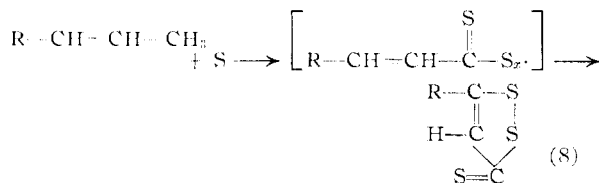


At 200°, similar substrates give 1,2-dithiole-3-thiones,²⁷ as in equation 8. Thiolethiones appear



to have exceptional stability,²⁸ and may arise by closure of a dithio acid radical followed by dehydrogenation. This intermediate thio acid radical is similar to those which might exist in the reaction reported here. In the oxidation discussed here, however, intramolecular closure is not possible and hydrolysis yields stable products. Thiolethione formation is also base catalyzed and H₂S pressure increases at a first-order rate. (Calculations based on data of Fields.²⁹)

Butyl rubber reacts to incorporate sulfur into the rubber hydrocarbon at a rate that is first order in sulfur and zero order in hydrocarbon.^{30a} This reaction also is base catalyzed.^{30b} The activation

(27) M. G. Voronkov and A. S. Broun, *Doklady Akad. Nauk SSSR*, **59**, 1437 (1948); B. Botcher and A. Luttringhaus, *Ann.*, **567**, 89 (1947); N. Lozac'h, *Compt. rend.*, **225**, 686 (1947).

(28) W. Hüchel, "Theoretical Principles of Organic Chemistry," Vol. I, Elsevier Publ. Co., New York, N. Y., 1955, p. 676; G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 145.

(29) E. K. Fields, *THIS JOURNAL*, **77**, 4255 (1955).

(30) (a) M. Gordon, *J. Polymer Sci.*, **7**, 485 (1951); (b) G. D. Kratz, H. H. Young and I. Katz, *Ind. Eng. Chem.*, **41**, 399 (1949); (c) R. H. Gerke, *ibid.*, **31**, 1478 (1939).

energy for vulcanization is roughly 30 kcal.,^{30c} and the dissociation energy of a long chain polysulfide is 33 kcal.³¹ It would appear, therefore, that the slow step in vulcanization is fission of an S-S bond followed by rapid attack on substrate, giving zero-order dependence on hydrocarbon.^{30a} The first-order dependence on substrate found in the reaction reported here is therefore distinctive and indicates attack of the sulfur radical on substrate, rather than production of sulfur radicals, must be rate limiting.

Finally, the reaction of sulfur with diphenylmethane at 200° is of interest. The detailed mechanism is in doubt since results by Moreau³² at 250° and Tsurugi³³ at 200° are in contradiction. Both find thiobenzophenone as final product but Tsurugi finds benzhydryl polysulfide is an intermediate. H₂S pressure increases at a first-order rate, the reaction is accelerated by light and the reaction is base catalyzed.³³

Acknowledgments.—I wish to thank many of my associates for helpful discussion, especially Drs. L. L. Ferstandig and W. G. Toland. Dr. B. A. Fries aided in setting up the liquid scintillation analysis. Mr. George Tamaki helped with the experimental work.

(31) D. M. Gardner and G. K. Fraenkel, *THIS JOURNAL*, **78**, 3279 (1956).

(32) R. C. Moreau, *Bull. soc. chim. France*, **628**, 918, 1044, 1049 (1955).

(33) J. Tsurugi, *Bull. Univ. Osaka Perfect*, **A5**, 161, 169, 173 (1957); *C. A.*, **51**, 15987c (1957); J. Tsurugi, H. Fukuda and T. Nakabayashi, *Nippon Kagaku Zasshi*, **76**, 111, 190 (1955); *C. A.*, **51**, 17846–17847 (1957).

RICHMOND, CAL.

[CONTRIBUTION 4956 FROM THE PURE CHEMISTRY DIVISION, NATIONAL RESEARCH COUNCIL OF CANADA, OTTAWA]

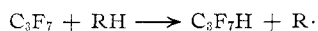
The Reactions of Perfluoro-*n*-propyl Radicals with Hydrogen and Deuterium

BY GLENN H. MILLER¹ AND E. W. R. STEACIE

RECEIVED APRIL 14, 1958

Perfluoro-*n*-propyl radicals were produced by the photolytic decomposition of perfluoro-di-*n*-propyl ketone using 3130 Å. radiation. Activation energies for the reactions C₃F₇ + H₂ → C₃F₇H + H (1) and C₃F₇ + D₂ → C₃F₇D + D (2) were found to be 12.3 ± 0.4 and 13.8 ± 0.5 kcal. per mole, respectively. A brief study of the competitive reaction C₃F₇ + H₂ + D₂ → C₃F₇H + C₃F₇D + etc., has shown the difference in activation energies between reactions 1 and 2 to be 1.7 kcal. per mole.

The initial step in the photolysis of perfluoro-di-*n*-propyl ketone has been shown to involve the formation of *n*-C₃F₇ radicals, the only reaction products being CO and C₆F₁₄.² The availability of these radicals makes possible a study of the abstraction reactions



A comparison of the activation energies and steric factors of these reactions with the corresponding reactions for CF₃, C₂F₅ and the hydrogenated analogs is of theoretical interest. In this work the *n*-C₃F₇ radicals have been reacted with hydrogen and deuterium.

(1) National Research Council of Canada Postdoctorate Fellow 1956–1957. Department of Chemistry, University of California, Santa Barbara College, Goleta. Presented at the 123rd Meeting of the American Chemical Society, April 16, 1958, San Francisco.

(2) G. H. Miller, G. O. Pritchard and E. W. R. Steacie, *Z. physik. Chem.*, **15**, 262 (1958).

Experimental

Apparatus and Procedure.—The apparatus used for these experiments was the same as was used for the previous investigation.² Light from a B.T.H. high pressure mercury lamp (type ME/D, 250 watts) was collimated *via* two quartz lenses and a stop. The 3130 Å. radiation was isolated by means of standard nickel chloride, potassium chromate, potassium hydrogen phthalate and Corning 9863 filters.³ The parallel beam had approximately the same diameter as the completely illuminated cell.

The quartz reaction vessel had a diameter of 5 cm., length of 10 cm. and a volume of 175 ml. It was connected to the vacuum system by means of a specially designed mercury cut-off which was mounted directly below the cell.⁴ A small freeze-out trap was connected to the top of the cell.

After the ketone (C₃F₇COC₃F₇) was admitted to the cell the pressure was measured by means of a cathetometer focused on a constant-volume manometer. The ketone was condensed at liquid nitrogen temperature until a zero manometer reading was obtained. Hydrogen or deuterium

(3) M. Kasha, *J. Optical Soc.*, **38**, 929 (1948).

(4) M. Weston, R. K. Brinton and G. H. Miller, to be published.

then was admitted to the desired pressure, the system was isolated and the reactants mixed by expanding into a one-liter Toepler pump four or five times. The total gas pressure always checked the sum of the individual pressures within experimental error.

Following the reaction (in which the ketone decomposition was allowed to proceed to less than 5%) the products were expanded directly into the analytical line which consisted of two Ward-LeRoy stills,⁵ a cold trap, a small mercury diffusion pump, a Pd thimble at approximately 380°, a gas buret and a Toepler pump for sample collection. The two stills and the cold trap were cooled to liquid nitrogen temperature and in these the C₆F₁₄, C₃F₇H or C₃F₇D, and the unreacted ketone were collected. The non-condensed mixture of hydrogen or deuterium plus carbon monoxide was allowed to stand exposed to the hot Pd thimble for 1 to 1.5 hours. After recording the volume of the remaining gas (CO), it was transferred by means of an additional Toepler pump to a second Pd thimble where it was allowed to stand overnight. The following morning the volume again was measured. Six such determinations showed that there was no change in volume during the overnight exposure to the second thimble, hence this step was omitted and the volume of carbon monoxide was read directly after the one exposure. Mass spectrographic analyses showed no hydrogen or CF₃ peak in the carbon monoxide fraction.

The C₃F₇H or C₃F₇D was collected by first allowing the cold trap and second still to warm to room temperature and then increasing the temperature of the first still to -105°. Mass spectrographic analyses indicated the absence of a 181 (C₆F₁₄) or 197 (ketone) peak in these fractions.

The mass spectra of C₃F₇H and C₃F₇D were complicated. Table I gives the main ion peaks with the relative heights

TABLE I
MASS SPECTRA OF *n*-C₃F₇H AND C₃F₇D

Mass no. of peak	Probable ion	Relative peak height with C ₃ F ₇ H	Relative peak height with C ₃ F ₇ D
31	CF	72	72
32	CFH	14	
33	CFD		12
43	C ₂ F	2	4
44	C ₂ FH(CO ₂)	9	
45	C ₂ FD		6
50	CF ₂	19	19
51	CF ₂ H	1100	68
52	CF ₂ D		1001
62	C ₂ F ₂	3	
63	C ₂ F ₂ H	9	
64	C ₂ F ₂ D		14
69	CF ₃	1000	1000
81	C ₂ F ₃	3	
82	C ₂ F ₃ H	32	
83	C ₂ F ₃ D		33
93	C ₃ F ₃	3	3
100	C ₂ F ₄ (Hg)	111 ^a	102 ^a
101	C ₂ F ₄ H (Hg)	58 ^a	
102	C ₂ F ₄ D (Hg)		73 ^a
119	C ₂ F ₅	60	59
120	C ₂ F ₅ H	1	
131	C ₃ F ₅	3	4
150	C ₃ F ₆		2
151	C ₃ F ₆ H	114	7
152	C ₃ F ₆ D		107
169	C ₃ F ₇	10	13

^a No correction was made for Hg peak heights.

and probable positive ions for the compounds *n*-C₃F₇H and *n*-C₃F₇D. The 51 and 151 peaks were due to the HD present in the reaction mixture and partly to exchange which occurred in the reaction cell. Other minor peaks due to the presence of hydrogen in the *n*-C₃F₇ reaction mixture were omitted. No isotope corrections were made and the large 70 isotope peak was omitted.

(5) D. J. LeRoy, *Can. J. Research*, **B28**, 492 (1950).

Materials.—The C₃F₇COC₃F₇ was prepared by the action of sodium on C₃F₇COOC₂H₅ in ether solution⁶ and was purified as previously described.² The deuterium was purchased from the Stuart Oxygen Co. and after passage through a palladium thimble it had a purity of 95.4% D₂ and 4.5% HD. Dry cylinder hydrogen also was purified by passage through palladium. Both gases were stored in 5-liter storage bulbs.

Results and Discussion

Perfluoro-di-*n*-propyl ketone when irradiated with light of 3130 Å. produces *n*-C₃F₇ radicals. When a mixture of the ketone and hydrogen is photolyzed, *n*-C₃F₇H is produced by the abstraction of one hydrogen atom, and similarly *n*-C₃F₇D is produced when deuterium is used. The experimental results obtained for these reactions are listed in Table II for hydrogen and Table III for

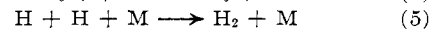
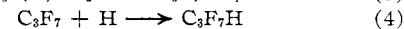
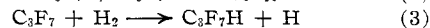
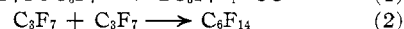
TABLE II
THE REACTION OF *n*-C₃F₇ RADICALS WITH HYDROGEN

Time, sec.	Temp., °K.	Reactants, moles/cc. × 10 ⁶		Products, moles/cc./sec. × 10 ¹²		<i>k</i> ₂ / <i>k</i> ₃ ^{1/2} , moles ^{-1/2} sec. ^{-1/2}	
		(C ₃ F ₇) ₂	H ₂	CO	C ₃ F ₇ H		C ₆ F ₁₄
9360	398	2.18	3.51	8.02	1.41	7.32	0.074
7200	408	1.80	2.50	7.89	1.85	6.96	.140
8640	425	1.93	2.79	7.07	2.90	5.62	.219
7200	434	1.89	2.56	7.30	3.46	5.57	.286
7500	444	1.82	2.52	7.22	3.16	5.64	.263
7500	453	1.54	2.14	7.45	4.87	5.01	.508
7200	483	1.57	2.74	9.68	12.50	3.43	1.23
7200	485	1.13	1.92	6.91	8.38	2.72	1.32
7500	486	1.36	2.15	7.85	9.64	3.03	1.29
6960	505	2.15	1.43	6.92	9.65	2.10	2.32
3780	508	1.82	0.89	2.22	2.59	0.92	1.52
5040	516	1.37	1.53	6.30	10.64	0.98	3.52

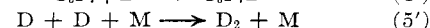
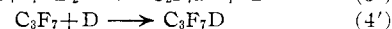
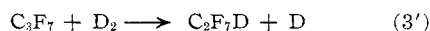
TABLE III
THE REACTION OF *n*-C₃F₇ RADICALS WITH DEUTERIUM

Time, sec.	Temp., °K.	Reactants, moles/cc. × 10 ⁶		Products, moles/cc./sec. × 10 ¹²		<i>k</i> ₂ / <i>k</i> ₃ ^{1/2} , moles ^{-1/2} cm. ^{3/2} sec. ^{-1/2}	
		(C ₃ F ₇) ₂	D ₂	CO	C ₃ F ₇ D		C ₆ F ₁₄
9120	430	1.91	2.96	4.40	0.64	4.08	0.054
9000	447	2.13	2.61	4.74	1.49	4.00	.143
7200	464	1.88	2.39	4.92	1.70	4.07	.176
7200	466	1.81	1.78	5.74	1.53	4.98	.193
8580	474	1.80	2.00	3.76	1.78	2.87	.262
7200	487	1.57	2.80	4.07	2.88	2.63	.317
7200	492	1.81	2.46	4.87	3.23	3.25	.364
7200	504	1.92	2.02	5.48	4.29	3.33	.582
5280	513	1.80	2.47	4.33	5.25	1.71	.812
7200	522	1.86	2.36	5.10	6.63	1.79	1.05
7200	537	1.56	1.44	3.03	4.32	0.87	1.61

the deuterium reactions. The only products noted were carbon monoxide, *n*-C₆F₁₄ and either *n*-C₃F₇H or *n*-C₃F₇D. The following reaction scheme will account for these



or for the deuterium reactions 1, 2 and



(6) M. Hauptschein and R. A. Braun, *THIS JOURNAL*, **77**, 4930 (1955).

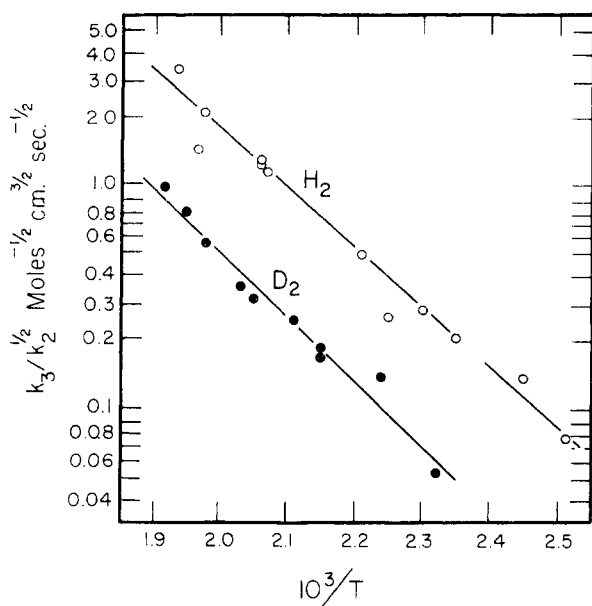


Fig. 1.—Arrhenius plots for the reaction of C_3F_7 radicals with H_2 or D_2 .

The values reported in the tables for the rate of C_6F_{14} production were calculated according to the formula

$$\text{rate } C_6F_{14} = \text{rate CO} - \frac{1}{2}(\text{rate } C_3F_7H)$$

This assumption had to be made since small amounts of C_6F_{14} could not be analyzed in the presence of the excess amount of unreacted ketone.² That such a treatment is valid gains support from the data of Ayscough and Polanyi⁷ for the CF_3 plus H_2 system where a similar approximation would have given values very close to those found by actual analysis.

In order to obtain values for k_3 it is necessary to consider the relative importance of reactions 4 and 5, *i.e.*, the fate of the H atom. Consideration of equations 1, 2, 3 and 4 leads to the expression

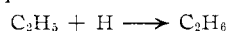
$$\frac{k_3}{k_2^{1/2}} = \frac{\text{rate } C_3F_7H}{2(\text{rate } C_6F_{14})^{1/2}(H_2)}$$

while reactions 1, 2, 3 and 5 give

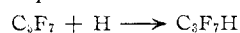
$$\frac{k_3}{k_2^{1/2}} = \frac{\text{rate } C_3F_7H}{(\text{rate } C_6F_{14})^{1/2}(H_2)}$$

The data reported in Tables II and III give k_3 values based on the first expression.

If one considers reactions of the hydrocarbon series it is certain that at normal pressures the hydrogen atom recombination reaction requires a third-body but the methyl radical recombination does not. Since the product of the reaction



is hot C_2H_6 as in the methyl recombination case, it seems likely that a third-body is not required. This is also true of the more complicated hydrocarbon systems such as the recombination of ethyl radicals and the reaction of H with C_3H_7 . Thus, by analogy, it is reasonable to predict that the reaction



will not require a third-body. Reaction 4 should

(7) P. B. Ayscough and J. C. Polanyi, *Trans. Faraday Soc.*, **52**, 960 (1956).

have a rate constant 200 or 300 times higher than reaction 5 and this would outweigh any concentration effect. In practice, however, the choice of reaction 4 or 5 is not critical for either would give the same apparent activation energies providing both are not included and as long as their relative importance does not vary with temperature. The agreement of the results obtained for $H_2 + D_2 +$ ketone as compared to the separate H_2 and D_2 results substantiate these conclusions.

Fig. 1 shows the Arrhenius plots for the two reactions, C_3F_7 with H_2 or D_2 . These were found to be linear over the temperature range studied. The values determined for the ratios of the rate constants using the method of least squares are for hydrogen

$$k_3/k_2^{1/2} = 4.37 \times 10^5 e^{-(12.3 \pm 0.4)10^3/RT} \text{ moles}^{-1/2} \text{ cm.}^{3/2} \text{ sec.}^{-1/2}$$

and for deuterium

$$k_3'/k_2^{1/2} = 6.01 \times 10^5 e^{-(13.8 \pm 0.5)10^3/RT} \text{ moles}^{-1/2} \text{ cm.}^{3/2} \text{ sec.}^{-1/2}$$

The calculated activation energies are

$$E_3 - \frac{1}{2}E_2 = 12.3 \pm 0.4 \text{ kcal./mole}$$

$$E_3' - \frac{1}{2}E_2 = 13.8 \pm 0.5 \text{ kcal./mole}$$

If one arbitrarily assumes a collision diameter of 5.2 Å. for the radical C_3F_7 along with the values of 2.8 Å. for hydrogen and 2.8 Å. for deuterium a calculation of the ratios of the steric factors for a temperature of 210° gives

$$P_3/P_2^{1/2} = 4.2 \times 10^{-3}$$

$$P_3'/P_2^{1/2} = 1.2 \times 10^{-2}$$

Reaction of C_3F_7 with H_2 and D_2 Mixtures.—

When a mixture of perfluoro-di-*n*-propyl ketone, hydrogen and deuterium is photolyzed, all of the reactions 1 through 5 and 3' to 5' will occur along with the combination of H and D atoms and the $D + H_2$ and $H + D_2$ reactions. If

$$\text{rate } C_3F_7H = k_3(C_3F_7)(H_2)$$

$$\text{rate } C_3F_7D = k_3'(C_3F_7)(D_2)$$

it follows that

$$\frac{k_3'}{k_3} = \frac{\text{rate } C_3F_7D(H_2)}{\text{rate } C_3F_7H(D_2)}$$

Thus from a knowledge of the initial hydrogen and deuterium concentrations along with the ratio of the rates of formation of C_3F_7H and C_3F_7D it is possible independently to determine the magnitude of the value $E_3' - E_3$ as well as the ratio A_3'/A_3 .

The ratio rate C_3F_7D /rate C_3F_7H was determined mass spectrometrically from the relative abundances of the CF_2H^+ (51) and CF_2D^+ (52) peaks, allowance being made for the C^{13} contributions and assuming the sensitivities and cracking patterns of the two molecules to be similar. Difficulty was encountered initially due to the appearance of a relatively high 51 ion peak when only D_2 and the ketone were photolyzed. Conditioning of the cell, however, produced blank values of 5.6 to 6.7 for the 51/52 ratio. To minimize errors a blank run (ketone plus D_2) was made immediately before a determination (ketone plus D_2 and H_2) and the necessary corrections then were applied. The results obtained are recorded in Table IV, and Fig. 2 gives the Arrhenius plot of the data.

TABLE IV
THE REACTION OF $n\text{-C}_3\text{F}_7$ RADICALS WITH HYDROGEN-DEUTERIUM MIXTURES

Run no.	Time, min.	Pressures, cm.			Temp., °K.	Mass spectrum peak heights		$\frac{d(\text{C}_3\text{F}_7\text{D})/dt}{d(\text{C}_3\text{F}_7\text{H})/dt}$	$\frac{k_3'}{k_3}$
		D ₂	H ₂	Ketone		51	52		
110	264	7		6	513	26	388		
112	180	4.74	3.02	4.55	502	980	373	0.391	0.249
128	121	4.17		4.21	485	68	1019		
129	120	4.12	1.07	4.02	485	1152	887	0.811	.216
130	120	3.96		4.11	526	52	779		
131	120	4.10	0.98	4.12	526	800	801	1.072	.257
132	120	4.03		4.12	542	100	1548		
133	120	4.14	0.99	4.13	542	936	1010	1.158	.277
134	90	4.12		4.17	575	35	612		
135	90	4.13	1.24	4.07	570	306	280	0.966	.290

Although only five determinations were made, within experimental error the results confirm the values already obtained. Using the method of least squares the value for the ratio of the rate constants is

$$k_3'/k_3 = 1.32e^{-1.7 \times 10^3/RT}$$

This gives a value of 1.7 for $E_3' - E_3$ which checks favorably with the value of 1.5 kcal. (13.8 - 12.3) from the separate determinations. This agreement rules out the importance of the H + D₂ and D + H₂ reactions.

The ratio of the frequency factors

$$A_3'/A_3 = 1.32$$

agrees with the independent value

$$\frac{A_3'/A_2^{1/2}}{A_3/A_2^{1/2}} = \frac{6.01}{4.37} = 1.38$$

It is interesting to note that this value checks favorably with that found by Pritchard, *et al.*, for the CF₃ plus hydrogen and deuterium system, *i.e.*, 1.45.⁸ Both of these values are close to the ratio of

(8) G. O. Pritchard, H. O. Pritchard, H. I. Schiff and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **52**, 849 (1956).

the relative collision numbers for the two reactions, 2^{1/2}.

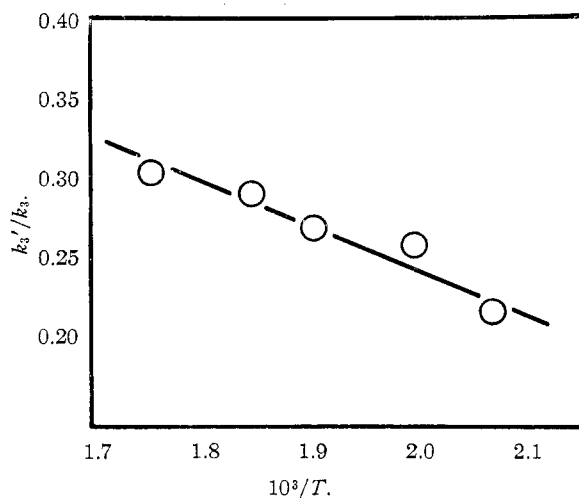


Fig. 2.—Arrhenius plot for the reaction of C₃F₇ radicals with H₂ plus D₂ mixtures.

OTTAWA, ONTARIO, CANADA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quantitative Correlation of the Infrared O-H Absorption Intensity in Aliphatic Alcohols with Substituent Constants

BY THEODORE L. BROWN

RECEIVED JULY 3, 1958

A linear relationship between the infrared O-H intensity and polar substituent constants, σ^* , has been found. The relationship is obeyed with good precision for fourteen aliphatic alcohols of varying structure. Deviations from the linear relationship are found for compounds in which internal hydrogen bonding is probable. The application of the relationship to determination of new values of σ^* , and as an aid in determination of structure is discussed.

Introduction

Studies of the infrared absorption band due to O-H in aliphatic alcohols have led to the conclusion that the intensity of the band is highly sensitive to the nature of the groups attached to the carbinol carbon.^{1,2} It has been found that there is a quantitative correlation of the intensity with the sum of the polar substituent constants,³ σ^* , of the

groups attached to the carbinol.⁴ In the present paper the results of further measurements on alcohols are reported. The purpose of this study is (a) to improve the precision of the correlation, (b) to correct or verify the results for methanol and 3-chloro-1-propanol, which were open to question, and (c) to uncover the cause or causes of deviation from the common behavior.

The variation in intensity throughout a series of

(1) T. L. Brown and M. T. Rogers, *THIS JOURNAL*, **79**, 577 (1957).
(2) T. L. Brown, J. M. Sandri and H. Hart, *J. Phys. Chem.*, **61**, 698 (1957).
(3) R. W. Taft in "Steric Effects in Organic Chemistry," M. S.

Newman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12.

(4) T. L. Brown, *Chem. Revs.*, **58**, 581 (1958).