

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

## Microwave Absorption and Molecular Structure in Liquids. LI. The Molecular and Intramolecular Relaxations of Two Substituted Biphenyls, 1-Naphthol, 2,6-Dimethylphenol and *p*-Diacetobenzene<sup>1,2</sup>

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The dielectric constants and losses at wave lengths of 1.25, 3.22, 9.98 cm. and 575 m. have been measured for *p*-phenylphenol, *p*-phenylacetophenone, 1-naphthol, 2,6-dimethylphenol and *p*-diacetobenzene in benzene solutions at temperatures from 20 to 60°. Refractive indices were determined for the sodium D line at 20°. The data obtained for all the compounds in benzene have been analyzed in terms of two relaxation times, the values of the short relaxation times being consistent with the intramolecular mechanisms of group rotation. In contrast to the case of 1-acetonaphthone, rotation of the OH group in 1-naphthol is not prevented by steric hindrance. In the 2,6-dimethylphenol molecule, OH group rotation contributes predominantly to the total observed loss, indicating that the rotating group is prevented from intermolecular interaction by the neighboring methyl groups. Over-all molecular rotation appears to be the predominant relaxation mechanism in the *p*-diacetobenzene molecule, suggesting high potential energy barriers hindering the acetyl group rotation. The heats of activation for rotational relaxation of the acetyl and OH groups are indistinguishable from the values of the resonance energies given by thermal data as the contribution of the respective groups.

The possibility of rotation of the polar acetyl and hydroxyl groups in molecules and the possible effects of steric hindrance and resonance energy are investigated in the present paper by determining the dielectric relaxation times of *p*-phenylphenol, *p*-phenylacetophenone, 1-naphthol, 2,6-dimethylphenol and *p*-diacetobenzene. The study of the 2,6-dimethylphenol and *p*-diacetobenzene molecules should be particularly interesting, since in the 2,6-dimethylphenol molecule, the OH group is situated between two neighboring methyl groups, and in the *p*-diacetobenzene molecule, there is no fixed molecular moment in the major axis. The study of the *p*-phenylphenol, *p*-phenylacetophenone and 1-naphthol molecules is a logical sequence of the previous studies made on the 1-acetonaphthone, 2-acetonaphthone, 4-acetyl-*o*-terphenyl and 2-naphthol molecules. It is of interest to ascertain the importance of the internal group rotation as a relaxation mechanism in these molecules.

### Experimental Methods

**Apparatus.**—The dielectric constants and losses of these molecules were measured in benzene solution by methods which have been previously described.<sup>4-7</sup>

**Purification of Materials.**—*p*-Phenylphenol, *p*-phenylacetophenone, 1-naphthol, 2,6-dimethylphenol and 1,4-diacetobenzene were obtained from the Eastman Kodak Co. *p*-Phenylphenol was recrystallized from benzene twice, and was then vacuum-dried in a desiccator containing anhydrous calcium chloride. The observed melting point was 164.2–165.1°.

*p*-Phenylacetophenone was recrystallized from ethanol and was vacuum-dried in the manner described above. The observed melting point was 120.3–121.2°.

1-Naphthol, 2,6-dimethylphenol and *p*-diacetobenzene were each recrystallized from benzene twice and vacuum-dried in the above manner. The observed melting points were 93.0–93.9°, 47.1–48.0° and 113.5–114.2°, respectively.

Benzene (Allied Chemical Corp.) was dried over Drierite (W. A. Hammond Drierite Co.) for several weeks and then was used without further purification.

### Experimental Results

Slopes  $a_0$ ,  $a'$ ,  $a_D$ , and  $a''$  were obtained by plotting the static dielectric constants  $\epsilon_0$ , the high-frequency dielectric constants  $\epsilon'$ , the refractive indices for the sodium D line, and the losses  $\epsilon''$  of the solutions against

the concentrations of the polar solutes. Cole-Cole plots<sup>8</sup> of  $a''$  vs.  $a'$  were made in order to determine the distribution parameter  $\alpha$  and the most probable relaxation time  $\tau_0$ .<sup>9</sup>

The experimental values for  $a_0$ ,  $a'$  and  $a''$  obtained for these compounds are listed after each compound in Table I. The concentration range of the two or three solutions measured for each substance is given as mole fractions in parentheses. The values obtained for  $\alpha$ ,  $a_\infty$ ,  $a_D$  and  $\tau_0$ , the "most probable relaxation time," are listed in Table II.

TABLE I

SLOPES FOR THE DEPENDENCE OF DIELECTRIC CONSTANT AND LOSS ON CONCENTRATION IN BENZENE SOLUTION

Wave length, cm.	20°		40°		60°	
	$a'$	$a''$	$a'$	$a''$	$a'$	$a''$
<i>p</i> -Phenylphenol (0–0.0068)						
1.25	1.12	0.59	1.10	0.64	1.12	0.65
3.22	2.06	1.03	2.03	1.02	1.90	1.01
9.98	2.98	0.71	2.82	0.53	2.50	0.52
575 m.	3.20		2.94		2.63	
<i>p</i> -Phenylacetophenone (0–0.0190)						
1.25	2.46	1.58	2.65	1.65	2.89	1.96
3.22	4.10	3.72	4.50	4.12	4.82	4.40
9.98	9.31	5.40	9.71	4.51	9.61	3.85
575 m.	13.85		12.69		11.77	
1-Naphthol (0–0.0262)						
1.25	1.72	0.94	1.89	0.90	2.09	0.81
3.22	2.43	1.09	2.51	.92	2.51	.76
9.98	3.08	0.73	3.00	.47	2.80	.31
575 m.	3.45		3.20		2.87	
2,6-Dimethylphenol (0–0.0263)						
1.25	1.99	0.95	1.89	0.90	1.78	0.88
3.22	2.42	.63	2.30	.58	2.15	.49
9.98	2.67	.35	2.47	.23	2.27	.17
575 m.	2.74		2.49		2.25	
1,4-Diacetobenzene (0–0.0192)						
1.25	3.28	1.85	3.75	2.25	4.13	2.48
3.22	6.28	3.87	6.58	3.70	6.83	3.25
9.98	9.50	2.96	9.18	2.56	9.00	2.01
575 m.	11.40		10.75		10.10	

### Discussion of Results

For each of the five compounds measured, analysis of the experimental data in Table I by the double-

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(2) This paper represents part of the work submitted by F. K. Fong to the Graduate School of Princeton University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(3) Sayre Fellow, 1959–1960.

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TABLE II

SLOPES,  $a_D$ , FOR THE DEPENDENCE OF THE SQUARE OF THE REFRACTIVE INDEX ON CONCENTRATION, WITH INFINITE FREQUENCY INTERCEPTS  $a_\infty$ , RELAXATION TIMES  $\tau_0$ , AND DISTRIBUTION

$t$ , °C.	$a_D$	PARAMETERS $\alpha$		$\alpha$
		$a_\infty$	$\tau_0$ ( $10^{-12}$ sec.)	
<i>p</i> -Phenylphenol				
20	0.79	0.85	19.0	0.09
40		.81	16.2	.07
60		.80	14.0	.01
<i>p</i> -Phenylacetophenone				
20	0.90	2.20	45.3	0.07
40		2.24	35.3	.06
60		2.30	27.0	.04
1-Naphthol				
20	0.745	0.95	14.4	0.10
40		.95	10.8	.10
60		.91	7.5	.09
2,6-Dimethylphenol				
20	0.224	0.29	5.3	0.11
40		.29	4.8	.07
60		.29	4.4	.0
1,4-Diacetobenzene				
20	0.323	2.59	24.6	0.11
40		2.63	19.0	.09
60		2.70	16.2	.08

arc method<sup>10</sup> yields values for  $\tau_1$ , the molecular relaxation time,  $\tau_2$ , the group relaxation time, and  $c_2$ , the relative weight of the group relaxation process, which are listed in Table III.

TABLE III

RELAXATION TIMES AND RELATIVE WEIGHTS OF THE GROUP RELAXATION PROCESSES BY THE DOUBLE-ARC METHOD

$t$ , °C.	$\tau_1 \times 10^{12}$ sec.	$\tau_2 \times 10^{17}$ sec.	$c_2$	
<i>p</i> -Phenylphenol	20	24	4	0.23
	40	20	4	.20
	60	17	3	.18
<i>p</i> -Phenylacetophenone	20	51	8.0	.12
	40	41	6.5	.12
	60	30	4.9	.11
1-Naphthol	20	15	3.4	.26
	40	11	3.4	.23
	60	8	3.2	.26
2,6-Dimethylphenol	20	13.7	3.4	.83
	40	9.7	3.3	.82
	60	6.1	3.2	.84
1,4-Diacetobenzene	20	27	7.7	.15
	40	22	6.2	.16
	60	18	4.9	.18

*p*-Phenylphenol.—*p*-Phenylphenol is sparingly soluble in benzene, and dielectric measurements made in this medium are subject to considerable experimental error. Double-arc analysis of the experimental data yields but an estimate of the two relaxation times. The environment of the OH group in the *p*-phenylphenol molecule is similar to that in the 2-naphthol molecule. Since no evidence of hydrogen bonding between solute molecules is found for a 0.60 molar per cent solution of 2-naphthol,<sup>10</sup> it may be concluded that the amount of hydrogen bonding between the *p*-phenylphenol molecules is too small to alter the dielectric results by more than the normal probable errors in the measurements.

The *p*-phenylphenol molecule is slightly longer than the 2-naphthol molecule, and, consistent with this, the most probable relaxation times,  $\tau_0$ , for *p*-phenylphenol

are slightly longer than those for 2-naphthol.<sup>10</sup> The large relaxation times,  $\tau_1$ , for *p*-phenylphenol, however, are indistinguishable from those for 2-naphthol.<sup>10</sup> Since experimental error is large for these sparingly soluble hydroxy compounds, closer comparisons do not seem to be profitable. The small relaxation times  $\tau_2$  for the OH group rotation in *p*-phenylphenol are also indistinguishable from those for the OH in 2-naphthol,<sup>10</sup> and are of the same magnitude as the values calculated by Aihara and Davies<sup>11</sup> from low frequency measurements for several other aromatic hydroxy compounds. The apparent contributions of group rotation in this molecule are a little smaller than those in 2-naphthol,<sup>10</sup> 2-methoxynaphthalene and 2-ethoxynaphthalene.<sup>12</sup>

*p*-Phenylacetophenone.—The Cole-Cole arcs for *p*-phenylacetophenone are similar to those for 2-acetonaphthone and 4-acetyl-*o*-terphenyl,<sup>13</sup> the dispersion regions  $a_0$ - $a_\infty$  for the three compounds being almost identical in magnitude. The distribution parameters  $\alpha$  are also of the same order, those for *p*-phenylacetophenone being slightly smaller. For reasons similar to those in the cases of 2-acetonaphthone and 4-acetyl-*o*-terphenyl,<sup>13</sup> it appears that acetyl group rotation is also present in the *p*-phenylacetophenone molecule. It is evident from Table III that this molecule relaxes predominantly by over-all molecular rotation, as is the case with the other two molecules.<sup>13</sup> The closeness of the  $c_2$ -values for these three molecules is consistent with the similarity of the three dipole moments. The relaxation time for over-all molecular rotation  $\tau_1$  of *p*-phenylacetophenone has the value  $51 \times 10^{-12}$  sec. at 20° as compared to the values  $33 \times 10^{-12}$  sec. for that of 2-acetonaphthone and  $100 \times 10^{-12}$  sec. for that of 4-acetyl-*o*-terphenyl. This is consistent with the fact that the volume swept out by the over-all molecular rotation of the *p*-phenylacetophenone molecule is intermediate between those by the 2-acetonaphthone and 4-acetyl-*o*-terphenyl molecules. The small relaxation times  $\tau_2$ , presumably due to the acetyl group rotation, as listed in Table III for *p*-phenylacetophenone, are in agreement with those previously obtained.<sup>13</sup>

1-Naphthol.—It has been found<sup>13</sup> that 1-acetophenone relaxes essentially by one simple process, the acetyl group being blocked by the adjacent hydrogen atom on the 8-position. The OH group in 1-naphthol, however, encounters no such hindrance as it rotates. It is possible to treat the dielectric data of 1-naphthol in terms of two relaxation times in much the same way as has been done for those of 2-naphthol.<sup>10</sup> The 1-naphthol molecule is slightly larger than the 1-fluoronaphthalene molecule. The relaxation times  $12.6 \times 10^{-12}$  sec. at 20°,  $9.9 \times 10^{-12}$  sec. at 40° and  $8.0 \times 10^{-12}$  sec. at 60° for 1-fluoronaphthalene in benzene<sup>13</sup> are consistently smaller than the corresponding values for 1-naphthol, as they should be if the relaxation times of the latter are those of molecular rotation only. The large relaxation time pertaining to the over-all molecular rotation  $\tau_1$  of 1-naphthol has the value  $15 \times 10^{-12}$  sec. at 20° as compared to the value  $23.6 \times 10^{-12}$  sec. for that of 2-naphthol. This is in agreement with the fact that 2-substituted naphthalenes usually have longer relaxation times than the corresponding 1-substituted compounds because of greater volumes swept out in rotation. The small relaxation times,  $\tau_2$ , for 1-naphthol are very close to those for 2-naphthol<sup>10</sup> and *p*-phenylphenol, all having values around  $3.5 \times 10^{-12}$  sec., indicating the similarity of the intramolecular process, namely the OH group rotation.

(11) A. Aihara and M. Davies, *J. Colloid Sci.*, **11**, 671 (1956).

(12) E. L. Grubb and C. P. Smyth, *J. Am. Chem. Soc.*, **83**, 4873 (1961).

(13) F. K. Fong and C. P. Smyth, *ibid.*, **85**, 548 (1963).

(10) F. K. Fong and C. P. Smyth, *J. Phys. Chem.*, **67**, 226 (1963).

The Cole-Cole arcs for 1-naphthol are similar to those for *p*-phenylphenol and 2-naphthol.<sup>10</sup> For all three compounds, the dispersion regions  $a_0$ - $a_\infty$ , 2.50 for 1-naphthol, 2.71 for 2-naphthol and 2.35 for *p*-phenylphenol, are similar in magnitude. The distribution parameters  $\alpha$  for these three compounds are also of the same order. All three molecules relax predominantly by over-all molecular rotation, the smaller contributions of group rotation in 1-naphthol being slightly smaller than those in 2-naphthol,<sup>10</sup> but larger than those in *p*-phenylphenol. The similarity in the values for  $a_0$ - $a_\infty$  for 1-naphthol and 2-naphthol is to be contrasted with the difference between the corresponding values 9.19 for 1-acetonaphthone and 12.35 for 2-acetonaphthone.

**2,6-Dimethylphenol.**—*o*-Toluidine has been found to have the relaxation time values  $5.5 \times 10^{-12}$  sec. at 20° by Vyas<sup>14</sup> and  $8.5 \times 10^{-12}$  sec. at 23° by Fischer,<sup>15</sup> both in benzene. *o*-Bromophenol, *o*-cresol and *o*-dichlorobenzene in benzene solution at 40° have relaxation times<sup>16</sup> of 7.7, 4.7 and  $8.8 \times 10^{-12}$  sec., respectively. All the above-mentioned molecules are smaller than the 2,6-dimethylphenol molecule, which would be expected to have longer relaxation times if it were rigid. The anomalously low most probable relaxation times listed in Table II for 2,6-dimethylphenol thus indicate the important role played by the intramolecular relaxation process. The dielectric data suffer from the lack of very high frequencies. It is nevertheless possible to treat them in terms of two relaxation times by the double-arc method,<sup>10</sup> and the results are listed in Table III. The small relaxation time  $\tau_2$  at 20° is in excellent agreement with the value calculated by Aihara and Davies<sup>11</sup> from low frequency measurements,  $3.5 \times 10^{-12}$  sec. for the OH in the same molecule. It is also in good agreement with the value 3.74 found by Davies and Meakins<sup>17</sup> for the OH in the analogous 2,4,6-tri-*t*-butylphenol in decalin, and the corresponding values found for *p*-phenylphenol, 1-naphthol and 2-naphthol.<sup>10</sup> The large relaxation time for over-all molecular rotation at 40° is 9.7, as compared to the corresponding relaxation time<sup>17</sup> of 7.7 for the *o*-bromophenol molecule, which presumably relaxes by one molecular process, the OH group being hydrogen-bonded to the bromine atom intramolecularly. This is consistent with the fact that the 2,6-dimethylphenol molecule is larger than the *o*-bromophenol molecule.

The value 2.45 for  $a_0$ - $a_\infty$  for 2,6-dimethylphenol at 20° is very close to those for *p*-phenylphenol, 1-naphthol and 2-naphthol; but, unlike these three compounds, a large part of this value is the contribution from the OH group rotation. The value 0.83 for  $c_2$  is more than three times those for *p*-phenylphenol, 1-naphthol and 2-naphthol. The ratio of the relative weights of group rotation and molecular rotation,  $c_2/c_1$ , is equal to 4.9 as compared with the corresponding ratios, 0.30 for *p*-phenylphenol, 0.35 for 1-naphthol and 0.39 for 2-naphthol. Since, for dilute solutions of these compounds in benzene, hydrogen bonding between solute molecules is not important,<sup>10</sup> this phenomenon is probably attributable to hydrogen bonding between the solute molecules and the  $\pi$ -electrons of the benzene molecules. It is then the unassociated OH group that relaxes to give the small relaxation time, which is normally found to be around  $3.5 \times 10^{-12}$  sec. The loss resulting from OH group rotation is proportional to the concentration of unassociated OH groups. In the 2,6-dimethylphenol molecule, the

OH group is partially screened from the benzene molecules by the neighboring methyl groups, and large contribution to the total loss by OH group rotation is made possible. From the heights of the two loss maxima obtained by Davies and Meakins<sup>17</sup> for 2,4,6-tri-*t*-butylphenol,  $c_2/c_1$  is estimated to be 8.2. These values of  $c_2/c_1$  are larger than the value 4.9 given by the data in Table III for 2,6-dimethylphenol, probably because the OH group in 2,4,6-tri-*t*-butylphenol is freer from molecular interaction than is that in 2,6-dimethylphenol, as the result of better screening by the large *t*-butyl groups.

**1,4-Diacetobenzene.**—If the acetyl groups were capable of free rotation, 1,4-diacetobenzene might be expected to give relaxation times characteristic of internal rotation only, since the fixed dipole moment components in the molecular axis are equal and oppositely directed. However, the relaxation times obtained for this compound are much larger than would be expected for a purely internal relaxation mechanism, suggesting considerable contribution from molecular rotation as a relaxation mechanism. In fact, the double-arc analysis of the dielectric data gives  $c_2 = 0.15$  (Table III), which shows that the relaxation is largely molecular rotation. The possibility of a mesomeric moment along the major axis as an explanation for this phenomenon is out of the question since such a mesomeric moment is negligibly small in comparison with the large group moment. A plausible explanation is that the potential energy barriers hindering rotation of the acetyl groups cause the molecules to exist in unstable *cis* and *trans* configurations, the *cis* configuration contributing to dielectric relaxation by molecular rotation. In the *p*-dimethoxybenzene molecule,<sup>18</sup> internal rotation is evidently the predominant mechanism,  $c_2$  being as large as 0.85. The dielectric behavior of *p*-diacetobenzene parallels that of benzoic acid in which group rotation around bonds may be prevented by the energy barrier arising from the conjugation between the carbonyl group and the phenyl rings.<sup>19</sup> It appears that the potential energy barriers hindering rotation of the acetyl groups are larger than those in the case of the methoxy groups, and that be-

TABLE IV  
ACTIVATION ENERGIES (KCAL./MOLE) AND ENTROPIES  
(E.U./MOLE) IN BENZENE SOLUTION

	<i>t</i> , °C.	$\Delta F^*$	$\Delta H^*$	$\Delta S^*$
<i>p</i> -Phenylphenol	20	2.90	1.0	-6.5
	40	3.03	1.0	-6.5
	60	3.16	1.0	-6.1
<i>p</i> -Phenylacetophenone	20	3.34	2.0	-4.9
	40	3.48	2.0	-4.7
	60	3.53	2.0	-4.6
1-Naphthol	20	2.63	2.3	-1.2
	40	2.66	2.3	-1.1
	60	2.66	2.3	-1.1
2,6-Dimethylphenol	20	2.56	2.4	-0.6
	40	2.58	2.4	- .6
	60	2.48	2.4	- .3
<i>p</i> -Diacetobenzene	20	2.97	1.3	-5.8
	40	3.09	1.3	-5.8
	60	3.20	1.3	-5.8
Acetyl group rotation	20	2.25	1.5	-2.7
	40	2.31	1.5	-2.7
	60	2.33	1.5	-2.6
Hydroxy group rotation	20	1.77	0	-6.0
	40	1.90	0	-6.1
	60	2.04	0	-6.1

(14) A. Vyas, *J. Sci. and Ind. Research*, **19B**, 49 (1960).

(15) E. Fischer, *Z. Naturforsch.*, **4a**, 707 (1949).

(16) H. N. Srivastava, *J. Sci. and Ind. Research*, **19B**, 149 (1960).

(17) M. Davies and R. J. Meakins, *J. Chem. Phys.*, **26**, 1584 (1957).

(18) E. L. Grubb and C. P. Smyth, *J. Am. Chem. Soc.*, **83**, 4873 (1961).

(19) F. K. Fong, Ph.D. Dissertation, Princeton University, 1962.

cause of this, group rotation is less probable. Since the Stuart-Briegleb models indicate that steric hindrance to rotation of the acetyl groups should be low, it appears probable that the energy of resonance of the acetyl groups with the benzene ring is the main source of the hindering potential barriers. The large relaxation time  $\tau_1$ , presumably due to the over-all molecular rotation, is consistent with the size of the molecule, which is roughly the same as that of *p*-phenylphenol. The small relaxation time  $\tau_2$  for the acetyl group rotation is indistinguishable from those previously determined for this group.

**Energies of Activation.**—The free energies  $\Delta F^*$ , heats  $\Delta H^*$  and entropies  $\Delta S^*$  of activation for dielectric relaxation, calculated from values for  $\tau_1$  in the usual manner,<sup>20</sup> are given in Table IV. The second decimal place has no absolute significance but is retained for  $\Delta F^*$  as possibly showing trends with temperature.

It is to be noted that the values of  $\Delta H^*$  and  $\Delta S^*$  for *p*-phenylphenol and *p*-phenylacetophenone are very close to those for 2-naphthol and 2-acetonaphthone, respectively, and that the values of  $\Delta S^*$  for *p*-phenylacetophenone, 2-acetonaphthone and 4-acetyl-*o*-terphenyl, where the acetyl groups are in similar environments, are practically indistinguishable from each other. For similar molecules, the values of  $\Delta H^*$  increase with increase of the molecular size. Thus

(20) E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4102 (1948).

the values of  $\Delta H^*$  are 1.8 for 2-acetonaphthone, 2.0, for *p*-phenylacetophenone, 2.5 for 4-acetyl-*o*-terphenyl, 0.7 for 2-naphthol and 1.0 for *p*-phenylphenol. The values of  $\Delta H^*$  for the acetyl and hydroxy group rotations may be related to the resonance energy contribution by the groups to their respective molecules.<sup>13</sup> The  $\Delta H^*$  value, 1.5 kcal./mole, in Table IV for the acetyl group rotation is the energy barrier which the group encounters as it rotates. It is indistinguishable from the value previously determined for the acetyl group rotation in the 2-acetonaphthone and 4-acetyl-*o*-terphenyl molecules<sup>13</sup> and the value for the resonance energy contribution of 1 kcal. to the acetophenone molecule<sup>21</sup> by the acetyl group determined calorimetrically. The  $\Delta H^*$  value for the OH group rotation is calculated from the small relaxation times  $\tau_2$  for 2,6-dimethylphenol. It has been possible to obtain the small temperature dependence of the OH group relaxation time for this molecule because of the predominance of the intramolecular group relaxation mechanism. The zero value of  $\Delta H^*$  does not necessarily mean that the OH group makes no resonance energy contribution to the aromatic system. It only suggests that its resonance energy contribution is of the order of, or smaller than, the average kinetic energy,  $kT$ . This finding is again in accord with the resonance study made on phenol by calorimetry.<sup>21</sup>

(21) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 99.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT SANTA BARBARA, GOLETA, CALIF.]

### Radical Recombination Reactions. III. Methyl and Heptafluoro-*n*-propyl Radicals

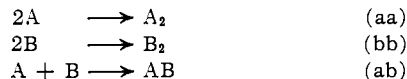
BY G. O. PRITCHARD, Y. P. HSIA AND G. H. MILLER

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The temperature dependence for the cross-combination ratio of the rate constants for  $\text{CH}_3$  and  $\text{C}_3\text{F}_7$  radicals is  $k_{ab}/(k_{aa}k_{bb})^{1/2} = 0.743 \pm 0.046 \exp(1440 \pm 50/RT)$  over the range 300 to 579°K. This is mainly due to the polar nature of perfluoroalkyl radicals, which results in a small potential barrier to their recombination.

#### Introduction

Kerr and Trotman-Dickenson<sup>1</sup> have found that the ratio of the rate constants  $k_{ab}/(k_{aa}k_{bb})^{1/2}$  for the cross-combination radical reactions is close to 2.0 in many



gas-phase systems. This is the expected value, calculated from simple collision theory, for reactions with no activation energy, and it is suggested that the results are a strong indication that all the combinations occur on every collision. Calvert<sup>2</sup> has pointed out that although the data are convincing for non-polar radicals, for the case of combinations between highly polar radicals the rate of association may be appreciably slower. A small temperature dependence for the cross-combination ratio for  $\text{CH}_3$  and  $\text{CF}_3$  radicals has been observed,<sup>3</sup> which was ascribed to the polar nature of the  $\text{CF}_3$  radical, leading to an activation energy for  $\text{CF}_3$  radical recombination of approximately 2 kcal./mole. This interpretation gains support from the recent studies by Szwarc and his co-workers<sup>4</sup> on the photolysis of hexafluoroazomethane in iso-octane at

65°, which indicate a value of 1.5 kcal./mole for  $\text{CF}_3$  radical recombination. Kerr and Trotman-Dickenson<sup>1</sup> question the validity of the temperature dependence, but note that the high value of the ratio (3.2, and independent of the temperature) calculated by them from the results of Giacometti and Steacie<sup>5</sup> for  $\text{C}_2\text{H}_5$  and  $\text{C}_3\text{F}_7$  radicals is not unexpected for a case involving such a polar radical. (The inaccuracies in this determination will be discussed further.)

Subsequently in the system where  $A = \text{CF}_3$  and  $B = \text{C}_3\text{F}_7$  we obtained<sup>6</sup> a ratio of  $1.77 \pm 0.10$ , which was independent of temperature. This shows that  $E_{ab} = 1/2(E_{aa} + E_{bb})$ , but the values are not necessarily zero, and that  $p_{ab} = (p_{aa}p_{bb})^{1/2}$ , but again not necessarily that the steric factors are all unity. For the recombination of  $\text{C}_3\text{F}_7$  radicals the value may be much less than unity.<sup>7</sup>

More recently, the possibility of a potential barrier to  $\text{CCl}_3$  radical recombination has been suggested by Johnston and Goldfinger<sup>8</sup> owing to the unfavorable orienting effect of permanent dipoles.

The present investigation is concerned with the cross-combination ratio for  $\text{CH}_3$  and  $\text{C}_3\text{F}_7$  radicals. These were produced by the co-photolysis of  $\text{CH}_3\text{COCH}_3$  and  $\text{C}_3\text{F}_7\text{CHO}$  in the region of 3130 Å. The photo-decomposition of acetone is well established, and that

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