deviations at intermediate [I$^-$]. Instead they are distributed randomly around the curve which can be calculated applying (3b) (which gives about the same value for k_1). We conclude that with a probability of more than 99.5% (3b) represents the actual mechanism of the main paths of the reaction, and (4) as well as (3a), (3d), and (3e) can be ruled out. The standard deviation, *s*, calculated from (3b) is 6.9%, which is not far from the predicted experimental error. However minor paths of order zero and three with respect to H$^+$ are not ruled out and actually are strongly suggested by the results. Using the weight equations[17] we have calculated the standard deviations of the parameters of (3b) which are given in the text.

An analogous treatment was applied to the data of Table II with generally similar results. In particular (3b) is confirmed to be significantly superior to (3a) and (3d) and (3e) give a negative meaningless value for the rate constant corresponding to $(p,r) = (1,2)$. No definite conclusion can be reached from these runs about the relative merits of (3b) and (4) due to the narrow range of [I$^-$]. The purpose of these runs was in fact to rule out, even at $I = 3.00\ M$, the contribution of a path first order with respect to H$^+$ and second order with respect to I$^-$. This contribution can be ruled out with a probability of more than 97.5% ($\chi^2_{(3b)} = 17.6$ and $\chi^2_{(3a)} = 30.1$; for 16 degrees of freedom $\chi^2_{(90\%)} = 23.5$ and $\chi^2_{(97.5\%)} = 28.8$).

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The Homogeneous Ruthenium-Catalyzed Reduction of Nitrobenzene

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Dodecacarbonyltriruthenium, pentacarbonylruthenium, and tris(acetylacetonato)ruthenium(III) were found to promote the homogeneous reduction of nitrobenzene to aniline by carbon monoxide and hydrogen in good yields and conversions. At CO:H$_2$ ratios higher than 1, diphenylurea is also a product of the reaction and its yields increase gradually with the CO:H$_2$ ratio. Product balance at very high CO:H$_2$ ratios shows that carbon monoxide participates in the reduction and thus the stoichiometry of the reaction is probably $C_6H_5NO_2 + 2CO + H_2 \rightarrow C_6H_5NH_2 + 2CO_2$. A reaction mechanism is proposed in which a phenylnitrene intermediate stabilized by bonding to ruthenium in a binuclear complex undergoes either hydrogenolysis to give aniline or CO insertion and hydrogenolysis to give 2,2′-diphenylurea. Pentacarbonyliron is considerably less active than ruthenium in promoting the reduction of nitrobenzene; a possible interpretation of this fact is given.

Introduction

There are several advantages in studying the reduction of nitrobenzene by carbon monoxide and hydrogen catalyzed by soluble metal complexes. Nitrobenzene, an industrially important chemical, has been more often reduced with hydrogen on heterogeneous catalysts and no really homogeneous catalytic systems have been reported in detail. Besides that, rather simple organic materials easily recognizable by the usual physical-chemical methods were anticipated to arise from its reduction.

Nitrobenzene had been reduced before by making use of metal-carbonyl systems. Formation of aniline from nitrobenzene has been briefly mentioned apparently with carbon monoxide and hydrogen in the presence of octacarbonyldicobalt.[2] Although yields were not specified, this reaction was assumed by us to occur under catalytic conditions. Aniline was also obtained[3] from nitrobenzene in the presence of alkaline solutions presumably containing the FeH(CO)$_4^-$ anion. The latter system is substantially stoichiometric since the moles of nitrobenzene reduced correspond to or are only slightly more than the moles of pentacarbonyliron introduced in the reaction. Nitrobenzene was also reduced stoichiometrically by Fe(CO)$_5$ under ultraviolet or γ-ray irradiation to give nitrosobenzene.[4] The latter was isolated as monomeric and dimeric Fe(CO)$_3$ complexes. In view of the paucity of data available, it was interesting to see whether other metal carbonyls would catalyze the reduction of nitrobenzene to aniline.

The main prerequisites of a catalyst are that (a) it should not react in an irreversible way with the substrate, (b) it should provide a low-energy path for the formation of the intermediates, and (c) the intermediates should not be kinetically too stable. Ruthenium and osmium carbonyls appeared to satisfy the first requirement in view of their stability to oxidizing agents[5] in general and to nitrobenzene in particular. Further, formation of aniline from nitrobenzene in the presence of metal carbonyls as catalysts may involve reduction either by hydrogen exclusively or by carbon monoxide and hydrogen. The possibility that the first steps of

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TABLE I

NITROBENZENE REDUCTIONS WITH CARBON MONOXIDE AND HYDROGEN IN THE PRESENCE OF RUTHENIUM COMPOUNDS[a]

Run no.	Ruthenium compound	Nitrobenzene: ruthenium ratio	Initial p_{CO} and p_{H_2}, atm	Initial $CO:H_2:C_6H_5NO_2$ molar ratio	Intermediate $CO:H_2$ ratio[b]	Reaction time, hr	% products	
							Aniline	2,2′-Diphenylurea
1	$Ru_3(CO)_{12}$	400	100,100	. . .	. . .	6	66.5	. . .
2	$Ru(acac)_3$[c]	88	100,100	3.4:3.4:1	0.4	15	66.3	. . .
3	$Ru_3(CO)_{12}$	21	80,80	6.6:6.6:1	0.7	15	66.8	. . .
4	$Ru(CO)_5$	38	80,80	10.4:10.4:1	0.8	16	52.9	3.0
5	$Ru_3(CO)_{12}$	270	120,40	4.0:1.3:1	1.5	3.5	57.4	20.6
6	$Ru_3(CO)_{12}$	219	140,20	4.7:0.7:1	4.0	5	39.4	40.3
7	$Ru_3(CO)_{12}$	227	148,12	5.0:0.4:1	7.4	21	Not determined	54.0
8	$Ru_3(CO)_{12}$	359	200, . . .	. . .	. . .	20	. . .[d]	8.4

[a] The reactions were carried out without solvent except runs 3 and 4 in which the reaction mixture was diluted with benzene. The temperature of reaction was in general 140° (initial gas absorption) to 160°. [b] This is the hypothetical $CO:H_2$ ratio when 2 mol of CO has been used to reduce $C_6H_5NO_2$ to "phenylnitrene." [c] Tris(acetylacetonato)ruthenium(III). [d] A small gas absorption was observed. The infrared spectrum of the filtered reaction mixture was substantially that of unreacted nitrobenzene.

the reduction sequence may be carried out by hydrogen requires the use of a metal catalyst which is capable to activate molecular hydrogen and to form a rather labile hydrido compound. Previous studies on ruthenium and osmium carbonyls had indicated that while osmium forms the exceptionally stable[6] $OsH_2(CO)_4$, the corresponding hydridocarbonyl of ruthenium is unstable[7] and decomposes very readily at room temperature. This suggested a general tendency for osmium to form more stable metal–hydrogen bonds as compared with ruthenium, thus implying that osmium would less favorably than ruthenium fulfill requirement c if hydrogen transfer to nitrobenzene is the key step of the reaction sequence. On the other hand, a consideration of the available experimental data for the metal carbonyl derivatives of a vertical triad shows that the reactivity of the second-row transition metals is substantially higher than that of the two other metals. This is particularly true for reactions involving the labilization of a metal–carbon bond, such as the exchange $M(CO)_6$–^{14}CO (activation energies[8] for the exchange are 39 kcal/mol for $Cr(CO)_6$, 30.8 kcal/mol for $Mo(CO)_6$, and 40.4 kcal/mol for $W(CO)_6$) and the carbon monoxide displacement[9] from $MC_5H_5(CO)_2$ for which the order of reactivity is $Co < Rh > Ir$. This labile character of second-row transition metals in their compounds containing carbon monoxide groups may also be responsible for the much higher activity of rhodium as compared with cobalt as a catalyst of the hydroformylation reaction.[10] In consideration of this, ruthenium carbonyls appeared to be better catalysts for the reduction of nitrobenzene by making use of the $CO \rightarrow CO_2$ pathway than both iron and osmium.

Therefore, ruthenium appeared to be the most promising as possible catalyst for the reduction of nitrobenzene to aniline with carbon monoxide and hydrogen. The results of the present investigation have shown that ruthenium carbonyls are effective catalysts for the reduction. We also hope that our study has thrown some light into the general problem of nitroaromatic compound reduction catalyzed by metal carbonyls.

Experimental Section

Tris(acetylacetonato)ruthenium(III) and dodecacarbonyltriruthenium were prepared as described earlier.[11]

Carbon monoxide was purchased from Fluka A.G., Buchs, Switzerland, and used without further purification. Nitrobenzene was freshly distilled before use.

Most of the reactions were carried out in a rocking stainless steel autoclave of 223-ml capacity, heated in an oil bath. Owing to the uniformity of heating and the good thermal contact provided by this experimental setup, reductions of nitrobenzene could be carried out without solvent. It is recommended, however, that one heats the reaction mixture initially very slowly as indicated in this section. Some of the reactions carried out in stainless steel autoclaves of the usual type heated by an external rocking electric oven resulted in strong heat being evolved. Also here very slow initial heating or, better, the use of a solvent resulted in controllable experiments.

Infrared spectra were measured with Perkin-Elmer spectrophotometers, Models 521 and 337, equipped with grating.

Reduction of Nitrobenzene.—We describe here only two experiments of reduction carried out with dodecacarbonyltriruthenium and tris(acetylacetonato)ruthenium(III), respectively, with CO and H_2 in an approximate ratio 1:1. This will exemplify the experimental procedure used; the effect of varying the $CO:H_2$ ratio on product distribution can be seen from the data of Table I.

(a) **In the Presence of $Ru_3(CO)_{12}$ (Run 1 in Table I).**—Dodecacarbonyltriruthenium (0.26 g, 0.407 mmol) was dissolved in 60.2 g of nitrobenzene (489 mmol; nitrobenzene:ruthenium ratio of 400) and allowed to react with hydrogen (100 atm) and carbon monoxide (100 atm). The reaction time was 6 hr at 135–160°. The temperature of the autoclave was 112° after 2 hr of heating and then gradually increased to 135° during 1 hr and 20 min. At this temperature gas absorption began and continued for 5 hr while the temperature reached the value of 160°. Carbon monoxide and hydrogen were then compressed again to 220 atm and the heating was maintained for 1 hr. After cooling, a pressure drop of 140 atm was observed. After filtration (recovered about 0.1 g of $Ru_3(CO)_{12}$), the reaction mixture was distilled and gave 30.3 g of substantially pure aniline (66.5% yield).

(b) **In the Presence of Tris(acetylacetonato)ruthenium(III) (Run 2 in Table I).**—Tris(acetylacetonato)ruthenium(III) (1.11 g, 2.79 mmol) was dissolved in nitrobenzene (30.12 g, 245 mmol; nitrobenzene:ruthenium ratio of 88) and heated during

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[6] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, **6**, 2092 (1967).

[7] M. I. Bruce and F. G. A. Stone, *Angew. Chem.*, **80**, 460 (1968).

[8] F. Calderazzo, R. Ercoli, and G. Natta in "Organic Syntheses *via* Metal Carbonyls," I. Wender and P. Pino, Ed., Vol. 1, John Wiley & Sons, Inc., New York, N. Y., 1968, p 175.

[9] F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 576.

[10] B. Heil and L. Markó, *Chem. Ber.*, **101**, 2209 (1968), and references therein.

[11] F. Calderazzo and F. L'Eplattenier, *Inorg. Chem.*, **6**, 1220 (1967).

15 hr at 160° with carbon monoxide (100 atm, 824 mmol) and hydrogen (100 atm, 824 mmol). After cooling a pressure drop of 85 atm was observed. The reaction mixture was filtered and the residue on the filter was washed with petroleum ether (bp 50–70°) and dried. An infrared spectrum of this solid (0.46 g) indicated the presence of $Ru_3(CO)_{12}$ contaminated with some 2,2′-diphenylurea. No bands due to unreacted nitrobenzene were observed in the infrared spectrum of the filtrate. The latter was distilled under vacuum and the main fraction (15.12 g; 66.3% yield) was substantially pure aniline, according to the infrared spectrum.

A control experiment was carried out with 60.2 g of nitrobenzene, carbon monoxide (100 atm), and hydrogen (100 atm) without any ruthenium being added. The autoclave content was heated to 160° for 7 hr. After cooling, an absorption of 10 atm was observed, to be compared with the absorption of 85 atm observed under the same conditions with half the amount of nitrobenzene in the experiment with $Ru_3(CO)_{12}$ described above. The infrared spectrum of the reaction mixture indicated the presence of large amounts of unreacted nitrobenzene.

Reduction of Nitrobenzene in the Presence of Pentacarbonyliron.—Nitrobenzene (7.22 g, 58.6 mmol) and 100 ml of benzene were introduced in the stainless steel autoclave together with $Fe(CO)_5$ (0.57 g, 2.91 mmol; nitrobenzene:iron ratio of 20), hydrogen (80 atm), and carbon monoxide (80 atm). After heating for 15 hr at 160°, the autoclave was cooled. The reaction mixture still contained considerable amounts of unreacted nitrobenzene. A spectrophotometric determination showed that a 29.2% conversion of nitrobenzene into aniline had occurred. Smaller amounts of azobenzene were observed.

Attempted Reaction of Aniline with CO to Form 2,2′-Diphenylurea.—Aniline (25.54 g, 274 mmol), 0.24 g of dodecacarbonyltriruthenium, carbon monoxide (140 atm), and hydrogen (20 atm) were heated in a stainless steel autoclave for 19 hr at 160°. After cooling no solid products were found in the reaction mixture and the infrared spectrum of the solution had bands due to aniline and to pentacarbonylruthenium. Diphenylurea was not present in any appreciable amount.

Results and Discussion

Dodecacarbonyltriruthenium has been found to promote the reduction of nitrobenzene to aniline by carbon monoxide and hydrogen. The yields given in Table I are usually calculated on distilled aniline; the figures given there certainly represent a lower limit. Of particular interest is the really catalytic character of the reaction: some of the reactions were run with substrate to ruthenium ratios of 400 and still reasonable rates were observed. Under the conditions which gave the best yields of aniline, *i.e.*, at a 1:1 ratio of carbon monoxide to hydrogen, the ruthenium is mostly present at the end of the reaction as the little soluble $Ru_3(CO)_{12}$. The latter, although sometimes contaminated with 2,2′-diphenyurea, can be reused for a subsequent reaction. A further advantage is that the reaction can be carried out without preformed $Ru_3(CO)_{12}$.

Tris(acetylacetonato)ruthenium(III) can be used instead. The results are the same (compare runs 1 and 2 of Table I) but longer reaction times have to be used. An induction time of 2 or 3 hr was usually observed with the acetylacetonate before gas absorption took place to any important extent. This may be understood when considering that ruthenium has to be reduced and carbonylated before the active species, whatever it is, may be formed. It is known[11,12] that tris(acetylacetonato)ruthenium(III) is reduced and carbonylated by hydrogen and carbon monoxide to give $Ru(CO)_5$ or $Ru_3(CO)_{12}$ depending on the solvent, carbon monoxide partial pressure, and temperature.

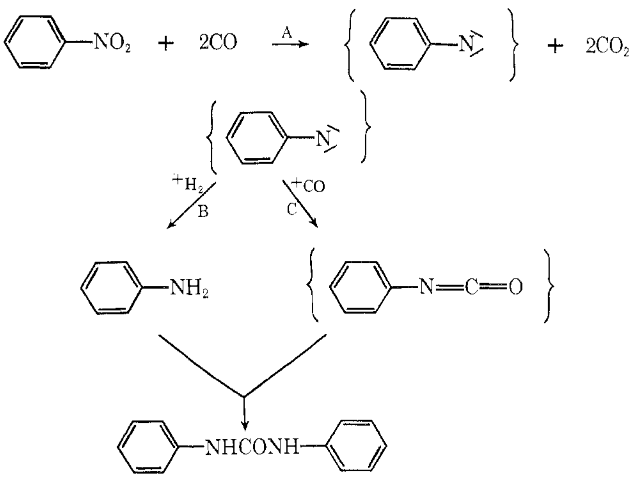
As expected, the reduction of nitrobenzene can be successfully carried out when ruthenium is initially introduced as $Ru(CO)_5$ (run 4 in Table I).

The effect of varying the $CO:H_2$ ratio is also indicated in Table I. While with 1:1 carbon monoxide–hydrogen mixtures, very small amounts of 2,2′-diphenylurea, if any, were found, at increasing $CO:H_2$ ratios aniline decreases and 2,2′-diphenylurea increases. Experiment 7 which had the highest $CO:H_2$ ratio gave the highest yield of the urea. The initial $CO:H_2:C_6H_5NO_2$ ratios are also to be considered. As it can be seen from experiments 5 and 6, despite the fact that the molar ratio hydrogen:nitrobenzene is around or lower than 1, about 80% of the initial nitrobenzene is converted into 2,2′-diphenylurea or aniline. The only way to explain this is by saying that the role of carbon monoxide is not only that of avoiding the decomposition of the catalyst at high temperatures under hydrogen pressure. Clearly carbon monoxide directly participates in the reduction of nitrobenzene. This is even more evident when considering the results of run 6 in which the 0.7 mol of hydrogen per mol of nitrobenzene initially introduced in the reaction was almost quantitatively found in the final products (0.39 mol as aniline and 0.20 mol as 2,2′-diphenylurea). This, together with the fact that CO_2 was detected spectroscopically in the final reaction mixtures, makes one believe that the correct stoichiometry of the reaction is

$$C_6H_5NO_2 + 2CO + H_2 \longrightarrow C_6H_5NH_2 + 2CO_2 \qquad (1)$$

The experimental facts can be explained by the reaction mechanism indicated in Scheme I. The formation of the intermediate phenylnitrene by carbon monoxide reduction of nitrobenzene (path A) is postulated. The latter can be formally considered to react either with hydrogen (path B) to give directly aniline or with CO (path C) to give phenyl isocyanate. Some of the species in Scheme I have been written in braces to specify that they are not believed to be present as such

Scheme I



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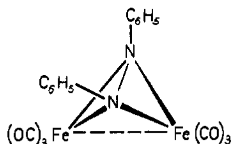
(12) G. Braca, G. Sbrana, and P. Pino, *Chim. Ind.* (Milan), **50**, 121 (1968).

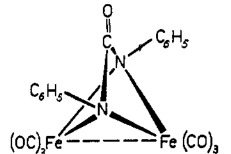
in solution even for short periods of time. They are probably stabilized by complexation to ruthenium. Although 2,2′-diphenylurea can of course arise from the reaction of phenyl isocyanate with aniline, the origin of the urea may be different and its formation may occur within the coordination sphere of the metal (*vide infra*).

Kmiecik[13] also assumed the presence of an intermediate nitrene in the reductive coupling of nitroaromatic compounds; in this reaction, which was carried out in the presence of catalytic amounts of pentacarbonyliron, the reducing agent is carbon monoxide. It is interesting to notice that when in our reacting system we substituted $Ru_3(CO)_{12}$ with $Fe(CO)_5$ and kept all the other conditions unchanged, aniline formation took place to a considerably smaller extent and some coupling products of reduced nitrobenzene (azobenzene) were found. Over a reaction time which is sufficient with ruthenium to convert nitrobenzene quantitatively into reduced products, still about 50% of unreacted nitrobenzene was found spectroscopically. This may be understood in terms of a much lower catalytic activity of iron as compared with ruthenium. This is also indicated by the more drastic conditions used by Kmiecik for his reductive coupling (200–210°; nitrobenzene:iron ratio of 10–20) as compared with the conditions required by our catalytic system (135–160°; nitrobenzene:ruthenium ratios as high as 400).

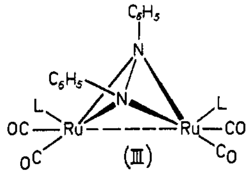
Thus, once again one finds that a second-row transition metal in its complexes containing carbonyl groups shows a much higher kinetic lability than its lighter congener. The lower catalytic activity of iron as compared with ruthenium in nitrobenzene reduction can be explained in several different ways. One possible explanation is that iron stabilizes the intermediate phenylnitrene, thus retarding its further reaction either with hydrogen (path B of Scheme I) or with CO (path C) or with itself and nitrobenzene to give azobenzene and azoxybenzene, respectively. This view is substantiated by the isolation[14] of a bis-phenylnitrene (or azobenzene) complex of iron of formula $Fe_2(CO)_6(NC_6H_5)_2$ to which structure I was assigned. This compound is spontaneously converted in solution into the urea-type of complex (II). The structure of the latter compound has been recently elucidated by X-ray diffraction.[15] A trinuclear $Fe(CO)_3$ compound with a proposed nitrene-like structure was also isolated from the reaction of nitromethane with $Fe_2(CO)_9$.[14] The carbonyl insertion to give II suggests that the N–N bond in complex I is rather labile and undergoes CO insertion rather easily. It is attractive to regard the ruthenium-catalyzed reduction of nitrobenzene to aniline and 2,2′-diphenylurea as occurring through the formation of two intermediate complexes of ruthenium analogous to I and II.



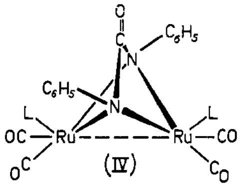
(I)



(II)



(III)



(IV)

Phenylnitrene shown in Scheme I should then be better regarded as being generated on the metal complex by two subsequent reductions by coordinated carbon monoxide groups and there remaining as a ligand in a more stable form as indicated in III. Complex III can then undergo hydrogenation to aniline or CO insertion between the N–N bond to give complex IV. The latter by hydrogenation would give 2,2′-diphenylurea. The ligands L on the ruthenium atoms may be either carbon monoxide groups or hydrido ligands.

Under the assumption that complexes of the type described above are responsible both for the reductive coupling of nitrobenzene[13] catalyzed by iron and for our ruthenium-catalyzed reduction, the lower catalytic activity of iron may be ascribed to a less labile iron–nitrogen bond in I relative to the ruthenium–nitrogen bonds in structures III and IV.

Since disubstituted ureas can be obtained by dehydrogenative carbonylation of primary amines[16] in the presence of $Mn_2(CO)_{10}$, the question arose whether this was also the origin of 2,2′-diphenylurea in our catalytic system. The failure to obtain 2,2′-diphenylurea from aniline and carbon monoxide in the presence of $Ru_3(CO)_{12}$ (a low partial pressure of hydrogen was also used in order to reproduce the reaction conditions) supports the idea that phenylnitrene or, better, a metal-stabilized bisphenylnitrene is the precursor to 2,2′-diphenylurea.

Finally, we have to comment on the result of run 8 in Table I, which was carried out with no additional hydrogen other than that contained in the commercially available carbon monoxide (about 2%). This reaction was expected to give either phenyl isocyanate or azobenzene or azoxybenzene. There was substantially no reaction and none of the products expected was found. The small amount of 2,2′-diphenylurea observed may arise from the hydrogen present as impurity in the gas; once all the hydrogen had been consumed to produce the urea, the reaction stopped. A reasonable explanation is that, although hydrogen does not participate directly in the stoichiometry of the reduction of nitrobenzene to complexed phenylnitrene, its presence is probably necessary to promote the formation of the active ruthenium carbonyl species. If this species is binuclear, hydrogen may be involved in the labilization of the ruthenium–ruthenium bonds of dodecacarbonyltriruthenium. We are investigating the scope of this reaction and trying to get some further evidence in favor of the proposed intermediates.

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