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TITLE

STUDY OF CHEMICAL REACTIONS UNDER THE INFLUENCE OF ULTRASOUND

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Study of Chemical Reactions under the Influence of Ultrasound

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At Los Alamos we are interested in sonochemistry because there is potential for accelerating reactions involving the synthesis of certain nitro compounds and for milder reaction conditions to reduce the possibility of decomposition. We have initiated the study of the nitration of 2,4-dihydro-3*H*-1,2,4-triazol-3-one with concentrated nitric acid under sonication. The preparation of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine, and oxidation of 3,6-diamino-1,2,4,5-tetrazine were also studied. Sonication reaction conditions and results of these reactions under ultrasound will be discussed in detail.

Keywords: sonochemistry; nitration; oxidation; reaction rate

INTRODUCTION

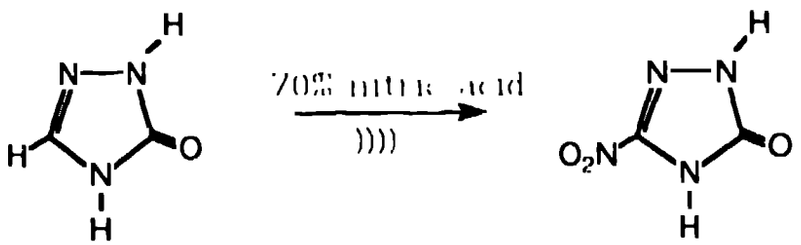
It is well-known that rate enhancement of chemical reactions accompanied with higher production yield in both homogeneous and heterogeneous reaction systems has been demonstrated under the influence of ultrasonic irradiation [1]. For example, the production yield of 2,2'-dinitrobiphenyl from 2-iodonitrobenzene via the Ullmann coupling reaction in the presence of copper powder was 80% under sonication; without ultrasound, the yield was less than 2% [2]. The hydrogenation rate of soybean oil was increased 100-fold by a combination of copper chromite catalysis and ultrasound [3]. At Los Alamos, we are interested in sonochemistry for the following reasons: 1) to accelerate reactions involving the synthesis of certain nitro compounds, 2) for milder reaction conditions -- reducing the possibility of decomposition, 3) for preparation of explosive molecules and intermediates that might not be possible by conventional methods, and 4) for preparation of novel compounds with unusual properties. In this paper, the chemical reactions studied under sonication will be described, and the findings of the ultrasonic effect on the reaction rates will also be reported.

EXPERIMENTS AND RESULTS

Sonicator W-385 (Heat Systems) equipped with a 0.5 inch probe, operating at 20 kHz with a variable power supply output was used for the study of ultrasonic effect on chemical reactions. Unless specified, the double amplitude is set at 60 μm. Reaction temperature was monitored by a thermocouple immersed in the reaction mixture. All reactions are laboratory scale.

Nitration of 2,4-dihydro-3*H*-1,2,4-triazol-3-one (TO)

5-Nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (NTO) is an explosive developed at Los Alamos. It is prepared by nitration of TO with nitric acid at elevated temperature [4], Reaction 1. In an attempt to prepare NTO at a lower nitration temperature, the nitration reaction was conducted ultrasonically. Before we began the nitration study, the ultrasonic effect on nitric acid was investigated by sonicating 14 ml of 70% nitric acid for 20 minutes at both 26 and 36°C, which were the same reaction temperatures used for the nitration study. Immediately after sonication, samples of sonicated acid were analyzed by ion chromatography (IC). No nitrous acid was detected from the chromatogram, indicating that nitric acid is stable to sonication. We then continued our nitration study by reacting TO with nitric acid. Thus, to a Suslick cell filled with 13 ml 70% nitric acid was added TO (2.38 g, 0.028 mol), and the mixture was sonicated for 50 minutes. Formation of NTO was identified by ^{13}C nmr spectroscopy. A total of 5 experiments has been carried out.



TO NTO

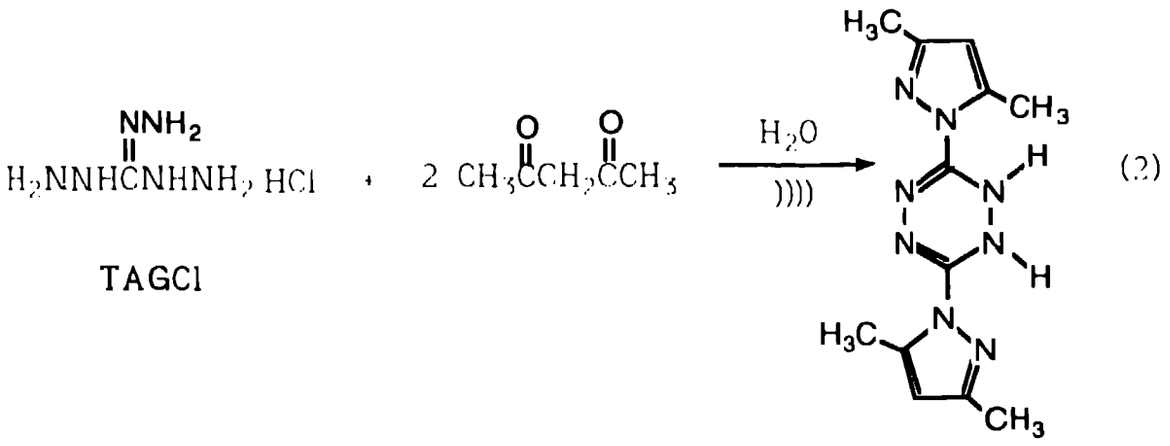
Experimental results from this study demonstrated that NTO can be prepared at the two reaction temperatures studied under the influence of ultrasonic irradiation. However, the titanium probe was eroded by the acid. This halted the experiment. We are investigating the use of a cup-horn apparatus to continue our study.

Preparation of 3,6-Bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (DHTZ)

This reaction was studied for a shorter reaction time than reported [5] for the preparation of DHTZ. 2,4 - Pentanedione (7.3 ml, 0.071 mol) was added to a mixture of water (36 ml) and triaminoguanidine (TAGCl) (5 g, 0.036 mol) in a 50 ml beaker, and the two-phase system was sonicated at ambient temperature (~25°C) for different reaction times, and at both 60- and 80-µm power setting, Reaction 2.

Without ultrasound, it required four hours to prepare DHTZ with 85% yield by stirring the starting materials in water at 70°C. However, when the same reaction was subjected to ultrasound, the reaction time was reduced significantly. The yield of DHTZ is directly proportional to the energy output and reaction time. Figure 1 illustrates the yield of DHTZ as a function of

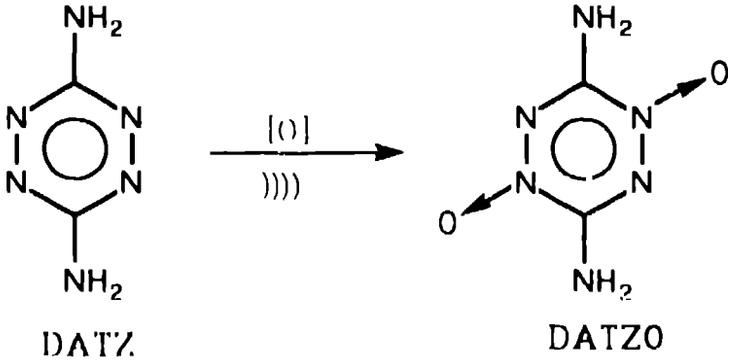
reaction time at the two power outputs. It can be seen that a production yield of 85% was obtained after 10 minutes of sonication at higher power output.



(2)

Preparation of 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (DATZO)

DATZO was prepared by oxidation of 3,6-diamino-1,2,4,5-tetrazine (DATZ) with OXONE® in water at 25°C [6], Reaction 3. Thus, DATZ (0.56 g, 0.005 mol) was added to a solution of OXONE® (6.15 g, 0.005 mol) in water (25 ml), and the mixture was sonicated at different reaction temperatures and times.



(3)

Without ultrasound, it required 20 hours to prepare crude DATZO with 85% yield. And, according to ^{1}H nmr analysis, more decomposition products were obtained when the reaction temperature was increased to 40°C or higher. However, higher yield of DATZO was realized when the same reaction was carried out at higher reaction temperature and under the influence of ultrasound. Figure 2 shows that a 96% DATZO yield was obtained at a reaction temperature around 47°C in one hour.

CONCLUSION

Several chemical reactions were studied under the influence of ultrasonic irradiation. They were studied for production yield improvement as well as reaction rate enhancement. Experimental results from this study demonstrate that, under the reaction condition described, ultrasonic irradiation does lead to the acceleration of certain organic chemical reactions in both homogeneous and heterogeneous systems.

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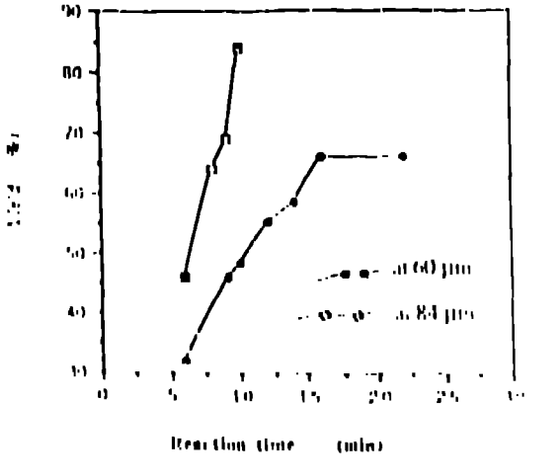

Figure 1. Yield of DHTZ vs reaction time under sonication

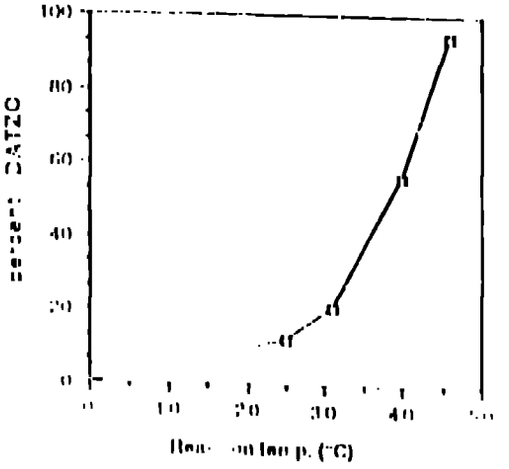

Figure 2. Yield of DATZO vs reaction temperature