This formula is convenient for determining the barrier height as a function of ϵ_v and the tunneling frequency, ν. Using an upper limit for ν of 15 kHz, and ϵ_v = 1209 cm^{-1} for the HN bending mode in ethylenimine,[15] gives a lower limit to V.

$$V = 4065 \text{ cm}^{-1} = 11.6 \text{ kcal} \tag{28}$$

This lower limit for the barrier height is very close to the activation energy of 11.0 (11.9) kcal for nitrogen inversion (or proton tunneling) in 2,2,3,3-tetramethylaziridine (tetramethylethylenimine).[16] As we have found the tunneling frequency to be low, it is likely that tunneling adds little to the measured rates in the magnetic resonance experiments. Therefore, the measured activation energy is likely to be a good measure of the barrier height. Our upper limit for V in ethylenimine is, however, much lower than given in a recent calculation (34 kcal).[17]

We can now define the potential constants in $V(s)$ in eq 14. It is also necessary to list the reduced mass which we assume is equal to the proton mass.

$$k = 1.45 \times 10^{20} \text{ ergs/cm}^4$$

$$k' = 2.17 \times 10^{6} \text{ ergs/cm}^2$$

$$s_m = \pm 0.86 \times 10^{-8} \text{ cm}$$

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

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Free Radical Addition of Trifluoroacetonitrile to Propylene[1]

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Abstract: A study is reported of the rate of the gas-phase addition of CF_3CN to propylene over the range 400–450°. Under conditions such that $CF_3CN \gg C_3H_6$, the rate equation is $\partial[CF_3(C_3H_6)CN]/\partial t = 10^{14\pm2}\exp(-51.5/RT)[CF_3CN][C_3H_6]$ l. mol^{-1} sec^{-1}. The results are consistent with a free radical mechanism in which the initiation step is bimolecular, $CF_3CN + C_3H_6 \rightarrow CF_3 + C_3H_6CN$, and in which chain termination is due to hydrogen abstraction from C_3H_6 by trifluoromethyl radicals.

The telomerization of CF_3I with ethylene has been investigated in the homogeneous gas phase (309°) by Bell.[3] A similar study, but with CF_3CN and C_2H_4, in the range 365–445° was reported by Flannery and Janz,[4] the rate equation being

$$\partial[CF_3CH_2CH_2CN]/\partial t = 10^{7.0\pm0.4}\exp(-27 \pm 3/RT) \times [CF_3CN][C_2H_4] \text{ l. mol}^{-1}\text{ sec}^{-1} \tag{1}$$

under conditions of excess CF_3CN (as required to minimize the formation of telomers[5]). The present communication reports the results of a study of the addition of CF_3CN to C_3H_6, under conditions such that $CF_3CN \gg C_3H_6$. With propylene two addition products could be expected under such conditions. The structures of these compounds and the relative amounts were explored; these have been reported elsewhere.[6] Thus at 400°, it was found that both the 1:1 adducts $CF_3CH_2CH(CN)CH_3$ (I) and $NCCH_2CH(CF_3)CH_3$ (II) were present in the product, with I being predominant (89 ± 1%) in the mixture. When vinyl fluoride is used as the olefin,[7] this addition reaction yields essentially $CF_3CH_2CH(CN)F$. These results are consistent with CF_3 radicals as the primary chain carrier, as was proposed in our earlier work with CF_3CN and ethylene.[4,5,7]

With knowledge of the structures of the products from the addition of CF_3CN to propylene, a quantitative study of the reaction energetics appeared feasible. The results of such an investigation are given in this communication.

Experimental Section

The apparatus and procedure were those described in detail in our earlier paper.[5]

The reactants, CF_3CN (Peninsular Chemical Research, Inc., 95% minimum purity) and C_3H_6 (Matheson Co., Inc., 99% minimum purity), were degassed under high vacuum and triply distilled at low temperature prior to use.

Kinetic data were obtained by manometric techniques. The over-all rate was monitored up to 40–50% conversions, relative to the initial olefin concentration. The total initial pressures ranged from 0.50 to 0.85 atm. For each experiment the initial reactant ratio (CF_3CN/C_3H_6) was adjusted to be from 8.5 to 8.9, this being the upper limit for excess of nitrile at which quantitative measurements of the addition products could be gained with our analytical facilities. A large excess of nitrile is important in order to minimize the formation of telomeric adducts other than the 1:1 addition compounds. The analyses of the gaseous and liquid products were by gas chromatography and infrared spectroscopy.

In the gaseous fraction, unconverted CF_3CN and C_3H_6 and small amounts of CF_3H (typically ~1.0 mol %) were observed. No evidence was found for the formation of C_2F_6, HCN, $(CN)_2$, or gaseous compounds that would arise from propylene pyrolysis.

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[1] Based in part on a thesis submitted by B. H. in partial fulfillment of the requirements for the Ph.D. degree, June 1968, Rensselaer Polytechnic Institute.

[2] To whom all correspondence should be addressed.

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The composition of the liquid fraction was found to be essentially $CF_3(C_3H_6)CN$ (~97%). A small quantity of aliphatic nitriles (about 1%, 3-butenenitrile and *n*-butyronitrile) and materials which corresponded to propylene polymerization products (similarly in small amounts, about 2%) were noted. Higher telomers (*e.g.*, $CF_3(C_3H_6)_2CN$) were not detected.

A limited series of free radical promotion–inhibition types of experiments were undertaken to confirm that the general features were in accord with the free radical characteristics established for the CF_3CN–C_2H_4 system.[5] It was found that the rate was enhanced by ethylene oxide (*e.g.*, a threefold increase at 390° with less than 4% initiator); with NO (<0.05%, 390°), the rate was markedly inhibited, dropping rapidly to about one-half the uninhibited value. The reaction homogeneity was explored for similar reasons. It was found that a tenfold surface-to-volume ratio increase did not lead to a significant change of the reaction rate.

The partial pressures, reactant ratios, and temperatures, for the kinetic studies in the range 400–450°, are given in Table I. The reaction order for C_3H_6, from these data, was found to be unity. The dependence for CF_3CN similarly conformed to first order, but owing to the large excess of nitrile in the mixture (as required to minimize the formation of telomeric adducts) this result is not as definitive as that for the olefin. Support for the first-order nitrile dependence was gained from the derivation of the over-all rate law, which established (as noted in detail elsewhere[4]) that the kinetic data could be satisfactorily accounted for by a second-order rate equation. The results are given in the last column of Table I.

Table I. Second-Order Rate Constants for the CF_3CN–C_3H_6 Reaction

	—Initial	reactant	mixture—	Mole ratio	$k \times 10^3$,
Temp, °K	P_{CF_3CN} (atm)	$P_{C_3H_6}$ (atm)	P_{total} (atm)	CF_3CN/C_3H_6	l. mol^{-1} sec^{-1}
683.7	0.746	0.088	0.834	8.5	5.17
684.4	0.687	0.081	0.768	8.5	4.90
683.3	0.628	0.074	0.702	8.5	5.06
679.9	0.572	0.067	0.639	8.5	4.63
680.3	0.562	0.066	0.628	8.5	5.06
680.7	0.478	0.056	0.534	8.5	5.24
697.7	0.551	0.062	0.613	8.9	9.22
698.2	0.508	0.057	0.565	8.9	11.53
695.7	0.455	0.051	0.506	8.9	10.68
698.2	0.607	0.068	0.675	8.9	9.67
705.0	0.597	0.066	0.645	8.7	17.8
705.7	0.529	0.061	0.590	8.7	20.8
722.4	0.628	0.070	0.698	8.9	43.0
723.5	0.574	0.064	0.638	8.9	40.2
720.4	0.524	0.059	0.583	8.9	39.7
722.7	0.751	0.086	0.837	8.7	37.4
721.9	0.690	0.079	0.769	8.7	42.6
721.2	0.631	0.072	0.703	8.7	40.7

The temperature dependence for the rate constants, expressed in the Arrhenius form (least-squares method), is

$$k = 10^{14\pm2}\exp(-51.5 \pm 2/RT)\ \text{l. mol}^{-1}\ \text{sec}^{-1} \qquad (2)$$

where uncertainty limits are root-mean-square deviations. A graphical representation of this dependence is shown in Figure 1.

Discussion

The results of promotion–inhibition and surface-to-volume ratio experiments are consistent with the view that the addition of CF_3CN to propylene is a free radical process, occurring homogeneously in the gas phase, much as for the case when ethylene is the olefin with CF_3CN.[4,5] The relative amounts of the two isomeric 1:1 adducts,[6] I and II, are further support for the hypothesis advanced elsewhere[5,7] that the trifluoromethyl radical is the primary chain carrier in these systems.

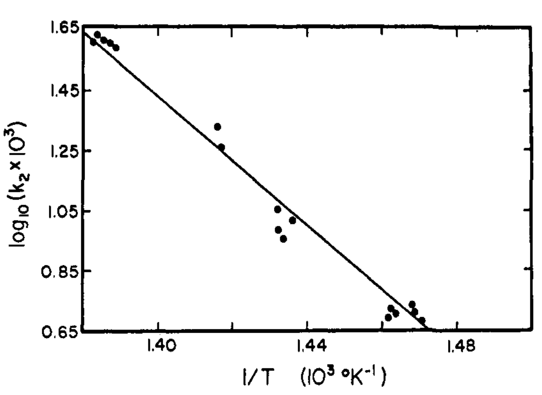
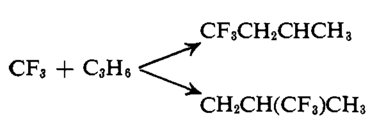


Figure 1. The Arrhenius graph of the second-order rate constants for the free radical addition reaction of CF_3CN to propylene: $CF_3CN + C_3H_6 \rightarrow (CF_3CH_2CH(CN)CH_3$ and $CNCH_2CH(CF_3)CH_3)$.

In such a free radical process[8] the propagation steps would be the addition of CF_3 radicals to propylene, *i.e.*



$$CF_3 + C_3H_6 \begin{cases} \nearrow CF_3CH_2\dot{C}HCH_3 & (3a) \\ \searrow \dot{C}H_2CH(CF_3)CH_3 & (3b) \end{cases}$$

followed by a subsequent reaction with CF_3CN

$$CF_3CH_2CHCH_3 + CF_3CN \longrightarrow CF_3CH_2CH(CN)CH_3 + CF_3 \qquad (4a)$$

$$CH_2CH(CF_3)CH_3 + CF_3CN \longrightarrow NCCH_2CH(CF_3)CH_3 + CF_3 \qquad (4b)$$

where, in the above, the need for distinguishing between paths a and b is not important for the derivation of the over-all rate law.

The analytical data showed that CF_3H was present, but only in small amounts (~1.0%). It is known from the work of Haszeldine and Steele[9] that CF_3 radicals readily abstract hydrogen from propylene (*e.g.*, at ambient temperatures). The presence of CF_3H in our studies is thus undoubtedly due to an abstraction process such as

$$CF_3 + C_3H_6 \longrightarrow CF_3H + C_3H_5 \qquad (5)$$

which also produces the allyl radical. The recognized stability of the allyl radical[10–16] indicates that it should not interfere to a significant degree with the free radical steps leading to $CF_3(C_3H_6)CN$. On the other hand, the propylene–allyl radical reaction, *i.e.*

$$C_3H_5 + C_3H_6 \longrightarrow C_6H_{11} \qquad (6)$$

would lead to a series of products due to propylene polymerization.[16] In this study such compounds were observed in small, but nevertheless real, amounts. The abstraction process (reaction 5) thus corresponds effec-

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tively to a termination step. This is in marked contrast to the CF_3CN–C_2H_4 system, where chain termination is through radical recombination steps.[4,5]

If the mode of initiation remains unspecified, steps 3, 4, and 5 comprise a net mechanism for the formation of the 1:1 adducts. If kinetic chains are long and the stationary-state condition is imposed, the expression for the over-all reaction rate law simplifies to

$$\partial[CF_3(C_3H_6)CN]/\partial t = (k_3/k_5)r_i \qquad (7)$$

where r_i is the rate of the initiation step. Inspection of this rate law shows that it is of the form that derives from generalized considerations for the formation of small molecules by free radical processes, providing an "allylic termination" is operative.[8]

Relative to the nature of the initiation step, a bimolecular reaction, *e.g.*

$$CF_3CN + C_3H_6 \longrightarrow CF_3 + C_3H_6CN \qquad (8)$$

is inherent in the derivation of an over-all rate law that is first order in both CF_3CN and C_3H_6. This initiation is analogous to that for the CF_3CN–C_2H_4 system (*i.e.*, see ref 4, eq 2). Experimental evidence that supports the assumption of a bimolecular initiation process, *e.g.*, eq 8, is found in the two aliphatic nitriles, 3-butenenitrile and *n*-butyronitrile. These compounds were both confirmed to be present (in small amounts) by our analytical studies of the composition of the product mixture. Thus if the initiation step leads to the formation of the $NCCH_2CHCH_3$ radical, a disproportionation reaction would directly account for the 3-butenenitrile and *n*-butyronitrile, as observed. While the formation of the $CH_2CH(CN)CH_3$ radical is not ruled out as a simultaneous occurrence, the two nitriles corresponding to the disproportionation of the latter, *i.e.*, isobutyronitrile and methacrylonitrile, were not detected, and it would appear that this reaction path is much less favored. The initiation step (reaction 8) may thus be represented as

$$CF_3CN + C_3H_6 \longrightarrow CF_3 + NCCH_2CHCH_3 \qquad (9)$$

and from this it follows that

$$r_i = k_9[CF_3CN][C_3H_6] \qquad (10)$$

so that the over-all rate expression for the free radical addition of CF_3CN to propylene becomes

$$\partial[CF_3(C_3H_6)CN]/\partial t = \frac{k_9k_3}{k_5}[CF_3CN][C_3H_6] \qquad (11)$$

i.e., second order for the over-all process.

From eq 11 it follows that the over-all activation energy may be expressed as a function of three elementary activation energies

$$E_0 = E_9 + E_3 - E_5 \qquad (12)$$

The value of E_9 would not be expected to differ greatly from that for the corresponding process in the CF_3CN–C_2H_4 system and may be equated to this accordingly. An experimental measurement of the latter is in progress in our laboratory;[17] a preliminary value is 50 ± 1 kcal mol^{-1}. This is to be compared with the earlier prediction[4] of about 55 ± 5 kcal mol^{-1}. No such data are known for E_3 and E_5, and thermodynamic estimation techniques must be used to advance this approach further. For this purpose we have summarized in Table II the activation energies for a series of hydrogen abstractions by CH_3 and CF_3 radicals. These data and the appropriate reaction enthalpies[18–21] give the empirical equation

Table II. Energies of Activation for Some Hydrogen-Abstraction Reactions: $R + HS \rightarrow RH + S$

HS	E_{CH_3}	Ref	E_{CF_3}	Ref
H_2	10.0, 11.1	*a,b*	8.8	*d*
CH_4	12.8	*b*	10.3, 11.0	*e*
C_2H_6	10.4	*c*	7.5	*e*
C_3H_8			6.5	*e*
n-C_4H_{10}	8.3	*c*	5.1	*f*
i-C_4H_{10}	7.5	*c*	4.7	*f*
t-C_4H_{10}	7.6	*c*	4.7	*e*
neo-C_5H_{12}	10.2	*b*	7.6	*d*
c-C_6H_{12}	8.3	*c*	5.0	*g*
C_6H_6	9.2	*c*	6.3	*g*
$C_6H_5CH_3$	8.3	*c*	5.4	*g*

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$$E_{CF_3} = E_{CH_3} - 1.80 \pm 0.27|\Delta H_{rCH_3}| - 0.30|\Delta H_{rCF_3}| \qquad (13)$$

where $|\Delta H_r|$ is the absolute numerical value of the exothermicity of the reaction with the respective radicals. Equation 13 finds precedent in the Evans–Polanyi relation, first advanced for hydrocarbons,[22] and considered elsewhere in detail.[16] Our relation (eq 13) predicts E_{CF_3} to ±5% of the experimental values given in Table II. Miyoshi and Brinton[23] have reported the results given in reactions 14 and 15. Using

$$CH_3 + C_3H_6 \longrightarrow C_4H_9 \quad E = 8.80 \text{ kcal mol}^{-1} \qquad (14)$$

$$CH_3 + C_3H_6 \longrightarrow CH_4 + C_3H_5 \quad E = 8.20 \text{ kcal mol}^{-1} \qquad (15)$$

these, and eq 13, values of 5.5 and 5.3 kcal mol^{-1} are gained for E_3 and E_5, respectively. The calculated value for E_0, the activation energy for the over-all reaction, is thus about 50 kcal mol^{-1}. This value, while admittedly approximate, is in good agreement with the experimentally observed value, 51.5 ± 2 kcal mol^{-1}, and is independent support for the mechanism advanced here.

A measure of the kinetic chain length is possible if one compares the rate of the over-all reaction and the rate of initiation. Thus for the present system the kinetic chain length is

$$\frac{10^{14}\exp(-51.5/RT)}{10^{11}\exp(-50/RT)} \geq 10^2\,(440°) \qquad (16)$$

The value of the corresponding factor for the free radical

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addition of CF_3CN to ethylene was found[4] to be 2×10^2 at the same temperature.

It is striking, at first, that the free radical additions of CF_3CN to propylene and ethylene differ so markedly in the values of E_0, the energy of activation for the over-all reaction (51.5 kcal mol^{-1} with C_3H_6 and 27 kcal mol^{-1} with C_2H_4). Consideration of these systems in detail shows that an abstraction reaction, leading to an allyl radical is a feature of the propylene system and is not an inherent part of the ethylene system. The difference thus may be attributed, in large part, to the "allylic termination." The bimolecular initiation step undoubtedly involves a transition-state configuration in which there is considerable interaction between the π bonds of $C{\equiv}N$ and $C{=}C$, and the possibility of a charge-transfer species suggests itself. Without additional data this is, at best, speculative and further discussion is deferred accordingly.

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Methyl Group Inductive Effect in the Toluene Ions. Comparison of Hückel and Extended Hückel Theory[1]

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Abstract: An HMO perturbation analysis is made of the methyl group splitting of the unsubstituted benzene ion degeneracy and of the effective methyl group Q values in aromatic positive and negative ions. The necessity for including both hyperconjugative and inductive interactions between the ring and the methyl group is demonstrated; the inductive effect, in particular, is shown to be required to obtain an energy level ordering in agreement with esr data. These results are contrasted with extended Hückel calculations, which yield the correct level ordering and reasonable spin distributions with nonempirical (NEMO) parameters that are apparently very different from the usual HMO parameters and without explicit introduction of an inductive effect. When the nonorthogonal orbitals used in the extended Hückel theory are replaced by an orthogonalized (OAO) set, the NEMO and HMO Hamiltonian matrices are found to be very similar in form. Moreover, the substituted carbon (C^1) is shown to have a Coulomb integral (α_1) that differs from the unsubstituted carbon α values. This suggests that the overlap between C^1 and the methyl group is a source of the HMO inductive effect.

In spite of its approximate nature, Hückel molecular orbital (HMO) theory has proved itself extremely useful in elucidating problems concerned with the electronic structure of π-electron systems. A case in point is provided by the esr spectra of the toluene and related anion radicals. Although quantitative calculation of the hyperfine splitting constants of these radicals requires the inclusion of a complex set of factors due to the vibronic coupling of two near-degenerate electronic states,[4–7] it is well known that the dominant features of the spin distribution can be obtained from the simple HMO theory.[8] Moreover, by means of HMO theory it is possible to decompose the methyl group–aromatic orbital interaction into contributions from hyperconjugation and from an inductive effect, and thereby to understand the differences between the esr spectra of the positive and negative ions derived from the same neutral hydrocarbon.

A number of authors have concluded that in HMO theory, and in a Pariser–Parr ASMO–CI model, both hyperconjugation and the inductive effect are important for deriving the correct spin distribution[6,9,10] as well as other properties.[11,12] In particular, inclusion of the inductive effect appears to be essential for obtaining the correct ordering of the near-degenerate levels.[10,11] However, Hoffmann[13] has pointed out that if an extended Hückel theory calculation[14] is made for the toluene system, the correct level ordering is obtained without the need for explicit resort to an inductive effect. Corresponding results have been obtained by Newton[15] with SCF parameters in the extended Hückel theory (NEMO).[16] Moreover, since the parameters

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