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## Abstract

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# MECHANISM OF FORMATION OF EXCITED FORMALDEHYDE MOLECULES IN OXIDATION REACTIONS

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It is known that the glow accompanying the cold-flame oxidation of various organic substances is associated with excited formaldehyde molecules. An extensive literature is devoted to the study of the kinetics of reactions in cold flames; in it, in particular, the question of the pathways of formation of excited formaldehyde is discussed (see, for example, the reviews ($^{1,2}$)). It has not been possible to resolve this question unambiguously, since the kinetics of cold-flame oxidation is very complex. However, as a result of a number of kinetic studies ($^{3-6}$), by the present time there has apparently been established a general opinion that excitation occurs in reactions proceeding with the participation of alkoxyl radicals. Applied to the simplest of them—the methoxyl radicals—the following reactions are considered most probable:

$$CH_3O + CH_3O \rightarrow CH_3OH + CH_2O + 76 \text{ kcal } (^2), \qquad \text{(I)}$$

$$CH_3O + OH \rightarrow H_2O + CH_2O + 98 \text{ kcal } (^6), \qquad \text{(II)}$$

$$CH_3O + CH_3 \rightarrow CH_4 + CH_2O + 82 \text{ kcal}, \qquad \text{(III)}$$

the thermal effect of which is close to the excitation energy of formaldehyde (77 kcal) ($^7$).

In our work ($^9$), using the example of the oxidation reaction of acetaldehyde ($^{18}$), it was shown that the formation of excited formaldehyde molecules is not a distinctive feature of cold-flame oxidation (temperature range 205–240°), but can be observed at considerably lower temperatures (100–180°). This opened up the possibility of studying the mechanism of formation of excited formaldehyde molecules in model systems with a known radical composition.

The aim of the present work was to choose that one of the processes (I, II, III) which is actually responsible for chemiluminescence. As sources of free radicals of a definite kind, the following substances were used:

Fig. 1

Figure 1: Fig. 1

1. A source of $CH_3$ radicals—di-tert-butyl peroxide $(CH_3)_3COOC(CH_3)_3$—was obtained by the action of hydrogen peroxide on tert-butyl alcohol and was purified by distillation in vacuum. 2. Sources of $CH_3O$ radicals (8): a) methyl nitrate $CH_3ONO_2$—was obtained by nitration of methyl alcohol; b) methyl nitrite $CH_3ONO$—was obtained in an exchange reaction of isoamyl nitrite with methyl alcohol, and purified by repeated freezing; c) dimethyl peroxide $CH_3OOCH_3$—was obtained by the reaction of dimethyl sulfate with hydrogen peroxide, and purified by freezing. 3. A source of $CH_3O$- and OH-radicals (8)—methyl hydroperoxide $CH_3OOH$—was synthesized by the method of Rieche (11). An approximately 80% aqueous solution was purified by distillation in vacuum. The pure hydroperoxide was not isolated from the solution. Measurements of chemiluminescence were carried out on a photometric apparatus of high sensitivity, a description of which is given in (10).

The intensity of the light emitted in slow reactions is so small that the use even of a special light-intensity spectrometer (19) proves possible only in individual cases. Therefore, in the present work, to determine the spectral composition of the glow (and, consequently, to identify the excited formaldehyde), the following procedure was used. Under conditions in which, on the light-intensity spectrometer, it was possible to obtain

spectrum of formaldehyde (9), the emission spectrum was simultaneously recorded with a set of 10 light filters with a sharp short-wavelength cutoff. In Fig. 1 (curve 1), the points represent the result of the corresponding recalculation of the differences in the intensity of the light transmitted by two adjacent light filters. Curves 2 and 3 were obtained in an analogous way at a light intensity insufficient for recording the spectrum with a spectrograph. The differences between curves 1, 2, and 3 lie within the experimental error. Subsequently, the obtaining of curves of this type was considered proof of the formation of excited formaldehyde.

Fig. 1. Emission spectrum of excited formaldehyde, recorded with a set of light filters.
1 —50 mm $CH_3CHO$ + 47 mm $O_2$, $t = 182°$; 2 —50 mm $CH_3CHO$ + 35 mm $O_2$, $t = 182°$; 3 —50 mm $CH_3CHO$ + 35 mm $O_2$, $t = 121°$.

**Decomposition of methyl nitrate and methyl nitrite.** The assumption that chemiluminescence arises as a result of process (I) is based to a considerable extent on the results of the work of Gray (12-14), who found that the thermal decomposition of some alkyl nitrates and alkyl nitrites is accompanied by emission of light. Luminescence was observed at high temperatures (300–400°) under conditions characteristic of flame formation. The spectrum of formaldehyde was obtained in a stationary flame of the thermal decomposition of methyl nitrate. Apin, Hariton, and Todes ($^{15}$) studied the kinetics of the decomposition of methyl nitrate at 210–240° and did not observe luminescence. Steacie ($^{16}$) studied the decomposition of methyl nitrite ($CH_3ONO$) at 190–240° and likewise did not observe luminescence.

In the present work the decomposition of methyl nitrite (55 mm Hg) was carried out at 250°, and also that of methyl nitrate (40 mm Hg) at the same temperature. No luminescence could be detected, and only at 295° was an explosion of methyl nitrite observed, with a bright flash of light. The simplest interpretation of the facts listed is that the luminescence observed at high temperatures arises not in the act of disproportionation of the initially formed $CH_3O$ radicals, but in certain secondary reactions.

**Decomposition of dimethyl peroxide.** For an additional assessment of the possible role of reaction (I), thermal decomposition of dimethyl peroxide $CH_3OOCH_3$ was carried out, in which two $CH_3O$ radicals are formed in the primary step. The experiment showed that the decomposition of dimethyl peroxide (100 mm Hg) at 155° proceeds without luminescence, although the reaction, recorded from the pressure increase, proceeds rapidly. These experiments, as well as the experiments on the decomposition of methyl nitrate and methyl nitrite, make it possible definitely to reject elementary step (I) as a reaction leading to chemiluminescence.

**Joint decomposition of dimethyl and di-tert-butyl peroxides.** The joint decomposition of dimethyl peroxide and di-tert-butyl peroxide, which form methoxyl and methyl radicals, respectively, was carried out in order to check the possible role of process III in the excitation of chemiluminescence. In the experiments, a mixture of dimethyl peroxide (22 mm Hg) and di-tert-butyl peroxide (22 mm Hg) at 155° decomposed without luminescence, although the reaction proceeded rapidly. These experiments make it possible to exclude process III from the number of reactions leading to chemiluminescence.

**Decomposition of methyl hydroperoxide.** If luminescence arises in reaction (II), then it should be observed during the decomposition of $CH_3OOH$, in which $CH_3O$ and OH radicals are formed. Chemiluminescence was indeed observed in this reaction, beginning at 130°. At 175°, in the decomposition reaction of methyl hydroperoxide (10 mm Hg), a spectrum of formaldehyde was obtained. For an additional verification of the conclusion that excited formaldehyde is formed by reaction II, experiments were carried out on the joint decomposition of methyl hydroperoxide and dimethyl peroxide. Methyl hydroperoxide was first introduced into the reactor and a certain intensity of formaldehyde emission was established; then dimethyl peroxide was added, which itself does not give luminescence but increases the concentration of the $CH_3O$ radicals responsible for the luminescence. As was to be expected, at different ratios of the components and different temperatures, additions of dimethyl peroxide sharply increase the luminescence intensity, and the spectrum of the intensified emission proves to be the spectrum of formaldehyde. An analogous effect was observed when dimethyl peroxide was added to decomposing tert-butyl hydroperoxide.

**Effect of formaldehyde additions.** If excited formaldehyde is formed in a chemical reaction, and not as the result of energy transfer, then additions of formaldehyde should not lead to luminescence or intensify the observed luminescence. Addition (15 mm Hg) of formaldehyde to ditertiary butyl peroxide (15 mm Hg) decomposing at 108°, where a large amount of energy is released upon recombination of methyl radicals, does not lead to luminescence; and addition of formaldehyde to a system in which oxidative decomposition of ditertiary butyl peroxide is taking place (the same composition plus 2 mm Hg of oxygen), accompanied by chemiluminescence (emission of excited formaldehyde), does not lead to intensification of the luminescence. The participation of an energy-transfer process in the formation of excited formaldehyde is also rejected by the experiments of Gaydon [17]. Thus, excited formaldehyde is formed only in a chemical reaction.

The totality of the experiments performed makes it possible, with a high degree of certainty, to ascribe the formation of excited formaldehyde in cold flames and in other chemical reactions to the elementary process

$$\mathrm{CH_3O + OH \rightarrow H_2O + CH_2O^*}.$$

The advantage of this process in comparison with the others (I and III) is the larger thermal effect.

In the present work the question remains open as to the possibility of formation of excited formaldehyde in reactions of hydroxyl with other alkoxyl radicals according to reaction (4)

$$\mathrm{RCH_2O + OH \rightarrow ROH + CH_2O}.$$

The thermal effect of such reactions is close in magnitude to the thermal effect of the reactions (I) and (III) rejected by us, but it is unknown whether this characteristic is decisive in the present case.

Since the introduction into a chemical system of $CH_3O$ radicals in the form of readily decomposing dimethyl peroxide, hyponitrites, etc., presents no difficulty, the luminescence of formaldehyde may serve as a convenient indicator for detecting hydroxyl radicals. Obviously, conversely, hydroxyl may be an indicator for methoxyl (and possibly alkoxyl) radicals.

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