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PRODUCTION OF HYDROGEN FROM THE REACTION OF THE ANION RADICAL OF NAPHTHALENE WITH WATER AND ETHANOL IN LIQUID AMMONIA

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Summary The reaction of sodium naphthalenide in liquid ammonia with water and ethanol was found to occur by two competing pathways yielding the protonation product and hydrogen gas Under the experimental conditions of this study, the major pathway was the reaction producing hydrogen gas

In a recent communication, Szwarc[1] and his colleagues disputed an earlier claim by Stevenson[2] <u>et al</u> that the radical anion of naphthalene reacts with water to produce hydrogen gas The net reaction in question is

$$2Ar^{\overline{\cdot}} + 2H_2O \rightarrow 2Ar + H_2 + 2OH^- \qquad (1)$$

where Ar is naphthalene and $Ar^{\overline{\cdot}}$ its radical anion The H_2 evolution via equation 1 is in sharp contrast to the protonation reaction via equation 2

$$2Ar^{\overline{\cdot}} + 2H_2O \rightarrow ArH_2 + Ar + 2OH^- \qquad (2)$$

Due to its synthetic utility, the latter reaction (Birch reduction) has received considerable attention and a number of studies[3] concerning the kinetics and mechanisms of these protonation reactions have been reported

During our work dealing with the kinetics of the reaction of sodium naphthalenide with water and ethanol in liquid ammonia it became apparent that this reaction has two pathways, namely, equations 1 and 2 Table 1 gives a summary of some of our results that show unequivocally that hydrogen gas results when sodium naphthalenide is exposed to water or ethanol in liquid ammonia (equation 1) Moreover, the results given in Table 1 strongly suggest that perhaps product analysis (especially determining whether hydrogen gas is produced) is required before the interpretation of a number of reported studies[3] concerned with the kinetics and mechanisms of protonation of radical anions can be considered valid

The experimental procedure used in the present study precludes the possibility that the evolved hydrogen was produced by any reaction other than equation 1 The equipment and purification procedures were similar to those previously described [4] Usually, several hours were required

TABLE 1 Hydrogen gas production from the reactions of sodium naphthalenide with water and ethanol in liquid ammonia

RUN	Volume NH_3 ml	mmolx10^{-2} sodium	mmolx10^{-1} naphthalene	mmol ROH[a]	mmolH_2x10^{-2} Recovered	% Reaction 1
D92	59.0	9.80	1.07	7.43	4.48	91
D90	56.8	5.63	3.11	28.0	2.06	73
D89	47.5	5.68	5.68	22.9	2.83	100
D64	61.8	2.31	2.00	21.2	1.17	101
D56	63.7	1.06	5.68	5.52	3.68	61
D54	58.3	6.90	5.01	1.46	3.28	40
H64	60.4	2.86	1.35	3.49	0.929	65
H68	60.2	2.67	1.15	5.60	0.734	55

[a] ROH is water with reaction at -34 for runs D92,D90, and D89 In all other experiments, ROH is ethanol with reaction at -45

for the green sodium naphthalenide solution to bleach indicating a very slow reaction compared to results reported in other solvents of lower dielectric constant[3] Finally, the hydrogen gas (confirmed by its mass spectrum) was collected and the amount measured following procedures reported elsewhere[5]

The results given in Table 1 show that equation 1 is the major pathway for the reaction under our experimental conditions In a few experiments, g.c analysis showed the presence of the dihydronaphthalene in quantities much less than the stoichiometric amount estimated from equation 2, and the sum of the H_2 and dihydronaphthalene recovered was consistent with the initial sodium At the present time, we offer no explanations as to why the large variation was observed in the percent reaction via equation 1

References

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