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CHEMICAL SYNTHESSES WITH A QUENCHED FLOW  
REACTOR. HYDROXYTRIHYDROBORATE  
AND PEROXYNITRITE

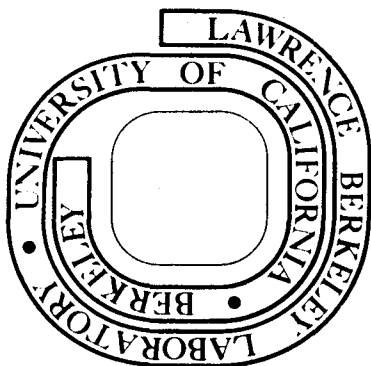
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## ABSTRACT

for Communication 2217-T253

Chemical Syntheses with a Quenched Flow  
Reactor. Hydroxytrihydroborate and Peroxynitrite.

The technique of mixing two streams of reactant solutions in a reaction tube with downstream injection of a solution containing a quenching reagent has been applied to the synthesis of species in aqueous solution. Up to 94% yields of  $\text{BH}_3\text{OH}^-$  were obtained by quenching  $\text{H}_2\text{OBH}_3$  (formed from  $\text{H}^+$  +  $\text{BH}_4^-$ ) with  $\text{OH}^-$ , and up to 82% yields of  $\text{ONOO}^-$  were obtained by quenching  $\text{HOONO}$  (formed from  $\text{H}^+$  and  $\text{H}_2\text{O}_2 + \text{NO}_2^-$ ) with  $\text{OH}^-$ .

Chemical Syntheses with a Quenched Flow  
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Sir:

The technique of mixing two streams of reactant solutions in a reaction tube with downstream injection of a solution containing a quenching reagent has been used for studying the kinetics of fast reactions,<sup>1</sup> but does not seem to have been applied to laboratory synthesis. The method is ideal for a synthesis involving the formation of an intermediate species which (1) must be prepared under conditions such that its half-life is in the range between a millisecond and several seconds and (2) can be stabilized by rapid reaction with a quenching reagent. We now report the successful use of this method for preparing solutions of two different compounds in high yield, sodium hydroxytrihydroborate and sodium peroxynitrite. Each synthesis involves the formation of an unstable intermediate species which is stabilized by deprotonation with hydroxide ion.

The apparatus consists of a Lucite rod bored to a depth of 10 cm with a 3-mm hole. Two 1.5-mm holes for the introduction of the reactants enter from the side of the rod, joining the 3-mm tube tangentially at its inner end. A third 1.5-mm hole, for the quenching solution, enters the tube at a point 5 cm from the two reactant holes. The holes are connected to glass tubes on the outside of the rod; these are connected through glass and Teflon needle valves to siphon tubes inserted into three separate bottles. The bottles can be simultaneously pressurized with nitrogen gas

at a regulated pressure from a cylinder. Before each run, the needle valves are adjusted so that the flow rates of the three solutions are equal. The reaction tube is mounted vertically, and the quenched product is collected in a beaker placed beneath the open end of the tube.

Wang and Jolly<sup>2</sup> have shown that, in methanol-water solution at  $-78^{\circ}$ , the borohydride ion reacts very rapidly with strong acid to form  $\text{H}_2\text{OBH}_3$ . This species hydrolyzes under these conditions with a half-life of about 300 sec, but it can be deprotonated to form the relatively stable  $\text{BH}_3\text{OH}^-$  ion, which has a half-life of several hours at room temperature. An estimated effective activation energy for the  $\text{H}_2\text{OBH}_3$  hydrolysis of 12 kcal/mole<sup>3</sup> corresponds to a half-life of about 20 msec at  $0^{\circ}$ . Thus, it seemed reasonable to attempt the synthesis of  $\text{BH}_3\text{OH}^-$  using the quenched flow reactor with aqueous solutions initially at  $0^{\circ}$  and with a reaction time (time between the initial mixing of  $\text{H}^+$  and  $\text{BH}_4^-$  and the quenching with  $\text{OH}^-$ ) of the order of 20 msec or less. Our experimental data are given in Table I. The change in the percentage yield of  $\text{BH}_3\text{OH}^-$  with change in reaction time was qualitatively as expected. Relatively high yields, essentially independent of reaction time, were obtained for reaction times of 10-21 msec; the yield dropped off for a reaction time of 26 msec. The decrease in the percentage yield with increasing concentration of the solutions may be due to the corresponding increase in the reaction temperature caused by the increased heat of reaction.

The reaction of nitrous acid with hydrogen peroxide in acidic solution yields peroxynitrous acid.



Table I

Data for  $\text{BH}_3\text{OH}^-$  Syntheses

Reaction time, msec	Reagent Concns., M			Product Temp., °C <sup>a</sup>	Yield of $\text{BH}_3\text{OH}^-$ , % <sup>b</sup>
	$\text{BH}_4^-$	$\text{H}^+$	$\text{OH}^-$		
26	0.3	0.45	0.6	6	75
21	0.3	0.45	0.6	6	87
16	0.3	0.45	0.6	6	94
10	0.3	0.45	0.6	6	86
10	1.0	2.5	3.0	16	65
10	3.0	4.5	6.0	37	51

<sup>a</sup>Temp. of  $\text{BH}_3\text{OH}^-$  soln. Reagent solutions cooled to 0°. <sup>b</sup>Determined from amount of  $\text{H}_2$  evolved upon complete hydrolysis.

This acid decomposes to nitric acid with a half-time of 7 sec at 0°, but the conjugate base, peroxyxynitrite ion, is relatively stable in alkaline solutions.<sup>5-8</sup> The literature procedure for the synthesis of peroxyxynitrite involves the mixing of an acidic peroxide solution with a nitrite solution, immediately followed by treatment with excess base. Yields of 45-50% have been reported.<sup>6</sup> We have carried out this synthesis with our quenched flow reactor, using equal flow rates of the following solutions at 0°: 0.6 M  $\text{KNO}_2$ , a solution 0.6 M in HCl and 0.7 M in  $\text{H}_2\text{O}_2$ , and 3 M NaOH. The product solution was analyzed spectrophotometrically.<sup>6</sup> The reaction times (msec) and corresponding percentage yields follow: 44, 44%; 88, 67%; 88, 68%; 230, 77%; 280, 72%; 450, 82%. The relatively low yield obtained for the shortest reaction time (44 msec) was probably a consequence of incomplete reaction of the nitrous acid with the hydrogen peroxide.

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- (3) This is admittedly an optimistically low estimate of the activation energy. At -78° the acid-independent hydrolysis of  $\text{H}_2\text{OBH}_3$  has a rate

comparable to that of the acid-dependent hydrolysis.<sup>2</sup> The former reaction would be expected to have an activation energy near 20 kcal/mole, thus making the hydrolysis too rapid for a quenched flow reactor operated near room temperature. We have no explanation for the discrepancy.

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