size are attributed to changes in internal strain accompanying the change in coördination number of a ring atom (I-strain). The I-strain concept permits the chemistry of the small rings (3-, 4-members), the common rings (5-, 6-, 7) and the medium rings (8- to 12-) to be correlated and systematized.

LAFAYETTE, INDIANA RECEIVED JUNE 16, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF OKLAHOMA]

Chromyl Chloride Oxidation of Methylcyclohexane

BY ALBERT TILLOTSON AND BRUCE HOUSTON

The Étard reaction which has been extensively studied as a means of introducing the carbonyl group into side chains on aromatic rings and into olefinic compounds appears to have received little attention as an oxidizing agent with saturated hydrocarbons.

Étard[1] reported the formation of chlorinated ketones from pentane and from hexane. He did not establish the structures of these or give the yields obtained. Crook[2] obtained high yields of an addition product by the action of chromyl chloride on 2,7-dimethyloctane whose analysis corresponded to $C_{10}H_{22}(CrO_2Cl_2)_4$. He obtained on hydrolysis of this product small amounts of material which gave aldehydic reactions with semicarbazide and with Schiff reagent but which were not further identified.

We have now found that methylcyclohexane shows little tendency to react with chromyl chloride in carbon tetrachloride solution at 35°. However, the addition of less than 1% of an olefin initiated a moderately rapid reaction. This resulted in the formation of an 85% yield of a solid addition product. The chromium content of this material indicated a formula of $C_6H_{11}CH_3(CrO_2Cl_2)_2$ and on hydrolysis gave a 25% yield of hexahydrobenzaldehyde. No other organic product of the hydrolytic reactions was identified.

This observation on the effect of olefins is in accord with that of Kishner[3] who observed that 2,6-dimethyloctane was moderately stable to permanganate at 100° but was oxidized rather rapidly at 50° in the presence of menthene. The authors have made similar observations on the effect of olefins on the oxidation of methylcyclohexane with lead tetraacetate, although in this case the character of the resulting products appears to be very different from those obtained with chromyl chloride.

Experimental

Materials.—The methylcyclohexane was Phillips Petroleum Co. "Pure Grade," guaranteed to be not less than 99% pure with the most likely impurities listed as ethylcyclopentane. The chromyl chloride was prepared by the method of Law and Perkin.[4]

Étard Addition Product.—Preliminary tests were run by placing in each of five test-tubes 3 ml. of methylcyclohexane and 0.3 ml. of chromyl chloride in 7 ml. of carbon tetrachloride. One drop of an olefin was added to each of the first three tubes, and a drop of benzene to the fourth. The olefins used were cyclohexene, 2-methyl-2-butene and pinene. Immediate red-brown precipitates were noted in each of the tubes with added olefins. The tube with the benzene underwent a gradual darkening as it stood, whereas no change was noted in the tube without olefins or aromatic until twenty minutes had elapsed. Then it became slowly darker but no filterable material was noted after several hours.

A solution of 77.5 g. (0.5 mole) of chromyl chloride in 2 volumes of carbon tetrachloride was slowly added to 49 g. of methylcyclohexane in 2 volumes of carbon tetrachloride. The temperature was maintained between 33° and 38°. At the end of 15 minutes after starting the addition of chromyl chloride, no sign of reaction was noted and 0.3 ml. of 2-methylbutene was added. Precipitation began immediately. The chromyl chloride addition required 5 hours. The precipitate was then filtered and washed with carbon tetrachloride. After 4 days a further quantity of solid had precipitated from the filtrate and it was added to the solid previously obtained. About two-thirds of the total yield came down during the first 5-hour period. On drying *in vacuo* 87 g. of a fine, red-brown hygroscopic powder was obtained. Gravimetric analyses for chromium were made. *Anal.* Calcd. for $C_6H_{11}CH_3(CrO_2Cl_2)_2$: Cr, 25.49. Found: Cr, 26.09.

When some of the addition product was added to cold water, considerable heat was evolved and gave what appeared to be a true solution.

Hexahydrobenzaldehyde.—Two hundred ml. of crushed ice and water and 50 ml. of ether were placed in a separatory funnel. One-tenth mole (40.8 g.) of the addition product was added a few grams at a time with vigorous shaking after each addition. The water layer was extracted with two more portions of ether and the extracts dried over magnesium sulfate. The ether was then removed under reduced pressure and from the crude residue 2.8 g. of a liquid boiling between 75 and 80° at 20 mm. was collected. Eight-tenths gram of a black residue remained in the flask which would not distil at 150° at 20 mm. Darzens and Lefebure[5] reported a boiling point of 75–78° at 20 mm. for hexahydrobenzaldehyde. The compound obtained here also gave the Schiff aldehyde test and the derivatives subsequently described.

Attempts to improve the yield of recoverable oxidation product were made by: (a) decomposing the addition product in a water solution of sodium bisulfite instead of water; (b) using benzene in place of ether as an extracting agent; (c) converting the aldehyde to the hexahydrobenzoic acid and steam distilling this. None of these resulted in a measurable gain of product.

Hexahydrobenzaldehyde Semicarbazone.—This was prepared in the usual manner. After 2 recrystallizations from 50% alcohol, the melting point was 178°. Bouveault[6] reported a m.p. of 176°. *Anal.* Calcd. for $C_6H_{11}CHN\text{-}NH\text{-}CO\text{-}NH_2$: N, 24.83. Found: N, 24.83.[7]

Hexahydrobenzoic Acid.—Twice the calculated volume of hydrogen peroxide solution was added to 1 g. of hexahydrobenzaldehyde. The water was removed by evaporation at 2 mm. pressure; a solid melting between 26 and 30°. Hiers and Adams[8] reported the m.p. of hexahydrobenzoic acid to be 29–30°.

Summary

Methylcyclohexane gave a good yield of a solid addition product with chromyl chloride in the

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[1] Étard, *Compt. rend.*, **84**, 951 (1877).

[2] K. E. Crook, M.S. Thesis, University of Oklahoma, 1926.

[3] Kishner, *J. Russ. Phys.-Chem. Soc.*, **45**, 1788 (1913); Brooks, "The Non-Benzenoid Hydrocarbons," Chemical Catalog Co., Reinhold Publishing Corp., New York, N. Y., 1922, p. 57.

[4] Law and Perkin, *J. Chem. Soc.*, **91**, 191 (1907).

[5] Darzens and Lefebure, *Compt. rend.*, **142**, 715 (1906).

[6] Bouveault, *Chem. Centr.*, **74**, II, 1437 (1903).

[7] Micro-Dumas analysis by Mr. C. C. Hobbs of this Laboratory.

[8] Hiers with Adams, THIS JOURNAL, **48**, 2392 (1926).

presence of small amounts of olefins. In the absence of unsaturated compounds, the reaction did not take place at a practical rate under the conditions used.

This addition product, on decomposing with water, gave a 25% yield of hexahydrobenzaldehyde. No other oxidation product was identified.

NORMAN, OKLAHOMA RECEIVED MAY 27, 1950

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, NAVAL RADIOLOGICAL DEFENSE LABORATORY]

The Association of Cerous Ion with Iodide, Bromide and Fluoride Ions[1]

BY STANLEY W. MAYER AND S. DAVID SCHWARTZ

The association constant for $CeCl^{+2}$ has recently been measured by Connick and Mayer.[2] The ion exchange measurements of ion-pair formation between Ce^{+3} and the other important halides are reported in this paper.

Theoretical

It has been shown[2,3] that the equilibrium constant for the exchange between cerous and sodium ions may be written as

$$K_a = \frac{[Ce_R^{+3}][Na^+]^3}{[Ce^{+3}][Na_R^+]^3} = \frac{(Ce_R^{+3})(Na^+)^3\gamma_{Ce_R^{+3}}\gamma^6_{\pm NaX}}{(Ce^{+3})(Na_R^+)^3\gamma^4_{\pm CeX_3}\gamma^3_{Na^+_R}} \qquad (1)$$

where brackets denote activities, parentheses denote concentrations in moles per 1000 g. of water or moles per 1000 g. of resin. The subscript R indicates that the ion is in the resin. X is a univalent anion.

The radiations from Ce^{141} and Ce^{144} nuclides were used to determine (Ce_R^{+3}) and (Ce^{+3}), allowing (Ce_R^{+3}) to be kept small relative to (Na_R^+). Consequently $\gamma_{Ce_R^{+3}}$ and $\gamma_{Na_R^+}$ were essentially constant throughout the measurements.

$$\frac{K_a\gamma^3 Na_R^+}{\gamma_{Ce_R^{+3}}} = A = \frac{(Ce_R^{+3})(Na^+)^3\gamma^6_{\pm NaX}}{(Na_R^+)^3(Ce^{+3})\gamma^4_{\pm CeX_3}} \qquad (2)$$

Ion exchange measurements have established the empirical relationship[2] for the mixed electrolyte activity coefficients of trace concentrations of cerous perchlorate

$$\gamma^4_{\pm Ce(ClO_4)_3} \text{ in } Y \text{ molal } NaClO_4 = b\gamma^3_{\pm NaClO_4,Y}\gamma_{\pm CeCl_3,Y} \qquad (3)$$

where b is a constant, Y is equal to the molality of sodium ion, and $\gamma_{\pm CeCl_3,Y}$ denotes the mean activity coefficient of $CeCl_3$ in Y molal $CeCl_3$ solution.

This relationship has been applied[2] to other univalent anions to calculate the mixed electrolyte activity coefficients of cerous salts. Then

$$Ab = B = \frac{(Ce_R^{+3})(Na^+)^3\gamma^3_{\pm NaX,Y}}{(Ce^{+3})(Na_R^+)^3\gamma_{\pm CeCl_3,Y}} = \frac{\text{Count}_{Ce_R^{+3}}(Na^+)^3\, g_{H_2O}\, \gamma^3_{\pm NaX,Y}}{\text{Count}_{Ce_{Aq}^{+3}}(Na_R^+)^3\, g_R\, \gamma_{\pm CeCl_3,Y}} \qquad (4)$$

where Count denotes the count per second obtained from the tracer cerous ion in the indicated phase, and g_R denotes grams of resin.

All the factors of the right-hand member of (4) are experimentally measurable if the anion, X, does not form an ion-pair with Ce^{+3}. Then the value of B for the exchange between Ce^{+3} and Na^+ can be calculated.

In order to determine the constant for ion-pair formation with the anion, Z, the exchange is then carried out in the presence of a known concentration of Z.[4] Equation (4) and the measured value of B are then utilized to calculate (Ce^{+3}), making the correction for the (CeZ^{+2}) in the resin.[2]

$$\sum_{n=0}(CeZ_n) = (Ce^{+3}) + \sum_{n=1}(CeZ_n) \qquad (5)$$

For the case in which the only ion-pair formed is CeZ^{+2}

$$K_a = \frac{(CeZ^{+2})\gamma_{CeZ^{+2}}}{(Ce^{+3})(Z^-)\gamma_{Ce^{+3}}\gamma_{Z^-}} = K_m K_\gamma \qquad (6)$$

where K_m is the concentration quotient and K_γ is the activity coefficient quotient.

For those cases in which other ions than CeZ^{+2} are formed, the method of Leden[5] or the graphical method of Connick and McVey[6] can be employed to calculate the reaction constants.

Experimental

Materials.—Dowex 50[7] resin, 100–200 mesh, was used as the cation exchanger throughout these measurements. The resin was thoroughly washed with acid and water. It was then neutralized with sodium hydroxide solution, washed, and finally dried in air. The capacity of the resin was 3.11 equivalents per 1000 g.

The purified mixture of Ce^{141}–Ce^{144} fission product, secured from the Oak Ridge National Laboratory, contained less than 1% of radiochemical impurities.

All the sodium salts were of reagent grade, and were dried to a moisture content of not more than one-tenth of one per cent.

Procedure.—The method was similar to that heretofore employed.[2,8] For the measurements involving bromide and iodide ions the concentration of cerous ion was 10^{-4} molal. For the equilibrations with fluoride ion (Ce^{+3}) was decreased to 10^{-6} molal because of the low solubility of cerous fluoride.

Results

In a series of eight replicate ion exchange equilibrations between 0.501 molal sodium perchlorate and 1.0 × 10^{-4} molal cerous perchlorate, B was found to have the mean value 13.9, with a standard deviation of 0.4. In a series of four replicate ion exchange equilibrations between 0.501 molal sodium iodide and 1.0 × 10^{-4} molal cerous perchlorate, B was again found to have the mean value of 13.9, with a standard deviation of 0.4. The

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(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Atlantic City Meeting, September, 1949.

(2) R. E. Connick and S. W. Mayer, THIS JOURNAL, to be published.

(3) G. E. Boyd, J. Schubert and A. W. Adamson, *ibid.*, **69**, 2818 (1947).

(4) J. Schubert, *J. Phys. Coll. Chem.*, **52**, 340 (1948).

(5) I. Leden, *Z. physik. Chem.*, **188**, 160 (1941).

(6) R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

(7) W. C. Bauman and J. Eichhorn, *ibid.*, **69**, 2830 (1947).

(8) E. R. Tompkins and S. W. Mayer, *ibid.*, **69**, 2859 (1947).