Table II: Activity Coefficient Ratio of Ammonia in Aqueous Salt Solutions

Salt molality	Ammonia molarity	$f_{NH_3}/f^0_{NH_3}$	Number of observations	Std dev of the mean
		LiBr		
0.0	1.034	1.00	4	
0.50	1.050	0.936	3	0.015
1.00	1.046	0.892	3	0.020
2.00	1.053	0.810	4	0.012
3.00	1.054	0.718	4	0.014
4.00	1.050	0.606	4	0.018
6.00	1.026	0.404	4	0.020
		NaCl		
0.0	0.806	1.00	3	
0.505	0.838	1.049	3	0.004
1.02	0.831	1.107	3	0.010
2.09	0.805	1.220	2	0.019
3.77	0.774	1.361	3	0.016
5.59	0.783	1.520	3	0.002
		$NaClO_4$		
0.0	0.988	1.00	3	
0.50	0.982	0.993	3	0.015
1.00	0.981	0.993	2	0.015
2.00	0.978	1.003	3	0.049
3.00	0.982	0.997	3	0.037
4.00	0.984	0.992	3	0.015
6.00	1.000	1.005	2	0.006

ever, the present data do not justify any such curve fitting.

The wide range of sensitivity of the mass spectrometer makes it ideal for the measurement of ammonia activities over a large range of ammonia and salt concentrations. The precision obtained (2–3%) was somewhat reduced by minor instrumental difficulties, but the major source of error was due to the adsorption of water on the glass walls of the inlet system of the mass spectrometer. Ammonia, with its affinity for water, was probably absorbed to some extent. This difficulty was minimized by allowing the system to reach equilibrium during each mass spectral determination. More precise results could be obtained by introducing the sample directly into the ion source through a fine capillary inlet. With this modification and with higher instrument stability, a precision of better than 1% could be expected. The effect of changes in the hydrolysis of ammonia in the different salt solutions is not included in the present study. However, it is expected that this factor will not have a significant effect on the observed activity results. Furthermore, indications are that the mass spectrometer can be successfully applied to the simultaneous activity determination of water. Since the peak height ratio between OH^+ and H_2O^+ is constant after correcting for contributions from other sources, the OH^+ peak is a direct measure of the water vapor partial pressure. Because of the adsorption problem, measurements of the water activity were not made in this study, but there should be no difficulty once the direct capillary inlet is constructed. Since the mass spectrometer can both quantitatively and qualitatively analyze the vapor sample, this technique should be applicable to the simultaneous determination of activity of several volatile species in complex multicomponent systems.

Free Radical Addition of Perfluoroacetonitrile to Vinyl Fluoride

by G. J. Janz and J. B. Flannery

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In the free-radical addition of perfluoroalkylnitriles and propylene, two isomeric products are formed. Correspondingly, with vinyl fluoride and CF_3CN, one would predict two possible structures for the compound, CF_3CH_2CHFCN (I) and CF_3CHFCH_2CN (II), resulting from the equimolar addition reaction. The results of a series of experiments are reported in this note for the addition reaction CF_3CN and CH_2CHF. Only one of the two possible isomeric compounds, namely, CF_3CH_2CHFCN, is apparently formed. A precise kinetic study was found impossible since the formation of higher telomeric compounds could not be suppressed to less than 13%. These results are examined relative to related studies[1,2] with C_2H_4 and propylene.

Experimental Details and Results

The reactants, CF_3CN (95% min, bp −64°, Peninsular Chemresearch, Inc.) and CH_2CHF (bp −51°, E. I. du Pont de Nemours and Co., Inc.) were degassed three times under high vacuum at −195°. Analysis by gas chromatography showed the purity of both reactants to be better than 99%.

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(1) G. J. Janz, N. A. Gac, A. R. Monahan, and W. J. Leahy, *J. Org. Chem.*, **30**, 2075 (1965).

(2) N. A. Gac and G. J. Janz, *J. Am. Chem. Soc.*, **86**, 5059 (1964).

The reaction vessel for accumulation of products was a 5-l. Pyrex flask heated with a Glas-Col mantle. Premixed reactants were transferred from an all-glass vacuum manifold to the reactor by conventional vacuum-transfer methods.

A series of reactions between CF_3CN and vinyl fluoride was run to accumulate sufficient addition product for structural characterization. The initial mole ratio of nitrile to olefin was 5:1, the total initial pressure 600–700 mm, and the reaction temperature 400 ± 5°. Reaction times were 12–24 hr. No attempt was made to estimate either the conversions or product yields.

Analysis by gas chromatography (Beckman GC-2a chromatograph, 6-ft × 0.25-in. o.d. column with 30 wt % di-*n*-decyl phthalate on 40–60 mesh C-22 firebrick; 53-cm^3/min He carrier, at 130, 160°) showed the liquid product to be largely that corresponding to 1:1 addition. Small amounts of higher boiling materials (probably 2:1 telomers) were also present.

The 1:1 addition product was purified by multiple fractionations, using chromatographic fraction-collection techniques. Aliquots were examined by microelemental analysis,[3] infrared spectroscopy (Perkin-Elmer Model 21, NaCl optics), mass spectroscopy,[4] and nmr (Varian A-60 spectrometer, TMS external standard). The results were as follows.

Microelemental Analysis. Anal. Calcd for CF_3CH_2CHFCN: C, 34.04; H, 2.13; N, 9.93. Found: C, 34.18; H, 2.25; N, 10.02.

Infrared Spectra. The infrared frequencies (cm^{-1}) and intensities are 3000 (m), 2285 (w), 2110 (vw), 2010 (vw), 1730 (vw), 1630 (vw), 1520 (w), 1430 (vs), 1405 (vs), 1345 (s), 1315 (vs), 1280 (vvs), 1250 (vvs), 1180 (vvs), 1150 (vvs), 1080 (vs), 1040 (s), 1020 (m), 963 (m), 942 (s) 904 (w), 870 (vs), 850 (sh), 843 (s), 789 (w), 741 (m), 668 (s) (w, weak; m, medium; s, strong; v, very; sh, shoulder). The observed bands at 1315, 1180, and 1150 cm^{-1} coincide with 1321 (±9) and 1140 (±9) cm^{-1} reported[5] for the symmetrical and antisymmetrical deformations in CF_3. The band at 2285 cm^{-1} confirms the nitrile group.[6] The intense bands at 1280 and 1250^{-1} are in accord with the C–F stretching mode and that at 3000 cm^{-1} corresponds to the C–H stretch.[6]

Nmr Spectra. The proton nmr data are understood if the structure of the product is CF_3CH_2CHFCN. Thus, a double triplet at 5.79 ppm confirmed F on a methynyl carbon, with a methylene carbon adjacent (J_{H-H} = 6 cps, J_{F-H} 46 = cps). A complex multiplet, found at 3.2 ppm, is in accord with $-CH_2-$ bonded to CF_3- and $-CHF-$. Finally, the F^{19} resonance with CH_2- protons decoupled[7] gave a doublet for CF_3 due to coupling with $-CFH-$ (J_{F-F} = 7.6 cps). No evidence was found for the isomeric compound, CF_3CHFCH_2CN.

The results of a series of experiments to determine the kinetic behavior of the CF_3CN, CH_2CHF system are summarized in Table I. Pressure–time measurements were made using the same experimental assembly as described for the $CF_3CN-C_2H_4$ kinetic study.[2] The rate constants $k_{3/2}$ were calculated according to the rate law established elsewhere[2] for the $CF_3CN-C_2H_4$ reaction. Analysis of products (vpc) showed the presence of up to 13% higher telomers relative to the 1:1 addition product. This is to be compared with the results for the $CF_3CN-C_2H_4$ reaction,[2] where telomer formation was below 3%, even for initial nitrile–olefin ratios as low as 5:1.

Table I: CF_3CN-CH_2CHF Kinetics Studies

a. Reaction Conditions

Run	T, °C	$(CH_2CHF)/(CF_3CN)$	P^0_{total}, mm[a]	$P^0_{CF_3CN}$, mm[a]	$P^0_{CH_2CHF}$, mm[a]
NVF-1	448.3	0.177	506.1	430.1	76.0
NVF-2	443.2	0.110	588.0	529.8	58.2
NVF-3	441.5	0.110	538.3	485.1	53.2

b. Rate Constants

Run	ΔP_{total}, mm	% conversion[b]	$k_{3/2} \times 10^4$, (mole l.$^{-1}$)$^{-1/2}$ sec^{-1}
NVF-1	11.0	14.5	35
NVF-2	15.8	27.2	14
NVF-3	4.8	9.1	7.6

[a] Superscript zero refers to initial conditions. [b] Based on molar consumption of vinyl fluoride.

Discussion

The microelemental analysis, infrared spectra, and nmr spectra confirm that the 1:1 addition product in the reaction of CF_3CN with CH_2CHF is CF_3CH_2CHFCN (I). The presence of the isomeric compound, CF_3CHFCH_2CN (II), was not detected chroma-

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[3] Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[4] J. B. Flannery and G. J. Janz, *J. Chem. Eng. Data*, **10**, 387 (1965).

[5] R. R. Randle and D. A. Whiffin, *J. Chem. Soc.*, 1311 (1965).

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

[7] C. W. Wilson, III, and L. O. Moore, Union Carbide Co., Research Laboratory, S. Charleston, W. Va., are thanked for results of F^{19} nmr.

tographically or spectrally. While the formation of II in amounts small relative to I is not ruled out, the predominant formation of I provides further support for the view that the primary chain carrier in the propagation cycle of this free-radical reaction is the CF_3 radical. Recent studies of a related system, CF_3I and vinyl fluoride, have revealed the formation of both CF_3CH_2CHFI (I′) and CF_3CHFCH_2I (II′), with I′ in large excess.[8] This is additional support for the viewpoint that, in these processes, the monoolefin addition reaction proceeds by preferential attack by the CF_3 radical.

While precise kinetic data were not attained in the present study (at the highest nitrile to olefin ratios possible, the telomer formation could not be suppressed to less than 13%), the results in Table I are nevertheless sufficient to assess the CF_3 radical affinities for the two monoolefins, CH_2CHF and CH_2CH_2, at 441°. The data for the CH_2CH_2, CF_3CN addition reaction are reported elsewhere.[2] Thus at 441°, in the gas phase, for these two processes, the rate constants are as shown in Table II. It is clear from this comparison that the CF_3 radical affinities for ethylene and vinyl fluoride are very nearly in the ratio 7:1 at 441°. The only previously reported CF_3 radical affinities for these two monoolefins are those of Pearson and Szwarc.[9] In the temperature range of 65–180°, the CF_3 radical affinity for ethylene was observed to be 5–10 times greater than that of vinyl fluoride. The agreement is striking and, if significant, implies that the ratio of the CF_3 radical affinities in the gas phase for these two monoolefins remains essentially constant for a surprisingly wide range of temperatures (up to 440°). The present studies (with CF_3CN) are to be extended to evaluate this approach for the study of radical affinities for a range of monoolefins at moderately high temperatures.

Table II

System	$k_{3/2}$, (mole l.$^{-1}$)$^{-1/2}$ sec^{-1}
CH_2CH_2–CF_3CN	5.1×10^{-3}
CH_2CHF–CF_3CN	7.6×10^{-4}

Acknowledgment. This work was made possible in large part by a grant-in-aid from the American Chemical Society Petroleum Research Fund. J. B. F. acknowledges with thanks the award of a N.A.S.A. Traineeship for advanced work in this area of research.

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