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Reaction between NaH and Hexamethylphosphoramide (HEMPA)

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The reaction between NaH and HEMPA at 120 °C yields two anionic species: $O{=}P{-}[N(CH_3)_2]_2$ *(A) and Na* $N(CH_3)_2$ *(B), which are also obtained from the reaction between Na and HEMPA at 25 °C. Nevertheless, the percentage of (A) and (B), determined quantitatively, is different in the two reactions. These mixtures are employed in the polymerization of butadiene to yield polymers with prevailing 1,2 enchainments.*

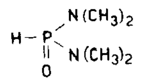
Introduction

The use of NaH in binary or ternary catalytic systems for polymerization reactions is well known [1, 2]; less data are available on the use of NaH alone [3], probably because of its poor solubility in organic solvents. In order to obtain soluble species for use in polymerization reactions, we have investigated the reaction of NaH with hexamethylphosphoramide (HEMPA) to yield two soluble anionic species. The complete characterization of these species including their exact yields, is now reported. The catalytic activity of such anions in the polymerization of butadiene has also been tested.

Experimental

Materials

NaH employed was an ANIC product with a ϕ = 80 μ. Na was used as finely subdivided sand. Azobenzene, benzophenone and HEMPA were pure Fluka products and were used without other purification. CH_3SO_2Cl, $PhCH_2Cl(Br)$ were also FLUKA products and were distilled and dried by treatment on P_2O_5 (C. Erba). Butadiene was an ANIC product, dried by azeotropic distillation. The solvents diethyl ether, THF (tetrahydrofuran), n-hexane, benzene (all Erba) and HEMPA (Merck) were used after standard purification and fractional distillation under nitrogen. The compound,

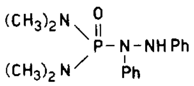


was prepared by literature methods [4, 5] and its metallation to give the corresponding anion (A) was carried out with LiBut at 0 °C or with $NaNH_2$ in liquid ammonia.
$NaN(CH_3)_2$ (B) was prepared according to ref. 6.

Procedure

The NaH–HEMPA reaction was carried out for 4 h at 120 °C with HEMPA as solvent. The mixture was then filtered and Na was determined by atomic absorption to monitor the concentration of active species.

The reaction Na–HEMPA was carried out following the literature [7]. The characterization of the products was done with azobenzene at 40 °C for 3 hours (ratio 1:1) for the species (A) to give the corresponding



and with $PhCH_2Cl$ and CH_3SO_2Cl for the species B.

The quantitative determination of the species (A) and (B) was made both from the Na by atomic absorption and from the $(CH_3)_2NH$ (Kjeldahl method) formed in the complete hydrolysis (KOH in water) of the two species.

Butadiene polymerization was carried out in a glass bottle under N_2, by first introducing the catalyst in HEMPA then adding THF (total volume = 20 ml), followed by sealing with an inert cap and injection of butadiene.

The polymer was recovered (after 8 h) by pouring the reaction mixture into methanol, drying at 40 °C for 12 h, and weighing.

Analyses

NMR and MS investigations were carried out with Varian mod. H-A 100 and LKB 9000 instruments, respectively.

The microstructure of polybutadienes was investigated by IR (Perkin–Elmer Mod. 21).

Na and Li were determined by atomic absorption using a Perkin–Elmer mod. 503 instrument.

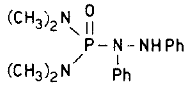
Results and Discussion

Qualitative Aspects of the Reaction NaH–HEMPA

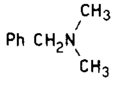
Nothing is reported in the literature on the reaction NaH–HEMPA. Upon mixing NaH with HEMPA, no reaction occurred up to 100–110 °C and NaH remained insoluble in the reaction medium. At 120 °C a progressive formation of a deep red solution was observed, accompanied by gas evolution consisting of H_2 and $NH(CH_3)_2$.

The product was characterized by reaction with electrophiles such as azobenzene, benzyl halides and methansulfonyl chloride.

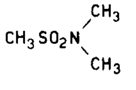
The following derivatives (I), (II), (III) have been isolated,



I

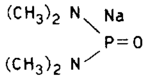


II

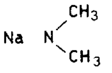


III

I from species (A), II and III from species (B).

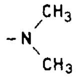


(A)



(B)

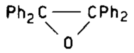
Spectroscopic data confirm these structures. In particular, for (I) mass data show: m/e 135(100); 44(46); 45(34); 77(34); $M^{+\cdot}$ 318(27); 92(20); 93(17); 183-(16); 46(15) and the NMR spectrum in $CDCl_3$ shows the following chemical shifts (in ppm from HMDS): 7.60–6.60 (Ph, m); 5.82 (–NH– s); 2.53



^{1}HNMR and m.s. spectra of the derivative (II) agree with reported data.

M.S. data of the derivative III show: m/e 44(100), 43(48), 42(45); $M^{+\cdot}$ 123(22), 122(8), 79(8), 41(8), 45(7), 81(6).

The formation of species (A) is also confirmed indirectly [8] by the isolation of



from the reaction mixture upon treatment with benzophenone.

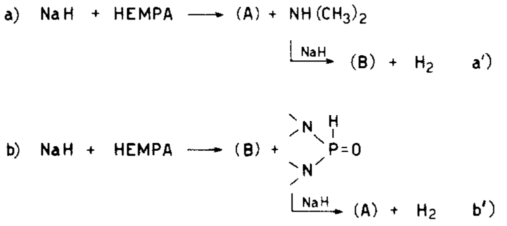
As has been reported, the species (A) and (B) have also been found in the reaction products of buthyllithium [8] or alkaline metals [7] with HEMPA.

In the butyllithium reaction, butane evolution is noted along with the formation of (A) and (B). In the reaction between alkaline metals and HEMPA, radical anionic species, whose stability depends on the nature of counterions (Li > Na > K), are formed first. The decomposition of these radical anions yields the species (A) and (B), with dimethylamine evolution, according to the reported mechanism [7].

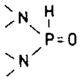
In the reaction between NaH and HEMPA at 120 °C, gas evolution (H_2 and $(CH_3)_2NH$) also occurs. The overall reaction may be as follows:

$$NaH + HEMPA \rightarrow (A) + (B) + NH(CH_3)_2 + H_2$$

through the intermediate steps:



In our opinion reaction (b) is less likely than (a) because



has a pK_a lower than that of $NH(CH_3)_2$ [9]; reaction (b′) is more likely than (a′) for the same reason and because of the high volatility of the amine which could prevent the metalation reaction. Hence both (a) and (b) probably contribute to the overall reaction, through the cleavage of the P–N bond.

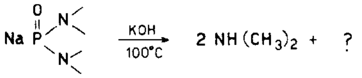
Quantitative aspects

Up until now, there were no data in the literature on the exact quantities of species (A) and (B) formed. Some preliminary attempts to evaluate the reaction products of species (A) and (B) with benzyl halides *via* V.P.C. were unsuccessful. Similarly, little reliable data are obtained by determining the adduct (I) gravimetrically (species A reacted with azobenzene) or by titrating the amine evolved in the reaction of (B) with triphenylmethane:

$$NaN(CH_3)_2 + Ph_3CH \rightarrow Ph_3CNa + (CH_3)_2NH$$

We have succeeded in evaluating quantitatively (A) and (B) by analyzing the pure species prepared as reported in the experimental part.

Species (A), upon treatment with KOH at 100 °C, yields quantitatively two mol of titratable dimethylamine,



while species (B), obviously, gives rise to 1 mol.

Since under the same experimental conditions HEMPA does not yield dimethylamine, it is possible to calculate (A) (x mol) and (B) (y mol) by the system:

TABLE I. Comparison between the Reactions NaH–HEMPA and Na–HEMPA, with Quantitative Determination of the Species Produced

Na, mmol	NaH, mmol	HEMPA, ml	Temp., °C	Time, hr	Yield[a], %	A%, mol		B%, mol
						Analytical Method	Gravimetric Method	
–	6	20	100	4	0			
–	12	20	120	4	90	63	65	37
6.5	–	20	25	8	95	53	55	47

[a] Calculated by analysis of Na in solution.

$$x + y = Na_{tot}$$

$$2x + y = NH(CH_3)_{2\,tot}$$

In Table I the quantitative determination of the amounts of species (A) and (B) obtained in the reactions NaH–HEMPA and Na–HEMPA is reported. In the same table the results of the gravimetric evaluation of the species (A) (reaction with azobenzene) are reported for comparison.

The constancy of such data over time shows the high stability of the two anionic species in HEMPA.

Anionic Polymerization of Butadiene

The reaction products of NaH–HEMPA at 120 °C and Na–HEMPA at 25 °C (after decomposition of the radical anion) were used as catalysts in the polymerization of butadiene.

NaH alone is not active in polymerization; the reaction mixture NaH–HEMPA yields 1,2-polybutadiene with a vinyl content higher than that obtained by the system Na–HEMPA.

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