TABLE IV

THE REACTION OF n-C_3F_7 RADICALS WITH HYDROGEN–DEUTERIUM MIXTURES

Run no.	Time, min.	Pressures, cm. D_2	H_2	Ketone	Temp., °K.	Mass spectrum peak heights 51	52	$\frac{d(C_3F_7D)/dt}{d(C_3F_7H)/dt}$	$\frac{k_3'}{k_3}$
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 $H + D_2$ and $D + H_2$ 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 CF_3 plus hydrogen and deuterium system, *i.e.*, 1.45.[8] Both of these values are close to the ratio of the relative collision numbers for the two reactions, $2^{1/2}$.

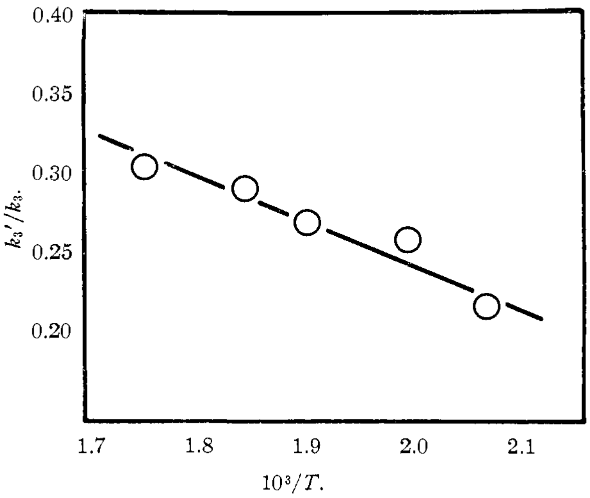

Fig. 2.—Arrhenius plot for the reaction of C_3F_7 radicals with H_2 plus D_2 mixtures.

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

[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

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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

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[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).

compounds possessing a common functional group has been related in several instances to the substituent constants characteristic of attached groups. Functional groups studied include cyanide,[5,6] carbonyl,[7] aromatic OH[8,9] and aromatic NH_2.[10,11]

Experimental

The procedure employed is similar to that previously described.[1] A Perkin–Elmer Model 21 spectrometer fitted with sodium chloride optics was employed. The cell thickness was 1.00 mm., the slit spectral width was calculated as 15.5 cm.$^{-1}$; the integration was carried out numerically over an interval of 150 cm.$^{-1}$. A concentration range of 0.08–0.01 molar was employed for the solutions.

All of the alcohols employed were obtained commercially and were carefully purified prior to use. Reagent grade carbon tetrachloride was dried with anhydrous magnesium sulfate prior to use as solvent.

The value of intensity obtained for each of the alcohols studied is listed in Table I. The values reported are those calculated from the measured band areas and do not contain any correction for wing absorption.[12] Values for methanol and 3-chloro-1-propanol were reported previously. It was felt that the value for methanol might be low, however, because of possible sampling error caused by the compound's volatility. In the present work special precautions were taken to avoid this source of error and the value obtained is 0.05 intensity unit higher than that previously obtained.[1] Because the intensity for 3-chloro-1-propanol seemed unusually high, this compound also was restudied, using a different sample. The result, however, is precisely that obtained previously.[1]

TABLE I

VALUES OF INTENSITY FOR THE INFRARED O–H ABSORPTION IN SOME ALIPHATIC ALCOHOLS, MEASURED IN CARBON TETRACHLORIDE

Compound	Intensity[a]
Methanol	0.50
3-Chloro-1-propanol	.63
1,3-Dichloro-2-propanol	.77
2-Nitro-2-methyl-1-propanol	.87
2-Chloroethanol	.60
2,2,2-Tribromoethanol	.75
Furfuryl alcohol	.56
Tetrahydrofurfuryl alcohol	.60

[a] In units of 1×10^4 mole^{-1} l. cm.$^{-2}$.

Correlation of Intensities with Values of σ^*.—The alcohols are considered as compounds of the form $R_1R_2R_3C{-}OH$. The O–H intensity is to be compared with the sum of the σ^* values for the three R groups. Values of σ^* for a number of functional groups are given by Taft.[3] In a few instances where a value is not available it can be estimated by comparison with similar groups. This has been done for the following compounds.

CBr_3: The value of σ^* for CH_2Cl is 1.05, that for CH_2Br is 1.00. The difference in σ^* for CH_2F and CH_2Cl is 0.05, while for CHF_2 and $CHCl_2$ the difference is 0.11. This is good indication that the difference in σ^* for the CCl_3 and CBr_3 groups should be roughly three times larger than that for CH_2Cl and CH_2Br, which is 0.05. Accordingly, since the σ^* value for CCl_3 is 2.65, it is taken as 2.50 for CBr_3.

$H_2C{=}CH$: σ^* for $CH_3CH{=}CH$ is 0.36, for $C_6H_5CH{=}CH$ it is 0.41; substitution of hydrogen for phenyl in the latter group should result in only a very slight change in σ^*, since the electron-withdrawal properties of the two groups are closely similar (σ^* for methyl, hydrogen and phenyl are 0.00, 0.49 and 0.60, respectively). A value of 0.40 is therefore chosen for $H_2C{=}CH$.

$HC{\equiv}C$: σ^* for the $C_6H_5C{\equiv}C$ group is 1.35. The value for the $HC{\equiv}C$ group is undoubtedly a little less than this; a value of 1.30 has been chosen.

$(CH_3)_2CNO_2$: σ^* for $CH_2NO_2CH_2$ is 0.50. With one less methylene group the value is increased to about 2.8 times this value,[3] or 1.30 for CH_2NO_2. (This compares well with 1.30 for CH_2CN, a similar group.) Substitution of two methyls for hydrogen lowers this by about 0.2 (the difference in σ^* for ethyl and *t*-butyl is 0.20), so that σ^* for the $(CH_3)_2CNO_2$ group is 1.10.

Although the values of σ^* estimated as above are not as precise as the established values, they are almost certainly within 0.1 of the correct value, and this order of precision is all that is required for the purpose at hand.

Using the estimated and established values of σ^*, the intensity is graphed in Fig. 1 *vs.* the sum of the σ^*-values for the three groups attached to carbinol, utilizing the intensity results for seventeen alcohols (ref. 1, 2 and Table I). The alcohols not identified on the figure are, in order of decreasing intensity: trichloroethanol, tribromoethanol, ethylenechlorohydrin, propargyl alcohol, 3-butyn-2-ol, benzyl alcohol, 2-methyl-3-butyn-2-ol, methanol, allyl alcohol, *n*-propyl alcohol, *sec*-butyl alcohol, *t*-butyl alcohol, triethylcarbinol and tri-isopropylcarbinol.

Discussion of Results

Correlations of absorption intensity with molecular reactivity parameters are largely empirical, and there is no general basis as yet on which to choose a suitable function for the variables. In some cases log *A* has been correlated with substituent constants, in other instances simply the intensity itself seems to afford meaningful results. In the present study it does appear that the intensity rather than its logarithm is best correlated with σ^*.

Inspection of Fig. 1 shows that for fourteen of the alcohols the relationship between σ^* and intensity is linear. The deviations of the other three compounds are well outside the range of experimental error and will be discussed below. The linearity of the relationship is strikingly good; the standard deviation from the line is less than 0.01.

The qualitative significance of the observed variation of intensity with changing electron-withdrawal power of the attached groups has been discussed previously.[1]

In a recent study of the O–H absorption in aliphatic alcohols Flett[13] has pointed out the prevalence of internal hydrogen bonding, as evidenced by the frequencies of band maxima, and semi-quantitative estimates of intensity changes. The O–H intensity is known to be extremely sensitive to hydrogen bonding and generally increases markedly when hydrogen bonds are formed.[14,15] It seems quite probable that very weak hydrogen bonding should be detectable by accurate intensity measurements before any noticeable change occurs in the frequency or gross band shape.

The abnormally high intensity for 3-chloro-1-propanol and 2-nitro-2-methyl-1-propanol can be explained as due to intramolecular hydrogen bonding, with formation of a six-membered ring. Hydrogen bonding to other than first row elements possessing lone pairs is known to be relatively weak. Further, the formation of five-membered rings by

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(5) M. R. Mander and H. W. Thompson, *Trans. Faraday Soc.*, **53**, 1402 (1957).

(6) T. L. Brown, THIS JOURNAL, **80**, 794 (1958).

(7) H. W. Thompson, R. W. Needham and D. Jameson, *Spectrochim. Acta*, **9**, 208 (1957).

(8) P. J. Stone and H. W. Thompson, *ibid.*, **10**, 17 (1957).

(9) T. L. Brown, *J. Phys. Chem.*, **61**, 820 (1957).

(10) S. Califano and R. Moccia, *Gazz. chim. ital.*, **87**, 58 (1957).

(11) P. J. Krueger and H. W. Thompson, *Proc. Roy. Soc.* (*London*), **243A**, 143 (1957).

(12) D. A. Ramsay, THIS JOURNAL, **74**, 72 (1952).

(13) M. St. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957).

(14) H. Tsubomura, *J. Chem. Phys.*, **24**, 927 (1956).

(15) C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).

intramolecular hydrogen bond formation is less satisfactory than when the rings are six-membered. From both these considerations it is not surprising that interaction of the hydroxyl hydrogen with halogen in the 2-halo alcohols does not produce any noticeable deviation from the usual behavior in the O–H intensity. This is not to say that there is no interaction in a compound such as 2-chloroethanol. From a study of internal rotation in this compound it has been concluded that a weak interaction does indeed exist.[16] It does not necessarily follow, however, that it amounts to hydrogen bonding in the strict sense.[17,18] Since only five-membered rings can be formed to chlorine by hydrogen-bonding in 1,3-dichloro-2-propanol, it is not clear why the intensity for this compound should be higher than that predicted from the linear relationship, and it remains for the time being an anomalous case.

An interesting application of these considerations is afforded by the results for furfuryl and tetrahydrofurfuryl alcohols (Table I). While it is true that five-membered rings might be formed in these compounds, hydrogen bonding would not be expected to be very strong. In furfuryl alcohol the oxygen atom is rendered less basic by resonance with the remainder of the furan ring, so that the oxygen in tetrahydrofurfuryl alcohol should be better suited for hydrogen bonding than it is in the former compound. If hydrogen bonding were not a consideration, the intensity for the saturated compound would be lower than that for the other, since the saturation of the ring undoubtedly makes it less electron-withdrawing. The fact that the intensity is higher is good evidence that there is some hydrogen bonding in tetrahydrofurfuryl alcohol although it is not possible to say whether there is any in furfuryl alcohol itself, since the value of σ^* for the 2-furan ring is not known.

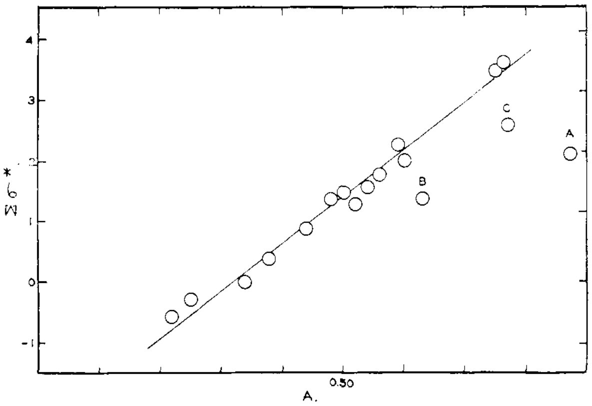

Fig. 1.—Infrared O–H intensity *vs.* sum of the polar substituent constants, σ^*, of the R groups in compounds of the form $R_1R_2R_3C$–OH: A, 2-nitro-2-methyl-1-propanol; B, 3-chloro-1-propanol; C, 1,3-dichloro-2-propanol.

Applications

A least-squares treatment of the data for the fourteen alcohols which obey the linear relationship in Fig. 1 leads to the following equation for the line: $\sigma^* = 7.88A - 2.52$. Using this equation new values of σ^* can be determined from intensity data when there is only one unknown group in the set R_1, R_2 and R_3. Using the intensity data for the set of three alcohols containing the cyclopropyl group,[2] the value of σ^* for the cyclopropyl group is determined to be $+0.11 \pm 0.03$.[19] The correlation presented here should prove to be useful in diagnostic work involving compounds of uncertain structure. For example, if a compound of known molecular weight contains an O–H group which might be in any one of two or three possible positions, a careful determination of the O–H intensity in carbon tetrachloride solution may permit a decision as to its location.

Acknowledgments.—The writer wishes to acknowledge the help of Drs. Harold Hart and M. M. Kreevoy, who first pointed out the correlation presented here.

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[16] S. Mizushima, "Structure of Molecules," Academic Press, Inc., New York, N. Y., 1953, p. 61.

[17] C. A. Coulson, *Research*, **10**, 149 (1957).

[18] C. G. Cannon, *Spectrochim. Acta*, **10**, 341 (1958).

[19] In a previous reference to the correlation reported in this paper,[4] a somewhat different value of σ^* for the cyclopropyl group was obtained. This results from the fact that the data were fewer and the acetylenic compounds were not included in the correlation. The value reported here, although not much different, is considered the more reliable.

[CONTRIBUTION FROM THE DEPARTMENT OF ENGINEERING, UNIVERSITY OF CALIFORNIA]

The Dielectric Constant of *cis*- and *trans*-Decahydronaphthalene and Cyclohexane as a Function of Temperature and Frequency

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The dielectric constant of *cis*- and *trans*-decahydronaphthalene as a function of temperature and frequency was measured using highly purified material. The relationship of dielectric constant and temperature were linear in the liquid region between 60 c.p.s. and 4 megacycles. The loss factor was less than 0.0002 in all cases. Re-examination of the discontinuity of the dielectric constant during the freezing process of *trans*-decahydronaphthalene and cyclohexane indicated the presence of several transient solid phases before the stable phase was reached.

Introduction

In a previous publication the dielectric constants of *cis*- and *trans*-decahydronaphthalene as a function of temperature were given.[1] In the course of the measurements certain anomalous behaviors of

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[1] W. F. Seyer and G. M. Barrow, THIS JOURNAL, **70**, 802 (1948).