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Abstract

Full Text

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FORMATION OF EXCITED FORMALDEHYDE MOLECULES DURING LOW-TEMPERATURE OXIDATION OF ACETALDEHYDE

(Presented by Academician V. N. Kondrat' ev on 11 VI 1962)

In work (^{1}) the existence of chemiluminescence in the reaction of low-temperature gas-phase oxidation of acetaldehyde was reported. In contrast to previous observations (see, for example, (^{2})), according to which chemiluminescence exists in the temperature region adjacent to the region of cold flames (above 200°), in work (^{1}) luminescence was detected at much lower temperatures. The experiments showed that already at 100° the luminescence is sufficiently intense and the kinetics of the change in its intensity can be measured quite reliably. Observation of luminescence in a low-temperature reaction became possible owing to the use of a highly sensitive photometric method (^{3}).

The present work was undertaken in order to determine the chemical nature of the luminescing particles in the acetaldehyde oxidation reaction. It is shown in the work that the luminescence in this reaction is associated with the formation of excited formaldehyde molecules. As is known, formaldehyde is a source of radiation of cold flames arising during the oxidation of various compounds ($^{4-6}$) (hydrocarbons, ethers, aldehydes).

Fig. 1. Kinetic curve of chemiluminescence in the acetaldehyde oxidation

reaction. Temperature 182°, acetaldehyde pressure 50 mm Hg, oxygen pressure 47 mm Hg.

As a result of a number of kinetic studies ([7–9]), it has apparently become generally accepted that excited formaldehyde is formed in reactions of alkoxy radicals, and the suggestion has been made that formaldehyde luminescence may account for chemiluminescence in those reactions in which alkoxy radicals are undoubtedly formed: decomposition of various peroxide compounds ([11]), alkyl nitrites and alkyl nitrates ([12,13]), and low-temperature oxidation of hydrocarbons ([14]).

Possible reactions leading to the formation of excited formaldehyde molecules are considered, for example, to be the following:

$$CH_3O + CH_3O \rightarrow CH_3OH + CH_2O^* \tag{1}$$

$$RCH_2O + OH \rightarrow ROH + CH_2O^*, \tag{2}$$

$$RCH_2O + R' \rightarrow RR' + CH_2O^*. \tag{3}$$

(This does not exclude other possibilities for the formation of CH_2O^*, for example in systems containing atomic oxygen ([10]).)

The suggestion that excited formaldehyde molecules are formed in reactions of alkoxy radicals appears plausible. However, it has not yet been proved by direct experiments. In the case of acetaldehyde oxidation, the mechanism of which has been studied in detail ([18]), luminescence of formaldehyde could also be expected, since the formation of methoxy radicals in this reaction is very probable ([15]). On the other hand,

on the other hand, it was impossible to exclude the possibility of formation of other electronically excited molecules, for example of such a strongly fluorescing substance as diacetyl. This possibility, in particular, was noted in work (16).

Thus, determination of the source of radiation in the slow gas-phase oxidation of acetaldehyde is important not only for clarifying the relation between the kinetics of this reaction and chemiluminescence, but also for solving the more general question of the nature of luminescence in gas-phase reactions proceeding with the participation of oxygen or oxygen-containing compounds. In order to identify the luminescing particles, in the present work spectra were recorded of the chemiluminescence accompanying the oxidation of acetaldehyde. For this purpose a high-aperture spectrometer developed by R. F. Vasil' ev, S. M. Petukhov, and T. N. Zhuchkova was used.

Description of the apparatus in which the reaction was carried out is given in work (1). The chemiluminescence spectrum was recorded in a reaction carried out at 182°. For the experiments, the following mixture composition was chosen:

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

50 mm Hg of acetaldehyde and 47 mm Hg of oxygen. In a mixture of this composition the chemiluminescence intensity was highest.

Fig. 2. *A*—chemiluminescence spectrum in the acetaldehyde oxidation reaction. Spectral slit width 4 mμ.
B—scheme of the fluorescence spectrum of formaldehyde $^{(17)}$

Fig. 3. Kinetic curves of chemiluminescence in the acetaldehyde oxidation reaction, recorded with a spectrometer at different wavelengths (mμ). 1—λ = 510, 2—λ = 425, 3—λ = 370 mμ. Spectral slit width ~ 20 mμ. Mixture composition: 50 mm Hg acetaldehyde and 35 mm Hg oxygen.

The kinetic curve of chemiluminescence is shown in Fig. 1. As can be seen from the figure, the curve has two maxima of luminescence. At the second maximum there is a section on which the luminescence intensity changes little with time. In this section the spectrum shown in Fig. 2 was recorded. The spectrum was recorded with a slit width of 2 mm, which corresponds to a spectral width of ~ 4 mμ. In Fig. 2, for comparison, a scheme of the fluorescence spectrum of formaldehyde, taken from work $^{(17)}$, is presented. It is evident from the figure that the positions of the bands and the distribution of intensities practically coincide. The maximum of luminescence corresponds to the broadest band c_0 of the fluorescence spectrum. Thus, from comparison of the spectra it follows that in the acetaldehyde oxidation reaction the luminescing particles are excited molecules of formaldehyde. The formation of formaldehyde in the reaction products was also detected by chemical analysis.

In view of the fact that the luminescence intensity decreased strongly when the temperature was lowered, we could not record spectra at lower temperatures. However, with the aid of light filters it was shown that the position of the luminescence maximum and the general form of the spectrum do not change in the temperature range 180—120°. From this it may be concluded that even at temperatures below 180° the second luminescence maximum is associated with formaldehyde. To clarify the nature of the chemiluminescence in the region of the first maximum (see Fig. 1), kinetic curves of luminescence (at 182° and mixture composition 50 mm CH_3CHO + 35 mm O_2) were recorded at three fixed values-

wavelengths (370, 425, and 510 mμ) corresponding to the edges and the middle of the observed spectrum. In setting up these experiments it was assumed that the ratio between the luminescence intensities at the first and second maxima would depend on wavelength if different particles were luminescing.

The experiments showed that the intensity ratio remains practically unchanged (Fig. 3). Consequently, in the region of the first maximum as well, the luminescence is associated with excited formaldehyde molecules, which apparently are the only emitters in the reaction under study.

Using the oxidation of acetaldehyde as an example, it is evident that reactions leading to the formation of excited formaldehyde molecules are not a distinctive feature of cold flames, but occur already at considerably lower temperatures.

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REFERENCES

1. L. M. Postnikov, V. Ya. Shlyapintokh, V. F. Shuvalov, ZhFKh, **36**, No. 10, 2284 (1962).
2. M. Pretre, Bull. Soc. chim. France, (4), **51**, 1132 (1932).
3. R. F. Vasil' ev, O. N. Karpukhin, V. Ya. Shlyapintokh, ZhFKh, **35**, 461 (1961).
4. V. N. Kondratjev, Zs. Phys., **63**, 322 (1930).
5. V. N. Kondrat' ev, *Kinetics of Chemical Gas Reactions*, Publishing House of the Academy of Sciences of the USSR, 1958.
6. A. G. Gaydon, *Spectroscopy of Flames*, IL, 1957.
7. J. Bardwell, C. N. Hinshelwood, Proc. Roy. Soc., A **205**, 375 (1951).
8. A. D. Walsh, Trans. Farad. Soc., **43**, 297 (1947).
9. A. G. Gaydon, Proc. Roy. Soc., A **230**, 1 (1955).
10. H. C. Bailey, R. G. W. Norrish, Proc. Roy. Soc., A **212**, 311 (1952).
11. E. J. Harris, Proc. Roy. Soc., A **173**, 126 (1939).
12. P. Gray, Proc. Roy. Soc., A **200**, 114 (1949).
13. P. Gray, Chem. Rev., **59**, 239 (1959).

14. M. Lucquin, J. Chim. Phys., **55**, 827 (1958).

15. M. Niclause, Thèse, Nancy, 1953.

16. H. W. Holden, K. O. Kutschke, Canad. J. Chem., **39**, 1952 (1961).

17. G. Herzberg, K. Franz, Zs. Phys., **76**, 720 (1932).

18. N. M. Emanuel' , article in the collection *Kinetics of Chain Oxidation Reactions*, Publishing House of the Academy of Sciences of the USSR, 1950, p. 185.

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