[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Further Studies on a Molecular Rearrangement Induced by Ultrasonic Waves

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The rearrangement of an azide under the influence of ultrasonic waves was first studied by Porter and Young.[1] They subjected solutions of benzazide to the influence of ultrasonic vibrations using a magnetostriction oscillator functioning at a frequency of 16,000 cycles per second.

The purpose of the experimental work reported in this paper was to study the effect of changes in vibration frequency upon the rate of the rearrangement. A piezoelectric oscillator was used in place of the magnetostriction machine previously employed. The reaction vessel was a glass tube having a thin glass membrane bottom which permitted the passage of vibrations from the quartz crystal oscillator. The tube was one inch in diameter and nine inches long. It was surrounded by a large condenser jacket, and water at constant temperature was circulated through this jacket to keep the temperature of the solution constant.

The piezoelectric oscillator used in these experiments was similar to a machine built by Salisbury and Porter.[2]

The plate power input for the experiments varied from 100 to 250 watts. The vibrating crystal was mounted between a heavy brass bottom electrode and a thin silver top electrode, and the whole assembly was immersed in transformer oil. The heavy wires leading to the electrodes were equipped with glass shields to prevent corona discharge and sparking. When the machine was in operation, the reaction vessel was lowered into the oil until the glass membrane was close to the top electrode. The proper distance was determined by the appearance of cavitation phenomena in the solution.

Experimental

Preparation of the Chemicals.—The benzazide was prepared by the interaction of sodium azide and benzoyl chloride. Sodium azide (37 g.) was dissolved in 100 cc. of distilled water. In another flask, 70.0 g. of benzoyl chloride was dissolved in 125 cc. of acetone. Both solutions were cooled to 0° in an ice-bath, then mixed and shaken for thirty minutes, returning the mixture to the ice-bath occasionally to keep the temperature near 0°. The solution was then allowed to separate into two phases and the acetone-rich phase was withdrawn, the other being discarded. The solution was poured over cracked ice, whereupon the azide crystallized out in a fairly pure state. The product was filtered, washed with water, recrystallized once from acetone by addition of water and dried over calcium chloride in a desiccator; yield, 40 g., m. p. 32°.

Aniline was selected as the solvent for the benzazide because it absorbs much less gas from the atmosphere than does benzene. Ordinary commercial aniline was allowed to stand over calcium chloride for twenty-four hours, after which it was distilled from zinc dust and animal charcoal in an atmosphere of nitrogen. It was stored in an atmosphere of nitrogen for twenty-four to forty-eight hours before using.

For each of the experiments, a solution consisting of 5 g. of benzazide in 50 cc. of aniline was prepared. The aniline was subjected to the action of the oscillator for one hour before the azide was added, in order to drive out nitrogen in excess of the quantity which the aniline was able to retain while vibrating.

Five determinations of the rate of rearrangement were made. Three experiments were made with a frequency of 478 kilocycles per second, and two were carried out at 275 kilocycles per second. The rate of decomposition of the azide was determined by measuring the volume of nitrogen evolved from the solution while vibration of constant intensity was applied. As an indication of the rate of azide decomposition the following table is presented:

Time, minutes	N_2, cc.	Time, minutes	N_2, cc.
0	0.00	45	5.29
5	1.08	50	5.68
10	1.54	55	6.29
15	2.05	60	6.82
20	2.35	65	7.37
25	2.78	70	8.03
30	3.26	75	8.52
35	3.94	80	9.12
40	4.58		

This run was made at 32.4° with a power input of 200 watts and with a crystal oscillating at 478 kilocycles per second. Complying with the Editor's request for a brief report all other rate measurements are omitted.

A rate constant as determined from direct measurements could not be regarded as a measure of the effect produced by vibration alone, since some thermal rearrangement of the azide occurs. The thermal effect could be computed for each experiment, however, since the rates of rearrangement of benzazide at 25° and at 35°, under the influence of heat alone, were known. Porter and Young had found the rate constant at 25° to be 0.762×10^{-5}, and at 35° equal to 3.68×10^{-5},

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[1] Porter and Young, THIS JOURNAL, **60**, 1497 (1938).

[2] W. W. Salisbury and C. W. Porter, *Rev. Sci. Instr.*, **10**, 142 (1939).

time being expressed in minutes. From these two rates, the activation energy calculated from the equation

$$A = \frac{RT_2T_1}{(T_2 - T_1)} \ln \frac{k_2}{k_1}$$

was found to be equal to 29,400 cal./mole. Using this value of the activation energy and the known rate at one temperature, the rate of thermal rearrangement at the temperature used in each experiment was calculated, and, by subtracting this from the over-all rate, the rate of rearrangement due to the ultrasonic vibrations alone was obtained.

In order to determine the effects of different frequencies upon the reaction, it was necessary to know the rates at which energy was being supplied to the solutions or some quantities directly proportional to these rates. The necessary data were obtained from calorimetric measurements. After concluding an experiment on an azide solution, water was placed in the same reaction tube, and an air-jacket (instead of a water-jacket) was used. A measured volume of water (50 cc.) was transferred to the tube and vibration was applied. The rate of temperature rise of the water was measured. The rate of rise, in degrees per minute, was converted into calories per second, assuming that the specific heat of water is constant and equal to 1.00. The absorption of heat by the glass could be ignored, for it would be the same in heating the azide solution as in heating the water.

This procedure determined a rate of addition of energy which was proportional to, but not equal to, the rate of supply of energy to the azide solution. Equality cannot be assumed, for the coefficients of acoustic absorption of the azide solution and of water must be different. The actual value of the proportionality factor is unimportant since the same azide concentration, the same solution volume and the same volume of water was used in each experiment. The proportionality factor may be assumed to be constant.

No linear relationship exists between energy input and energy supplied in vibrational form, for different crystals possess different degrees of efficiency in converting electrical into acoustical power, and with a given crystal the efficiency of the oscillator varies with the input of power. This makes it impossible to use oscillator input as a quantitative measure of the energy being supplied to the solution, and therefore the calorimetric data must be relied upon.

The results of five runs show that, within the limits of experimental error, the rate of rearrangement induced by ultrasonic vibrations is directly proportional to the energy absorbed by the solution, and is independent of the frequency of the vibrations.

Summary

The rate of rearrangement of benzazide in aniline solution has been studied at frequencies of 16, 275 and 478 kilocycles per second and with power inputs ranging from 100 watts to 250 watts. The rate of rearrangement has been found to be directly proportional to the energy of the vibration and independent of the frequency.

BERKELEY, CALIFORNIA RECEIVED AUGUST 26, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Photolysis of Methyl Bromide[1]

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The photolysis of alkyl halides is a convenient source of hydrocarbon free radicals; the immediately ensuing secondary reactions yield data from which the properties and reactivities of those radicals can be deduced. Up to the present, such work has dealt almost entirely with the iodides. The products finally obtained have been accounted for, in general, on the basis of probable secondary reactions, either between the radicals themselves, or between the radicals and the molecules present. Since the absorption spectra of methyl iodide and methyl bromide are qualitatively similar, the latter band being somewhat broader and displaced toward shorter wave lengths,[3] it is to be expected that the primary

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(1) Paper presented before the Division of Physical and Inorganic Chemistry, St. Louis Meeting of the American Chemical Society, April, 1941.

(2) Abstract from a thesis presented in partial fulfillment of the requirements for the degree of doctor of philosophy at New York University, June, 1941.

(3) Herzberg and Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930).