The association of a series of carboxylic acids, RCOOH, in the vapor state has been measured.

The association of the same series of acids has been measured in solution, using diethyl ether as solvent.

It is pointed out that the same theoretical considerations apply not only to the organic acids, but to any other types of organic compound which associate by hydrogen bridge formation.

AMES, IOWA RECEIVED MAY 19, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

The Electron-Sharing Ability of Organic Radicals. XIII. The Effect of the Radicals in the Solvent Molecule

BY FRANC A. LANDEE AND I. B. JOHNS

As mentioned in the preceding paper, hydrogen bridge formation is of paramount importance in the association of compounds containing active hydrogen atoms, such as the carboxylic acids. The normalizing effect of many solvents is doubtless due to the formation of hydrogen bridges between the compound and the oxygen of the solvent. If this be true the electron donor power of the oxygen atom of a given solvent type, such as the ketones, nitro compounds, esters, etc., should be variable depending on the electron-sharing ability of the radicals attached to the carbonyl, nitro, carboxyl, etc., group.

In the formation of the covalent bond in the hydrogen bridge, there is no transfer of charge, or if such transfer takes place it must be completely and rapidly reversed. Accordingly such bonds should not be influenced by the dielectric constant of the medium.

The present paper shows that the normalizing effect of benzaldehyde on *p*-chlorophenol is due to the association of the solvent with the phenol, most probably by hydrogen bonding. It is also shown that the electron-sharing ability of the radicals in a series of ketones determines the normalizing power of these solvents on benzoic acid and on ethanol, and that the dielectric constants of these ketones have no noticeable influence.

Experimental

Proof that Association with the Solvent is the Cause of the Normalizing Effect.—The method chosen to show the formation of complexes between the solvent and solute and the effect on the molecular weight of the solute was as follows. First, a substance of fair associating power was added to benzene and its molecular weight at various concentrations measured cryoscopically. Then to known solutions of this compound were added measured amounts of a non-associating compound and the total depression of the freezing point measured. The apparatus used was that described in an earlier publication from this Laboratory.[1]

If there were no reaction between the two solutes then their effects would be additive. Any deviation from this behavior was interpreted as being due to association between the two solutes. Several pairs of compounds were investigated in this manner. Since all pairs gave the same results, data are presented only for *p*-chlorophenol and benzaldehyde.

The data pertaining to the molecular behavior of *p*-chlorophenol in benzene are listed in Table I.

TABLE I

ASSOCIATION OF *p*-CHLOROPHENOL IN BENZENE AS A FUNCTION OF CONCENTRATION

Grams of solute in 100 g. of solvent	Moles solute in 100 g. solvent × 10^2	F. p. depression, °C.	Calcd. mol. wt.	% Association
0.847	0.659	0.338	128.9	0
1.168	.91	.457	131	2
1.658	1.29	.640	133	3
2.010	1.56	.772	134	4
2.438	1.89	.921	136	6
3.155	2.45	1.172	139	8
3.210	2.49	1.172	141	10
3.912	3.04	1.391	144	12
4.341	3.38	1.535	145	13
4.609	3.58	1.599	148	15
4.964	3.86	1.562	151	17
5.29	4.12	1.794	152	18

Benzaldehyde in benzene exhibited a nearly normal molecular weight, 109 ± 1, over the range 1.4 to 7.1 moles/100 g. of solvent.

In Table II are presented the data for solutions of both benzaldehyde and *p*-chlorophenol in benzene.

The status of the two solutes can be determined from these data in the following way, using the second determination in Table II as example. Since there is present 0.0126 mole of benzaldehyde in one form or another, then 0.648° (0.0126 ×

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[1] I. B. Johns and R. M. Hixon, THIS JOURNAL, **56**, 1333 (1934).

TABLE II

THE FREEZING POINTS OF SOLUTIONS CONTAINING BOTH *p*-CHLOROPHENOL AND BENZALDEHYDE AS SOLUTES IN BENZENE AS A SOLVENT

0.0338 mole *p*-chlorophenol in 100 g. benzene in all cases.

Moles C_6H_5CHO in 100 g. C_6H_6	Total moles of solute in 100 g. C_6H_6	F. p. depression (found), °C.	Moles of solute calcd. from f. p. depression
0.000	0.0338	1.535	0.0298
.0126	.0464	1.870	.0364
.0252	.0590	2.275	.0443
.0378	.0716	2.690	.0523
.0504	.0842	3.170	.0617

51.4), of the freezing point lowering can be attributed to the aldehyde. This leaves a lowering of 1.222° to be caused by the phenol, exclusive of the phenol molecules that are associated with the benzaldehyde. From a graph of the data in Table I it was found that a solution having a freezing point depression of 1.222° contains 0.0259 mole of *p*-chlorophenol per 100 g. of benzene and that 0.0217 mole exists as single molecules while the remaining 0.0042 mole exists as the dimer. Therefore the complete molecular distribution of the phenol in this solution is:

		Total moles
Single molecules	0.0217	0.0217
Double molecules	.0021	.0042
Solvated molecules	.0079	.0079
		.0338

These results and those calculated for the other concentrations are given in Table III and are plotted on Fig. 1.

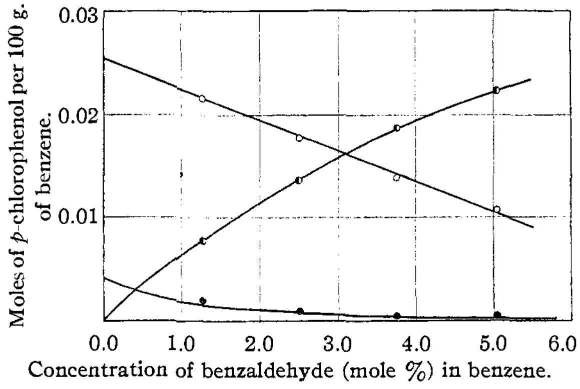

Fig. 1.—O, single molecules; ●, double molecules; ◐, solvated molecules.

The curves of this graph show clearly that the hydrogen of the phenol is able to form associated bonds with the aldehyde group and that as the concentration of the aldehyde increases the association of the phenol with itself decreases.

TABLE III

THE MOLECULAR STATUS OF *p*-CHLOROPHENOL AND BENZALDEHYDE SIMULTANEOUSLY DISSOLVED IN BENZENE AS A SOLVENT

0.0338 mole *p*-chlorophenol in 100 g. benzene in all cases.

		Calcd. moles present as			
Run	Moles C_6H_5CHO in 100 g. C_6H_6	Phenol single molecules	Phenol doubled molecules	Phenol solvated molecules[a]	Aldehyde single molecules
1	0.0	0.0257	0.00405	0.00	0.00
2	.0126	.0217	.0021	.0079	.0047
3	.0252	.0179	.0011	.0137	.0115
4	.0378	.0140	.0005	.0188	.0190
5	.0504	.0108	.0003	.0224	.0280

[a] This also represents the moles of benzaldehyde present in combined form.

Similar studies in benzene using *p*-chlorophenol with ethyl benzoate and *p*-chlorophenol with nitrobenzene show that the strengths of the solvating action of the groups are, in the order of increasing effect, NO_2, $COOC_2H_5$, CHO. This also suggests that the method employed can serve as a quantitative method for determining the normalizing effects of solvents, the amount of the solvent that must be added to benzene in order to produce a given reduction in the association of a solute being inversely proportional to its normalizing effect, provided it is not itself associated in benzene.

Electron-Sharing Ability of the Radicals and the Normalizing Power of a Series of Ketones.—The molecular weights of two solutes, namely, benzoic acid and ethyl alcohol were determined in a series of ketones. The solvents were chosen to give as wide a separation in the electron-sharing ability of the attached radicals as possible and to possess as nearly as possible the same melting points.

Most of the determinations were carried out cryoscopically. In acetone the vapor-pressure method was used. It was found that some of the solvents, notably benzophenone, crystallized so slowly that excessive supercooling was encountered unless the temperature of the water-bath was raised to the fusion temperature of the solvent as soon as the latter had been induced to crystallize by seeding. In this way a uniform supercooling could be obtained for all the solvents used. The freezing points were not corrected for this supercooling since the correction is less than the over-all accuracy of the cryoscopic method in these solvents.

Naphthalene was used to determine the molal freezing point constants of the solvents. Acetophenone, m. p. 19°, was found to have a molal freezing point lowering of 5.67. Garelli and Montanari[2] had reported 5.65. The value for benzophenone, m. p. 46°, was found to be 9.80 compared with 9.88 reported by Eykman.[3] The constant found for *p,p'*-dichloroacetophenone, m. p. 142°, is 10.15, none having been reported before.

In Tables IV to VII inclusive are given the data concerning the ketones.

TABLE IV

ASSOCIATION OF BENZOIC ACID IN ACETONE AS A FUNCTION OF CONCENTRATION (VAPOR PRESSURE LOWERING METHOD)

Grams solute in 100 g. solvent	Moles solute in 100 g. solvent $\times 10^2$	Mole % solute	Calcd. mol. wt.	Association index
4.07	3.33	1.90	115	0.942
5.34	4.37	2.48	118	.966
6.12	5.02	2.84	117	.960
8.64	7.08	3.95	121	.991

To check the method, naphthalene was employed and found to have a molecular weight of 128 in the concentration range 2.65 to 3.45 g. per 100 g. of acetone.

TABLE V

ASSOCIATION OF BENZOIC ACID AND ETHYL ALCOHOL IN ACETOPHENONE AS A FUNCTION OF CONCENTRATION

Grams solute in 100 g. solvent	Moles solute in 100 g. solvent $\times 10^2$	Mole % solute	F. p. depression, °C.	Calcd. mol. wt.	Association index
		Benzoic Acid (122)			
0.816	0.67	0.80	0.34	135	1.11
2.581	2.12	2.48	1.05	138	1.13
3.250	2.66	3.10	1.30	141	1.16
5.063	4.15	4.75	1.95	147	1.20
5.895	4.83	5.48	2.22	150	1.23
		Ethyl Alcohol (46)			
1.54	3.34	3.86	1.52	57.2	1.24
2.17	4.71	5.35	2.03	60.5	1.31
2.89	6.28	7.02	2.60	63.0	1.37
3.52	7.65	8.42	3.06	65.0	1.41

TABLE VI

ASSOCIATION OF ETHYL ALCOHOL AND BENZOIC ACID IN BENZOPHENONE AS A FUNCTION OF CONCENTRATION

Grams solute in 100 g. solvent	Moles solute in 100 g. solvent $\times 10^2$	Mole % solute	F. p. depression, °C.	Calcd. mol. wt.	Association index
		Benzoic Acid (122)			
1.410	1.16	2.07	0.93	149	1.22
2.548	2.09	3.66	1.60	156	1.28
4.201	3.44	5.89	2.53	163	1.34
5.115	4.19	7.09	2.91	173	1.42
6.082	4.99	8.33	3.35	178	1.46
		Ethyl Alcohol (46)			
1.421	3.09	5.33	2.13	65.5	1.42
2.539	5.51	9.12	3.46	71.8	1.56
2.762	6.01	9.85	3.61	75.0	1.63
2.938	6.38	10.4	3.80	75.6	1.64
3.162	6.88	11.1	3.91	79.2	1.72

TABLE VII

ASSOCIATION OF BENZOIC ACID IN *p,p'*-DICHLOROBENZOPHENONE AS A FUNCTION OF CONCENTRATION

Grams solute in 100 g. solvent	Moles solute in 100 g. solvent $\times 10^2$	Mole % solute	F. p. depression, °C.	Calcd. mol. wt.	Association index
2.390	1.96	4.76	1.85	131	1.07
3.495	2.86	6.66	2.53	140	1.15
4.283	3.51	8.08	3.00	145	1.19
5.721	4.69	10.5	3.92	148	1.21
6.40	5.25	11.6	4.25	153	1.25

From the above tables of data graphs were drawn from which the association indices of the two solutes at like concentrations were obtained by interpolation. The indices for benzoic acid at 0.01 mole per cent. and for ethanol at 0.03 mole per cent. are given in Table VIII. However, since we are studying the reaction or possible reaction between the molecules of the solvent and the solute, we should compare the indices at the same mole fraction in each case. This has been done and the indices at 0.01 and 0.03 mole fraction are included in the table. Due to differences in molecular volumes of the solvents, neither method is exactly that required for perfect comparison.

The data of Table VIII are shown graphically in Fig. 2. It is clearly seen that as the electron-sharing ability of the radicals attached to the carbonyl group increases, the association of the solute increases. This means that an increase in the electron-sharing ability of the radicals decreases the electron donor power of the oxygen of the carbonyl group, thus decreasing the extent of association of the solute with the solvent and allowing greater association of the solute molecules with themselves. No such relation can be seen between the dielectric constant of the solvent and association of the solute.

In the case of acetophenone and methyl propyl ketone, the only unsymmetrical ketones used, the value for the electron-sharing ability employed in Table VIII and in Fig. 2 is the average of the values for the two radicals. The numerical values were taken from the graph in the first paper of this series.[4]

One point is definitely out of line, namely, that

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[2] Garelli and Montanari, *Gazz. chim. ital.*, **24**, II, 229 (1894).

[3] Eykman, *Z. physik. Chem.*, **4**, 497 (1889).

[4] R. M. Hixon and I. B. Johns, THIS JOURNAL, **49**, 1786 (1927).

TABLE VIII

ASSOCIATION INDICES OF BENZOIC ACID AND ETHYL ALCOHOL AT STANDARD CONCENTRATIONS IN VARIOUS SOLVENTS OF THE TYPE RCOR TOGETHER WITH VARIOUS PHYSICAL CONSTANTS OF THE SOLVENTS

Solvent	Temp. of detn., °C.	Dielectric const. of solvent	Av. E. S. A. of the two R groups concerned	Association indices of solutes: Benzoic acid, 0.01 mole in 100 g.	Benzoic acid, 1 mole %	Ethyl alcohol, 0.03 mole in 100 g.	Ethyl alcohol, 3 mole %
$CH_3—CO—CH_3$	40	(19.0)	−1.45	0.94	0.93	0.99	0.98
$CH_3—CO—C_3H_7$	102	(12.0)	−1.50	.93	.93+[a]	..	..
$CH_3—CO—C_6H_5$	19	18.0	+1.40	1.11	1.10	1.22	1.20
$C_6H_5—CO—C_6H_5$	46	12.0	+4.2	1.21	1.14	1.41	1.33
$Cl—C_6H_4—CO—C_6H_4—Cl$	142	....	+5.1	1.07	1.03	..	..
$ClCH_2—CO—CH_2Cl$	41	(18.0)	+6.7	1.2–1.3	1.2–1.3	..	..
$Cl—CO—Cl$	9	4.5	+8.5	2.12	2.13[b]	..	..

[a] Beckmann, Fuchs and Gernhardt, *Z. physik. Chem.*, **18**, 473 (1895). [b] Beckmann, *Z. anorg. allgem. Chem.*, **55**, 371 (1907).

for benzoic acid in *p,p'*-dichlorobenzophenone. The low result here may be understood when it is remembered that this determination was made at a temperature of 142° or about 110° above the mean determination temperature of the other solvents. It is well known that an increase in temperature decreases association, Beckmann[5] having found the molecular weight of benzoic acid in benzene to be 233 at the freezing point and 193 at the boiling point at a concentration of 0.25 molal.

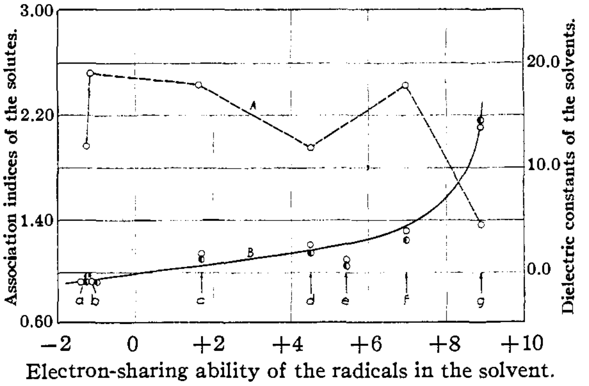

Fig. 2.—A, dielectric constants of solvents; B, association indices of benzoic acid; ○, $^1/_{100}$ mole in 100 g.; ◐, 1 mole %: a, methyl *n*-propyl ketone; b, acetone; c, acetophenone; d, benzophenone; e, *p,p'*-dichlorobenzophenone; f, *sym*-dichloroacetone; g, phosgene.

Though the heat of reaction of the single benzoic acid molecule associating to the double molecule is known with considerable accuracy from the work of Hendrixson[6] and of Szyszkowski[7] this energy is not of value for correcting the above mentioned index since the reaction is not from the single molecule to the double molecule but from the solvated to the double molecule.

Association in the Liquid State.—Unfortunately no method above criticism is known for determining the molecular weight of a liquid, if such a term can even be said to have a meaning. All methods available involve the study of some physical constant of the compound in question and the comparison of this value with the calculated value as derived from a study of the same constant for liquids that are known or appear to be normal. The deviation of the found and calculated value of the constant is interpreted as being due to association and the degree of association is proportional to the degree of deviation.

The boiling point of a liquid compound is one of the constants adapted to such a study and an empirical relationship known as Longinescu's[8] relation has been derived that shows a relationship between the absolute boiling point of a liquid, its density at 0° and the number of atoms of any type in the molecule. The relation is

$$T/d\sqrt{n} = K$$

This constant has been evaluated by a study of normal liquids such as chlorobenzene, carbon disulfide, ethylene bromide, ethyl cinnamate, octyl ether, etc., and found to have a value of 100. Therefore

$$n = [T/d(100)]^2$$

and since acetic acid has a boiling point of 118° (391°K.) and has a density of 1.065 at 0°, we may substitute these values in the above equation and find that "*n*" or the number of atoms in each molecule in the liquid state is equal to 13.5. Since the formula CH_3COOH requires but 8, we may say that the association index in this case is 13.5/8 or about 1.7. Propionic acid by the same calculation gives an index of about 1.6, while benzoic acid with a boiling point of 249° (522°K.)

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(5) E. Beckmann, *Z. physik. Chem.*, **2**, 729 (1888).

(6) Hendrixson, *Z. anorg. allgem. Chem.*, **13**, 73 (1897).

(7) Szyszkowski, *Z. physik. Chem.*, **131**, 175 (1927).

(8) Longinescu, *Chem. Rev.*, **6**, 381 (1929).

and a density of 1.15 has an association index of 1.3.

It is realized that this method is only approximate and that the results must be considered more from a qualitative than a quantitative standpoint. Nevertheless these results do compare favorably with those secured by other methods, so they may contain some elements of truth. Therefore this relation was used to calculate the association indices of a series of substituted carboxylic acids. These results are plotted in Fig. 3 against the electron-sharing ability of the substituted radical. The result is precisely that expected. The associations decrease in a regular fashion as the electron-sharing ability of the substituted radical increases.

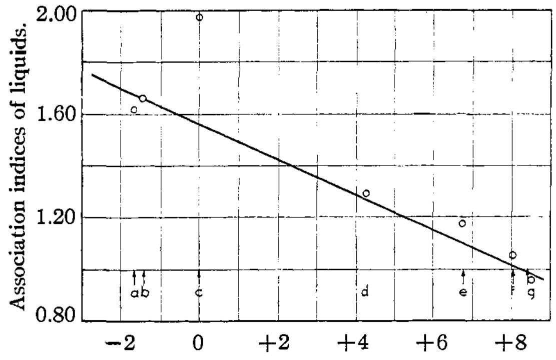

Fig. 3.—Substituted radicals in RCOOH: a, C_2H_5; b, CH_3—; c, H—; d, C_6H_5—; e, CH_2Cl—; f, $CHCl_2$—; g, CCl_3-.

Another method of estimating association in the liquid is that due to Ramsay and Shields involving the measurement of the surface tension and the density of the liquid being studied. Though the Ramsay–Shields equation has been modified by many investigators and the results determined using this method have been criticized on many grounds, it is nevertheless true that methods involving the surface tension are still considered valuable in determining association in the liquid phase. In Fig. 4 is given a curve that shows the variation of the association indices of compounds of the type ROH as a function of the electron-sharing ability of the substituted radical. As may be seen the agreement with the hypothesis is good. This curve was plotted from data obtained by investigators using the old Ramsay–Shields equations. Newer investigations involve a function of the surface tension and the density at the boiling point of the liquid being examined. This function called the "specific cohesion" is doubtless a better indication of association in the liquid state. This is especially true of the higher molecular weight compounds. In Fig. 4 is also given a curve of the same type as the one mentioned previously except that the specific cohesion function was used to obtain the data.

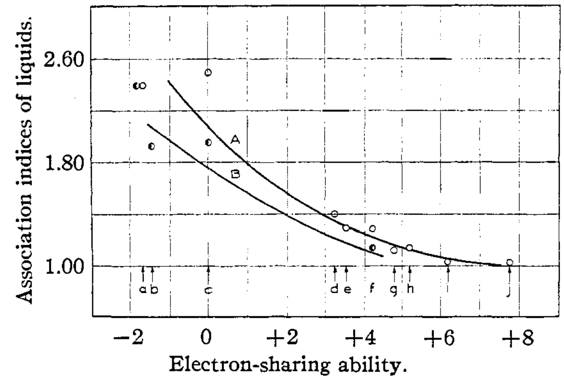

Fig. 4.—Substituted radicals in R—OH: a, C_2H_5—; b, CH_3—; c, H—; d, p-$CH_3C_6H_4$—; e, m-$CH_3C_6H_4$—; f, C_6H_5—; g, o-$CH_3C_6H_4$—; h. p-ClC_6H_4—; i, o-ClC_6H_4—; j, *sym*-$Cl_3C_6H_2$—; A, by Ramsay–Shields equation; B, by specific cohesion equation.

Still another method of measuring association in the liquid is that due to Bingham and his coworkers which involves measurements of the fluidity of the compound in question. Data obtained by this method have been plotted in Fig. 5. It seems to be a characteristic of this method that high results are obtained. By their fluidities, even compounds such as chlorobenzene, biphenyl, ethylene chloride, and so forth, are judged to be appreciably associated. This is contrary to the finding of other methods in most cases.

In conclusion it may be stated that apparently

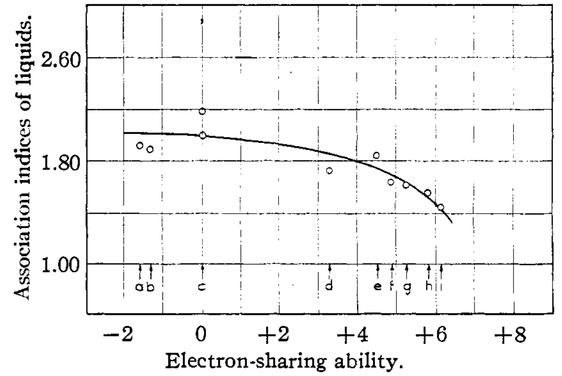

Fig. 5.—Substituted radicals in ROH: a, C_2H_5—; b CH_3—; c, H—; d, p-$CH_3C_6H_4$—; e, C_6H_5—; f, o-$CH_3C_6H_4$—; g, p-ClC_6H_4—; h, m-ClC_6H_4—; i, o-ClC_6H_4—.

no matter by what method one measures association in the liquid phase, one finds that the observed values depend upon the electron-sharing abilities of the radicals concerned. This dependence is in the same direction as that predicted, and found, for association of organic compounds in solution. Hence the contributing factors in each case must be the same, *i. e.*, the presence of doubly covalent hydrogen.

Summary

1. Data are presented which show that the normalizing effect of a solvent is due to the association of the solvent with the solute. This relation was found by studying the behavior in benzene of two compounds together, one, called the solute (*p*-chlorophenol) in fixed concentration, the second, called the solvent (benzaldehyde) in variable concentration.

2. Data are presented which show that the normalizing power of a series of ketones depends in a regular way on the electron-sharing ability of the radicals attached to the carbonyl group.

3. Both the data and the theoretical considerations indicate that the dielectric constant of a solvent has little if any effect on associations due to hydrogen bonding.

AMES, IOWA RECEIVED MAY 19, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Photolysis of Azomethane

BY C. V. CANNON[1] AND O. K. RICE

Azomethane has been considered particularly adapted to decomposition studies because this reaction is apparently a unimolecular one which has no chain (or else a very short one) and is comparatively free from complicating side reactions. A number of investigators[2] have studied the thermal and photochemical decompositions. Ramsperger[3] showed that the unimolecular rate constant of the thermal process falls off at low pressures, due to lack of activating collisions and Sickman and Rice[4] measured the collisional activating efficiency of various inert gases. Forbes, Heidt and Sickman,[5] studying the photochemical decomposition, believed that they had discovered a lowering in the quantum yield caused by collisional deactivation of the excited molecules at high pressures. This was especially noticeable at long wave lengths, which was to be expected, since the life of an excited molecule almost certainly depends in an inverse way on the energy it contains.[6] These less highly excited molecules would be expected to have long lives, during which collisional activation could occur. It was our purpose in the present work to check this result of Forbes, Heidt and Sickman, and to see whether deactivation could also be found to occur through collision with inert gas molecules.

Although determinations of the *absolute* quantum yield would not be necessary to show deactivation, lack of agreement among earlier investigators made it desirable to redetermine this quantity. Ramsperger,[7] using filters to obtain monochromatic light, found the quantum yield at 3660 Å. to be approximately 2. His energy measurements, however, involved large corrections for red and infrared light. Forbes, Heidt and Sickman[5] reported a value for the quantum yield that approaches unity as a maximum at low pressures. These authors used the increase in the total pressure as a measure of the amount of azomethane which had reacted.

Careful analyses[8,9,10] of the products of the photodecomposition prove the reaction to be much more complicated than was originally believed and throw doubt on quantum yield determinations depending solely upon the pressure increase during reaction, since such calculations assume either an over-all decomposition giving nitrogen and ethane, or a pressure increase that is proportional to the extent of decomposition. However, other quantum yield determinations by

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[1] Du Pont Fellow in Chemistry, 1939–40; present address, Northwestern University, Evanston, Illinois.

[2] For references see Taylor and Jahn, *J. Chem. Phys.*, **7**, 470 (1939).

[3] Ramsperger, THIS JOURNAL, **49**, 1495 (1927).

[4] Sickman and Rice, *J. Chem. Phys.*, **4**, 239, 242, 608 (1936).

[5] Forbes, Heidt and Sickman, THIS JOURNAL, **57**, 1935 (1935).

[6] For a detailed theory see Rice and Ramsperger, *ibid.*, **49**, 1617 (1927).

[7] Ramsperger, *ibid.*, **50**, 123 (1928).

[8] Burton, Davis and Taylor, *ibid.*, **59**, 1038 (1937).

[9] Burton, Davis and Taylor, *ibid.*, **59**, 1989 (1937).

[10] Davis, Jahn and Burton, *ibid.*, **60**, 10 (1938).