Fig. 4.—Cole–Cole arc plot for 0.626-mole fraction of chloroform with diazabicyclo[2.2.2]octane at 20°.

amine is increased, a large distribution of relaxation times is observed. The heat of formation[23] for the chloroform–triethylamine complex is −4 kcal. per mole. The heat of formation of the chloroform–diazabicyclo-[2.2.2]octane complex should be of similar magnitude, which would mean a hydrogen bond of greater strength than in the chloroform–dioxane complex. The large distribution in the relaxation times for the chloroform–diazabicyclo[2.2.2]octane mixture can be accounted for by assuming that rotation of both the uncomplexed chloroform and the chloroform–amine complex contribute to the relaxation.

The Cole–Cole arc obtained for the 0.626-mole fraction of chloroform–diazabicyclo[2.2.2]octane mixture is

(23) C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, J. Chem. Phys., **23**, 1244 (1955).

presented in Fig. 4. As indicated in Table III, the mixture with a higher mole fraction of chloroform showed a smaller distribution. For the 0.626-mole fraction of chloroform mixture, it was possible to obtain two relaxation times by using a double arc method.[15] The relaxation time attributed to the rotation of the complex was 80×10^{-12} sec., for which the reduced relaxation time is 39. The relaxation time of the uncomplexed chloroform molecules is 14×10^{-12} sec., for which the reduced relaxation time is 7, and the relative contribution, C_1, of the uncomplexed molecules to the total relaxation process is 0.65. For the mixture with 0.909-mole fraction of chloroform, the fraction of complexed chloroform molecules would be expected to be much smaller. With such a small value for C_2, it is impossible to obtain a good separation. For a value of 7×10^{-12} sec. for uncomplexed chloroform molecules, good fit was obtained by assuming values for the complex between 20×10^{-12} and 35×10^{-12} sec. The latter value gives a reduced relaxation time close to that of the complex in the mixture discussed above.

The measurements on chloroform mixed with various substances indicate that hydrogen bonding influences the dielectric relaxation in several ways. In dilute solutions, the relaxation time is increased by hydrogen bonding to the solvent. This is evident from comparison of the behaviors of chloroform in cyclohexane, carbon tetrachloride, benzene, and dioxane. As the concentration of chloroform is increased, there is competition between the solvent and chloroform for the hydrogen bond. In all of these solvents, the results are consistent with a mechanism involving the rotation of the chloroform molecule, but in the mixtures of chloroform with diazabicyclo[2.2.2]octane, an additional relaxation mechanism involves the rotation of a complex between the amine and chloroform.

Microwave Absorption and Molecular Structure in Liquids. LIV. Dielectric Relaxation and Intramolecular Hydrogen Bonding in Hydroxy- and Methoxyacetophenones[1,2]

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Dielectric constants and losses at microwave frequencies as well as static dielectric constants and refractive indices of solutions are reported for o-hydroxyacetophenone and o-methoxyacetophenone in cyclohexane and dioxane solution, and for m-methoxyacetophenone in dioxane. These values were used to calculate dielectric relaxation times and Cole–Cole distribution parameters. Infrared carbonyl stretching frequencies are reported for o-hydroxyacetophenone and o-methoxyacetophenone in cyclohexane, carbon tetrachloride, and dioxane. o-Hydroxyacetophenone behaves as a rigid molecule because of the intramolecular hydrogen bond between the hydroxyl and acetyl groups. Resonance between the substituents and the benzene ring as well as steric inhibition to group rotation causes o-methoxyacetophenone also to behave as a rigid molecule. Group rotation is observed for m-methoxyacetophenone, for which steric repulsion is absent.

This study of substituted acetophenones is a continuation of that by Antony, Fong, and Smyth[4] on the dielectric relaxation and intramolecular hydrogen bonding in the halophenols. Substituents *ortho* to the hydroxy group on the benzene ring are capable of forming intramolecular hydrogen bonds with that group. A stronger hydrogen bond is expected for an acetyl group

ortho to the hydroxy than for a chlorine or bromine atom, because oxygen is a better proton acceptor than chlorine or bromine, and because the intramolecular hydrogen bond is sterically more favored in o-hydroxyacetophenone. The dielectric relaxation time of o-hydroxyacetophenone was measured in cyclohexane and in dioxane, the former solvent being considered incapable of participating in hydrogen bonding, the latter solvent being a fairly strong proton acceptor. Measurements were also made on o-methoxyacetophenone in cyclohexane and dioxane, because the methoxy compound is in many ways similar to the hydroxy compound but does not form hydrogen bonds. The infrared spectra in the region of the carbonyl stretching frequency were measured for these two compounds in cyclohexane, car-

bon tetrachloride, and dioxane as an aid in ascertaining the effect of the solvent on the intramolecular hydrogen bond. Finally, the dielectric relaxation time of m-methoxyacetophenone was determined in dioxane, because in this compound the methoxy and acetyl groups do not sterically hinder each other.

Experimental Methods

Purification of Materials.—m-Methoxyacetophenone (b.p. 128° at 11 mm.), o-hydroxyacetophenone (b.p. 101° at 14 mm.), and o-methoxyacetophenone (b.p. 110° at 9 mm.) were distilled under vacuum. These materials were purchased from Aldrich Chemical Co. Dioxane was distilled from sodium and cyclohexane was fractionally distilled. Reagent grade carbon tetrachloride from Allied Chemical Corp. was used without further purification.

Apparatus.—Dielectric constants and losses were measured by methods previously described.[5-8] Infrared spectra were measured on a Perkin–Elmer 421 grating spectrometer.

Experimental Results

Slopes a_0, a', a_D, and a'' were obtained by plotting the dielectric constants ϵ_0, the high frequency dielectric constants ϵ', the refractive indices for the sodium D line, and the losses ϵ'' of the solutions against the concentrations of the polar solutes. Values of the distribution parameter α and the most probable relaxation time τ_0 were obtained from Cole–Cole plots of a' against a''.[9,10] The concentration range in mole fraction is given in Table I in parentheses after the name of the solute.

TABLE I
SLOPES FOR THE DEPENDENCE OF DIELECTRIC CONSTANT AND LOSS ON CONCENTRATION

Wave length, cm.	20°		40°		60°	
	a'	a''	a'	a''	a'	a''
o-Hydroxyacetophenone (0–0.0156) in cyclohexane						
1.25	3.6	2.4	4.4	2.3		
3.22	7.2	3.4	7.4	2.8		
10.0	10.3	2.0	9.4	1.5		
25.0	10.7	0.8	9.7	0.5		
575 m.	10.9		10.0			
o-Hydroxyacetophenone (0–0.0306) in dioxane						
1.25	2.7	2.6	3.3	2.8	3.9	3.1
3.22	5.1	4.9	6.9	4.4	8.0	3.9
10.0	12.5	5.7	12.4	4.1	11.8	2.9
25.0	15.8	2.6	14.4	1.7	13.0	1.25
575 m.	16.1		14.7		13.4	
o-Methoxyacetophenone (0–0.0090) in cyclohexane						
1.25	5.4	2.7	5.9	3.0	5.8	3.4
3.22	8.9	5.3	9.6	4.8	10.0	4.1
18.5	16.6	3.1	14.8	2.1	13.3	1.4
25.0	17.0	2.3	15.2	1.6	13.5	1.1
575 m.	17.4		15.3		13.6	
o-Methoxyacetophenone (0–0.0187) in dioxane						
1.25	4.7	3.4	5.1	3.6	6.0	3.8
3.22	8.8	8.6	10.6	8.9	11.3	8.2
10.0	20.4	9.6	20.3	7.5	19.1	4.5
575 m.	25.4		22.6		20.3	
m-Methoxyacetophenone (0–0.0298) in dioxane						
3.22	3.4	2.2	3.9	2.4	4.5	2.6
10.0	7.6	4.0	8.1	3.2	8.4	2.4
25.0	10.7	3.0	10.0	2.1	9.2	1.4
50.0	11.7	1.8	10.7	1.3	10.0	0.9
575 m.	12.4		11.7		10.8	

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(10) C. P. Smyth, "Dielectric Behavior and Structure," McGraw–Hill Book Co., Inc., New York, N. Y., 1955, Chapter 11.

TABLE II
SLOPES, a_D, FOR THE DEPENDENCE OF THE SQUARE OF THE REFRACTIVE INDEX ON CONCENTRATION, WITH INFINITE FREQUENCY INTERCEPTS a_∞, RELAXATION TIMES τ_0, AND DISTRIBUTION PARAMETERS, α

t, °C.	a_D	a_∞	τ_0	α
o-Hydroxyacetophenone in cyclohexane				
20	0.4	3.0	16.4	0
40		3.3	13.8	0
o-Hydroxyacetophenone in dioxane				
20	0.5	2.5	31.0	0.05
40		2.7	24.0	.06
60		2.7	17.6	.10
o-Methoxyacetophenone in cyclohexane				
20	0.5	4.6	26.4	0.04
40		4.5	19.8	.02
60		4.6	15.9	0
o-Methoxyacetophenone in dioxane				
20	0.55	4.0	33.5	0
40		4.3	26.1	0
60		4.4	20.1	0
m-Methoxyacetophenone in dioxane				
20	0.5	2.4	46.5	0.14
40		2.4	35.2	.18
60		2.2	23.5	.24

Discussion of Results

The infrared absorption spectrum[11] of o-hydroxyacetophenone reveals no absorption band in the region around 3600 cm.$^{-1}$, where OH absorption normally occurs in phenolic compounds. This indicates the nearly complete absence of free OH. The intramolecularly hydrogen-bonded OH band is probably shifted into the CH stretching region. It is thus more useful in the case of o-hydroxyacetophenone to consider the shift in the carbonyl frequency. For acetophenone dissolved in carbon tetrachloride, the carbonyl band occurs[12] at 1693 cm.$^{-1}$. A shift in this frequency is observed when there are substituents on the ring. For m- and p-substituents, this shift can be related to their electron-withdrawing or -releasing power. The carbonyl band for o-hydroxyacetophenone appears at 1638 cm.$^{-1}$ in the Raman spectrum.[13] The shift is interpreted as being caused by intramolecular hydrogen bonding. Our measurements of the infrared carbonyl frequencies of o-hydroxyacetophenone and o-methoxyacetophenone in three different solvents are given in Table III.

TABLE III
CARBONYL STRETCHING FREQUENCIES, CM.$^{-1}$

Solvent	o-Hydroxyaceto-phenone	o-Methoxyaceto-phenone
Cyclohexane	1637	1665
Carbon tetrachloride	1640	1676
Dioxane	1635	1666

For o-hydroxyacetophenone, no band appeared in the region between 1660 and 1690 cm.$^{-1}$ in cyclohexane or dioxane solution, and in carbon tetrachloride, no band appeared between 1670 and 1690 cm.$^{-1}$, but the major band at 1640 cm.$^{-1}$ obscured the region below 1670 cm.$^{-1}$. This is taken as evidence that virtually all of the carbonyl in o-hydroxyacetophenone is intramolecularly hydrogen bonded. This is confirmed by the

(11) N. M. Cullinane, R. A. Woolhouse, and V. V. Bailey-Wood, *Rec. trav. chim.*, **80**, 116 (1961).

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

(13) G. Michel, *Bull. soc. chim. Belges.*, **68**, 643 (1959).

nearly complete absence of a distribution of dielectric relaxation times for *o*-hydroxyacetophenone in cyclohexane and dioxane, which indicates that the molecule is rigid.

The molecular model of *o*-methoxyacetophenone indicates that rotation of the methoxy group is highly hindered sterically by the adjacent acetyl group. Rotation of the acetyl group is hindered considerably less by the methoxy, but previous measurements[14] on *p*-diacetobenzene indicate little rotation of the acetyl group on the benzene ring, presumably because of double-bond character of the group bond to the ring. In addition, any resonance of the methoxy group with the benzene ring should further increase the double-bond character of the bond between the acetyl group and the benzene ring. Both the *o*-methoxyacetophenone and the *o*-hydroxyacetophenone might, therefore, be expected to relax largely by over-all molecular rotation. This is, in fact, the case both in cyclohexane solution and in dioxane solution, for the distribution parameter is zero or negligible in every case. In contrast, *m*-methoxyacetophenone shows a sizable, though not large, distribution in dioxane. In this case, there is no steric inhibition of rotation of either group, and, because the groups are *meta* to each other, resonance of the methoxy group with the benzene ring does not increase the double-bond character of the bond between the acetyl group and the ring. Because of the complexity of the motions of this molecule, it does not seem practical to attempt to analyze the data into more than one relaxation time. The large differences between a_∞ and a_D in Table II indicate libration of the polar groups around their bonds to the ring. A similar large difference was evident in the values for *p*-diacetobenzene.[14] The difference is considerably larger for *o*-methoxyacetophenone, in which both the acetyl and the sterically hindered methoxy group may librate.

The τ_0 value for *m*-methoxyacetophenone appears to be large in comparison with the values reported for the *o*-substituted compounds in dioxane solution. This could be, at least in part, the result of the greater length of this molecule in contrast with the compact shape of the *o*-substituted acetophenones. *o*-Methoxyacetophenone is a slightly larger molecule than *o*-hydroxyacetophenone and has, therefore, a larger relaxation time in cyclohexane. The methoxy compound would be expected to have a slightly larger relaxation time than the hydroxy compound in dioxane as well, but the difference between the two is negligible. The high relaxation time of *o*-hydroxyacetophenone in dioxane could be the result of a solute–solvent interaction because of the tendency of the hydroxy group to form hydrogen bonds with dioxane, even though no such bonds are actually formed. Dioxane is a more viscous solvent than cyclohexane and this in part accounts for

the larger relaxation times observed for both solutes in dioxane than in cyclohexane. This hypothesis has also been used to explain the exceptionally high relaxation times found[4] for some halophenols.

The dipole moment of *o*-hydroxyacetophenone was calculated from the data in Tables I and II as 2.72 D. in cyclohexane and 3.00 D. in dioxane. Assuming that all of the molecules are in the configuration shown below, the dipole moment is expected to be 3.21 D.; if the HO bond moment[15] is taken as 1.51 D., the
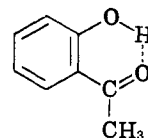
CO bond moment[15] for the hydroxy group as 0.99 D., and the moment[16] due to the acetyl group as 2.65 D. The angle[15] COH is taken as 115°. The angle[15] between the acetyl group moment and the bond between the acetyl group and the benzene ring is taken as 125°. A dipole moment along the direction of the hydrogen bond would decrease the dipole moment of the molecule.

The dipole moment for *o*-methoxyacetophenone, 3.39 in cyclohexane, 3.73 in dioxane, was calculated in a similar manner. Because of steric repulsion between the methoxy and the acetyl group, and because of resonance of these two groups with the benzene ring, the molecule probably assumes the two configurations shown below. The moment[15] of the OCH₃ group is assumed to be 1.25 D. The angle, θ, between the
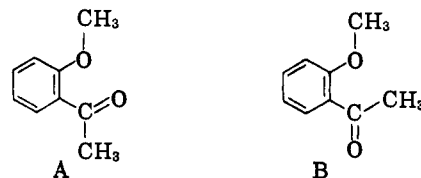
methoxy group moment and the bond between the methoxy oxygen and the benzene ring is calculated to be 70° according to the equation

$$\mu = m_1(2 - 2\cos^2\theta)^{1/2}$$

where μ is 1.72, the dipole moment of *p*-methoxyanisole, and m_1 is 1.25, the dipole moment of anisole. Using these bond moments and those given above for *o*-hydroxyacetophenone, 3.43 D. is expected for configuration A and 3.98 D. for B. The molecular model suggests that configuration A might be favored over configuration B. In any case, a larger moment is expected for *o*-methoxyacetophenone than for *o*-hydroxyacetophenone and this is what is observed.

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