the 2α -acetate of 2.7%, and the 2β -acetate of 34.0%. Those from 6e-OTs were the olefin mixture of 57.1%, the 2α -acetate of 1.7%, and the 2β -acetate of 35.4%. Those from 7e-OTs were the olefin mixture of 58.1%, the 2α -acetate of 1.6%, and the 2β -acetate of 34.0%. Those from 11e-OTs were the olefin mixture of 55.2%, the 2α -acetate of 1.1%, and the 2β -acetate of 31.9%.

Registry No.—1e, 2529-06-8; 1e-OTs, 19124-24-4; 2e, 36284-21-6; 2e-OTs, 39003-14-0; 3e, 36126-50-8; 3e-OTs, 39003-16-2; 4e, 36407-90-6; 4e-OTs, 36126-60-0; 5e, 36126-54-2; 5e-OTs, 39062-17-4; 6e, 36126-58-6; 6e-OTs, 39010-18-9; 7e, 36284-22-7; 7e-OTs, 39010-20-3; 8e, 36126-73-5; 8e-OTs, 39010-22-5; 9e, 36126-63-3; 9e-OTs, 39010-24-7; 10c, 36126-75-7; 10e-OTs, 39010-26-9; 11e, 34824-00-5; 11e-OTs, 36126-61-1; p-toluenesulfonyl chloride, 98-59-9.

The Cycloaddition of Ethylene to Acrylonitrile

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The thermal and catalyzed cycloadditions of ethylene to an acrylonitrile were investigated experimentally and theoretically. At 300-345° and 1000 atm ethylene pressure, up to 30% conversion of acrylonitrile to cyclobutanecarbonitrile were obtained. The reaction reached equilibrium under these conditions. This was shown by obtaining the thermodynamic properties of cyclobutanecarbonitrile by spectroscopic means, and calculating the free-energy change for the reaction: $\Delta F^{\circ} = -21,500 + 45.52T$. Below 300° kinetic control occurred. A catalyst search revealed weak acceleration by nickel(0) compounds. This is the second example of cycloaddition of ethylene catalyzed by a transition metal.

In connection with work on the synthesis and polymerization of 1-bicyclobutanecarbonitrile,² the need arose for a ready synthesis of cyclobutanecarbonitrile as a possible intermediate. The cycloaddition of ethylene to acrylonitrile suggested itself as such a route.

$$\underbrace{\underbrace{}}_{\pm} \overset{\mathrm{CN}}{\to} \underbrace{\Box}_{\cdot} \overset{\mathrm{CN}}{\to} \underbrace{\Box}_{\bullet} \overset{\mathrm{CN}}{\to} \underbrace{\Box}_{\bullet} \overset{\mathrm{CN}}{\to} \underbrace{\Box}_{\bullet} \overset{\mathrm{CN}}{\to} \underbrace{\Box}_{\bullet} \overset{\mathrm{CN}}{\to} \underbrace{\Box}_{\bullet} \overset{\mathrm{CN}}{\to} \underbrace{\Box}_$$

Although this reaction has not been reported previously, cyclodimerization of each of these olefins to itself is known. Coyner and Hillman³ showed that acrylonitrile underwent cyclodimerization at 200° in 20% yield, and this reaction has subsequently received much attention in the patent literature.4-7 The biradical mechanism was ascribed to this reaction.³



Recently Back and coworkers⁸ carried out the thermal cyclodimerization of ethylene to cyclobutane. At

$$\overline{\pm} \rightarrow \square$$

 450° with a reaction time of 5-20 min, a 0.02% conversion to cyclobutane was achieved.

The results of our studies on the cycloaddition of ethylene to acrylonitrile form the basis of the present report.

- (1) Address correspondence to Department of Chemistry, University of Arizona, Tucson, Arizona 85721.
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- (3) E. C. Coyner and W. S. Hillman, J. Amer. Chem. Soc., 71, 324 (1949).
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Results

Thermal Cycloadditions .-- The reactions were carried out in stainless steel pressure vessels at elevated temperatures. It was found necessary to work at 300-345° to obtain significant conversions to cyclobutanecarbonitrile. Ethylene, at 1000 atm pressure, was used in large excess over acrylonitrile (17:1-30:1) to form the desired cycloaddition and to minimize the competing cyclodimerization of acrylonitrile. This pressure was about optimum; use of 3000 atm led to lower decomposition temperatures and tar formation.⁹ Polymer and tar formation were minimized by adding inhibitors. Best results below 300° were achieved with *p*-methoxyphenol or 2,6-di-*tert*-butylresorcinol; above 300° these inhibitors were used in conjunction with cupric salts. Addition of a little water⁶ to the reaction mixtures was also beneficial in minimizing tar formation. The results are summarized in Table I. There is considerable scatter owing to experimental difficulties. However, under best conditions, up to 30% of the acrylonitrile charged can be converted to cyclobutanecarbonitrile.

Calculation of Equilibrium Constants.-It was considered important to establish whether the observed yields were limited by equilibrium or by kinetic factors. To this end we calculated the free-energy change of the cycloaddition reaction as a function of temperature, using spectroscopic methods to determine the individual free energies.

The thermodynamic properties of ethylene¹⁰ and of acrylonitrile^{11,12} as functions of temperature were al-ready available. The heat of formation of cyclobutanecarbonitrile was also known.13 For the variation of

(11) F. Halverson, R. F. Stamm, and P. J. Whalen, J. Chem. Phys., 16, 808 (1948).

⁽⁹⁾ A referee has suggested that cycloadditions of acrylonitrile work best in the gas phase, and that the deleterious effect of increased pressure consists of increasing the amount of liquid phase.

⁽¹⁰⁾ National Bureau of Standards Circular 500 (1952).

⁽¹²⁾ H. L. Finke, J. F. Messerly, and S. S. Judd, J. Chem. Thermo., 4, 359 (1972).

⁽¹³⁾ H. K. Hall, Jr., and J. H. Baldt, J. Amer. Chem. Soc., 93, 140 (1971).

		THERMA	L CYCLOADI	DITION OF ETH	IYLENE TO AC	RYLONITRILE.	Experime	NTAL RESULT	rs ^a	
	Initial mmol of	Concn of				• . • •.				
Temp,	acrylo-	ethylene, moll -1	0.08 hr	0.17 hr	Cyclo 0 25 hr	0.5 hr	lie tound, mmo	2 hr	3 hr	4 hr
225	150	14.2	0.00 m	0.17 11	0.1-0.2	0.0			0 11	1
220	900	12.6			0.1-0.2			7-8		
200	300	12.2						(2 runs)		
210	000	10.0						2-7	1-13	3-11
								(4 runs)	(5 runs)	(2 runs)
300	150	13.0		9	3-8	5	9-21	11-14	(0 - 4	(=)
000	200			-	(2 runs)	-	(2 runs)	(3 runs)		
	300	13.0			13	7	5-11	6-36		
							(4 runs)	(4 runs)		
325	150	12.5		10 - 24	12 - 26	9-36	19	. ,		
				(8 runs)	(10 runs)	(17 runs)				
335	150	12.3		17-18						
				(2 runs)						
	300	12.3		14 - 47		20 - 65				
				(4 runs)		(27 runs)				
	600	12.3		20 - 82						

TABLE I THERMAL CYCLOADDITION OF ETHYLENE TO ACRYLONITRILE. EXPERIMENTAL RESULTS^a

^a Conditions: Pressure vessel volume, 0.4 l.; ethylene, 1000 atm pressure at reaction temperature (concentration calculated from gas density at given pressure and temperature); water, 2 ml, added to all runs to inhibit resin formation; inhibitors below 300°, 0.15 g of 2,5-di-*tert*-butylhydroquinone or of 2,6-di-*tert*-butylcatechol; inhibitors at or above 300°, same plus 0.15 g of cupric chloride, cupric acetate, cupric bromide, or cupric fluoroborate.

24

16 - 33

(3 runs)

(7 runs)

14-44

(13 runs)

thermodynamic properties of this compound with temperature, the fundamental frequencies were obtained from the work of Lord and Blackwell¹⁴ (Table II). The important ring-puckering vibration is given as a harmonic oscillator approximation in Table II. The actual potential function, obtained by far-infrared measurements, is given by Carreira and coworkers.¹⁵ and the energy levels are given in Blackwell's thesis.¹⁴ From the fundamental vibrational frequencies in Table II, the variation of thermodynamic properties with temperature was calculated.¹⁶ The harmonic oscillator approximation was used for all vibrations, for which the detailed energy levels were used. The thermodynamic properties are given as functions of temperature in Table III. Combination of the free energies leads to the free-energy change for the reaction of ethylene and acrylonitrile, $\Delta F_{\tau}^{\circ} = -21,500 + 45.52T$. The reaction is strongly favored at room temperature but is progressively disfavored at higher temperatures.

345

150

12.0

11 - 12

(2 runs)

Having this relationship, we were now able to calculate the equilibrium constants for our reaction conditions (see Experimental Section for details). Table IV compares the values found for the equilibrium constant with those calculated for various temperatures. Agreement above 300° is good considering the difficult nature of the experiments, and indicates that the equilibrium has been achieved. Support for this proposal is afforded by the independence of yield with time at these temperatures, although the variation from run to run makes this somewhat tenuous.

Also, under these conditions the reaction was shown to be reversible, by heating cyclobutanecarbonitrile at

- Ortonininini			JI CHOBO I MINDOMINIO CALIMINI
Type of	No. of con- tribu-	Funda- mental vibration frequency,	
vibrations	tions	cm -1	Description
A' (20)	1	138^a	Ring puckering ^a
	1	260	Ring-CN bending
	1	518	C–CN bending
	1	588	CH ₂ rocking
	1	719	CH ₂ rocking
	1	748	Ring deformation
	1	007	C CN at not a hing

TABLE II

FUNDAMENTAL VIBRATIONS FOR CYCLOBUTANECARBONITRILE

	r	000	OII2 TOOKINg
	1	719	CH_2 rocking
	1	748	Ring deformation
	1	887	C-CN stretching
	1	939	Ring breathing
	1	1046	Ring deformation
	1	1109	CH deformation (in plane)
	1	1250	CH ₂ twist
	1	1330	CH_2 wagging
	2	1449	CH ₂ deformation
	1	2239	CN stretch
	5	2950	CH_2 stretch
A'' (13)	1	176^{b}	Ring–CN bending
	1	480	C-CN bending
	1	673	CH ₂ rocking
	1	784	Ring deformation
	1	921	Ring deformation
	1	1109	CH deformation
	2	1212	CH ₂ twisting
	2	1250	CH_2 wagging
	1	1462	CH_2 deformation
	2	2998	CH stretch

^a Estimated from the observed far-infrared transitions as the harmonic frequency needed to represent the contribution of the ring-puckering vibration to the thermodynamic functions: R. C. Lord and C. S. Blackwell, unpublished results. ^b From far-infrared type B band (gas).

325° for 0.5 hr under 1000 atm pressure of ethylene. Acrylonitrile was present in the product, as established by gas chromatography.

⁽¹⁴⁾ C. S. Blackwell, Ph.D. Thesis, M. I. T., June 1971, Chapter 2; R. C. Lord, private communication.

⁽¹⁵⁾ C. S. Blackwell, L. A. Carreira, J. R. Durig, J. M. Karriker, and R. C. Lord, J. Chem. Phys., 56, 1707 (1972).

⁽¹⁶⁾ N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, pp 463-484.

TABLE III

THERMODYNAMIC PROPERTIES OF CYCLOBUTANECARBONITRILE⁴

Temp,	$H_T^\circ - E_0^\circ$	•	$F_T^\circ - E_0^\circ$			
۰ĸ	T	H_T°	T	F_T°	S°	$C_{\mathbf{p}}$
0	0	39.62	0	39.62	0	0
298, 2	13.22	43 , 56	-60.10	21.69	73.32	22.37
400	16.48	46.21	-64.43	13.84	80.92	29.53
500	19.70	49.47	-68.46	5.39	88.16	35.46
600	22.75	53.27	-72.32	-3.78	95.07	40.31
700	25.55	57.50	-76.04	-13.61	101.60	44.32
800	28.11	62.11	-79.63	-24.01	107.74	47.69

^a Assumptions: symmetry $C_{\rm s}$, $\sigma = 1$; electronic contributions negligible; all vibrations are harmonic oscillations except ring puckering, the energy levels for which are taken directly from Table I; ring puckering angle 30°. Parameters: $I_{\rm A} =$ 0.092132×10^{-37} g cm⁻²; $I_{\rm B} = 0.334808 \times 10^{-37}$ g cm⁻²; $I_{\rm C} =$ 0.376698×10^{-37} g cm⁻²; mol wt, 81.110.

TABLE IV

Compari Found I	son of Calc Equilibrium	CULATED AND	
ΔFt° kcal I nol-1	10 ² K _{calcd} , l. mol ⁻¹	$10^{2}K_{exptl},$ l. mol ⁻¹	Ratio of exptl/calcd
6.6	0.49	1	2.4
6.1	0.66	0.7	1.0
	0.66	0.8	1.3
	0.66	0.5	0.8
5.6	0.89	1	1.3
			Av 1.4 ± 0.4
4.5	1.9	0.5	0.27
	1.9	0.4	0.19
3.4	4.6	0.1	0.028
2.4	10	0.04	0.0039
1.2	30	0.006	0.00019
	COMPARI FOUND I ΔF_t° kcal I nol^{-1} 6.6 6.1 5.6 4.5 3.4 2.4 1.2	COMPARISON OF CALC FOUND EQUILIBRIUM ΔF_t° kcal $10^2 K_{calcd}$, nol ⁻¹ l. mol ⁻¹ 6.6 0.49 6.1 0.66 0.66 0.66 5.6 0.89 4.5 1.9 1.9 3.4 4.6 2.4 10 1.2 30	COMPARISON OF CALCULATED AND FOUND EQUILIBRIUM CONSTANTS ΔF_t° kcal $10^2 K_{calcd}$, $10^2 K_{exptl}$, nol ⁻¹ 1. mol ⁻¹ 1. mol ⁻¹ 6.6 0.49 6.1 0.66 0.66 0.8 0.66 0.5 5.6 0.89 4.5 1.9 0.4 3.4 2.4 10 0.006 0.04

At lower temperatures, however, where equilibrium considerations would give more cyclobutanecarbonitrile, less is actually obtained. This suggests kinetic control at these temperatures. This is supported by the fact that here the yields appear to increase with time.

Catalyzed Cycloadditions.-Our results for the thermal cycloaddition showed that, at temperatures where reasonable rates could be obtained, the equilibrium amount of cyclobutanecarbonitrile was very small. It was appropriate to look for a catalyst which, giving higher rates at lower temperatures, would allow us to use lower temperatures with accompanying higher equilibrium concentrations of the desired product. Many compounds were screened as potential catalysts. These scouting experiments were carried out under milder conditions than the shaker tubes used above, namely in sealed glass ampoules containing 1300 psi of ethylene at 250-275° for 2-4 hr. Under these conditions, no cyclobutanecarbonitrile was detectable in the absence of catalysts. Weak acceleration under these conditions was demonstrated for several organonickel complexes, including π -cyclopentadienylnickel carbonyl, nickelocene, and π -cyclopentadienyl 2,3-biscarbomethoxy- 2π , 5-norbornadien-7-ylnickel (Table V). Use of various solvents (THF, hexane, acetonitrile) decreased yields. The formation of cyclobutanecarbonitrile was not proved to be a truly catalytic process; perhaps it is a stoichiometric reaction of π -bonded acrylonitrile or ethylene. 1,2-Dicyanocyclobutane (acrylonitrile dimer) also formed in these reactions,



but we cannot say whether its formation was catalyzed or thermal (this compound was also noted in the thermal cycloadditions).

Discussion

Thermal Cycloaddition. — The cycloaddition of ethylene to acrylonitrile can be accomplished in modest yields. The conditions, involving 1000 atm of ethylene at 300–345°, cannot be described as convenient. Also, scrupulous precautions to avoid oxygen or adventitious initiators must be taken to avoid polymer and tar formation. Nevertheless, this cycloaddition does represent a synthesis of cyclobutanecarbonitrile from cheap starting materials.

The conversions are limited by equilibrium factors above 300°, as shown by the agreement for calculated equilibrium constants with those found and by the independence of yield with time. The thermodynamic equation for the section is very similar to that given by Back and coworkers⁸ for cyclobutane, $\Delta F^{\circ} = -19,030$ + 42.38*T*. The cyano group, therefore, does not change the equilibrium position to any great extent.

This is not true, however, for the rates. Back and coworkers worked at $450-513^{\circ}$ to obtain reasonable rates of cyclodimerization of ethylene. Our reaction proceeds at $300-345^{\circ}$, consistent with stabilization of the biradical intermediate by one cyano group. Stabilization by two cyano groups, in the cyclodimerization of acrylonitrile, permits a further lowering of reaction temperature to $200-240^{\circ}$ with an accompanying greater equilibrium conversion to cyclodimer.¹⁷

Catalyzed Cycloaddition.—The possibility of metalcatalyzed cycloaddition of two olefins has been much discussed lately (for recent reviews, see ref 18). Experimental examples, however, have been limited until recently to strained olefins such as norbornene, norbornadiene, and 1-methylcyclopropene, and to conjugated dienes such as butadiene. Very recently, however, Cannell¹⁹ showed that ethylene cycloadds to butadiene under the influence of tetrabenzyltitanium and related soluble titanium catalysts. Our discovery



of weak catalysis by nickel(0) compounds is the second example of the catalysis of an ethylene cycloaddition.

⁽¹⁷⁾ Reports from several laboratories⁵⁻⁷ agree that at 240-250° for 4 hr a 13-15% yield is obtained. At 200° a 5% yield is obtained in this time,⁸ but this is undoubtedly kinetically controlled.

⁽¹⁸⁾ For recent reviews, see (a) W. Keim in "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971, pp 59-91; (b) F. D. Mango and J. H. Schachtschneider, *ibid.*, pp 223-295.

⁽¹⁹⁾ L. G. Cannell, J. Amer. Chem. Soc., 94, 6867 (1972).

TABLE	V-
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"CATALYSIS" OF CYCLOBUTANECARBONITRILE FORMATION^a

		UNITED IS IS	OF OF CHODOF	THORE OF THE		•	
Tube volume, ml	Acrylo- nitrile, ml	Catalyst	Temp, °C	Time, hr	Cyclobutane- carbonitrile, mmol	1,2-Dicyano- cyclobutane, mmol	Polymer
400	60	$(C_5H_5)_2Ni$	250	2	5	24	Moderate
400	60	$(C_5H_5)_2Ni$	250	4	8	28	Moderate
400	60	3	250	2	6-8	21 - 54	Moderate
400	30	$(C_5H_5)_2Ni$	275	2	7	5	Moderate
- C - 111	1000	halana wa nalamanti (1 m of catalmat				

^a Conditions: 1000 atm of ethylene, no solvent, 0.1 g of catalyst.

Experimental Section

Raman spectra were determined on a Cary Model 81 instrument equipped with a helium-neon laser. Thermodynamic properties were calculated using the formulas given by Colthup, *et al.*¹⁶ The computer programs gave good agreement with test compounds from the literature.²⁰

Pressure Tube Procedure (Table V).—A 400-ml, stainless steel shaker tube was flushed with nitrogen and the catalyst candidate or inhibitor was loaded under a stream of nitrogen. The tube was closed, cooled in Dry Ice-acetone and acetone, and alternately evacuated and flushed with nitrogen five times. A loading vessel charged with acrylonitrile and solvent was then connected to the evacuated tube and the acrylonitrile and solvent were transferred under vacuum. The tube was closed and filled with the desired amount of ethylene. After heating for the specified period of time, the tube was cooled in Dry Ice-acetone and the excess ethylene was vented very slowly through a gas trap cooled in Dry Ice-acetone. After the ethylene was vented, the contents were poured into a bottle and the tube was rinsed thoroughly with 20 ml of toluene. The rinse was placed in a separate bottle. The product mixture was flash distilled under reduced pressure into a gas trap cooled in liquid nitrogen until no further volatile material condensed. The polymer residue was analyzed for N. A small amount of tetramethylene sulfone was added to the distillate and rinse as an internal gc standard. The liquid samples were analyzed for acrylonitrile, cyclobutane-carbonitrile, 1,2-cyclobutanedicarbonitrile, and 2-methylene-glutaronitrile by gas chromatography. The gc column, used at 150° for the first two and 225° for the latter two, was a 6 ft \times 0.25 in. stainless steel column packed with 20% silicone gum nitrile (XE-60) on 60/80 Chrom P; flow rate of 30 cc/min He.

The shaker tubes were conditioned by boiling them with dimethylformamide and drying under nitrogen.

Carius Tube Procedure (Table V).-The reaction vessel was a 60-ml heavy-walled glass Carius tube. The metal complex or catalyst candidate was placed in a drybox if the sample was air or moisture sensitive. The tube was connected with gum-rubber tubing to a glass three-way stopcock, which was connected to a vacuum pump and to a 2.25-1. stainless steel cylinder. The cylinder (which had been alternatively evacuated and filled with ethylene five times to remove oxygen) in turn was connected to a source of reagent grade ethylene. The Carius tube was evacuated to less than 0.1 mm pressure and then cooled in liquid N_2 . The 2.25-1. cylinder was filled with the desired amount of ethylene (as indicated by a pressure gauge). The desired amount of acrylonitrile (Matheson Coleman and Bell Chromatoquality, purged with argon and dried over molecular sieves, Type 3A) was delivered into the tube with a hypodermic syringe through the rubber tubing connecting the tube to the stopcock (the tube leading to the pump was clamped off). The stopcock was then opened, allowing the ethylene to condense into the tube. Excess ethylene which had not condensed was pumped off. The tube was sealed and heated for 16 hr at $150-275^{\circ}$ in a shielded oven. The tube was then cooled in liquid nitrogen and connected by means of a piece of gum-rubber tubing to a source of positive nitrogen. The glass tip of the tube was broken, and the excess ethylene was allowed to evaporate. The residual product was removed and analyzed by gc.

The column used was 21-in., 10% butanediol succinate on 60-80 Gas-Chrom Z. The column temperature was programmed for 100° (3 min) to 200° at 15° /min with a flow rate of 10 cc/6.5

in. Peak area ratios were translated into moles of acrylonitrile, and cyclobutanemono- or dicarbonitrile by the following formulas (TMS = tetramethylene sulfone, AN = acrylonitrile, CBN = cyclobutanecarbonitrile, DCN = 1,2-cyclobutanedicarbonitrile).

mmol of AN	= mmol o	$f TMS(2,0) \frac{\text{peak area AN}}{1}$
		peak area TMS
mmol of CBN	= mmol o	f TMS(1.26) peak area CBN
		peak area TMS
mmol of DCN	= mmol c	of TMS(1.01) peak area DCN
		peak area TMS

The conversion factors were determined by making up standard solutions with known amounts of AN and the cyclobutanecarbonitriles as well as TMS.

Calculations.—The results of Table I were converted to equilibrium constants as follows

$$K_{\text{exp}} = \frac{a_{\text{CBN}}}{a_{\text{AN}}a_{\text{E}}} = \frac{\gamma_{\text{CBN}}c_{\text{CMN}}}{\gamma_{\text{AN}}c_{\text{AN}}c_{\text{E}}}$$

where CBN = cyclobutanecarbonitrile, AN = acrylonitrile, E = ethylene, c's are concentrations, and a's are activities. The activity coefficients of the two nitriles are expected to be approximately equal and were cancelled. The activity coefficient of ethylene, $\gamma_{\rm E}$, can be obtained by comparing the observed pressure to that calculated from the perfect gas law. Over the temperature ranges under consideration it had the value 1.66 ± 0.03 . The values of $c_{\rm E}$ were obtained from the known gas densities, the pressure vessel volume, and the molecular weight of ethylene. Therefore

$$K_{exp} = \frac{\text{mmol CBN}_{t}}{(\text{mmol AN}_{0} - \text{mmol CBN}_{t}) \cdot 1.66c_{\text{E}}}$$

The sources of error in this treatment include the loss of AN through dimerization and resin formation.

A brief attempt was made to calculate the equilibrium constant as the ratio of the rates of the forward and back reactions. The former were calculated for the runs at 225 and 250°. The latter were obtained by extrapolation of the reported thermolysis rates of cyclobutanecarbonitrile at much higher temperatures.²¹ Agreement of the equilibrium constant obtained in this way with that calculated from thermodynamics was poor. However, the great difference in conditions under which the two rate constants were obtained ($k_{\rm forward}$ at 225° in 1000 atm of supercritical ethylene; $k_{\rm reverse}$ at 1 atm at 500°) is doubtless responsible.

Registry No.—Ethylene, 74-85-1; acrylonitrile, 107-13-1; cyclobutanecarbonitrile, 4426-11-3.

Acknowledgments.—We are deeply indebted to Miss Ellen Wallace for the laser Raman middle-infrared spectra; to Mrs. Ann Alexander of the Engineering Department for the computer programs for the thermodynamic properties; to the personnel of the Pressure Research Laboratory for endless pressure runs; to Drs. E. Bromels and S. C. Cherkofsky for helpful discussions; and to Professor R. C. Lord of the Massachusetts Institute of Technology, without whose invaluable assistance, patient encouragement, and contribution of data (together with Dr. C. S. Blackwell) this work could not have been performed.

^{(20) (}a) Spiropentane: D. W. Scott, H. L. Finke, W. N. Hubbard, and J. P. McCullough, *J. Amer. Chem. Soc.*, **72**, 4668 (1950). (b) Chloroform: ref 16. (c) Ethylene: G. J. Janz, "Thermodynamic Properties of Organic Compounds," Academic Press, New York, N. Y., 1967, p 26. (d) Trifluoro-acetonitrile: *ibid.*, p 22.

⁽²¹⁾ S. Sarner, D. M. Gale, and A. B. Richmond, J. Phys. Chem., 76, 2817 (1972).