

the flask. The top of the condenser was attached to a gas buret through a three-way stopcock by means of flexible rubber tubing. All stopcocks and joints were lubricated with Dow-Corning silicone grease. The system was often checked for leaks by pressuring it with carbon dioxide, but always found to be satisfactory.

The reaction vessel was constantly agitated during the course of a kinetic experiment by a shaking device attached to the reaction flask.

The constant temperature bath consisted of a stainless steel beaker (9 × 6.5 in.), filled with Fisher bath wax, and inserted into a metal can (12 × 9 in.), with the space between the vessels packed with insulating material. The wax was heated to within 10–20° of the desired temperature by means of a 750 watt immersion heater. Final temperature control was maintained by means of a vapor pressure type thermostat, attached to a 125-watt knife blade heater through a relay. The shaking motion of the reaction flask in the wax bath was sufficient to provide adequate circulation, since temperature control to within 0.2° could generally be maintained during an experiment.

A kinetic measurement was preceded by cleaning of the reaction flask. At the beginning stages of the work, sulfuric acid-dichromate was used, but it was found that hot caustic was equivalent to the acid wash as far as the effect on the rates was concerned. In either case, the flask was repeatedly rinsed with distilled water and acetone, and dried overnight at 120°. Glass wool was placed in the reaction flask and the latter inserted into the constant temperature bath and attached to the condenser. The entire apparatus was flushed with carbon dioxide, which was dried by passing it through

Drierite. The solvent to be used in the experiment was thoroughly saturated with carbon dioxide at room temperature, then injected into the reaction flask by means of a syringe. The shaker was started, and the system equilibrated for approximately 1 hr. In order to start a kinetic measurement, a weighed sample of the carboxylic-carbonic anhydride was injected into the solvent in the reaction flask through the stopcock, the opening of which was protected from the atmosphere by a rubber diaphragm. After the addition of sample, which generally took less than 30 sec., the shaker was started, and readings of carbon dioxide evolution were taken at appropriate time intervals, depending on the speed of the particular decomposition. A shield surrounding the gas buret was effective in keeping its temperature fairly constant. The decomposition was allowed to continue until a constant volume of gas was evolved, and this was taken as V_{∞} . Each volume was corrected to volume at STP and a plot of $\log(V_{\infty} - V)$ versus time was made.

In the catalyzed decompositions, the catalyst was added to the solvent before the latter was saturated with carbon dioxide, or if insoluble, it was placed in the reaction flask.

When hydrogen chloride was used as catalyst, a small quantity was bubbled into dibutyl carbitol, and its concentration determined by titration with standard sodium hydroxide, using 95% ethanol as solvent. The end-point was determined with a pH meter. Solutions with a desired concentration of hydrogen chloride were made up by dilution of this stock solution with pure dibutyl carbitol, and the concentrations were always checked by titration.

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Trifluoroacetonitrile Addition Reactions. I. Ethylene

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It is shown that trifluoroacetonitrile reacts readily with ethylene in the homogeneous gas phase at moderately high temperatures (300°–500°) with the formation of 4,4,4-trifluorobutyronitrile when the reactants are mixed in equimolar ratio at atmospheric pressure. Some evidence for the formation of another product, most likely 4,4,4-trifluorocapronitrile in smaller amounts is reported. Equilibrium yields of 4,4,4-trifluorobutyronitrile as predicted from thermodynamics are apparently readily attained at 400°, *i.e.* thermodynamic control can be achieved.

In the preceding communications in this series the reactions of simple dienes with trifluoroacetonitrile have been described. The nitrile group exhibited dienophilic properties with the facile formation of 2-trifluoromethyl-substituted pyridines at atmospheric pressure and moderately high temperatures (350°–520°). The present paper is the first in a series describing the results of similar studies of the reactions of simple olefins and acetylenes with trifluoroacetonitrile in this laboratory. The thermal addition of trifluoroacetonitrile to ethylene, and the thermodynamics of the process are reported.

EXPERIMENTAL

Chemicals. The trifluoroacetonitrile (b.p. –68°) was a commercial sample (Columbia Organic Chemicals) of mini-

mum 95% purity. The ethylene (b.p. –104°) was a commercial C.P. grade sample (Matheson Co.). Portions of both chemicals were repeatedly redistilled by vacuum transfer techniques to remove dissolved air and other noncondensable gases before use in the experiments.

Apparatus and procedure. A static system was used, since an interest was to explore the thermal stabilities of the reactants, and the possibility of thermodynamic control for the addition reaction. Vacuum transfer techniques were used in an all glass system as illustrated in Fig. 1. Predetermined amounts of the reactants (sufficient to give a pressure of about 1 atm. initially at the reaction temperature) were transferred from the ampoules (B) to the storage trap (A). The 5-l. reaction vessel (J) was attached in place of one of the ampoules by its side arm to the manifold, evacuated, filled with the reactants from the trap, and sealed off with a torch after the reaction charge had been frozen (–195°) into the small finger type trap. The flask J was then positioned in the furnace and resealed to the vacuum manifold as shown in Fig. 1. The reaction temperature was monitored by two chromel-alumel thermocouples. On completion of an experiment the contents of the flask J were transferred to a cold trap E (–195°) and J was removed from the system. The nature of the product mixture in E was investigated by the conventional techniques as described below.

(1) G. J. Janz and M. A. De Crescente, *J. Org. Chem.* **23**, 765 (1958); J. M. S. Jarvie, W. E. Fitzgerald, and G. J. Janz, *J. Am. Chem. Soc.* **78**, 978 (1956).

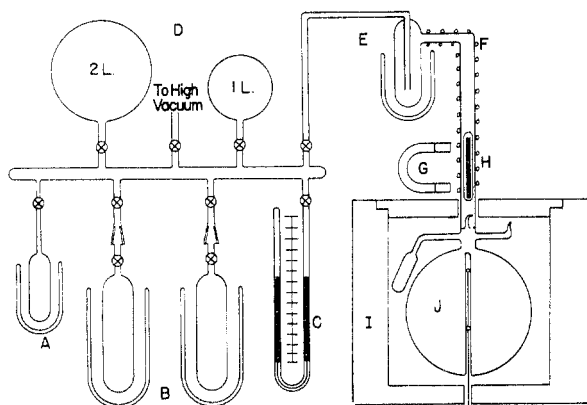


Fig. 1. Static system. A, Liquid nitrogen degassing trap. B, Input assembly. C, Closed-end Hg manometer. D, Calibrated storage volume. E, Liquid nitrogen freeze-out trap. F, Heating tape. G, Permanent magnet. H, Metal-in-glass hammer for breaker seal. I, Electric furnace. J, Reaction chamber

RESULTS

Thermal stability of pure reactants. The pyrolysis of ethylene is so well-known² that only a limited number of experiments were undertaken to investigate its rate of pyrolysis in the temperature range of this investigation (350°–450°). No data for trifluoroacetonitrile were known and a similar series of experiments was undertaken, the temperature range being extended to 550°. The results of these experiments may be briefly summarized as follows. Under the conditions of the experiments—*i.e.*, degassed samples, clean vessels—no appreciable pyrolysis of ethylene was observed at 400° (ethylene recovery, 99 mole %) but the presence of methane and hydrogen was detected in the products at 450°C (ethylene recovery, 75 mole %). For the trifluoroacetonitrile experiments, no traces of hexafluoroethane or cyanogen were detected in the pyrolysis products even at 550°. The gas chromatograms indicated that the limited pyrolysis corresponded to removal of the impurities in the commercial trifluoroacetonitrile (most probably trifluoroacetic acid or the amide). After twenty hours at 550°, 450°, and 400° respectively, 98.5, 99.0, and 100 mole % respectively of the initial trifluoroacetonitrile were recovered unchanged.

Addition reaction. The results for a series of experiments for equimolar mixtures of trifluoroacetonitrile and ethylene for the temperature range 350°–450° are summarized in Table I. It is significant that both reactants are gaseous at room temperature so that the liquid product must be attributed to an addition reaction or, less probably, to a selfpolymerization of one of the reactants. The evidence from the thermal stabilities of the reactants, and from the exact correspondence of the conversions of each reactant at 350° is strong sup-

port for an addition reaction. The fact that the trifluoroacetonitrile conversion does not exceed 60% at 400° suggests the possibility of thermodynamic control. The correspondingly higher conversions of ethylene may be understood in the light of a more complex process at 400° with the formation of additional products having more than one ethylene per mole of trifluoroacetonitrile as a possibility. The significance of the values calculated for K_p in the last column of Table I is discussed later.

Identification of products. The unchanged trifluoroacetonitrile and ethylene were quantitatively analyzed by gas chromatography. The liquids from the experiments all at 400° ± 3° were combined for distillation analysis. The gas chromatograph of this mixture indicated two main components, one in large excess, being present, and a number of minor peaks indicating some components of less extensive simultaneous reactions. Distillation in a semimicro Podbielniak apparatus separated two fractions, one low boiling (b.p. 139°–140°/760 mm.) and the other higher boiling (b.p. 197°–198°/760 mm.) in the approximate weight ratio of 8:1 respectively and which, within the limits of the technique, composed 90–95% of the unrefined liquid mixture.

(i) The lower boiling liquid product was identified as 4,4,4-trifluorobutyronitrile.

Anal. Calcd. for $C_4H_4F_3N$: H, 3.3; N, 11.4; F, 46.3. Found: H, 3.44, 3.48; N, 11.30, 11.07; F, 45.55, 45.83.

An aliquot was hydrolyzed in methanolic sodium hydroxide yielding an acid shown to be 4,4,4-trifluorobutyric acid (I. R. spectra, b.p. 162° lit. 166°).³ The physical properties and infrared spectrum for 4,4,4-trifluorobutyronitrile have not been reported previously and were observed as follows: n_D^{25} , 1.565; d_4^{25} , 1.21 g./ml.; infrared spectrum (Perkin-Elmer Model 21; sodium chloride region) shows clearly that absorption at 2280 cm^{-1} confirms the nitrile group (*cf.* perfluoronitriles⁴ 2275 ± cm^{-1} , it is slightly shifted from the 2240–2260 region characteristic of aliphatic mono- and dinitriles⁵). Bands at 1309, 1180, and 1142 cm^{-1} are in accord with the literature values,⁶ 1321 ± 9, 1179 ± 7, and 1140 ± 9 cm^{-1} for the symmetrical and antisymmetrical deformation modes of CF_3 . The bands, 1230–1287 cm^{-1} and at 3000 cm^{-1} are in the regions for C—F and C—H stretching modes⁷ respectively. The infrared spec-

(3) E. T. McBee *et al.*, *J. Am. Chem. Soc.* **70**, 2910 (1948); **76**, 3722 (1954).

(4) D. G. Weiblen, *Fluorine Chemistry*, Vol. 2, Academic Press Inc., New York, 1954.

(5) R. E. Kiston and N. E. Griffith, *Anal. Chem.* **24**, 334 (1952).

(6) R. R. Randle and D. M. Whiffen, *J. Chem. Soc.* 1371 (1955).

(7) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1958.

(2) C. D. Hurd, *The Pyrolysis of Carbon Compounds*, Chem. Cat. Co., New York (1929).

TABLE I
 TRIFLUOROACETONITRILE-ETHYLENE ADDITION REACTION

Temp.	Time, hr.	C ₂ H ₄			CF ₃ CN			Liquid ^a Product (Total) (g.)	K _p (expt.)
		In (moles)	Out (moles)	Conversion (mole %)	In (moles)	Out (moles)	Conversion (mole %)		
348	20.3	0.0490	0.0460	6.12	0.0475	0.0446	6.12	0.359	0.03
366 ^b	89.0	0.0440	—	—	0.0455	—	—	1.98	0.4
397	25.0	0.0491	0.0105	79.0	0.0475	0.0446	50.1	3.03	0.7
399	20.3	0.0486	0.0145	70.5	0.0481	0.0232	51.6	3.68	1.0
400	92.0	0.0501	0.0	100	0.0503	0.0205	59.5	3.41	1.2
401	48.0	0.0496	0.0	100	0.0499	0.02063	58.5	3.59	1.3
401	67.5	0.0503	0.0	100	0.0503	0.0232	54.2	3.34	0.9
499	46.2	0.0451	0.0	100	0.0451	0.0149	66.5	3.60	—

^a Liquid at 25° and 1 atm. pressure. ^b Trifluoroacetonitrile was prepyrolyzed at 550° for this experiment.

trum, within the limits of the preceding analysis, is in support of the structure 4,4,4-trifluorobutyronitrile for the addition product (b.p. 140°). An NMR spectrogram relative to fluorine showed only a triplet, identifying all the fluorine atoms as equivalent, in this structure. An alternate structure 2,4,4-trifluorobutyronitrile thus is seen as most improbable. Additional support for the structure 4,4,4-trifluorobutyronitrile for this product is seen in the NMR spectrum which showed a high order splitting of the proton resonance, due to the perturbation of the trifluoromethyl and nitrile groups in the sample, these groups being quite similar in electronegativity. In the alternate structure this would not be expected as the groups FCH₂ and CF₂CN differ considerably in electronegativity and the protons are no longer all equivalent.

(ii) The higher boiling product (b.p. 190°), gained in much smaller amounts under the present conditions of reaction, has not been investigated at present except to note that the infrared spectrum showed the frequencies characteristic of CN, CF₃, and CH₂ as in the preceding compound, and that the NMR spectrum confirmed that all fluorine atoms were equivalent and, in addition, that the protons were in a more aliphatic environment, *i.e.*, less perturbed, in comparison with the results for 4,4,4-trifluorobutyronitrile. The results are in accord with the identification of this product as CF₃(CH₂)_nCN, where $n > 2$. Comparison of the boiling point range with those of related aliphatic nitriles shows that its boiling point (190°) is as would be predicted for $n = 4$, *i.e.*, 6,6,6-trifluorocapronitrile. The product has not been investigated further.

Thermodynamic considerations. In view of the experimental results at 400° relative to the conversions of trifluoroacetonitrile, an estimate of the thermodynamics for the simple addition reaction



seemed of interest to evaluate the yields relative to thermodynamic control for the overall process.

The standard free energy change for the reaction is readily obtained from the expression:

$$\Delta F_T^\circ = \sum_{p-r} \Delta(F^\circ - H_0^\circ)_T + \Delta H_0^\circ \quad (2)$$

where \sum_{p-r} expresses the differences in the summation function for the products and the reactants, and ΔH_0° is evaluated from the relation:

$$\Delta H_0^\circ = - \sum_{p-r} \Delta(H^\circ - H_0^\circ)_{298} + \Delta H_{298}^\circ \quad (3)$$

in which ΔH_{298}° is the heat of reaction at 25° and must be known or calculated from heat of formation data. A summary of the necessary thermodynamic data over the temperature range 350°–550° is given in Table II. Relative to the estimates of data in Table II, it is sufficient to note that the thermodynamic functions for 4,4,4-trifluorobutyronitrile were calculated by the method⁸ of group equations and a knowledge of the data for propane,⁹ *n*-pentane,⁹ and trifluoroacetonitrile.¹⁰ The values for the heats of formation for trifluoroacetonitrile and 4,4,4-trifluorobutyronitrile were similarly calculated by the principle of additivity⁸ using the values for acetonitrile¹¹ and propane,⁹ and *n*-pentane⁹ as parents and the recently reported¹² precise values of 46.5 kcal./mole for the difference in the bond energies $E(\text{RCF}_3 - \text{RCH}_3)$ where R is any hydrocarbon group. The values in Table II are reported to more significant figures than the data for the parent compounds can justify for the sake of internal consistency in the equilibrium calculations. Since ΔF° is directly propor-

(8) G. J. Janz, *Estimation of Thermodynamic Properties of Organic Compounds*, Academic Press Inc., New York, 1958.

(9) F. D. Rossini, *et al.*, Ed., *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, Pa., 1953.

(10) G. J. Janz and S. C. Wait, Jr., *J. Chem. Phys.* **26**, 1766 (1957).

(11) N. S. Kharasch, *Bur. Standards J. Research* **2**, 359 (1929).

(12) W. D. Good, D. R. Douslin, D. W. Scott, A. George, J. L. Lacina, J. P. Dawson, and G. Waddington, *J. Phys. Chem.* **63**, 1133 (1959).

TABLE II
THERMODYNAMIC DATA FOR PREDICTION OF K_p IN THE TRIFLUOROACETONITRILE-ETHYLENE ADDITION REACTION

Substance		C_2H_4		CF_3CN		$CF_3CH_2CH_2CN$		\sum_{p-r}
Function	Temp.	kcal./mole	Ref.	kcal./mole	Ref.	kcal./mole	Ref.	(kcal./mole)
ΔH_f°	298.1°K	12.50	^a	-126.7	^b	-136.9	^b	-22.70
$\frac{(F^\circ - H_0^\circ)}{T}$	600°K	50.70	^a	69.15	^c	87.18	^b	19.60
	800°K	54.19		74.54		96.11		26.10
$\frac{(H^\circ - H_0^\circ)}{T}$	298.1	8.47	^a	12.68	^c	19.78	^b	-1.37

^a See ref. 9. ^b Estimated, this work. ^c See ref. 10.

tional to the absolute temperature, the values over the temperature range of the experiments are readily gained by interpolation, and from the well known expression:

$$\Delta F^\circ = -RT \ln K_p \quad (4)$$

the following values for equilibrium constant are predicted for the formation of trifluorobutyronitrile by the trifluoroacetonitrile-ethylene addition reaction:

T	350°	400°	450°
K_p (theor.)	4.8	1.2	0.4

These are to be compared with the values in Table I from the experimental data and the expression:

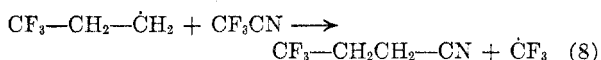
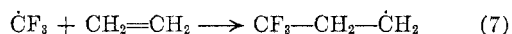
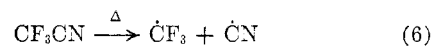
$$K_p = \frac{1}{RT} \frac{C_3}{C_1 C_2} \quad (5)$$

where C_1 , C_2 and C_3 are the concentrations (moles/l) of trifluoroacetonitrile, ethylene and 4,4,4-trifluorobutyronitrile at equilibrium. For this purpose it was assumed as a first approximation that the liquid was entirely 4,4,4-trifluorobutyronitrile and that the equilibrium conversion of ethylene was equal to that for trifluoroacetonitrile as the reactants contribute in this ratio to the formation of the above product. The conversions at 348° (Table I) clearly support the latter assumption. Comparison shows that thermodynamic control, *i.e.*, equilibrium yields, can be attained readily at 400°, whereas at 350° the reaction is under kinetic control even after reaction times of ninety hours. The results should be interpreted qualitatively rather than quantitatively in view of the estimates necessary for the theoretical calculations and the assumptions in the treatment of the experimental data. Indirect support for the assumption that 4,4,4-trifluorobutyronitrile is in large part the only addition product at 350°-400° is seen in the close agreement with the theoretically predicted K_p values at 400°.

DISCUSSION

The salient results may be briefly restated in that it has been shown that trifluoroacetonitrile reacts readily with ethylene in the homogeneous gas phase at moderately high temperatures (300°-500°) with the formation of 4,4,4-trifluorobutyro-

nitrile as the main product when the reactants are mixed in equimolar ratio at atmospheric pressure. Some evidence for the formation of another product in smaller amounts, *i.e.*, 6,6,6-trifluorocapronitrile was noted. Equilibrium yields predicted from thermodynamics can apparently be readily attained at 400°, *i.e.*, thermodynamic control can be achieved. The experiments do not lend themselves to kinetic interpretation but some speculation on the mechanism is of interest and possible by analogy with related addition processes. A close correspondence in the reactivities of trifluoroacetonitrile and cyanogen in the gas phase with 1,3-dienes at moderately high temperatures has been demonstrated elsewhere.¹ That incipient formation of free trifluoromethyl radicals may occur from trifluoroacetonitrile by simple thermal dissociation or a suitable trace catalyst seems probable as this is known for cyanogen.¹³ The reaction may thus be understood by a mechanism rather similar to the free radical addition of hydrogen bromide to olefins,¹⁴ *i.e.*:



with termination steps which need not be detailed for the present. The investigations are being extended to gain an insight on the nature of the reaction mechanism and the possible role of trifluoroacetonitrile as a telogen¹⁵ as distinct from the thermodynamics of the overall process.

Acknowledgment. This work was made possible in part by fellowship grant support from the Monsanto Chemical Company and Union Carbide Chemical Company. Dr. C. M. Huggins (General Electric Company) is thanked for information on the NMR spectra reported in this work. The experimental contributions of C. A. Wahl and W. J. Leahy are gratefully acknowledged.

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(14) C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, 1957.

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