by oxidation. Therefore, in the absence of a detailed examination of the reaction the significance of the rate constants obtained for cyclobutanol cannot be assessed.

The fact that the 5-, 7- and 8-membered ring alcohols react faster than cyclohexanol[10] is as would be anticipated on the basis of other reactions involving a covalency change from four to three or five.[3] It is striking, however, that the variation in rates covers such a small range (4.9 to 13.5). Normally the variation is of the order of one hundredfold.

Another point of interest lies in the fact that isopropyl alcohol is oxidized more slowly than cyclohexanol; whereas the reverse would have been expected. Whether this is due to variation in the equilibrium constants of equation (1) or to other factors cannot be determined from the available data.

Experimental

Alcohols.—The alcohols were purchased or prepared by conventional procedures. They were carefully fractionated through a Podbielniak-type column 6 mm. × 100 cm. (Todd Scientific Co.). In those cases where the refractive index differed from literature values a refractionation was performed to ensure the correctness of our value. Data are given in Table II.

TABLE II

PHYSICAL CONSTANTS OF THE ALCOHOLS

	B.p., °C.	n^{20}_D Obs.	n^{20}_D Lit.	Ref.
2-Propanol	82.5	1.3778[a]	1.3758[b]	*c*
Cyclobutanol	125–126	1.4328	1.4347[b]	*d*
Cyclopentanol	140–141	1.4531	1.4530	*e*
Cycloheptanol	183–184	1.4773	1.4705–1.4753	*f*
Cycloöctanol	128–130 (50 mm.)	1.4823[b]	1.4844	*g*

[a] At 21°. [b] At 25°. [c] A. Weissberger and E. Proskauer, "Organic Solvents," Oxford University Press, Oxford, 1935, p. 27. [d] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949). [e] C. R. Noller and R. Adams, *ibid.*, **48**, 1084 (1926). [f] J. Böeseken and C. J. A. Hanegraaff, *Rev. trav. chim.*, **61**, 69 (1942); A. I. Vogel, *J. Chem. Soc.*, 1336 (1938); L. Ruzicka, P. Plattner and H. Wild, *Helv. Chim. Acta*, **28**, 395 (1945). [g] L. Ruzicka and H. A. Boekenoogen, *ibid.*, **14**, 1319 (1931).

The melting point (24.0°, lit.[11] 25.15°) was taken as the most sensitive criterion of purity for cyclohexanol which has a very large cryoscopic constant[10] (377 deg./mole/100 g.).

The perchloric acid was J. T. Baker C.P.

C.P. chromic acid was crystallized once from water. The same 0.01 M stock solution was used in all experiments.

Sodium perchlorate was crystallized from water, dried at 110° to constant weight and stored in a desiccator.

Kinetic Method.—The method of Westheimer and Novick[6a] was followed. All reactions were carried out at 40.0 ± 0.01°. In each run the ionic strength was 0.40 and the chromic acid concentration 0.001 to 0.002 M. In some cases the alcohol concentrations were as low as 0.013 M because of limited solubility. Each alcohol was run in duplicate at perchloric acid concentrations of 0.10 and 0.25 M. Since the change in hydrogen ion concentration during the course of the reaction is negligible, the integrated rate expression [ref. 6a, equation (14)] was modified to

$$k_{\text{obsd}}t = \frac{8}{3}\int_0^x \frac{dx}{(a - x)\{-K^1 + [K^{12} + 8K^1(b - x)]^{1/2}\}} \quad (3)$$

where $k_{\text{obsd}} = k_1\,[H^+] + k_2\,[H^+]^2$, a is the initial alcohol concentration, b is the initial chromic acid concentration, x is the concentration of chromic ion and $K_1 = 0.015 = [HCrO_4^-]^2/[Cr_2O_7^=]$. The integration was performed graphically and k_1 and k_2 computed from values of k_{obsd} at the two acid concentrations.

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(7) N. Menschutkin, *Ann.*, **195**, 334 (1879); **197**, 193 (1879).

(8) N. J. Demjanow and M. Dojarenko, *Ber.*, **40**, 2594 (1907); N. J. Demjanow, *ibid.*, **41**, 43 (1908).

(9) *Cf.* ref. 4 on the rearrangements accompanying the deamination of cyclobutylamine and cyclopropylmethylamine.

(10) The apparent inversion in order for k_1 values of cyclopentanol and cyclohexanol may be due to experimental error which amounted to about ±2% in k_{obsd}.

(11) H. N. Wilson and A. E. Heron, *J. Soc. Chem. Ind.*, **60**, 168 (1941).