Calculations of the dissociation constant for the tetrakis-(diethyldithiocarbamato)-uranate(VI) ion were made according to the method of Foley and Anderson,[12] which utilizes solution pairs having the same concentration of the complex but differing in concentrations of the free complex forming ions. Such data were available directly from the Yoe and Jones type of plot, the continuous variation curves, or appropriate dilutions of these solutions in 1 M sodium perchlorate. Calculated values for three solution pairs gave six values ranging from 1.5×10^{-18} to 6.9×10^{-18} at 25° for the equilibrium defined by the equation

$$K = \frac{[UO_2^{++}][X^-]^4}{[UO_2X_4^{-2}]}$$

where X is diethyldithiocarbamate. The free energy of formation of the complex as calculated from the values of K is about 23 to 25 kcal./mole. The values for the dissociation constants are at best approximations. The hydrolysis of the uranyl ion, which is appreciable at pH values above 3, and the hydrolysis of the dithio acid salt are both neglected as is also equilibrium with other complexes. In the region of low pH, where hydrolysis of uranyl ion does not occur, the dithio acids are decomposed thus precluding any measurements.

The spectrum of the ethylxanthate complex was similar to that of the dithiocarbamate complex except that the maximum occurred in the vicinity of 360 mμ and then rose very steeply as the wave length decreased beyond 340 mμ. The complex absorbed much more strongly in ethanol than in water, indicating considerable dissociation in the latter solvent. For this reason the continuous variation curves were run in ethanol. Plotting according to the method of Yoe and Jones gave values for the extinction coefficient in ethanol of 2.5×10^3 at 345 mμ and 2.2×10^3 at 360 mμ. Similar calculations made for solutions of the solid in alcohol give the values 2.2×10^3 at 345 mμ and 1.9×10^3 at 360 mμ. The insolubility of the solid complex in non-polar solvents limits the value of the spectral data insofar as obtaining information about the structure of the solid is concerned. The existence of UO_2X_2 in solutions of the solid in ethanol suggests that it may be a double salt of the type $KX \cdot UO_2X_2$, where X is the ethylxanthate group. The data in no way preclude the possibility of the existence of tris- or tetrakis- complexes. No definite conclusions concerning the structure of the solid appear to be justified, on the basis of these data.

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[12] R. T. Foley and R. C. Anderson, THIS JOURNAL, **71**, 909 (1949).

[CONTRIBUTION FROM U. S. NAVAL ORDNANCE TEST STATION]

Photolysis of Acetone-d_6 in the Presence of n-Butane and of n-Butane-2,2,3,3-d_4. A Study of the Abstraction of Primary and Secondary Hydrogen by Methyl Radicals

BY JAMES R. McNESBY AND ALVIN S. GORDON

RECEIVED FEBRUARY 20, 1956

Mixtures of n-butane-2,2,3,3-d_4 and acetone-d_6 and of n-butane and acetone-d_6 were irradiated with a medium pressure mercury arc. From the analysis of the methanes produced the activation energies for the following reactions were deduced: $CD_3 + CH_3CD_2CD_2CH_3 \rightarrow CD_3H + CH_2CD_2CD_2CH_3$, $E = 11.4$ kcal.; $CD_3 + CH_3CD_2CD_2CH_3 \rightarrow CD_4 + CH_3CDCD_2CH_3$, $E = 11.4$ kcal.; $CD_3 + CH_3CH_2CH_2CH_3 \rightarrow CD_3H + CH_3CHCH_2CH_3$, $E = 9.3$ kcal. In the system acetone-d_6–butane-d_4, it was found that H is abstracted by CH_3 and CD_3 at about the same specific rate. The pre-exponential factors in the Arrhenius equations for abstraction of primary and secondary hydrogen from n-butane are in the ratio 1.5 compared with the statistical ratio of 1.5. In n-butane-d_4 the ratio of pre-exponential factors for abstraction of primary hydrogen and secondary deuterium is 0.92 compared with a statistical ratio of 1.5.

Introduction

The comparison of the relative rates of abstraction of D from acetone-d_6 and H from hydrocarbons by the CD_3 radical has proved a valuable tool for precise measurement of the activation energies of such metathetical reactions. Measurements made upon hydrocarbons containing more than one kind of hydrogen, $e.g.$, butane, cannot be interpreted unambiguously. For this reason we have prepared practically pure $CH_3CD_2CD_2CH_3$ by the photolysis of α,α'-diethyl ketone-d_4[1] and studied the photolysis of acetone-d_6 in its presence.

Results and Discussion

1. Acetone-d_6 and n-Butane-2,2,3,3-d_4.—Mixtures of acetone-d_6 and butane-d_4 were photolyzed in the temperature range 356–450°, employing a previously described technique.[2] The advantage of working in this temperature range is that the secondary butyl radical formed upon abstraction of D from butane-d_4 is thermally unstable and decomposes to give propylene and a light methyl radical. It has therefore been possible to compare the relative rates of abstraction of H and D by the CH_3 radical, as well as by the CD_3 radical, in the

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[1] J. R. McNesby, C. M. Drew and Alvin S. Gordon, *J. Phys. Chem.*, **59**, 988 (1955).

[2] J. R. McNesby and Alvin S. Gordon, THIS JOURNAL, **76**, 4196 (1954).

same system. The reactions of present interest in this system are

$$CD_3COCD_3 \longrightarrow 2CD_3 + CO \tag{1}$$

$$CD_3 + CH_3CD_2CD_2CH_3 \longrightarrow CD_4 + CH_3CDCD_2CH_3 \tag{2}$$

$$CH_3 + CH_3CD_2CD_2CH_3 \longrightarrow CH_3D + CH_3CDCD_2CH_3 \tag{2a}$$

$$CD_3 + CH_3CD_2CD_2CH_3 \longrightarrow CD_3H + CH_2CD_2CD_2CH_3 \tag{3}$$

$$CH_3 + CH_3CD_2CD_2CH_3 \longrightarrow CH_4 + CH_2CD_2CD_2CH_3 \tag{3a}$$

$$CD_3 + CD_3COCD_3 \longrightarrow CD_4 + CD_3COCD_2 \tag{4}$$

$$CH_3 + CD_3COCD_3 \longrightarrow CH_3D + CD_2COCD_3 \tag{4a}$$

$$CH_3CDCD_2CH_3 \longrightarrow CH_3CD{=}CD_2 + CH_3 \tag{5}$$

$$CH_2CD_2CD_2CH_3 \longrightarrow CH_2{=}CD_2 + CD_2CH_3 \tag{6}$$

The rates of formation of the various methanes are

$$R_{CD_4} = k_2(CD_3)(CH_3CD_2CD_2CH_3) + k_4(CD_3)(CD_3COCD_3) \tag{\textit{1}}$$

$$R_{CD_3H} = k_3(CD_3)(CH_3CD_2CD_2CH_3) \tag{\textit{2}}$$

$$R_{CH_3D} = k_{2a}(CH_3)(CH_3CD_2CD_2CH_3) + k_{4a}(CH_3)(CD_3COCD_3) \tag{\textit{3}}$$

$$R_{CH_4} = k_{3a}(CH_3)(CH_3CD_2CD_2CH_3) \tag{\textit{4}}$$

Since the reactions have been carried out only to about 1% completion, it is possible to write

$$\frac{R_{CD_4}}{R_{CD_3H}} = \frac{(CD_4)}{(CD_3H)} = \frac{k_4A}{k_3B} + \frac{k_2}{k_3} \tag{\textit{5}}$$

and

$$\frac{R_{CH_3D}}{R_{CH_4}} = \frac{(CH_3D)}{(CH_4)} = \frac{k_{4a}A}{k_{3a}B} + \frac{k_{2a}}{k_{3a}} \tag{\textit{6}}$$

where A = (acetone-d_6) and B = (n-butane-2,2,3,3-d_4). It is evident from equation *5* that the ratio CD_4/CD_3H, when plotted against the acetone-d_6/butane-d_4 ratio, should give a straight line whose slope is k_4/k_3 and whose intercept on the CD_4/CD_3H axis is k_2/k_3. Three master mixtures of acetone-d_6–n-butane-2,2,3,3-d_4 were used. Each mixture was photolyzed with a medium pressure mercury arc at three temperatures and the methane fractions analyzed with a high resolution mass spectrometer. The results are shown in Table I, and the plots of CD_4/CD_3H *vs.* A/B are shown in Fig. 1.

Four minor sources of CD_3H are present because the reactants are incompletely deuterated.

$$CD_2H + CD_3COCD_3 \longrightarrow CD_3H + CD_2COCD_3 \tag{7}$$

$$CD_3 + CD_2HCOCD_3 \longrightarrow CD_3H + CD_2COCD_3 \tag{8}$$

$$CD_3 + CH_3CDHCD_2CH_3 \longrightarrow CD_3H + CH_3CDCD_2CH_3 \tag{9}$$

$$CD_2H + CH_3CD_2CD_2CH_3 \longrightarrow CD_3H + CH_3CDCD_2CH_3 \tag{10}$$

Acetone-d_6 alone gives CD_3H/CD_4 = 4%. From the analysis of the deuterated acetone, it is calculated that 1.3% of the radicals are CD_2H, so that reaction (8) must account for the remaining 2.7% of CD_3H produced from the photolysis of the acetone-d_6 alone.

Since Fig. 1 indicates that k_2/k_3 is about unity and since practically all of the CD_3H in the mixture came from butane-d_4, the amount of CD_4 coming from butane-d_4 was equal to the total CD_3H, with the remaining CD_4 coming from acetone-d_6. Four per cent. of the CD_4 from acetone-d_6 was subtracted from the total to correct for reactions (7) and (8). Since 2.7% of the CD_4 appears as CD_3H from reaction (8) in the case of acetone-d_6 alone, it was assumed that about the same percentage of the CD_4 formed from the butane-d_4 appeared as CD_3H from reaction (9). As previously noted, 1.3% of the radicals produced from acetone-d_6 are CD_2H, and they abstract H and D from butane-d_4 with equal facility. Thus reaction (10) results in CD_3H to the extent of 1.3% of the CD_4 from butane-d_4. The corrections for reactions (9) and (10) total 4% of the CD_4 arising from the butane-d_4.

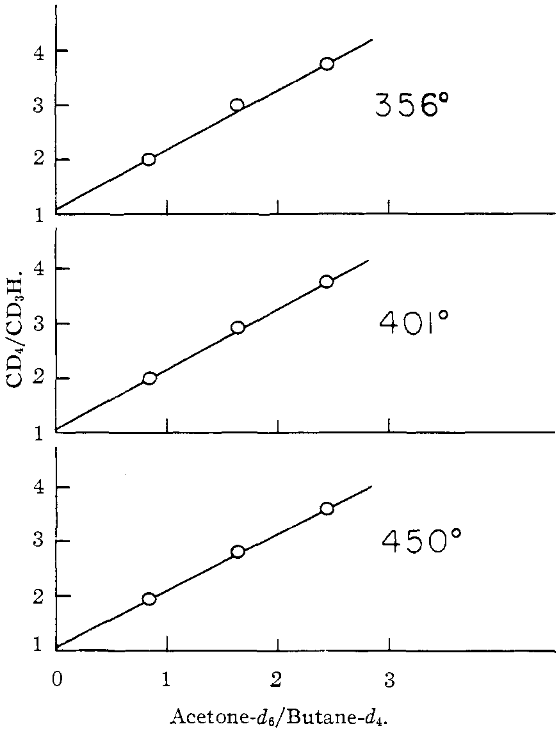

Fig. 1.—Photolysis of acetone-d_6 in the presence of butane-d_4.

The corrections on CH_4 were made on a similar basis, assuming that the total extraneous CH_4 arises from

$$CH_3 + CD_2HCOCD_3 \rightarrow CH_4 + CD_2COCD_3 \tag{11}$$

$$CH_3 + CH_3CDHCD_2CH_3 \longrightarrow CH_4 + CH_3CDCD_2CH_3 \tag{12}$$

Figures in parentheses in Table I are quite inaccurate due to the small amounts of CH_3D and CH_4 in the particular experiments indicated. High resolution mass spectrometry was employed to distinguish mass 16, 17 and 18 peaks due to water from those due to methane fragments. The CH_3D/CH_4 ratios are not significantly different from the corresponding CD_4/CD_3H ratios. The corrected data indicate that CH_3 abstracts H and D from the system with the same activation energy differences as does CD_3.

It is very difficult to see a trend in k_2/k_3 with temperature. From the data it appears that $E_3 - E_4 = 0.1 \pm 0.1$ kcal. Since it has already been es-

TABLE I

PHOTOLYSIS OF ACETONE-d_6 IN THE PRESENCE OF n-BUTANE 2,2,3,3-d_4[a]

t, min.	3	4	3	2	3	1	1	1.5	1
T, °C.	356	356	356	401	401	401	450	450	450
A/B	0.84	1.65	2.45	0.84	1.65	2.45	0.84	1.65	2.45
CD_3H	24.4	46.8	26.5	26.3	50.3	13.6	35.9	44.2	26.5
CD_4	48.7	138.8	99.3	52.4	146.1	50.8	69.9	124.3	96.3
CH_4	9.4	12.1	5.0	21.8	23.9	6.0	48.9	26.2	12.9
CH_3D	20.2	39.5	20.1	43.0	71.7	19.7	97.7	76.9	49.9
CD_4/CD_3H	2.00	2.99	3.74	1.99	2.91	3.74	1.95	2.62	3.63
CH_3D/CH_4	(2.1)	(3.3)	(4.0)	1.97	3.00	(3.3)	2.00	2.94	(3.9)
$(CD_4)_A$	23.3	90.9	71.6	25.0	93.6	36.6	32.5	78.1	68.6
$(CH_3D)_A$	10.7	27.2	15.1	20.9	47.5	13.6	48.1	50.5	36.8
$(CD_4)_B$	25.4	48.9	27.7	27.4	52.5	14.2	37.4	46.2	27.7
$(CH_3D)_B$	9.5	12.3	5.0	22.1	24.2	6.1	49.6	26.6	13.1
$(CH_4)_B$	9.4	12.1	5.0	21.8	23.9	6.0	48.9	26.2	12.9
$(CD_3H)_B$	25.0	48.1	27.3	27.0	51.7	13.9	36.9	45.5	27.3
$(CD_3/CH_3) = (CD_4)_A/(CH_3D)_A$	2.18	3.34	4.74	1.20	1.97	2.69	0.68	1.55	1.86
$(CD_4/CH_3D)_B$	2.67	3.98	5.5	1.24	2.17	2.33	0.75	1.74	2.11
k_2/k_{2a}	(1.2)	(1.2)	(1.2)	1.0	1.1	(0.9)	1.1	1.1	(1.1)
k_2/k_3	1.08			1.06			1.07		
k_4/k_3	1.08			1.10			1.04		

[a] CD_3H and CH_4 have been corrected as indicated in the text. A/B = relative molar concentrations of acetone-d_6 and butane-d_4. $(CD_4)_A$ = CD_4 formed from acetone-d_6. $(CD_4)_B$ = CD_4 formed from butane-d_4. Numbers are mass spectrometer peak heights. The total pressure was about 35 mm. for each run.

tablished that $E_4 = 11.3$ kcal.,[3-5] it follows that $E_3 = 11.4$ kcal. and $E_2 = 11.4$ kcal.

From two independent studies,[6,7] the energy of activation $E_{13} = 11.4 \pm 0.2$.

$$CD_3 + C_2H_6 \longrightarrow CD_3H + C_2H_5 \tag{13}$$

Thus the activation energy for the abstraction of primary H is, within a small experimental error, independent of whether the H is abstracted from ethane or butane-d_4.

Table I includes the amounts of the various methanes arising from each of the abstraction reactions. From these results the rate of reaction of CD_3 and CH_3 with the D atoms of butane-d_4 may be compared.

$$\frac{R_{(CD_4)A}}{R_{(CH_3D)A}} = \frac{(CD_4)_A}{(CH_3D)_A} = \frac{k_4A(CD_3)}{K_{4a}A(CH_3} \tag{7}$$

It has previously been shown that $k_4 = k_{4a}$.[4] It follows that

$$CD_3/CH_3 = (CD_4)_A/(CH_3D)_A \tag{8}$$

$$\frac{(CD_4)_B}{(CH_3D)_B} = \frac{k_2(CD_3)(B)}{k_{2a}(CH_3)(B)} = \frac{k_2(CD_4)_A}{k_{2a}(CH_3D)_A} \tag{9}$$

$$k_2/k_{2a} = [(CD_4)_B(CH_3D)_B]/[(CD_4)_A/(CH_3D)_A] \tag{10}$$

The values of k_2/k_{2a} were calculated in this way. It is doubtful whether the ratio is significantly greater than 1.0, but it is certainly not less than 1.0. It must be concluded that CH_3 and CD_3 abstract D from butane-d_4 at about equal rates over the temperature range studied.

2. Acetone-d_6 and n-Butane.—A mixture of acetone-d_6 and n-butane was made up in the ratio butane/acetone-d_6 = 2.04. This mixture was photolyzed from 250–450° and the product methanes analyzed as above. The literature cracking pattern of CD_3H includes 51.1% of the parent at mass 17. In the 250° experiments where the *sec*-butyl radical is quite stable, CD_3H and CD_4 are the important methanes. Negative residuals at mass 17 were encountered under these conditions. If 49.5% is used rather than 51.1% for the CD_3H cracking pattern at mass 17, no negative residuals were encountered and values of the CH_4/CH_3D ratio were commensurate with the CD_3H/CD_4 ratios. In the work with acetone-d_6 and butane-d_4 such an error in the cracking pattern of CD_3H would be negligible, since relatively large amounts of CH_3D were generated during the reaction.

In the acetone-d_6–n-butane system the methane forming reactions are

$$CD_3 + CD_3COCD_3 \longrightarrow CD_4 + CD_2COCD_3 \tag{4}$$

$$CD_3 + CH_3CH_2CH_2CH_3 \longrightarrow CD_3H + CH_2CH_2CH_2CH_3 \tag{14}$$

$$CD_3 + CH_3CH_2CH_2CH_3 \longrightarrow CD_3H + CH_3CHCH_2CH_3 \tag{15}$$

$$CH_3 + CD_3COCD_3 \longrightarrow CH_3D + CD_3COCD_2 \tag{16}$$

$$CH_3 + CH_3CH_2CH_2CH_3 \longrightarrow CH_4 + CH_2CH_2CH_2CH \tag{17}$$

$$CH_3 + CH_3CH_2CH_2CH_3 \longrightarrow CH_4 + CH_3CHCH_2CH_3 \tag{18}$$

The CH_3 radicals are formed in

$$CH_3CHCH_2CH_3 \longrightarrow CH_3 + CH_3CH{=}CH_2 \tag{19}$$

In the initial stages of reaction

$$CD_3H/CD_4 = (k_{14}B)/(k_4A) + (k_{15}B)/(k_4A)$$

From the data in Table I, it is a sufficiently accurate approximation to write $k_{14}/k_4 = 0.93$ on the assumption that the abstraction of primary H is unaffected by the mass of the hydrogen atoms in the secondary positions. Since $B/A = 2.04$

$$k_{15}/k_4 = \frac{CD_3H/CD_4 - 1.90}{2.04}$$

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[3] J. R. McNesby, T. W. Davis and A. S. Gordon, THIS JOURNAL, **76**, 823 (1954).

[4] J. R. McNesby and A. S. Gordon, *ibid.*, **76**, 1416 (1954).

[5] M. H. J. Wijnen, *J. Chem. Phys.*, **22**, 1075 (1954).

[6] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **77**, 4719 (1955).

[7] M. H. J. Wijnen, *J. Chem. Phys.*, **23**, 1357 (1955).

TABLE II

PHOTOLYSIS OF ACETONE-d_6 IN THE PRESENCE OF n-BUTANE

t, min.	T, °C.	CD_4	CD_3H	CD_2H_2	CH_3D	CH_4	CD_2 Cor.	$\frac{CH_4}{CH_3D}$	k_{15}/k_4
5	250	17.6	185.2	(0.0)	(0.4)	(5)	10.48	. . .	4.21
10	250	33.1	351.7	0.7	(1.5)	(10)	10.59	. . .	4.26
4	303.5	13.7	127.1	0.3	10.9	104.3	9.24	9.57	3.60
10	303.5	43.0	391.6	1.2	32.6	249.1	9.07	9.17	3.51
3	355	13.2	108.5	0.4	29.7	256.3	8.18	8.63	3.08
6	355	29.5	240.3	3.2	61.7	530.6	8.11	8.60	3.04
3	397	12.6	96.2	0.9	50.3	392.0	7.60	7.53	2.79
6	397	37.1	279.9	6.1	132.7	1051.9	7.50	7.93	2.75
4	449	28.0	199.5	5.0	131.1	969.0	7.09	7.39	2.54

The pertinent data are given in Table II. From the slope of the Arrhenius plot for k_{15}/k_4, $E_4 - E_{15}$ is calculated to be 2.0 kcal. Since E_4 is 11.3 kcal.,[5,8] it follows that $E_{15} = 9.3$ kcal.

As in the acetone-d_6–n-butane-2,2,3,3-d_4 mixtures, these data indicate that CH_3 abstracts H and D with the same activation energy difference as does CD_3. It is of interest to note that the difference in energy of activation for the abstraction of secondary D and H by CD_3 from butane is 2.1 kcal., a value in excess of the zero point energy difference of H_2 and D_2. Some previous work[6,8] also indicates that zero point energy differences are not sufficient to account for the difference in rate of abstraction of D and H by methyl radicals.

It is of interest to calculate the ratio of preëxponential factors in the Arrhenius equations, A_3/A_{15}, corresponding to the abstraction of primary and secondary hydrogen. In this discussion we assume that $A_3 = A_{14}$.

As may be seen in Fig. 1, k_2/k_4 varies very little with temperature. From this observation A_3/A_4 may be calculated as 0.93.

From Fig. 2, $A_4/A_{15} = 1.61$, so that

$$\frac{A_4}{A_{16}} \times \frac{A_3}{A_4} = \frac{A_3}{A_{15}} = 1.50$$

This is the ratio of the number of primary hydrogen atoms to the number of secondary hydrogen atoms, so that the entropy of activation per hydrogen atom of the attack on primary hydrogen is the same as for the attack on secondary hydrogen.

We may also compare A_3/A_2, the ratio for the abstraction of primary hydrogen to the abstraction of secondary deuterium in butane-d_4.

From the intercepts in Fig. 1, $k_3/k_2 = 0.93$, independent of temperature. Thus $A_3/A_2 = 0.93$. This ratio is far from the ratio of the number of primary hydrogen atoms to secondary deuterium atoms in the butane-d_4. We can offer no explanation for this discrepancy at the present time. Since $E_{14} = 11.4$ kcal. and $E_{15} = 9.3$ kcal., it is concluded that the difference in activation energy for abstraction by CD_3 of primary and secondary H is 2.1 kcal. Considering the numerous approximations that were necessary in the work of Allen[9] at a single temperature, his estimate of 2.1 kcal. for the difference in abstraction activation energies of primary and secondary H from propane is remarkably close to our precisely measured value for the case of butane.

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. Andreas V. Jensen and Mrs. Helen R. Young in mass spectrometer analysis.

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[8] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **76**, 1416 (1954).

[9] A. O. Allen, *ibid.*, **63**, 708 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

An Electron Diffraction Investigation of the Molecular Structure of 1,1,1-Trifluoroethane[1]

BY JAMES L. BRANDT AND R. L. LIVINGSTON

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The interatomic distances in methylfluoroform have been determined by electron diffraction using the visual correlation procedure. Sectored electron diffraction photographs were used in the interpretation of some of the features. The following results were obtained: C–F = 1.33 ± 0.02 Å., C–C = 1.52 ± 0.04 Å., and ∠CCF = 111.5° ± 1.5°.

Two previous electron diffraction investigations[2] of the structure of methylfluoroform gave the following conflicting results: C–C = 1.45 ± 0.04 Å. as compared to 1.53 ± 0.04 Å., C–F = 1.33 ± 0.03 Å. compared to C–F = 1.36 ± 0.02 Å. and ∠FCF = 108.5 ± 2° against 107 ± 3°. Edgell and Roberts,[3] in a microwave spectroscopic study, obtained a moment of inertia perpendicular to the threefold axis of $161.80 \pm 0.07 \times 10^{-40}$ g. cm.^{2}. They showed that this moment of inertia was compatible with the following parameters: C–C = 1.54 Å., C–F = 1.33 Å., C–H = 1.043 Å.,

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[1] From the Ph.D. thesis of James L. Brandt, Purdue Research Foundation Fellow in Chemistry, 1951–1952.

[2] R. W. Allen and L. F. Sutton, *Acta Cryst.*, **3**, 46 (1950).

[3] W. F. Edgell and A. Roberts, *J. Chem. Phys.*, **16**, 1002 (1948).