

acid has given improved yields of *nor*- and *bis-nor*-desoxycholic acids. The yield of *etio*-desoxycholic acid also has been improved by the following steps: (1) ozonolysis of 3,12-diacetoxy-*ter-nor*-cholanyldiphenylethylene; (2) condensation of the resulting 3,12-diacetoxy-*etio*-cholanyl

methyl ketone with benzaldehyde; (3) ozonolysis of the condensation product; and (4) oxidation of the resulting glyoxal with periodic acid to give 3,12-diacetoxy-*etio*-cholanolic acid, followed by hydrolysis.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AND MILLS COLLEGE]

A Molecular Rearrangement Induced by Ultrasonic Waves

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Acid azides of the type $RCON_3$ are converted, through the Curtius reaction, into nitrogen and isocyanates.¹ Some other azides, including those derived from sulfonic acids, yield nitrogen, when heated, but do not, as a rule, undergo the rearrangement.²

Benzazide, $C_6H_5CON_3$, yields nitrogen and phenyl isocyanate at measurable rates when heated in the solid state or in any solvent and we selected this compound for treatment with ultrasonic vibrations. The rate of the thermal decomposition of the compound in the solid state has been measured by Vasilevskii and others.³

We present in this paper the rates of rearrangement of benzazide in benzene solution and in aniline solution at 25° with and without the application of vibrational energy.

The vibrator—a magnetostriction oscillator—is so constructed that the energy input may be varied between 100 and 1500 watts. The efficiency of the machine, however, is less than 5%. The vibrating unit is a nickel tube, 2.7 cm. in diameter, which is closed at the upper end. Tubes of various lengths are used for frequencies ranging from 10,000 to 50,000 cycles per second. The lower end of the nickel tube is surrounded by concentric coils of insulated wire. One coil is part of the oscillating circuit to which power is supplied, at the resonance frequency of the rod, by two self-exciting vacuum tubes. Adjustment to resonance is made by a variable condenser which, with the coil, controls the frequency of the oscillations. The vacuum tube plate voltage used in most of this work was 1500 v. and the plate current 300 m. a. The outside coil carries a direct current to produce a steady magnetic field which polarizes the rod. A current of 3.5 amp. from a 110-v. d. c. supply was used in this coil. A polarizing field is necessary to prevent the flux in the rod from reversing and causing the rod to vibrate feebly at double the fundamental frequency.

The benzene solution of benzazide was placed in a glass

cell covering the upper end of the nickel tube as shown in Fig. 1. The evolved nitrogen was measured in a slender buret. It had been determined by other experiments that the thermal decomposition of benzazide is not catalyzed by nickel.

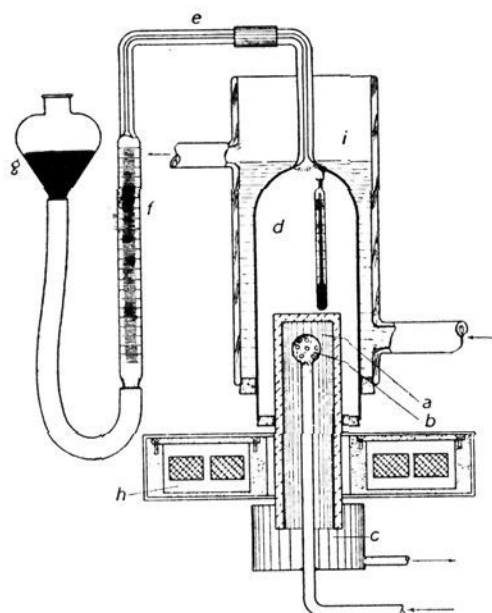


Fig. 1.—The parts shown are: a, nickel tube; b, perforated glass bulb from which a spray of water from the thermostat plays upon the inner surface of the tube; c, tank from which water is returned to the thermostat; d, glass cell containing the solution of benzazide; e, capillary tube; f, buret; g, leveling bulb; h, cross section of coils surrounding the nickel rod; i, water jacket surrounding the cell.

The vibrational energy imparted to the liquid surrounding the upper half of the nickel tube was estimated calorimetrically and also by measuring the amplitude and frequency of the vibrations. Several measurements were made and values ranging from 10 to 15 watts were obtained. The average corresponds to a vibrational energy of 12 watts. The amplitude is 0.00015 cm. in the 16-cm. tube and the vibration frequency in this tube is 16,000 cycles per sec. (The tube is a 0.5 wave length oscillator and the velocity of sound in nickel is 4800 m. per sec.)

(1) Curtius and Darapsky, *Ber.*, **35**, 3229 (1902).

(2) Alfred Bertho, *J. prakt. Chem.*, **120**, 89 (1928).

(3) Vasilevskii, Blotshtein and Kustrya, *Khim. Zhur., Ser. A*, **5**, 1652 (1935).

The amplitude of vibration in an 8-cm. tube, which we frequently used, has not been measured.

The temperature control was accomplished by pumping water from a large thermostat into the vibrating tube and into a chamber surrounding the cell. In this way the azide solution could be held within 0.3° of any desired temperature.

The rates of thermal decomposition of benzazide at 25 and 35° are shown in Table I.

TABLE I

THERMAL DECOMPOSITION OF BENZAZIDE

The nitrogen was measured at the temperature at which it was evolved, the buret and capillary delivery tube as well as the reaction flask being completely submerged in the water of the thermostat. A correction for the vapor pressure of benzene has been made in each case.

Time, hours	I Temp. 25°; azide 1.427 g.; vol. benzene 100 cc.		II Temp. 35°; azide 1.410 g.; vol. benzene 100 cc.	
	Vol. N ₂	% N ₂	Vol. N ₂	% N ₂
3	0.23	0.10	1.21	0.50
6	.52	.22	2.90	1.20
10	.94	.40	5.37	2.22
15	1.48	.63	7.50	3.10
21	2.17	.92	10.28	4.25
24	2.48	1.05	12.46	5.15
36	3.68	1.56

The velocity constant, k , calculated from the equation

$$k = \frac{1}{t} \log \frac{a}{(a-x)}$$

is equal to 0.00191 at 25° and 0.000898 at 35°. From these values and the equation

$$A = \frac{RT_2T_1}{T_2 - T_1} \log_e \frac{k_2}{k_1}$$

we find the activation energy equal to 27,700 calories per mole.

Nitrogen and oxygen are very soluble in benzene and when ordinary dry benzene, saturated with air, is used as a solvent, the first gas which escapes under the influence of ultrasonic waves is largely dissolved air. On the other hand, if the benzene is completely degassed, by prolonged boiling, then used as a solvent for the azide, the first nitrogen produced from the azide fails to escape. We found the only satisfactory method was to subject the benzene to treatment with the oscillator until no more gas could be driven out, then add the azide and continue the treatment. It requires about one hour of steady vibration to bring 100 cc. of benzene to the equilibrium state with respect to dissolved air.

In later experiments we used aniline as a solvent and excluded air. Aniline dissolves less than one-third as much nitrogen as does benzene. The aniline was refluxed to remove all dissolved air, then distilled in an atmosphere of nitrogen. It was stored under one atmosphere of nitrogen until needed and transferred to the reaction cell without exposure to air. The oscillator was then operated until no more gas could be driven out. The azide was then added and the process continued. The rates of degassing of 95-cc. samples of benzene and aniline are given in Tables II

and III and shown graphically in Figs. 2 and 3 (Curve II, Fig. 2 and Curve IV, Fig. 3).

TABLE II

PARTIAL REMOVAL OF DISSOLVED AIR FROM BENZENE BY ULTRASONIC WAVES

Vol. benzene 95 cc.; temp. 25°; cycles 16,000

Time, min.	Vol. N ₂ , cc.	Time, min.	Vol. N ₂ , cc.
0	..	55	0.96
5	0.40	60	.97
10	.60	65	.98
15	.70	70	.99
20	.78	75	1.00
25	.83	80	1.01
30	.87	85	1.01
35	.90	90	1.02
40	.92	95	1.02
45	.94	100	1.02
50	.95	105	1.03
		110	1.03

TABLE III

PARTIAL REMOVAL OF DISSOLVED NITROGEN FROM ANILINE BY ULTRASONIC WAVES

Vol. aniline 95 cc.; temp. 25°; cycles 16,000.

Time, min.	Vol. N ₂ , cc.	Time, min.	Vol. N ₂ , cc.
0	..	40	0.13
5	0.03	45	.13
10	.05	50	.14
15	.07	55	.14
20	.09	60	.15
25	.10	65	.15
30	.11	70	.15
35	.12	75	.15

TABLE IV

EVOLUTION OF NITROGEN FROM A BENZENE SOLUTION OF BENZAZIDE. BENZENE SATURATED WITH AIR

Vol. benzene 95 cc.; temp. 25°; wt. azide 1 g.; cycles 16,000.

Time, min.	Vol. N ₂ , cc.	Time, min.	Vol. N ₂ , cc.
0	..	35	1.05
5	0.43	40	1.08
10	.64	45	1.13
15	.76	50	1.20
20	.86	55	1.22
25	.93	60	1.25
30	1.00	65	1.30

TABLE V

EVOLUTION OF NITROGEN FROM A BENZENE SOLUTION OF BENZAZIDE. BENZENE PREVIOUSLY DEGASSED TO EQUILIBRIUM STATE

Vol. benzene 95 cc.; temp. 25°; wt. azide 3 g.; cycles 16,000.

Time, min.	Vol. N ₂ , cc.	Time, min.	Vol. N ₂ , cc.
0	..	35	0.44
5	0.07	40	.50
10	.18	45	.55
15	.25	50	.63
20	.30	55	.68
25	.35	60	.75
30	.40	65	.80

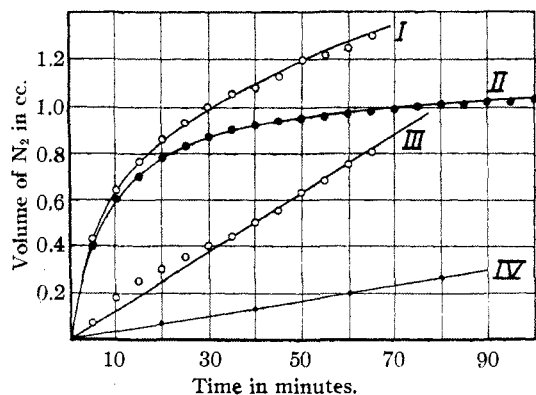


Fig. 2.—I, evolution of N₂ from 1 g. of benzazide in 95 cc. of benzene saturated with air; II, evolution of N₂ from 95 cc. of benzene alone; III, evolution of N₂ from 3 g. of benzazide in benzene previously brought to equilibrium state with respect to dissolved air; IV, rate of thermal decomposition of 3 g. of benzazide in benzene at 25°.

TABLE VI

EVOLUTION OF NITROGEN FROM BENZAZIDE IN ANILINE PREVIOUSLY DEGASSED TO EQUILIBRIUM CONDITION
Vol. aniline 95 cc.; temp. 25°; wt. azide 8 g.; cycles 16,000.

Time, min.	Vol. N ₂ , cc.	Time, min.	Vol. N ₂ , cc.
0	..	25	1.50
5	0.25	30	1.75
10	.55	35	2.05
15	.85	40	2.30
20	1.20	45	2.60

TABLE VII

EVOLUTION OF NITROGEN FROM BENZAZIDE IN ANILINE PREVIOUSLY DEGASSED TO EQUILIBRIUM STATE
Vol. aniline 95 cc.; temp. 25°; wt. azide 3 g.; cycles 16,000.

Time, min.	Vol. N ₂ , cc.	Time, min.	Vol. N ₂ , cc.
0	..	35	0.63
10	0.17	40	.72
15	.25	45	.80
20	.35	50	.87
25	.44	55	.95
30	.53	60	1.05

An attempt has been made to answer the question as to whether the molecules are activated by vibrational energy or whether local heating is responsible for the decomposition of the azide. The temperature rise due to compression of the liquid by the sound wave is negligible, only a few hundredths of a degree. This can be estimated from the equation

$$\frac{\Delta T}{T} + (\gamma - 1) \frac{\Delta V}{V} = 0 \quad (1)$$

which holds approximately for liquids when extremely small volume changes are involved. We measured the amplitude, a , of the vibration in

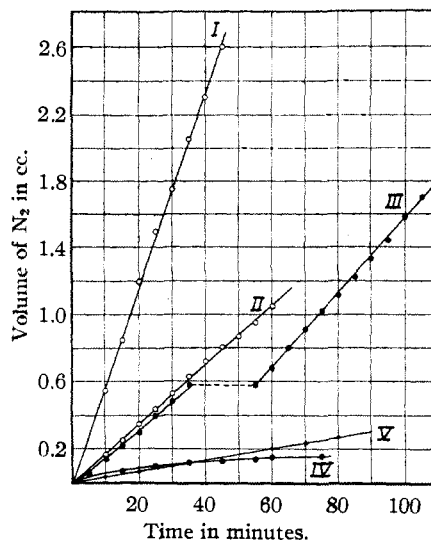


Fig. 3.—I, evolution of N₂ from 8 g. of benzazide in aniline; II, evolution of N₂ from 3 g. of benzazide in aniline; III, evolution of N₂ from 3 g. of benzazide in aniline. Oscillator not in operation between 35 and 55 min. intervals; IV, evolution of N₂ from aniline alone which had been freed from air, then saturated with nitrogen; V, rate of thermal decomposition of 3 g. of benzazide in aniline.

TABLE VIII

EVOLUTION OF NITROGEN FROM BENZAZIDE IN ANILINE PREVIOUSLY DEGASSED TO EQUILIBRIUM STATE

Vol. aniline 95 cc.; temp. 25°; wt. azide 3 g.; cycles 16,000. Power off at 35 min. Turned on again at 55 min.

Time, min.	Vol. N ₂ , cc.	Time, min.	Vol. N ₂ , cc.
0	..	55	0.58
5	0.06	60	.68
10	.14	65	.80
15	.22	70	.91
20	.30	75	1.02
25	.40	80	1.11
30	.48	85	1.22
35	.58	90	1.33
40	.58	95	1.44
45	.58	100	1.58
50	.58	105	1.70

the 16-cm. tube and found it to be 0.00015 cm. (one-half of the total excursion of the end of the rod).⁴ The velocity of sound in benzene was

(4) The end of the vibrating rod (which is electrically at ground potential) was used as one plate of a small condenser. The other plate (which was insulated and polarized with a high-voltage direct current in such a way that the quantity of electricity was substantially constant) was mounted on a screw micrometer head. The insulated condenser plate was brought into contact with the rod while it was at rest and then backed off a known distance. The vibrator was then started and an alternating voltage was induced in the insulated condenser plate due to variations of capacity according to the formula $Q = cv$ where Q is a constant quantity of electricity, c a varying capacity and v the voltage. The alternating component of

taken as 1.2×10^5 cm./sec. The frequency was 16,000 per sec. and the wave length, λ , in the solution was, therefore, 7.5 cm. From the equation

$$\Delta V/V = 2\pi a/\lambda \quad (2)$$

we have $\Delta V/V = 12.56 \times 10^{-5}$. For benzene γ or (c_p/c_v) is approximately 1.4 and the value of $\Delta T/T$ in equation (1) becomes 5.03×10^{-5} . At 25° (298 A.) the value of ΔT is less than 0.02° . If the use of equation (1) involves a fifty-fold error, the temperature effect due to compression of the liquid is still negligible.

The collapse of cavitation bubbles, on the other hand, is said to be a source of very great local temperature and pressure effects.⁵

A phenomenon often called cavitation constituted our most reliable method of tuning the oscillating circuit to the resonance frequency of the nickel tube. This was the appearance of many small bubbles which sometimes grew in size and ultimately escaped by rising to the surface of the liquid, but which usually grew and diminished in size alternately for a few seconds, then disappeared. These are bubbles of benzene vapor formed in expanding regions around nuclei of nitrogen molecules. They disappear in compression areas due to condensation of the vapor and increased solubility of the nitrogen or they grow and escape. The opalescence or turbulence caused by vast numbers of minute cavities, formed too quickly to be saturated with vapor of the medium and collapsing within the time interval of a half cycle, appeared in only one of our experiments. The rate measured in this run was much faster than in any other, but since we failed to duplicate the measurements they are not reported in this paper. With the 8-cm. tube the oscillator is operating, apparently, at the threshold of true cavitation conditions. This conclusion is in harmony with Boyle's calculations of amplitudes and frequencies required to give rise to cavitation phenomena.⁶

Equations relating to the adiabatic compression of a gas, if applied to the sudden collapse of a bubble, indicate the possibility of enormous temperature changes; but bubbles of vapor

this varying voltage was measured by a vacuum tube voltmeter. The measured voltage has the same ratio to the polarizing voltage as the amplitude (half excursion) of the rod has to the total separation of the rod and condenser plate.

(5) Bondy and Söllner, *Trans. Faraday Soc.*, **31**, 835 (1935); Lord Rayleigh, *Phil. Mag.*, [6] **34**, 94 (1917).

(6) Boyle, *Trans. Roy. Soc. Canada*, [3] **16**, 157 (1922).

gradually diminishing in size and surviving thousands of compression waves cannot give rise to abnormal local temperatures.

From a consideration of the amplitude and frequency of the oscillator, the velocity of propagation of the sound wave and the density of the liquid, we find that the peak pressure in benzene cannot exceed 2.8 atmospheres. The pressure variation, p , due to the wave, is given by the equation

$$p = 2\pi f a c \rho_0$$

in which c is the velocity of the wave, ρ_0 the density of the liquid, a the amplitude and f the frequency. From this equation we obtain a value of p equal to 1.48×10^6 dynes per sq. cm. or about 1.4 atmospheres. The pressure range is twice the pressure variation or 2.8 atmospheres. The vapor pressure of benzene reaches 2.8 atmospheres at 117° and this is the highest local temperature theoretically attainable in a saturated bubble of benzene vapor. This would be a temperature high enough to account for the measured rates, but since the bubbles persist through comparatively long time intervals, and disappear gradually, this maximum temperature is not approached.

Freundlich and Söllner found that the liquefaction of gels by ultrasonic waves is dependent upon cavitation.⁷ The application of an external pressure sufficient to stop the appearance of cavitation bubbles or reduction of the external pressure to the point where the bubbles escaped from the liquid instead of condensing, destroyed the sound wave effects.

The frequencies employed in our experiments are so far below the natural resonance frequencies of the molecule that the direct absorption of vibrational energy by the azide seems impossible. On the other hand, there is no obvious source of sufficient heat to produce the observed results. We submit the data without an adequate explanation.

Summary

The rates of rearrangement of benzazide in benzene and in aniline under the influence of ultrasonic waves have been compared with the rate of thermal decomposition at the same temperature. The rate of rearrangement is greatly accelerated by the application of vibrational energy.

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(7) Freundlich and Söllner, *Trans. Faraday Soc.*, **32**, 966 (1936).