

proton splittings is greater in the case of the deuterated compound. This fact is accounted for in the model we have presented by attributing a slightly larger ΔE (about 200 calories larger according to the present best estimate) to the deuterated system.

We are at present in the process of modifying our Strand Lab Model 601 X-band spectrometer so that we may follow the temperature variations in hyperfine splittings more precisely to get information about unpaired spin distribution in both ground and excited states. We point out that such an analysis would in many cases provide both the magnitude and the sign of coupling constants.

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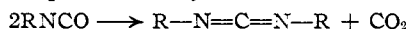
RECEIVED MARCH 7, 1962

A NEW SYNTHESIS OF MONO- AND POLYCARBODIIMIDES

Sir:

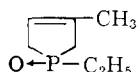
There are many simple, well-known condensation reactions which can be carried out on difunctional monomers with the production of linear polymers. However, those which can give polymers with sufficiently high molecular weight to be useful are quite limited in number.

We wish to call attention to a unique catalyzed condensation reaction in which an isocyanate is converted quantitatively to a carbodiimide



This reaction not only is suitable for the preparation in very high yield of a wide variety of mono-carbodiimides but, surprisingly, can be used to produce a new type of tough, high molecular weight condensation polymer in which the recurring unit is the $-\text{N}=\text{C}=\text{N}-$ link.

The most active catalyst for this reaction, 1-ethyl-3-methyl-3-phospholine-1-oxide

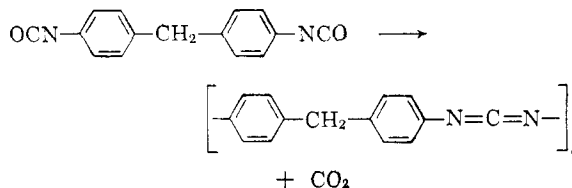


was prepared according to McCormack.¹ An example of its use is the preparation of 4,4'-dinitrodiphenyl carbodiimide, a hitherto unreported compound. *p*-Nitrophenyl isocyanate (21.0 g., 0.128 mole) was melted and treated with 0.03 g. of catalyst at about 60°. Carbon dioxide was evolved almost explosively and in a matter of 1-2 min. the mixture had set to a crystalline mass. The last traces of carbon dioxide were removed *in vacuo* and 18 g. (100%) of a yellow crystalline solid melting at 165-170° was obtained. One recrystallization from petroleum ether-chloroform gave an analytical sample, m.p. 164-166°. *Anal.* Calcd. for $\text{C}_{13}\text{H}_8\text{N}_4\text{O}_4$: C, 54.9; H, 2.81; N, 19.7. Found: C, 54.8, 54.7; H, 2.88, 3.02; N, 19.9, 20.0.

To produce a polymer, the following procedure is typical. To a solution of about 20 g. of a diisocyanate in 150 ml. of a suitable solvent, such as benzene, xylene, carbon disulfide, was added about 0.03 g. of the catalyst. The polymerization proceeded

(1) W. C. McCormack, U. S. Patents 2,883,736-9 (Dec. 22, 1953).

smoothly in all cases studied at temperatures from 25 to 250°. At 250° the evolution of carbon dioxide was extremely fast, while at room temperature 24 hr. or more was required for completion of the polymerization. For example, polymerization of methylene bis-(4-phenyl isocyanate) in boiling xylene gave a tough, Nylon-like lump of polymer in four hours.



This was pressed at 250° to a clear, crystalline, orientable film with a tenacity of about 50,000 p.s.i. an initial modulus of 410,000 p.s.i. and an elongation of 20% at 25°.

The proposed structure of the polymers is based on (1) method of formation, (2) ultimate analyses, and (3) infrared analysis which in all cases showed the very characteristic $\text{N}=\text{C}=\text{N}$ band at 4.76 microns.² In view of the reactivity of the carbodiimide link,³ the polymers are remarkably inert to boiling acid, alkali and amines. This presumably is because of lack of penetration of the reagent.

(2) G. D. Meakins and R. J. Moss, *J. Chem. Soc.*, 993 (1957).

(3) H. G. Khorana, *Chem. Revs.*, **53**, 145 (1953).

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RECEIVED FEBRUARY 14, 1962

NEW, HIGHLY ACTIVE METAL CATALYSTS FOR THE HYDROLYSIS OF BOROHYDRIDE

Sir:

We wish to report that the treatment of aqueous solutions of platinum, ruthenium and rhodium salts with aqueous sodium borohydride produces finely-divided black precipitates which are exceedingly active catalysts for the hydrolysis of the borohydride ion.

It has been known since the original discovery of sodium borohydride¹ that aqueous solutions of the salt exhibit a remarkable stability to hydrolysis. The hydrolysis can be facilitated by acids, or by certain metal ions.² Among the metals investigated, iron, cobalt and nickel salts appeared to be most effective, with cobalt being superior to the other two. This discovery led to the development of sodium borohydride pellets containing a small quantity of cobalt chloride. Such pellets, placed in contact with water, rapidly liberated hydrogen, and thereby provided an easily portable source of the gas.²

In the course of examining the interaction of sodium borohydride with a number of heavy metals,

(1) H. I. Schlesinger, H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **75**, 186 (1953).

(2) H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *ibid.*, **75**, 215 (1953).

we observed that many of these also exert a powerful catalytic effect on the hydrolysis of borohydride. The platinum family metals proved to be unusually effective and were subjected to a detailed study.

TABLE I
TIME REQUIRED FOR LIBERATION OF ONE-HALF OF THE AVAILABLE HYDROGEN FROM AQUEOUS SODIUM BOROHYDRIDE

Metal	Compound used	Time, min.
Iron	FeCl ₂	38
Cobalt	CoCl ₂	9
Nickel	NiCl ₂	18
Ruthenium	RuCl ₃	0.3
Rhodium	RhCl ₃	0.3
Palladium	PdCl ₂	180
Osmium	OsO ₄	18.5
Iridium	IrCl ₄	28
Platinum	H ₂ PtCl ₆	1

The following procedure was utilized. A stirred solution of 1.00 g. of sodium borohydride in 45.0 ml. of water in a 125 ml. erlenmeyer flask was maintained in a constant temperature bath at 25°. Reaction was initiated by injecting 5.0 ml. of a 0.100 M solution of the appropriate metal salt with a hypodermic syringe. The salt was instantly reduced with the formation of a deep black, finely-divided solid. The hydrogen evolved was passed through a wet-test meter, and the volume realized at regular intervals of time was noted. The results are summarized in Table I.

It is evident that the effectiveness of osmium and iridium is modest, approximating the previously known activities of iron, cobalt and nickel. Moreover, palladium exhibits much poorer catalytic activity. However, platinum is a highly effective catalyst, with a half-life approximately one-tenth that of cobalt, and both ruthenium and rhodium are even more active catalysts. In these last cases, the activities are so high that the half-lives can only be considered to be approximate—the solutions evolve hydrogen almost explosively with the injection of the metal salt solution.

The black powder produced by treating chloroplatinic acid with sodium borohydride was isolated and analyzed. It was essentially pure platinum. Consequently, it appears that sodium borohydride reduces these platinum metals to the elementary state, in a form which exhibits high catalytic activity for the hydrolysis reaction.

We are exploring the catalytic activity of these products for other reactions.

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RECEIVED MARCH 14, 1962

A SIMPLE PREPARATION OF HIGHLY ACTIVE PLATINUM METAL CATALYSTS FOR CATALYTIC HYDROGENATION

Sir:

The treatment of platinum metal salts with aqueous sodium borohydride results in the immediate formation of finely-divided black precipitates which are active catalysts for the hydrolysis

of sodium borohydride.¹ We wish to report that these materials are also highly active catalysts for the hydrogenation of typical olefins, such as 1-octene. Indeed, the platinum catalyst obtained by this simple procedure exhibits an activity of nearly 100 per cent. greater than that of commercial platonic oxide (Adams catalyst²) now widely used for laboratory hydrogenation, and the rhodium catalyst realized in this procedure is even more active.

The apparatus utilized for following the rates of hydrogenation of 1-octene consisted of a 100-ml. round-bottom flask, fitted with a magnetic stirrer, an inlet for hydrogen, an outlet leading to a short manometer, and an injection port fitted with a rubber serum cap. The flask was immersed in a 25° constant temperature bath. Hydrogen was conveniently generated in an adjacent flask by adding a 1.00 M solution of sodium borohydride in a buret to aqueous acid. In the hydrogenation flask was placed 1.0 ml. of 0.20 M chloroplatinic acid, then 40 ml. of anhydrous ethanol. The flask was briefly flushed with nitrogen. The catalyst was generated *in situ* by injecting 5.0 ml. of a 1.00 M solution of sodium borohydride in ethanol. The excess borohydride was destroyed and a hydrogen atmosphere achieved by injecting 4.0 ml. of 6 M hydrochloric acid. The 1-octene, 40 mmoles, was injected into the vigorously stirred solution. Hydrogen absorption began immediately. The standard solution of sodium borohydride was added to the generating flask (previously flushed with hydrogen) at such a rate as to maintain the pressure in the apparatus at approximately atmospheric. The results reveal an essentially linear absorption of hydrogen, complete in 16 to 18 minutes.

min.	%	min.	%
0	0	10	68
2.0	10	12	80
4.0	21	14	92
6.0	31	16	98
8.0	43	18	100

Under identical conditions, the reaction utilizing commercial platonic oxide was complete in 26 to 28 minutes.

Table I summarizes the results realized with the various platinum metal catalysts.

TABLE I
RATES OF HYDROGENATION OF 1-OCTENE BY VARIOUS PLATINUM METAL CATALYSTS PRODUCED *in Situ* BY BOROHYDRIDE REDUCTION

Metal ^a	Compound used	Time, min. ^b	
		50%	100%
Ruthenium	RuCl ₃	70	(170)
Rhodium	RhCl ₃	7	20
Palladium	PdCl ₂	16	(90)
Osmium	OsO ₄	45	(110)
Iridium	IrCl ₄	32	(80)
Platinum	H ₂ PtCl ₆	9	17
(Platinic oxide)	PtO ₂	14	27

^a 0.2 mmole for 40 mmoles of 1-octene. ^b Values in parentheses are estimated times for complete reaction.

(1) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 1493 (1962).

(2) R. Adams and R. L. Shriner, *ibid.*, **45**, 2171 (1923).