will be noted in Table II, the salt extracted by alcohol when carbonate alone is present amounts to only 0.6 to 0.7 mg. per cc. of alcohol. After careful trituration of crystals of potassium carbonate and saturated solution with 94% alcohol, the amount of carbonate extracted was found, as an average of nine determinations, to be about 1.09 mg. per cc. of alcohol.

Much of this work was done in the Rijksinstituut voor de Volksgezondheid, Utrecht, Holland. The author's sincere thanks are due Dr. J. F. Reith, Head of the Chemical Division there, who demonstrated his methods, and offered valuable suggestions and criticisms.

Summary

1. Iodate can be quantitatively reduced in hot alkaline solution by means of hydrazine sulfate.

2. Efficient extraction of iodide can be made with alcohol from a saturated solution of potassium carbonate, without danger of occlusion by crystals.

3. Alkaline solutions containing iodide should not be boiled in porcelain dishes before extraction of the iodide.

4. Fluoride delays the re-oxidation of iodide which takes place after a titrimetric determination of iodine.

PHILADELPHIA, PENNA. RECEIVED JUNE 15, 1936

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

The Reduction of Aromatic Compounds with Hydrogen and a Platinum Oxide–Platinum Black Catalyst in the Presence of Halogen Acid

BY J. H. BROWN, H. W. DURAND AND C. S. MARVEL

While reducing hot alcoholic solutions of some bromophenylolefins to the corresponding paraffins by hydrogen in the presence of Adams, Voorhees and Shriner's platinum catalyst,[1] we observed that in some runs more than the expected amount of hydrogen was absorbed, and hydrogen bromide was formed. Further investigation showed that this reaction involved not only removal of bromine from the benzene ring, but also reduction of the benzene ring to a hexahydro derivative. Since Adams and Marshall[2] have found that, in general, aromatic compounds are very slowly reduced in alcohol and only with moderate rapidity in glacial acetic acid, with platinum oxide–platinum black as a catalyst, it has seemed worth while to investigate our chance observation in greater detail.

When bromobenzene was dissolved in alcohol at about 55° and shaken with the catalyst in the presence of hydrogen, rapid absorption of hydrogen occurred, and cyclohexane was formed. By interrupting the reduction when one equivalent of hydrogen per molecule of bromobenzene had been absorbed, the product obtained was an impure sample of benzene, but the reaction did not seem to offer a satisfactory scheme for removal of halogen from a benzene derivative. Other aryl halides, such as *o*-, *m*- and *p*-bromotoluene, *p*-dibromobenzene, chlorobenzene and *p*-dichlorobenzene, were also readily reduced to halogen acid and the cyclohexane derivative. However, not all aryl halides could be reduced readily, as shown by the fact that iodobenzene, *o*-bromobenzoic acid, α-chloronaphthalene and α-bromonaphthalene were not affected in our experiments.

Since the reduction of an aryl halide apparently was taking place in two steps—first, removal of halogen acid, and then reduction of the ring—and more rapidly than the usual reduction of the ring alone, it seemed probable that the liberated halogen acid must be an activator for the platinum catalyst for reduction of aromatic compounds. This was verified by reducing various aromatic compounds in alcoholic solution in the presence of various concentrations of hydrogen chloride and bromide. Some of the first reductions were carried out after preheating the solutions to 50–70°, but later it was found that this was not necessary, as reduction took place rapidly, and the temperature of the mixture soon rose to this point without outside heating. Benzene, toluene, xylene, mesitylene, ethylbenzene, cymene, diphenyl and anthracene were readily reduced, whereas naphthalene and phenanthrene were not affected. There seemed to be no choice between hydrogen chloride and hydrogen bromide as an activator.

When functional groups are present in the aro-

---

[1] Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 452.

[2] Adams and Marshall, THIS JOURNAL, **50**, 1970 (1928).

TABLE I

REDUCTION OF ARYL HALIDES

Compound reduced	Mols of H_2 absorbed[a]	Time, min.	Halogen acid formed, mols	Product of reduction
Bromobenzene	0.185	240	0.0486	Cyclohexane d^{20}_4 0.7767 n^{20}_D 1.4274
Bromobenzene	.06	14	.0422	Benzene
o-Bromotoluene	.17	135	.0479	Methylcyclohexane d^{20}_4 0.7689 n^{20}_D 1.4227
m-Bromotoluene	.2	240	.047	Methylcyclohexane n^{20}_D 1.4362
p-Bromotoluene	.14	300	.044	Methylcyclohexane n^{20}_D 1.4357
p-Dibromobenzene	.22	210	.085	Cyclohexane n^{20}_D 1.4261
Chlorobenzene	.2	210	.049	Cyclohexane n^{20}_D 1.4255
p-Dichlorobenzene	.21	300	.073	[b] Cyclohexane n^{20}_D 1.4282

[a] Calculated roughly from drop in pressure during reduction. [b] Some *p*-dichlorobenzene remained at the end of this run.

matic molecule, there is very little regularity in the effect of halogen acid on the ease of reduction. Phenol and ethyl benzoate were reduced more rapidly in the presence of halogen acid than in its absence. Benzaldehyde and benzoic acid were no more readily reduced in the presence of halogen acid. Anisole, in the presence of halogen acid, gave cyclohexane. It is of interest that, while naphthalene and its α-chloro and α-bromo derivatives were unaffected, α- and β-naphthol both reduced readily in the presence of hydrogen chloride to give the corresponding tetrahydronaphthols. This is the normal course of reduction for α-naphthol, but in the case of β-naphthol sodium and amyl alcohol reduction gives mainly the alcohol[3] and very little phenol.

Adams and Marshall[2] pointed out that alcohol is usually the best solvent for reductions making use of this platinum catalyst, although for aromatic hydrocarbons they had better results with acetic acid. When the catalyst is activated with halogen acid, alcohol again becomes the better solvent, although the activity of the catalyst in acetic acid is slightly improved by hydrogen chloride.

Hamilton and Adams[4] have shown that pyridine derivatives reduce much more readily if they are first converted to the halogen acid salt. This may be due to the same sort of activation of the catalyst which has been observed with hydrocarbons of the benzene series. Zelinsky, Packendorff and Packendorff[5] have reported that ketones can be reduced to the corresponding hydrocarbons over a catalyst of platinized charcoal, provided a little palladium chloride is added to raise the activity of the catalyst. Later Packendorff[6] showed that reduction of chloroplatinic acid in the presence of platinized charcoal gave a catalyst which was effective for the reduction of a carbonyl group to a methylene group. This probably was an activating effect of halogen acid similar to that which we have observed.

Experimental Part

Reduction of Aryl Halides.—A solution of 0.05 mole of the aryl halide in exactly 100 cc. of ethyl alcohol was placed in a reduction outfit[7] and warmed to 55°. To the warm mixture 0.1 g. of platinum oxide catalyst[1] was added and the mixture was reduced under a hydrogen pressure of about 3 atmospheres. The drop in pressure was noted from time to time in order to know when reduction was complete. When no more hydrogen was absorbed, the reaction mixture was removed from the outfit and an aliquot portion of the solution was titrated to show the amount of halogen acid produced. The reaction mixture was then diluted, and the reduction

TABLE II

EFFECT OF HALOGEN ACID ON CATALYTIC REDUCTION OF BENZENE

Halogen acid used	Time for complete reduction, min.	Pressure drop[a]
None	70	None
1 drop alcoholic HCl[b]	49	6.9
0.2 cc. alcoholic HCl	29	7.3
1.0 cc. alcoholic HCl	31	7.0
5.0 cc. alcoholic HCl	30	7.3
6.0 cc. alcoholic HCl	23[c]	7.3
1 drop alcoholic HBr[d]	36	7.4
0.5 cc. alcoholic HBr	34	7.1
5.0 cc. alcoholic HBr	79	5.9
0.02 g. I_2	720	None
0.2 cc. alcoholic HCl[e]	39	7.6

[a] The theoretical absorption of hydrogen should cause a drop in the pressure of 7.1–7.2 lb. [b] This solution was prepared by saturating 95% ethyl alcohol with dry hydrogen chloride at room temperature. [c] In this experiment 0.25 g. of catalyst was used. [d] This solution was prepared by saturating 95% ethyl alcohol with dry hydrogen bromide at room temperature. [e] The solution was not preheated in this reduction.

---

(3) Bamberger and Kitschelt, *Ber.*, **23**, 885 (1890).

(4) Hamilton and Adams, THIS JOURNAL, **50**, 2260 (1928).

(5) Zelinsky, Packendorff and Packendorff, *Ber.*, **66**, 872 (1933); **67**, 300 (1934).

(6) Packendorff, *ibid.*, **67**, 905 (1934).

(7) Adams and Voorhees, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 53.

TABLE III

REDUCTION OF AROMATIC HYDROCARBONS

Compound reduced	Amount used	Halogen acid used	Time, hrs.	Product
Benzene	10 cc.	2 cc. aqueous HCl (sp. gr., 1.19)	4	Cyclohexane[a]
Toluene	10 cc.	None	3.5	No reduction
Toluene	10 cc.	1 cc. 48% aqueous HBr	10	Methylcyclohexane[b]
Toluene	10 cc.	5 cc. alc. HCl	3	Methylcyclohexane[b]
Xylene[c]	10 cc.	2 cc. alc. HCl	6	Dimethylcyclohexane[d]
Mesitylene	10 cc.	2 cc. alc. HCl	6	1,3,5-Trimethylcyclohexane[e]
Ethylbenzene	9.25 cc.	1 cc. alc. HBr	5.5	Ethylcyclohexane[f]
Cymene	13.4 g.	0.5 cc. alc. HCl	2.25	Hexahydrocymene[g]
Diphenyl	7.7 g.	5 cc. alc. HCl	10	Dicyclohexyl[h]
Anthracene	4.55 g.	5 cc. alc. HCl	15.5	Octa- and perhydroanthracenes[i]

[a] B. p., 81–81.5°; n^{20}_{D} 1.4314. [b] B. p., 99–101°; n^{20}_{D} 1.4359. [c] Technical xylene. [d] B. p., 113–124°; d^{20}_{4} 0.773; n^{20}_{D} 1.4258. [e] B. p., 134–136°; n^{20}_{D} 1.4320. [f] B. p., 131–132°; n^{20}_{D} 1.4329. [g] B. p., 168–169°; n^{20}_{D} 1.4395; d^{20}_{4} 0.8038. Adams and Marshall[2] report n^{20}_{D} 1.4370; d^{25}_{4} 0.8061. In their experiment 13.4 g. of cymene in glacial acetic acid was reduced with 0.2 g. of catalyst in seven and one-half hours. [h] B. p., 220-228°; n^{20}_{D} 1.4792; d^{20}_{4} 0.8804. [i] Octahydroanthracene, m. p., 73–74°; perhydroanthracene, m. p. 61–62°.

TABLE IV

REDUCTION OF AROMATIC DERIVATIVES

Compound	Amount	Time of reduction	Product	Physical properties of product
Phenol	9.4 g.	32 min.	Cyclohexanol	n^{22}_{D} 1.4652
Phenol	9.4 g.	3 hrs.[a]	Cyclohexanol	n^{22}_{D} 1.4652
Ethyl benzoate	7.5 cc.	4 hrs.	Ethyl hexahydrobenzoate	B. p. 190–194°; n^{15}_{D} 1.4481; d^{20}_{4} 0.9649
Acetophenone	6 g.	12 hrs.	Ethylcyclohexane[b]	B. p. 130–132°; n^{20}_{D} 1.4447
Anisole	10.8 g.	6 hrs.	Cyclohexane	B. p. 79–80°; n^{20}_{D} 1.4272
α-Naphthol	7.2 g.	4 1/2 hrs.	5,6,7,8-Tetrahydronaphthol-1	M. p. 68–69°
β-Naphthol	7.2 g.	10 hrs.	5,6,7,8-Tetrahydronaphthol-2	M. p. 59–60°

[a] No halogen acid has added to this run. [b] This material contained a little ethylbenzene.

product isolated in the usual manner. The results of some of the experiments are summarized in Table I.

Under the same experimental conditions iodobenzene, α-bromonaphthalene, α-chloronaphthalene and *o*-bromobenzoic acid were not affected.

Reduction of Benzene.—A series of experiments, using 5 cc. of freshly distilled, thiophene-free benzene in 100 cc. of 95% ethyl alcohol at 70° with 0.125 g. of platinum oxide catalyst, different amounts of hydrogen chloride and bromide and a hydrogen pressure of about three atmospheres, gave the results shown in Table II.

From these results, it is evident that both hydrogen chloride and hydrogen bromide activate the platinum oxide catalyst for the reduction of benzene. With hydrogen chloride, any amount beyond a trace seems to have little effect. Too much hydrogen bromide seems to be undesirable. Iodine is not an activator for the catalyst. No attempt was made to isolate the product of reduction in these runs.

To test the effect of halogen acid on the catalyst in acetic acid solution, two reductions were carried out, using 5 cc. of benzene, 0.1 g. of platinum oxide and 50 cc. of glacial acetic acid. To one of these batches, 0.5 cc. of alcoholic hydrogen chloride was added. The run without hydrogen chloride was complete in seventy minutes, whereas the run with it was complete in fifty-four minutes.

Reduction of Aromatic Hydrocarbons.—The standard reduction experiment was carried out by dissolving the aromatic hydrocarbon in 100 cc. of alcohol at 70°, using 0.1 g. of platinum oxide catalyst and 45 pounds (3 atm.) of hydrogen pressure. The halogen acid used to activate the catalyst was varied. The reduction products were isolated and identified, although little effort was made to determine exact yields. The results of some of our experiments are collected in Table III.

No evidence of reduction of either naphthalene or phenanthracene could be obtained using the general conditions outlined above, although various amounts of aqueous and alcoholic hydrogen chloride and bromide were added as activators for the platinum catalyst.

Reduction of Some Aromatic Derivatives.—Attempts were made to reduce some phenols, aromatic ethers, acids, esters, aldehydes and ketones, using the platinum oxide catalyst and halogen acids. Some of these derivatives reduced readily, and some not at all. The standard procedure was to use about 0.1 mole of compound, 100 cc. of alcohol, 0.1 g. of catalyst and 0.5 cc. of alcoholic hydrogen chloride at 70° under 3 atmospheres of hydrogen. The results are summarized in Table IV.

Benzaldehyde and benzoic acid were not reduced under the same conditions.

Summary

Small amounts of hydrogen chloride and hydrogen bromide increase the effectiveness of platinum oxide–platinum black as a catalyst for the hydrogenation of most aromatic rings.

URBANA, ILLINOIS RECEIVED JUNE 25, 1936