[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE ETHYL GASOLINE CORPORATION]

The Vapor-phase Oxidation of Hydrocarbons. III. Chemiluminescence of *n*-Heptane

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Introduction

The emission of a visible chemiluminescence is known to accompany the autoxidation of a wide variety of compounds,[1] and may in fact be a general characteristic of such reactions.[2] The spectra observed[3] are markedly different from those of the true flames which accompany complete combustion. Pseudo-flames or flashes, each accompanied by a brief expansion of the luminescent gas, were observed by Pope, Dykstra and Edgar[4] in the slow combustion of a *n*-octane–air mixture in the neighborhood of 250°, some 400° below the true inflammation point. The same phenomenon was noted by Prettre, Dumanois and Laffitte[5] in their observations of the luminescence of pentane–air mixtures, and it has become the characteristic of the so-called "lower ignition point" of such mixtures.[6]

In connection with our study of the autoxidation of *n*-heptane[7] it seemed desirable to observe this luminescence. Although the oxidation is of the "homogeneous," chain-mechanism type, evidence from various sources shows clearly that the nature of the furnace walls plays an important role, and it was hoped that a study of the luminescence might add to our knowledge of this effect.

Experimental Method

Five different furnaces were used, each made of Pyrex glass. Their description and method of use follows.

No. 1.—This furnace, 2.3 cm. in diameter, was a duplicate of our standard furnace,[7] except that the insulation was removed on one side, leaving a window 1 cm. in width running the length of the reaction chamber (65 cm.), and the exit end of the tube was not constricted but was covered with a glass plate to permit an end-on view. Through a small hole in the center of this plate could be inserted rods of different materials in order to note the effect of such surfaces on the luminescence. The oxygen and nitrogen–fuel streams were introduced through a preheater as previously described[7] and were mixed at the "inlet," giving in effect a theoretically equivalent (2%) mixture of fuel vapor in air. Temperatures were measured by a thermocouple inserted through a preheater to a fixed point, 1 cm. from the inlet.

No. 2.—This furnace was the same in design and operation as No. 1, except that the reaction chamber was 4.8 cm. in diameter, 25 cm. in length from the inlet to the side exit-tube, and 7.5 cm. further in length to the end window. This wide furnace gave larger, more clearly visible glows and flames than did No. 1, but there was some uncertainty as to the temperature conditions at different points therein; for this reason No. 3 was constructed.

No. 3.—This was a 2.5 by 60 cm. vertical tube suspended in a glass boiling-tube containing benzophenone. The oxygen and nitrogen–fuel streams were led in at the standard rates through 2-mm. preheater tubes which were joined together at, and sealed into, the bottom of the furnace. The upper end of the furnace was open for end-on observations or for the insertion of rods or a thermocouple. The incoming gases and the lower 34 cm. of the furnace wall were at a uniform, constant temperature of 314°; this was later reduced to 280° by the addition of halowax oil to the bath. With fuel present the maximum temperature in the interior of the furnace was 13° higher than that of the vapor-bath outside.

In general, the design and operations of furnaces No. 1–3 duplicate in all essential particulars the experimental conditions used in our previous investigations.[4,7] The furnaces received the fuel charge as a diffuse stream which had ample contact with the walls. To avoid, as far as possible, the effect of surface, the following two set-ups were used.

No. 4.—This was No. 1 mounted vertically with the exit side-tube, through which a current of air was forced, at the top. The top end was closed by a cork supporting a buret, from which liquid heptane was delivered drop-wise. Under the open bottom end was a beaker to catch the falling drops and make them audible. The temperature at top and bottom was approximately uniform, and was about 300°.

No. 5.—This was No. 2, except that the regular preheating and mixing device was replaced by a length of 0.15-cm. capillary tubing through which was forced a mixture of nitrogen and fuel vapor, while air or oxygen flowed in slowly through the annular space between the capillary and the preheater wall. At proper gas velocities, tests showed that the capillary delivered a well-defined jet along the furnace axis, 10-20 cm. in length. This procedure was used after attempting, without success, to study the reaction of crossed beams of air and fuel according to the method of Alyea and Haber.[8]

Since the amount of light emitted from each of the fur-

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[1] Milas, *Chem. Rev.*, **10**, 328 (1932).

[2] Moureu and Dufraisse, "Reports of the Solvay International Council on Chemistry," Brussels, April 1925, p. 524; Bäckström, *Medd. K. Vetenskapsakad. Nobelinst.*, **6**, No. 16 (1927).

[3] Emeleus, *J. Chem. Soc.*, 1733 (1929).

[4] Pope, Dykstra and Edgar, THIS JOURNAL, **51**, 1875 (1929).

[5] Prettre, Dumanois and Laffitte, *Compt. rend.*, **191**, 414 (1930).

[6] See, for example, Zerbe and Eckert, *Z. angew. Chem.*, **45**, 593 (1932).

[7] Beatty and Edgar, THIS JOURNAL, **56**, 102, 107 (1934).

[8] Alyea and Haber, *Z. physik. Chem.*, **B10**, 193 (1930).

naces is relatively small, it was necessary to work in a completely dark room. The observations were made with the assistance of Mr. Lester B. Roberts, to whom we are indebted.

Results

The results obtained with furnaces Nos. 1, 2 and 3 were entirely similar, and showed with increasing temperature six distinct phenomena, as follows.

(1) A diffuse, uniform blue glow appears at about 250°, and increases in intensity and extent, nearly filling the furnace tube. Then (2) at the "lower ignition temperature" of 270° a belt or ring of blue-white "cold flame" is suddenly formed about 15 cm. from the inlet and, dividing, moves slowly along the surface in both directions, then dies out, leaving the furnace dark. At once the uniform glow builds up again and the process is repeated. The appearance of the moving "flame" is accompanied by a momentary pressure increase. The interval between the "flames" is at first ten to twelve seconds and decreases as the temperature is raised, until (3) at 300° the "flames" become continuous, forming a spot or small region of intense glow at or near the inlet. A rapid rise of temperature is now noted in the gas; the reaction is going with its maximum velocity. Now (4) a further increase in temperature causes the spot to become diffuse and spread down the tube, finally filling it completely with a uniform glow. This striking negative temperature coefficient effect is in entire accord with the results of gas analyses which show a decreased rate of oxygen consumption in this temperature range.[7] Finally (5) at the inflammation point (about 525°) the mixture ignites at a point some 15 cm. from the inlet, and fast-moving, greenish-blue flames (not explosion waves) move in both directions, at intervals of five seconds. (6) With further increase in temperature the inflammation becomes continuous and occurs at the inlet. The flames of (5–6) are true, hot flames and are accompanied by complete combustion of the fuel, while at temperatures below the inflammation point less than half of the theoretical amount of oxygen is consumed.

Surfaces of smooth and rough Pyrex glass, solid and gauze copper, and iron were introduced into the reaction zone at different temperatures, but had no noticeable effect on the glows in any case, although iron is known to catalyze these oxidations. Wide variations in the various rates of oxygen, nitrogen and fuel feeds were without marked effect on the results.

In view of the definite indication of surface reaction at the lower ignition point where the first moving "flames" appear (stage 2, above), the results obtained in furnace No. 4 are of considerable interest. With the buret-tip stopper set in tightly, vaporization preceding the falling of the drops of liquid heptane caused the appearance of a bright, steady glow at the top of the furnace. The fuel drops falling through did not change this glow, and remained themselves invisible. However, by raising the buret-tip stopper enough to give a slight upward ventilation, the pre-drop vaporization effect was eliminated, and the tube remained dark until the actual fall of the fuel drop. Below 300° the drop was *followed* by a trail of diffuse glow, filling the tube, strongest at the top, and lasting for an appreciable length of time. However, on raising the temperature the light appeared *simultaneously* with the falling drop, and consisted of a narrow pencil of intense glow, extending the entire length of the furnace along its axis, clearly far removed from the surface; it was of very brief duration and exhibited no afterglow.

Analogous results were obtained with furnace No. 5 at 350°. In general only diffuse glows appeared, but under proper operating conditions (low concentration of fuel and low jet speed) it was possible to observe a small ball of concentrated glow hanging in space, 0.5–2 cm. from the capillary tip. Copper gauze on a glass rod introduced to the 2-cm. point was without visible effect.

Results for 3-Heptene.—Results obtained using 3-heptene in furnace No. 2 were in accord with the known resistance to oxidation of this fuel compared with n-heptane.[7] The low-temperature diffuse glow was very faint; at the lower ignition point only one or two feeble, slow-moving "flames" were seen at the top of the furnace; at higher temperatures a diffuse glow filled the furnace, being strongest 15 cm. from the inlet. Copper gauze on a glass rod inserted at 5 or 15 cm. was without noticeable effect.

Discussion.—Since the reactions as a whole are very complex, no attempt will be made here to offer a detailed interpretation of each of the different phenomena observed in these experiments. We may, however, note the following points.

The results give evidence for the existence of a surface effect, but do not permit drawing any definite conclusions as to its nature. While the low-temperature diffuse glow appears perfectly homogeneous, there is no doubt whatever that the moving "flames" at the lower ignition point are largely surface phenomena; their distinctly ring-shaped appearance is in marked contrast to that of the true flames observed at the inflammation point.

Although light emission is observed at all temperatures from the beginning of oxidation up to the inflammation point, it is not at all certain that each one of the sequence of reactions occurring at a given temperature is luminescent. Hence, the experiments with the falling fuel drops and the vapor jet give only strong indication, and not definite proof, of the possibility of oxidation occurring without the aid of a surface as a starting point. The failure to observe any effect of various surfaces introduced into the center of the furnace may have been due to their small area.

In general, the observations over the entire temperature range of the slow oxidation of *n*-heptane are in complete accord with our knowledge of the amount, velocity and temperature coefficient of that reaction,[7] and are similar to the results of Prettre, Dumanois and Laffitte[5] for the oxidation of pentane.

Summary

The autoxidation of a theoretically equivalent (2%) mixture of *n*-heptane in air from the temperature of initial reaction (250°) to the point of inflammation (525°) emits a visible chemiluminescence, which appears as a steady, diffuse glow except at the "lower ignition point" (270–300°) where moving "cold flames" sweep along the furnace walls. By directing the fuel charge into the center of the furnace, the glow may be observed there, entirely removed from the walls.

The autoxidation of 3-heptene emits a luminescence differing from that of *n*-heptane in a manner corresponding to the relative rates of reaction of the two fuels.

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The Hydrolysis of Substituted Benzenesulfonanilides

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Since Hinsberg first pointed out the value of benzene sulfonchloride as a reagent for distinguishing between primary, secondary and tertiary amines, many substituted aromatic sulfonyl chlorides[1] and aliphatic sulfonyl chlorides[2] have been used for this purpose. Although many of these yield solid derivatives suitable for identification all have one disadvantage in that the original amine cannot be readily recovered.

The usual hydrolysis according to the equation

$$RSO_2NHR' + H_2O \longrightarrow RSO_3H + R'NH_2$$

requires the use of strong acid and drastic conditions.[3] Since sodium benzene sulfonate is cleaved by alkalies a similar splitting of sulfonamides should be accomplished according to the equation

$$RSO_2NHR' + 3NaOH \longrightarrow RONa + R'NH_2 + Na_2SO_3 + H_2O$$

However, benzenesulfonanilide was unaffected by fusion with 80% sodium hydroxide at 250°. Hence, in order to make this reaction useful, a means of weakening the carbon–sulfur linkage is necessary. One promising way of accomplishing this would be the introduction of ortho and para nitro groups which are known to accelerate the alkaline hydrolysis of *o*- and *p*-nitrochlorobenzenes[4] and *o*- and *p*-nitranilines.[5] This prediction has been fulfilled in the present investigation.

Ortho and para nitrobenzene sulfonchlorides were prepared according to the method of Fierz, Schlittler and Waldmann.[6] The 2,4-dinitrobenzene sulfonchloride was prepared by the action of phosphorus pentachloride on 2,4-dinitrobenzene sodium sulfonate. The latter compound was obtained by the nitric acid oxidation of 2,4,2′,4′-tetranitrodiphenyl disulfide. The substituted

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[1] Witt and Uerményi, *Ber.*, **46**, 296 (1913); Marvel and Smith, THIS JOURNAL, **45**, 2696 (1923); Marvel, Kingsbury and Smith, *ibid.*, **47**, 166 (1925); Johnson and Ambler, *ibid.*, **36**, 372 (1914).

[2] Marvel, Helfrick and Belsley, *ibid.*, **51**, 1272 (1929); Marvel and Gillespie, *ibid.*, **48**, 2943 (1926).

[3] The use of concentrated sulfuric acid or chlorosulfonic acid as hydrolytic agents is prohibited in the case of sulfonamides of aromatic amines since the latter are readily sulfonated. Rearrangement may also occur. Halberkann, *Ber.*, **55**, 3074 (1922).

[4] Kenner, *J. Chem. Soc.*, **105**, 2717 (1914); Sprung, THIS JOURNAL, **52**, 1650 (1930).

[5] Merz and Ris, *Ber.*, **19**, 1749 (1886).

[6] Fierz, Schlittler and Waldmann, *Helv. Chim. Acta*, **12**, 667 (1929).