

carbons without the use of a heavy atom solvent system.<sup>36,37</sup>

**E. Relation of the Spectroscopic Results to Ketone Photochemistry.** One of the most thoroughly studied photochemical reactions of the carbonyl compounds is the photoreduction in the presence of good hydrogen atom donors.<sup>38-41</sup> From studies of a number of aromatic ketones it appears that the reactive species is an  $n, \pi$  triplet state.<sup>38-41</sup> In those ketones where the lowest triplet state is a  $\pi, \pi$  triplet state, the molecules are considerably less reactive, or totally unreactive. Our triplet-state assignments in the benzophenone series are therefore consistent with the observations that the 4,4'-dimethyl-, -dimethoxy-, and -dibromobenzophenone all readily photopinacolize.<sup>38</sup> The "anomalous" non-reactivity of *p*-hydroxybenzophenone has been previously considered by Porter<sup>27</sup> in terms of the excited state *pK*. Many of the butyrophenones are known to undergo a photochemical reaction which is analogous

(36)  $S \rightarrow T_{\pi, \pi}$  transitions have also been observed in a number of coumarin derivatives without the use of heavy atom solvents: W. Rothman and D. R. Kearns, presented at the Western Regional Meeting the American Chemical Society, Los Angeles, Calif., Nov 1965.

(37) A. Marchetti and D. R. Kearns, unpublished data.

(38) J. N. Pitts, H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(39) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(40) J. K. S. Wan, R. N. McCormick, E. J. Baum, and J. N. Pitts, *ibid.*, **87**, 4409 (1965).

(41) G. S. Hammond and P. A. Leermakers, *ibid.*, **84**, 207 (1962).

to the type II cleavage of ketones, and again reactivity can generally be correlated with relative ordering of the  $n, \pi$  and  $\pi, \pi$  triplet states.<sup>42</sup> In both 4'-chloro- and 4'-methylbutyrophenone the lowest triplet state has been assigned as an  $n, \pi$  triplet state, and both compounds show a high quantum yield for the type II process.<sup>43</sup> In *p*-hydroxy- and *p*-acetamidobutyrophenone, on the other hand, the lowest triplet state is a  $\pi, \pi$  triplet state, and these molecules do not undergo a type II photochemical reaction.<sup>30</sup> Similarly, the non-reactivity of 2-naphthaldehyde has already been attributed to the fact that the lowest triplet state is a  $\pi, \pi$  triplet state.<sup>44</sup>

As we pointed out in section A, all of the acetophenone derivatives which we studied, including 4'-acetamido-, 4'-bromo-, 4'-hydroxy-, 4'-methoxy-, and 2,4'-dibromoacetophenone, have a  $\pi, \pi$  triplet state as their lowest triplet state. Therefore, to the extent that the correlation between reactivity and location of the  $n, \pi$  triplet state is valid, these substituted acetophenones should be photochemically less reactive than acetophenone.

**Acknowledgments.** The support of the U. S. Public Health Service, Grant No. G. M. 10499, is most gratefully acknowledged.

(42) J. N. Pitts, L. D. Hess, E. J. Baum, E. A. Schuck, and J. S. Wan, *Photochem. Photobiol.*, **4**, 305 (1965).

(43) E. J. Baum and J. N. Pitts, private communication.

(44) L. A. Singer and P. D. Bartlett, *Tetrahedron Letters*, 1887 (1964).

## Free-Radical Addition of Trifluoroacetonitrile to Ethylene. III. Temperature Dependence and Reaction Energetics<sup>1,2</sup>

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*Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York. Received June 30, 1966*

**Abstract:** A study is reported of the rate of the gas-phase addition of  $CF_3CN$  to ethylene over the range 365–445°. Under conditions such that  $CF_3CN \gg C_2H_4$ , the rate equation is  $(\partial/\partial t)[CF_3CH_2CH_2CN] = 10^{7.0 \pm 0.4} \exp(-27 \pm 3/RT)[CF_3CN][C_2H_4]$  mole l.<sup>-1</sup> sec<sup>-1</sup>. Examination of this result relative to the over-all reaction energetics shows the initiation process to be bimolecular,  $CF_3CN + C_2H_4 \rightarrow CNCH_2CH_2 + CF_3$ , and the kinetic chain length for the propagation cycle about 200 at 440°.

The telomerization of  $CF_3I$  with ethylene has been investigated in the homogeneous gas phase (309°) by Bell.<sup>4</sup> A similar study, but with  $CF_3CN$  and  $C_2H_4$  at a higher temperature (442°), was reported by Gac and Janz.<sup>5</sup> Both centered on the propagation steps of these free-radical processes. The present communication reports the results of a study of the  $CF_3CN-C_2H_4$  addition reaction over a temperature range from 365 to

445°. The results are examined for their significance relative to the reaction energetics of such gas-phase telomerizations and the mode of initiation of the free-radical mechanism.

### Kinetics

The reactants,  $CF_3CN$  (Peninsular Chemresearch, Inc., 99% minimum) and  $C_2H_4$  (Matheson Co., Inc., 99% minimum), were degassed under high vacuum and triply distilled at low temperatures prior to use.

The apparatus and procedure have been described in detail elsewhere.<sup>5</sup> Kinetic data were obtained by manometric techniques. Total initial reactant pressures were between 450 and 700 mm. The initial mole ratio of nitrile to olefin was maintained constant at 8.7:1.0. Analyses of both liquid and gaseous products

(1) Based in part on a thesis submitted by J. B. F. in partial fulfillment of the requirements for the Ph.D. degree, Oct 1965, Rensselaer Polytechnic Institute, Troy, N. Y.

(2) Presented at the 152th National Meeting of the American Chemical Society, Division of Physical Chemistry, New York, N. Y., Sept 1966.

(3) Author to whom inquiries should be addressed.

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

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

were obtained by gas chromatography and infrared spectroscopy.

The over-all rate of reaction of  $\text{CF}_3\text{CN}$  with  $\text{C}_2\text{H}_4$  to form  $\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}$  was measured at temperatures in the range 365–445°. Total system pressure was monitored for sufficient time to allow typically 40–60% conversion of reactants (based on initial concentration of ethylene). Product analyses established that the liquid products had the same composition as previously reported<sup>5</sup> for similar reaction conditions, *i.e.*, the major constituent was  $\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}$ , with small amounts (<3 mole %) of  $\text{CH}_2=\text{CHCN}$ ,  $\text{CH}_3\text{CH}_2\text{CN}$ , and  $\text{CF}_3(\text{CH}_2\text{CH}_2)_2\text{CN}$ .

Semiquantitative analysis of gaseous fractions by low-temperature chromatography confirmed  $\text{C}_2\text{F}_6$  and  $\text{CF}_3\text{H}$  as the only gaseous products. Trace amounts of  $\text{C}_2\text{F}_6$  (<0.1 mole %, based on total starting materials) were formed, while as much as 1.5 mole % of  $\text{CF}_3\text{H}$  was detected. No evidence for  $(\text{CN})_2$  in the products was found.

The kinetic data were examined to establish the order relative to each of the reactants. The kinetic order with respect to  $\text{C}_2\text{H}_4$  was found to be first order, as reported previously.<sup>5</sup> The order with respect to  $\text{CF}_3\text{CN}$  could not be confirmed from the rate data and remains indeterminate under present experimental conditions. This difficulty arises because of the large excess of nitrile that is necessary to repress the formation of higher telomers, *i.e.*,  $\text{CF}_3(\text{CH}_2\text{CH}_2)_n\text{CN}$ ,  $n = 2, 3, \dots$ . The kinetic order relative to  $\text{CF}_3\text{CN}$  was thus gained indirectly from a knowledge of the over-all reaction energetics and the kinetic steps of this free-radical process (*vide infra*).

The analysis of pressure-time data and calculation of kinetic rate constant were facilitated through computer programs developed as part of this study. The programs evaluated the initial total pressure as a function of time. Initial partial pressures of reactants were also thus calculated using the known initial mole ratio. Values of an integrated rate expression  $\log X_t$  were gained for each data point, and a quadratic expression for  $\log X_t$  as a function of time was generated by least-squares analysis. The rate constants were derived from the limiting initial gradient of this expression, *i.e.*, at  $t = 0$ .

Rate constants were calculated by two rate laws: (a) the three-halves-order rate expression advanced earlier

$$k_{3/2} = \frac{2.303(RT)^{1/2}}{(a-b)^{1/2}} \frac{\partial}{\partial t} \log X_{3/2} \quad (1)$$

where

$$X_{3/2} = \left[ \frac{(a-x)^{1/2} + (a-b)^{1/2}}{(a-x)^{1/2} - (a-b)^{1/2}} \right] \quad (2)$$

and (b) a second-order rate law

$$k_2 = \frac{2.303RT}{(a-b)} \frac{\partial}{\partial t} \log X_2 \quad (3)$$

where

$$X_2 = \left[ \frac{b(a-x)}{a(b-x)} \right] \quad (4)$$

In the above,  $t$  is time (sec),  $a$  is initial nitrile concentration,  $b$  is initial olefin concentration, and  $x$  is the pro-

gressive concentration of product. The results are in Table I. Comparison with the data from the previous

Table I. Three-Halves and Second-Order Rate Constants for  $\text{C}_3\text{FCN}-\text{C}_2\text{H}_4$  Reaction

Expt	Temp, °K	$10^3 k_{3/2}$ , (mole/l.) <sup>-1/2</sup> sec <sup>-1</sup>	$10^2 k_2$ , (mole/l.) <sup>-1</sup> sec <sup>-1</sup>
1	715.2	5.6	5.0
2	716.1	5.0	5.3
3	714.9	5.4	5.6
4	717.3	5.2	5.3
5	714.8	4.5	4.5
6	714.5	5.4	5.0
7	714.6	5.0	5.8
8	698.6	2.6	2.4
9	697.8	2.5	2.4
10	697.8	2.6	2.5
11	697.6	2.8	2.8
12	697.4	3.4	3.7
13	697.4	4.0	4.3
14	694.0	2.7	2.7
15	692.2	2.7	2.6
16	692.6	2.8	3.0
17	683.7	2.0	1.8
18	684.3	2.0	1.8
19	683.5	2.4	2.2
20	683.6	2.5	2.5
21	682.9	2.8	2.7
22	681.6	2.8	2.9
23	672.0	1.5	1.6
24	670.7	1.5	1.2
25	669.7	1.5	1.3
26	669.1	1.2	1.0
27	667.8	0.91	0.90
28	667.2	0.99	0.89
29	667.6	1.1	1.1
30	666.6	1.2	1.1
31	661.7	1.1	1.0
32	661.0	1.0	1.0
33	643.2	0.75	0.79
34	641.7	0.54	0.55
35	638.6	0.68	0.65
36	635.9	0.52	0.46

study<sup>5</sup> at 440° shows that the results are in good agreement. A least-squares analysis of the calculated rate constants in terms of the Arrhenius relationship gives

$$k_{3/2} = 10^{9.7 \pm 0.3} \exp[(-26 \pm 2)/RT] \quad (5)$$

$$k_2 = 10^{7.0 \pm 0.4} \exp[(-27 \pm 3)/RT] \quad (6)$$

The error limits are root-mean-square deviations. A graph of  $\log k_2$  vs.  $1/T$  is in Figure 1.

The values of the over-all energy of activation are 26 and 27 kcal mole<sup>-1</sup>, corresponding to three-halves and second-order reaction schemes, respectively. The reaction mechanisms described by these two possible rate laws are summarized for comparison in Table II. The propagation and termination processes were confirmed in the detailed study by Gac and Janz.<sup>5</sup> The identity of  $\text{CF}_3$  as the primary chain carrier has also been confirmed elsewhere.<sup>5-7</sup> The identification of  $\text{C}_2\text{F}_6$  and  $\text{CF}_3\text{H}$  and the absence of  $(\text{CN})_2$  in the reaction products are additional support for  $\text{CF}_3$  as the principal chain carrier. Inspection (Table II) shows that the two schemes differ in the nature of the initiation process.

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

(7) G. J. Janz and J. B. Flannery, *J. Phys. Chem.*, **70**, 2061 (1966).

Table II.<sup>a</sup> Mechanism for CF<sub>3</sub>CN-C<sub>2</sub>H<sub>4</sub> Addition Reaction

Initiation	$\text{CF}_3\text{CN} \xrightarrow{k_i} \text{CF}_3 + \text{CN}$	(i)
$\frac{3}{2}$ order		
2nd order	$\text{CF}_3\text{CN} + \text{C}_2\text{H}_4 \xrightarrow{k_b} \text{CF}_3 + \text{CNCH}_2\text{CH}_2$	(b)
Propagation	$\text{CF}_3 + \text{C}_2\text{H}_4 \xrightarrow{k_4} \text{CF}_3\text{CH}_2\text{CH}_2$	(4)
	$\text{CF}_3\text{CH}_2\text{CH}_2 + \text{CF}_3\text{CN} \xrightarrow{k_5} \text{CF}_3\text{CH}_2\text{CH}_2\text{CN} + \text{CF}_3$	(5)
Termination	$\text{CF}_3 + \text{CF}_3 \xrightarrow{k_6} \text{C}_2\text{F}_6$	(6)
	$\text{CF}_3 + \text{CF}_3\text{CH}_2\text{CH}_2 \xrightarrow{k_7} \text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$	(7)
	$\text{CF}_3\text{CH}_2\text{CH}_2 + \text{CF}_3\text{CH}_2\text{CH}_2 \xrightarrow{k_8} \text{CF}_3(\text{CH}_2\text{CH}_2)_2\text{CF}_3$	(8)

<sup>a</sup> Numbering of above equations is that given in ref 5.

For over-all second-order kinetics, the initiation step is a molecule-molecule reaction leading to free-radical species; for the three-halves-order scheme, a first-order dissociation of CF<sub>3</sub>CN is the initiation step. It is of interest to examine this problem from the viewpoint of the over-all reaction energetics and bond dissociation energies to see if sufficient insight can be gained to distinguish between these two initiation steps and to establish the over-all reaction order.

### Discussion

With a stationary state in CF<sub>3</sub> and CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> and the assumption of long kinetic chains, it follows that the over-all rate of the three-halves-order process in Table II is

$$R_0 = \frac{\partial}{\partial t}[\text{CF}_3\text{CH}_2\text{CH}_2\text{CN}] = R_i^{1/2} \left[ \frac{k_4[\text{C}_2\text{H}_4]}{2k_6 + 2k_7 \frac{k_4}{k_5} M + 2k_8 \left( \frac{k_4}{k_5} \right)^2 M^2} \right]^{1/2} \quad (7)$$

where  $M = [\text{C}_2\text{H}_4]/[\text{CF}_3\text{CN}]$ , and the rate of initiation  $R_i = k_i[\text{CF}_3\text{CN}]$ , when  $[\text{CF}_3\text{CN}] \gg [\text{C}_2\text{H}_4]$ . Thus, from (7), the apparent energy of activation,  $E_o$ , is given by

$$E_o = \frac{1}{2}E_i + E_4 - E_t \quad (8)$$

with  $t$  denoting the rate-controlling termination step, *i.e.*, (6), (7), or (8) of Table II.

The value for  $E_4$ , estimated from related data<sup>8-11</sup> for CH<sub>3</sub> and CF<sub>3</sub> addition to ethylene, and for CH<sub>3</sub> recombination,<sup>12</sup> is about 7 kcal mole<sup>-1</sup>. Activation energies for radical recombinations are generally close to zero;  $E_t$  is thus assumed to be negligible. If (i) is the initiation step,  $E_i$  would be close to the bond dissociation energy  $D(\text{F}_3\text{C}-\text{CN})$ , *i.e.*,  $107 \pm 3$  kcal mole<sup>-1</sup> (*cf.* Appendix I). With these values, (8) predicts  $E_o \sim 60 \pm 2$  kcal mole<sup>-1</sup>. The observed value of  $E_o$  corresponding to an over-all three-halves-order rate law is  $26 \pm 2$  kcal mole<sup>-1</sup>. This discrepancy cannot be reconciled by assuming a unimolecular dissociation of CF<sub>3</sub>CN in the falloff region, for Kassel theory<sup>13</sup> would require

(8) J. M. Pearson and M. Szwarc, *Trans. Faraday Soc.*, **59**, 553 (1964).

(9) M. Feld and M. Szwarc, *J. Am. Chem. Soc.*, **82**, 3791 (1960).

(10) R. P. Buckley and M. Szwarc, *Proc. Roy. Soc. (London)*, **A240**, 396 (1957).

(11) R. K. Brinton, *J. Chem. Phys.*, **29**, 781 (1958).

(12) R. Gomer and G. B. Kistiakowsky, *ibid.*, **19**, 85 (1951).

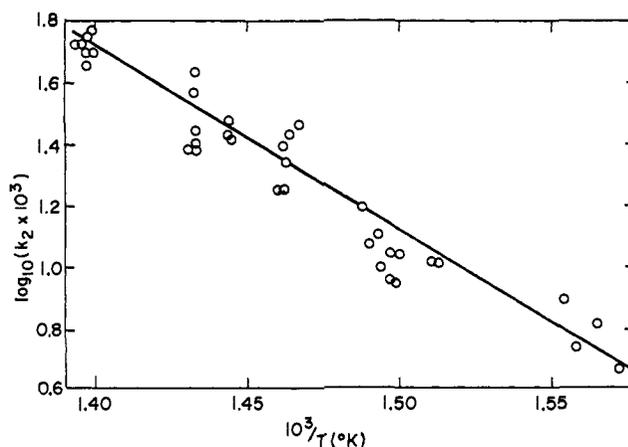
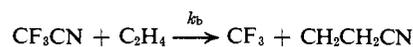


Figure 1. Arrhenius plot for CF<sub>3</sub>CN-C<sub>2</sub>H<sub>4</sub> reaction, second-order kinetics, least-squares equation:  $k_2 = 10^{7.0 \pm 0.4} \exp(-27 \pm 3RT)$ .

the implausible result that the number of internal degrees of freedom in CF<sub>3</sub>CN be about 82 at 440°. The unimolecular dissociation of CF<sub>3</sub>CN thus appears ruled out as a significant factor in the kinetics of the over-all process.

The mechanism proposed for the second-order process (step b in Table II) depends on the bimolecular initiation process



The expression for the rate of initiation,  $R_i$ , thus takes the form

$$R_i = k_b[\text{CF}_3\text{CN}][\text{C}_2\text{H}_4] \quad (9)$$

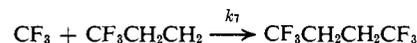
From this it follows that the over-all rate of reaction,  $R_o$ , is given by

$$R_o = \frac{k_b^{1/2} k_4}{\left[ 2k_6 + 2k_7 \frac{k_4}{k_5} M + 2k_8 \left( \frac{k_4}{k_5} \right) M^2 \right]^{1/2}} [\text{CF}_3\text{CN}]^{1/2} [\text{C}_2\text{H}_4]^{1/2} \quad (10)$$

It follows from the limits imposed by the mole ratios in the present study that this reduces to

$$R_o = \left[ \frac{k_b k_4 k_5}{2k_7} \right]^{1/2} [\text{CF}_3\text{CN}][\text{C}_2\text{H}_4] \quad (11)$$

*i.e.*, the rate is second order over-all, but is first order with respect to both ethylene and CF<sub>3</sub>CN. The rate-controlling chain-termination step in the scheme corresponding to (11) is (step 7, Table II)



This is consistent with the analytical and kinetic results of this and the previous studies.<sup>5,14</sup>

From (11), the value observed for the over-all energy of activation,  $E_o$ , may be expressed as

$$E_o = \frac{1}{2}[E_b + E_4 + E_5 - E_7] \quad (12)$$

Comparison of the value for  $E_o$  calculated from (12)

(13) C. N. Hinshelwood, "The Kinetics of Chemical Change," Oxford University Press, London, 1955, p 79.

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

with that determined experimentally is necessary to test the proposed second-order mechanism.

Values for  $E_4$  and  $E_7$  are given above. The chain-transfer reaction (5) is in a class for which activation energies are low, *ca.* 3–6 kcal mole<sup>-1</sup>.<sup>15</sup> While the activation energy,  $E_b$ , for bimolecular initiation is not known, it can be equated in first approximation to the enthalpy change  $\Delta H_b$  for reaction b. The latter can be gained as follows.

The heats of formation for all species in (b), except that for CNCH<sub>2</sub>CH<sub>2</sub>, are known (*cf.* Tables IV and VI). Calculation of the latter by: (i) a method of group equations, and (ii) a bond-energy comparison, gives the value

$$\Delta H_f^{\circ}{}_{298}(\text{CNCH}_2\text{CH}_2(\text{g})) = 58 \pm 3 \text{ kcal mole}^{-1} \quad (13)$$

Thus, the enthalpy change for initiation by (b) is

$$\Delta H_b \sim 60 \pm 5 \text{ kcal mole}^{-1} \quad (14)$$

With these estimates, the predicted  $E_o$ , from (12), falls in the range of 32–39 kcal mole<sup>-1</sup>. The agreement with the experimental value for  $E_o$ ,  $27 \pm 3$  kcal mole<sup>-1</sup>, is all that could be expected in view of the uncertainties in the thermochemical data and the estimates required in these calculations. The predicted value for  $E_o$ , while subject to large uncertainties, nevertheless gives strong support for the second-order rate law as a description of the over-all process.

The formation of free radicals through reaction of molecular species is known.<sup>16,17</sup> In the present system, the established participation of CF<sub>3</sub> radicals in product-forming chains, and the absence of the CN radical, are additional support for the bimolecular initiation scheme. Further, the products, CH<sub>3</sub>CH<sub>2</sub>CN and CH<sub>2</sub>=CHCN, are understood through the disproportionation and abstraction reactions of the cyanoethyl radical, CNCH<sub>2</sub>CH<sub>2</sub>. This feature of the observed results is thus also in accord with the bimolecular initiation process (Table II).

A measure of the kinetic chain length can be obtained from a comparison of the rate of the over-all reaction to the rate of initiation. In this system

$$\text{kinetic chain length} \sim \frac{10^7 \exp(-27/RT)}{10^{10} \exp(-44/RT)} \sim 2 \times 10^2 (440^\circ) \quad (15)$$

assuming a "normal" bimolecular preexponential for (b), and using  $E_b$ <sup>18</sup> from (12). This chain length compares well with the value of 300 determined earlier,<sup>5</sup> using ethylene oxide as a radical initiator. The assumption of long kinetic chains advanced earlier<sup>5</sup> is confirmed. The predominance of CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN in this process, with a large excess of nitrile in the initial reactant mixture, follows from reactions 4 and 5 (Table II) as the sole propagation steps in this gas-phase free-radical process.

## Appendix I

**Thermochemical Considerations.** Knowledge of the C–C bond dissociation energy of CF<sub>3</sub>CN,  $D(\text{F}_3\text{C}-\text{CN})$ ,

(15) N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," Vol. 1, Pergamon Press, New York, N. Y., 1958, p 4.

(16) N. N. Semenov, *ref 15*, pp 260–271.

(17) S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, **16**, 397 (1965).

(18)  $E_b$  for this estimate was obtained from (12) using the experimental  $E_o = 27$  kcal mole<sup>-1</sup>. Thus  $E_b = 44$  kcal mole<sup>-1</sup> in (15).

is important. While a thermochemical estimate of  $D(\text{F}_3\text{C}-\text{CN})$  has been reported,<sup>14</sup> this differs from a more recent experimental value derived from electron-impact studies.<sup>19</sup> The possible approaches to this problem are as follows. The bond dissociation energy,  $D(\text{F}_3\text{C}-\text{CN})$ , can be derived from thermodynamic data for the processes



or



if the value for  $\Delta H_f^{\circ}{}_{298}(\text{CF}_3\text{CN}(\text{g}))$  is known. Since the latter value has not been established by combustion calorimetry, the estimation of a reliable value is considered from various empirical and semiempirical techniques.

An alternate is to calculate  $D(\text{F}_3\text{C}-\text{CN})$  from electron-impact data, but this requires the value of the appearance potential  $A(\text{CF}_3^+)$  of CF<sub>3</sub><sup>+</sup> from CF<sub>3</sub>CN and the ionization potential  $I(\text{CF}_3)$  of the CF<sub>3</sub> radical. The former has been determined,<sup>19</sup> but uncertainty exists over the latter. This is also examined further in this approach.

**Estimates of  $\Delta H_f^{\circ}{}_{298}(\text{CF}_3\text{CN}(\text{g}))$ .** (a) **Andersen-Beyer-Watson-Bryant Method.**<sup>20–22</sup> The method of group contributions<sup>20,21</sup> has recently been extended by Bryant<sup>22</sup> for estimation of thermodynamic properties of fluorocarbons. This method was applied to calculate  $\Delta H_f^{\circ}{}_{298}(\text{CF}_3\text{CN}(\text{g}))$  using data obtained from the sources cited.<sup>20–22</sup> The calculation, shown in Table III, yields  $\Delta H_f^{\circ}{}_{298}(\text{CF}_3\text{CN}(\text{g})) = -131.6$  kcal mole<sup>-1</sup>.

Table III. Heat of Formation of CF<sub>3</sub>CN(g) by Group Contributions

	$\Delta H_f^{\circ}$ , kcal mole
Base group, CH <sub>4</sub>	-17.9
Primary CH <sub>3</sub> substitution	-2.4
Secondary CH <sub>3</sub> substitution (1,1)	-4.5
(2,1)	-6.6
(3,1)	-8.1
Trisubstituted fluorine (3 × 43.7)	-131.1
CN group replacing CH <sub>3</sub>	39.0
$\Delta H_f^{\circ}{}_{298}(\text{CF}_3\text{CN}(\text{g}))$	-131.6

(b) **Method of Group Equations.**<sup>21</sup> An earlier estimate<sup>14</sup> by the method of group equations<sup>21</sup> gave  $\Delta H_f^{\circ}{}_{298}(\text{CF}_3\text{CN}(\text{g})) = -126.7$  kcal mole<sup>-1</sup>. Known heats of formation of benzotrifluoride,<sup>23</sup> acetonitrile,<sup>24</sup> and toluene<sup>25</sup> were used in the equation

$$\Delta H_f^{\circ}(\text{CF}_3\text{CN}) = \Delta H_f^{\circ}(\text{C}_6\text{H}_5\text{CF}_3) + \Delta H_f^{\circ}(\text{CH}_3\text{CN}) - \Delta H_f^{\circ}(\text{C}_6\text{H}_5\text{CH}_3) \quad (18)$$

Recently, more reliable values of  $\Delta H_f^{\circ}{}_{298}$  for benzotri-

(19) G. P. Van der Kelen and P. J. DeBievre, *Bull. Soc. Chim. Belges*, **69**, 379 (1960).

(20) J. W. Andersen, G. H. Beyer, and K. M. Watson, *Natl. Petroleum News*, **36**, 476 (1944).

(21) G. J. Janz, "The Estimation of Thermodynamic Properties of Organic Compounds," Academic Press Inc., New York, N. Y., 1958.

(22) W. M. D. Bryant, *J. Polymer Sci.*, **56**, 277 (1962).

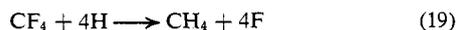
(23) W. D. Good and D. W. Scott, *J. Phys. Chem.*, **60**, 1080 (1956).

(24) P. J. Hawkins and G. J. Janz, *J. Chem. Soc.*, 1479 (1949).

(25) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

fluoride<sup>26</sup> and acetonitrile<sup>27</sup> have been determined to be  $-148.29$  and  $21.0$  kcal mole<sup>-1</sup>, respectively. These, with the established  $\Delta H_f^\circ{}_{298}(\text{C}_6\text{H}_5\text{CH}_3) = 11.95$  kcal mole<sup>-1</sup>,<sup>25</sup> gives for  $\Delta H_f^\circ{}_{298}(\text{CF}_3\text{CN}(\text{g}))$  the value  $-139$  kcal mole<sup>-1</sup>.

(c) **Bond Energy Comparison.**<sup>28</sup> The difference in thermochemical bond energies  $E(\text{C-F}) - E(\text{C-H})$  in aliphatic compounds was derived by Good and co-workers<sup>28</sup> from hypothetical reactions of the type



For similar conformations of product and reactant, the heat of reaction depends on the difference in bond energies of bonds created and destroyed in substitution.

Data on heats of formation of fluorinated organics, though sparse, have increased considerably. The current "best" values for  $\Delta H_f^\circ{}_{298}$  are in Table IV. Also included are the relevant heats of formation of hydrocarbons, and heats of atomization of hydrogen and fluorine, needed to revise earlier calculations.<sup>28</sup> Model reactions and associated endothermicities are listed in Table V.

**Table IV.** Thermodynamic Data for Fluorocarbons and Hydrocarbons

Compound	$\Delta H_f^\circ{}_{298}(\text{g})$ , kcal mole <sup>-1</sup>	Compound	$\Delta H_f^\circ{}_{298}(\text{g})$ , kcal mole <sup>-1</sup>
CF <sub>4</sub>	-218.3 <sup>a</sup>	C <sub>6</sub> F <sub>6</sub>	-220.4 <sup>i</sup>
C <sub>2</sub> F <sub>6</sub>	-316.5 <sup>b</sup>	c-C <sub>6</sub> F <sub>10</sub>	-449.6 <sup>j</sup>
n-C <sub>7</sub> F <sub>16</sub>	-789.0 <sup>c</sup>	CH <sub>4</sub>	-17.889 <sup>k</sup>
c-C <sub>6</sub> F <sub>11</sub> CF <sub>3</sub>	-675.3 <sup>c</sup>	C <sub>2</sub> H <sub>6</sub>	-20.236 <sup>k</sup>
c-C <sub>6</sub> F <sub>11</sub> C <sub>2</sub> F <sub>5</sub>	-769.7 <sup>c</sup>	n-C <sub>7</sub> H <sub>16</sub>	-44.89 <sup>k</sup>
C <sub>2</sub> F <sub>4</sub>	-162(-151.7) <sup>d</sup>	c-C <sub>6</sub> H <sub>11</sub> CH <sub>3</sub>	-36.9 <sup>k</sup>
CF <sub>2</sub> CH <sub>2</sub>	-79.6 <sup>e</sup>	c-C <sub>6</sub> H <sub>11</sub> C <sub>2</sub> H <sub>5</sub>	-41.0 <sup>k</sup>
CF <sub>2</sub> CFH	-113.3 <sup>e</sup>	C <sub>2</sub> H <sub>4</sub>	12.496 <sup>k</sup>
CF <sub>3</sub> CFCF <sub>2</sub>	-259 <sup>b</sup>	CH <sub>3</sub> CHCH <sub>2</sub>	4.879 <sup>k</sup>
CF <sub>3</sub>	-115 ± 5 <sup>b</sup>	CH <sub>3</sub>	32.0 <sup>l</sup>
CF <sub>3</sub> H	-162.6 <sup>f</sup>	C <sub>3</sub> H <sub>8</sub>	-24.820 <sup>k</sup>
CF <sub>3</sub> CH <sub>3</sub>	-169 <sup>g</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	11.950 <sup>k</sup>
C <sub>2</sub> H <sub>5</sub> CF <sub>3</sub>	-185(-176) <sup>g,m</sup>	C <sub>6</sub> H <sub>6</sub>	19.820 <sup>k</sup>
C <sub>2</sub> H <sub>3</sub> CF <sub>3</sub>	-155 <sup>g</sup>	c-C <sub>6</sub> H <sub>10</sub>	-1.70 <sup>k</sup>
C <sub>6</sub> H <sub>5</sub> CF <sub>3</sub>	-148.29 <sup>h</sup>	H	52.09 <sup>l</sup>
C <sub>6</sub> H <sub>5</sub> F	-26.48 <sup>i</sup>	F	18.9 ± 1 <sup>l</sup>

<sup>a</sup> C. R. Patrick, *Tetrahedron*, **4**, 26 (1961). <sup>b</sup> C. R. Patrick, *Advan. Fluorine Chem.*, **2**, 1 (1961); and ref 12. <sup>c</sup> Reference 19. <sup>d</sup> F. W. Kirkbridge and F. G. Davidson, *Nature*, **174**, 79 (1954); G. A. Neugebauer and J. L. Margrave, *J. Phys. Chem.*, **60**, 1318 (1956). <sup>e</sup> V. P. Kolescov, A. M. Martynov, S. M. Shtekher, and S. M. Skuratov, *Russ. J. Phys. Chem.*, **36**, 1118 (1962). <sup>f</sup> G. A. Neugebauer and J. L. Margrave, *J. Phys. Chem.*, **62**, 1043 (1958). <sup>g</sup> Reference 20. <sup>h</sup> Reference 16. <sup>i</sup> W. D. Good and D. W. Scott, *Pure Appl. Chem.*, **2**, 77 (1961). <sup>j</sup> Reference 18. <sup>k</sup> F. D. Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons," Circular C461, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C. 1947. <sup>l</sup> Reference 17. <sup>m</sup> See text for duplicate values.

The difference in bond energies is given<sup>28</sup> by  $a$  for  $\geq \text{CF}$  relative to  $\geq \text{CH}$ ; by  $b$  for  $> \text{CF}_2$  relative to  $> \text{CH}_2$ ; and by  $c$  for  $-\text{CF}_3$  relative to  $-\text{CH}_3$ . Solution of appropriate equations for reactions 1 through 9 in Table V gives for  $a$ ,  $b$ , and  $c$  the values 9.25, 11.65, and

(26) W. D. Good, J. L. Lacina, B. L. DePrater, and J. P. McCullough, *J. Phys. Chem.*, **68**, 579 (1964).

(27) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1952.

(28) 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 V.** Heats of "Model" Reactions

No.	Reaction	$\Delta H_f^\circ{}_{298}$ , kcal mole <sup>-1</sup>
1	CF <sub>4</sub> + 4H → CH <sub>4</sub> + 4F	67.7
2	n-C <sub>7</sub> F <sub>16</sub> + 16H → n-C <sub>7</sub> H <sub>16</sub> + 16F	213.1
3	CF <sub>3</sub> + 14H → CH <sub>3</sub> + 14F	173.7
4	C <sub>2</sub> F <sub>5</sub> + 16H → C <sub>2</sub> H <sub>5</sub> + 16F	197.7
5	C <sub>2</sub> F <sub>6</sub> + 6H → C <sub>2</sub> H <sub>6</sub> + 6F	97.1
6	CF <sub>3</sub> + 3H → CH <sub>3</sub> + 3F	49.4
7	CHF <sub>3</sub> + 3H → CH <sub>4</sub> + 3F	45.1
8	CF <sub>3</sub> CH <sub>3</sub> + 3H → CH <sub>3</sub> CH <sub>3</sub> + 3F	49.2
9	CF <sub>3</sub> C <sub>2</sub> H <sub>5</sub> + 3H → C <sub>3</sub> H <sub>8</sub> + 3F	60.6 (51.6) <sup>a</sup>
10	C <sub>2</sub> F <sub>4</sub> + 4H → C <sub>2</sub> H <sub>4</sub> + 4F	31.4
11	C <sub>3</sub> F <sub>6</sub> + 6H → C <sub>3</sub> H <sub>6</sub> + 6F	64.7
12	CF <sub>3</sub> C <sub>2</sub> H <sub>5</sub> + 3H → C <sub>3</sub> H <sub>8</sub> + 3F	60.3
13	CF <sub>2</sub> CH <sub>2</sub> + 2H → C <sub>2</sub> H <sub>4</sub> + 2F	25.7
14	C <sub>2</sub> F <sub>3</sub> H + 3H → C <sub>2</sub> H <sub>4</sub> + 3F	26.2
15	c-C <sub>6</sub> F <sub>10</sub> + 10H → c-C <sub>6</sub> H <sub>10</sub> + 10F	116.0
16	C <sub>6</sub> H <sub>5</sub> CF <sub>3</sub> + 3H → C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> + 3F	60.7
17	C <sub>6</sub> H <sub>5</sub> F + H → C <sub>6</sub> H <sub>6</sub> + F	13.1
18	C <sub>6</sub> F <sub>6</sub> + 6H → C <sub>6</sub> H <sub>6</sub> + 6F	41.1

<sup>a</sup> See text for explanation of duplicate values.

16.1, respectively. These are compared to  $a$ ,  $b$ , and  $c$  of 7.2, 12.0, and 15.5, respectively, derived earlier.<sup>28</sup>

The endothermicity of reaction 9 in Table V is high by about 10 kcal mole<sup>-1</sup> when compared to related reactions 1 through 8. This reaction heat depends on a heat of formation of CF<sub>3</sub>C<sub>2</sub>H<sub>5</sub> estimated<sup>29</sup> from electron-impact data using a measured appearance potential  $A(\text{C}_2\text{H}_5^+)$  for the ethyl ion from this compound and a literature value for  $I(\text{C}_2\text{H}_5)$ . However, data from the same source<sup>29</sup> for  $A(\text{CF}_3^+)$  from CF<sub>3</sub>C<sub>2</sub>H<sub>5</sub>, and  $I(\text{CF}_3) = 10.1$  eV,<sup>30</sup> give  $\Delta H_f^\circ(\text{C}_2\text{H}_5\text{CF}_3) = -176$  kcal mole<sup>-1</sup>, from which the heat of reaction 9 is 51.6 kcal mole<sup>-1</sup>. This value is consistent with those for related processes and suggests that the  $A(\text{C}_2\text{H}_5)^+$  of Steele and Stone<sup>29</sup> probably represents an excited species.

No internally consistent set of  $a$ ,  $b$ , and  $c$  values were found for reactions representing substitution in olefins or aromatics.

One point which does emerge, however, is that values of  $c$  for  $E(\text{CF}_3) - E(\text{CH}_3)$  for groups adjacent to sp<sup>2</sup> carbons are higher by about 5 kcal mole<sup>-1</sup> than the corresponding  $c$  value for the aliphatic series. This indicates that a heat of formation calculated for CF<sub>3</sub>CN using the  $c = 16.1$  from the aliphatic compounds should be regarded as a maximum value. The problem of F substitution in  $\pi$ -bonded systems relative to thermodynamic properties has been recognized by Cox.<sup>31</sup> Since sufficiently reliable data are lacking, the question is not pursued further here.

Assuming invariance of  $c = 16.1 \pm 0.6$ , the heat of the reaction



is  $\Delta H^\circ = 48.3 \pm 1.8$  kcal mole<sup>-1</sup>. With  $\Delta H_f^\circ{}_{298}(\text{CH}_3-$

(29) W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3450 (1962).

(30) J. B. Farmer, I. H. S. Henderson, F. P. Lossing, and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

(31) J. D. Cox, H. A. Gundry, and A. J. Head, *Trans. Faraday Soc.*, **59**, 653 (1964).

$\text{CN}(\text{g}) = 21.0 \text{ kcal mole}^{-1}$ ,<sup>27</sup> one obtains  $\Delta H_f^\circ_{298}(\text{CF}_3\text{CN}(\text{g})) \leq -127 \pm 3 \text{ kcal mole}^{-1}$ .

**Estimate of  $D(\text{F}_3\text{C}-\text{CN})$  from Thermochemical Data.** The thermochemical estimates of  $\Delta H_f^\circ_{298}(\text{CF}_3\text{CN}(\text{g}))$  can be used to obtain  $D(\text{F}_3\text{C}-\text{CN})$  from the heats of reactions 16 and 17 above.

For (16),  $D(\text{H}_3\text{C}-\text{CN}) = 103 \text{ kcal mole}^{-1}$  was used.<sup>32</sup> Reaction 17 yields  $D(\text{F}_3\text{C}-\text{CN})$  directly, with  $\Delta H_f^\circ(\text{CN}(\text{g})) = 92 \pm 2 \text{ kcal mole}^{-1}$ .<sup>32</sup> Calculated quantities are in Table VI.

Table VI. Bond Dissociation Energy of  $\text{CF}_3\text{CN}$

$\Delta H_f^\circ_{298}$ ( $\text{CF}_3\text{CN}(\text{g})$ ), kcal mole <sup>-1</sup>	$D(\text{F}_3\text{C}-\text{CN})$ , kcal mole <sup>-1</sup>
$-127 \pm 3$	102
-132	107
-139	114

From the thermochemical data  $D(\text{F}_3\text{C}-\text{CN})$  emerges close to, or slightly higher than,  $D(\text{H}_3\text{C}-\text{CN})$ . Relative bond strengths in methyl and trifluoromethyl halides and hydrides are helpful to improving estimates of  $D(\text{F}_3\text{C}-\text{CN})$ . Pertinent data are in Table VII. Possibly excepting the bromides, the  $\text{CF}_3$  compounds have  $D(\text{F}_3\text{C}-\text{X})$  1-3 kcal mole<sup>-1</sup> higher than the  $\text{CH}_3$  analogs. Thus, by comparison with  $D(\text{H}_3\text{C}-\text{CN})$ ,  $D(\text{F}_3\text{C}-\text{CN}) = 107 \text{ kcal mole}^{-1}$  is most probable, with  $\Delta H_f^\circ_{298}(\text{CF}_3\text{CN}(\text{g})) = -132 \text{ kcal mole}^{-1}$ .

Table VII. Bond Strengths in  $\text{CH}_3-$  and  $\text{CF}_3-$  Compounds

Compound	$D(\text{R}-\text{X})$ , kcal mole <sup>-1</sup>
$\text{CH}_3-\text{I}$	$54 \pm 2^a$
$\text{CF}_3-\text{I}$	$57 \pm 4^b$
$\text{CH}_3-\text{Br}$	$67 \pm 2^{c,d}$
$\text{CF}_3-\text{Br}$	$64.5 \pm 2^b$
$\text{CH}_3-\text{Cl}$	$80 \pm 2^c$
$\text{CF}_3-\text{Cl}$	$83 \pm 3^e$
$\text{CH}_3-\text{F}$	$108 \pm 5^f$ ( $107 \pm 12^g$ )
$\text{CF}_3-\text{F}$	$121 \pm 4^e$
$\text{CH}_3-\text{H}$	$103.8 \pm 5^g$
$\text{CF}_3-\text{H}$	$106.2 \pm 0.5^g$
$\text{CH}_3-\text{CN}$	$104.2^h$ ( $103$ ) <sup>i</sup>
$\text{CF}_3-\text{CN}$	$107 \pm 3^i$

<sup>a</sup> C. A. McDowell and B. G. Cox, *J. Chem. Phys.*, **20**, 1496 (1952).

<sup>b</sup> M. Szwarc and A. H. Sehon, *ibid.*, **19**, 656 (1951). <sup>c</sup> F. P. Lossing, K. U. Ingold, and I. H. S. Henderson, *ibid.*, **22**, 1489 (1954). <sup>d</sup> M. Szwarc, *Chem. Rev.*, **47**, 75 (1950). <sup>e</sup> Reference 21. <sup>f</sup> V. H. Dibeler and R. M. Reese, *J. Res. Natl. Bur. Std.*, **54**, 127 (1955). <sup>g</sup> J. C. Amphlett, J. W. Coombler, and E. Whittle, *J. Phys. Chem.*, **70**, 593 (1966). <sup>h</sup> Reference 31. <sup>i</sup> Reference 32. <sup>j</sup> This work.

**Estimate of  $D(\text{F}_3\text{C}-\text{CN})$  from Electron-Impact Data.** The appearance potential of  $\text{CF}_3^+$  from  $\text{CF}_3\text{CN}$  was reported<sup>19</sup> as  $A(\text{CF}_3^+) = 14.5 \pm 0.1 \text{ ev}$ . This, with the ionization potential of  $\text{CF}_3$ ,  $I(\text{CF}_3)$ , can be used to derive  $D(\text{F}_3\text{C}-\text{CN})$ .

$$D(\text{F}_3\text{C}-\text{CN}) \leq A(\text{CF}_3^+) - I(\text{CF}_3) \quad (21)$$

The ionization potential  $I(\text{CF}_3)$  is widely discussed. Dibeler<sup>33</sup> reported  $I(\text{CF}_3) = 8.9 \text{ ev}$ , from measured

(32) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, pp 126-132.

(33) V. H. Dibeler, R. M. Reese, and F. L. Mohler, *J. Chem. Phys.*, **20**, 7 (1952).

$A(\text{CF}_3^+)$  and  $A(\text{CH}_3^+)$  from  $\text{CF}_3\text{CH}_3$ , and the value  $I(\text{CH}_3) = 10.07 \text{ ev}$ . Farmer<sup>30</sup> found  $I(\text{CF}_3) = 10.10 \pm 0.05 \text{ ev}$  by measuring  $A(\text{CF}_3^+)$  from hexafluoroazomethane. Lossing<sup>34</sup> suggested  $I(\text{CF}_3) = 10.2 \text{ ev}$ , but derived quantities using this value agreed poorly with known heats of formation. In a later report, Dibeler<sup>35</sup> recommended  $I(\text{CF}_3) = 9.3 \text{ ev}$ .

The low  $I(\text{CF}_3) = 8.9 \text{ ev}$  leads to  $D(\text{F}_3\text{C}-\text{CH}_3)$  and  $D(\text{F}_3\text{C}-\text{CF}_3)$  of 117 and 124 kcal mole<sup>-1</sup>, respectively. This should be discarded, since  $D(\text{H}_3\text{C}-\text{CH}_3)$  is only 83 kcal mole<sup>-1</sup>.<sup>36</sup>

Van der Kelen<sup>19</sup> accepted  $I(\text{CF}_3) = 9.3 \text{ ev}$  and found  $D(\text{F}_3\text{C}-\text{CN}) = 120 \pm 4 \text{ kcal mole}^{-1}$ . However, Bibby and Carter<sup>37</sup> used  $I(\text{CF}_3) = 9.35 \text{ ev}$  to obtain  $D(\text{F}_3\text{C}-\text{CF}_3) = 139.5 \text{ kcal mole}^{-1}$ , a high value, particularly in light of recent work.<sup>38</sup> The reported  $D(\text{NC}-\text{CN}) = 112 \text{ kcal mole}^{-1}$ <sup>32</sup> indicates  $D(\text{F}_3\text{C}-\text{CN})$  must be below 120 kcal mole<sup>-1</sup>. Resonance stabilization cannot contribute to the extent in  $\text{CF}_3\text{CN}$  that it does in cyanogen. Even the recent evidence<sup>39</sup> for  $D(\text{NC}-\text{CN}) = 125 \pm 8 \text{ kcal mole}^{-1}$  supports this view.

Farmer<sup>30</sup> used the directly determined  $I(\text{CF}_3) = 10.10 \pm 0.05 \text{ ev}$  with measured  $A(\text{CF}_3^+)$  from  $\text{CF}_4$ ,  $\text{CF}_3\text{H}$ , and  $\text{CF}_3\text{Cl}$  to derive bond energies  $D(\text{F}_3\text{C}-\text{F})$ ,  $D(\text{F}_3\text{C}-\text{H})$ , and  $D(\text{F}_3\text{C}-\text{Cl})$  consistent with other data on these compounds. Using  $I(\text{CF}_3) = 10.10 \pm 0.05 \text{ ev}$  with  $A(\text{CF}_3^+) = 14.5 \pm 0.01 \text{ ev}$ ,<sup>19</sup> one obtains  $D(\text{F}_3\text{C}-\text{CN}) = 101 \pm 3 \text{ kcal mole}^{-1}$ . For  $D(\text{H}_3\text{C}-\text{CN})$ , McDowell and Warren<sup>40</sup> found 103 kcal mole<sup>-1</sup>; this is generally accepted.<sup>32,41-43</sup> Similarly, if  $I(\text{CF}_3)$  is taken as 10.10 ev, then more reasonable  $D(\text{F}_3\text{C}-\text{CH}_3)$  and  $D(\text{F}_3\text{C}-\text{CF}_3)$  values of  $90 \pm 4$  and  $97 \pm 4 \text{ kcal mole}^{-1}$ , respectively, are obtained.<sup>33,37,44,45</sup>

With  $D(\text{F}_3\text{C}-\text{CF}_3) = 93 \pm 4 \text{ kcal mole}^{-1}$ ,<sup>46</sup> and  $A(\text{CF}_3^+)$  from  $\text{C}_2\text{F}_6$  as  $14.3 \pm 0.1 \text{ ev}$ ,<sup>33</sup> one obtains  $I(\text{CF}_3) = 10.3 \pm 0.2 \text{ ev}$ . This with  $A(\text{CF}_3^+)$  from  $\text{CF}_3\text{CN}$ <sup>19</sup> gives  $D(\text{F}_3\text{C}-\text{CN}) = 96.5 \pm \text{kcal mole}^{-1}$ .

Recently, Lossing and co-workers<sup>47</sup> have argued for  $I(\text{CF}_3) \sim 9.5 \text{ ev}$ , since  $I_{\text{vert}}(\text{CF}_3) = 10.1 \text{ ev}$  probably includes 0.6 ev excitational energy. Though inconsistencies in  $A(\text{CF}_3^+)$  from different compounds are large, the data are more readily reconciled with  $I(\text{CF}_3) \sim 9.5 \text{ ev}$ . In this case,  $D(\text{F}_3\text{C}-\text{CN})$  may be as high as 115 kcal mole<sup>-1</sup>. It is clear that the electron-impact data are insufficient to generate an estimate of  $D(\text{F}_3\text{C}-\text{CN})$  as accurately as the thermochemical approach.

(34) F. P. Lossing, P. Kebarle, and J. B. DeSousa, "Advances in Mass Spectrometry," Pergamon Press, New York, N. Y., 1959, p 431.

(35) V. H. Dibeler, R. M. Reese, and F. L. Mohler, *J. Res. Natl. Bur. Std.*, **57**, 113 (1956).

(36) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 262.

(37) M. M. Bibby and G. Carter, *Trans. Faraday Soc.*, **59**, 2455 (1963).

(38) E. Tschuikow-Roux, *J. Phys. Chem.*, **69**, 1075 (1965).

(39) W. Tsang, S. H. Bauer, and M. Cowperthwaite, *J. Chem. Phys.*, **36**, 1768 (1962).

(40) C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1954).

(41) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth and Co. (Publishers), Ltd., London, 1954.

(42) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 1, Reinhold Publishing Corp., New York, N. Y., 1954.

(43) A. H. Sehon and M. Szwarc, *Ann. Rev. Phys. Chem.*, **8**, 439 (1957).

(44) G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 313 (1952).

(45) P. Corbett, A. M. Tarr, and E. Whittle, *Trans. Faraday Soc.*, **59**, 1609 (1963).

(46) E. Tschuikow-Roux, *J. Chem. Phys.*, **43**, 2251 (1965).

(47) I. P. Fisher, J. B. Homer, and F. P. Lossing, *J. Am. Chem. Soc.*, **87**, 957 (1965).

The limits of the electron-impact estimate, *i.e.*, 96–115 kcal mole<sup>-1</sup>, bracket the value of  $107 \pm 3$  kcal mole<sup>-1</sup> estimated from thermochemical data. The latter value is thus used in all discussions.

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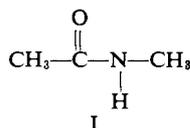
## Deuterium–Hydrogen Exchange in a *cis*-Lactam Amide Group

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**Abstract:** Rates of deuterium–hydrogen exchange have been measured for 2-pyrrolidone (II) at 11.0 and 19.5°, and compared with values for two *trans* amides, N-methyl- and N-ethylacetamide. The *cis* amide shows markedly faster exchange rates, a higher activation energy, and a larger entropy of activation. The amide nitrogen seems more accessible in the *cis* amide but the energy for placing a D<sup>+</sup> on it is greater.

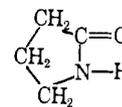
There are numerous factors that may influence the rates of hydrogen–deuterium exchange in biological macromolecules. Before the observed kinetics can be interpreted in terms of structure and conformation of a macromolecule, it will be necessary to examine the behavior of simple model systems under a variety of environmental conditions. N-Methylacetamide (I) has



been used as one such model in several laboratories.<sup>2–4</sup> Its rate of N–H → N–D exchange has been found sensitive to D<sup>+</sup> or OD<sup>-</sup> in several different solvent systems, and also subject to catalysis by a number of acids (*e.g.*, formic, acetic) and bases (imidazole, amines).

It seems almost certain that the amide group in N-methylacetamide is in the *trans* form, as depicted in I, in view of the large dielectric constant of this substance as well as its infrared and nmr properties.<sup>5–7</sup> The *trans* state is also that of amide groups in either the  $\alpha$  helix or  $\beta$  form of polypeptides or proteins. On the other hand, it is possible that in some environments, a *cis* form of the amide might exist, even if only as a transient state. It seemed of interest, therefore, to compare the rate of deuterium–hydrogen exchange in a *cis* amide with that in a *trans* state.

Large cyclic lactams can fold in various ways, but the five-membered ring compound 2-pyrrolidone (II)



II

must have the amide group locked in a *cis* configuration. The kinetics of its exchange reaction with D<sub>2</sub>O were examined, therefore, under a variety of conditions.

### Experimental Section

**Materials.** 2-Pyrrolidone was obtained from the Dyestuff and Chemical Division of General Aniline and Film Corp., New York, N. Y. It was vacuum distilled at 3 mm pressure, and the fraction boiling at 88–90° was collected. N-Methylacetamide was obtained from Eastman Organic Chemicals and distilled at atmospheric pressure. The fraction boiling at 205–206° was collected. N-Ethylacetamide was provided by Lachat Chemicals, Chicago, Ill. The fraction boiling at 68–69° at a pressure of 3 mm was collected. The purity of this material was checked by nmr spectroscopy and vapor phase chromatography and found to be greater than 99%.

Heavy water containing a minimum of 99.8% D<sub>2</sub>O was purchased from Bio-Rad Laboratories, Richmond, Calif. A solution of 38% DCl in D<sub>2</sub>O was also obtained from Bio-Rad and was diluted as necessary.

Sodium acetate was obtained from Eastman Organic Chemicals and used directly.

**Preparation of Reaction Mixtures.** A solution of 0.02 M sodium acetate in D<sub>2</sub>O was prepared as the buffer medium for H–D exchange. The necessary pD was reached by addition of small quantities of 1 M DCl to the buffer.

The amide to be studied, contained in a 250- $\mu$ l Hamilton syringe, was injected into a 1-cm quartz cell containing 2.5 cc of buffer. The cell was manually shaken, centrifuged to remove air bubbles, and then placed in the spectrophotometer. An optical reference cell contained the same buffer solution but no amide.

**Optical Measurements.** Rates of exchange were followed by the increase in absorption at 1.43  $\mu$  for both N-methylacetamide and N-ethylacetamide and 1.41  $\mu$  for 2-pyrrolidone as measured in a Cary Model 14R recording spectrophotometer. The quartz cells were the Infrasil type sold by Precision Cells Inc., New York, N. Y.

**pH Measurements.** All pH values were measured with a Beckman Model G pH meter at 25°. The meter was standardized with H<sub>2</sub>O buffer solutions and the meter reading converted to pD values

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