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Kinetics and Mechanism of the Free-Radical Addition of Trifluoroacetonitrile to Ethylene¹

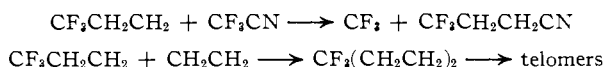
BY N. A. GAC AND G. J. JANZ

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A kinetic study is reported for the free-radical addition of CF_3CN to CH_2CH_2 at 442° and atmospheric pressure. The reaction is an example of the general class of telomerization reactions. An average chain length of about 300 is observed when kinetic control is such that $\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}$ is the predominant product. The cross-combination ratio for the CF_3 and $\text{CF}_3\text{CH}_2\text{CH}_2$ termination reactions is $2.2 + 0.5$. The recombination of CF_3 radicals does not become the exclusively controlling termination process until the $\text{CF}_3\text{CN}:\text{CH}_2\text{CH}_2$ ratio approaches $10^5:1.0$. The limiting form of the rate equation is found to be $d[\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}]/dt = 38.7 \times 10^{-8}[\text{C}_2\text{H}_4][\text{CF}_3\text{CN}]^{1/2}$.

Introduction

Thermally initiated addition reactions of CF_3CN with monoolefins are being investigated in this laboratory.²⁻⁵ For example, the formation of 4,4,4-trifluorobutyronitrile ($\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}$), with some 6,6,6-trifluorocapronitrile ($\text{CF}_3(\text{CH}_2)_4\text{CN}$) in smaller amounts, is observed^{2,3} when CF_3CN and C_2H_4 are heated at 400° and normal pressures. The rate of reaction is clearly diminished by addition of small amounts of an inhibitor, NO (see ref. 3), and promoted by an initiator, $(\text{CH}_2)_2\text{O}$ (see Discussion). From a limited study of the temperature dependence of the rate for this system, in the range $350\text{--}450^\circ$, an estimate of the energy of activation for the formation of $\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}$ has been advanced.³ The over-all rate was approximately $3/2$ order, but the kinetic data were insufficient to characterize the details of the reaction mechanism. The appearance of the 2:1 stoichiometric compounds in the products is suggestive of a gas-phase, free-radical, telomerization process. The gas chromatographic results showed that the formation of $\text{CF}_3(\text{CH}_2\text{CH}_2)_2\text{CN}$ relative to $\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}$ decreased as the $\text{C}_2\text{H}_4:\text{CF}_3\text{CN}$ reactant ratio decreased. This was understood as a competition between reactions such as



The generalized mechanism for this class of reactions⁶

(1) Abstracted in part from the thesis submitted by N. A. G. in partial fulfillment of the requirements for the Ph.D. degree, Rensselaer Polytechnic Institute, Jan., 1964.

(2) G. J. Janz and J. J. Stratta, *J. Org. Chem.*, **26**, 2169 (1961).

(3) J. J. Stratta, Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, N. Y., 1961.

(4) W. J. Leahy, Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, N. Y., 1961.

(5) N. A. Gac and G. J. Janz, *J. Am. Chem. Soc.*, in press.

(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 6.

leads to quite complex differential rate expressions. With the exception of the kinetic studies with CF_3I and ethylene by Bell,⁷ data for such thermally initiated processes at moderately high temperatures and normal pressures appear almost nonexistent. The present communication reports the results of an investigation of the kinetics and mechanism of the $\text{CF}_3\text{CN}-\text{CH}_2\text{CH}_2$ reaction at 440° and atmospheric pressures.

Experimental

The reactants, CF_3CN (95% minimum purity, Peninsular Chemresearch, Inc.), C_2H_4 (99% minimum purity, Matheson Co., Inc.), and ethylene oxide (99.7% minimum purity, Matheson Co., Inc.), were degassed and vacuum transferred to suitable small metal cylinders for use as required. The CF_3CN was further redistilled at low temperatures prior to use.

Apparatus and Procedure.—The design of the experimental assembly and vacuum-transfer manifold is shown in Fig. 1. The reaction flask (1 l.) was conditioned⁸ by a 24-hr. ethylene pyrolysis at 480° . To premix the reactants a larger flask (5 l.) and magnetically coupled stirring device was adopted. Homogeneity of the gaseous reactant mixtures was cross-checked with gas chromatographic analysis. The reaction furnace (11 in. i.d. \times 22 in.) could be used simply as an air thermostated zone ($\pm 0.1^\circ$), or with a molten salt bath about the reaction flask to further improve the heat transfer. The latter technique was used in the free-radical sensitization studies.

With the reactant mixture introduced to the hot zone, time and pressure readings (± 0.05 mm.) were made to gain the data for the kinetic analysis. The time average for such pressure readings was 20–30 sec.; all times were measured with an electric stopwatch. Two pressure and time readings were made every 100 sec. in the first 1000-sec. period of each kinetic experiment. Readings were continued at less frequent intervals for the duration of these experiments (~ 30 min.). The flask contents were "rapid-quenched" at liquid N_2 temperatures at the completion of an experiment. Gaseous compounds were separated in the conventional manner from the liquid products by vacuum-transfer techniques and stored in calibrated flasks (Fig. 1) until aliquots were required for analysis (gas chromatography (25°) and infrared spectroscopy). The liquid compounds were weighed, and ali-

(7) T. N. Bell, *J. Chem. Soc.*, 4973 (1961).

(8) W. D. Walters, "Technique of Organic Chemistry," Vol. VIII, Interscience Publishers, New York, N. Y., 1953, Chapter V, p. 235.

Peak	1	2	3	4	5
$M^0 = 0.008$	0.016	0.015	0.0024	1.0	0.0025
$M^0 = 0.185$	0.0028	0.013	0.029	1.0	0.028
Identity	C_2H_4CN	C_2H_5CN	$CF_3(CH_2)_4CF_3$	$CF_3CH_2CH_2CN$	$CF_3(CH_2)_4CN$

quots were removed for analytical attention by gas chromatography (Beckman GC-2 chromatograph; di-*n*-decyl phthalate on C-22 firebrick, 160°).

Results

It was apparent from the mechanism advanced (see Discussion) that an experimental investigation of the free-radical mechanism would be possible most readily if the studies were limited to the region of $[CF_3CN] \gg [C_2H_4]$, *i.e.*, low values for the mole ratio of ethylene to CF_3CN . To define the necessary limits for this ratio, the composition of the product was investigated as a function of the ratio $C_2H_4:CF_3CN$, hereafter designated by M . It was found that the relative rate of formation of $CF_3(CH_2CH_2)_2CN$ to $CF_3CH_2CH_2CN$ was directly proportional to M as would be predicted in a telomeric process.¹ Results for two such experiments, for high and low values of M , are shown in Table I; the identity of the compounds and amounts (relative to $CF_3CH_2CH_2CN$ taken arbitrary as 1.0) in the "reaction crude" are indicated in Table I. Formation of "side" products in amounts greater than 3 mole % relative to the 1:1 addition product was thus readily minimized by using values of $M^0 \leq 0.2$. In the preceding study, the identity of the peaks was confirmed by the techniques of n.m.r. spectroscopy, as well as gas chromatography, infrared spectra, and physical properties (boiling point and refractive index).

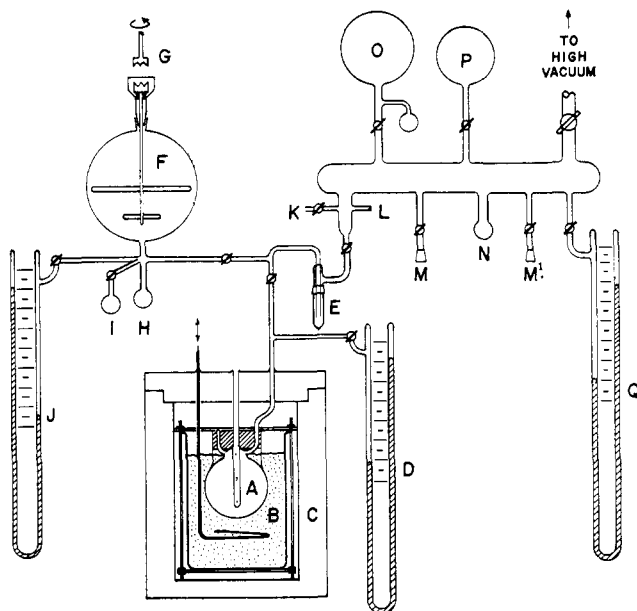


Fig. 1.—Manometric assembly for gas-phase kinetic studies at moderately high temperatures and normal pressures. Legend: (A) 1-l. water-calibrated reactor with thermocouple well; (B) 40% $NaNO_2$ -7% $NaNO_3$ -53% KNO_3 molten salt bath; (C) reactor furnace; (D) 10-mm. o.d. Hg-in-glass reactor manometer; (E) product recovery trap; (F) 5-l. water-calibrated mixer; (G) 6-pole Alnico magnet stirrer assembly; (H) 50-ml. mixer transfer trap; (I) 50-ml. mixer isolation trap; (J) 10-mm. o.d. Hg-in-glass mixer manometer; (K) connection to McLeod vacuum gauge; (L) connection to product accumulation system manifold; (M, M') $\frac{1}{8}$ 14/53 manifold inlets; (O) 2-l. water-calibrated storage bulb; (P) 1-l. water-calibrated expansion bulb; (Q) 12-mm. o.d. Hg-in-glass manifold manometer.

trarily as 1.0) in the "reaction crude" are indicated in Table I. Formation of "side" products in amounts greater than 3 mole % relative to the 1:1 addition product was thus readily minimized by using values of $M^0 \leq 0.2$. In the preceding study, the identity of the peaks was confirmed by the techniques of n.m.r. spectroscopy, as well as gas chromatography, infrared spectra, and physical properties (boiling point and refractive index).

The kinetic data and results are shown in Tables II and III for fixed initial pressures of CF_3CN and C_2H_4 , respectively, in the reactant mixtures. The runs at constant initial CF_3CN pressures in Table II were made initially to test the order of the reaction with respect to ethylene. The pressure-time data in the initial periods appeared to be pseudo-first order, but the first-order rate constants were found to vary with ethylene pressure. They are numerically equal to the pseudo- $k_{1/2}$ divided by $[CF_3CN]^{1/2}$ given in Table II. Limits of error are shown, from a complete analysis, and the correction of the results to a common temperature was possible using the previously reported value³ for E_{act} (≈ 45 kcal. mole⁻¹). The data and results for these mixtures with ethylene oxide present, as a means of varying the initiation rate,⁹⁻¹¹ are

TABLE II
DATA AND RESULTS FOR EXPERIMENTS WITH CONSTANT INITIAL PRESSURES OF CF_3CN

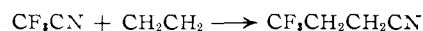
Expt.	T , °C.	a , mm. CF_3CN	b , mm. CH_2CH_2	M^0 (CH_2CH_2/CF_3CN)	T^a	
					$k_{1/2}$, (moles/l.) ^{-1/2} sec. ⁻¹	$T = 442^{\circ a, b}$ $\times 10^2$
A-15	441.2	361.1	4.7	0.013	12 ± 4	13 ± 4
A-16	441.7	361.4	4.7	0.013	15 ± 2	15 ± 2
A-2	442.9	359.5	8.8	0.0245	14 ± 5	14 ± 4
A-1	442.0	329.9	8.1	0.0245	16 ± 2	16 ± 2
A-6	443.7	359.7	9.4	0.026	17.6 ± 0.2	17.6 ± 0.2
A-7	442.5	360.5	9.4	0.026	23 ± 1	23 ± 1
A-9	441.9	360.9	11.7	0.0325	8.7 ± 0.3	8.7 ± 0.3
A-10	442.4	360.0	11.7	0.0325	10.4 ± 0.6	10.2 ± 0.6
A-8	442.6	361.1	15.8	0.0439	7.5 ± 0.3	7.3 ± 0.3
A-3	441.9	360.3	17.5	0.0485	6.9 ± 0.4	6.9 ± 0.4
A-4	442.4	359.9	17.5	0.0485	7.3 ± 0.4	7.2 ± 0.4
A-11	442.9	358.7	28.6	0.0820	5.3 ± 0.1	5.1 ± 0.1
A-12	442.0	362.4	28.9	0.0820	5.3 ± 0.2	5.3 ± 0.2
A-17	440.3	386.4	43.7	0.113	4.12 ± 0.05	4.42 ± 0.05
A-18	437.4	362.6	44.6	0.123	3.62 ± 0.06	4.44 ± 0.06
A-19	440.4	364.3	45.6	0.125	3.81 ± 0.06	4.09 ± 0.06
A-5	442.8	360.0	48.9	0.136	3.24 ± 0.06	3.13 ± 0.08
A-14	440.8	360.9	51.9	0.144	2.99 ± 0.08	3.16 ± 0.08
A-13	440.8	360.4	57.6	0.160	2.97 ± 0.08	3.13 ± 0.08

^a Initial values, *i.e.*, for $M = M^0$. ^b $k_{1/2}T$ normalized to $T = 442^\circ$.

shown in Table IV. The rate increases are 10- and 14.4-fold, respectively, with 1.28 and 2.72% sensitizer present, relative to the unsensitized rate. This corresponds to a rate increase exactly proportional to $[(CH_2)_2O]^{1/2}$. Gas chromatographic analysis of the reaction "crudes" showed that the relative amounts of products were substantially the same in the sensitized and unsensitized experiments.

Discussion

The preceding results have the features that characterize telomerization reactions with the difference that CF_3CN does not participate as would be forecast by analogy with CCl_3CN ,⁶ *i.e.*, as $\cdot F$ and $\cdot CF_2CN$ but as $\cdot CF_3$ and $\cdot CN$. A simple molecular reaction for the formation of $CF_3CH_2CH_2CN$, *i.e.*



(9) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954, p. 229.

(10) A. Maccoll, "Technique of Organic Chemistry," Vol. VIII, Part 1, Interscience Publishers, Inc., New York, N. Y., 1961, Chapter X.

(11) S. W. Benson, *J. Chem. Phys.*, **40**, 105 (1964).

TABLE III
DATA AND RESULTS FOR EXPERIMENTS WITH CONSTANT
INITIAL PRESSURES OF C₂H₄

Expt:	T, °C.	b, mm. CH ₂ CH ₂	a, mm. CF ₃ CN	M ⁰ (C ₂ H ₄ / CF ₃ CN)	T ^a	T = 442 ^{°a,b}
					k ₁ ^{1/2} , (moles/l.) ^{-1/2} sec. ⁻¹	× 10 ⁴
b = 5.0 mm.						
B-2	441.7	5.0	629.1	0.0080	18 ± 1	19 ± 1
B-1	441.9	5.0	556.8	0.0090	16 ± 1	15 ± 1
B-5	441.1	5.0	410.6	0.012	13 ± 1	13 ± 1
B-6	440.8	5.0	410.2	0.012	14 ± 1	14 ± 1
A-16	441.7	4.7	361.4	0.013	15 ± 2	15 ± 2
A-15	441.2	4.7	361.1	0.013	12 ± 4	13 ± 4
b = 50.8 mm.						
C-1	442.2	52.7	486.9	0.108	4.2 ± 0.1	4.2 ± 0.1
C-2	441.9	51.6	477.9	0.108	3.8 ± 0.1	3.8 ± 0.1
C-3	442.7	49.7	493.5	0.109	4.20 ± 0.08	4.20 ± 0.08
A-5	442.8	48.9	360.0	0.136	3.24 ± 0.06	3.13 ± 0.06
A-14	440.8	51.9	360.9	0.144	2.99 ± 0.08	3.16 ± 0.08
b = 58.0 mm.						
D-8	441.2	60.0	435.5	0.139	3.0 ± 0.2	3.1 ± 0.3
D-5	442.6	57.9	400.4	0.145	3.26 ± 0.06	3.17 ± 0.06
D-4	441.0	57.9	400.3	0.145	2.86 ± 0.08	2.99 ± 0.09
A-13	440.8	57.6	360.4	0.160	2.97 ± 0.08	3.13 ± 0.08
D-7	441.4	57.5	310.2	0.185	2.35 ± 0.07	2.41 ± 0.07
D-6	441.4	57.8	312.4	0.185	2.44 ± 0.07	2.51 ± 0.07

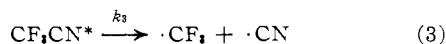
^a Initial values, *i.e.*, for $M = M^0$. ^b $k_1^{1/2}$ normalized to $T = 442^\circ$.

TABLE IV
ETHYLENE OXIDE SENSITIZED EXPERIMENTS

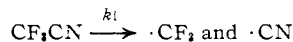
No.	T, °C.	M ⁰ (C ₂ H ₄ / CF ₃ CN)	a, mm.	b, mm.	P ⁰ (CH ₂) ₂ O, mm.	Init. rate,
						min. sec. ⁻¹ × 10 ²
A-18	437.2	0.123	326.6	44.6	0	1.25
E-1	437.0	0.123	358.3	44.1	5.2	12.5
E-2	438.2	0.123	350.9	43.2	11.0	18.0

is clearly ruled out since the reaction is not first order with respect to ethylene. Moreover, ethylene oxide sensitization, nitric oxide inhibition, and the formation of "side" products favors a free-radical mechanism. The following mechanism may be advanced in accord with the product composition at low ratios of M .

(i) initiation



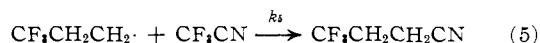
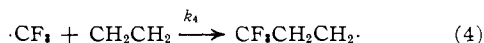
Steps 1b and 2b are negligible¹²⁻¹⁵ under conditions where telomerization is minimized. It follows also that under such reaction conditions the initiation process may be simply expressed as



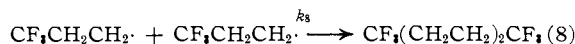
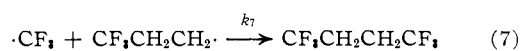
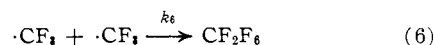
and that the rate of initiation, R_i , is accurately described¹⁶ by the first-order process

$$R_i = k_1[\text{CF}_3\text{CN}]$$

(ii) propagation



(iii) termination



The nitrile abstraction reactions such as step 5, although somewhat unusual, have been previously postulated.^{17,18}

While it is recognized that both the CF₃ and CN radicals may participate in the chain-initiation steps, the results of related studies with propylene as the olefin⁵ are strong support for the viewpoint that attack by CF₃ is the important step in the chain-initiation process. It can be readily shown from the steady-state condition for the formation of $\cdot\text{CF}_3$ and $\text{CF}_3\text{CH}_2\text{CH}_2\cdot$, *i.e.*

$$0 = k_1[\text{CF}_3\text{CN}] - 2k_6[\cdot\text{CF}_3]^2 - 2k_7[\cdot\text{CF}_3][\text{CF}_3\text{CH}_2\text{CH}_2\cdot] - 2k_8[\text{CF}_3\text{CH}_2\text{CH}_2\cdot]^2 \quad (9)$$

with the assumption of a long-chain mechanism, *i.e.*

$$k_4[\cdot\text{CF}_3][\text{CH}_2\text{CH}_2] = k_5[\text{CF}_3\text{CH}_2\text{CH}_2\cdot][\text{CF}_3\text{CN}] \quad (10)$$

that the over-all rate is

$$R_0 = \frac{d}{dt} [\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}] = \frac{k_1^{1/2}k_4[\text{CH}_2\text{CH}_2][\text{CF}_3\text{CN}]^{1/2}}{\left(2k_6 + 2k_7 \frac{k_4}{k_5} M + \left(\frac{2k_8k_4^2M^2}{k_5^2}\right)^{1/2}\right)} \quad (11)$$

The relatively low yields of the termination products relative to $\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}$ qualitatively confirm that the long-chain assumption is approached at sufficiently low M values. The above equation (11) transforms to

$$\frac{dx}{dt} = [(b-x)(a-x)]^{1/2} \times [(\gamma + \beta M + \alpha M^2)]^{1/2} \quad (12)$$

in terms of partial pressures, where a and b are the initial pressures of the reactants, and x is the pressure at time t of the product $\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}$, and the parameters α , β , and γ are given by $\alpha = (2k_8k_4^2/k_5^2)(k_1k_4)^{-1}$, $\beta = (2k_7k_4/k_5)(k_1k_4)^{-1}$, and $\gamma = 2k_6(k_1k_4)^{-1}$.

Inspection of (12) shows that for the experimental conditions minimizing telomerization, *i.e.*, $[\text{CF}_3\text{CN}] \gg [\text{C}_2\text{H}_4]$, a three-halves-order rate law is predicted

$$\frac{dx}{dt} = \gamma^{-1/2}[b-x][a-x]^{1/2} \quad (13)$$

This result is also predicted if the initiation process, and steps 4, 5, and 6 only are considered in the derivation of the rate equation; under these conditions, *i.e.*, as $M \rightarrow 0$, the termination rate is the $\cdot\text{CF}_3$ recombination, *i.e.*, step 6. A limiting three-halves-order rate expression is also predicted for the case when $[\text{CF}_3\text{CN}] \ll [\text{C}_2\text{H}_4]$, *i.e.*, M is very large; this case is hypothetical since large excesses of C_2H_4 in the reactant mixture lead to telomerization, a condition under which the proposed mechanism is not applicable.

(17) A. B. King and E. W. R. Steacie, *Can. J. Chem.*, **37**, 1737 (1959).

(18) D. E. McElcheran, M. H. J. Wijnen, and E. W. R. Steacie, *ibid.*, **35**, 1216 (1957).

(12) M. Volpe and H. S. Johnston, *J. Am. Chem. Soc.*, **78**, 3903 (1956).

(13) H. F. Cordes and H. S. Johnston, *ibid.*, **76**, 4264 (1954).

(14) D. J. Wilson and H. S. Johnston, *ibid.*, **75**, 5763 (1953).

(15) H. S. Johnston, *ibid.*, **75**, 1567 (1953).

(16) S. W. Benson, *J. Chem. Phys.*, **22**, 46 (1954):

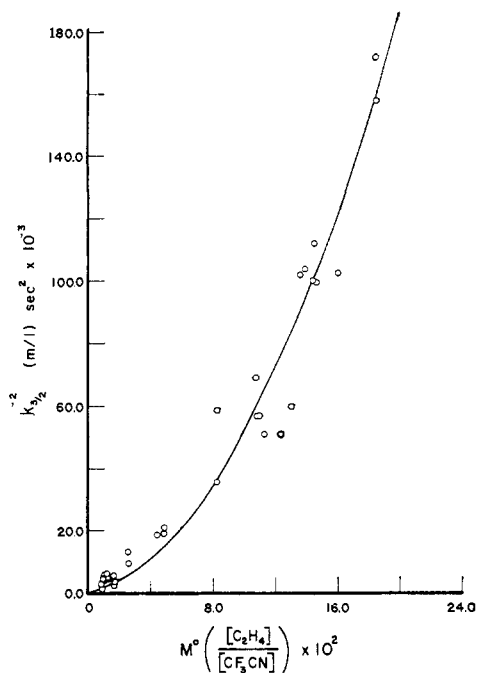


Fig. 2.—Graphical analysis of the $k_{1/2}^{-2}-M^0$ relation for the $\text{CF}_3\text{CN}-\text{C}_2\text{H}_4$ reaction at 442° . Legend: the experimental values, O, are shown relative to the parabolic curve fit (least-squares analysis) to the equation $k_{1/2}^{-2} \times 10^{-3} = 41.5M^2 + 0.931M + 0.00665$.

A form of the rate equation (12) more suitable for interpretation of the experimental data is

$$k_{1/2} = (\alpha M^2 + \beta M + \gamma)^{-1/2} = \left(\frac{RT}{a-b} \right)^{1/2} \frac{d}{dt} \ln X_t \quad (14)$$

where

$$X_t = \frac{(a-x)^{1/2} + (a-b)^{1/2}}{(a-x)^{1/2} - (a-b)^{1/2}}$$

It follows that the pseudo-three-halves-order rate constants can be gained by graphical analysis of the $\log X_t-t$ relationship at fixed temperatures; the ratio M is most precisely known at $t = 0$, *i.e.*, where $M = M^0$, the ratio of reactants as initially charged into the hot zone.

The values listed for $k_{1/2}$ (Tables II and III) were thus determined using the initial slopes of the $\log X_t-t$ graphs. It is seen that these are functions of M as predicted in eq. 14. Thus, as b is increased (*i.e.*, M is increased, Table II), $k_{1/2}$ decreases; as a is decreased (*i.e.*, M is decreased), the values of $k_{1/2}$ decrease. This shows that $k_{1/2}$ is a function of M only, but not necessarily that given by eq. 14. The dependence is demonstrated by the following considerations.

Quantitative evaluation of the parameters α , β , and γ is readily achieved if the expression for the pseudo-three-halves-order rate constant is rearranged in the equation of a parabola

$$k_{1/2}^{-2} = \alpha M^2 + \beta M + \gamma \quad (15)$$

The results of this analysis are illustrated in Fig. 2; the equation for the solid curve through the experimental points is

$$k_{1/2}^{-2} \times 10^{-3} = 41.5M^2 + 0.931M + 0.00665 \quad (16)$$

The three-halves-order rate law, for the limit where $M = 0$, *i.e.*, telomerization entirely suppressed, is thus found to be (at $T = 442^\circ$)

$$d[\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}]/dt = 38.7 \times 10^{-3} [\text{CH}_2\text{CH}_2][\text{CF}_3\text{CN}]^{1/2} \text{ mole sec.}^{-1} \quad (17)$$

The experimental conditions under which telomerization will be minimized, and the value of the cross-combination ratio $[k_7/(k_6^{1/2}k_8^{1/2})]$ can be gained from a knowledge of the values of α , β , and γ for this system. Thus the relative rates of the termination steps are given by

$$R_7/R_6 = (\beta/\gamma)M \text{ and } R_8/R_6 = (\alpha/\gamma)M^2 \quad (18)$$

and the cross-combination ratio for $\cdot\text{CF}_3$ and $\text{CF}_3\text{-CH}_2\text{CH}_2\cdot$ is

$$k_7/(k_6^{1/2}k_8^{1/2}) = \beta/(\gamma^{1/2}\alpha^{1/2}) \quad (19)$$

If it is assumed that step 6 ($\text{CF}_3\cdot$ recombination) is controlling when its rate is 100-fold greater than R_7 and R_8 , it is seen that this condition would not be attained until the mole ratio (M) had the values 0.7×10^{-4} and 13×10^{-4} , respectively. Recombination of $\text{CF}_3\cdot$ apparently does not become the controlling termination step until the excess of CF_3CN to C_2H_4 is in the ratio $10^5:1.0$. The value for the cross-combination ratio (eq. 19) is found to be 2.2 ± 0.5 for the present studies at 442° . This is to be compared with a value of 1.8 (± 0.1) and 2.08 (at 440°) for the cross-combination ratios in the radical recombination studies for $\text{CF}_3\cdot$ and $\text{C}_3\text{F}_7\cdot$,¹⁹ and $\text{CH}_3\cdot$ and $\text{C}_3\text{F}_7\cdot$,²⁰ respectively.

An estimate of the chain length is of interest in view of importance of this assumption to the derivation of the kinetic expressions. The (time-average) kinetic chain length can be gained from a knowledge of the over-all reaction rate and the rate of the initiation step and can be shown to have the form

$$\frac{R_0}{R_i} = \frac{(R_0^s)^2}{(R_0R_i)} \left(\frac{[\text{CH}_2\text{CH}_2]_0}{[\text{CH}_2\text{CH}_2]_s} \right)^2 \quad (20)$$

where

$$R_0^s = k_4 \left(2k_6 + 2 \frac{k_7k_4}{k_6} M + 2 \frac{k_8k_4^2}{k_6^2} M^2 \right)^{-1/2} R_i^{1/2} [\text{C}_2\text{H}_4]$$

is the over-all rate in the sensitized experiment. The derivation of eq. 20 assumes that only the rate of initiation (initiation process) is changed. This is supported by the product analysis already considered for the sensitized and unsensitized experiments, and the dependence of R_0^s in $[(\text{CH}_2)_2\text{O}]^{1/2}$. Using the two sets of results for ethylene oxide sensitized and unsensitized experiments (Table IV; E-1, A-18, and E-2, A-18, respectively), the values for the chain lengths are 270 and 280 at 442° . In this calculation the kinetic data for ethylene oxide decomposition in this temperature range¹¹ were used for R_i^s . The propagation cycle repeats approximately 300 times for each initiating radical formed or for each chain terminated.

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The salient features for the over-all thermally initiated $\text{CF}_3\text{CN}-\text{C}_2\text{H}_4$ reaction, at low values for the reactant ratio $\text{C}_2\text{H}_4:\text{CF}_3\text{CN}$, appear well-understood in the light of free-radical telomerization kinetics in which the $\text{CF}_3\cdot$ radical is dominant in the chain-initiation step. These investigations are being extended to olefins and nitriles of related structures to gain a further insight on the reaction energetics; the question of using these processes with suitably selected experimental conditions, for the measurement

of $\text{CF}_3\cdot$ radical affinities in the gas phase at moderately high temperatures, is also being explored as part of this work.

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Chromatographic Separation of Isotopic Methanes

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Isotopic methanes are separated chromatographically by using a charcoal column (-3.5 to 150°). Retention times progressively decrease with increasing D or T substitutions. This decrease is consistent with the expected decrease in polarizabilities with increasing D or T substitutions.

Introduction

Isotopic molecules often exhibit markedly different retention times in gas-solid adsorption chromatography.^{1,2} This fact is utilized in the present paper to develop a chromatographic technique for analyzing mixtures of deuterated and tritiated methanes.

Experimental

The four D isomers were obtained from Merck Sharp and Dohme Co., Ltd., Montreal, Canada. A mixture containing four T isomers was prepared by allowing 0.016 mole of CH_4 to stand for 2 months in the presence of 4.4 c. of T_2 , which initiated tritiation by undergoing β -decay.³ A chromatograph of the resulting mixture gave four peaks. These were identified by assuming that the peak sequence is the same as that observed with D isomers where CD_4 , CD_3H , CD_2H_2 , and CDH_3 come off the column in this order. The identification was further checked in two ways. First, CH_3T was prepared by mercury-sensitized photolysis of a CH_4-T_2 mixture. This photolysis was reported⁴ to give predominantly monosubstituted methane, and the retention time of the principal peak coincided with that of a peak identified as CH_3T . A mixture of T isomers in which CT_4 was the major component (mass spectrometry) was prepared as follows. T_2 purchased from the Oak Ridge National Laboratories was found to contain small amounts of highly tritiated methane. This mixture was sparked with a Tesla coil and passed through a molecular sieve trap (-160°), which retained the methane but not tritium.⁵ The methane recovered by subsequently warming the molecular sieve column gave a single peak whose retention time coincided with that of a peak originally identified at CT_4 .

A 1520-cm. stainless steel column (0.152-cm. i.d.) was prepared by joining two 760-cm. columns which contained 0.0082 g./cm. of 80–100 mesh, high-activity charcoal purchased from Burrell Corp., Pittsburgh, Pa. Two such columns were prepared. One column was used for the experiments at -3.5 and 24° , while the

other was used above 50° . Helium was used as a carrier gas, and the flow rate measured at the outlet was kept constant at 56.6 cc./min. regardless of column temperature.

To maintain the helium flow rate of 56.6 cc./min., it was necessary to employ high inlet pressures of above 10 atm. Sample injections at these pressures were accomplished with a gas-sampling valve, equipped with a Viton A O-ring, purchased from Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

Experiments were performed using these mixtures: binary mixtures with 3:2 mole ratio of the components CH_4-CD_4 , CH_4CHD_3 , $\text{CH}_4-\text{CH}_2\text{D}_2$, and $\text{CH}_3\text{D}-\text{CD}_4$; a mixture of CH_4 with the four D isomers, each component having the same concentration; 4.4 c. of the four T isomers diluted in 0.016 mole of CH_4 ; and 0.5 mc. of C^{14}H_4 diluted in 0.016 mole of CH_4 . In most experiments, sample size for a single injection was 1.3 moles of the mixture. A thermal conductivity cell was used for CH_4 and D isomer detections, while a 3-cc. ion chamber was employed for C^{14}H_4 and T isomer detections. Signals from both detectors were registered on a Brown dual-pen potentiometric recorder.

Results and Discussion

Figure 1 gives a chromatogram containing peaks of C^{14}H_4 , CH_4 , and CH_2D_2 . The retention times of

TABLE I
THE RATIO, $t(\text{CH}_4)/t(\text{ISOTOPES})$, OF RETENTION TIMES
USING A CHARCOAL COLUMN

Isomers	24°	-3.5°
CH_4^a	1.000	1.000
CH_3D	1.015	1.016
CH_2D_2	1.029	1.033
CHD_3	1.042	1.051
CD_4	1.061	1.068
CH_3T	1.013	1.017
CH_2T_2	1.030	1.031
CHT_3	1.048	1.053
CT_4	1.068	1.078

^a $t(\text{CH}_4) = 78.0$ and 180.3 min. at 24 and -3.5° , respectively.

TABLE II
RETENTION TIMES AT DIFFERENT TEMPERATURES

Temp., $^\circ\text{C}$.	$t(\text{CH}_4)$, min.	$t(\text{CH}_4)/t(\text{CD}_4)$	$t(\text{CH}_4)/t(\text{CT}_4)$
50	41.63	1.049	1.065
75	26.70	1.041	1.052
100	19.30	1.035	1.043
125	14.40	1.027	1.030
150	11.25	1.014	1.014

(1) For the isotope effect in adsorption chromatography, see, for example, these references: (a) W. R. Moore and H. R. Ward, *J. Am. Chem. Soc.*, **80**, 2909 (1958); (b) S. Ohkoshi, Y. Fujita, and T. Kwan, *Bull. Chem. Soc. Japan*, **31**, 770 (1958); (c) P. L. Gant and K. Yang, *Science*, **139**, 1548 (1959); (d) W. J. Hanbach and D. White, *J. chim. phys.*, **60**, 97 (1963); (e) E. Glueckauf, *Endeavour*, **20**, 42 (1961); (f) J. W. Root, E. K. Lee, and F. S. Rowland, *Science*, **143**, 676 (1964).

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