dipole–dipole effect. Thus the partial molal heat of vaporization of water falls. This trend continues until dipole–dipole effects become increasingly significant, when the partial molal heat of vaporization of water increases linearly with dielectric constant up to about 90% by weight of water. In solutions more concentrated in water than 90% by weight an accelerated increase of partial molal heat of vaporization of water is observable. This increase is due perhaps to the increased magnitude of dipole–dipole forces relative to dipole-induced dipole forces and perhaps also due to increased hydrogen bonding among water molecules alone.

With reference to the dioxane curve, the initial increase of the partial molal heat of vaporization of dioxane can be explained by the increased forced holding each dioxane molecule as the proportion of water increases. The increased forces arise perhaps from both induced polarity in dioxane molecules and hydrogen bonding between water and dioxane molecules. These increased forces reach a maximum at the azeotrope composition shown by the dotted line in Fig. 9. Beyond the azeotrope composition, dipole–dipole forces among water molecules become increasingly important relative to dipole-induced dipole forces among the water and dioxane molecules. Thus the restraining forces on dioxane becomes less and the partial molal heat of vaporization of dioxane falls, less rapidly at first and then more rapidly and finally precipitously as predominant dipole–dipole interacting molecules, in a sense, squeeze out the dioxane.

A further study of the heats of vaporization of the dioxane–water system at several temperatures is planned, since the rate of change of heat of vaporization with temperature at any given composition would be theoretically useful, and the data taken at other temperatures would tend to check the present study qualitatively without the labor of repeating it.

Since the calorimeter was designed for the most general applicability, it is planned to study other types of liquid mixtures.

FAYETTEVILLE, ARKANSAS RECEIVED SEPTEMBER 21, 1951

[CONTRIBUTION FROM THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON]

The Reaction of Cyanogen and Related Nitriles with 1,3-Dienes. III. Kinetic Study of the Cyanogen–Butadiene Cyclization Reaction[1]

BY P. J. HAWKINS AND G. J. JANZ[2]

The reaction of cyanogen with butadiene at moderately high temperatures in the gas phase yields 2-cyanopyridine as product. The present communication reports on a kinetic study of this cyclization—dehydrogenation reaction. The constant pressure continuous flow method was used to obtain the kinetic data for the temperature range of 325 to 450°. The reaction is homogeneous and over-all second order, first order with respect to each of the reactants. The energy of activation is 31.6 ± 0.2 kcal./mole, and the frequency factor, 1.6×10^{-12} sec.$^{-1}$ g. mole^{-1} l. A comparison of these data with those reported for diene reactions at high temperatures is made.

It has been seen in Parts I and II of this series[3] that the reaction of cyanogen with butadiene to give 2-cyanopyridine previously reported[4] is one of a more general group of reactions of organic nitriles with conjugated dienes. This generality favors a Diels–Alder type of mechanism for this cyclization–dehydrogenation reaction. The (C≡N) group thus has the role of the dienophilic component of the dienophile, and because the conditions are favorable for aromatization, the reaction is accompanied by a simultaneous dehydrogenation, giving the pyridinic derivative as product. Alder[5] has mentioned in his observations on the formation of pyridinic nuclei by this reaction that when hydrogen is present in the 2- and 5-positions of the adduct, dehydrogenation to a pyridine derivative takes place under the normal conditions of the reaction. A kinetic study of the cyanogen–butadiene cyclization was thus undertaken to gain quantitative data concerning the energy of activation and collision frequency factor in a reaction leading to the direct synthesis of the pyridine nucleus. A constant pressure–continuous flow method seemed to offer the best means for this experimental study, for by restricting the reaction to small conversions the complications due to side reactions can be avoided. In consequence of the possible complexity of this system, and the small conversions thus necessary, the rate of reaction was measured by the formation of cyanopyridine rather than by disappearance of either of the reactants.

Experimental

Description of Flow Apparatus.—Three capillary type flowmeters were used to measure and control the rates of flow of the three gases, cyanogen and butadiene and nitrogen. The former two gases met in a mixing tube fitted with glass beads and were passed through a calcium chloride tube before reaching the reaction vessel in the hot zone. The nitrogen, when used, was passed through a phosphorus pentoxide tube before entering the system. The reaction vessel was all Pyrex, with capillary inlet and outlet tubes to the constant temperature reaction volume, and a thermocouple well extending the length of the reaction zone. The products of the reaction and unchanged reagents were collected in three receivers, the first being cooled to −80° and the latter two, −192°. The pressure immediately before the reaction was measured by a manometer, and the tem-

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[1] Abstracted in part from the thesis submitted by P. J. Hawkins in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at University College, London.

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[3] P. J. Hawkins and G. J. Janz, *J. Chem. Soc.*, 1479, 1485 (1949).

[4] G. J. Janz, R. G. Ascah and A. G. Keenan, *Can. J. Research*, **B25**, 272 (1947); G. J. Janz and A. G. Keenan, *ibid.*, **B25**, 283 (1947); G. J. Janz and P. J. Hawkins, *Nature*, **162**, 28 (1948).

[5] K. Alder, "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 503.

perature by three Eureka nichrome thermocouples at various positions in the thermocouple well.

The furnace assembly consisted of an aluminum block, 6 in. in diameter and 20 in. long with a 2-in. diameter hole bored centrally in which the reaction vessel rested. The free space within the furnace resulting from the use of various sized reaction vessels was packed (to the limits of the aluminum block) with aluminum sections, the remaining space between the block and the outside of the lagging being packed with plaster of paris sections. The block insulated with asbestos paper was wound in one section with nichrome resistance wire and thermally insulated with asbestos pipe lagging. The thermoregulator entered the aluminum block radially as shown and controlled the power input to the winding through a Sunvic relay.

The temperature variation during the course of an experiment was not greater than 0.5° which at 400° implies an error in the rate constant of approximately ±2%. No significant gradient could be detected along the body of the reaction vessel at the largest flow rates used in the kinetic runs.

Materials (a) Cyanogen.—The method previously described[4] for the preparation was used. The crude cyanogen was twice distilled through acidified silver nitrate solution to remove hydrogen cyanide and dried by passing the gas through phosphorus pentoxide. The pure sample was distilled into a small steel cylinder fitted with a needle valve.

The purity was estimated using a simple gas buret in conjunction with a gas absorption apparatus described by Burton and Davies.[6] A known volume of cyanogen was absorbed in sodium hydroxide solution and determined by Ricca's method. The purity of the cyanogen by this method was in all cases found to be greater than 99%.

(b) Butadiene.—A commercial sample (Imperial Chemical Industries, Ltd.) was used without further purification. Analysis by the method of Tropsch and Mattox[7] gave a purity of 98–99%. The gas was stored in a small steel cylinder fitted with a needle valve.

(c) Nitrogen.—Commercial nitrogen was passed through Fieser's solution to remove oxygen and dried by passing over phosphorus pentoxide.

Method of Operation.—Initially the reaction vessel and receivers were pumped down and held at 1–2 mm. pressure to ensure the apparatus was gas tight. The system was then flushed with nitrogen using a flow rate equal to the total rate of flow to be used with the reactants. During this period, the butadiene and cyanogen flows were adjusted by their respective needle valves, using a bypass to take these gases. The run was started when the air had been flushed from the system by turning a special valve to cut off the nitrogen and admit the flow of the butadiene–cyanogen mixture to the reaction zone.

The gases were thus passed for an appropriate time to give sufficient product for analysis, during which time temperature gradients were measured. At the end of a run, the system was flushed with nitrogen again as above to sweep out the reaction zone, and to remove any cyanopyridine in the exit tube (maintained at 200° during this operation).

The unchanged reagents were next distilled from the receivers under a nitrogen atmosphere. The last traces of cyanogen butadiene, and hydrogen cyanide were removed by pumping the receivers down to 50 mm. pressure, keeping the receivers at about 0°. It had been previously determined that this pressure did not remove a significant amount of cyanopyridine. Acetone was finally used to wash the receivers and exit tubes, and this mixture was analyzed for cyanopyridine.

Methods of Analysis (a) The Determination of 2-Cyanopyridine.—The contents of the receivers were refluxed for approximately 15 minutes with 50 cc. of 10% sulfuric acid solution to extract the cyanopyridine and transferred to a normal Kjeldahl steam distillation apparatus. The cyanopyridine was hydrolyzed with an excess of 10% sodium hydroxide solution and the evolved ammonia absorbed in 100 cc. of 2% boric acid solution. The solution was titrated with approximately 0.05 *N* standard hydrochloric acid using brom cresol green *n* methyl red as indicator.[8,9]

The hydrolysis has been shown to be quantitative and the method to be unaffected by the acetone used in the extraction.

Cyanogen alone was passed through the reaction vessel under conditions similar to those of the kinetic runs to determine that no products capable of giving ammonia on alkaline hydrolysis were formed by polymerization and that the procedure adopted was efficient in completely removing unchanged cyanogen.

Results and Discussion

A summary of the experimental data and the rate constants calculated from these data over the temperature range 320 to 450° is given in Table I.[10]

The Calculation of Rate Constant.—A strictly rigorous treatment of flow systems requires a consideration of volume changes resulting from a difference in the number of moles of products and reactants and of concentration due to their interdiffusion. Some simplification is possible, if, in the second effect, the limiting cases of complete and negligible diffusion are assumed and equations have been derived for these conditions.[11] In the present work, where the percentages of reaction were necessarily small and conditions were not such as to justify the assumption of either of these limiting cases, an approximate formula has been used which corrects volume and concentration terms in the unintegrated rate equation to the arithmetical means of the initial and final values.

$$k_2 = \frac{V_1^2}{V_r}\left(\frac{Ne}{(N_{A_1})(N_{B_1})}\right) \text{ cc. mole}^{-1} \text{ sec.}^{-1} \qquad (1)$$

where V_1 = volume (cc.) of gases entering the reactor at the reaction temperature and pressure, *i.e.*, (a + b + c) where a = cyanogen, b = butadiene and c = nitrogen. V_r = the volume of the reaction zone (cc.). N_{A_1}, N_{B_1} = number of moles of cyanogen and butadiene, respectively, entering the reaction vessel per second. Ne = number of moles of cyanopyridine leaving the reaction vessel per second.

The equation used to calculate k_2 was

$$k_2 = \frac{V_2^2}{V_r}\left[\frac{Ne}{\left(N_{A_1}\left(1 - \frac{\alpha_1}{2}\right)\right)\left(N_{B_1}\left(1 - \frac{\alpha_2 + \alpha_3}{2}\right)\right)}\right] \qquad (2)$$

where $V_2 = a + b\left(1 - \frac{\alpha_3}{4}\right) + c$. α_1, α_2 = the fractional conversions of cyanogen and butadiene, respectively, due to the formation of cyanopyridine, α_3 is the fractional conversion of butadiene due to dimerization assumed to be occurring alone. Equation (2) was applied to data of experiments in which the percentage reaction was greater than 1%. The simple equation (1) was used in other cases. These results are listed as $k_2(1)$ and $k_2(2)$ in Table I, respectively. Calculation of the rate constants with the various equations assuming the cases of complete diffusion and negligible diffusion[11] gave results not significantly different from these obtained by (1) and (2) above. The butadiene dimerization contribution was calculated from the

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(6) M. Burton and T. W. Davies, *Ind. Eng. Chem., Anal. Ed.*, **9**, 139 (1937).

(7) H. Tropsch and W. J. Mattox, *ibid.*, **6**, 104 (1934).

(8) T. S. Ma and G. Zuazaga, *ibid.*, **14**, 280 (1942).

(9) E. W. Meker and E. C. Wagner, *ibid.*, **5**, 396 (1933).

(10) For detailed tables supplementary to this article order Document 3416 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(11) G. M. Harris, *J. Phys. & Colloid Chem.*, **51**, 505 (1947).

data reported by Rowley and Steiner[12] and Kistiakowsky and Ransom.[13] As it was not always possible to obtain a range of data at any one temperature, a temperature coefficient of 3% per degree (an approximate figure determined from the activation energy subsequently derived) was used to reduce constants within a small range to a fixed temperature for purposes of comparison. These are listed in Table I as $k_2(T)$. From a consideration of the limits of error in the operation of flow methods, *i.e.*, the flowmeters, the measurement of the reaction volume, temperature and pressure, and the total time of gas flows, a variation of 10–15% is possible in the rate constant. A reproducibility of this order was found in the kinetic data.

At 400° the initial partial pressures of the reagents was varied from 0.10 to 0.75 atmosphere for both butadiene and cyanogen. Nitrogen was used as a third gas to effect the reduction of partial pressures when necessary to attain small percentages of reaction. The rate factors may be seen to remain constant within experimental error. The reaction is therefore considered to follow the second order rate equation

$$\text{rate} = k_2[(CN)_2][C_4H_6]$$

where the expressions in brackets stand for the respective concentrations. The reaction also was found to be homogeneous in the gas phase. This may be seen from a comparison of the results of runs 26–29 (Table I) with the mean value of 90.2 for the rate constant in the unpacked runs at 400°. In these four experiments the surface to volume ratio was increased approximately twelvefold in the packed reaction vessels. The tendency to a decrease in rate factor in the packed experiments is likely due to a constant experimental error introduced in determining the free space in the packed vessels. The small effect on the rate factor with the great increase in the surface/volume ratio thus shows that the reaction is essentially homogeneous. The use of a clean reaction vessel in each experiment, and avoidance of prolonged runs, minimized complications that might possibly arise from a carbon-like deposit in the reactor found on the walls after several experiments, especially at the higher temperatures. At each temperature also, data were obtained for series of contact times to ensure that the rate factors were independent of the reaction time. This was necessary since at very short contact times the percentage of the reaction time required by the gases to reach the reaction temperature may become significant and thus result in low values for the rate constants *e.g.*, runs 62–64 at 400° (Table I). At the temperatures of 450 and 400° the rate constants were found to be independent of the percentage reaction occurring, within small limits. However at temperatures below 400° an increase in the rate factor is found with an increase in the percentage reaction, the effect becoming more marked with decreasing temperature, *e.g.*, runs 84–87 at 322° and runs 54, 92–93 at 372.5° (Table I). It has not been possible so far to find a satisfactory explanation for this increase, but in view of the complexities of the system, it is not unlikely that side reactions are responsible for the formation of other hydrolyzable nitriles which are determined as cyanopyridine. As it was not possible to avoid this complication, the rate factors were corrected to zero percentage conversion, and these corrected rate constants k°_2 were used in the determination of the parameters of the Arrhenius equation.

In the derivation of the energy of activation ΔE and the B factor by the method of least squares and in obtaining the standard deviation all data have been used. The experimental activation energy was obtained from a plot of log k°_2 against $1/T$ where the points lie well along a straight line.

The rate constants k°_2 at 10° temperature intervals over the range covered in this investigation are listed in Table II. The activation energy calculated from this plot is 31.6 ± 0.2 kcal., and the rate as a function of temperature can be expressed by the following Arrhenius equation

Table II

Rate Constants[a] for the Cyanogen–Butadiene Reaction over the Temperature Range 325–450°

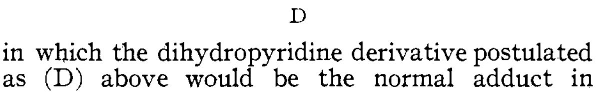
Temperature, °C.	k^0_2 cc. mole^{-1} sec.$^{-1}$	Temperature, °C.	k^0_2 cc. mole^{-1} sec.$^{-1}$
320	3.597	390	60.53
330	5.598	400	86.10
340	8.610	410	121.4
350	13.00	420	168.8
360	19.28	430	233.0
370	28.80	440	316.6
380	41.69	450	436.0

[a] Interpolated from the experimental results plotted as log k°_2 against $1/T$ (°K.).

$$k = (1.6 \pm 0.2) \times 10^{12}e^{-31,600/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1} \quad (3)$$

Calculation of the collision number (Z) from the kinetic-theory relation using the mean molecular collision diameters of butadiene and cyanogen as 5.70 and 4.91 Å., respectively, gave a value for Z of 3.9×10^{14}. A steric factor of 10^{-2} is thus required to account for the deviation of the actual reaction from the behavior of the simple collision theory. A comparison of these data with those reported for related high temperature gaseous cyclization reactions is given in Table III. It is seen that the steric factor in the orthodox high temperature Diels–Alder reaction is 10^2 to 10^3 greater than in this reaction.

The reaction of cyanogen with butadiene may be formulated as



D

in which the dihydropyridine derivative postulated as (D) above would be the normal adduct in an orthodox Diels–Alder association reaction. Theoretical considerations[3] on the thermodynamic stability of dihydropyridine relative to pyridine have shown that the dihydro compound is thermodynamically quite unstable, and thus, if formed

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[12] D. Rowley and H. Steiner, *Faraday Society Discussions*, April (1951), Preprint 18.

[13] G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, **7**, 373 (1939).

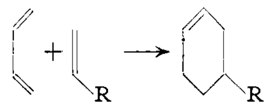
TABLE III

FREQUENCY FACTORS AND ENERGIES OF ACTIVATION FOR SOME HIGH TEMPERATURE DIELS–ALDER REACTIONS

Diene	Dienophile	Temperature range T, °C.	Frequency factor cc.$^{-1}$ mole^{-1}	Energy of activation, kcal.	Ref.
Butadiene	Acrolein	155–332	1.46×10^9	19,700	(14)
Butadiene	Crotonaldehyde	242–300	0.9×10^9	22,000	(15)
Butadiene	Butadiene	173–386	9.2×10^9	23,690	(13)
		418–650	1.4×10^{11}	26,800	(12)
Butadiene	Ethylene	487–648	3.0×10^{10}	27,500	(12)
Butadiene	Cyanogen	325–450	1.6×10^{12}	31,600	(This work)

under conditions favoring aromatization, would be expected to pass over to the pyridine. Alder has also reported[5] that in Diels–Alder reactions leading to the formation of pyridinic nuclei, the dihydro intermediates spontaneously lose hydrogen under the conditions of the reaction to form, as end product, a pyridine derivative. This reaction thus differs from the orthodox Diels–Alder association reactions in that the "adduct" formed as the product in the normal reactions is here unstable and never found as end-product of the reaction.

The four 1,3-butadiene reactions listed in Table III are all examples of the classical and orthodox Diels–Alder reaction in which the olefinic group



of the dienophile adds to the diene to give a tetrahydrobenzene derivative as product. The investigations of these reactions have established certain kinetic characteristics for the high temperature Diels–Alder associations. They have been found to be homogeneous and of the second order; first order with respect to the diene, and first order with respect to the dienophile. The reaction of cyanogen with butadiene has also been found to be essentially an homogeneous reaction, and of the second order; first order with respect to butadiene, and first order with respect to cyanogen. A more striking characteristic of these high temperature Diels–Alder associations is found in the parameters of the Arrhenius equation. The energies of activation in the case of the associations involving butadiene are quite low, and the frequency factors are considerably less than the collision number calculated from the kinetic theory, and independent of the associating species. Examination of the data in Table III shows that for the orthodox Diels–Alder reactions involving butadiene, the energies of activation fall in the region of 18 to 28 kcal., the exact value being dependent on the "reactivity" of the dienophile, *i.e.*, on the extent to which the polar group adjacent to the olefinic linkage enhances the polarizability of the dienophilic link. In the butadiene–cyanogen reaction the energy of activation was found to be considerable greater, *i.e.*, about 4 kcal. larger than for the reaction of butadiene with ethylene under comparable conditions. The relatively large activation energy is associated with a more stabilized initial state in this system than in the other comparable reacting systems.

A further difference is observed on comparison of the frequency factors for the normal Diels–Alder reactions with that found for the butadiene–cyanogen reaction. Thus for the four orthodox Diels–Alder reactions involving butadiene the frequency factors are, within experimental error, identical at moderately high temperatures. The *B* factors of these reactions are 10^9 to 10^{10}, and smaller than the normal values for bimolecular association reactions by a factor of 10^3. The fact that the frequency factor is much less than that for normal bimolecular associations and also the calculated collision frequency can be accounted for by the loss of rotational degrees of freedom in the association.[15] The independence of this factor relative to the nature of the associating species is interpreted also statistically as a similarity in the nature of the transition complex, the bond rearrangements, and the steric factors in these reactions. The recent work of Rowley and Steiner[12] confirms that the assumption of a similarity of transition state and final reaction product in the Diels–Alder association reactions is in the main correct. In the case of the cyanogen–butadiene reaction the frequency factor was found to be 10^{12}, which is larger by a factor of 10^2 than the factors in the orthodox Diels–Alder reaction. Whilst the orthodox reactions have been confined to reactions involving olefinic dienophiles, and the present reaction of a nitrile dienophile is therefore not strictly comparable, it might nevertheless be expected in view of the cyclization present in each case that the entropy factors, and thus the *B* factors would be alike for these reactions. The numerically larger frequency factor in the cyanogen–butadiene reaction can be interpreted in the transition complex having a much looser structure than in the case of the orthodox Diels–Alder reactions. This can be met if the configuration of the activated complex does not correspond as closely to the final reaction product as in the classical diene association reactions. The corresponding entropy change in passing from the initial state to the transition state is thus less in this reaction than in the orthodox Diels–Alder reactions.

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(15) M. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, **34**, 614 (1938).