852. *The Reduction of Carbon Monoxide by Lithium Aluminium Hydride.*

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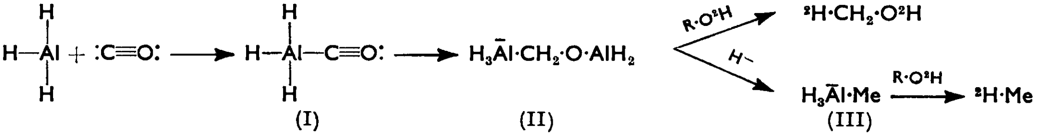
The reduction of carbon monoxide by lithium aluminium hydride has been studied with the aid of deuterium and carbon-14.

Contrary to earlier reports,[1] carbon monoxide is absorbed by solutions of lithium aluminium hydride to form a complex which gives methanol and methane on alcoholysis.[2] In preliminary experiments it was never possible to account for more than about 92% of the carbon monoxide absorbed but it was not clear whether the techniques of isolation were at fault or whether there were other minor products. The reaction was therefore examined by using [^{14}C]carbon monoxide, and the yield of methanol and the presence or absence of by-products established by dilution analysis. In this way a satisfactory balance of total carbon and total isotope was obtained (Table 1). About 99·5% of the isotope appeared in methanol and in the gaseous product of the alcoholysis, and there was no evidence of the formation of any other compound from carbon monoxide.

The lithium aluminium hydride reduction of carbon dioxide [2] differs from that of carbon monoxide in that the rate of reaction in comparable conditions is much greater and there is no formation of methane or carbon monoxide. The reduction of carbon dioxide appears to proceed by way of intermediates derived from formate and formaldehyde, both of which are always present in the products of this reaction but are absent from those from carbon monoxide. The following reaction scheme is suggested.[2a] The first step is the co-ordination of carbon monoxide with aluminium hydride (existing in equilibrium with aluminohydride ion) to give a carbonyl hydride (I), the carbonyl group of which undergoes reduction in the usual manner to give compound (II) which is susceptible to further attack by hydride or aluminohydride ion at the C–O bond to form the methylaluminium compound (III); on alcoholysis (II) yields methanol and (III) methane. Carbon monoxide is much less soluble in organic solvents than carbon dioxide and this, or a low rate of reaction in the co-ordination stage, may be the cause of the slower reaction observed in this case. It will be seen that the formation of the intermediate (II) from carbon monoxide requires two, and of the methylaluminium compound (III) three hydrogen atoms per molecule, and from the relative proportions of methanol and methane in the product the theoretical requirement of hydride is easily calculated. In Run 2 (Table 2) a consumption of 7·75 mmoles was expected, in good agreement with the observed value of 8·14. The intermediate (II) will clearly exist mainly in this simple form only in the earlier stages of the reaction, and when



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[1] Brown, Finholt, Nystrom, and Schlesinger, Abs. 110th Amer. Chem. Soc. Meeting, 1946, 27p.

[2] Cox, Turner, and Warne, *J.*, 1950, 3167.

[2a] Cf. Paddock, *Chem. and Ind.*, 1953, 63.

more than one molecule of carbon monoxide has been absorbed for each two molecules of hydride every additional molecule of monoxide reacting will link two molecules of (II). The molecular size will of course be diminished by the reaction leading to the methylaluminium compound. In a typical experiment the solution became turbid at about 0·6 mol. of carbon monoxide per mol. of hydride and by the time 1·2 mol. per mol. had been absorbed a large amount of white solid had separated. As would be expected the yield of methane increased with the ratio of hydride to carbon monoxide, and with increase in time and temperature.

Confirmation of the structures of (II) and (III) was obtained by means of tracer experiments with deuterium, for on decomposing the reaction complex with tetrahydrofurfuryl [^{2}H]alcohol, [$^2H_1$]methane and [^{2}H]methan[^{2}H]ol were formed. No methane was obtained having more than one deuterium atom; this confirms the presence of an unsubstituted methyl group in the intermediate (III).

TABLE 1. *Run* 2.

	Carbon (mg. atoms)	Specific activity (c per mg.-atom of carbon)	Total activity (c)
CO reacting ...	12·60	$1{\cdot}39 \times 10^{-7}$ [a]	$17{\cdot}5 \times 10^{-7}$
Gaseous product	6·12 [b]	$1{\cdot}32 \times 10^{-7}$	$8{\cdot}07 \times 10^{-7}$
MeOH	6·57 [c]	$1{\cdot}39 \times 10^{-7}$ [d]	$9{\cdot}15 \times 10^{-7}$
Residual MeOH (R_1)	0·0025 [c]	$1{\cdot}39 \times 10^{-7}$ [d]	$0{\cdot}0035 \times 10^{-7}$
Activity in R_2...	0·06 [c]	$1{\cdot}39 \times 10^{-7}$ [d]	$0{\cdot}08 \times 10^{-7}$
Total products	12·75	—	$17{\cdot}3 \times 10^{-7}$
Discrepancy ...	+ 0·15 (1·2%)	—	$-0{\cdot}2 \times 10^{-7}$ (1·1%)

[a] Mean of specific activity at beginning and at the end of the experiment. [b] From the analysis and total quantity of mixed gases, assuming that unsaturated hydrocarbons had four carbon atoms. [c, d] Values marked *d* are assumed to be the same as that marked *a*; values marked *c* are calculated on this assumption.

TABLE 2. *Stoicheiometry of the reaction* (*Run* 2).

	mmoles	mmoles
$LiAlH_4$ taken	12·83	—
H_2 in gaseous product	18·75	—
Hydride consumed ...	—	8·14
CO absorbed	—	12·60
Total C in gaseous product (as CO_2) ...	6·12	—
C_nH_{2n+2} (n = 1·02) ...	5·84	—
Methane	—	5·73 [a]
Methanol	—	6·57
Hydride required (calc.)	—	7·75

[a] Minimum value, the saturated hydrocarbon contaminant in the methane being assumed to be ethane.

EXPERIMENTAL

Specific activities are expressed in curies per mg.-atom of carbon and total activities in curies.

Materials.—Tetrahydrofurfuryl alcohol was purified by fractional distillation, the fraction of b. p. 80°/21 mm. being used. Tetrahydrofurfuryl [^{2}H]alcohol was prepared by mixing 99·7% deuterium oxide (2·31 g., 115 mmoles) with tetrahydrofurfuryl alcohol (21·35 g., 209 mmoles). After being kept overnight, the water was removed by azeotropic distillation with benzene (*ca.* 40 g.) in a Dean and Stark apparatus. The benzene was distilled off and the residual alcohol allowed to undergo exchange a second time with deuterium oxide (3·00 g., 150 mmoles). The water was removed as before, and on distillation tetrahydrofurfuryl [^{2}H]alcohol (13·0 g.) was collected at 78—80°/21—23 mm. On the assumption that equilibrium was reached at both stages with no isotope effect, and that the excess of water was completely removed after the first stage without the loss of any alcohol, a deuterium content of *ca.* 80 atoms % was expected in the hydroxyl group; the actual value was 76% (see below). Tetrahydro(tetrahydrofurfuryloxy)pyran, b. p. 135°/25 mm., was prepared as described by Cox, Turner, and Warne.[2]

Lithium aluminium hydride solution was prepared by stirring the coarsely crushed material with tetrahydrotetrahydrofurfuryloxypyran in a carefully dried apparatus. The solution was filtered with the aid of Celite 545 into a flask (Fig. 1) from which it could be dispensed without coming into contact with air. All operations were carried out in dry oxygen-free nitrogen.

Analyses.—Lithium aluminium hydride solutions were estimated by decomposition with excess of tetrahydrofurfuryl alcohol in a simple gas-volumetric apparatus. The results were reproducible to about 0·2%. Felkin's[3] iodimetric method was not applicable to the estimation of lithium aluminium hydride in the presence of tetrahydro(tetrahydrofurfuryloxy)pyran.

All deuterium analyses were carried out in the mass spectrometer. Methane and methanol

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[3] Felkin, *Bull. Soc. chim. France*, 1951, 347.

were introduced directly. Deuterium in the hydroxyl group of tetrahydrofurfuryl alcohol was determined as methane after reaction with an excess of methylmagnesium iodide in *n*-butyl ether.

As samples of deuteromethanols were not available for standardising the mass spectrometer, it was assumed that the sensitivities for the deuterated compounds were the same as for methanol. In the case of the methane analyses, the spectrum of pure methane obtained on our instrument was very similar to that published for methane and consequently it was considered justifiable to use published data for the mass spectrum of monodeuteromethane in our calculations. The isotopic composition of the methanol was calculated from the ratios of the peaks at m/e 32 and 34 and at m/e 33 and 34. The analyses of methane and monodeuteromethane mixtures were obtained from the peak heights at $m/e = 15$, 16, and 17. Accurate quantitative analyses were not required for the purpose of determining the course of the reactions and any errors introduced by the above assumptions would not affect our proposals for the mechanisms.

Samples were burned and counted for ^{14}C as described by Turner and Warne.[4]

FIG. 1.

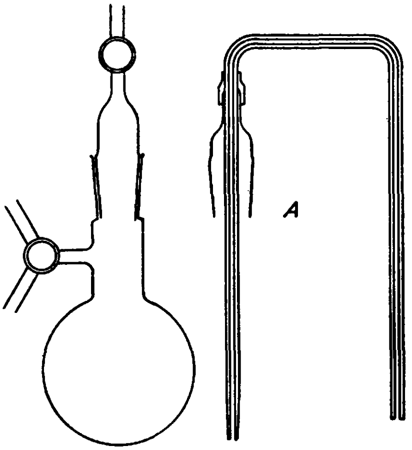
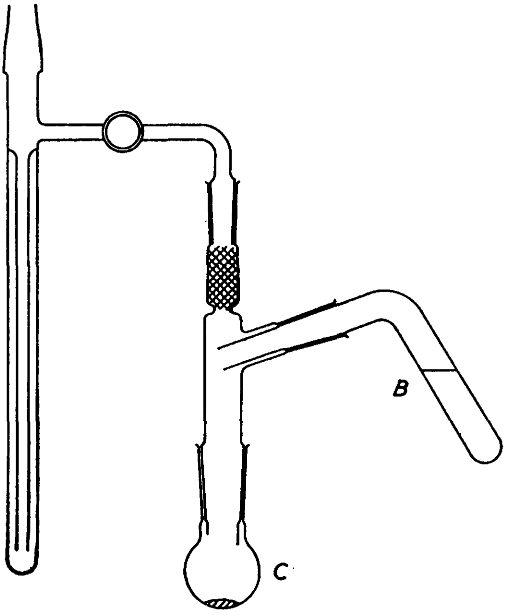


FIG. 2.



Apparatus.—A vacuum manifold of small volume, generally similar to that described by Cox and Turner (Fig. 1),[5] was connected through a Töpler pump to a calibrated storage bulb fitted with a manometer. The reactions were carried out in vessels attached to the manifold.

Preparation of [^{14}C]*Carbon Monoxide.*—The apparatus in Fig. 2 was connected to the manifold through a second trap (not shown). The side-tube *B* contained outgassed 100% sulphuric acid (*ca.* 10 ml.) which could be tipped by rotation about the joint on sodium [^{14}C]formate (15—25 mmoles) in flask *C*. The first trap was cooled by solid carbon dioxide and the second by liquid nitrogen. After thorough evacuation of the apparatus the acid was added to the formate and the carbon monoxide evolved was pumped into the storage bulb. The reaction took place readily in the cold and the yield of carbon monoxide was almost quantitative.

Reaction of Carbon Monoxide with Lithium Aluminium Hydride.—(i) *General.* Lithium aluminium hydride solution (*ca.* 14 g. of a solution containing 0·877 mmole of hydride per g.) was blown under nitrogen pressure through the siphon *A* against a countercurrent of nitrogen into flask *D* (Fig. 3) which had been baked for several hours at 120°. The quantity was determined by weighing before and after delivery. The flask was attached to the trap *E* and thoroughly evacuated while the hydride solution was stirred at room temperature. Stirring was effected by a magnetically operated stainless iron capsule which allowed thorough emulsification of gas and liquid. The stirring was interrupted while carbon monoxide was pumped into the

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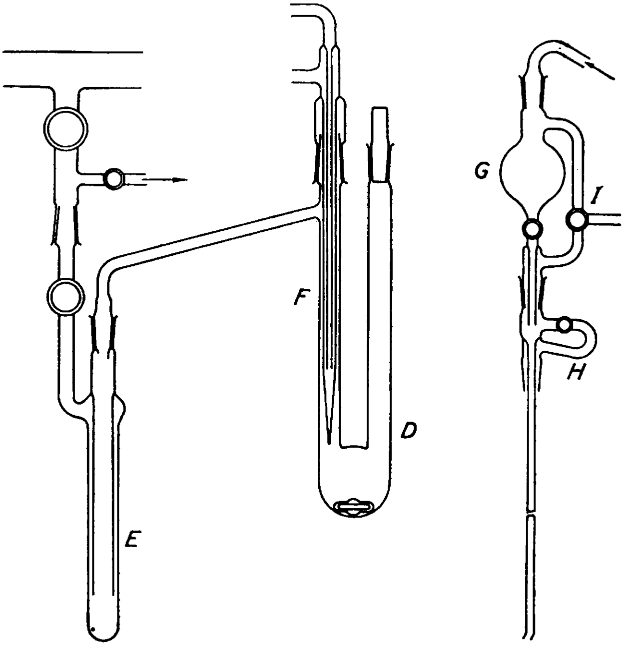
[4] Turner and Warne, *J.*, 1953, 789.

[5] Cox and Turner, *J.*, 1950, 3176.

flask and manifold from the storage bulb to give a pressure of about one atmosphere; there was no detectable reaction during the addition. The solution was then stirred vigorously and heated rapidly to 55—60° whereupon a steady absorption of carbon monoxide occurred with some evolution of heat. More gas was pumped in when required. When sufficient had been absorbed the mixture was cooled to 0° and the bulk of the remaining carbon monoxide was pumped back into the storage bulb and a correction applied for the few millimetres' pressure left in the manifold. Finally the reaction mixture was evacuated until the pressure in the system did not exceed that due to the solvent. Samples of the original and the residual carbon monoxide were taken for isotope analysis.

Dry oxygen-free nitrogen was admitted to the manifold and then to the reaction flask, and the apparatus *GH* (Fig. 3) was connected to *D* in place of the stopper in an ascending current of nitrogen. The funnel *G* contained a 100% excess (based on the hydride taken) of tetrahydrofurfuryl alcohol. The apparatus was quickly evacuated and after cooling of trap *E* in liquid nitrogen the alcohol was added to the reaction product with stirring. The mixture of permanent gases which was evolved was transferred by the Töpler pump into the storage bulb until the pressure in the apparatus fell to *ca.* 10 mm. Hg, the vapour pressure of methane at liquid-nitrogen temperature. At this stage the liquid nitrogen around the trap *E* was replaced by solid carbon dioxide, cold water was passed through the finger condenser *F*, and the reaction mixture was stirred at about 60°. Pumping was continued until the pressure in the manifold had fallen to 0·1 mm. Samples of the gaseous product of the reaction were taken for chemical and isotope analysis.

FIG. 3.



The flask and attachments were then isolated from the manifold and dry nitrogen was admitted at *I*. *E* was cooled in liquid nitrogen, the flask heated to 100° with stirring, and the methanol together with some solvent and tetrahydrofurfuryl alcohol were distilled in a current of nitrogen under conditions of partial reflux into trap *E*. In a typical experiment about 5 g. of distillate were collected containing some 6—10 mmoles of methanol. The methanol was concentrated by distillation *in vacuo* at room temperature as described by Cox, Turner, and Warne[2] but it was not possible to effect a quantitative separation; the yield was therefore determined indirectly. It was first established (Run 1), by preparation of the pure 3 : 5-dinitrobenzoate, that the specific activity of methanol produced in the reaction is identical, within experimental error, with that of the carbon monoxide reduced. The yield of methanol in another experiment (Run 2) was then determined by isotope dilution analysis. A quantity of pure methanol was added to the first distillate, and a sample of pure methyl 3 : 5-dinitrobenzoate isolated as before; from the specific activities of the diluted methanol and the original carbon monoxide, and the weight of methanol used for dilution, the weight of methanol in the first distillate could be calculated. It was further established by the dilution method that the removal of methanol from the reaction mixture during the first distillation was essentially complete.

(ii) *Experiments with isotopically labelled compounds.* (*a*) Run 1. A solution containing lithium aluminium hydride (11·63 mmoles) was allowed to absorb $[^{14}\text{C}]$carbon monoxide (15·95 mmoles; specific activity $1{\cdot}39 \pm 0{\cdot}01 \times 10^{-7}$, specific activity of residual carbon monoxide $1{\cdot}38 \pm 0{\cdot}01 \times 10^{-7}$) at *ca.* 60° during $1\frac{3}{4}$ hr. Towards the end of the reaction stirring became difficult owing to the deposition of a large amount of the white reaction complex. The mixture was decomposed by the addition of tetrahydrofurfuryl $[^{2}\text{H}]$alcohol (9·0 ml., *ca.* 100% excess; 76 atoms % deuterium in the hydroxyl group). A total of 11·19 mmoles of gaseous products were formed (see Table 3) of which 99% consisted of hydrogen and saturated hydrocarbons C_nH_{2n+2}. The saturated hydrocarbons ($n = 1{\cdot}02$) must contain at least 98% by volume of methane; the major gaseous products were therefore hydrogen (7·22 mmoles) and methane (3·78—3·86 mmoles). A sample of the mixture of gases was burned to carbon dioxide (specific activity $1{\cdot}29 \pm 0{\cdot}01 \times 10^{-7}$). Mass-spectrometric assay of the mixed gases showed the methane to contain CH_4 (57%) and $CH_3{}^2H$ (43%). The methanol was distilled from the reaction mixture and partially purified by distillation and a sample was converted into the pure 3 : 5-dinitrobenzoate which, on combustion, gave carbon dioxide of specific activity $1{\cdot}71 \pm 0{\cdot}01 \times 10^{-8}$ (corresponding to methanol of specific activity $1{\cdot}37 \pm 0{\cdot}01 \times 10^{-7}$). Mass-spectrometric assay showed the methanol to contain $CH_2{}^2H{\cdot}O^2H$ (25%), $CH_3{\cdot}O^2H$ plus $CH_2{}^2H{\cdot}OH$ (46%), and $CH_3{\cdot}OH$ (29%).

TABLE 3. *Analyses in Bone and Wheeler apparatus of gaseous products after decomposition* (%).

Gas	CO_2	C_nH_m (unsat.)	O_2	CO	H_2	C_nH_{2n+2}	N_2	n of C_nH_{2n+2}
Run 1	0·1	0·2	0·1	0·3	64·5	34·5	0·3	1·02
Run 2	0·1	0·1	0·0	0·2	75·1	23·4	1·1	1·02

(*b*) Run 2. Lithium aluminium hydride solution (containing 12·83 mmoles of hydride) absorbed at *ca.* 60° $[^{14}\text{C}]$carbon monoxide (12·60 mmoles; specific activity $1{\cdot}40 \pm 0{\cdot}01 \times 10^{-7}$) generated from sodium formate (specific activity $1{\cdot}39 \pm 0{\cdot}01 \times 10^{-7}$); the carbon monoxide remaining at the end of the reaction had specific activity $1{\cdot}38 \pm 0{\cdot}01 \times 10^{-7}$. On adding tetrahydrofurfuryl alcohol (10 ml.) a total of 24·96 mmoles of gaseous products was evolved which (Table 3) contained 18·75 mmoles of hydrogen and 5·84 mmoles of saturated hydrocarbon C_nH_{2n+2}, containing at least 5·72 mmoles of methane, and on combustion gave carbon dioxide of specific activity $1{\cdot}32 \pm 0{\cdot}01 \times 10^{-7}$.

The methanol was distilled from the alcoholysis product, and a total of 4·90 g. of crude product (P_1) was collected. The residue (R_1) from the distillation (total activity *ca.* $8 \times 10^{-9} =$ *ca.* 0·45% of original total activity in the $[^{14}\text{C}]$carbon monoxide reacting) was mixed with pure methanol (1·00 ml., 24·8 mmoles) and separated by distillation into a residue (R_2) and a methanol fraction (P_2) which was converted into pure methyl 3 : 5-dinitrobenzoate. On combustion this gave carbon dioxide of specific activity $<5 \times 10^{-12}$; the methanol thus had specific activity $<4 \times 10^{-12}$ or a total activity of $<1 \times 10^{-9}$. This is the activity derived from <0·1% of the methanol produced in the reaction. The crude distillate (P_1), which therefore contained at least 99·9% of the methanol produced in the reaction, was mixed with pure methanol (0·740 g.; 23·15 mmoles) and after two distillations gave two residues (R_3 and R_4) and a methanol concentrate (*ca.* 0·7 g.; P_3) which was converted into pure methyl 3 : 5-dinitrobenzoate. On combustion carbon dioxide was obtained with specific activity $3{\cdot}83 \pm 0{\cdot}01 \times 10^{-9}$, corresponding to methanol of specific activity $3{\cdot}06 \pm 0{\cdot}01 \times 10^{-8}$. Assuming the methanol produced in the reaction to have specific activity $1{\cdot}39 \pm 0{\cdot}01 \times 10^{-7}$, the yield was therefore 6·57 mmoles. The residues R_3 and R_4 contained a total activity of *ca.* 3×10^{-7}. This is the activity of *ca.* 10 mmoles of the diluted methanol. The total methanol *after* dilution was 29·7 mmoles, and the amount recovered as a concentrate about 22 mmoles. It is therefore probable that the activity in these residues was largely due to incompletely removed methanol.

A sample of methanol prepared by reduction of carbon monoxide gave a negative reaction for formaldehyde by the chromotropic acid test. Glycol was sought by a dilution method in the less volatile fractions (R_3 and R_4) obtained in the working up of the crude methanol distillate (P_1) in Run 2. By assuming that specific activity of the glycol carbon would be the same as the original carbon monoxide it was shown that less than 0·03% of the monoxide was converted into glycol. Similarly it was shown that formate present in R_2 was 0·004% of the [^{14}C]carbon monoxide absorbed. This may well have arisen from traces of [^{14}C]carbon dioxide present in the original carbon monoxide.

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