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Abstract

Full Text

PHYSICAL CHEMISTRY

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IGNITION OF METHANE MIXTURES IN SHOCK WAVES

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High-temperature oxidation of hydrocarbons of the methane series reveals an interesting feature: with increasing temperature, the ignition delays of air mixtures for all the fuels studied ⁽¹⁾ tend toward the ignition delays of methane mixtures. In the present work, therefore, the ignition of methane mixtures with oxygen and various inert diluents was studied in detail, with the aim of determining the dependence of ignition delays on pressure and on the concentration of the components.

Ignition of the mixtures was carried out in reflected shock waves in the shock tube described in ⁽²⁾. The course of the process was monitored by means of a pressure transducer and a two-electrode ionization probe, located on the end flange of the tube, a photomultiplier, and continuous slit schlieren photography of the wave motion. The ignition delays were determined mainly from the ionization current. The onset of the intense reaction was taken to be the moment at which the oscilloscope trace recording the ionization current broke away from the zero line. The choice of this recording method was due to the fact that the delays in this case were determined more sharply; moreover, it gave good agreement with methods based on recording the photocurrent or on Toeppler photography. Ignition delays determined from pressure records were almost always somewhat overestimated, which is connected with the lower sensitivity of the pressure transducer and with the small change in pressure during explosion.

The parameters of the mixture behind the reflected shock waves were calculated by the method described in ⁽¹⁾. For methane, enthalpy tables exist only up to temperatures of 1200°C. For higher temperatures we calculated the enthalpies on the assumption that methane is a rigid rotor and that the vibrations in the molecule are harmonic. The measured and calculated pressures in the reflected wave agree to within $\pm 10\%$ over a fairly wide range of Mach numbers for almost all the mixtures investigated. Unfortunately, measurements of the gas parameter most important for the chemical reaction—the temperature—were not carried out. Since, as a consequence of nonideality of the flow in the shock tube, the character of reflection of shock waves in gases with different thermodynamic properties is different, it is quite probable that the temperature behind the reflected wave will not correspond exactly to the calculated value. Although, as

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

direct measurements show, these deviations cannot be very large.

The first series of experiments was carried out in order to determine the influence of pressure on the ignition delays of stoichiometric mixtures of methane with air. The temperature coefficient of the ignition delays was not constant over the entire temperature range of the measured times. Very large for low temperatures and long times, it decreases for times shorter than $\sim 20 \mu\text{sec}$, and the decrease is the greater the lower the initial pressure. In the range of times longer than $20 \mu\text{sec}$, the ignition delays igni-

can be expressed, with a rather large scatter, by the equation $\tau = 2 \cdot 10^{-16} P^{-1.2} \exp(85 \text{ kcal/mole}/RT) \cdot \text{sec}$, where the pressure P is expressed in atmospheres (the range of its variation is 3–90 atm). For times shorter than $20 \mu\text{sec}$, $\tau = 2 \cdot 10^{-8} P^{-0.6} \exp(26 \text{ kcal/mole}/RT) \cdot \text{sec}$. The temperatures in the formulas are equilibrium temperatures. If it is assumed that during the reaction time the vibrational degrees of freedom in nitrogen do not have time to become excited (which may well occur at low pressures), then the ignition delays shift into the region of higher temperatures (see Fig. 1, dashed line) by approximately 100° .

Fig. 1. Dependence of the logarithm of the ignition delays on reciprocal temperature: **a** –mixture 10% CH_4 + 90% air, $P_0 = 50 \text{ mm Hg}$; **b** –mixture 10% CH_4 + 20% O_2 + 70% Ar, $P_0 = 100 \text{ mm Hg}$.

Fig. 2. Dependence of the logarithm of ignition delays on reciprocal temperature: **a** –mixture 10% CH_4 + 90% air, $P_0 = 12.5 \text{ mm Hg}$; **b** –mixture 10% CH_4 + 90% air, $P_0 = 50$; **c** –mixture 10% CH_4 + 90% O_2 , $P_0 = 12.5$; **d** –mixture 10% CH_4 + 90% O_2 , $P_0 = 50 \text{ mm Hg}$.

To determine the influence of the concentrations of the substances participating in the reaction on the ignition delays, we carried out experiments with mixtures $\text{CH}_4 + 2\text{O}_2$, 81% CH_4 + 20% O_2 , 10% CH_4 + 90% O_2 , and 2% CH_4 + 98% air. Unfortunately, because of the rather large scatter of the experimental points and because of the doubts that arose in calculating the temperature and were associated with the different character of shock-wave reflection in gases with different thermodynamic properties, it was not possible to obtain quantitative data on the dependence of the ignition delays on the concentrations of the reactants.

It can, however, be stated with certainty that strong dilution of the mixture with oxygen lowers the temperature coefficient of the ignition delays in the range of

times greater than $20 \mu\text{sec}$ (see Fig. 2). Strong dilution of the mixture with methane slightly shortens the ignition delays in comparison with air mixtures at $\tau > 20 \mu\text{sec}$. The temperature coefficient of the ignition delays in this case is somewhat greater than for air mixtures, and the ignition delays did not depend on pressure when the latter was varied by a factor of 10.

A comparison of the ignition delays of mixtures diluted with nitrogen and argon shows that mixtures diluted with nitrogen have shorter ignition delays, although the thermal theory of explosion would lead one to expect the opposite picture. The greater the degree of dilution, the greater this discrepancy. The latter can probably be associated either with the different effectiveness of nitrogen and argon in transferring energy in collisions, or with different degrees of deviation of the temperature behind the reflected wave from the calculated values.

For mixtures of methane with argon there is a fairly extensive body of material on the study of the thermal decomposition of CH_4 in shock tubes^(3,5). The decomposition reaction is monomolecular, with an activation energy of about 90 kcal/mole. Assuming that the chain length of the oxidation reaction under our conditions is close to unity and that the reaction with which the oxidation process begins is methane decomposition, we calculated the value of the adiabatic ignition delay, using the experimental values of the decomposition constant for a stoichiometric mixture of methane with argon-air and a mixture of 5% ($\text{CH}_4 + 2\text{O}_2$) + 95% air. Within the scatter of the experimental points, the calculated ignition-delay values coincide with those measured by us.

Thus, it may be said that for mixtures with an excess of CH_4 or strongly diluted with an inert gas, at pressures on the order of atmospheric pressure, the rate of the oxidation reaction at the initial stage is determined by the rate of thermal decomposition of methane. It is quite possible that the chain length of oxidation and the role of the initiation reaction $\text{CH}_4 + \text{O}_2 = \text{HO}_2 + \text{CH}_3$ increase with increasing oxygen concentration and pressure and with decreasing temperature. The possibility of competition between chain oxidation initiated by the reaction $\text{CH}_4 + \text{O}_2 = \text{HO}_2 + \text{CH}_3$ and radical oxidation with thermal decomposition of methane was pointed out in work⁽³⁾ at lower temperatures and for rich mixtures.

The region of ignition delays shorter than $20 \mu\text{sec}$ proved very interesting. Unfortunately, it has not yet been clarified whether the decrease in the temperature coefficient of the ignition delays determined by us in this region is a consequence of a change in the course of the reaction itself or of some other causes.

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CITED LITERATURE

1. S. M. Kogarko, A. A. Borisov, *Izv. AN SSSR, OKhN*, 1960, No. 8, 1348.
2. A. A. Borisov, S. M. Kogarko, A. V. Lyubimov, *Zhurn. prikl. mekh. i tekhn. fiz.*, No. 3, 175 (1960).
3. G. B. Skinner, R. A. Ruehrwein, *J. Phys. Chem.*, 63, No. 10, 1736 (1959).
4. G. I. Kozlov, V. G. Knorre, *Inzh. fiz. zhurn.*, 4, No. 7, 11 (1961).
5. V. Kevorkian, C. E. Heath, M. Boudart, *J. Phys. Chem.*, 64, No. 8, 964 (1960).

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

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