Experimental

3-Ethoxy-7,9-diaminoacridinium Methiodide.—To a solution of 5.5 g. of the diaminoacridine base (m. p. 124°) in 50 cc. of methanol 5 g. of methyl iodide was added at room temperature. After standing for twelve hours the salt separated as a yellow powder; yield 50%. The substance was soluble in water or methyl alcohol and insoluble in acetone. After repeated crystallization from water–acetone (1:5) it melted at 332–334°, dec. The solubility in water at 35–38° was 1:2,000.

Anal. Calcd. for $C_{16}H_{18}O_2N_3I$: N, 10.6. Found: N, 11.1.

Methochloride.—A filtered solution of 2 g. of the diaminoacridine base in 100 cc. of methanol was saturated with gaseous methyl chloride in an autoclave and the autoclave then heated slowly to 95–100° in the course of two hours; the pressure rose to 8–10 atmosphere. Upon standing, a greenish-yellow powder precipitated and this when crystallized from a mixture of glacial acetic acid and ethyl acetate melted at 357–358°. Solubility in water at 25° was 1:1,000.

Anal. Calcd. for $C_{16}H_{18}ON_3Cl$: N, 13.8. Found: N, 13.5.

Methosulfate.—To a filtered solution of 2.5 g. of the diaminoacridine in a 1:4 mixture of methanol and acetone a solution of 3 g. of dimethyl sulfate in 3 cc. of acetone was added. In the course of two days at room temperature 1.2 g. of bright yellow salt precipitated. After crystallization from methanol–acetone it melted at 235°. Solubility in water at 35–38° was 1:1,000.

Anal. Calcd. for $C_{17}H_{21}O_5N_3S$: N, 11.5. Found: N, 11.0.

TABLE I

BIOLOGICAL TESTS

Bacteriostatic (A) and bactericidal (B) activity (duplicate series) against *Staphylococcus aureus*: 0 = no growth, + = turbid, showing growth·

Substance	Dilution in tryptic broth	A Bacterial growth after 24 hr. at 37° Series I	Series II	B Viable bacteria counts[a] Series I	Series II
Methiodide	5,000	0	0	0	0
	10,000	0	0	0	0
	50,000	+	+		
Methochloride	5,000	0	0	0	0
	10,000	0	0	0	0
	50,000	+	+		
Methosulfate	5,000	0	0	0	0
	10,000	0	0	0	0
	50,000	+	0	Many	Many
Rivanol	5,000	0	0	Many	0
	10,000	0	0	Many	Many
	50,000	+	+		

[a] In 1/1000 cc. of test dilutions showing inhibition (bacteriostasis) after twenty-four hours at 37° as recorded under a.

Slightly different results were obtained with *Bacterium coli*. All substances tested were bacteriostatic at a dilution of 1:50,000, but only the methochloride was bactericidal at a dilution of 1:10,000.

Toxicity determinations kindly carried out by Professor S. Adler of the Hebrew University, Jerusalem, showed that the quaternary salts have the same order of toxicity as Rivanol:

Under the skin of mice:

Maximum tolerated dose = 0.095 g./kg.
Maximum lethal dose = 0.1 g./kg.

In the abdominal cavity of mice:

Maximum tolerated dose = 0.065 g./kg.
Maximum lethal dose = 0.07 g./kg.

THE DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE   RECEIVED OCTOBER 1, 1945

Molecular Complexes with 2,4,7-Trinitrofluorenone. II[1]

BY MILTON ORCHIN,[2] LESLIE REGGEL[2] AND E. OSCAR WOOLFOLK[2]

In a previous communication[3] it was shown that 2,4,7-trinitrofluorenone (T.N.F.) formed molecular complexes with a variety of polynuclear hydrocarbons. All of these complexes were composed of one mole of the hydrocarbon and one mole of T.N.F. We have now found that T.N.F., in common with picric acid and s-trinitrobenzene, forms complexes with some hydrocarbons in other than 1:1 molar proportions. The behavior of 1,4-diphenylbutadiene is of particular interest. As can be seen from Fig. 1, this hydrocarbon forms two compounds with T.N.F., one corresponding to a molar ratio of 1:2 and the other to 3:1 of the hydrocarbon to T.N.F. The 1:2 compound is quite stable and is easily obtained pure from solution; the 3:1 compound cannot be obtained pure, since recrystallization leads to the isolation of the more stable, more insoluble 1:2 compound.
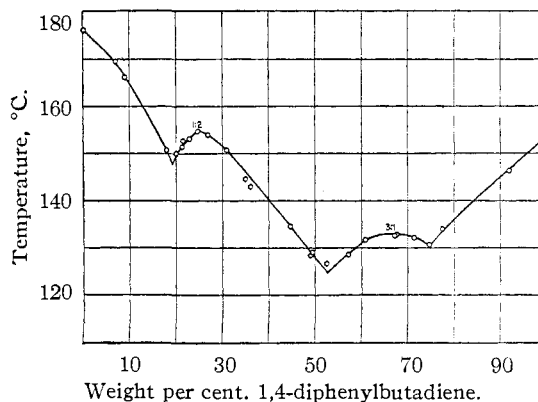

Fig. 1.—Melting point–composition curve: 2,4,7-trinitrofluorenone–1,4-diphenylbutadiene.

In an extension of the use of T.N.F. to some simple low-molecular weight derivatives of naphthalene, it has been found that, in several instances, extensive dissociation of the complex takes place when alcohol or benzene is used as a solvent for the complex. However, if acetic acid is used in these cases, it is frequently possible to isolate a complex. It appears that, in general, s-trinitrobenzene or picric acid is to be preferred to T.N.F. for the characterization of very soluble,

(1) Published by permission of the Director, U. S. Bureau of Mines. Not copyrighted.
(2) Organic Chemist, Central Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.
(3) Orchin and Woolfolk, THIS JOURNAL, 68, 1727 (1946).

TABLE I

MOLECULAR COMPLEXES WITH T. N. F.

Polynuclear component	Solvent	Appearance of complex	M. p. complex, °C.	Molar ratio T. N. F./ component	Molecular formula of complex	N Analyses,[a] % Calcd.	Found
1,4-Diphenylbutadiene[b]	EtOH–PhH	Dark red needles	154.2–154.8	2	$C_{42}H_{24}N_6O_{14}$	10.1	10.3
2,3-Benzfluorene[c]	EtOH–PhH	Silky orange needles	221.2–222.0				8.5
1,2'-Dinaphthyl[d]	HOAc–H₂O	Orange-red needles	145.0–146.9	2	$C_{46}H_{24}N_6O_{14}$	9.5	9.6
Naphthalene	HOAc	Yellow needles	151.2–154.0	1	$C_{23}H_{13}N_3O_7$	9.5	9.7
2-Methylnaphthalene	HOAc	Orange needles	124.6–126.0	2	$C_{37}H_{20}N_6O_{14}$	10.9	11.1
2-Naphthol	HOAc	Red prisms	175.3–177.1	1	$C_{23}H_{13}O_8N_3$	9.2	9.4
2-Methoxynaphthalene	HOAc	Red prisms	133.0–134.1	1	$C_{24}H_{15}O_8N_3$	8.9	9.0
1-Naphthol	HOAc	Red prisms	195.2–196.2	1	$C_{23}H_{13}O_8N_3$	9.2	9.4
1-Bromonaphthalene	HOAc	Bright yellow prisms	171.4–172.8	1	$C_{23}H_{13}BrN_3O_7$	8.0	8.3
2-Bromonaphthalene	HOAc	Bright yellow needles	138.0–140.1	1	$C_{23}H_{13}BrN_3O_7$	8.0	8.2
1-Pyrenol[e]	EtOH–PhH	Dark brown needles	234.0–235.4 (dec.)	1	$C_{29}H_{15}N_3O_8$	7.9	8.0
Acridine[f]	EtOH–PhH	Orange needles	163.6–165.1	1	$C_{26}H_{14}N_4O_7$	11.3	11.3
13-Picenol[e]	EtOH–PhH	Black crystals	272–273	1	$C_{35}H_{19}N_3O_8$	6.9	7.3
13-Acetoxy-5,6-dihydro-picene[e]	EtOH–PhH	Red-orange needles	200.5–201.2[g]	1	$C_{37}H_{23}O_9N_3$	6.4	6.6
5-Acetoxy-13,14-dihydro-picene[e]	EtOH–PhH	Dull orange crystals	255–258.5	1	$C_{37}H_{23}O_9N_3$	6.4	6.9
Diphenylene oxide	HOAc	Yellow needles	158.9–160.4	1	$C_{25}H_{13}N_3O_8$	8.7	9.1
2-Benzylnaphthalene[h]	HOAc	Orange-yellow needles	124.3–125.4	1	$C_{30}H_{19}N_3O_7$	7.9	8.2
20-Methylcholanthrene[i]	PhH	Olive green needles	253.0–253.6		$C_{34}H_{21}N_3O_7$	7.2	7.4
2-Phenylnaphthalene[j]	EtOH–PhH	Orange-yellow needles	169.5–170.5	1	$C_{29}H_{17}N_3O_7$	8.1[k]	8.0

[a] Microanalyses by the Arlington Laboratories, Fairfax, Virginia, using the Dumas method. All of the samples were dried *in vacuo* at 56° except the naphthalene–T. N. F. complex. This complex decomposed even with such mild treatment, so it was air dried for twenty-four hours prior to analysis. [b] "Organic Syntheses," Coll. Vol. II, 229 (1943). [c] The analysis of the complex with 2,3-benzfluorene does not correspond to any simple molar proportion of hydrocarbon to T. N. F. Since the past history of our sample, melting point 212.2–213.8°, was unknown, it was compared with an authentic sample kindly furnished by Professor C. F. Koelsch. The two hydrocarbon samples were identical (ultraviolet absorption spectra and mixed melting point) and the T. N. F. complexes of the samples were identical (mixed melting point). The hydrocarbon can easily be recovered unchanged from the complex by selective adsorption on alumina. Attempts to obtain a melting point–composition curve were unsuccessful because mixtures of the two compounds decomposed when heated to the melting point in the presence of each other although each component alone was stable at 225°. The decomposition may be due to some oxidation–reduction. Repeated recrystallization of the sample of our complex changed neither the melting point nor the nitrogen content. [d] Orchin and Reggel, THIS JOURNAL, **69**, 505 (1947). [e] Gift of Professor M. S. Newman. [f] The best grade of commercial material (which was very impure) was carefully chromatographed and a fraction obtained which gave pure acridine, m. p. 108.1–110.1°. [g] Put in bath at 175°; sinters 188°. Melts when put in bath at 190°. [h] Prepared by the dehydrogenation of 2-benzoyl-5,6,7,8-tetrahydronaphthalene, unpublished work. [i] Gift of Mr. B. D. Polis. [j] Friedel, Orchin and Reggel, unpublished work. [k] Dumas microanalysis by Dr. T. S. Ma, University of Chicago.

low molecular weight derivatives of naphthalene. It has been reported[4] that 2-phenylnaphthalene fails to form a complex with picric acid. We have found that this hydrocarbon readily forms a complex with T.N.F.[5]

The complexes with T.N.F. that we now wish to report are shown in Table I. An improved procedure for the preparation of T.N.F. is given below.[6]

Experimental[7]

2,4,7-Trinitrofluorenone.—A 250-cc. dropping funnel, a thermometer and a mechanical stirrer were suspended

(4) Kruber, Marx and Schade, *Ber.*, **71B**, 2478 (1938).

(5) We also were unable to prepare a picrate of 2-phenylnaphthalene. The failure to isolate a complex with a particular hydrocarbon in a particular manner is a poor criterion for complex compound formation since the use of other solvents may very well result in the isolation of a complex. It is probable that many of the hydrocarbons reported as not forming complexes would show complex compound formation if studied by means of a melting point–composition curve.

(6) 2,4,7-Trinitrofluorenone is now available from the Farchan Research Laboratories, 609 E. 127th Street, Cleveland, Ohio.

through the ground-glass joints of a three-necked, 3-liter, round-bottom flask (hood). Exclusion of the atmosphere was unnecessary. A mixture of 900 cc. of red fuming nitric acid (sp. gr. 1.59–1.60) and 675 cc. of concentrated sulfuric acid (sp. gr. 1.84) was placed in the flask. The stirrer was started, the acid mixture cooled to 20° and the cooling bath removed. A solution of 45 g. (0.25 mole) of fluorenone in 135 cc. of glacial acetic acid was added dropwise to the acid mixture over a period of about forty minutes. At the end of the addition, the temperature of the reaction mixture was about 45°. The stirrer, thermometer and funnel were removed, the flask was attached to a reflux condenser with a ground-glass joint, and ground-glass stoppers were placed in the other two openings. The reaction mixture was refluxed for one hour and then poured slowly with shaking onto 7000 g. of cracked ice in a 12-liter flask. The product separated as a yellow solid and was filtered by suction and washed with 5 liters of water. The product and 2000 cc. of water were placed in a 5-liter round-bottom flask, and steam was passed into the mixture for one hour to dissolve and remove acidic impurities. The product was filtered by suction, washed with water until the washings were no longer acid to congo

(7) We wish to thank Margaret B. Wolak for assistance with a portion of the experimental work. All melting points are corrected.

red paper, and air-dried overnight. The material was further dried by placing it in a 1-liter round-bottom flask connected to a water pump and the flask was heated in a water-bath at 80–90° for several hours. The product was a yellow powder weighing 74 g. (94% of the theoretical amount) and melted at 166–171°.

The crude product was dissolved in 350 cc. of boiling glacial acetic acid and the hot solution filtered by suction through a Büchner funnel. If crystals separated in the filtrate, the suction flask was heated to bring all of the material into solution and then left to cool. The small yellow needles that separated were filtered with suction and washed successively with small quantities of alcohol, water, and alcohol. The yield was 59–61 g. (75–78% of the theoretical amount) of 2,4,7-trinitrofluorenone, melting at 175.2–176.0°. Additional material was recovered from the mother liquor by dilution with water; the precipitate was filtered with suction and dried. Crystallization from acetic acid gave about 5 g. of pure material, melting point 175.2–176.0°, which was usually slightly darker than the first crop.

Complex Compound Formation.—Equimolar proportions of the pure T.N.F. and the polynuclear component were dissolved separately in the same solvent (alcohol, benzene or acetic acid) and the two hot, nearly saturated solutions mixed. After separation of the solid, colored complex it was recrystallized from the solvent indicated in the table. In a few instances where acetic acid was used, the complex did not separate until the saturated solution was left at room temperature for six to twelve hours.

Melting Point *versus* Composition Diagram.—Pure 1,4-diphenylbutadiene and T.N.F. were weighed into small Pyrex test-tubes in various molar proportions. The total weight of the mixture was usually about 200 mg. The test-tubes were sealed, placed in a shaking apparatus, and heated in an oil-bath with shaking until the mixture was completely fluid. The bath was removed, the tubes opened and the solid melt transferred as quantitatively as possible to a small mortar. The mixture was ground and the melting point determined with a capillary tube in the usual fashion.

RESEARCH AND DEVELOPMENT DIVISION
OFFICE OF SYNTHETIC LIQUID FUELS
U. S. DEPARTMENT OF THE INTERIOR
BUREAU OF MINES   RECEIVED JANUARY 31, 1947
CENTRAL EXPERIMENT STATION
PITTSBURGH, PENNSYLVANIA

The Solubility of Iodine in Concentrated Hydriodic Acid Solutions

BY C. F. POWELL AND I. E. CAMPBELL

This paper presents data on the solubility of iodine in 45 to 67% hydriodic acid. No data are reported in the literature on the solubility of iodine in acid stronger than 10%.

Experimental

Hydriodic acid was prepared in a modified form (Fig. 1) of the synthesis and absorption train described by Caley and Burford.[1] Difficulty experienced with temperature control and sagging of the heated parts in using the original version led to its modification. A 102-hour run, using 435 g. of resublimed iodine (Baker C. P. grade) in the vaporizer and 200 ml. of distilled water in the absorber, produced a 66.7% acid, conversion being better than 90%. Weaker concentrations of acid were prepared when needed by dilution of the 66.7% acid with air-free distilled water.

Three 7-ml. samples of each of five concentrations were

(1) E. R. Caley and M. G. Burford, "Inorganic Syntheses," 1st ed., McGraw-Hill Book Company, Inc., New York, 1939, Vol. 1, pp. 159–162.
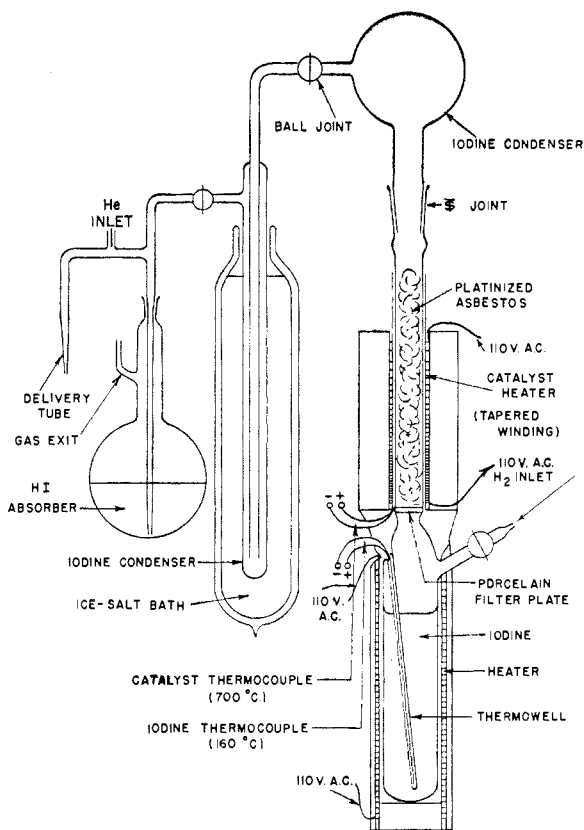

Fig. 1.—Hydrogen iodide preparation apparatus (scale: one sixth).

run into glass ampules containing about 30 g. (an excess) of iodine in a helium atmosphere, and sealed off. The helium used was purified by passing over calcium metal turnings heated to 600°.

After being agitated in a thermostated water-bath at 25.00 ± 0.05° for three days, each ampule was broken in a helium atmosphere and the sample filtered at the equilibrium temperature through a dry asbestos mat into a smaller, weighed ampule holding 3 ml. Two samples were taken from each saturation ampule. These samples, after being sealed off in a helium atmosphere, were reweighed by standard weighing methods, and the weights reduced to vacuum.

The first of each sample pair was analyzed for free iodine by breaking the ampule in a flask containing 100 ml. of distilled water, 20 g. of Baker C. P. potassium iodide, and 5 g. (an excess) of Baker C. P. sodium bicarbonate, and titrating with 1 N sodium thiosulfate using 1 ml. of a 0.25% starch solution as indicator. The 1 N thiosulfate solution was standardized against resublimed iodine.[2]

The second ampule of each pair was broken in a flask containing 100 ml. of distilled water, 2 or 3 ml. of 12 N sulfuric acid, and 25.00 ml. of 1 N potassium iodate solution made up with Baker C. P. potassium iodate and standardized against the 1 N thiosulfate solution described above. After boiling off all free iodine (addition of a small marble chip facilitated complete removal) the hydrogen iodide content of the sample was obtained by determining the excess iodate in the cooled solution by adding an excess of Baker C. P. potassium iodide and titrating with 1 N thiosulfate solution.[3]

(2) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, 8th ed., John Wiley & Sons, Inc., New York, N. Y., 1935, p. 599.

(3) H. Dietz and B. M. Margosches, *Chem.-Ztg.*, II, 1191 (1904).