PHYSICAL CHEMISTRY

A. I. SERBINOV, Ya. K. TROSHIN

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. I. SERBINOV, Ya. K. TROSHIN
and Corresponding Member of the Academy of Sciences of the USSR K. I. SHCHELKIN

KINETIC PARAMETERS OF THE PROCESSES OF DETONATION, AUTOIGNITION, AND ISOTHERMAL OXIDATION OF BENZENE

Attempts are known in the literature to use gas detonation to obtain data on the rate of combustion of homogeneous mixtures of fuel with oxidizer. Quite recently, thanks to the development of a schlieren method for studying the structure of the gas-detonation zone ([1]), and also after the instability of the detonation wave had been clarified ([2]), it became possible to estimate the time of the chemical reaction in the gas-detonation zone. The linear size of the inhomogeneity, recorded in the form of an imprint on the weakly smoked end of a tube, is related by a simple relation to the magnitude of the ignition delay τ in a plane shock wave

$$\tau = \frac{\Delta y}{2D\sqrt{\frac{2\gamma(\gamma-1)}{\gamma+1}}}, \tag{1}$$

where: Δy is the mean linear size of the imprint, D is the velocity of propagation of the detonation, and $\gamma = \frac{c_p}{c_v} \simeq 1.4$.

By measuring the mean magnitude of the inhomogeneities at different detonation-wave velocities, one can calculate the ignition delay at different temperatures in a plane shock wave.

In Fig. 1, in coordinates $\lg\tau - \frac{1}{T}$, the results of measurements for a benzene-oxygen mixture are presented. Attention should be drawn to the extremely small values of the ignition delay in the detonation wave, lying within the limits of a microsecond and fractions thereof.

The very small ignition delays measured for the first time are comparable with the time of vibrational excitation of such diatomic molecules as oxygen ([4]) and carbon monoxide (5), measured at temperatures of 2500 and 5000°K, respectively, i.e., at a considerably higher temperature than at the compression front of gas detonation.

It is evident from Fig. 1 that all the points lie well on a straight line satisfying the equation

$$\tau = A' e^{\frac{E_k}{RT}} \tag{2}$$

with an apparent activation energy E_k of 37 kcal/mole and a pre-exponential factor $A' = 10^{-11.2}$ sec.

Table 1 compares all the values of E_k known to us, determined by various authors for mixtures of benzene with air or oxygen under conditions of thermal explosion and during isothermal oxidation. A large scatter is clearly seen in the values of the apparent activation energy determined by different authors.

However, if all the primary experimental values of τ measured by the authors are plotted on one graph, then, as is seen from Fig. 2, all the points, irrespective of the method of work, lie in a narrow band. If, in addition, theoretical limiting straight lines are constructed as was done in work (16)

Table 1

Values of the apparent activation energy E_k for thermal explosion and isothermal oxidation of benzene mixtures with air or oxygen, reported by various authors

E_k, kcal/mole	Designation in Fig. 2	Experimental method	Source
37		τ during detonation	Authors of the present paper
60		τ in a shock tube	Kogarko and Borisov (6)
–		τ when benzene is injected into a bomb with heated air at a pressure of 30 atm	Serbinov (7)

E_k, kcal/mole	Designation in Fig. 2	Experimental method	Source
60 and 20		τ when a benzene–air mixture is admitted into a heated vessel, $p_0 = 4$ ata, $\alpha = 0.65$	Sokolik, Gen, and Yantovskii (8)
–		τ during ignition of benzene droplets in a heated open vessel	Serbinov
50		From the time of isothermal oxidation of 10% benzene	Fort and Hinshelwood (9)
78		From the time of isothermal oxidation of 10% benzene. From the maximum oxidation rate	Ambé (10)
56		τ at the autoignition temperature	Zabetakis et al. (11)
–		Same	Jackson (12)
44		τ in an adiabatic apparatus	Taiman (13)
61		Same	Yost (14)
–		» »	Taylor et al. (15)

it is seen that all the points with ignition-delay values from tens of seconds down to tenths of a microsecond (a change of more than 8 orders of magnitude) fit well between the limiting straight lines with activation energies of 58 and 62 kcal/mole; i.e., all the experiments are described by the Arrhenius equation

Fig. 1. Temperature dependence of the ignition delay of a benzene-oxygen mixture in a detonation wave

Figure 1: Fig. 1. Temperature dependence of the ignition delay of a benzene-oxygen mixture in a detonation wave

Fig. 2. Generalized temperature dependence of the time of isothermal oxidation and ignition delay of benzene in air or oxygen

Figure 2: Fig. 2. Generalized temperature dependence of the time of isothermal oxidation and ignition delay of benzene in air or oxygen

$$\tau_{\text{sec}} = 10^{-14.6} e^{60\,000/RT} \tag{3}$$

with a single value for all experiments, $E = 60 \pm 2$ kcal/mole, for a pre-exponential factor $A = 10^{-14.6}$ sec, adopted as identical for all molecules with a frequency of valence vibrations of the order of 1000–1700 cm^{-1} (16).

It should be noted that the experimental points joined by the solid straight line with $E_k = 44$ kcal/mole and the dashed straight line with $E_k = 61$ kcal/mole, plotted from the data of Taiman (13) and Yost (14), respectively, as well as two points taken from the work of Taylor et al. (15), fall completely outside the general dependence (shifted into the region of low temperatures by almost 300°C). The reason for such a deviation is apparently the presence, in the cylinder of the adiabatic apparatus of Taiman and Yost, of lubricating oil, which caused ignition at such a low temperature. In Taylor' s adiabatic apparatus, in which graphite lubricant was used, ignition of the benzene-air mixture was caused by the piston striking the retaining ring, esta—

Fig. 1. Temperature dependence of the ignition delay of a benzene-oxygen mixture in a detonation wave.

Fig. 2. Generalized temperature dependence of the time of isothermal oxidation and ignition delay of benzene in air or oxygen

renewed inside the combustion chamber for fixing the compression ratio. It is clear that, when the piston strikes, the temperature of the mixture near the stop ring must be considerably higher than the temperature calculated by the authors for the central part of the compression chamber. In Fig. 2, in the region $\lg \tau = 2.5$, the primary data of Fort and Hinshelwood (9) on the time of isothermal oxidation of 10% benzene in a mixture with oxygen are also plotted. As can be seen from the graph, their experiments, represented by five points, coincide with our limiting straight line at 62 kcal/mole.

The uppermost straight line was constructed by us by recalculating the data of Ambé (10), who investigated the slow oxidation of benzene in its mixture with oxygen. To determine the oxidation time of 10% benzene plotted on the graph, we used the reaction-rate constant for oxidation with the degree of conversion noted by the author. The large slope obtained for this straight line, corresponding to an apparent activation energy $E_k = 78$ kcal/mole, can be explained by a progressive increase in the reaction rate owing to slight self-heating of the mixture, the greater the higher the initial temperature of the experiment. Therefore, at the very lowest temperatures, where self-heating was minimal, the points deviate least of all from the mean activation energy, equal to 60 kcal/mole.

Thus it may be asserted that all the experimental data, with the exception of the obviously inaccurate experiments of Teichmann (^{13}) and Taylor (^{15}), indicate a value of the activation energy for benzene of 60 kcal/mole, with a pre-exponential factor of the theoretical magnitude for monomolecular reactions.

Returning to the results of our measurements of τ in the detonation wave, it should be noted that the experimental points at the smallest values of τ begin to deviate from the general dependence $E = 60$ kcal/mole in such a way as if some factor retarding the ignition reaction had appeared. Such a factor may be assumed to be the time of vibrational relaxation of the benzene molecule. Under this assumption, from the ignition lag in the detonation wave one can estimate the time of excitation and redistribution over the bonds of the energy of valence vibrations in the benzene molecule under detonation conditions.

For this purpose, from the ignition lag measured at a given temperature in the detonation wave (equation 2) it is necessary to subtract that τ which would have occurred at the same temperature if the time of vibrational excitation of the benzene molecule did not retard the ignition process (equation 3), i.e., to calculate from Fig. 2, at the given value of $\frac{1}{T}$, the difference between the ordinates of two straight lines—the experimental one with $E_k = 37$ kcal/mole and the extrapolated straight line with $E = 60$ kcal/mole, with the theoretical value of the pre-exponential factor.

In spite of the linear size of the difference of ordinates increasing because of the logarithmic scale, the absolute magnitude of the time of excitation and redistribution of the energy of valence vibrations of the benzene molecule under detonation conditions may be estimated at 0.3–0.5 μsec.

The authors express their gratitude to Academician V. N. Kondrat' ev for discussion of the work and valuable comments.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
24 III 1962

REFERENCES CITED

1. Yu. N. Denisov, Ya. K. Troshin, DAN, **125**, 110 (1959).

2. B. P. Volin, Ya. K. Troshin, G. I. Filatov, K. I. Shchelkin, *Zhurn. prikl. mekh. i tekhn. fiz.*, No. 2, 78 (1960).
3. K. I. Shchelkin, ZhETF, **36**, 600 (1959).
4. Morton Camac, *J. Chem. Phys.*, **34**, 448 (1961).
5. D. L. Matthews, *J. Chem. Phys.*, **34**, 639 (1961).
6. S. M. Kogarko, A. A. Borisov, *Izv. AN SSSR, OKhN*, 1960, No. 8, 1348.
7. A. I. Serbinov, *Combustion in Transport Piston Engines*, Izd. AN SSSR, 1951, p. 267.
8. A. S. Sokolik, M. Ya. Gen, S. A. Yantovskii, ZhFKh, **21**, 1263 (1947).
9. R. Fort, C. N. Hinshelwood, *Proc. Roy. Soc.*, A**127**, 218 (1930).
10. J. Amiel, C. R., **196**, 1122 (1933); **197**, 984 (1933).
11. M. G. Zabetakis, A. L. Furno, G. W. Jones, *Ind. and Eng. Chem.*, **46**, 2173 (1954).
12. J. Jackson, *Ind. and Eng. Chem.*, **43**, 2869 (1951).
13. H. Teichmann, *Zs. f. Elektrochem.*, **47**, 297 (1941).
14. V. Iost, *Explosions and Combustion in Gases*, Moscow, 1952, p. 526, Fig. 222.
15. C. F. Taylor, E. S. Taylor et al., *SAE Quart. Trans.*, **4**, 232 (1950).
16. A. I. Serbinov, DAN, **129**, 627 (1959).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.