

I. The remainder was composed of higher boiling hydrocarbons most probably tri-(methylcyclohexyl)-benzene.

Proof of Structure. Fraction B.—Eighteen grams of B dissolved in 30 ml. of benzene was dehydrogenated by passing it over chromia-alumina catalyst⁵ at 450°, according to the procedure described previously.³ The solution was passed five times over the catalyst at an hourly liquid space velocity of 0.10, and the crystals removed between each pass. The gases, 8.3 liters, produced during the dehydrogenation consisted of 21% methane and 79% hydrogen. The crystalline material, amounting to 6.5 g., melted after crystallization from absolute ethanol at 202–205°.

Anal. Calcd. for C₁₀H₁₄: C, 93.87; H, 6.12. Found: C, 93.58; H, 6.56.

The melting point of a known sample of *p*-terphenyl, which was crystallized from ethanol, was 206–207.5°. The mixed melting point of the two samples was 204–205°. The infrared spectra showed that the sample obtained from dehydrogenation contained about 95% of *p*-terphenyl. Minor intensity bands at wave lengths of 12.3 μ which are characteristic of *m*-disubstituted aromatics were present.

Fraction A.—The product, 16.2 g., was dehydrogenated as indicated above. After four passes 12.0 g. of liquid and 7.7 liters of gas were recovered, the latter was composed of 86.6% hydrogen and 11.3% methane. From the liquid hydrocarbons 1.2 g. of solid separated on cooling, which after crystallization from ethanol melted at 83–85°. It did not depress the melting point of an authentic sample of *m*-terphenyl. The infrared spectra of the two compounds were identical.

The liquid product obtained from dehydrogenation distilled at 204–230° at 12 mm., *n*_D²⁰ 1.6070. Since the original product appears, according to infrared spectra and physical constants to consist of a pure compound, it is possible that during dehydrogenation a migration of a methyl group occurred.

Spectroscopic Data.—The wave lengths of the absorption bands of I (fraction B), II (fraction A), *p*-terphenyl and *m*-terphenyl are listed below in order of decreasing band intensity, expressed in microns.

I—*p*-di-(1-methylcyclohexyl)-benzene—6.88, 12.04, 6.60, 9.82, 7.27, 9.03, 10.37, 7.40, 7.66, 9.04, 7.14, 10.78 and 11.64.

II—*m*-di-(1-methylcyclohexyl)-benzene(?)—14.10, 12.58, 7.24, 7.02, 6.21, 6.69, 11.12, 10.32, 7.36, 9.00, 7.68, 8.33, 11.56, 11.66, 13.07, 10.75, 9.75, 8.12, 8.65, 9.60 and 12.07.

p-Terphenyl—13.32, 14.39, 11.90, 12.97, 13.81, 9.89, 9.28, 10.95 and 8.96.

m-Terphenyl—13.33, 14.33, 14.29, 13.07, 12.48, 11.16, 9.26, 9.67 and 9.83.

(5) R. C. Archibald and B. S. Greensfelder, *Ind. Eng. Chem.*, **37**, 356 (1945).

THE IPATIEFF HIGH PRESSURE AND
CATALYTIC LABORATORY
DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

Spectral Absorption of Solutions of Iodine in Liquid Hydrogen Fluoride

By L. I. KATZIN AND J. J. KATZ

RECEIVED AUGUST 3, 1953

It is generally accepted that the colors of solutions of iodine reflect specific solvation interactions, the "violet" solutions in solvents like carbon tetrachloride, carbon disulfide or aliphatic hydrocarbons displaying no effect of solvent on the vapor-like absorption of the iodine, and the various red through brown solutions in the benzenoid hydrocarbons and oxygenated solvents showing shifts of the peak of the absorption toward the ultraviolet in relation to the strength of the specific interaction

between the iodine and the solvent.^{1–7} Mass action constants for formation of monosolvates have been determined for many of these systems, and similar relations have been shown for solutions of bromine in benzenoid hydrocarbons.⁸

Water as a solvent shifts the iodine spectrum in the same sense as do the oxygenated organic compounds. A recent publication⁹ on another oxygenated inorganic solvent, 96% sulfuric acid, reports that iodine shows a red color (absorption at 502 $m\mu$ instead of the 517 $m\mu$ of carbon tetrachloride or 450 $m\mu$ of water), while in the oxygenated organic solvent, trifluoroacetic acid, iodine shows an absorption maximum at 515 $m\mu$. We have hereby been stimulated to publish our observations on the absorption of iodine in liquid hydrogen fluoride, for which we find a broad absorption maximum centering at about 514 $m\mu$. The solution is violet colored. Tracing the absorption with a Cary recording spectrophotometer, we can find no second absorption peak down to the limit of the instrument (and the cell system) at 220 $m\mu$. This is therefore apparently not analogous to the case of iodine in *cis*-dichloroethylene, trichloroethylene and tetrachloroethylene, in which optically "violet" solutions show an intense absorption in the ultraviolet, in the vicinity of 270–280 $m\mu$, which gives evidence of complex formation.^{10,11}

If the color of the iodine solution in hydrogen fluoride is due to minimal solvent-solute interaction, addition of a strong-base solvent, such as diethyl ether, should affect the absorption. If iodine is dissolved in a mixture of one part by weight diethyl ether to 10 parts hydrogen fluoride, the solution is a red-orange, and the absorption peak is shifted down to about 508 $m\mu$. With 33% ether, the orange color is more marked, and the absorption peak is at about 500 $m\mu$. With a solution composed of 75% ether and only 25% hydrogen fluoride, a yellow-brown solution is found, with a principal absorption at about 360 $m\mu$ (it was followed only down to 340 $m\mu$) and a lesser shoulder or peak with its maximum at about 460 $m\mu$. The latter corresponds presumably to the iodine absorption in ether, and the intense 360 $m\mu$ peak is undoubtedly the long-wave length peak of the triiodide ion doublet, the second member falling below 300 $m\mu$.

Qualitatively similar color changes could be seen for methanol-hydrogen fluoride mixtures as solvent, but spectral observations were impractical because of apparently accelerated reaction between the iodine and the nickel of the observation cell in this system. All of the colors seemed further

- (1) J. H. Hildebrand and B. L. Glascock, *THIS JOURNAL*, **31**, 26 (1909).
- (2) J. Groh, M. Radvanyi, L. Urbanek and K. Lanyi, *Z. anorg. u. allgem. Chem.*, **162**, 287 (1927).
- (3) J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948).
- (4) H. A. Benesi and J. H. Hildebrand, *THIS JOURNAL*, **71**, 2703 (1949).
- (5) R. S. Mulliken, *ibid.*, **72**, 600 (1950).
- (6) J. A. A. Ketelaar, C. van de Stolpe and H. R. Gersmann, *Rec. trav. chim.*, **70**, 499 (1951).
- (7) J. S. Ham, *J. Chem. Phys.*, **20**, 1170 (1952).
- (8) R. M. Keefer and L. J. Andrews, *THIS JOURNAL*, **72**, 4677 (1950).
- (9) R. E. Buckles and J. F. Mills, *ibid.*, **75**, 552 (1953).
- (10) L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **74**, 458 (1952).
- (11) J. A. A. Ketelaar and C. van de Stolpe, *Rec. trav. chim.*, **71**, 805 (1952).

shifted to the violet than with the ether system (*i.e.*, iodine in methanol was orange-brown, addition of fractional amounts of hydrogen fluoride gave orange-red solutions, and this color persisted over a large range of HF-methanol mixture compositions; a violet coloration appeared at higher methanol concentrations than in the ether system).

A noticeable characteristic of the system was the difference in solubility of iodine in the oxygenated solvents and in hydrogen fluoride. Starting with even a dilute solution of iodine in methanol, addition of hydrogen fluoride to about 75% by weight precipitated iodine, and precipitation continued with further addition of hydrogen fluoride. Iodine dissolves slowly in pure hydrogen fluoride.

Some question might be raised concerning the relatively small effects of the lower concentrations of the oxygenated electron donors on the iodine spectrum. It should be pointed out that hydrogen fluoride will compete with the iodine for the electrons of the donor, so that the effective concentration of the latter is considerably diminished. From the evidence as a whole it does not seem that hydrogen fluoride interacts significantly with iodine dissolved in it.

Visual observations and solution make-up were performed with test-tubes formed of fluoride-resistant aluminum phosphate glass ("Fluorex"). The experimental procedures for following absorption spectra in liquid hydrogen fluoride will be described elsewhere.¹²

(12) J. J. Katz and H. H. Hyman, *Rev. Sci. Instruments*, to be published.

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS

Significance of Fungus Growth in Analytical and Radiochemical Work with Strontium-containing Solutions¹

By S. Z. LEWIN, PETER J. LUCCHESI AND JOHN E. VANCE
RECEIVED JULY 15, 1953

Dipping-type Geiger-Mueller tubes employed in an investigation of rates of dissolution of radioactively-labeled crystals of strontium sulfate in distilled water were observed, in runs at room temperature, to acquire an activity which increased regularly with time. The activity was in the form of an adherent deposit on the surface of the tube, for when removed from the solution and rinsed repeatedly with water, the tube gave practically the same high count as it had when immersed in the solution. The activity recorded by the tube did not decrease at all when the tube was left immersed in a large volume of a solution containing a high concentration of stable Sr^{++} , showing that the radioactive strontium deposited on the tube does not enter into exchange with strontium ions in solution. Firm wiping of the tube removed a large part of the activity, but vigorous scrubbing with a mild abrasive was necessary to remove the remainder. The same effects were observed with glass, stainless steel, and

(1) This work was supported in part under Contract No. AT (30-1)-1256 between the Atomic Energy Commission and New York University.

glyptal-coated dip tubes at room temperature, but they were no longer observed when the experiments were carried out at temperatures near 0°.

These observations suggested that the deposit on the G-M tube might be a fungus capable of ingesting strontium. To test this hypothesis, the solution from one of the runs (consisting of two liters of water approximately saturated with $Sr^{89}SO_4$) was made 0.5% in dextrose, and set aside for one month at room temperature. A luxuriant growth of mold mycelium was present at the end of this period; it was filtered, air-dried and measured for radioactivity. A 0.24-g. sample of the mold mycelium gave 937 ± 10 counts per minute over background; the same weight of the solution gave 5 c.p.m.

The effect of $SrSO_4$ on the rate of growth of the fungus was investigated by preparing a number of 1% dextrose solutions, half of which were saturated with strontium sulfate, and inoculating all with equal amounts of the mold mycelium obtained as described above. After one day, the solutions containing $SrSO_4$ were decidedly more turbid, due to the mold, than the other solutions; after one month, the strontium-containing solutions had large colonies of mycelium which did not adhere to the walls of the flask, whereas the solutions containing the same nutrient, but no $SrSO_4$, showed only a thin growth which adhered firmly to the glass surface.

The fungus, when cultured on bread slices, produced black colonies having the appearance characteristic of *Rhizopus nigricans*. It is concluded that this mold grows in solutions of strontium sulfate (even when the only nutrient available is what falls into the solution from the laboratory air), that its growth is actually accelerated by the presence of the Sr^{++} , and that it ingests strontium and incorporates it into its structure in a form that does not exchange with strontium ions in solution.

Analyses of solutions of $SrCl_2$ and $SrSO_4$ in water by a colorimetric procedure² show that the concentration of strontium ions in these solutions may decrease considerably with time; for example, a 0.06% solution of $SrCl_2$ in distilled water in a glass-stoppered flask decreased in concentration by about 60% over a three-month period.

It follows that the possibility of loss of Sr^{++} due to fungus activity must be considered in all analytical and radiochemical work with strontium-containing solutions.

(2) P. J. Lucchesi, S. Z. Lewin and J. E. Vance, *Anal. Chem.*, in press.

CHEMISTRY DEPARTMENT
NEW YORK UNIVERSITY
NEW YORK 3, N. Y.

The Preparation of Ethyl 1,1,2,2,3,4-Butene-3-hexacarboxylate

By C. G. OVERBERGER AND PETER KABASAKALIAN
RECEIVED JULY 1, 1953

In connection with other work, we attempted to synthesize ethyl 1,1,2,2,3,4-cyclobutanehexacarboxylate (I). Reid and Sack¹ have recently re-

(1) E. B. Reid and M. Sack, *THIS JOURNAL*, **73**, 1985 (1951).