

was isolated. Similar results were obtained with sodium ethoxide.

Three grams of the colorless oxidation product, dissolved in benzene (50 ml.) and then chilled in an ice-bath, showed no change when treated with sodium amalgam and ethanol. Upon addition of acetic acid slightly more than two grams of starting material was recovered.

$(C_6H_5)_2C=N-O-N=C(C_6H_5)_2$ , IV.—*Anal.* Calcd. for  $C_{26}H_{20}ON_2$ : C, 82.98; H, 5.32. Found: C, 83.05; H, 5.36.

A sample (1.0 g.) was boiled for one-half hour with acetic acid containing a small amount of acetic anhydride. The solution was then made alkaline and heated for one hour.

The addition of water containing sodium bicarbonate caused the separation of benzophenone oxime (0.09 g.).

### Summary

The oxidation of benzophenone oxime is described. The products of oxidation are nitrogen, benzophenone, diphenylketazine oxide and the benzophenone oxime ester of *aci*-diphenylnitromethane. The behavior of some of these oxidation products has been investigated and an attempt has been made to account for their formation.

MINNEAPOLIS, MINNESOTA

RECEIVED APRIL 6, 1942

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

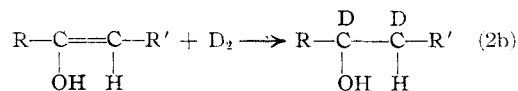
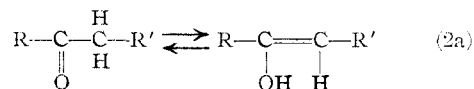
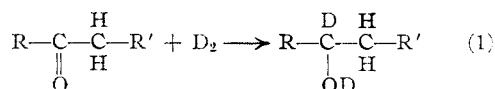
## The Mechanism of the Catalytic Reduction of Some Carbonyl Compounds<sup>1</sup>

BY LEIGH C. ANDERSON AND N. W. MACNAUGHTON

Deuterium oxide has been used by many investigators for studying reactions of hydrogen. Much of the work has dealt with inorganic compounds and in reactions where the deuterium ion was involved. Among the studies involving deuterium and organic compounds, it might be mentioned that exchange reactions between ethylene and deuterium<sup>2</sup> were found to accompany hydrogenation. It was found, also, that rapid exchange with deuterium took place with benzene in the presence of catalysts.<sup>3</sup> Farkas and Farkas<sup>4</sup> have stated that in the vapor phase both acetone and isopropyl alcohol are converted to propane with either hydrogen or deuterium over a platinum catalyst. From the relative rates of the reactions of the two organic compounds they concluded that the reduction to the hydrocarbon takes place directly from acetone rather than through the alcohol as an intermediate.

This paper presents a discussion of the mechanism of the reactions which occur when butyraldehyde, acetone, and several other aldehydes and ketones were catalytically reduced to alcohols with a mixture of hydrogen (80 parts) and deuterium (20 parts).<sup>5</sup> Two mechanisms may be

postulated for the manner in which a carbonyl group is converted to an alcohol group by the use of deuterium: (1) direct addition of deuterium to the carbonyl group (Eq. 1), and (2) enolization of the carbonyl compound followed by addition of deuterium to the resulting ethylenic linkage (Eqs. 2a and 2b).



The difference in the deuterio compounds that would be formed according to these two mechanisms is readily apparent because the product from Eq. 1 contains an OD bond and a CD bond whereas that from Eq. 2b contains two CD bonds. The former compound on oxidation should yield a compound free from deuterium and the latter compound, in the absence of exchange during oxidation, should oxidize to a compound with a deuterium on the alpha carbon atom. The presence of either a CD bond or an OD bond in the compound under investigation is readily ascertained by the appearance of the characteristic bands at about  $\Delta\nu$  2150 and  $\Delta\nu$  2500 in the Raman spec-

(1) The material presented in this paper constitutes a portion of a dissertation submitted by N. W. MacNaughton to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements of the Ph. D. degree, August, 1941.

(2) Horiuchi and Polanyi, *Nature*, **134**, 377-8 (1934); Farkas, Farkas and Rideal, *Proc. Roy. Soc. (London)*, **A146**, 630 (1934).

(3) Horiuchi, Ogden and Polanyi, *Trans. Faraday Soc.*, **30**, 663-5 (1934); Horiuchi and Polanyi, *ibid.*, **30**, 1164-72 (1934).

(4) Farkas and Farkas, *THIS JOURNAL*, **61**, 1336-41 (1939).

(5) The deuterium oxide used in the preparation of deuterium for this investigation was purchased by a grant from the Research Funds

of the Horace H. Rackham School of Graduate Studies. Preliminary experiments indicated that a mixture of deuterium and hydrogen would yield results as conclusive as pure deuterium and the mixture was used, therefore, in order to conserve the heavy isotope.

TABLE I

Hydrogenation			Raman data			
Compound	Catalyst	T°	Reduction product		Oxidation product CD	Type of addition
			CD	OD		
<i>n</i> -Butyraldehyde	Pt	25	×	×	No	Keto
<i>n</i> -Butyraldehyde	Ni	25	Strong	Weak	No	Keto <sup>a</sup>
<i>n</i> -Butyraldehyde	Pt	150	×	×	Trace	Mostly keto
<i>n</i> -Butyraldehyde	CuCr	150	×	×	Trace	Mostly keto
<i>n</i> -Butyraldehyde	Pt	250	×	No	Strong	Mostly enol
<i>n</i> -Butyraldehyde	CuCr	250	×	No	Strong	Mostly enol
Acetone	Pt + NaOC <sub>2</sub> H <sub>5</sub>	25	×	×	No	Keto
Acetone	Pt	25	×	×	No	Keto
Acetone	Ni	25	Strong	Weak	No	Keto <sup>a</sup>
Acetone	Pt	200	×	×	Weak	Consid. enol
Acetone	CuCr	200	×	×	Weak	Consid. enol
Acetone	Ni	200	×	×	Weak	Consid. enol
Acetaldehyde	Pt	25	×	×	No	Keto
Diethyl ketone	Pt	25	×	×	No	Keto
Methyl ethyl ketone	Ni	25	Strong	Weak	No	Keto <sup>a</sup>

×, moderately strong band. <sup>a</sup> Oriented addition of HD to CO group.

trum of the compound. The procedure for determining the mechanism, therefore, involved (1) reduction and determination of the Raman spectrum of the catalytic reduction product and (2) oxidation and determination of the Raman spectrum of the oxidized product. If the carbonyl compound after reduction with the deuterium showed both OD and CD bands and both of these were lost during the subsequent oxidation, it was concluded that the original reduction occurred through addition to the CO group as shown in Eq. 1. Similarly, when the reduced product showed a strong CD band and the oxidized product still showed such a band, it was concluded that the original reaction had been largely through addition of the deuterium to the enol form of the carbonyl compound (Eqs. 2a and b). The presence of the weak OD band which usually accompanied the strong CD band in the latter case, can be accounted for by the simultaneous occurrence of a small amount of ketonic addition or by some exchange of the hydroxyl hydrogen at the surface of the catalyst.

A number of conclusions can be drawn from the summary of the more important data which are presented in Table I. The mechanism of reduction to alcohols of the carbonyl group in the simple aldehydes and ketones is very dependent upon the temperature, ketonic addition being predominant at low temperatures and more enolic addition taking place at higher temperatures. The same results are obtained in the presence of nickel, platinum and copper chromite catalysts.

It was thought that enolic reduction of acetone

might be induced by hydrogenating acetone in the presence of sodium ethylate. Only ketonic addition could be observed when the experiment was tried at 25° with a nickel catalyst.

Since the reducing agent used in this investigation was a mixture of hydrogen and deuterium which undoubtedly formed HD in the presence of the catalyst, it is apparent that several monodeutero products were produced which are not indicated in Eqs. 1 and 2. For example, the addition of HD to a CO bond could yield either  $=C_{OD}^H$  (A) or  $=C_{OH}^D$  (B). If (A) and (B) are formed in equivalent amounts, the strength of the CD and OD bands in the Raman spectra will be the same with the HD as if a mixture containing 20% of pure deuterium had been present.<sup>6</sup> Evidence was obtained that oriented addition occurs when HD added to the carbonyl group in the presence of Raney nickel at low temperatures and does not occur when platinum is used. Oxidation of the low temperature reduction products obtained by hydrogenations using either Raney nickel or platinum catalysts showed the mechanism to be keto addition. The Raman spectra of the reduction products from the platinum catalysts had OD and CD bands of approximately equal intensity and the addition, therefore, must have yielded nearly equivalent amounts of (A) and (B). On the other hand, the Raman spectra of the alcohols from the Raney nickel reductions showed a strong

(6) This statement is based on data obtained in this Laboratory from the catalytic reduction of acetone with 99+ per cent. deuterium using a platinum catalyst at room temperature. The OD and CD Raman bands of the resulting alcohols were of nearly equal intensity.

CD band together with a weak OD band. Since oxidation proved ketonic addition, it must be concluded that there was a predominance of the reaction yielding (B). In other words, when Raney nickel was used at room temperature, there must have been oriented addition of the HD molecule to the carbonyl group with a greater tendency for the H to go to the O and the D to the C than for the reverse type of addition. These effects were not due to exchange reactions because experiments on exchange showed the latter to be negligible during the time and under the conditions used for the hydrogenations.

Two types of exchange reaction can occur between deuterium and the alcohols produced in the reductions under discussion: exchange of the hydroxyl hydrogen and exchange of hydrogen attached to carbon. A number of experiments were carried out with isopropyl alcohol and *n*-butyl alcohol and the deuterium-hydrogen mixture under conditions similar to those used for the reduction of the corresponding carbonyl compounds. No exchange could be detected at any temperature up to 250° in the absence of a catalyst. Platinum up to 250° and nickel at 25° caused exchange on the oxygen but not on the carbon. Nickel and copper chromite at 250° yielded deuterio compounds wherein exchange had occurred not only on the carbinol carbon but also on the one next to it. It would appear that dehydrogenation, enolization, and hydrogenation were all associated in the latter type of exchange.

Evidence was obtained that exchange did not occur with isopropyl alcohol as long as any acetone was present in the hydrogenation unit. These reductions were stopped, therefore, before reaching completion and the products separated for examination.

An interesting observation was noted in connection with the Raman spectra of the compounds involved in this investigation. The reduction of aldehydes to primary alcohols led only to one strong CD line at about  $\Delta\nu$  2165 (see band at 2 in

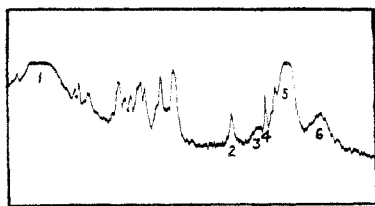


Fig. 1.—*n*-Butyl alcohol from butyraldehyde reduced with Cu-Cr at 200°.

Fig. 1). The reduction of ketones to secondary alcohols produced two CD lines separated by about 50 to 60 frequency units (see bands at 2 in Figs. 2, 3 and 4). The relative heights of these two CD lines of secondary alcohols were dependent on the location of the deuterium in the molecule. The two bands were practically the same height when the addition had occurred at low temperatures and no deuterium was to be found in the oxidation product, that is, when the alcohol had been formed by ketonic addition (Figs. 2 and 3). When the alcohol had been formed by

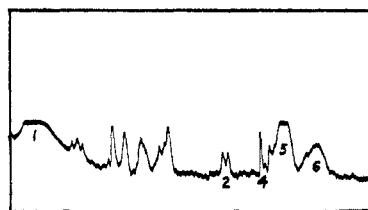


Fig. 2.—Isopropyl alcohol from acetone reduced with nickel at 25°.

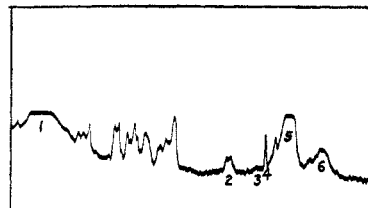


Fig. 3.—Methylethylcarbinol from methyl ethyl ketone with nickel at 25°.

enolic addition and oxidation showed one of the deuterium atoms to be on the alpha carbon, the CD line of higher frequency difference was much more intense (Fig. 4).

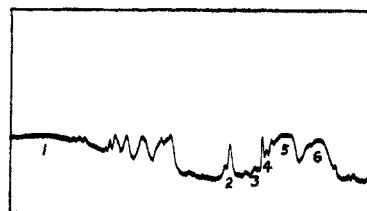


Fig. 4.—Isopropyl alcohol from acetone reduced with nickel at 200°.

Previous work from this Laboratory<sup>7</sup> has shown that the exchange reaction between acetone and deuterium oxide is inappreciable in the presence of acids and, consequently, the oxidation reactions in this work were carried out with chromic acid solutions. Therefore, since exchange reactions should be negligible and since all such oxidations

(7) Halford, Anderson and Bates, *THIS JOURNAL*, **56**, 491 (1934).

were carried out under similar conditions, the variations in deuterium content of the oxidized compounds should be truly indicative of the reduction mechanism.

### Experimental

The organic liquids to be reduced were purified by distillation through fractionating columns prior to hydrogenation. About 30–40 g. of organic material was used in each experiment with 0.1 to 0.2 g. of platinum oxide (plus a few crystals of ferrous chloride), 5–10 g. of Raney nickel or 3–5 g. of copper chromite. The platinum catalyst was prepared according to the directions of Adams, Voorhees and Shriner,<sup>8</sup> the copper chromite was made according to Calingaert and Edgar,<sup>9</sup> and the Raney nickel was prepared from the commercially available aluminum–nickel alloy according to the directions of Covert and Adkins.<sup>10</sup> At the completion of the reaction the shaking mechanism of the hydrogenation unit was stopped. After releasing the excess gas from the cold reaction vessel, the organic products were separated from the catalyst and fractionally distilled. About 20 g. of the middle portion of the alcohol fraction was placed in the Raman tube.

The deuterium–hydrogen mixture was prepared by heating a mixture of twenty parts of 99.6% deuterium oxide and eighty parts of water with powdered iron and a little ferrous chloride in an autoclave at 320° for several hours. The cold gas mixture was passed through Dessigel to remove water vapor prior to use. The deuterium mixture that remained in the hydrogenator after completion of a reaction was pumped through activated charcoal to remove organic vapors and returned to the generator. Hydrogenations at room temperature were carried out at 30–40 pounds gas pressure and at elevated temperatures at 1000 to 1200 pounds pressure. All exchange reactions were studied at about 1000 pounds pressure in order to assure the presence of sufficient deuterium for exchange.

The Raman spectra were ascertained by the use of the apparatus described in a previous publication from this Laboratory.<sup>11</sup> Two 3-mm. thick filters were used around the Raman tube: one was filled with 3% cobalt thiocyanate solution, the other with a 2% solution of benzophenone in 95% sulfuric acid. The latter filter has not been described hitherto. It is superior to many others which have been tried because it filters out a larger portion of the 4047

(8) Adams, Voorhees and Shriner, "Organic Syntheses," vol. 8, p. 92 (1928).

(9) Calingaert and Edgar *Ind. Eng. Chem.*, **26**, 878 (1934).

(10) Covert and Adkins, *THIS JOURNAL*, **54**, 4116 (1932).

(11) Halford, Anderson and Kissin, *J. Chem. Phys.*, **5**, 927 (1937).

mercury radiation without as much loss of the 4358 line which was the exciting radiation. This filter must be replaced frequently because on continued radiation decomposition products are formed which absorb the 4358 line. The presence of CD and OD bands was ascertained from microphotometer tracings which were made of all the spectrographic plates.

Four copies of microphotometer tracings from the Raman spectra plates are presented as illustrative of the data obtained in the work. The lines and bands of importance have been indicated as follows: (1) exciting source (4358 Hg line); (2) CD bands; (3) OD band; (4) 4916 Hg reference line; (5) CH bands; (6) OH band.

The CD lines shown in the tracings occur at the following frequencies ( $\Delta\nu$ ): Curve 1, 2165; Curves 2 and 3, 2120 and 2185; Curve 4, 2095 and 2145.

### Summary

1. At low temperatures, the catalytic reduction of acetaldehyde, butyraldehyde, acetone, methyl ethyl ketone, and diethyl ketone occurs through addition of hydrogen to the carbonyl group in the presence of nickel, platinum and copper chromite.

2. At elevated temperatures, the catalytic reduction of the compounds indicated above occurs to a considerable extent through addition of hydrogen to the carbon to carbon double bond of the enol form.

3. In the presence of Raney nickel, the HD molecule adds to a carbonyl group at low temperatures with preferential formation of the CD and OH bonds.

4. Deuterium is exchanged for the hydroxyl hydrogen of either isopropyl alcohol or *n*-butyl alcohol in the presence of nickel at 25° and in the presence of platinum at temperatures up to 250°.

5. With nickel or copper chromite catalysts at 250°, deuterium exchanges for hydrogen on both the carbinol carbon atom and the adjacent carbon atom of isopropyl alcohol and of *n*-butyl alcohol, indicating that dehydrogenation, enolization and hydrogenation reactions were all involved in these exchanges.