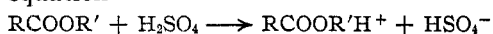


[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

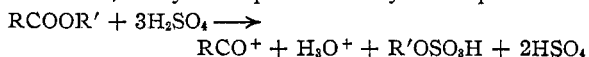
The Behavior of Organic Acids and Esters in Sulfuric Acid¹

BY LESTER P. KUHN AND ALSOPH H. CORWIN

Three types of behavior have been observed for organic acids and esters in sulfuric acid solution. Type I, which is by far the most common, was discovered by Hantzsch² and may be represented by the equation



Esters which ionize in this manner have a van't Hoff "*i*" value of 2 and when their sulfuric acid solutions are poured into water or alcohol they are recovered unchanged. The second type of behavior is exhibited by stronger acids such as trichloroacetic acid, which does not ionize at all and has an "*i*" value of 1. Type III, which was discovered by Hammett³ and studied further by Newman,⁴ may be represented by the equation



When R' is H, the "*i*" value is 4 and when R' is an alkyl group the "*i*" value is 5. The sulfuric acid solution containing the ions RCO⁺ yields the acid RCOOH when poured into water and the ester RCOOR' when poured into the alcohol R'OH. This type of ionization is exhibited by certain sterically hindered benzoic acids such as 2,6-dimethylbenzoic acid and mesitoic acid and their esters. This type of ionization has been called complex ionization whereas type I has been called normal ionization. We prefer to use the term "cationization" for the normal ionization process and "acylization" instead of "complex ionization," since these terms describe the product that is formed in each case and hence are self-explanatory. Hammett has shown that electron-attracting groups in the acid inhibit acylation and that 3,5-dibromomesitoic acid and 2,4,6-tribromobenzoic acid undergo cationization only.

Our interest in this problem stems from the fact that acylation in sulfuric acid has long been a standard method for securing selective hydrolysis of ester groups in the pyrrole series.⁵ In the preceding paper⁶ we have extended the study of this reaction in the pyrrole series. In the present paper we describe a type of ionization which we believe is related to acylation but differs from it in that the "*i*" value is somewhat smaller and the sulfuric acid solutions always yield the free acid

RCOOH whether poured into alcohol or water. We also show that the mode of ionization is strongly influenced by the electronic character of both R and R'.

Measurement of Ionization.—Two methods were used to determine the extent to which an ester undergoes acylation. In the first, which may be called the hydrolysis method, we measured the yield of free acid obtained when a sulfuric acid solution of an ester was poured into ice water. For the aromatic esters the organic acid was isolated from the reaction mixture and weighed. Because the isolation of the acid was not quantitative, a correction factor was obtained by starting with the free acid and performing a control experiment. The results are given in Table I. The second column contains the actual yield of acid and the third contains the corrected yield. The aliphatic acids were not isolated but were determined by potentiometric titration.

TABLE I
ACYLIZATION AS DETERMINED BY HYDROLYSIS

Compound	Yield of acid, %	Corrected yield, %
Aromatic Esters		
Benzoic acid	77	
Ethyl benzoate	0	0
Chloroethyl benzoate	1	...
Trichloroethyl benzoate	33	43
Cellosolve benzoate	26	33
Cellosolve benzoate (53°, 5 min.)	65	85
Cellosolve <i>p</i> -chlorobenzoate	21	26
Cellosolve 3,4-dichlorobenzoate	0	0
Cellosolve <i>p</i> -nitrobenzoate	0	0
Anisic acid	87	
Methyl anisate	42	48
Ethyl anisate	16	18
Chloroethyl anisate	76	87
Cellosolve anisate	87	100
Aliphatic Esters		
Ethyl acetate	1.7	
Chloroethyl acetate	30	
Cellosolve acetate	67	
Trichloroethyl acetate	52	
Chloroethyl chloroacetate	3	
Cellosolve chloroacetate	0	

It can be seen from Table I that electron-attracting groups in the alcohol portion of the ester and electron-repelling groups in the acid portion of the ester facilitate acylation, while electron attracting groups in the acid portion of the ester inhibit it. In the series of benzoate esters, the introduction of an electron attracting chloride into the alcohol portion of the ester results in a small amount

(1) Presented at the Atlantic City Meeting of the American Chemical Society, April, 1947. This paper is from the Doctoral Dissertation of Lester P. Kuhn, The Johns Hopkins University.

(2) Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908); **65**, 41 (1909).

(3) (a) Hammett and Deyrup, *THIS JOURNAL*, **55**, 1900 (1933); (b) Treffers and Hammett, *ibid.*, **59**, 1708 (1937); (c) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 45-48, 54-56, 277-285.

(4) (a) Newman, *THIS JOURNAL*, **63**, 2431 (1941); (b) Newman, Kuivila and Garrett, *ibid.*, **67**, 1704 (1945).

(5) Fischer and Walach, *Ber.*, **58**, 2820 (1925).

(6) Corwin and Straughn, *THIS JOURNAL*, **70**, 2968 (1948).

TABLE II					Ethyl Acetate					
FREEZING POINT DEPRESSION MEASUREMENTS										
Wt.	Δm	F. p., °C.	ΔT	"i"						
		Trichloroethyl Alcohol				.1028	.0158	3.954		
		4.423					3.760	.185	1.91	
0.1921	0.0181	4.094	0.329	2.96			3.757	.188	1.94	
....	4.089	.334	3.00						
		Ethyl Cellosolve								
		3.760								
.2300	.0343	2.980	.780	3.73						
....	2.972	.788	3.77	.2742	.0300	2.522	.558	3.05	
		Ethyl Benzoate								
		4.286								
.2160	.0193	4.065	.221	1.86						
....	4.052	.234	1.97						
.3711	.0332	3.634	.418	2.05	.1260	.00885	4.193	.192	3.53	
....	3.634	.418	2.05	4.195	.190	3.50	
		Chloroethyl Benzoate								
		4.450								
.3252	.0237	4.128	.322	2.21	.2268	.01865	4.100	.212	1.75	
....	4.123	.327	2.24	4.093	.219	1.81	
		3.615								
.3364	.0244	3.283	.332	2.22						
		Trichloroethyl Benzoate								
		4.320								
.2235	0.0119	4.110	0.210	2.87						
....	4.120	.200	2.74						
		Cellosolve 3,4-dichlorobenzoate								
		4.320								
.2294	.0117	4.159	.161	2.24						
....	4.156	.164	2.28						
		Cellosolve Benzoate								
		3.664								
.2437	.0170	3.220	.444	4.27						
....	3.200	.464	4.47						
		Anisic Acid								
		3.210								
.2524	.0223	2.750	.460	3.38						
....	2.750	.460	3.38						
.2070	.0182	2.375	.375	3.38						
....	2.375	.375	3.38						
		Methyl Anisate								
		4.264								
.2513	.0203	3.860	.404	3.25						
....	3.814	.450	3.62						
....	3.794	.470	3.78						
		Ethyl Anisate								
		4.680								
.2278	.0170	4.379	.301	2.88						
....	4.364	.316	3.02						
		Chloroethyl Anisate								
		3.462								
0.2490	0.0158	3.103	.359	3.72						
....	3.036	.426	4.41						
....	3.025	.437	4.53						

of acylation while three chloride atoms increase it considerably. Ethyl cellosolve benzoate yields an oxonium ion at the ether linkage as shown by the "i" value of 3.75 for cellosolve obtained from freezing point depression measurements (Table II). The oxonium ion is strongly electron attracting and is almost as effective as three chloride atoms. The introduction of the chloride atom into the benzene ring of cellosolve benzoate reduces the extent of acylation and two chloride atoms suppress it completely, as does one nitro group. Anisic acid esters show a greater tendency toward acylation than the corresponding benzoates because of the electron release of the methoxy group. To determine the effect of temperature, the cellosolve benzoate in sulfuric acid was kept at 53° for five minutes and the yield of acid was found to have increased about 2.5 times above that obtained by the normal procedure at room temperature for two minutes. The aliphatic esters parallel the benzoates but here the oxonium ion is more effective than the three chloride atoms in the trichloroethyl group. This is the first time that aliphatic esters have been shown to undergo acylation and it is interesting to note that for a given alcohol, the acetate ionizes further than the benzoate.

The second method for determining the mode of ionization is the determination of "i" values from freezing point depression measurements, given in Table II. In some cases the "i" value increases with successive readings, indicating that the ionization is not instantaneous. The weight of the sample added is in the first column, the number of moles of solute per 1000 g. of solvent in the second. The third contains the freezing points obtained

with the Beckmann thermometer, the fourth contains the freezing point depression, and the last has the "*i*" values calculated by means of the equation used by previous workers

$$"i" = \frac{\Delta T}{6.154(1 - 0.0047i)\Delta m}$$

where *t* is the difference between the freezing point of 100% sulfuric acid and the observed freezing point.

The effect of the electronic character of the substituents upon the "*i*" values and hence upon the mode of ionization as shown in Table II corroborates the evidence obtained from Table I. In anisic acid we see for the first time an aromatic acid without an ortho substituent which exhibits acylation. The extent of the reaction decreases in going from anisic acid to methyl anisate to ethyl anisate, in agreement with the decreasing order of electron attraction, H > Me > Et. The acetates again show a greater tendency toward acylation than the benzoates.

The fact that Newman⁴ found that *o*-benzoylbenzoic acid forms an acyl ion whereas the ethyl ester ionizes normally can probably be attributed to the greater electron attracting character of hydrogen as compared with ethyl, a result similar to that found in the anisic acid series.

The acylation of anisic acid is surprising at first glance since Treffers and Hammett^{5b} have shown that 3,4,5-trimethoxybenzoic acid forms only a normal cation. The electron release or the —T effect⁷ of the methoxy group which is responsible for the acylation requires that the molecule assume a planar configuration. The methoxy groups in the 3 and 5 positions of the trimethoxybenzoic acid prevent the methoxy group in the 4 position from lying in the plane of the ring because of steric hindrance and hence the —T effect is not operative. The interference between the groups is shown in Fig. 1, where trimethoxybenzoyl ion is

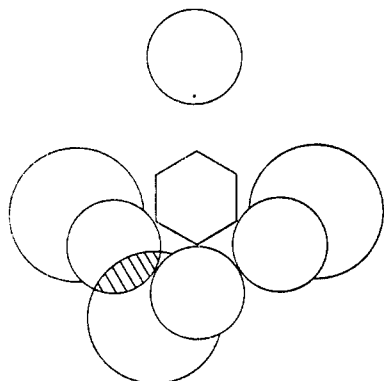


Fig. 1.—The 3,4,5-trimethoxybenzoyl ion: isolated circle shows position of the carbonyl oxygen. Shaded portion represents the overlapping tendency of the methyl group of the 4-OCH₃ and the oxygen of the 5-OCH₃.

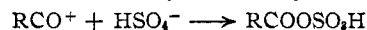
(7) Johnson, "Organic Chemistry," by Gilman, 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1846.

drawn to scale using the bond distances and van der Waals radii given by Pauling.⁸

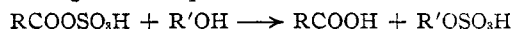
The case observed here is the converse of that discussed by Westheimer and Metcalf⁹ in which steric damping of resonance produced facilitation of a reaction. In our case, steric damping of resonance hinders the completion of a reaction and we thus have "remote steric hindrance."

Discussion

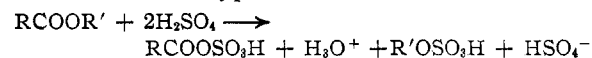
On the basis of the data given thus far, it would appear that the ionization process of these esters is the same as that studied previously by Hammett and by Newman, except that in this case the reaction does not go to completion. To get further evidence concerning the nature of the process, certain of the esters were dissolved in sulfuric acid and poured into cold methanol. Instead of getting the expected methyl ester, the free acid was obtained. These results can be explained if we assume that the ionization of substances such as cellosolve benzoate or anisic acid proceeds in the same manner as in the case of derivatives of mesitoic acid, but the acyl cation is unstable and reacts with a bisulfate ion to yield an acyl sulfate



We have prepared benzoyl and acetyl sulfates according to the methods described in the literature¹⁰ and we find that they react with alcohols according to the equation



This mode of reaction is observed when the acyl sulfate is dissolved in sulfuric acid and the sulfuric acid solution poured into alcohol and also when the acyl sulfate is allowed to react directly with alcohol in the absence of sulfuric acid. The over-all reaction for this type of ionization is



When R' is H, the theoretical "*i*" value is 3 and when R' is another monovalent group the "*i*" value is 4. The fact that the "*i*" value of anisic acid is slightly more than 3 indicates that some anisoyl cations may remain as such. An approximately 15% yield of methyl anisate was obtained when a sulfuric acid solution of anisic acid was poured into cold methanol.

Our picture of this mechanism of ionization would be substantiated if we could demonstrate the short-lived existence of the positive acyl ion. In a recent paper, Newman and Gildenhorn¹¹ have shown that mesitoic acid in sulfuric acid undergoes a Schmidt reaction with sodium azide at 0°, nitrogen and carbon dioxide being evolved. It is suggested by these investigators that the evolution of gas from such a reaction at 0° might be

(8) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(9) Westheimer and Metcalf, *THIS JOURNAL*, **63**, 1339 (1941).

(10) German Patent 275,846; *Friedl.*, **11**, 1191 (1912-1914).

(11) Newman and Gildenhorn, *THIS JOURNAL*, **70**, 317 (1948).

used as a diagnostic criterion for the presence of acyl cations. We have used a modification of this method on the esters described previously. Since we wish to demonstrate a transient entity, we have added the diagnostic reagent, sodium azide, first and then have added the acid or ester under investigation. Table III gives the results of these experiments.

TABLE III

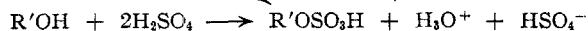
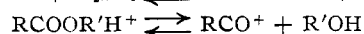
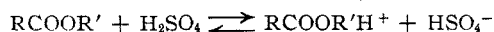
VOLUME OF GAS FROM SCHMIDT REACTION IN SULFURIC ACID

Theoretical for 2 moles of gas per mole of ester, 405 ml.

Compound	Gas after one hour, ml.
Ethyl benzoate	0
Benzoic acid	275
Cellosolve benzoate	280
Trichloroethyl benzoate	340
Benzoyl sulfate	275
Anisic acid	290
Ethyl anisate	0
Acetic acid	0
Cellosolve acetate	40
Acetyl sulfate	0

Our change in the sequence of addition of the reagents has resulted in a marked change in the results obtained with benzoic acid from those recorded by Newman and Gildenhorn.¹¹ Either gas evolution with sodium azide at 0° is not a criterion for the presence of acyl ions, or we must conclude that benzoic acid forms an unstable benzoyl ion which is present in such small quantity that it does not affect freezing point measurements but does react with the diagnostic reagent present in the solution. That we obtained some gas with cellosolve acetate might be considered as an indication of the existence of the acetyl ion, since neither acetic acid nor acetyl sulfate gives any gas evolution. Since the solubility of sodium azide is not large in sulfuric acid, the unstable acetyl ion has a better chance to react with a bisulfate ion than with a hydrazoic acid molecule. For this reason, a good yield of gas from any acetate ester under these conditions is hardly to be expected.

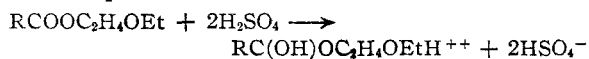
Day and Ingold¹² describe the mechanism of acyl ion formation in the following manner



Our observations are in accord with the preceding equations. In their interpretation of this mechanism, however, Day and Ingold assumed that changes in the electronic character of R' would have no effect on the extent of acylation. Our results show that this assumption is not valid.

The yield of acyl ions or the rate of their formation depends not only upon the electronic character of R and R' but also upon the basicity of the ester RCOOR'. Although step 2 is the rate-

determining step in the mechanism given by Day and Ingold, it is obvious that for the reaction to proceed, the equilibrium of step 1 must be favorable. If the ester is so weakly basic that it does not take a proton from the solvent, step 2 cannot take place. Such esters resemble trichloroacetic acid in their behavior. The freezing point data indicate that we have several examples of this inhibition of acylation due to the weak basicity of the esters. Cellosolve chloroacetate and cellosolve dichlorobenzoate would be expected to have "i" values of 3 if they ionized normally according to the equation



The fact that their "i" values are only slightly more than 2 indicates that the Cl atoms in R and the oxonium ion in the cellosolve portion of the esters weaken the basicity and thus prevent the complex ionization. In this manner we can explain why in the series of esters, cellosolve benzoate, cellosolve chlorobenzoate and cellosolve dichlorobenzoate, which yield benzoic acid to the extent of 33, 26 and 0%, respectively, in the hydrolysis experiments (see Table I), the yield of acyl ion drops off so sharply in going from the second to the last member of the series.

The equilibrium of step 1 can also be rendered unfavorable by the addition of bisulfate ions to the solution. We have found that the addition of bisulfate ions may decrease the yield of acyl ion as much as 50%, a further confirmation of the mechanism presented.

Experimental

Reaction with Sodium Azide.—Eleven millimoles of sodium azide was added slowly to 15 ml. of 98–100% sulfuric acid in a 50-ml. erlenmeyer flask which was contained in an ice-bath and equipped with a magnetic stirrer. Most of the sodium azide did not dissolve in the acid. The flask which contained a side arm through which solids or liquids could be added without opening the system to the air, was then connected to a graduate which was filled with saturated sodium chloride solution and inverted over more saline in a large evaporating dish. The gas was collected by displacement of the liquid in the graduate. Nine millimoles of acid or ester was added to the sodium azide in sulfuric acid slowly and with constant stirring. The amount of gas collected in one hour was measured and is given in Table III. In the case of benzoic acid, a 55% yield of aniline hydrochloride was isolated by neutralization, extraction with ether and addition of dry hydrogen chloride.

Preparation of Esters.—The aromatic esters were prepared by heating equimolecular quantities of acid and alcohol in benzene in the presence of 2–3 g. of toluene-sulfonic acid as catalyst in a benzene still until the theoretical amount of water had come off. The solution was then washed with water, dilute sodium bicarbonate, and water, and dried over sodium sulfate. The esters were obtained by fractional distillation. Only the middle portion of the distillate was used. The aliphatic esters were prepared by treating the acid anhydride with a 10% excess of alcohol in the presence of dry pyridine for twenty-four hours at room temperature. The solution was then poured into cold water, extracted with ether and the ether extract washed with water, dilute hydrochloric acid, water, dilute sodium bicarbonate and water, and then dried over sodium sulfate. The pure esters were obtained by

(12) Day and Ingold, *Trans. Faraday Soc.*, **37**, 694 (1941).

TABLE IV
 PHYSICAL CONSTANTS OF ESTERS

Ester	B. p., °C.	Mm.	d_{25}^{25}	n_D^{25}	Calculated, %			Found			
					C	H	Cl	C	H	Cl	
Chloroethyl benzoate	105	1									
Trichloroethyl benzoate	106-107	1	1.352	1.5343	42.60	2.76	42.01	42.66	2.89	41.99	
Cellosolve benzoate	142	5									
Cellosolve <i>p</i> -chlorobenzoate	131	1	1.160	1.5130	57.77	5.69	15.53	57.73	5.60	15.00	
Cellosolve 3,4-dichlorobenzoate	159-160	1	1.250	1.5272	50.20	4.56	26.90	50.05	4.52	26.40	
Cellosolve <i>p</i> -nitrobenzoate	218	35									
Methyl anisate	48 (m. p.)										
Ethyl anisate	122	1									
Chloroethyl anisate	155	4	1.222	1.5421	55.94	5.13	16.55	55.70	4.90	16.33	
Cellosolve anisate ^a	140	1	1.094	1.5142	64.29	7.14	...	64.39	6.85	...	
Chloroethyl acetate	73	64									
Cellosolve acetate	154	760									
Trichloroethyl acetate	71	24									
Chloroethyl chloroacetate	100	20									
Cellosolve chloroacetate	108	20	1.133	1.4374	42.99	7.16	21.19	43.00	6.96	21.13	

^a Obtained from Carbide and Carbon Chemicals Co.

fractional distillation as above. The esters and their boiling points are given in Table IV. For those esters which have not been previously reported in the literature, other physical constants and analytical data are given.

Freezing Point Depression Measurements.—The procedure for determining the freezing point depressions has been described by Newman, *et al.*^{4b} No essential modifications were made.

Hydrolysis Experiments.—Approximately 2 g. of ester was dissolved in 15 ml. of 99-100% sulfuric acid in a 50-ml. erlenmeyer glass stoppered flask. After standing for two minutes the solution was poured into 150 ml. of ice and water. In the case of the aromatic esters the mixture was then extracted three times with 50-ml. portions of ether. The ether solution was washed three times with 5% sodium carbonate solution. The alkaline wash was acidified with dilute hydrochloric acid to precipitate the organic acid which was filtered on a tared sintered glass funnel and dried in a vacuum desiccator over phosphoric anhydride and weighed. To correct for losses the experiment was repeated starting with the free acid. Thus with benzoic acid a 77% yield was obtained. Therefore the actual yields of benzoic acid from its esters were divided by 0.77 to give the corrected yields. In the case of the aliphatic esters, after pouring into ice and water the mixture was transferred to a 1-liter 3-necked flask fitted with a stirrer, thermometer and buret and contained in an ice-bath. It was diluted to 500 ml. with cold distilled water. The temperature was kept below 10° throughout the titration. The pH was adjusted to 3-4 by the addition of a solution of 200 g. of sodium hydroxide and 20 g. of barium hydroxide in 500 ml. of distilled water. The solution was then titrated with approximately 1 *N* sodium hydroxide, the pH being measured after the addition of each ml. with the aid of a Beckman pH meter. The titration curve so obtained was plotted and the volume of standard alkali required to go from pH 3.8 to pH 8.5 was determined. A blank was run for each ester by adding the

ester to 500 ml. of distilled water and ice and then adding the sulfuric acid. The titration was carried out as before and the volume of standard alkali required for the blank was subtracted from that required for the hydrolyzate to give the number of moles of acid obtained from the known weight of ester. The results are given in Table V.

Effect of Bisulfate.—Two grams of cellosolve benzoate was allowed to stand in 15 ml. of 100% sulfuric acid for two minutes, then poured on to ice; yield of benzoic acid, 26%; corrected yield, 34%.

Two grams of cellosolve benzoate was added to 15 ml. of 100% sulfuric acid containing 3 g. of potassium bisulfate and allowed to stand for two minutes; yield of benzoic acid, 20%; corrected yield, 26%.

ABSORPTION SPECTRA OF ETHYL BENZOATE

(a) In Hexane; no significant absorption above 300 $m\mu$		(b) In Concentrated Sulfuric Acid; no significant absorption above 340 $m\mu$	
Log k	λ	Log k	λ
1	295 $m\mu$	1.4	330 $m\mu$
2	290	2.7	320
2	280	3.0	310
2.9	270	3.3	300
2.8	260		

Summary

1. Measurements have been made of the extent of acyl ion formation in a group of aliphatic and aromatic esters in which both the acid group and the alcoholic group have been varied.

2. It has been found, contrary to previous predictions, that the nature of the alcoholic group is a critical variable in determining the extent of acylation.

3. Sufficiently electron-attracting alcohols are capable of inducing acylation in derivatives of benzoic and *p*-chlorobenzoic acids, the first cases in which this phenomenon has been observed in aromatic acid derivatives lacking ortho substituents.

4. Acylation can be induced similarly in aliphatic acid derivatives.

5. The extent of acylation is greater in acetates than in benzoates.

 TABLE V
 HYDROLYSIS OF ALIPHATIC ESTERS

Ester	—Millimoles of—			Hydrolysis, %
	Ester	Alkali	Alkali in blank	
Ethyl acetate	29	11.5	11.0	1.7
Chloroethyl acetate	17	14.7	9.6	30.0
Trichloroethyl acetate	12.5	14.9	8.4	52.0
Cellosolve acetate	16.6	19.8	8.6	67.0
Cellosolve chloroacetate	8.7	5.7	5.5	3.0
Chloroethyl chloroacetate	6.0	5.0	5.0	0

6. As would be predicted, the effect of an electron attracting group is opposite in the alcohol portion of the ester and in the acid portion of the ester.

7. Acylation is observed in anisic acid even though it is absent in 3,4,5-trimethoxybenzoic acid.

8. This effect is attributed to "remote steric hindrance" in the trimethoxy acid.

9. Evidence is presented that benzoyl and acetyl ions are unstable in solution and react with bisulfate ions to form acyl sulfates.

10. It has been found that the sequence of the addition of reagents in the "Schmidt reaction" with sodium azide in sulfuric acid alters the results obtained.

BALTIMORE 18, MD.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Some Systems of Carbon Halides with Dioxane, Pyridine and Cyclohexane

BY S. M. SCHOLASTICA KENNARD¹ AND P. A. MCCUSKER

In a previous paper² a study of molecular compound formation between silicon halides and dioxane, by means of solid-liquid equilibrium data and dielectric data on dilute solutions, was reported. The indication of weak molecular compound formation between silicon tetrabromide and dioxane suggested the desirability of carrying out similar studies on some carbon halide-dioxane systems. For the purpose of observing whether compounds of electronic character similar to dioxane would show similar behavior toward carbon halides, the carbon tetrachloride-pyridine system was also investigated.³

Experimental Procedures

Purification of Materials.—C. p. carbon tetrachloride, chloroform and cyclohexane were refluxed over phosphorus pentoxide and fractionally distilled. These materials were handled throughout with a minimum of exposure to moist air. Reagent grade pyridine was let stand over potassium hydroxide for three weeks and fractionally distilled. The fraction used had a b. p. of 113° and melted at -41.8°.

Determination of Melting Points.—Melting points were determined as previously described.² In the carbon tetrachloride-pyridine work very careful regulation of the rate of cooling and stirring was necessary to obtain sufficient undercooling to give a good equilibrium mixture. This was especially necessary to obtain the points in the region around 75 mole per cent pyridine.

Results

The melting point-composition data for the carbon tetrachloride-dioxane system are listed in Table I and diagrammed in Fig. 1.

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(2) Kennard and McCusker, *THIS JOURNAL*, **70**, 1039 (1948).

(3) After the original manuscript containing these results was submitted for publication, Davidson, VanderWerf and Boatright, *THIS JOURNAL*, **69**, 3045 (1947), presented a graph of the carbon tetrachloride-pyridine system. Although their results are essentially the same as ours, we are including in this paper a table of the melting points for this system.

TABLE I
MELTING POINTS OF CARBON TETRACHLORIDE-DIOXANE SOLUTIONS

Mole % dioxane	M. p., °C.	Mole % dioxane	M. p., °C.
0.0	-22.7	38.4	-18.5
2.7	-23.8	41.1	-18.8
3.5	-24.0	42.9	-19.2
4.1	-24.2	45.0	-19.4
4.9	-24.6	47.2	-19.8
6.0	-24.2	48.9	-20.0
7.7	-23.4	51.4	-17.6
8.4	-23.1	55.6	-13.1
9.0	-23.0	58.6	-11.2
9.8	-22.7	60.4	-9.9
10.9	-22.4	61.7	-9.2
12.4	-21.8	64.5	-7.3
14.1	-21.2	67.7	-5.3
16.2	-20.4	71.3	-3.7
20.5	-19.2	72.8	-2.9
23.0	-18.8	75.5	-1.6
25.0	-18.6	78.2	-0.2
25.8	-18.6	80.2	0.9
26.4	-18.5	82.6	2.2
28.4	-18.4	84.6	3.4
30.7	-18.2	86.2	4.3
31.2	-18.4	88.4	5.5
32.3	-18.4	91.2	7.0
33.1	-18.3	95.4	9.5
34.9	-18.3	96.7	10.1
35.5	-18.4	100.0	11.8
37.0	-18.4		

Two eutectics appear, one at 5.2 mole per cent dioxane, m. p. -24.7°, and the other at 49.5 mole per cent dioxane, m. p. -20.2°. The maximum between the two eutectics is fairly sharp and occurs at 33¹/₃ mole per cent dioxane, m. p. -18.2°.

Data for the chloroform-dioxane system are listed in Table II and are plotted in Fig. 2.

The behavior of chloroform with dioxane closely parallels that of carbon tetrachloride. Two eutectics again occur, one at -76.2° containing 12.6 mole % dioxane and the other at -60.0,