Mechanism of Autoignition in Benzene-Air Mixtures

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ALTHOUGH considerable research has been done on the slow oxidation of benzene, the rapid autoignition reactions occurring at higher temperatures and pressures have not been thoroughly investigated. The present work on benzene-air autoignition indicates that this reaction can be approximately described by a second-order rate equation with low activation energy, and that the benzene molecule degrades to acetylenes and oxidized products.

The first experiments were conducted with a rapid compression machine (2) to obtain an expression relating the rate of reaction to the temperature and partial pressures of the reactants. The machine was developed under the direction of F. A. F. Schmidt, Institut für Wärmetechnik und Verbrennungsmotoren, Technische Hochschule, Aachen. Homogeneous fuel-air mixtures were compressed rapidly to temperatures and pressures on the order of 800° K. and 20 atm. The succeeding combustion occurred at constant volume in a few milliseconds, while pressure was continuously recorded. An experiment to detect the reaction products of partial autoignition of benzene was carried out in a single-cylinder, variable-compression-ratio CFR engine (2), from which the spark plug had been removed and which promoted reaction by compressing the premixed charge to a high temperature and pressure of about 900° K. and 40 atm. The reaction was quenched by rapid expansion of the gases during the downward stroke of the piston, and a sample of the partially reacted gases removed from the exhaust system was analyzed in a mass spectrometer. The motored engine work and gas analysis were done in the Engine Fuels and Mass Spectrometry Sections of the National Bureau of Standards.

DETERMINATION OF RATE EQUATION

If the benzene-oxygen reaction followed a second-order rate law, it could be described by an expression such as:

$$-\frac{d[B]}{dt} = k[B][O_2]e^{-E/RT} \qquad (1)$$

where [B] is benzene concentration, $[O_2]$ is oxygen concentration, t is time, k is the reaction velocity constant, and the exponential factor contains the activation energy, E, the universal gas constant, R, and the absolute temperature, T.

A corresponding empirical formula for direct correlation with experimental data from the rapid-compression machine can be written as:

$$-\frac{dp_B}{dt} = A'p^2 x_B x_{O_2} e^{-b/T} \qquad (2)$$

where p is the total pressure in kilograms per square centimeter, x_B and x_{O_2} are mole fractions of benzene and oxygen, t is time in seconds, T is temperature in ° K., and A' and b are empirical constants (11).

The use of this equation involves a number of assumptions:

1. The process is adiabatic and heat losses to the walls are negligible. (This approximation results in little error over the comparatively short period before combustion has gone to equilibrium.)

2. The benzene molecule can continue to exist at all temperatures encountered, and its specific heat can be extrapolated to temperatures above 1500° K. (At higher temperatures this assumption probably becomes untenable, but the benzene concentrations have become small and the resultant specific heat of the total mixture will be only slightly affected.)

3. Each incremental pressure rise is caused by the release of heat at constant volume corresponding to complete combustion of a small portion of the benzene to carbon dioxide and water. (Subsequent discussion of the chemical reaction shows that most of the reacted benzene goes to end products rapidly; errors due to this assumption will be large at the higher temperatures reached near the end of combustion.)

4. Combustion continues until all carbon and hydrogen in the original fuel are in the form of carbon dioxide and water; the back reactions are neglected. (The temperature rise will not be as high as predicted during the later parts of the reaction.)

5. The total number of moles in the combustion chamber does not change during the reaction. (The calculated probable increase would be 1.5% or less, which lies within the accuracy of experimental measurement.)

6. The reaction is homogeneous. [During the earliest or initiating phases of autoignition this assumption may be essentially valid. There is photographic evidence, however, that the subsequent reaction may progress via the growth of multiple flame nuclei (9).]

The temperature and pressure at the end of compression (which corresponds to the beginning of the induction period) were computed isentropically from the initial state, the compression ratio, and the mean specific heat ratio of the mixture. The subsequent increase in temperature and total pressure caused by complete combustion at constant volume of a fraction Δp_B of the benzene was computed, using the heat of combustion of benzene and the specific heat of the mixture. The temperature and pressure were then plotted as a function of the quantity of fuel burned for the cases of stoichiometric and 0.5 stoichiometric.

A series of experiments was made at constant compression pressure and varying compression temperature, and the time delay, τ, to the first detectable pressure rise was measured in each case. The logarithm of the delay was plotted against the reciprocal temperature; the slope of the straight line connecting the points is equal to constant b in Equation 2. This procedure is equal to substituting temperature and delay values from any two experiments into the formula

$$b = \frac{\ln \tau_2/\tau_1}{1/T_2 - 1/T_1} \qquad (3)$$

The slope has a value of 5840° K., which corresponds to an apparent activation energy of 11.6 kc.

The time required to burn the first increment of fuel Δp_B can be determined as a function of A' from Equation 2, when the values derived for b and the mean temperature, pressure, and composition of the mixture during this part of the reaction are substituted in the equation. This procedure is repeated with successive increments, and p_B is replaced by the corresponding computed total pressure, producing a curve of pressure vs. $A't$.

When the calculated pressure curve for stoichiometric mixture was plotted on the same pressure scale as an experimental pressure curve, and the time scale was adjusted to give a coefficient, A', of 0.179×10^6, a reasonable agreement of the two curves was obtained, particularly in the early stages of reaction (Figure 1). When the same A' was applied to the theoretical curve for a 0.5 stoichiometric mixture, it approximated the corresponding experimental curve.
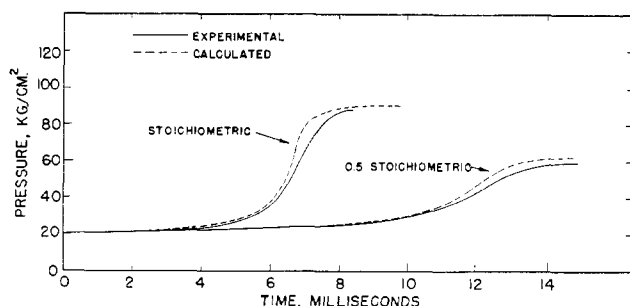

Figure 1. Pressure-time diagrams of benzene autoignition

Differences between the theoretical and experimental curves become increasingly large starting at about the point where the temperature and pressure are double their initial values. The discrepancies are probably due to the simplifying assumptions used for calculating the theoretical curve. Each of the first four assumptions has the effect of predicting a reaction rate which is too high by an amount that increases with increasing temperature (and decreasing partial pressure of unburned fuel).

J. C. Livengood has shown by flame photographs that the reaction of benzene may proceed by propagation of flame fronts outward from one or more ignition centers. Under these circumstances the rate of pressure rise should be a direct function of total area of the flame front, as appears to be the case in the MIT photographs. If the assumption of reaction homogeneity is discarded, the calculated apparent activation energy would apply only to the reactions initiating the first flame nucleus. Both the initiating and propagating mechanisms, however, would appear to follow the bimolecular rate law.

DETERMINATION OF REACTION PRODUCTS

A 0.5 stoichiometric benzene-air mixture was compressed in the motored engine at 900 r.p.m. to a temperature and pressure just below that which caused autoignition to occur. The corresponding peak compression temperature and pressure were on the order of 900° K. and 40 atm. Products expanded into the exhaust were collected in an evacuated sample bottle, separated into two fractions at liquid nitrogen temperature, and analyzed mass spectrometrically; 1.5% of the benzene had decomposed under these conditions. The products are listed in Table I.

DISCUSSION

Perhaps the most striking feature of this degradation pattern is that, although only 1.5% of the fuel molecules had decomposed, 73% of the carbon atoms and 55% of the hydrogen atoms involved had already completely oxidized to carbon dioxide and water. The most difficult step in the reaction is evidently an early one; once the molecule has been attacked and the ring destroyed, the subsequent reactions are apparently very rapid.

As no phenyl derivatives were detected, it appears that breaking of the ring occurs very shortly after the first attack on the molecule. This is in direct contrast to the pattern found in slow oxidation experiments (1, 3, 5, 6), where phenol and often quinone or hydroquinone were found in sizable quantities. The apparent

activation energy of the over-all reaction was found to be about 11.6 kcal. in the present work; values of over 50 kcal. in the slow oxidation experiments suggest a considerable difference in the free-radical mechanisms in the two cases.

Once the benzene molecule has been attacked, degradation is rapid and apparently progresses via a splitting of the aromatic nucleus and decomposition into two- and four-carbon acetylenes. No obvious mechanism suggests itself by which formaldehyde, methanol, carbon dioxide, and water may be formed. Ferguson and Broida, however, found these as well as other partially oxidized compounds among the combustion products of acetylene-atomic oxygen flames (4). It is therefore conceivable that the oxygenated products of benzene combustion arise from oxidation of acetylenic intermediates.

Porter (10) has suggested that carbon formation may occur via some very rapid mechanism involving the polymerization of acetylene. In light of the present evidence that benzene decomposes to acetylenes during the combustion process, this scheme appears plausible for carbon formation from benzene and perhaps from the other aromatics. Evidence for the decomposition and carbon formation from benzene via acetylenes was published by Ingold and Lossing (7), who studied benzene pyrolysis products with a mass spectrometer. At the lowest temperature reported, acetylene and butadiyne were the most prevalent degradation products containing carbon. As the temperature was raised, butadiyne disappeared and acetylene concentration decreased rapidly as the amount of carbon formed increased.

Table I. Degradation Products of Benzene Oxidation

(1.5% of benzene decomposed)

Component	Moles of Component / Mole of benzene decomposed	Fraction of Carbon from Decomposed Benzene	Fraction of Hydrogen from Decomposed Benzene
1-Butene-3-yne	0.10	0.07	0.07
Butadiyne	0.09	0.06	0.03
Acetylene	0.17	0.06	0.06
Methanol	0.38	0.06	0.25
Formaldehyde	0.11	0.02	0.04
Carbon dioxide	4.36	0.73	..
Carbon monoxide	Trace	..	..
Water (by difference)	1.60	..	0.55
Total	6.81	1.00	1.00

In summary, the over-all reaction in benzene autoignition at high temperatures and pressures can be described by a second-order rate equation with an apparent activation energy of about 11.6 kcal. The reaction seems to follow an entirely different course from that observed in low-temperature slow oxidation; 2- and 4-carbon acetylenes are the only hydrocarbon intermediates found. The carbon dioxide, water, methanol, and formaldehyde detected may be oxidation products of acetylenes.

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