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. Acylization 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. RECEIVED[13] JUNE 7, 1948

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[13] Original manuscript received October 24, 1947.

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

Some Systems of Carbon Halides with Dioxane, Pyridine and Cyclohexane

BY S. M. SCHOLASTICA KENNARD[1] AND P. A. MCCUSKER

In a previous paper[2] 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.

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 $33^{1}/_{3}$ 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,

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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.

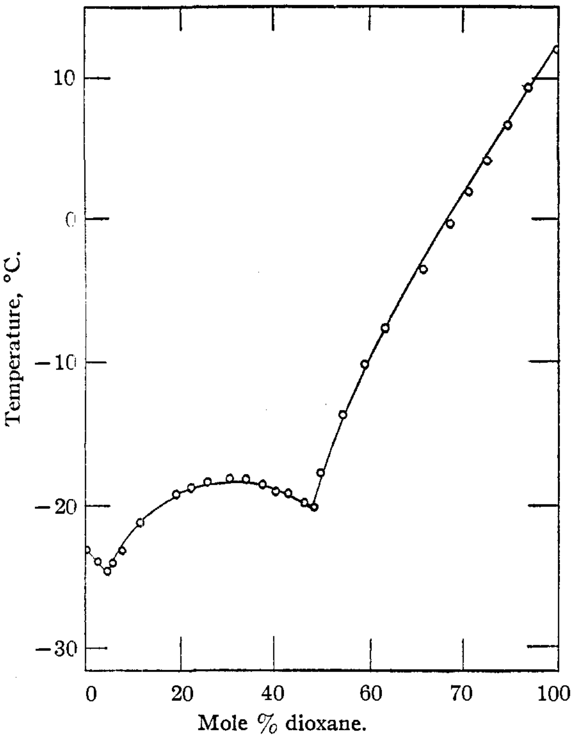

Fig. 1.—Melting point-composition curves for carbon tetrachloride–dioxane.

containing 37.5 mole % dioxane. A maximum shows up in the liquidus curve at $33^1/_3$ mole % dioxane, m. p. −59.2°.

Melting point–composition data for the system carbon tetrachloride–pyridine are listed in Table III.

The graph of the data for the carbon tetrachloride–pyridine system shows the same compound as reported by Davidson, *et al.*[3] An additional feature of our results is the observation of metastable melting points appearing in the region 75 to 82 mole % pyridine. In this region 2 sets of melting points were found. In some determinations solid would separate and melt completely at the lower temperature listed in the table. In other cases, especially when extreme undercooling occurred, the higher melting solid would form. Less frequently separation of the higher melting solid would occur before complete melting of the lower melting solid and a sudden rise in temperature would be observed. This behavior may be due to the separation of the compound, when the lower melting points are observed, and the separation of pyridine as the solid phase when the higher melting points are found.

As an example of an electronically inert molecule, of geometry similar to that of dioxane and pyridine, cyclohexane was selected and its behavior toward carbon tetrachloride studied by means of melting point–composition data. The data for this system are listed in Table IV and diagrammed in Fig. 3.

TABLE II

MELTING POINTS OF CHLOROFORM–DIOXANE SOLUTIONS

Mole % dioxane	M. p., °C.	Eutectic, °C.	Mole % dioxane	M. p., °C.
0.0	−63.5		44.1	−40.3
3.1	−67.0		45.0	−38.6
5.1	−69.2		45 8	−36.3
8.1	−71.6		47.2	−33.4
18.1	−68.0		48.2	−32.0
18.9	−67.0		49.2	−30.2
21.7	−64.6		51.3	−27.5
22.8	−63.3		52.4	−26.0
24.6	−62.3		54.2	−23.3
27.4	−60.6		57.6	−19.5
29.2	−60.0		62.5	−14.2
30.6	−59.6		64.0	−12.4
32.0	−59.6		65.1	−11.8
33.1	−59.6		67.6	− 9.5
34.1	−59.6		69.3	− 8.0
34.8	−59.6		71.9	− 5.8
35.5	−59.7		74.0	− 4.3
35.6	−60.0	−60.0	76.7	− 2.6
35.9	−60.0		77.8	− 1.6
36.6	−59.6		79.2	− 0.6
36.8	−58.3		81.1	0.5
36.8	−59.6		82.8	1.6
37.5	−57.0	−60.0	86.9	4.2
38.1	−55.3		88.4	5.6
38.5	−54.3	−60.0	91.2	7.2
39.4	−52.5	−60.0	92.6	8.1
41.1	−47.5		94.8	9.1
41.8	−45.5		96.6	10.3
42.2	−43.3		94.1	11.1
43.4	−42.0		100.0	11.8

TABLE III

MELTING POINTS OF CARBON TETRACHLORIDE–PYRIDINE SOLUTIONS

Mole % pyridine	M. p., °C.	Eutectic, °C.	Mole % pyridine	M. p., °C.	Eutectic, °C.
100.0	−41.8		62.5	−53.1	
98.0	−43.2		58.2	−50.4	
95.7	−45.1		54.2	−48.2	
93.8	−46.3		51.0	−47.3	
87.4	−50.6		48.5	−45.7	
83.7	−53.4		45.4	−44.6	
82.6	−55.0 (−69.5)		42.7	−43.6	
81.6	−55.6 (−69.0)		38.7	−43.4	
80.3	−56.3		33.1	−43.3	
78.7	−57.5 (−67.5)		31.4	−43.7	
77.5		−66.0	27.8	−44.5	
76.2		−66.0	25.9	−45.2	
75.1	−60.5 (−65.0)		24.8	−45.5	
72.9	−62.8		23.8	−45.8	−48.3
72.6	−64.1		23.1	−46.6	−48.3
72.0	−66.0		22.1	−47.1	−48.3
70.9	−61.7	−66.0	21.4	−48.3	−48.3
69.2	−60.5		19.6	−44.8	
68.6	−58.5		15.7	−40.3	
67.0	−57.4		7.2	−30.1	
64.9	−55.6		0.0	−22.7	

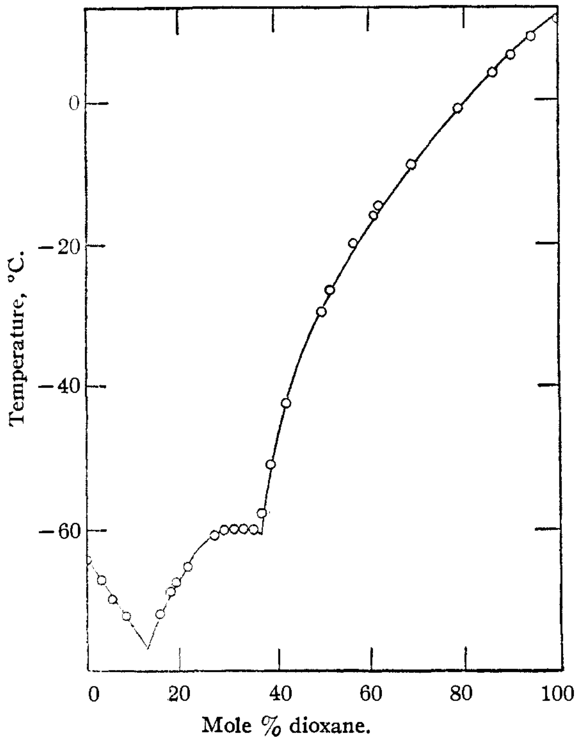

Fig. 2.—Melting point–composition curves for chloroform–dioxane.

TABLE IV

MELTING POINTS OF CARBON TETRACHLORIDE–CYCLOHEXANE SOLUTIONS

Mole % cyclohexane	M. p., °C.	Mole % cyclohexane	M. p., °C.
0.0	−22.7	43.3	−26.8
4.0	−26.0	51.5	−23.5
6.5	−27.7	53.8	−22.0
10.8	−29.3	57.5	−20.6
11.1	−29.8	60.0	−19.0
15.5	−30.6	69.0	−13.0
30.2	−30.2	84.2	− 3.9
32.5	−29.6	95.8	3.1
32.6	−29.5	100.0	6.4
37.9	−28.2		

The region between 15 and 25 mole % cyclohexane showed erratic behavior and reproducible melting points were not obtained for these solutions. Of greatest interest, for purposes of comparison, is the lack of any evidence of compound formation at $33^1/_3$ or higher mole % cyclohexane.

Discussion

The similarity of the behavior of carbon tetrachloride toward dioxane and pyridine with respect of compound formation is notable. Apparently the nature of the interaction of these compounds is such that a common feature of the dioxane and pyridine is involved. The failure of cyclohexane to show similar compound formation with the carbon halide suggests that the electronic character of the dioxane oxygen and pyridine nitrogen may be responsible for the compound formation. It is also to be observed that the melting point of the pyridine compound is considerably higher in relation to the two eutectic temperatures than that of the dioxane compound. This would indicate a greater stability for the pyridine compound than for the dioxane compound.

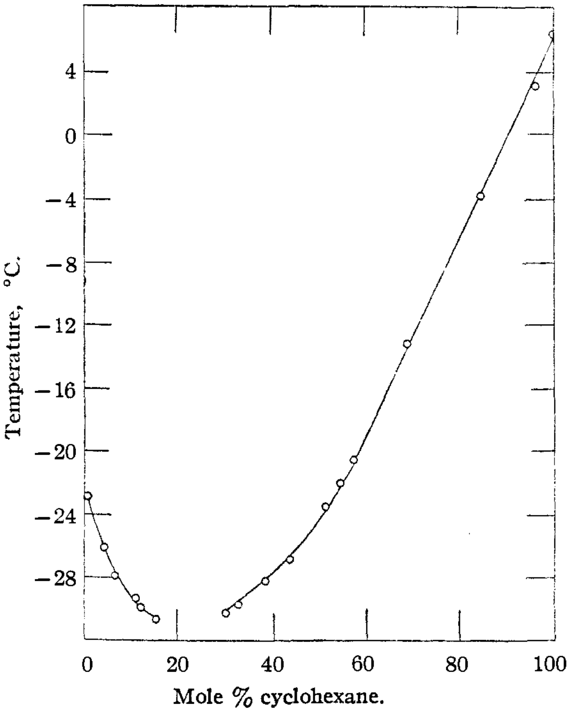

Fig. 3.—Melting point–composition curves for carbon tetrachloride–cyclohexane.

Chloroform and carbon tetrachloride show an exactly similar behavior toward dioxane but combine in different ratios with pyridine.[3] In the dioxane case the assumption that hydrogen bonding is responsible for the compound formation with chloroform is made less satisfactory because of the similar behavior of carbon tetrachloride. In the pyridine case, as Davidson, *et al.*,[3] observed, hydrogen bonding may more plausibly be assumed to be involved in the compound formation.

Summary

1. Melting point–composition data have been obtained for the following systems: carbon tetrachloride–dioxane, chloroform–dioxane, carbon tetrachloride–pyridine and carbon tetrachloride–cyclohexane.

2. Molecular compounds containing 2 moles of carbon halide and 1 mole of pyridine and dioxane have been observed.

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RECEIVED MAY 28, 1948