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Abstract

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Spectroscopic Study of Cold-Flame Luminescence during the Nitration of Propane with Nitrogen Dioxide

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Vapor-phase nitration of alkanes with nitrogen dioxide, carried out under definite conditions of temperature, pressure, and composition of the initial mixture, is accompanied by the occurrence of cold flames ([1–3]). As we have shown, such cold-flame nitration, in its external features, is similar to the long-known cold-flame oxidation of hydrocarbons by free oxygen. Indeed, in both cases, first, during the induction period of the cold flame, i.e., during the time from the introduction of the mixture into the reactor to the moment of ignition, a self-accelerating reaction proceeds with an increase in pressure; second, at the end of the induction period there occurs a sharp pressure jump, characterizing the explosive course of the reaction, and the pressure jump is followed by its sharp fall; and, third, synchronously with the pressure jump, in the hottest part of the reactor there appears the front of a very weakly actinic cold flame, propagating through the mixture at a rate of 10–30 cm/sec and exceeding the ambient temperature by only 50–150°; after passing through the mixture the flame is extinguished, and in time this extinction coincides with the end of the sharp pressure drop.

The principal difference so far established by us between cold-flame oxidation and nitration of alkanes consists in the fact that extinction of the cold flame and the pressure drop after its jump occur, in the case of oxidation, when a considerable part of the initial substances is still present in the mixture, whereas in the case of nitration they occur at the moment when the nitrogen dioxide in the mixture has been completely consumed.

In the 1930s V. N. Kondrat' ev established that the source of cold-flame luminescence during the oxidation of alkanes and other organic compounds is electronically excited formaldehyde ([4]). Many hypotheses were advanced regarding the pathways of its formation, and all of them reduced to the fact that excited formaldehyde arises through the interaction of free radicals. Quite recently V. F. Shuvalov, R. F. Vasil' ev, L. M. Postnikov, and V. Ya. Shlyapintokh ([5,6]) succeeded in making this more concrete, showing that during the oxidation of alkanes excited formaldehyde arises according to the reaction:

Fig. 1. Reactor diagram

Figure 1: Fig. 1. Reactor diagram

$$CH_3O + OH \rightarrow CH_2O + H_2O. \tag{1}$$

The above-mentioned similarity in the phenomenology of cold-flame phenomena during the oxidation and nitration of alkanes led us to the assumption that in both of these reactions there exists a common source of cold-flame radiation, namely excited formaldehyde. In order to test this, in the present work a spectroscopic study was carried out of cold flames during the nitration of propane with nitrogen dioxide.

A grating spectrometer with photoelectric recording, designed at the Institute of Chemical Physics of the Academy of Sciences of the USSR (7), was used. Its light receiver is an FEU-19 photomultiplier.

The most difficult task in using photoelectric recording of flames is stabilization of the jet of reacting gases. The cold flame was stabilized in a conical quartz reactor with axial symmetry (see Fig. 1). Stabilization of the jet was achieved by means of 5 fine-control valves, arranged two each on the hydrocarbon and nitrogen dioxide feed lines (feed valves) and one downstream of the reactor. To stabilize the pressure in the feed lines, thermostatted ballast vessels were placed between the feed valves, in which a constant pressure was maintained. As a result, the pressure of the jet with an established flame front could be maintained in the reactor for several hours with an accuracy of up to 2 mm on a dibutyl phthalate manometer. The reactor was placed in a furnace with electric heating and an external water cooler. The furnace was located in a light-tight chamber.

Fig. 1. Reactor diagram

Thus, the jet apparatus that was created provided high stability of the flame front and thereby made it possible to record the spectra of cold flames with a photoelectric spectrometer.

The flame spectrum given below was recorded under the following jet conditions: nitrogen dioxide feed—290 ncm^3/min, propane feed—268 ncm^3/min; pressure in the reactor 400 mm Hg; initial reactor temperature 365°.

The flame spectrograms are shown in Figs. 2 and 3. The geometrical width of the spectrometer slit was 0.5 mm, which corresponds to a spectral width of 2 mμ (7). The scanning speed was 160 Å/min (Fig. 2) and 40 Å/min (Fig. 3). In Fig. 2 two spectrograms recorded during forward and reverse scanning are superposed. It is evident that the number of peaks and their mutual arrangement coincide.

Fig. 2. Spectrogram of the cold nitration flame under forward and reverse scanning

Figure 2: Fig. 2. Spectrogram of the cold nitration flame under forward and reverse scanning

Fig. 2. Spectrogram of the cold nitration flame under forward and reverse scanning

In Fig. 3, on the same wavelength scale, are shown: first, the spectrogram of the cold flame of the nitration reaction obtained by us (solid curve); second, the scheme of the fluorescence spectrum of electronically excited formaldehyde given in the work of Herzberg and Franz (8); and, third, an analogous spectrum scheme constructed by us from the numerical data of Brandt' s work (9) (dashed lines). The spectrogram obtained by us is superposed on the spectrogram from work (8) according to the most intense band, C_0.

From Fig. 3 the complete identity of the cold-flame spectrum obtained by us with the spectra from works (8, 9) is evident. This shows for the first time that the source of the cold-flame glow arising in the system $RH + NO_2$ under certain conditions is electronically excited formaldehyde.

In stationary flames of the thermal nitration of propane on mixtures enriched with nitrogen dioxide, in addition to the formaldehyde glow, a glow was found in a longer-wavelength region of the spectrum

(500-600 mμ). As follows from Figs. 2 and 3, this long-wavelength luminescence is insignificant in typical cold flames. Gradual enrichment of the mixture with nitrogen dioxide (mixtures of the composition $C_3H_8 + 2NO_2$, $C_3H_8 + 3NO_2$, and $C_3H_8 + 4NO_2$ were studied) leads to an increase in the brightness of the flame. Visually, a red component appears in the flames. A sharp increase is observed in the intensities of the formaldehyde and long-wavelength luminescence. The intensity of the long-wavelength luminescence increases more rapidly than that of formaldehyde and, beginning with the composition $C_3H_8 + 2NO_2$, the intensities are approximately equal. The nature of the source of this luminescence is not clear and requires additional study.

Identification of excited formaldehyde in the cold flame of alkane nitration is of great significance for understanding the mechanism of thermal nitration. The finding of excited formaldehyde undoubtedly indicates the participation of free radicals in this reaction—apparently alkoxyl and hydroxyl radicals. Thus, the radical-chain scheme of thermal nitration proposed by us (10), which includes alkoxyl and hydroxyl radicals, is also confirmed.

We consider it our pleasant duty to express our gratitude to V. Ya. Shlyapintokh, L. M. Postnikov, and F. F. Shuvalov for providing a unique domestic spectrometer and for assistance in setting it up.

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Fig. 3. Spectrogram of the cold flame of propane nitration (solid curve), diagrams of the formaldehyde fluorescence spectra from paper (8) (solid lines) and from paper (9) (dashed lines). The peaks on the ordinate axis refer to the spectrogram from paper (8), and the letters at the vertical marks refer to the spectrogram from paper (8).

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Note: Figure translations are in progress. See original paper for figures.