

tuted for H<sub>2</sub> in another experiment. Thus we believe that the reaction is between ammonia and hydrogen and gives some species of empirical composition NH<sub>4</sub>. We observe this species as an ion, but this observation does not necessarily imply that the NH<sub>4</sub> species is adsorbed on the surface as an ion. Incidentally, it should be pointed out that the rate of NH<sub>4</sub><sup>+</sup> formation is dependent upon the first power of the H<sub>2</sub> pressure rather than [H<sub>2</sub>]<sup>1/2</sup>. This behavior suggests that ammonia reacts with H<sub>2</sub> molecules rather than atoms adsorbed on the surface.

The author is indebted to Drs. E. H. Taylor and Russell Baldock of this Laboratory and to Professor P. H. Emmett of Johns Hopkins University, a consultant to the Laboratory, for stimulating discussions during the course of this investigation.

(2) Operated for the U. S. Atomic Energy Commission by Union Carbide Corporation.

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RECEIVED FEBRUARY 3, 1962

#### TEMPERATURE DEPENDENCE OF PROTON HYPERFINE SPLITTINGS<sup>1</sup>

Sir:

We have found that the isotropic proton hyperfine splittings in the potassium toluenide electron spin resonance (e.s.r.) absorption spectrum are

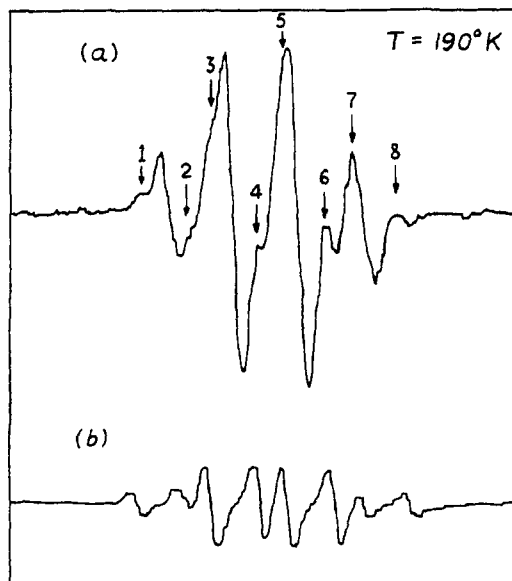


Fig. 1.—High field group of lines in the first derivative of the e.s.r. absorption spectra of (a) the 4:1 mixture of potassium *p*-deuteriotoluenide and undeuterated toluenide and (b) potassium toluenide alone. The positions of the eight lines from the toluenide are indicated by numbered arrows in (a); magnetic field decreases from left to right; solvent was 1:1 tetrahydrofuran to 1,2-dimethoxyethane.

slightly temperature dependent in the temperature range 160 to 270° K. Although changes in individual splittings could not be followed over the whole temperature range, we have been able

(1) This work has been supported in part by the National Science Foundation.

to estimate the change in the sum of the alkyl and para proton splittings as +1 gauss and in the sum of the meta and ortho proton splittings as -1 gauss. Proton hyperfine splittings were found to be temperature dependent in a similar degree in the case of other monoalkylbenzenides. The temperature dependence showed little variation with a change in size of the alkyl group. We have observed no such behavior of the proton splittings in the spectra of other free radical ions such as potassium benzenide, or naphthalenide.

The temperature dependence of these splittings may be understood on the basis of a thermally accessible electronic<sup>2</sup> excited state. Considering that transitions occur between these states at a rate rapid compared to frequency separations of hyperfine lines to be averaged, one expects to observe a spectrum which is a weighted average of the ground and excited state spectra. The supposition of a thermally accessible excited state is not unreasonable in view of the evidence for orbital degeneracy in the benzene anion.<sup>3</sup> Forming the indicated statistical average leads to the expression

$$\log \left( \frac{S_T - S_0}{S_1 - S_T} \right) = -\Delta E/RT \quad (1)$$

for  $S_T$ , the value of the hyperfine splitting at temperature  $T$ . The corresponding splittings for the ground and excited states are denoted by  $S_0$  and  $S_1$ , respectively,  $\Delta E$  is the energy difference between the states and  $R$  the gas constant. The data for toluenide may be fit with  $\Delta E$  between 1.5 and 2.0 kilocalories/mole and reasonable values for  $S_0$  and  $S_1$ .

In addition to accounting for the temperature dependence of proton hyperfine splittings, equation (1) also indicates the possibility of a deuterium isotope effect resulting from differences in vibrational energies associated with the electronic states of interest in deuterated and undeuterated anions. Such an isotope effect has been observed in the case of *p*-deuteriotoluenide ion. Figure 1(a) shows the group of lines occurring at high field for a 4:1 mixture of deuterated to undeuterated toluenide.<sup>4</sup> The group as a whole is asymmetric indicating that the centers of the two sets of lines, one from the toluenide (indicated with numbered arrows in Fig. 1), the other from the *p*-deuteriotoluenide anion, are shifted with respect to each other. Figure 1(b) is the high field group of lines in the e.s.r. spectrum of potassium toluenide. A closer inspection of Fig. 1(a) reveals that the *p*-deuteriotoluenide lines are shifted toward high field compared to their expected positions. The complete spectrum of this mixture retains over-all inversion symmetry. The low field lines are asymmetric in the opposite sense to their counterparts at high fields and the center line has a center of inversion. Clearly, the sum of the ortho and meta

(2) For simplicity the terms electronic and vibrational are used even though the Born-Oppenheimer separation may not apply.

(3) M. C. Townsend and S. I. Weissman, *J. Chem. Phys.*, **32**, 309 (1960).

(4) For an e.s.r. absorption spectrum of the toluenide ion see (a) J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 498 (1961), or (b) V. V. Voevodskii, S. P. Solodovnikov and V. M. Chibrikov, *Doklady Akad. Nauk SSSR*, **120**, 1982 (1959).

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  $\Delta E$  (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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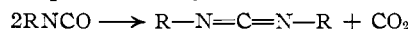
RECEIVED MARCH 7, 1962

### A NEW SYNTHESIS OF MONO- AND POLYCARBODIIMIDES

Sir:

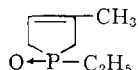
There are many simple, well-known condensation reactions which can be carried out on difunctional monomers with the production of linear polymers. However, those which can give polymers with sufficiently high molecular weight to be useful are quite limited in number.

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

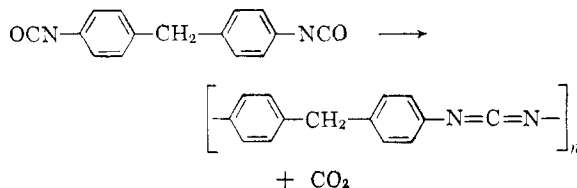


was prepared according to McCormack.<sup>1</sup> An example of its use is the preparation of 4,4'-dinitrodiphenyl carbodiimide, a hitherto unreported compound. *p*-Nitrophenyl isocyanate (21.0 g., 0.128 mole) was melted and treated with 0.03 g. of catalyst at about 60°. Carbon dioxide was evolved almost 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.<sup>2</sup> In view of the reactivity of the carbodiimide link,<sup>3</sup> 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.*, **63**, 145 (1953).

(4) To whom inquiries should be directed.

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JOHN J. MONAGLE

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 borohydride<sup>1</sup> that aqueous solutions of the salt exhibit a remarkable stability to hydrolysis. The hydrolysis can be facilitated by acids, or by certain metal ions.<sup>2</sup> 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.<sup>2</sup>

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).