results in the formation of a variety of products mainly as a result of free radical chain reactions.[3e]

From the available evidence it seems that the thermal decomposition of methyl cyclobutyl ketone may be a unimolecular reaction. Since no significant fall-off in the rate constant was detected at 10 mm., the pressure region of the fall-off appears to be below that of cyclobutane[4] as might be anticipated for a molecule with a greater number of vibrational degrees of freedom. The frequency factor for the decomposition lies within the limits expected for a unimolecular reaction. The frequency factor A of a unimolecular gas reaction can be expressed as

$$A = \kappa e(kT/h)e^{\Delta S^{\ddagger}/R}$$

where κ is the transmission coefficient and $\Delta S^{\ddagger}$ is the entropy of activation.[18] From the experimental value of the frequency factor and with the assumption that the transmission coefficient is unity, one can calculate that the entropy of activation at 400° is +4.3 cal./deg. mole. A positive value would be expected for a reaction involving the cleavage of the ring.

In comparison with the thermal decompositions of cyclobutane[4] and ethylcyclobutane[5] the activation energy for the decomposition of methyl cyclobutyl ketone is 7.5–8.0 kcal./mole lower. Although this decrease in activation energy is partially compensated by a lower frequency factor (smaller apparent entropy of activation), the methyl cyclobutyl ketone decomposition takes place at temperatures approximately 50° lower than the decompositions of ethylcyclobutane and cyclobutane (for similar rates). In this connection it is to be noted that the product methyl vinyl ketone possesses some resonance energy which would not be associated with the corresponding product in the decomposition of ethylcyclobutane or cyclobutane. The effect of resonance in the product may result in some lowering of the activation energy if the decomposition proceeds by a direct formation of methyl vinyl ketone and ethylene. As an indication of the resonance energy of methyl vinyl ketone, there is the value of the resonance energy for crotonaldehyde which was reported to be 2.9 kcal./mole.[19] On the basis of certain corrections for polar and hyperconjugation effects[20] a higher value (7.3 kcal./mole) has been suggested recently. If the rate-determining step in the decomposition involves the formation of a biradical (by the breaking of the ring C–C bond nearest the carbonyl group), there should be more resonance in the biradical formed from methyl cyclobutyl ketone than in the corresponding biradical from an alkyl derivative of cyclobutane. The presence of any resonance in the biradical should lower somewhat the activation energy of the formation of the biradical from methyl cyclobutyl ketone. In the comparison of the present results with those from the decompositions of other four-membered ring compounds it was observed that the frequency factor and the activation energy for methyl cyclobutyl ketone are much closer to those of cyclobutanone ($k = 3.6 \times 10^{14}\, e^{-52000/RT}$ sec.$^{-1}$) than to those of ethylcyclobutane or cyclobutane.

Acknowledgments.—The authors wish to acknowledge the financial assistance of the Celanese Corporation of America at the start of this study and the subsequent financial support of the National Science Foundation over the major portion of the investigation. They also wish to thank Mr. Carl Whiteman for making the infrared absorption measurements.

---

[18] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 295.

[19] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, THIS JOURNAL, **60**, 440 (1938).

[20] M. M. Kreevoy and R. W. Taft, Jr., *ibid.*, **79**, 4016 (1957).

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE A. AND M. COLLEGE OF TEXAS]

Quantitative Relationship between Structure and Reactivity for the Reactions between Diphenyldiazomethanes and Benzoic Acids in Toluene at 25°

BY C. KINNEY HANCOCK AND JOHN S. WESTMORELAND

RECEIVED AUGUST 26, 1957

Rate constants at 25° have been determined for the reaction of diphenyldiazomethane (DDM) with twelve *m*- or *p*-substituted benzoic acids (XBA's) in toluene. Correlation analysis of the data yields eq. 2: $\log k_2 = -0.1023 + 2.513\Sigma\sigma_B$ with $r = 0.9947$ and $s = 0.0913$. In a previous article,[1] correlation analysis of the data for the reaction of benzoic acid (BA) with twelve *m*- and/or *p*-substituted diphenyldiazomethanes (XDDM's) yielded eq. 1: $\log k_2 = -0.1440 - 1.570\Sigma\sigma_D$ with $r = 0.9987$ and $s = 0.0442$. If the structures of both reactants are varied simultaneously and the two effects are independent, it appears that the resulting data would be closely represented by eq. 4: $\log k_2 = -0.1231 - 1.570\Sigma\sigma_D + 2.513\Sigma\sigma_B$ where −0.1231 is the average of the intercepts from eq. 1 and 2, −1.570 and +2.513 are ρ_D and ρ_B from eq. 1 and 2, and $\Sigma\sigma_D$ and $\Sigma\sigma_B$ are the summations of σ-values in the XDDM and in the XBA. Rate constants at 25° have been determined for twenty-one reactions of XDDM's with XBA's in toluene. For these reactions plus two others from ref. 6, substitution of $\Sigma\sigma_D$ and $\Sigma\sigma_B$ values into eq. 4 yields calculated $\log k_2$ values which show an average deviation of 0.084 from experimental $\log k_2$ values. For the forty-six available reactions of XDDM's or DDM with XBA's or BA, the analysis of the multiple regression yields eq. 5: $\log k_2 = -0.1089 - 1.620\Sigma\sigma_D + 2.376\Sigma\sigma_B$ with $R = 0.9975$ and $s = 0.0783$. The very close fit of eq. 5 offers conclusive evidence that the effect of *m*- and/or *p*-substituents on the DDM is independent of the effect of *m*- or *p*-substituents on the BA.

Introduction

For the reaction at 25° in toluene of benzoic acid (BA) with diphenyldiazomethane (DDM) and with eleven *m*- and/or *p*-substituted diphenyldiazomethanes (XDDM's), it has been shown[1] that

---

[1] C. K. Hancock, R. F. Gilby, Jr., and J. S. Westmoreland, THIS JOURNAL, **79**, 1917 (1957).

$$\log k_2 = -0.1440 - 1.570\Sigma\sigma_D \qquad (1)$$

with a correlation coefficient r of 0.9987 and a standard deviation from regression s of 0.0442. In equation 1, -0.1440 is the value of $(\log k_2^0)_{\text{calcd.}}$, -1.570 is the slope ρ_D of the regression line, and $\Sigma\sigma_D$ is the summation[2a] of Hammett's[3] polar constants for the XDDM substituents.

For the reaction at 30° in ethanol of DDM with BA and with five *m*- or *p*-substituted benzoic acids (XBA's), Roberts, *et al.*,[4] found a ρ_B-value of 0.937 for the regression of $\log k_2$ on σ_B. Later, using the same temperature and solvent, for the reaction of DDM with BA and with seven *m*- or *p*-substituted XBA's, Benkeser, *et al.*,[5] found a ρ_B-value of 0.929 for the regression of $\log k_2$ on σ_B. Four of the XBA's were identical to four of those that were studied by Roberts, *et al.*

The objects of the presently reported study were: (1) to determine the relationship between $\log k_2$ and $\Sigma\sigma_B$ for the reactions of DDM with *m*- or *p*-substituted XBA's in toluene at 25°, (2) to obtain k_2-values for reactions between *m*- and/or *p*-substituted XDDM's and *m*- or *p*-substituted XBA's in toluene at 25° and (3) to determine the relationship between the effect of varying the structure in the XDDM and the effect of simultaneously varying the structure in the XBA.

Experimental

Materials.—All of the XBA's were procured from commercial sources and, where necessary, were recrystallized until melting point values agreed closely with previously reported reliable values. Other materials already have been described.[1]

Rate Measurements.—The general procedure has been described previously.[1] Because of limited solubility in toluene at 25°, it was necessary to reduce the initial molarities of three of the XBA's to the values indicated: 3-iodo-, 0.02; 4-methoxy-, 0.01; 3-nitro-, 0.006. In all cases, a ten-fold excess of XBA over XDDM was used. With 3-nitro-BA, matched cells with 5 cm. light paths were used because of the low initial optical density (OD). Matched cells with 1 cm. light paths were used in all of the other reactions. Due to short half-lives, after mixing the reactants at 25° and transferring a portion of the reaction mixture to the spectrophotometer cell, these reactions were followed on this sample in the cell: DDM and 3-nitro-BA; 4,4'-dibromo-DDM and 3-nitro-BA; DDM and 3-chloro-BA; DDM and 3-bromo-BA; 4,4'-dimethoxy-DDM and 3-bromo-BA; and DDM and 3-iodo-Ba.

Three or more determinations of k_2 were made on each reaction. The average deviation from the mean of replicate k_2-values exceeded 2% in only the cases of the following two reactions: 3,3'-dinitro-DDM and 4-methyl-BA, 2.9%; 4-chloro-DDM and 3-bromo-BA, 2.1%. The maximum deviation from the mean exceeded 3% in only the cases of the following four reactions: DDM and 3-bromo-BA, 4.6%; DDM and 4-*t*-butyl-BA, 3.6%; 3,3'-dinitro-DDM and 4-methyl-BA, 4.1%; 4-chloro-DDM and 3-bromo-BA, 3.1%.

Twelve other XBA's were procured from commercial sources but were not used because of low solubility in toluene at 25°. In general, it appeared that 3-substituted BA's were more soluble in toluene at 25° than were 4-substituted BA's and this accounts for the prevalence of the former in Tables I and II.

In some cases, after complete reaction of an XDDM with an XBA, the solution had a slight yellow color and a slight residual OD at the wave length measured. For the following reasons, it was concluded that this small residual OD was due to an unreactive impurity that was initially present in the XDDM solution: (1) Norris and Strain[6] concluded that colored solutions resulting from the complete reaction of 4,4'-dimethyl-DDM with several XBA's were due to di-*p*-tolylketazine that was initially present in the reaction mixture, (2) simultaneous runs of several different XBA's with the same XDDM preparation yielded solutions with the same residual OD, (3) different preparations of a particular XDDM gave different residual OD's when reacting with the same XBA and (4) on standing, decomposition of the XDDM solutions was observed and reaction of an aged XDDM solution with any XBA gave a higher residual OD than that resulting from the use of a fresh solution of the same XDDM with the same XBA.

Since non-interacting colored substances in the same solution give additive OD's,[7] in runs in which a measurable residual OD persisted after complete reaction, the residual OD was subtracted from each OD reading taken during the run. Data corrected in this manner gave well-aligned plots of log OD *versus* time.

Results and Discussion

Average k_2-values and corresponding $\Sigma\sigma_B$-values for the reactions of DDM with XBA's are given in Table I.[8] For 3,5-dimethyl-BA, $\Sigma\sigma_B$ is twice[2a] Hammett's σ-value for the 3-methyl substituent.

Excluding the data for 3-methoxy-BA and using a σ-value of -0.361[1] for 4-methoxy-BA, statistical treatment[9a] of the data of Table I yields with $r = 0.9947$ and $s = 0.0913$.

$$\log k_2 = -0.1023 + 2.513\Sigma\sigma_B \qquad (2)$$

TABLE I

RATE AND SUBSTITUENT CONSTANTS FOR THE REACTIONS OF DIPHENYLDIAZOMETHANE WITH SUBSTITUTED BENZOIC ACIDS IN TOLUENE AT 25°

Benzoic acid substituents	k_{2_1}, l. mole^{-1} min.$^{-1}$	$\Sigma\sigma_B$[2a, 3]
3-Nitro-	46.9	+0.710
3-Bromo-	8.59	+ .391
3-Chloro-	7.61	+ .373
3-Iodo-	6.62	+ .352
3-Methoxy-	0.773	− .003[a]
None	.645[b]	.000
3-Methyl-	.405	− .069
4-Isopropyl-	.305	− .151
4-Methyl-	.293	− .170
3,5-Dimethyl-	.279	− .138
4-*t*-Butyl-	.275	− .197
4-Methoxy-	.149	− .361[c]

[a] Calcd. from eq. 3. [b] Agrees with values of 0.649 in ref. 1 and of 0.642 in Ref. 10. [c] From Ref. 1.

In equation 2, -0.1023 is the value for $(\log k_2^0)_{\text{calcd.}}$, $+2.513$ is the slope ρ_B of the regression line and $\Sigma\sigma_B$ is the summation of Hammett's polar constants for the XBA substituents. It is apparent that the data of Table I are closely represented by equation 2.

By minimizing the squares of the deviations along the $\Sigma\sigma_B$-axis,[2b] equation 3 is obtained.

$$\Sigma\sigma_B = +0.0410 + 0.3938 \log k_2 \qquad (3)$$

---

(2) (a) H. H. Jaffé, *Chem. Revs.*, **53**, 230 (1953); (b) **53**, 254 (1953); (c) **53**, 251 (1953).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

(4) J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

(5) R. A. Benkeser, C. E. DeBoer, R. E. Robinson and D. M. Sauve, *ibid.* **78**, 682 (1956).

(6) J. F. Norris and W. H. Strain, *ibid.*, **57**, 187 (1935).

(7) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1948, p. 18.

(8) From the M.S. thesis of J. S. Westmoreland, The A. and M. College of Texas, Jan., 1957.

(9) G. W. Snedecor, "Statistical Methods," 4th Ed., The Iowa State College Press, Ames, Iowa, 1946: (a) Chaps. 6 and 7, (b) Chap. 13.

(10) A. B. Huefelmeyer and C. K. Hancock, THIS JOURNAL, **77**, 4746 (1955).

Substitution of the log k_2 value for 3-methoxy-BA in equation 3 yields a σ-value of -0.003. For the 3-methoxy substituent, Hammett[3] gives a σ-value of $+0.115$ with a probable error of 0.102. In view of the large uncertainty in Hammett's value (the probable error for 3-methoxy- is fourth largest of twenty-nine probable errors listed in ref. 3), it appears for the 3-methoxy group that -0.003 is not significantly different from $+0.115$ and that the former value is probably more applicable to the present reaction.

Average k_2-values and corresponding $\Sigma\sigma_D$ and $\Sigma\sigma_B$ values for the reactions of XDDM's with XBA's (including two reactions from Norris and Strain)[6] are given in Table II.

TABLE II

RATE AND SUBSTITUENT CONSTANTS FOR THE REACTIONS OF SUBSTITUTED DIPHENYLDIAZOMETHANES WITH SUBSTITUTED BENZOIC ACIDS IN TOLUENE AT 25°

Diphenyl-diazomethane substituents	Benzoic acid substituents	k_2, l./mole-min.	$\Sigma\sigma_D$	$\Sigma\sigma_B$
4,4'-Dimethoxy-	3-Bromo-	88.1	-0.722^a	$+0.391$
4,4'-Dimethyl-	3-Bromo-	25.0^b	$-$ .340	$+$ .391
4,4'-Dimethyl-	3-Chloro-	23.5^b	$-$ .340	$+$ .373
4,4'-Dimethoxy-	3-Methoxy-	14.6	$-$ $.722^a$	$-$ $.003^c$
4,4'-Dibromo-	3-Nitro-	5.71	$+$ .464	$+$ .710
4,4'-Dimethoxy-	4-Methyl-	4.87	$-$ $.722^a$	$-$ .170
4-Chloro-	3-Bromo-	2.91	$+$ .227	$+$ .391
4,4'-Dimethyl-	3-Methyl-	1.38^d	$-$ .340	$-$ .069
4,4'-Dichloro-	3-Bromo-	1.18	$+$ .454	$+$ .391
4,4'-Dimethyl-	4-*t*-Butyl-	1.13	$-$ .340	$-$ .197
4-Chloro-	3-Methyl-	0.192	$+$ .227	$-$ .069
4-Chloro-	4-*t*-Butyl-	.140	$+$ .227	$-$ .197
4-Chloro-	4-Methyl-	.133	$+$ .227	$-$ .170
4-Chloro-	3,5-Dimethyl-	.130	$+$ .227	$-$ .138
4,4'-Dichloro-	3-Methyl-	.0931	$+$ .454	$-$ .069
4,4'-Dibromo-	3-Methyl-	.0753	$+$ .464	$-$ .069
4,4'-Dichloro-	4-Methyl-	.0718	$+$ .454	$-$ .170
4,4'-Dichloro-	3,5-Dimethyl-	.0717	$+$ .454	$-$ .138
4,4'-Dibromo-	4-*t*-Butyl-	.0615	$+$ .464	$-$ .197
4,4'-Dibromo-	3,5-Dimethyl-	.0560	$+$ .464	$-$ .138
3,3'-Dinitro-	3-Bromo-	.0233	$+1.420$	$+$ .391
3,3'-Dinitro-	3,5-Dimethyl-	.00225	$+1.420$	$-$ .138
3,3'-Dinitro-	4-Methyl-	.00172	$+1.420$	$-$ .170

[a] Ref. 1. [b] Ref. 6. [c] Calcd. from eq. 3. [d] 1.46 reported in ref. 6.

If it be assumed that the effect of *m*- and/or *p*-substituents on the DDM is independent of the effect of *m*- or *p*-substituents on the BA, then it would appear that the data of Table II should be closely represented by the equation

$$\log k_2 = -0\ 1231 - 1.570\Sigma\sigma_D + 2.513\Sigma\sigma_B \quad (4)$$

In equation 4, -0.1231 is the average of the $(\log k_2{}^0)_{\text{calcd.}}$ values from equations 1 and 2, -1.570 and $+2.513$ are ρ_D and ρ_B from equations 1 and 2, and $\Sigma\sigma_D$ and $\Sigma\sigma_B$ are the summations of σ-values in the XDDM and in the XBA.

Values of $\Sigma\sigma_D$ and $\Sigma\sigma_B$ from Table II were substituted into equation 4 to obtain calculated log k_2 values. The deviations of these calculated values from the experimental log k_2 values were then obtained. It is interesting that twelve of the deviations are positive and the other eleven are negative. Also, whereas the absolute sum of the deviations is 1.936, the algebraic sum is only -0.052 which is remarkably close to zero. The latter would be the algebraic sum if equation 4 were the exact equation for the regression of log k_2 on $\Sigma\sigma_D$ and $\Sigma\sigma_B$. The average deviation of calculated log k_2 values from experimental log k_2 values is 0.084.

Equation 4 provides a close fit for the data of Table II. Moreover it is obvious that the data of Table I above and of Table I of ref. 1 are closely represented by equation 4. This offers conclusive evidence that the effect of *m*- and/or *p*-substituents on the DDM is independent of the effect of *m*- or *p*-substituents on the BA. Jaffé has reported[2c] that serious deviations were observed in previous attempts to correlate data, such as those in Table II, by an equation like equation 4.

Combining eleven log k_2 values from Table I of ref. 1 (omitting the log k_2 value for the reaction between DDM and BA), the twelve log k_2 values from Table I above and the twenty-three log k_2 values from Table II above, the multiple regression calculation[9b] yields

$$\log k_2 = -0.1089 - 1.620\Sigma\sigma_D + 2.376\Sigma\sigma_B \quad (5)$$

with multiple correlation coefficient $R = 0.9975$ and $s = 0.0783$. The average deviation from regression is 0.0645 and the maximum deviation from regression is only 0.1522. As would be expected, equation 5 provides a better fit for the data than does equation 4. A plot of experimental log k_2 values *versus* log k_2 values calculated from equation 5 is shown in Fig. 1.

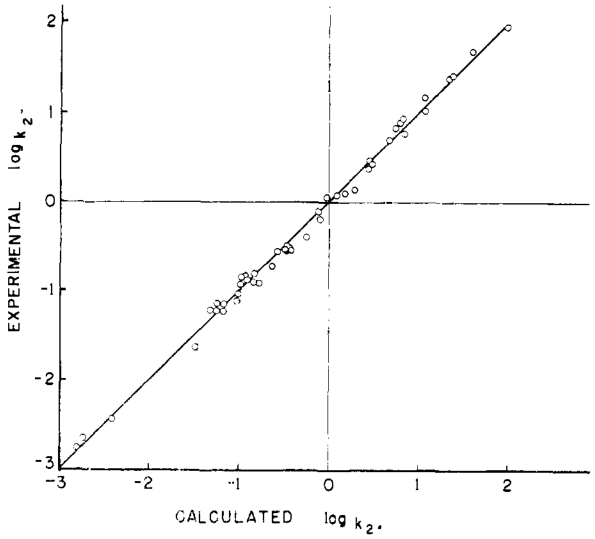


Fig. 1.—Relationship between experimental log k_2 values and log k_2 values calculated from equation 5 for forty-six reactions of diphenyldiazomethanes with benzoic acids in toluene at 25°.

Equation 5 may be re-arranged to

$$\log k_2 = -0.1089 + 1.620[(1.467\Sigma\sigma_B) - \Sigma\sigma_D] \quad (6)$$

where $1.467 = 2.376/1.620 = \rho_B/\rho_D$.

Finally, to emphasize that $\Sigma\sigma_D$ and $\Sigma\sigma_B$ are not directly additive, the analysis of the regression of log k_2 on $(\Sigma\sigma_B - \Sigma\sigma_D)$ yields[9a]

$$\log k_2 = -0.0609 + 1.769(\Sigma\sigma_B - \Sigma\sigma_D) \quad (7)$$

with $r = 0.9855$ and $s = 0.1860$. From a comparison of equations 5 and 7 and their corresponding correlation coefficients and standard deviations, it is apparent that equation 5 provides a much better fit for the data from the forty-six reactions under consideration.

Acknowledgments.—This study was supported in part by a research grant from the Robert A. Welch Foundation. The statistical calculations for equations 5, 6 and 7 were performed on an IBM-650 computer.[11]

[11] Computer Center, Texas Engineering Experiment Station, College Station, Texas.

COLLEGE STATION, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

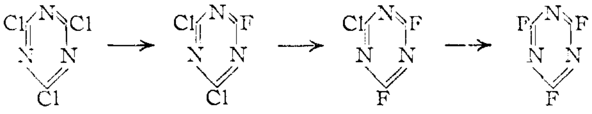
The Indirect Fluorination of Cyanuric Chloride[1]

BY ABE F. MAXWELL,[2] JOHN S. FRY[3] AND LUCIUS A. BIGELOW

RECEIVED AUGUST 6, 1957

Commercial cyanuric chloride has been subjected to indirect fluorination using various mixed antimony halides under different conditions. Pure $(CNF)_3$, $C_3N_3F_2Cl$ and $C_3N_3FCl_2$ have been prepared in 71, 24 and 20% yield, respectively, and fully characterized.

In connection with work being carried out in this Laboratory dealing with perfluorinated organic compounds containing nitrogen, it became desirable to prepare in considerable amounts the interesting compound cyanuric fluoride, $(CNF)_3$, which is 2,4,6-trifluoro-1,3,5-triazine. This compound could possibly prove a source not only of the unknown $NF_2CF_2NF_2$ but also of $CF_2{=}NF$ and FCN, the last of which is in controversy in the literature. The triazine $(CNF)_3$ already has been reported by Hückel[4] to boil at 150°, but this relatively high boiling point is unlikely, and the experimental data involved are no longer available as a result of the late war. Also it was to be expected that $(CNF)_3$ as well as the corresponding intermediates might be prepared readily from the presently commercially available cyanuric chloride $(CNCl)_3$, by the well known indirect fluorination procedures making use of the various antimony halides, according to the general scheme



I II III IV

It has been observed that when operating at atmospheric pressure neither SbF_3 alone nor SbF_5 can be used as reagents for this reaction, since the former sublimes and the latter is too reactive. However, SbF_3Cl_2, SbF_3 diluted with $SbCl_5$, and SbF_3 diluted with $SbCl_3$ readily form refluxing mixtures which decrease progressively in reactivity in that order. When cyanuric chloride I was refluxed under anhydrous conditions with SbF_3Cl_2 in such a manner that the lowest boiling portion was progressively distilled off, the fluorination went smoothly to completion; and when the crude product was carefully rectified analytically pure cyanuric fluoride IV, b.p. 74°, f.p. −38°, came over in 71% yield. This proves that the boiling point of 150° given in the literature is incorrect.

However, when I reacted with the milder reagent $SbF_3 + SbCl_5$, and the product distilled off and rectified, both IV and the analytically pure difluoride III, b.p. 113–114°, f.p. 22–23° were formed in 22 and 24% yields, respectively. Finally when I in large excess was treated with the still milder reagent $SbF_3 + SbCl_3$ and all of the product boiling below 190° rapidly distilled off, a mixture of liquid and solid was obtained, which upon rectification finally yielded the analytically pure monofluoride II, b.p. 155°, f.p. 2°, in approximately 20% yield. All of these were clear pungent liquids, extremely sensitive to hydrolysis, but otherwise very stable.

Experimental

The descriptions given below represent the best operating conditions so far developed for preparing the respective compounds. Some 5 to 10 exploratory runs were made in each case in order to determine these optimum conditions.

The research grade cyanuric chloride was kindly donated by the American Cyanamid Company and melted at 146°, corresponding to the literature value. The SbF_3 and $SbCl_5$ were Fisher technical and research grades, respectively, while the $SbCl_3$ was General Chemical reagent grade, which was dried *in vacuo* over $CaCl_2$ before use.

Preparation of Cyanuric Fluoride (IV).—In this case SbF_3 (100 g.) treated with Cl_2 until no more was absorbed at 100° in order to produce SbF_3Cl_2, and $(CNCl)_3$ (50 g.) were placed in a round-bottom flask equipped with a 12″ Vigreux column and a total reflux, partial take-off head. The material was refluxed using a Glass-col mantle and progressively distilled under completely anhydrous conditions until as nearly as possible all of the liquid product had passed over into the receiver. The distillate was then carefully rectified in a 12″ Podbielniak column and there was obtained 26.1 g. of $(CNF)_3$, b.p. 74°, corresponding to a yield of 71.4% based on the $(CNCl)_3$ used. There was no forerun and the still residue was insignificant. Pure $(CNF)_3$ boiled at 74°, froze at −38°, gave a positive test for fluorine, no test for chlorine and was very sensitive to hydrolysis.

Anal. Calcd. for $(CNF)_3$: F, 42.2; mol. wt., 135. Found: F, 42.4; mol. wt. (Victor Meyer), 135, 138.

Preparation of Cyanuric Difluorochloride (III).—Commercial $(CNCl)_3$ (170 g.), SbF_3 (340 g.) and $SbCl_5$ (85 g.) were placed in a round-bottom flask and electrically heated until the contents melted and refluxed. After 1 hr. the liquid product amounting to 60 cc. was distilled off, kept under an atmosphere of nitrogen and finally fractionated through the 12″ Podbielniak column. There were obtained $(CNF)_3$, b.p. 73° (20 cc.), transition (10 cc.), and the difluorochloride $C_3N_3F_2Cl$ (III), b.p. 113.5 (20 cc.). The

---

[1] This material was presented at the September, 1956, Meeting of the American Chemical Society in Atlantic City, and has been constructed from the Master's Theses presented by Abe F. Maxwell and John S. Fry to Duke University in June, 1956, and June. 1955, respectively.

[2] O. N. R. Research Assistant 1955–1956.

[3] O. N. R. Research Assistant 1954–1955.

[4] W. Hückel, *Nachr. Akad. Wiss. Göttingen, Math. Phys. Klasse*, 1, 55 (1946).