ments are being made of the pressures and compositions of vapors that will support explosive decomposition. Experimental results are reported here concerning the compositions of vapors at atmospheric pressure containing principally hydrogen peroxide and water, plus a small amount of oxygen, that may be exploded by a hot wire.

Experimental

In the experimental procedure, a vapor stream is passed through a flask and the effluent is analyzed at frequent intervals before the explosion is attempted. The vapor stream is supplied from a boiling aqueous hydrogen peroxide solution of high purity. Decomposition is kept to a minimum by keeping the amount of liquid in the boiler at any one time small relative to the boiling rate.

The vapors produced in the boiler are passed through the explosion flask and thence through a condenser. The concentration and volume of the condensate are determined while the volume of any non-condensable gas, assumed to be oxygen, is measured by a wet-test gas meter. These measurements are combined to give a complete vapor analysis as well as a material balance which can be used to check the steady-state operation of the system. It is assumed that negligible decomposition occurs in the explosion flask and condenser.

Initiation of the explosions in these experiments was accomplished by a platinum wire 0.01″ in diameter and 5 cm. long, which was welded across two 0.04″ diameter platinum leads sealed through glass into the explosion flask. Explosion was attempted by passing a current of 5 amperes through the wire, causing it to glow at a red heat.

In performing the experiments, hydrogen peroxide vapors were passed continuously through the explosion flask and analyzed until the measurements showed that steady state had been obtained. An attempt to explode the vapor was then made. After the attempt, the current through the wire was shut off and approximately thirty seconds allowed for the system to reach its previous steady state before ignition was again tried. At high hydrogen peroxide concentrations, the vapor will explode violently with complete destruction of the apparatus; however, with the vapor concentrations covered in the table below, the maximum effect has been an audible "pop." When the concentration was close to the explosion limit, no noise was heard; and the question as to whether or not an explosion had occurred was decided by close observation of the fog formed in the condenser. It has been possible to distinguish clearly between two cases on heating the wire: either (1) the fog is suddenly expelled from the condenser, or (2) there is no noticeable disturbance in the condenser. If there is a sudden expulsion of fog from the condenser, an explosion is considered to have occurred even though there has been no audible report.

Results.—The results are presented in Table I, which shows the vapor compositions studied and the observations on repeated explosion attempts with that vapor, at one atmosphere total pressure.

TABLE I

Partial press. in vapor, mm.			Observations	
H_2O_2	H_2O	O_2	Explosion	Attempts
153	517	99	0	10
178	550	22	0	10
198	559	5	1	9
198	557	6	3	10
204	487	69	10	10
222	524	19	10	10
226	523	15	10	10
231	518	6	10	10

The variation in the oxygen concentration in the vapor is due to improving operational technique which caused a decreasing amount of decomposition in successive runs. From energy considerations, reaction between water or oxygen and any of the species that could be present in this reacting mixture are unlikely; from this it would be expected that the oxygen to water ratio in the diluent gas should have little effect on the limit of explosive composition in terms of the partial pressure of hydrogen peroxide. This assumption is supported by the results obtained.

Discussion.—The results indicate definitely that with this experimental system, there is a reproducible explosion limit in the vicinity of 198 mm. partial pressure of hydrogen peroxide. In considering the significance of the results, it must be remembered, however, that the physical characteristics of the ignition system may appreciably affect the measured ignition limits.

The mechanism of the explosive reaction has not been thoroughly investigated, but a branched chain explanation seems unlikely because of energy considerations. It is probable that the reaction is carried through the mixture by unbranched chains—perhaps corresponding to the mechanism proposed by Haber and Willstätter for liquid phase decomposition,[4] with the initiating reaction in this case a breaking of the O–O bond in the hydrogen peroxide.[5,2] A continually increasing number of these chains may be thermally initiated as a result of the large heat of decomposition, thus producing an explosion which is essentially thermal in nature.

(4) F. Haber and R. Willstätter, *Ber.*, **64B**, 2844 (1931).

(5) P. Giguere, *Can. J. Research*, **25B**, 135 (1947).

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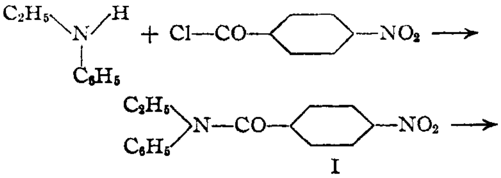
Synthesis of 4-(N-Ethylamino)-N-ethyl-N-phenylbenzamide[1]

BY W. A. SCHROEDER AND PHILIP E. WILCOX

In the course of recent experiments it was necessary to prepare 4-(N-ethylamino)-N-ethyl-N-phenylbenzamide (III) for which no method of synthesis seems to have been described in the literature. Two other new compounds, 4-nitro-N-ethyl-N-phenylbenzamide (I) and 4-amino-N-ethyl-N-phenylbenzamide (II), were intermediates in the synthesis of the desired compound. The series of reactions was



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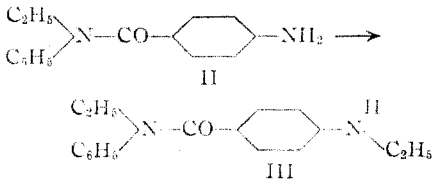
(1) This paper is based on work done for the Office of Scientific Research and Development under Contract OEMsr-881 with the California Institute of Technology.



Since only a small amount of the pure compound was required, no attempt has been made to improve the methods which are described below.

Experimental Part

Stem corrections were applied to melting points all of which were taken in melting point tubes in an electrically heated copper block.

4-Nitro-N-ethyl-N-phenylbenzamide (I).—To the vigorously stirred mixture of 22.0 g. of anhydrous potassium carbonate and a solution of 30.0 g. of 4-nitrobenzoyl chloride[2] in 100 ml. of ethyl ether, there was added slowly at room temperature a solution of 20.0 g. of Eastman Kodak Co. White Label N-ethylaniline. After addition was complete, the mixture was refluxed for thirty minutes and then the ether was evaporated in a stream of air. After the yellow residue had been heated to about 70° so that it became light orange in color and free N-ethylaniline was evident by its odor, it was washed with two 100-ml. portions of 3 *N* hydrochloric acid and finally with a large volume of water on the filter. The crude air-dried product weighed 42.5 g. (yield 97%) and melted at 111–114°. Material which had been twice recrystallized from ethanol melted at 119.5–120.5° and gave the following analysis.

Anal. Calcd. for $C_{15}H_{14}O_3N_2$: C, 66.64; H, 5.22; N, 10.37. Found: C, 66.34; H, 5.31; N, 10.36.

4-Amino-N-ethyl-N-phenylbenzamide (II).—The reduction of (I) followed essentially the procedure of "Organic Syntheses."[3] In a flask which was fitted with a reflux condenser and a mercury-sealed stirrer, 20.0 g. of crude (I), 20 ml. of 95% ethanol, 12 ml. of water and 18.0 g. of iron powder were mixed. After refluxing temperature had been attained, 1.5 ml. of 12 *N* hydrochloric acid in 3.5 ml. of 95% ethanol was added gradually with vigorous stirring, and the refluxing and stirring were continued for three hours. The acid was neutralized with 0.75 g. of sodium hydroxide in 20 ml. of ethanol and the precipitated iron compounds were filtered from the warm solution with the help of a layer of filter aid. Reaction flask and filter cake were washed with two 50-ml. portions of 95% ethanol. The product was isolated by cooling and then by concentration of the solution; the first two crops of white crystals weighed 9.6 g. and had a melting point of 161–162° which was not altered by recrystallization from ethanol. Further concentration and final dilution with water yielded 3.5 g. of less pure material of melting point 159.5–160.5°; the total yield was 13.1 g. or 74%. Analysis of the purer product gave these results.

Anal. Calcd. for $C_{15}H_{16}ON_2$: C, 74.94; H, 6.74; N, 11.93. Found: C, 75.11; H, 6.47; N, 11.76.

4-(N-Ethylamino)-N-ethyl-N-phenylbenzamide (III).—The ethylation of (II) was carried out by means of acetaldehyde–ammonia in the presence of zinc and sulfuric acid according to the procedure of G. Lockemann.[4] A 9.2-g. sample of (II), 100 ml. of ethanol, 340 ml. of water, 38 g. of concd. sulfuric acid and 38 g. of zinc dust were placed in a flask which was provided with a reflux condenser and an addition funnel. Then 2.5 g. of freshly prepared acetaldehyde–ammonia in 80 ml. of water was added to the refluxing solution in the course of forty minutes and refluxing was continued for one hour. The solution was filtered, made alkaline with 120 ml. of 15 *N* ammonium hydroxide, and kept at 5° for two days. The light tan crystalline precipitate was washed with three 50-ml. portions of 6 *N* ammonium hydroxide and a large quantity of water and was crystallized 5 times from ethanol and once from ethanol–water (approximately 1:1). The final product weighed 1.0 g. (yield 10%) and melted at 132.0–132.5°. Three grams of impure material were recovered from the mother liquors. Analysis of the purer sample yielded these results.

Anal. Calcd. for $C_{17}H_{20}ON_2$: C, 76.06; H, 7.53; N, 10.44; mol. wt., 268. Calcd. for $C_{19}H_{24}ON_2$ (the diethylamino compd.): C, 76.97; H, 8.17; N, 9.45; mol. wt., 296. Found: C, 76.03, 75.88; H, 7.50, 7.36; N, 10.42, 10.57; mol. wt., 272 (by Rast micro-method in cyclopentadecanone).

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[2] Prepared essentially by the method of "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 394.

[3] Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 160.

[4] G. Lockemann, *Chem. Zentr.*, **101**, II, 982 (1930).

Vapor Pressure of *cis*-2-Pentene, *trans*-2-Pentene and 3-Methyl-1-butene

BY DONALD W. SCOTT AND GUY WADDINGTON

A previous publication from this Laboratory[1] reported vapor pressure measurements on 1-pentene, 2-methyl-1-butene and 2-methyl-2-butene. Similar studies have now been made of the remaining three pentene isomers, *cis*-2-pentene, *trans*-2-pentene and 3-methyl-1-butene. The samples used for these measurements were API–NBS hydrocarbons made available by the American Petroleum Institute and the National Bureau of Standards through A.P.I. Research Project 44 on the "Collection, analysis, and calculation of data on the properties of hydrocarbons."[2]

The differences between the boiling and condensation temperatures observed for these samples at atmospheric pressure were: *cis*-2-pentene, 0.002°; *trans*-2-pentene, 0.001°; 3-methyl-1-butene, 0.006°. The purity of the compounds, as determined by a study of the melting points as a function of fraction melted, has been reported.[3] The vapor pressures were measured by an ebulliometric method. The apparatus described previously[4] was used after making certain modifications to adapt it for measurements with low-boiling materials. The section of the sample ebulliometer containing the thermometer-well for observing condensation temperatures was cooled by surrounding it with a coil of copper tubing through which was circulated an ethylene glycol–water mixture from a refrigeration unit. This same refrigerant was used in the condenser of the sample ebulliometer. Two liquid air traps were used to prevent diffusion of sample vapor into the water ebulliometer. Dry helium gas was used for the inert atmosphere in the apparatus.

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[1] Scott, Waddington, Smith and Huffman, THIS JOURNAL, **71**, 2767 (1949).

[2] The samples were purified at the National Bureau of Standards by the A.P.I. Research Project 6 on the "Analysis, purification, and properties of hydrocarbons" under the supervision of Frederick D. Rossini, from material supplied by the following laboratories: *cis*-2-pentene and *trans*-2-pentene, by the A.P.I. Research Project 45 on the "Synthesis and properties of hydrocarbons of low molecular weight" at the Ohio State University, under supervision of Cecil E. Boord; 3-methyl-1-butene, by the Houdry Process Corporation through the courtesy of E. A. Smith.

[3] Todd, Oliver and Huffman, THIS JOURNAL, **69**, 1519 (1947).

[4] Waddington, Knowlton, Scott, Oliver, Todd, Hubbard, Smith and Huffman, *ibid.*, **71**, 797 (1949).