

than in the absence of a field. However, no attempt to estimate the theoretical relative magnitude of these dielectric constants can now be made.

### Summary

1. Conductances of lead chloride have been measured in ethylene glycol-water mixtures which contain 0, 20, 40, 60, 80 and 100% glycol. The precision was 0.1%. The limiting conductances and the slopes were determined to an estimated precision of 0.2%.

2. Activity coefficients of lead chloride in these solvents have been compared with the Debye-Hückel limiting law by comparing the theoretical slopes of the limiting equation to the experimental slopes and the measured conductances have been compared with the Onsager

equation by comparing the theoretical slopes with the experimental slopes.

3. The discrepancies between theory and experiment have been attributed to a difference between the macroscopic and microscopic dielectric constants of the solutions, and the effective microscopic dielectric constants have been calculated from the experimental slopes of the curves in the cases of the Debye-Hückel and Onsager equations.

4. The known structural properties of these solvents have been used to show that such differences between macroscopic dielectric constants and microscopic dielectric constants in the presence and the absence of a field are qualitatively consistent with these structural properties.

COLUMBUS, OHIO

RECEIVED AUGUST 16, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

## Solvent Effect in the Curtius Rearrangement of Benzazide

BY MELVIN S. NEWMAN, SAMUEL HUNT LEE, JR.,<sup>1</sup> AND A. B. GARRETT

A study of the effect of the solvent on the rate of decomposition of benzazide is presented in this paper. This study was undertaken in an attempt to correlate the solvent effect on the kinetics of the reaction with some property of the solvents involved and also to seek for any further evidence as to the mechanism of the reaction. During this investigation we also observed unexpected reactions with nitromethane, acetic acid, butylamine, morpholine and piperidine.

In this rearrangement<sup>1a</sup> the R group shifts



from carbon to nitrogen in an irreversible intramolecular reaction exhibiting first order kinetics. The known experimental facts<sup>2</sup> indicate that the R group never leaves the influence of the molecule. The postulate<sup>3</sup> that on migration the R group carries with it the electrons which bind it to the carbon is in harmony with these facts and with the activated complex theory.<sup>4</sup>

### Experimental

**Materials Benzazide.**—One preparation<sup>5</sup> (70% of theoretical) was made from nitrous acid and benzhydrazide.<sup>6</sup>

(1) Du Pont Fellow, 1944. Material herein presented contained in the Ph.D. thesis of Samuel Hunt Lee, Ohio State University, August 1944. Present address: Department of Chemistry, University of Texas, Austin, Texas.

(1a) Curtius, *Ber.*, **27**, 778 (1894); *J. prakt. Chem.*, [2] **52**, 210 (1895).

(2) Wallis in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, Chapter 12.

(3) Whitmore, *THIS JOURNAL*, **54**, 3274 (1932); Hauser, *ibid.*, **62**, 933 (1940).

(4) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 86.

(5) Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Co., New York, N. Y., 1937, p. 153.

(6) Curtius and Struve, *J. prakt. Chem.*, [2] **50**, 295 (1894).

The white needles of the lachrymatory azide, after two recrystallizations each from acetone and petroleum ether (30-60°), melted at 27.0-27.5°.

Another preparation (50% of theoretical) was made from benzoyl chloride and sodium azide<sup>7b</sup> and recrystallized from acetone and petroleum ether using a Dry Ice-acetone bath and inverted filtration (suction through a sintered glass funnel) as was done before. A cooling curve for this product, also white needles, showed the freezing point to be 27.2° and attested to the purity of the sample. A melting curve on the same sample indicated a melting point of 27.2°. Plates from acetone melting at 32° have been reported,<sup>1,7</sup> but a m. p. of 26.0-28.0° has also been found.<sup>8</sup> In the present work plates were obtained only in the presence of water and melted at 26.5-27.4°, a mixed m. p. with the needles being 27.0-27.5°.

**Anilinium Chloride.**—Concentrated hydrochloric acid was added to purified aniline and the salt, precipitated by the addition of ether and recrystallized twice from hot water, melted at 196.4-197.4°.

**2,4-Dinitrophenylpyridinium Chloride.**—This was prepared from 1-chloro-2,4-dinitrobenzene and pyridine<sup>9</sup> and recrystallized three times from boiling ethanol to give needles with a slight cream color. No m. p. was taken because of the wide melting range and decomposition reported.<sup>10</sup>

**Solvents.**—In general, the solvent, in as pure a grade as could be obtained readily, was thoroughly dried and fractionated in a glass-helices-packed column at reflux ratios of 10:1 to 20:1. The middle, constant-boiling fraction was saturated with nitrogen, purified by passing through Fieser solution,<sup>11</sup> anhydrous calcium chloride, and phosphoric oxide, and the purified solvent was stored under this nitrogen in bottles paraffined to prevent the introduction of moisture. Solvents of a water white color were obtained in all cases.

**Apparatus.**—The reactions were run in a large, Thyra-ton-controlled<sup>12</sup> oil thermostat which gave temperature

(7) (a) Curtius and Hofmann, *ibid.*, [2] **53**, 518 (1896); (b) Barrett and Porter, *THIS JOURNAL*, **63**, 3434 (1941).

(8) Vasilevski, Bloshtein and Kustrya, *J. Gen. Chem.*, U. S. S. R., **5**, 1652 (1935).

(9) Vongerichten, *Ber.*, **32**, 2571 (1899).

(10) Zincke, Heuser and Moeller, *Ann.*, **333**, 296 (1904).

(11) Fieser, *THIS JOURNAL*, **46**, 2639 (1924).

(12) Garrett, *Ind. Eng. Chem., Anal. Ed.*, **10**, 324 (1938).

regulation to  $\pm 0.05^\circ$ . Rapid agitation of the reaction mixture was provided. The reaction system consisted of a reaction flask made from a 125-ml. Pyrex distilling flask, connected to a condenser by means of a ground glass joint, and a 100-ml. water-jacketed gas buret with a three-way stopcock and with mercury as the leveling fluid. The condenser and buret were joined by Koroseal tubing; all Koroseal-to-glass connections were sealed with glyptal.

A cathetometer was used to adjust and read the mercury levels.

**Procedure.**—The reaction flask was placed in the shaker as described and flushed with pure, dry nitrogen. After pipetting 25 ml. of solvent into it, the condenser was joined and, with the three-way stopcock open to the atmosphere, the flask shaken for at least half an hour to assure complete thermal equilibrium before introduction of the azide. The benzazide samples were weighed to  $\pm 0.1$  mg. in a capsule which was used to insert the azide into the reaction vessel. The rate data were taken at frequent intervals covering the time of about 90% decomposition. All runs were allowed to proceed to completion and duplicates were made for all but a few cases, the excellent agreement of the duplicate ones establishing the reliability of the single runs.

### Data and Discussion

A plot of  $\log (V_\infty - V)$  vs. time from the first order kinetics equation

$$\log (V_\infty - V) = \log V_\infty - 2.303kt$$

gives a straight line, from the slope of which the rate constant can be evaluated.

Data for a typical run are given in Table I and are plotted in Fig. 1 which also includes data for the duplicate run.

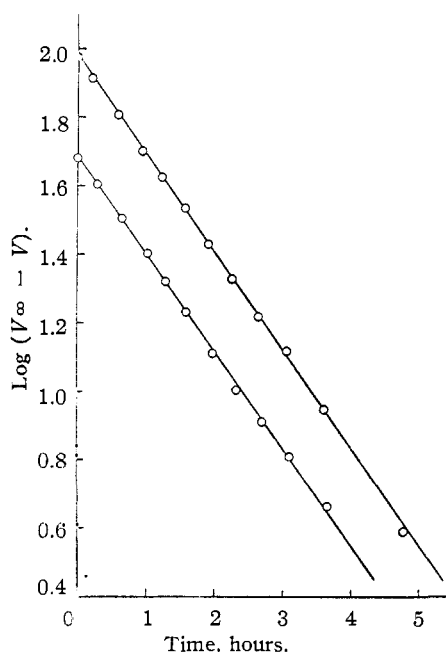


Fig. 1.

The phenomenon of supersaturation was avoided by agitating the reaction mixture.

The use of glass wool and glass beads indicated the absence of any surface effect.

The rate constant data for all solvents are tabulated in Table II together with values of the

TABLE I

#### TYPICAL RUN

Run No. 65: 25 ml. of dioxane at  $75^\circ$ , 0.6250 g. of benzazide.

Time, hours	Vol. at S. T. P., ml.	$\log (V_\infty - V)$
0	0	1.979
0.20	12.62	1.917
.57	30.72	1.809
.92	44.59	1.704
1.22	52.82	1.627
1.55	60.66	1.538
1.90	68.20	1.431
2.25	73.86	1.329
2.63	78.59	1.220
3.05	82.02	1.120
3.60	86.29	0.950
4.77	91.30	.491
5.85	93.59	.207

Rate constant for no. 65 (from slope of line in graph) = 0.660/hr. Rate constant for no. 66 (duplicate run) = 0.660/hr.  $V_\infty = 95.20$  ml. (99.9% theoretical volume).

energy of activation and entropy of activation. Consideration of Table II shows that there is a variation in the rate constants with respect to solvent decreasing from fifteen-fold at  $55^\circ$  to about eight-fold at  $75^\circ$ . For a particular solvent, the velocity constant increases three or four hundred per cent. for a ten degree rise in temperature. It is significant to note that benzazide alone has neither the largest nor the smallest rate constant, but that ten solvents have faster rates and only three slower ones. Probably the rate in *n*-heptane is more nearly the "true," or theoretical gas-phase, rate of decomposition than the rate for the azide by itself, since *n*-heptane is so inert a-solvent that it is difficult to understand how it could inhibit the rate by solvation or other causes.

There is no simple, direct correlation of rates with physical properties such as dielectric constant, dipole moment, boiling points, or viscosity although the dielectric constants and dipole moments in general seem to be larger for the faster rates.

The effectiveness series of solvents determined by Magat<sup>13</sup> parallels in general the order given in Table II.

The activation energies in Table II were obtained from the Arrhenius equation. The method of least squares<sup>14</sup> was employed to calculate the slope of the best straight line that could be drawn through the data for a plot of the logarithms of the rate constants for a particular solvent against the reciprocals of the absolute temperatures. The activation energies were computed from these calculated slopes.

The entropy of activation  $\Delta S^\ddagger$  was calculated from equation (2) where  $k_B$  is Boltzmann's constant and  $h$  is Planck's constant. This is derived

(13) Magat, *Z. physik. Chem.*, **A162**, 432 (1932).

(14) Bartlett, "The Method of Least Squares," Harvard Cooperative Society, Cambridge, Mass., 1915, pp. 62-78.

from the specific rate equation<sup>15</sup> in combination with the Arrhenius equation.

$$\Delta S^\ddagger = 2.303 R \left( \log A - 1 - \log \frac{k_b T}{h} \right) \quad (2)$$

The results of Porter and co-workers,<sup>7b,16</sup> corrected<sup>17</sup> for several typographical errors, are also presented in Table II and do not agree with the other data. No reason can be given here for this difference.

From the data of Vasilevski,<sup>8</sup> rate constants for benzazide alone at 20 and 35° were calculated and, including these data, the activation energy was found, by the method of least squares,<sup>14</sup> to be 31,000 calories per mole.

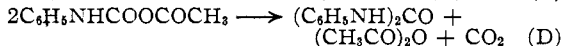
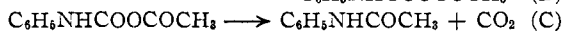
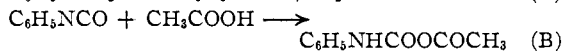
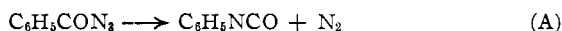
It is seen from Table II that  $E$  and  $\Delta S^\ddagger$  generally tend to increase and decrease together and, approximately, that when  $E$  and  $\Delta S^\ddagger$  are small,  $k$  is large and *vice versa*. A similar general relationship between  $E$  and  $\Delta S^\ddagger$  and  $k$  is pointed out by Moelwyn-Hughes.<sup>18</sup> Also noting this parallelism, Ogg and Rice<sup>19</sup> attempt an explanation in terms of solvation effects. On applying their explanation to the Curtius rearrangement, *i. e.*, benzazide decomposition, it seems that the activated complex must be solvated.

The relatively large entropy change is to be noted but the significance of this large change seems to remain obscure. Even with the facts known to date about this reaction there seems yet to be insufficient data to use it as a basis for a choice of mechanism of the reaction. Future study of this rearrangement should take this into consideration.

**Anomalous Solvent Effects.**—As previously mentioned, unexpected results were obtained in several solvents.

(1) In **acetic acid**, the decomposition of benzazide yielded about 165% of the theoretical amount of gas. However, when plots of  $\log(V_\infty - V)$  against time were made, in which  $V_\infty$  was the total (165% of theoretical gas) and  $V$  the volume at time  $t$  straight lines at all temperatures were obtained. This indicates that the reaction responsible for the excess gas takes place rapidly in comparison with the evolution of nitrogen from benzazide so that unimolecular kinetics is still observed.

The gas was undoubtedly produced by some combination of the following reactions<sup>20</sup>



(15) Glasstone, Laidler and Eyring, p. 199.

(16) Porter and Young, *THIS JOURNAL*, **60**, 1497 (1938).

(17) Barrett, private communication.

(18) Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford University Press, London, 1933, Chapter VI. Actually these authors considered the  $A$  factor but  $\Delta S^\ddagger$  is calculated from  $A$  by Equation (2).

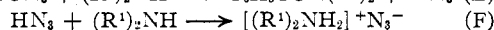
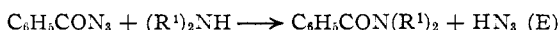
(19) Ogg and Rice, *J. Chem. Phys.*, **5**, 140 (1937).

(20) Dieckmann and Breest, *Ber.*, **39**, 3053 (1906).

If reaction C were entirely responsible for the excess gas, the excess would have been 100%; if reaction D, the excess would have been 50%. To check on these possibilities, 0.50 ml. of phenyl isocyanate was dissolved in acetic acid. At 55° the evolution of gas was complete in ten hours, whereas in the azide decomposition about fifty hours were required for completion of gas evolution. In addition gas analyses<sup>21</sup> showed the gas to be mainly carbon dioxide.

(2) In **nitromethane** there was obtained 25% excess gas. No explanation is offered for this unexpected result. A plot of  $(V_\infty - V)$  against time gave a hyperbola. A rate constant was calculated for these data from the slope of a line drawn tangent to the hyperbola at zero time with the assumption that the tangent represented the value of  $\log(V_\infty - V)$  if no secondary reaction had occurred.

(3) In **morpholine, piperidine and *n*-butylamine** no gas was evolved. This result must be caused by the high basicity of these amines which allows the following reaction to compete successfully with azide decomposition



Normal azide decomposition to produce nitrogen takes place in aniline because of its low basicity. However, reaction E for aniline is probably subject to catalysis by anilinium ions because when varying amounts of anilinium chloride were added to solutions of benzazide in

TABLE II  
RATE CONSTANTS AND ENERGIES AND ENTROPIES OF ACTIVATION

Solvent	Rate constants, per hr.			$E$ , cal./mole	$S^\ddagger$ at 65° E. U.
	At 55°	At 65°	At 75°		
Aniline	0.1921	0.579	1.782	25,400	10.7
Acetic acid <sup>a</sup>	.1347	.497	1.299	25,400	10.2
Acetonitrile	.1156	.401	1.293	27,300	15.6
<i>n</i> -Propanol	.0836	.328	1.188	30,100	23.5
Nitromethane <sup>a</sup>	...	.362	1.145	26,900	14.1
Piperidine	0.0781	.2220	0.765	26,300	11.5
Butanone	.0652	.2227	.707	27,000	13.5
Dioxane	.0556	.2032	.660	28,000	16.2
Ethyl acetate	.0533	.1794	.625	27,900	15.9
Benzene	.0457	.1551	.469	26,400	10.9
Azide alone	.0374	...	.481	29,000	18.4
Chlorobenzene	.0364	0.1452	.457	28,900	18.2
Triethylamine	.0267	.0847	.324	28,300	15.6
<i>n</i> -Heptane	.01324	.0549	.2132	31,600	24.2

<sup>a</sup> See discussion of Anomalous Solvent Effects for the assumptions used in calculating these values.

Data of Porter and Young:

Solvent	Rate constants per hr.		$E$ , cal./mole
	At 25°	At 35°	
Aniline	0.000439	0.002065	29,400
Benzene	.000436	.002206	28,300

(21) We would like to acknowledge the assistance of Prof. D. J. Demorest of the Department of Metallurgy, Ohio State University, for these analyses.

aniline, less than the theoretical amount of nitrogen was evolved on heating.

Furthermore, when slightly more than one equivalent of morpholine was added to a solution of benzazide in aniline, no gas at all was evolved on heating. If the added amount of morpholine was insufficient to react with benzazide according to equations E and F, then some nitrogen was evolved.

**Salt Effect.**—Investigation of the salt effect in this reaction yielded the data appearing in Table III.

The slight changes in rate with increasing salt concentration are within the limits of accuracy of the rate constant determinations.

TABLE III  
SALT EFFECT AT 65°

Run no.	Salt	Solvent	Molarity of Salt Azide		Rate per hr.
55	2,4-Dinitro-phenyl-	<i>n</i> -Propanol	0.0226	0.1202	0.330
56	Pyridinium chloride	<i>n</i> -Propanol	.0123	.1359	.323

The average rate in the *n*-propanol salt solutions, 0.3265/hour, agrees well with the mean rate in pure *n*-propanol, 0.328/hour. The lack of a salt effect is in accord with the theoretical conclusion of Wallis<sup>2</sup> about the mechanism of the reaction.

## Summary

1. The rate of decomposition of benzazide to phenyl isocyanate and nitrogen alone and in thirteen solvents has been measured at 55, 65 and 75°.

2. No simple correlation between rate constants and dielectric constant, dipole moment, viscosity or boiling point of the solvents is evident.

3. Energies and entropies of activation for the decomposition of benzazide alone and in these solvents have been calculated. Since large energies and entropies of activation are associated with small rate constants in general, solution of the activated complex is indicated.

4. No surface or salt effect is evident.

5. The decomposition of benzazide in primary and secondary aliphatic amines does not occur since reaction to form substituted benzamides is more rapid.

6. In acetic acid a secondary reaction leading to the formation of carbon dioxide occurs. The kinetics remain unimolecular. In nitromethane, another unidentified gas is obtained and the kinetics are complex.

7. Pure benzazide freezes and melts at 27.2° as determined by time-temperature cooling and heating curves. The present literature value is 32°.

8. The significance of the relatively large entropy change remains obscure.

COLUMBUS, OHIO

RECEIVED JUNE 17, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE GEORGIA SCHOOL OF TECHNOLOGY]

## The Tolymercaptopropanones and their Condensation with Isatins

BY O. NEWELL AND PAUL K. CALAWAY

In a previous paper<sup>1</sup> we have reported the utilization of 1-phenylmercapto-2-propanone in the preparation of substituted cinchoninic acids by the method of Pfitzinger.<sup>2</sup> The availability of the thiocresols suggested the preparation of the 1-tolymercapto-2-propanones and their ultimate condensation with isatin and 5-methylisatin, respectively, to produce six examples of a new type of substituted cinchoninic acid.

In our initial synthesis of 1-(*p*-tolymercapto)-2-propanone we followed the method used in earlier work<sup>1</sup> for the preparation of 1-phenylmercapto-2-propanone. The sodium salt of *p*-thiocresol was formed in boiling benzene, and chloroacetone was dropped into the mixture producing 1-(*p*-tolymercapto)-2-propanone. The latter was purified by distillation under diminished pressure. The yield obtained (55%) was not too good, and the reaction required several hours. Some discoloration of the sodium salt was noticed before

the completion of the reaction. Upon repetition of the synthesis, substituting toluene for benzene, and elevating the temperature of reaction to 100°, discoloration of the sodium salt was avoided, the reaction time was appreciably shortened, and the yield of 1-(*p*-tolymercapto)-2-propanone was increased to 85%. This percentage yield compares favorably with those reported by Hurd and Perletz<sup>3</sup> in their work on the synthesis of aryloxy ketones.

### Experimental

**Preparation of 1-(*p*-Tolymercapto)-2-propanone.**—A mixture of 24.8 g. (0.2 mole) of *p*-thiocresol and 200 cc. of toluene was introduced into a 500-cc., three-necked, round-bottomed flask equipped with an efficient, mercury-sealed mechanical stirrer, a dropping funnel and a condenser. The stirrer was started and 4.6 g. (0.2 mole) of finely divided sodium was added over a period of thirty minutes. After heating for two hours on a boiling water-bath all the sodium had dissolved and the sodium salt of the *p*-thiocresol separated as a white solid. The reaction mixture was allowed to cool to room temperature, 18.5 g. (0.2 mole) of chloroacetone was dropped in over a period of ten

(1) Knight, Porter and Calaway, *THIS JOURNAL*, **66**, 1893 (1944).

(2) (a) Pfitzinger, *J. prakt. Chem.*, **33**, 100 (1886); (b) **38**, 582 (1888); (c) **56**, 283 (1897).

(3) Hurd and Perletz, *THIS JOURNAL*, **68**, 38 (1946).