TABLE II

EFFECT OF IMMONIUM CHLORIDE CONCENTRATION ON PRODUCT COMPOSITION

Total volume, ml.	Chloroamino ketone hydrochloride product Wt., g.	M.p., °C.	I.R. value α-chloro ketone, %
	Run I		
10	0.33	168–169	18.5
40	.32	168–169	15.6
80	.33	169–170	12.6
	Run II		
10	.34	167–168	20.2
40	.33	167–168	17.4
80	.34	168–169	10.8

TABLE III

EFFECT OF EXCESS Cl^- ADDED AS Et_4NCl UPON PRODUCT COMPOSITION FROM *cis*-ETHYLENIMINE KETONE

Expt. no.	Molar equiv. Et_4NCl (excess Cl^- ion)	*threo*-Hydrochloride products Wt., g.	M.p., °C.	I.R. value (α-chloro ketone, %)
1	0	0.34	170–171	13.8
2	0	.33[a]	170–171	13.2
3	1	.34	170–171	14.5
4	1	.30	169–170	15.0
5	8	.33[a]	170–171	32.9
6	8	.34	167–168	32.9
7	16	.34	169–170	40.7
8	16	.33[b]	169–170	39.0

[a] *Anal.* Calcd. for $C_{23}H_{23}NOCl_2$: C, 68.99; H, 5.79. Found for expt. 2 product: C, 68.76; H, 5.83. Found for expt. 5 product: C, 69.38; H, 5.90. [b] Ring closure of expt. 8 *threo*-hydrochloride with triethylamine in benzene gave a 79% yield of *cis*-1-benzyl-2-phenyl-3-*p*-toluylethylenimine, m.p. 114–116°.

ence of Excess Chloride Ion.—(1) Methanol, pure tetraethylammonium chloride, two molar equivalents of hydrogen chloride and 0.3 g. (0.000916 mole) of the *cis*-ethylenimine ketone were quickly mixed to give 20 ml. of clear colorless solutions which were maintained in a thermostat at 25° for 24 hours. No precipitate appeared. All of the solvent was then evaporated from the solutions and the residues shaken with a mixture of 25 ml. of ether, 25 ml. of water and 0.098 g. (0.000916 mole) of benzylamine. The ether layers were washed with two 15-ml. portions of water and dried over Drierite for 20 minutes. The dry ether solutions were saturated with dry hydrogen chloride and the precipitated products removed immediately by filtration, washed with ether and dried in a vacuum desiccator. The I.R. values of the products were determined; see Table III for the results.

(2) Using conditions and techniques identical with those described in (1) above, samples of the *trans*-ethylenimine ketone (0.3 g., 0.000916 mole) were studied; see Table IV for results.

TABLE IV

EFFECT OF EXCESS Cl^- ADDED AS Et_4NCl UPON PRODUCT COMPOSITION FROM *trans*-ETHYLENIMINE KETONE

Expt. no.	Molar equiv. Et_4NCl (excess Cl^- ion)	*erythro*-Hydrochloride products Wt., g.	M.p., °C.	I.R. values (α-chloro-ketone, %)
1	0	0.33[a]	170–171	8.4
2	0	.32[a]	169–170	9.1
3	1	.34[b]	168–169	11.4
4	1	.33	168–169	12.0
5	8	.33	168–169	13.5
6	8	.32	167–168	13.8
7	16	.33[b]	169–170	14.9
8	16	.31	170–171	15.2

[a] Ring closure of the *erythro*-hydrochloride product from expt. 1 and 2 with triethylamine in benzene solution produced a 76% yield of *trans*-1-benzyl-2-phenyl-3-*p*-toluylethylenimine, m.p. 71–73°. [b] *Anal.* Calcd. for $C_{23}H_{23}NOCl_2$: C, 68.99; H. 5.79. Found for expt. 3 product: C, 68.78; H, 5.61. Found for expt. 7 product: C, 68.72; H, 5.70.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE WALKER LABORATORY, DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

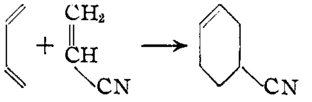
The Reaction of Cyanogen and Related Nitriles with 1,3-Dienes. V. Acrylonitrile and Butadiene[1]

BY G. J. JANZ AND N. E. DUNCAN[2]

RECEIVED MAY 29, 1953

The reactions of acrylonitrile and butadiene in the temperature region of 400° and atmospheric pressure are reported. In the uncatalyzed reaction, cyanocyclohexene only is formed, but in the presence of a chromia–alumina catalyst, vinylpyridine and cyanocyclohexene are obtained. The experimental data are correlated with the thermodynamic free energies and relative rates calculated for these reactions. The results indicate a considerable preferential catalysis of the pyridinic cyclization since the reactivity of the (C≡N) group is much more nearly that of the (C=C) group in presence of the catalyst than in the uncatalyzed reaction.

The addition of acrylonitrile to butadiene to yield 3-cyanocyclohexene (I) has been studied in toluene solution[3,4] and in aqueous dispersion.[5] This is an example of a typical Diels–Alder reaction in which a stable six-membered cyclic product is formed by 1,4-addition of the (C=C) group to butadiene. Acrylonitrile has in fact been classified by Alder and Rickert[6] as belonging in the group of dienophiles having greatest reactivity in the Diels–Alder reaction. At 400°, Janz and associates have found that the (C≡N) group of nitriles adds to butadiene yielding a 2-substituted pyridinic deriva-



(1)

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[1] Abstracted in part from the thesis submitted by N. E. Duncan in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at Rensselaer Polytechnic Institute, June, 1952.

[2] Cyanamid Research Fellow.

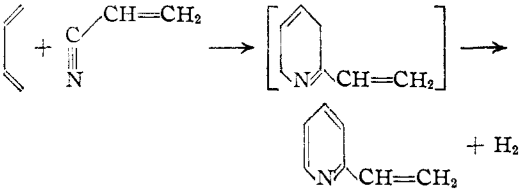
[3] A. A. Petrov and N. P. Sopov, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 2228 (1947).

[4] S. L. Jacobs, B.S. Thesis, Dept. of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y. (1951).

[5] W. D. Wolfe, U. S. Patent 2,217,632 (1940).

[6] K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

tive as product.[7] This cyclization–dehydrogenation reaction also may be explained as proceeding by a Diels–Alder type of mechanism in which the (C≡N) acts as the dienophilic group. Acrylonitrile presents the interesting case of a compound in which both groups (C=C) and (C≡N) are present and in conjugation. Reaction by virtue of the (C≡N) group would give 2-vinylpyridine (2) in this case, if the dihydropyridine loses hydrogen spontaneously under the reaction conditions as observed in the previous work.



(2)

This communication describes an experimental study of the reactions of acrylonitrile and butadiene in the temperature region of 400° at atmospheric pressure. The relative reactivity of the (C=C) and (C≡N) groups in acrylonitrile is considered in the light of thermodynamic and kinetic rate calculations.

Experimental

Materials.—Acrylonitrile (Eastman Kodak Co., prac. grade) was purified by fractional distillation after drying over anhydrous K_2CO_3 (observed: b.p. 76.5–77.5° (atm.), n^{25}_{D} 1.3889). Butadiene (Matheson Co., C.P. grade) was passed through activated alumina but otherwise used without purification. Two 4% Cr_2O_3–96% Al_2O_3 catalysts were used. The standard (STD) had a surface area of about 80 m.²/g., and the other (HSA) had a surface area approximately three times greater. The specifications, preparation and re-activation of these is described elsewhere.[8]

Procedure.—A continuous flow method with a fixed catalyst bed was used. The apparatus was similar to that described in detail in the catalyst evaluation.[8] Preliminary work had shown that at relatively long contact times with the catalysts, the reaction product obtained was quite complex, containing benzonitrile, cyanocyclohexene, propionitrile, and a mixture of basic products.[4] A short reaction time was selected for the present studies in order to minimize the effects due to secondary reactions.

Product Separation and Identification.—To accumulate a sufficient amount of material for separation and identification of the products, ten runs of two hour duration were made, each at about 400° and 4 seconds contact time. The catalyst was re-activated at the end of each two-hour period. This series of runs yielded 778 g. of crude product, collected at −80°. The crude product was used in working out the methods of analysis for the different reaction products. The unreacted butadiene was recovered by warming the crude product to 60°. Acrylonitrile was determined quantitatively by titration of a weighed aliquot of the mixture with dodecyl mercaptan reagent.[9] In this titration, the standard procedure was modified to permit a potentiometric determination of the end-point since the color of the crude product was sufficient to mask the normal end-point color. The amount of pyridinic base (as vinylpyridine) was obtained by a non-aqueous titration, using perchloric acid in glacial acetic acid solution.[10,11] The liquid products in the crude product were separated by fractional distillation in a semi-micro Podbielniak whirling band column after the high boiling tars had first been removed by an initial flash distillation at 15 mm. pressure. The fractions separated were: (i) b.p. 97.4° (760 mm.), (ii) b.p. 70–75° (20 mm.) and (iii) b.p. 81–85° (20 mm.). These were identified, on purification, as (i) propionitrile (observed: b.p. 97.4°, n^{25}_{D} 1.3645; lit. 97.1°, 1.3640); (ii) 2-vinylpyridine (observed: b.p. 70–75° (20 mm.) lit. 70–74° (20 mm.), mixed m.p. of picrate with vinylpyridine picrate gave no depression); (iii) 3-cyanocyclohexene (observed: b.p. 82.5–83.5° (20 mm.) n^{20}_{D} 1.4734; lit. 83° (20 mm.), 1.4736). Infrared absorption patterns were measured with a Perkin-Elmer recording spectrophotometer having a NaCl prism and a liquid cell thickness of 0.025 cm. In each case the close correspondence of the patterns with those for the authentic specimen confirmed the identification.

Reaction in the Homogeneous Gas Phase.—A two-hour run was made using an unpacked reactor to investigate the nature of the reactions in this system in the gas phase in this temperature range. Using acrylonitrile and butadiene in equimolar ratio, at 390°, and 6 sec. contact time, the material recovery as crude product (at −80°) was 99%. Analysis of the crude product for acrylonitrile established that 8 mole % was converted per pass. No vinylpyridine could be detected in the reaction products, but of the acrylonitrile converted, 77 mole % was accounted for as cyanocyclohexene.

Reaction over Cr_2O_3–Al_2O_3 Catalyst.—The reactions of acrylonitrile and butadiene over (a) the STD catalyst, (b) the HSA catalyst, and the thermal stability of acrylonitrile over the STD catalyst were investigated as follows: **Run (a)**.—The reaction conditions were: average temperature, 388°; contact time, 4.6 seconds; equimolar ratio of reactants in feed; duration of run, 6 hours; and STD catalyst (74.5 g., 56.6 cc. free space). Owing to the exothermic nature of the processes on the catalyst surface, a hot spot (70–75° rise in temperature) developed in the catalyst bed. The average bed temperature was obtained by graphical integration. The run was completed in three experiments of two hours each with a re-activation of the catalyst between each interval. Of the total input (271 g.), 94% was recovered (at −80°) as crude product for analysis, and the remainder as a gain in weight of the catalyst bed. The yields were calculated on the nitrile "converted" (*i.e.*, unrecovered) per pass through the hot zone. Analysis of the crude product established that the acrylonitrile conversion in this run was 40 mole %, and that the yields or cyanocyclohexene (10.8 g.) and vinylpyridine (1.23 g.) were 9.5 and 1.0 mole %, respectively, based on this conversion. A large amount of propionitrile (18.8 g.), equal to 32 mole % of the converted nitrile, was also found in the reaction product. **Run (b)**.—In this experiment the HSA catalyst rather than the STD catalyst was used. The reaction conditions were: average temperature, 438°; contact time, 4.0 sec.; equimolar ratio of reactants; duration of run, 2.0 hr., and 74.5 g. of catalyst, and total material input, 89.2 g. A considerably greater temperature rise (110°) was observed for the "hot spot," and the gain in weight of the catalyst bed was about four times as great as for the STD catalyst in run (i) for a two-hour period after re-activation. Of the material input, 76.4% was recovered as crude product (condensed at −80°), and 21.6% was accounted for as the gain in weight of the catalyst bed, the total material balance thus being 98 wt. %. Only 21 mole % of acrylonitrile was recovered unchanged from the crude product. Based on the acrylonitrile converted (79 mole %), the yields of cyanocyclohexene and vinylpyridine were 19 and 1.2 mole %, respectively. In addition, propionitrile (27 mole %) was again found in the product. **Run (c)**.—The object of this run was to observe the behavior of acrylonitrile at these temperatures. The reaction conditions were: average temperature. 370°; contact time, 4.6 sec.; equimolar ratio of acrylonitrile and nitrogen present in the feed; duration of run, 2.0 hours, STD catalyst, 74.5 g. During this run, the temperature rise (hot spot) was 50°. This hot spot required about ten minutes to pass through the catalyst bed. Of the total acrylonitrile input (47.4 g.), 87 wt. % was recovered as a clear colorless liquid, and 7 wt. % was accounted for as catalyst deposit. The refractive index of the liquid checked closely with that of pure acrylonitrile. This experiment was extended for a third hour, without re-activating the catalyst. No temperature rise in the catalyst bed was noted during this period. The catalyst bed did not gain further in weight, and 99 wt. % of the acrylonitrile input was recovered as a

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TABLE I

REACTION CONDITIONS, MATERIAL BALANCE AND YIELDS

		Input				Recovery				Yields, mole %		
Run	Catalyst	Temp., °C.	Contact time, sec.	Mole ratio, diene/nitrile	Total, g.	Liquid, g.	On catalyst	Total, wt. %	Nitrile mole. %, conversion	Cyano-cyclo-hexene	Vinyl-pyridine	Propio-nitrile
1	None	390	6.0	0.9	91.3	90.4	..	99	8.5	77	0.0	0.0
(a)	STD	388	4.6	1.0	270.6	253.5	17.7	100	40	9.5	1.0	32
(b)	HSA	438	4.0	0.9	89.2	68.1	19.2	98	79	19	1.2	27
(c)[a]	STD	370	4.6	1.0	47.4	41.2	3.3	94	..	..	...	..

[a] In this experiment the mole ratio refers to the nitrogen/acrylonitrile ratio.

clear colorless liquid product. An analysis by refractive index indicated that the liquid was essentially unchanged acrylonitrile. The thermal stability of acrylonitrile seems quite high under these conditions. Some decomposition occurs initially when a freshly activated catalyst is used. Butadiene likewise has been shown to have a good thermal stability.[12] In this temperature range vinylcyclohexene and ethylbenzene are formed when butadiene alone is passed over the Cr_2O_3-Al_2O_3 catalyst, the amount of ethylbenzene increasing with increasing reaction times.

The reaction conditions, material balance, and yields for the quantitative experiments are summarized in Table I.

Discussion

In the homogeneous gas phase at 400° and short contact time, acrylonitrile and butadiene formed cyanocyclohexene in good yields, and no detectable amounts of vinylpyridine. In the presence of the catalyst under similar conditions of contact time and temperature, vinylpyridine is formed as well as cyanocyclohexene. A third product, propionitrile, has also been obtained in appreciable amounts in the reaction over the catalyst. The latter may be accounted for by the hydrogenation of acrylonitrile occurring simultaneously with the cyclization reactions in this system. The hydrogen for this results from pyrolysis processes and aromatizations occurring on the catalyst at these temperatures. Further work is under way on the hydrogenation of acrylonitrile in the presence of these catalysts.

The addition of acrylonitrile to butadiene through the (C=C) and (C≡N) bonds would lead to the formation of cyanocyclohexene and vinylpyridine, respectively, as discussed earlier in this communication. The relative reactivity of these bonds in acrylonitrile can be predicted from thermodynamic and kinetic considerations. A measure of the thermodynamic feasibility of cyanocyclohexene formation (1) and vinylpyridine formation (2) is given by the free energy change for each reaction. This can be calculated at 650°K. from a knowledge of the heats of formation and entropies at 298°K., and the heat capacities for these compounds. For this purpose the thermodynamic data for cyanocyclohexene (ΔH^0_{298}, 30.9 kcal./mole; S^0_{298}, 89.7 e.u. and $C_p = 3.43 + 119 \times 10^{-3}T - 48.4 \times 10^{-6}T^2$) and vinylpyridine (40.3, 78.0, and $-6.01 + 114 \times 10^{-3}T - 45.5 \times 10^{-6}T^2$, respectively) were calculated by the method of group increments[13] from the data for methylcyclohexane[14] and methylpyridine.[15] Using these with the data for hydrogen[14] butadiene[16] and acrylonitrile,[17] the free energy changes for cyanocyclohexene and vinylpyridine formation from acrylonitrile and butadiene at 650°K. are −22 and −15 kcal./mole, respectively. These results refer to the ideal gaseous state and are necessarily qualitative in nature, but do show that both reactions are thermodynamically promising in this temperature range. In the homogeneous gas phase reaction at 400°, only cyanocyclohexene was formed.

Thus comparison of the experimental results (Run 1) and the free energy calculation suggest a kinetic control of the relative yields in the two reactions considered.

The relative rates for these two reactions would be given by the relation

$$k_1/k_2 = \exp.[(\Delta S^*_{12})/R - (\Delta E_{12})/RT]$$

if the rate controlling step in each reaction is the Diels–Alder step, *i.e.*, the cyclization. An estimate of the differences in energies of activation and entropies of activation (ΔE_{12} and ΔS^*_{12}, respectively) may be made from the kinetic rate data reported for acrolein and butadiene,[18] cyanogen and butadiene,[7] and butadiene dimerization,[19] in this temperature range. The reactivity of the C=C bond in acrylonitrile is quite comparable to the same group in acrolein,[6] but the C≡N bond is probably less reactive than the same bond in cyanogen.[7] Thus a value of −12 kcal./mole for ΔE_{12} seems reasonable. The value for ΔS^*_{12} is estimated as equal to the difference between the entropies of 3-cyanocyclohexene (96.0) and 2-vinyldihydropyridine (97.1) at 650°K. The latter values were calculated from S_{298} and heat capacities.[8]

These data in the above equation give the relative rates for the two reactions in question, k_1/k_2, as equal to 5800. In view of the assumptions necessary for these calculations, this result may be taken only as an indication that the formation of cyanocyclohexene is very much more rapid than vinylpyridine formation at these temperatures. The experimental results and the thermodynamic free energy calculations are in accord with the above, namely, that a kinetic control of the relative rates operates.

A measure of the relative activity of the (C=C) and (C≡N) groups of acrylonitrile in the presence of the catalyst is given by the ratio of the space-

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time-yields of cyanocyclohexene and vinylpyridine. The space-time-yield, defined in this instance in terms of millimoles of pyridinic product per hour per 100 cc. catalyst, is in the first approximation, a measure of the reaction rate. The space-time-yields for cyanocyclohexene and vinylpyridine in run (a) were 20 and 2.2, and run (b), 75 and 4.8, respectively. Thus with a freshly activated Cr_2O_3–Al_2O_3 catalyst, in the initial two-hour period, the $(C{=}C)$ group is only 9–15 times more reactive than the $(C{\equiv}N)$ group of acrylonitrile in the Diels–Alder reaction. The effect of the catalyst is to lower the energies of activations in these reactions. These results indicate a considerable preferential catalysis of the pyridinic cyclization reaction since the reactivity of the $(C{\equiv}N)$ group is much more nearly that of the $(C{=}C)$ group in the presence of the catalyst than in the homogeneous reaction.

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TROY, NEW YORK

[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, RESEARCH DIVISION, E. I. DU PONT DE NEMOURS AND COMPANY INC.]

Extensions of the Willgerodt Reaction. I

BY M. A. NAYLOR AND A. W. ANDERSON

RECEIVED MAY 25, 1953

The Willgerodt reaction has been successfully applied to certain olefins. Conditions giving high yields of propionamide and isobutyramide from propylene and isobutylene, respectively, are described. Butadiene and *n*-butylamine gave *n*-butyramide. Cyclohexene and vinylcyclohexene gave only tars. Under certain reaction conditions, polysulfides have been identified and are suggested as possible reaction intermediates.

Discussion

The Willgerodt reaction has been the subject of considerable laboratory work since its discovery in 1887.[1] The reaction generally involves treatment of an organic compound containing an appropriate functional group such as keto or hydroxyl, with ammonium polysulfide at elevated temperatures. Reaction results in the formation of amides containing the same carbon skeleton. Application of this reaction to aliphatic olefins and primary amines either has not been made or yields are too low to be of interest.[2]

From information in the literature, and certain work carried out in this Laboratory, it appeared that sulfur compounds were intermediates in the reaction and that compounds such as sulfides or polysulfides might be intermediates common to these reactions. Since it was known that H_2S along with organic sulfur derivatives formed when hydrocarbons were treated with sulfur and that sulfur compounds result from the action of sulfur or polysulfides on olefins, we felt that the Willgerodt reaction might be carried out on these materials.[3,4]

In attempting to carry out this reaction on propylene and isobutylene, it was found that under mild conditions (below 200°) considerable quantities of sulfuretted oils were formed. However, recycling such oils under more vigorous conditions (above 210–220°) resulted in their conversion to amide. The oils from isobutylene have been identified as mixtures of sulfides and polysulfides from which two fractions tentatively identified as diisobutyl disulfide and diisobutyl trisulfide (or mixture of isomers of these materials) have been separated. It appears that these materials may be intermediates in the reaction, particularly since we have shown them to be convertible to amides upon further processing.

We have found that, under appropriate conditions, propylene and isobutylene will react completely with aqueous ammonia and sulfur to give the corresponding amides in high yield. A complete list of the compounds examined with yields of products is given in Table I.

TABLE I

COMPOUNDS EXAMINED IN THE WILLGERODT REACTION

Compound	Product	Yield, %
Propylene	Propionamide	75
Isobutylene	Isobutyramide	70
Butadiene	*n*-Butyramide	10–20
Cyclohexene	Tar	...
Vinylcyclohexene	Tar	...
n-Butylamine	*n*-Butyramide	20

Although a number of modifications of the "ammonium polysulfide" reagent appear in the literature along with suggestions on the use of organic solvents in this reaction, it was found that appropriate mixtures of concentrated aqueous ammonia and elemental sulfur could be used quite satisfactorily. The use of specially prepared reagents was of no advantage in this work. It was

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