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APPLICATION OF ULTRASOUND TO ORGANIC REACTIONS: ULTRASONIC CATALYSIS ON HYDROLYSIS OF CARBOXYLIC ACID ESTERS

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Summary: Irradiation with ultrasound was found to facilitate the two-phase basic hydrolysis of aromatic carboxylic acid esters.

Although ultrasound has been known for more than 50 years,[1,2,3] its application to chemical reactions has not been investigated thoroughly. The general mechanism of sonochemistry (the chemistry of sound and ultrasound) is not known, but it is generally agreed that the phenomenon of cavitation (formation and collapse of micro-bubbles) is responsible for its chemical effects. It has been calculated that the cavitation phenomenon causes the temperature at the center of the collapsing bubbles to rise to 10^4 to 10^6 degrees Kelvin and its pressure to increase to up to several thousand atmospheres.[4] It has been reported that cavitation is able to generate free radicals in aqueous solutions.[4] In addition to these primary effects of cavitation, the secondary effects include emulsification, macroscopic heating due to sound absorption, and resonance characteristics of the medium and vessel.

We wish to report the results of our investigation on the effects of irradiation with ultrasound on the two-phase basic hydrolysis reactions of aromatic carboxylic acid esters. Since reactants are in different phases, reaction rates are usually slow. Techniques such as micelle catalysis[6] and phase transfer catalysis[7] have recently been developed, but their assistance in the study of aromatic ester saponification may not be felt for some time.

Ester saponifications were conducted under a variety of conditions so that meaningful comparisons could be made. Reaction conditions included: 90 min. reflux, 10 min. application of ultrasound, 60 min. application of ultrasound, 10 min. immersion in a 100° C oil bath, and 10 min. immersion in a 120° C oil bath.

The 90 min. reflux reaction was chosen as the basis for comparison, since it represents a conventional method of two-phase ester saponification.

Ultrasound was applied by an ultrasonic probe (at a frequency of 20,000Hz) which was immersed into the reaction mixture for the alloted time interval. Macroscopic heating of the reaction mixture due to the absorption of ultrasound was studied. It was found that the heating curve of the 100° C oil bath approximates that due to the application of ultrasound. In this way, any effects of ultrasound which are accountable solely to heating may be estimated.

For all saponifications studied, 1.0 g of ester was treated with 10.0 ml of a 20% sodium hydroxide solution. Table I summarizes the results of the reactions. Yields reported were determined by weighing the dried, recovered acid. Acid identity was checked by melting point and mass spectral analysis.

The saponification of methyl benzoate (1) went completely during 90 min. reflux (97%) and during a 10 min. application of ultrasound (98%). Since the reaction was effectively complete after 10 min. of ultrasound, a 60 minute application of ultrasound was not tested. Saponification for 10 min. in 100° C and 120° C oil baths resulted in yields of 13% and 77% respectively. The higher yield present in the 120° C oil bath reaction relative to the 100° C oil bath reaction is attributed to six minutes boiling which resulted from the heating.

Attempts to saponify methyl 2,4,6-trimethylbenzoate (2) were uniformly unsuccessful. It appears likely that the intensity and/or frequency of the ultrasound were not sufficient to achieve the desired result. It is possible that no set of ultrasonic conditions would be able to saponify 2. Since 90 min. of reflux and 60 minutes of ultrasound were unable to induce saponification, the relatively mild oil bath conditions were not tested.

The most dramatic result was obtained with methyl 2,4-dimethylbenzoate(3). The saponification of 3 occured to the extent of 15% for both the 90 min. reflux and the 10 min. ultrasound reactions. Upon saponification for 60 minutes with ultrasound, however, the reaction yield jumped to 94%.

Methyl 3,5-dimethylbenzoate (4) was the only ester for which the yield of the 90 min. reflux saponification was greater than that obtained by a 10 min. application of ultrasound; however, the difference was rather small (71% as compared with 62%). The highest yield was obtained after 60 minutes of sonication (96%). As with the other esters studied, the yield from the 100° C oil bath reaction was rather small (10%).

Clearly, the principal effect of applying ultrasound to the reaction vessels was not due to macroscopic heating. We feel that most of the observed catalysis in these reactions is probably due to the secondary cavitation effect of emulsification.

In conclusion, the use of ultrasound was found to catalyze two-phase ester saponifications to such an extent that reactions requiring 90 minutes of reflux could be accomplished after approximately 10 minutes of sonication. It is believed that application of ultrasound may serve to catalyze other heterogeneous reactions in a simple and facile manner.

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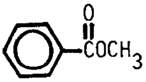
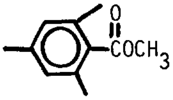
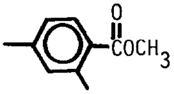
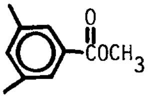
TABLE 1. SUMMARY OF SAPONIFICATION RESULTS

% Isolated Yield of Acid

Compound	Structure	90 min. Reflux	10 min. Ultra	60 min. Ultra	10 min 100° Oil	10 min 120° Oil
1		97	98	NT	13	77
2		0	0	0	NT	NT
3		15	15	94	4	NT
4		71	62	96	10	NT

NOTE: "NT" corresponds to "Not Tested".

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