

TABLE I

THE HEAT OF VAPORIZATION OF PHENYLHYDRAZINE

Temp., °C.	25	95	105	115
	125	135	145	240
Heat of vaporization, cal./mole	(14690)	13886	13788	13693
	13610	13526	13455	(12903)

Summary

The vapor pressure of phenylhydrazine has been measured by means of the isoteniscope over

the range 105–192° with a precision of about ± 0.4 mm. From the resulting data an empirical equation was derived by the method of least squares which reproduced these values to within the experimental precision.

From these values of the vapor pressure the latent heat of vaporization at temperatures from 25–240° has been computed and tabulated.

CORVALLIS, OREGON

RECEIVED JUNE 22, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Kinetics of the Transformation of Hydrazine Cyanate into Semicarbazide¹

BY ELTON M. BAKER AND E. C. GILBERT

The transformation of ammonium cyanate into urea has been the subject of numerous and exhaustive studies but the analogous reaction of hydrazine cyanate to form semicarbazide has never been subjected to critical examination. Such examination is complicated by the reactive nature of the substances involved and also by the fact that semicarbazide is definitely basic whereas urea is so weakly basic that for practical purposes its proton affinity in dilute aqueous solution is entirely negligible. The present work, however, represents a study of the kinetics of the reaction, simple salt effects, equilibrium measurements and the effect of temperature on the rate.

Experimental Part

Preparation of Materials.—Potassium Cyanate (Baker C. P.) was suspended in absolute ethanol by vigorous shaking, to dissolve any small amount of cyanide present. It was then collected on a filter, washed with ether and dried. It was then preserved in a vacuum desiccator and stored in the dark. Prepared in this manner, analysis by the Volhard method showed a purity of 99.6%.

Two neutral salts of hydrazine, the perchlorate and monohydrochloride, were prepared from Kahlbaum 100% hydrazine hydrate and the corresponding pure acids. These salts were recrystallized from 80% methanol and dried over sulfuric acid. They were analyzed by the iodate method.

For equilibrium measurements semicarbazide was necessary. Eastman Kodak Co. semicarbazide hydrochloride was recrystallized from 80% methanol, and checked for purity by Volhard analysis for chloride content. Foreign salts added to increase ionic strength were Baker C. P. quality.

Procedure.—The unexpected rapidity of the reaction precluded the preparation of pure hydrazine cyanate (free from other ions) from silver cyanate and hydrazine chloride in a manner analogous to that used by Warner and Stitt² to prepare ammonium cyanate.

All solutions were made up by adding hydrazine monochloride or perchlorate in solution to exactly equivalent amounts of potassium cyanate. This was accomplished by a vessel of special design which permitted almost instantaneous mixing of small amounts of these solutions. Measurements were made at 25 and 15° in a bath controlled to $\pm 0.05^\circ$.

The progress of the reaction was followed by withdrawing samples which were added to excess standard silver nitrate solution. The precipitated silver salts were filtered out and the excess silver ions in an aliquot portion were determined by titration with standard thiocyanate using ferric alum indicator.

From these results the amount of unreacted cyanate present at any time was calculable.

Equilibrium measurements were made from both forward and backward directions. Reaction mixtures of hydrazine and cyanate were allowed to react until the cyanate titer was constant. Similarly semicarbazide solutions of equivalent concentrations were allowed to stand at constant temperature and analyzed for cyanate from time to time. Equilibrium lies so far toward completion that the reverse reaction has no detectable effect in the early stages of the process.

Discussion

The rapidity of the reaction as measured was quite unexpected as the laboratory directions for the preparation of semicarbazide by this method³ called for elevated temperature and twenty to twenty-four hours of standing. It was therefore thought desirable to demonstrate that the reaction being followed was actually that which was postu-

(1) Taken from the thesis presented by Elton M. Baker in partial fulfillment of requirements for the Ph.D., Oregon State College, 1942. Published with the approval of the Monographs Publication Committee, O. S. C. Research Paper 67.

(2) Warner and Stitt, *THIS JOURNAL*, **55**, 4807 (1933).

(3) Beilstein, 4th edition, Vol. III, p. 98.

lated. This was done by adding benzaldehyde solution at intervals to samples of reaction mixture. With unchanged hydrazine the yellow insoluble compound benzalazine was formed, while with semicarbazide the white semicarbazone of the benzaldehyde was formed. This was also insoluble. The two were readily separated by differential solubility in ether and their identity established by mixed melting points with known samples. As the reaction proceeded the amount of yellow benzalazine rapidly decreased and that of the semicarbazone increased. Had it not been for the time lag in formation of these compounds it would have provided an excellent method of following the reaction. There thus is no reason to doubt that the reaction measured is that of the formation of semicarbazide. No evidence was ever found indicating the presence of carbonate, which is known to be a disturbing factor in the urea reaction.² This is probably due to the lower temperatures and shorter times used in this work.

The main points of interest lie in the conclusions that may be drawn concerning the possible mechanism of the reaction, the possibility of general or specific ion catalysis and the energy of activation.

The assumption that the process would likely prove to be bimolecular was borne out by the fact that in all cases the graph of time against the reciprocal of cyanate concentration was a very satisfactory straight line (Fig. 1) until the reaction was at least 50% complete.

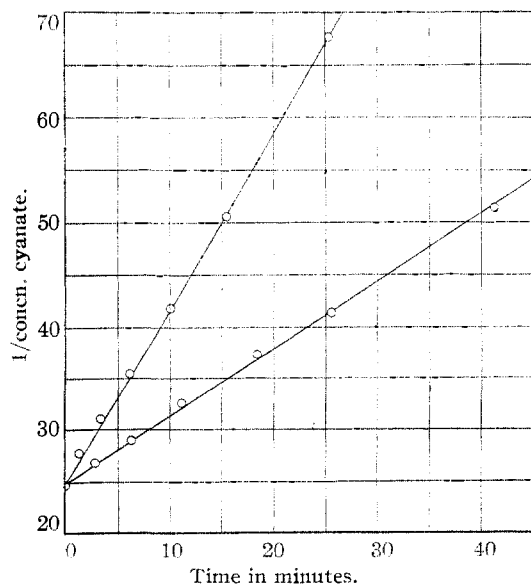


Fig. 1.—Graph showing bimolecular characteristics of reaction, also temperature effect: upper curve, temp. 25°; lower curve, temp. 15°.

For the elucidation of the mechanism useful evidence is obtainable from the effect of ionic strength on the velocity, as shown in Table I. Since the ionic strength diminished due to the disappearance of the hydrazine and cyanate ions during the reaction it was necessary to approximate the mean ionic strength during the time over which the constant was determined.

TABLE I
CONVERSION OF HYDRAZINE CYANATE INTO SEMICARBAZIDE AT 25°, DEPENDENCE OF THE BIMOLECULAR RATE CONSTANT UPON THE IONIC STRENGTH

Run	Initial molality	Molality of added salts	Mean ^a μ	Bimolecular k , mole liter ⁻¹ sec. ⁻¹
19	0.0250	0.0250 (1)	0.0488	0.0390
24	.0250	.0250 (1)	.0435	.0300
25	.0250	.0250 (2)	.0453	.0298
63	.0403	.0403 (1)	.0700	.0286
10	.0500	.0500 (1)	.0858	.0286
18	.0500	.0500 (2)	.0860	.0283
12	.0500	.0500 (3)	.0860	.0282
11	.0500	.0500 (1)	.0860	.0278
17	.0500	.1000 (3)	.1360	.0275
16	.0500	.1500 (3)	.1865	.0260
15	.0500	.2500 (3)	.2870	.0238
14	.0500	.4500 (3)	.4887	.0220

^a Mean ionic strength taking into account salts present plus mean concentration of hydrazine and cyanate ions during time used in establishing bimolecular constant, k : (1) potassium chloride only; (2) potassium perchlorate only; (3) potassium nitrate and chloride.

There was a definitely negative primary salt effect though the concentrations which it was necessary to use were too high to expect quantitative agreement with the limiting law. When the expression for the limiting law, modified to allow for higher ionic strength

$$\log k = \log k_0 + Z_1 Z_2 \frac{\sqrt{\mu}}{1 + A\sqrt{\mu}}$$

is used, excellent agreement is obtained even at the higher concentrations.

According to Brönsted's theory such a negative salt effect is to be expected for a reaction between ions of unlike charge, whereas if uncharged molecules were involved the salt effect should be negligible. The effect is shown graphically in Fig. 2, in which has been shown also the limiting slope (-1) predicted for a reaction in which the ions have unit positive and negative charges, in solutions of low ionic strength.

This evidence, like that in the urea conversion, points strongly to the theory that the rate governing step is one between ions, presumably hydrazine and cyanate.

The effect of temperature is also illustrated in Fig. 1 showing runs at 15 and 25° for solutions of low ionic strength. The mean k_{15} for 5 runs was 0.0107 and the mean k_{25} for 4 runs was 0.0284 giving a temperature coefficient of 2.65 for ten degrees, and a calculated energy of activation of 16,600 cal./mole. The data probably do not possess sufficient precision to merit calculation of the entropy of activation.

Equilibrium data are shown in Table II. Due to the greater time required for attainment of equilibrium at lower temperatures with the attendant complications of side reactions and oxidation only measurements at 25° are reported. Equilibrium is apparently reached only when approximately 97% of the hydrazine cyanate has reacted.

TABLE II
EQUILIBRIUM CONSTANT, AT 25°

$$K = \frac{(\text{MOLALITY OF CYANATE})^2}{(\text{MOLALITY OF SEMICARBAZIDE})}$$

Run	Molality of semicarbazide	Molality of cyanate	$K \times 10^6$
60	0.02409	0.00091	3.44
61 ^a	.03903	.00124	3.94
62 ^a	.03924	.00111	3.14
62 ^a	.03927	.00108	2.97
64	.03907	.00128	4.19

^a Semicarbazide was allowed to decompose into hydrazine cyanate. In all other runs the reactant was hydrazine cyanate.

Using the equilibrium data, in equations of Walker and Appleyard⁴ it was possible to calculate k_2 for the postulated reverse unimolecular decomposition of semicarbazide. This is shown in the summarizing table, Table III.

TABLE III

SUMMARY OF CONSTANTS
Conversion of Hydrazine Cyanate to Semicarbazide

Equilibrium constant K_{25}	($\mu = ca. 0.05$)	3.5×10^{-6}
Equilibrium constant K_{15}	($\mu = ca. .05$)	(2.9×10^{-6})
k_1 forward at 25°	($\mu = ca. .08$)	2.85×10^{-2} mole liter ⁻¹ sec. ⁻¹
k_2 reverse at 25°		9.98×10^{-7} mole liter ⁻¹ sec. ⁻¹
k_1 forward at 15°	($\mu = ca. .08$)	1.07×10^{-2} mole liter ⁻¹ sec. ⁻¹
k_2 reverse at 15°		4.93×10^{-8} mole liter ⁻¹ sec. ⁻¹
k_0 (extrap.) at 25°	($\mu = 0$)	4.46×10^{-2} mole liter ⁻¹ sec. ⁻¹
Temperature coefficient k_{25}/k_{15}		2.65
Energy of activation		16,600 cal. mole ⁻¹

Due to limitations imposed by the method of analysis which so far have not seemed avoidable, and the basicity of the semicarbazide, investigation of possible specific or general catalysis was confined to qualitative observations. Since

(4) Walker and Appleyard, *J. Chem. Soc.*, **69**, 193 (1896).

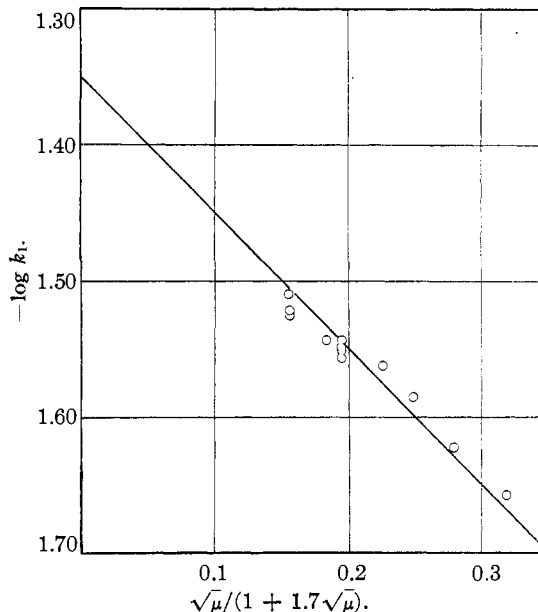


Fig. 2.—Change of velocity constant k_1 at 25° with change in ionic strength. Solid line is limiting slope for reaction between univalent ions of opposite charge.

the hydrazine salts were of the monovalent series and the potassium cyanate neutral the reaction mixture at the start was at a pH of approximately 6. As semicarbazide was formed, there was a gradual increase in pH . At this pH , calculation shows that the semicarbazide is practically entirely in the basic form. Buffers which are effective in this range have the disadvantage that practically without exception their silver salts are insoluble, unless acid is added, in which case error is introduced by the concomitant solubility of the silver cyanate.

One set of experiments using an acetate buffer at pH 5 (slightly lower than that of the unbuffered mixture) showed apparently an increase in reaction rate which might indicate a hydrogen ion catalysis. There was no change in the bimolecular characteristics, however. So far as could be de-

terminated, an increase in buffer concentration caused no increase in rate, indicating no general catalysis at least for the acetate-acetic acid buffer.

To convert semicarbazide predominantly into its salt requires a pH of about 2. Efforts were made to study the rate of reaction in this pH range by adding acid from a micro buret at a rate sufficient to keep the pH at 2.2 (in which case the acid added is a measure of the semicarbazide formed) following the procedure of earlier work.⁵ Evidence showed however that the cyanic acid was decomposing with little semicarbazide being formed, and this approach was not carried further.

(5) Gilbert, *THIS JOURNAL*, **51**, 3394 (1929).

Summary

1. The formation of semicarbazide from hydrazine cyanate takes place readily at room temperature.

2. Increase in ionic strength reduces the velocity of reaction in a manner which agrees with the postulate that the rate determining process is the reaction between the hydrazine and cyanate ions.

3. The reaction reaches an equilibrium far to the side of formation of semicarbazide.

4. Quantitative results are presented on the velocity constants of the reaction at 15 and 25°, the equilibrium constant, salt effects, temperature coefficient and heat of activation.

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RECEIVED AUGUST 6, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY, THE ILLINOIS INSTITUTE OF TECHNOLOGY, AND THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Role of Neighboring Groups in Replacement Reactions. I. Retention of Configuration in the Reaction of Some Dihalides and Acetoxyhalides with Silver Acetate¹

BY S. WINSTEIN² AND R. E. BUCKLES

Three mechanisms for nucleophilic replacement reactions at a saturated carbon atom are currently recognized.^{3,4} One is the now familiar⁵ bimolecular (S_N2) substitution with complete Walden inversion. A second mechanism (S_Ni) involves the rearrangement of an intermediate product^{3,6} in such a way that retention of configuration is the steric result.

The third mechanism has been termed unimolecular³ (S_N1) or polymolecular.^{3,4,7} It seems to consist of at least two steps, the most probable rate-determining step being an ionization. There are several indications that the carbonium ion intermediate is, in some respects, quite unfree.⁴ For example, the steric result of reaction by this mechanism generally is predominant inversion. Quite analogous to the S_N1 mechanism is a process

(1) A portion of the material reported in this paper was presented before the Organic Division at the St. Louis meeting of the American Chemical Society, April, 1941.

(2) National Research Fellow in Chemistry, Harvard University, 1939-1940.

(3) (a) Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1252 (1937); (b) Bateman, Church, Hughes, Ingold and Taher, *ibid.*, 979 (1940).

(4) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapters V and VI.

(5) (a) Olson, *J. Chem. Phys.*, **1**, 418 (1933); (b) Bergmann, Polanyi and Szabo, *Z. Physik. Chem.*, **20**, 161 (1933).

(6) Hughes, Ingold and Whitfield, *Nature*, **147**, 206 (1941).

(7) (a) Steigman and Hammett, *THIS JOURNAL*, **59**, 2536 (1937); (b) Parinacci and Hammett, *ibid.*, **59**, 2542 (1937); (c) Beste and Hammett, *ibid.*, **62**, 2481 (1940).

involving the electrophilic attack of a reagent such as silver ion on a halogen atom.^{3,4}

Ionization to an ion-pair, solvated in a way characteristic of ions, may be thought to be the rate-determining step in the S_N1 mechanism. Solvation of the ions makes this step feasible; therefore, the rate varies with the arrangement of solvent molecules around what is to be the ion-pair. Solvent molecules must be included in the transition state, without, however, drawing bonds between the solvent molecules and the carbonium ion.^{8,9,10} If the carbonium ion is very reactive it will react preferentially with a molecule in the solvation cluster to give inversion as the major steric result.³ There may thus be some connection between rates and final product compositions in mixed solvents.^{3,8} If reaction of the carbonium ion takes place after dissociation of the ion-pair, complete racemization is the steric result.⁷

(8) Winstein, *ibid.*, **61**, 1635 (1939).

(9) Balfe and Kenyon, *ibid.*, **62**, 445 (1940).

(10) It is possible that the failure of a tertiary halide with the halogen atom on a bridge-head to undergo solvolytic reaction, as demonstrated by Bartlett and co-workers, [*THIS JOURNAL*, **61**, 3184 (1939); **62**, 1183 (1940)] should be ascribed partly to the fact that the solvation energy of the cationic end of the ion-pair to be formed is apt to be much smaller than usual. Solvent is kept away from the cationic carbon atom by the hydrocarbon cage more effectively than is possible with the most highly hindered open-chain compounds in which the cationic carbon atom can flatten out.