É. A. BLYUMBERG, A. D. MALIEVSKII

and Corresponding Member of the Academy of Sciences of the USSR N. M. EMANUEL’

1961

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

É. A. BLYUMBERG, A. D. MALIEVSKII
and Corresponding Member of the Academy of Sciences of the USSR N. M. EMANUEL’

CRITICAL PHENOMENA IN THE LIQUID-PHASE OXIDATION OF BUTANE IN BENZENE

The high efficiency of methods for oxidizing low-molecular hydrocarbon gases in the liquid phase (1,2) has drawn interest to the use of inert solvents, which make it possible to preserve a liquid-phase system at elevated temperatures and thereby to ensure a high reaction rate. For the process of oxidizing liquefied butane, acetic acid—being the principal product of the reaction—can serve as such a solvent (3,4).

Fig. 1. **I** —kinetic curves for the accumulation of acetic acid during the oxidation of liquefied butane in benzene at 170° and a pressure of 50 atm: *a*—$\gamma_{\text{init}} \leq 0.4$, *b*—$\gamma_{\text{init}} = 0.49$, *v*—$\gamma_{\text{init}} = 0.61$, *g*—$\gamma_{\text{init}} = 0.92$; **II** —dependence of the amount of acetic acid formed in 2 hours of reaction on γ_{init} under the same conditions; **III** —change in γ with reaction time at 170° and a pressure of 50 atm.

In the present work, a study was carried out of the oxidation of butane in benzene, in the course of which a distinctive kinetic behavior of this solvent was established. It was found that the reaction rate and the maximum yields of the products of liquid-phase oxidation of butane in benzene depend on the ratio of the concentrations of butane and benzene $\gamma = [\mathrm{RH}]/[\mathrm{C_6H_6}]$. This dependence has a clearly pronounced critical character. There exists a certain value of the ratio $[\mathrm{RH}]/[\mathrm{C_6H_6}] = \gamma_{\text{cr}}$, below which butane oxidation does not proceed at all, while above it an ordinary autocatalytic reaction develops. The experiments were carried out in an autoclave-type apparatus specially adapted for the oxidation of liquefied hydrocarbon gases (2). To accelerate the process (to “remove” the induction period), cobalt stearate was used in an amount of 0.04 mole % relative to the initial butane. The course of oxidation was monitored from the kinetic curves for the accumulation of the main reaction products—acetic acid and methyl ethyl ketone—as well as from the intermediate product, *n*-butane hydroperoxide.

Figure 1 **I** gives the kinetic curves for the accumulation of acetic acid during the oxidation of liquefied butane in benzene at 170° and a pressure of 50 atm, illustrating the phenomenon of the critical concentration of benzene.

It is seen that the yield of acetic acid decreases as the amount of benzene in the initial mixture increases, down to the value $\gamma = 0.40$, at which

the reaction ceases completely. This phenomenon is especially clearly seen from Fig. 1, *II*, which gives the dependence of the amount of acetic acid formed in 2 hours of reaction on γ. A slight change in the value of γ near $\gamma_{\mathrm{cr}} = 0.40$ leads to an abrupt transition from the complete absence of reaction to butane oxidation at a considerable rate. It is not difficult to verify that in those cases when mixtures with $\gamma > 0.4$ are taken for the experiment, the reaction proceeds until, in the course of the process, the value $\gamma_{\mathrm{cr}} = 0.4$ is reached. For this purpose, by means of gas chromatography we followed the consumption of butane during the reaction and indeed observed stoppage of the process as

---

Fig. 2. Introduction of butane and benzene during the reaction at 170° and a pressure of 50 atm.
1 –kinetic curve of acetic acid accumulation at $\gamma_{\mathrm{init}} = 0.92$, transferred from Fig. 1, *I*. The points reflect the kinetics of acetic acid accumulation, beginning from the moment butane was added to $\gamma = 0.92$ to a mixture with $\gamma_{\mathrm{init}} = 0.40$, kept in the vessel:
a –0.5 hour, *b* –1.5 hours, *v* –2.5 hours, *g* –4 hours.
2 –curve of acetic acid accumulation upon adding fresh benzene to a mixture with $\gamma_{\mathrm{init}} = 0.92$ down to $\gamma = 0.40$. The moment of benzene addition is marked by an arrow.

---

soon as the value of γ fell to 0.4 (Fig. 1, *III*). When γ was artificially decreased to γ_{cr} during a reaction that had begun at $\gamma_{\mathrm{init}} = 0.92$, by adding fresh benzene, complete stoppage of the process was likewise observed (curve 2, Fig. 2). One more series of experiments was carried out. Fresh butane was added, to the ratio $\gamma > \gamma_{\mathrm{cr}}$, to a reaction vessel in which a mixture of butane with benzene at $\gamma \leq \gamma_{\mathrm{cr}}$ had been kept for a long time under reaction conditions. The oxidation reaction of butane then began immediately. The time for which the mixture had been kept under conditions of a nonproceeding reaction had no effect whatever on the character of the kinetic curves after dilution of the mixture with butane (the various points on curve 1 in Fig. 2). These experiments indicate that the observed critical phenomena are connected directly with the presence of benzene at a definite concentration, and not with the formation of any products of its transformation (for example, phenol). Apparently, benzene molecules react with peroxy radicals $\mathrm{RO}_2^\bullet$, forming a new complex radical $[\mathrm{C}_6\mathrm{H}_6\mathrm{RO}_2]^\bullet$, considerably less active than $\mathrm{RO}_2^\bullet$ and, as a result, incapable of further chain propagation.

Thus, the interaction of benzene with $RO_2^\bullet$ is in fact a chain-termination reaction, and the competition of this reaction with the hydroperoxide-formation reaction underlies the phenomena observed by us in the oxidation of butane in benzene.

For a theoretical consideration of such a mechanism of the process, let us introduce into the generally accepted scheme of liquid-phase oxidation the reaction of formation of the complex radical $[C_6H_6RO_2]^\bullet$ as the only path of chain termination (we neglect quadratic termination $RO_2^\bullet + RO_2^\bullet$):

$$RO_2^\bullet + RH \xrightarrow{k_2} RO_2H + R^\bullet \text{ —chain propagation,}$$

$$RO_2H \xrightarrow{k_3} RO_2^\bullet \text{ —chain branching,}$$

$$RO_2^\bullet + C_6H_6 \xrightarrow{k_4} [C_6H_6RO_2]^\bullet \text{ —chain termination.}$$

Here RH is butane. If the concentration of butane is taken as constant (for the early stage of the process), then the scheme leads to a system of two linear

differential equations:

$$\frac{d[RO_2H]}{dt} = k_2[RO_2^\bullet][RH] - k_3[RO_2H], \tag{1}$$

$$\frac{d[RO_2^\bullet]}{dt} = w_0 - k_4[RO_2^\bullet][C_6H_6] + k_3[RO_2H], \tag{2}$$

where w_0 is the rate of formation of radicals. Assuming the concentration of radicals $[RO_2^\bullet]$ to be stationary and solving the system of equations (1), (2), we obtain:

$$[RO_2H] = \frac{w_0}{1 - \frac{k_4}{k_2}\frac{[C_6H_6]}{[RH]}} \left\{ \exp\left[\left(\frac{k_2}{k_4}\frac{[RH]}{[C_6H_6]} - 1 \right) k_3 t \right] - 1 \right\}. \tag{3}$$

It follows from equation (3) that, as $t \to \infty$, the quantity $[RO_2H]$ tends to a constant value when $\frac{k_4}{k_2}\frac{[C_6H_6]}{[RH]} > 1$, and increases when $\frac{k_4}{k_2}\frac{[C_6H_6]}{[RH]} < 1$.

Thus, the ratio $\frac{k_4}{k_2} = \frac{[RH]}{[C_6H_6]}$ is the condition for transition from a slowly developing process to a rapid autocatalytic one. The formation of complex radicals of the type $[C_6H_6RO_2]$ has also been proposed in the work of other authors, for example, in studies of the photochlorination reaction of 2,3-dimethylbutane in organic solvents (5), the reaction of triphenylmethyl radicals with a series of benzene derivatives (6), the polymerization reaction of styrene in bromobenzene (7), the decomposition reaction of di-tert-butyl peroxide in cyclohexane in the presence of benzene and chlorobenzene (8), the decomposition reaction of benzoyl peroxide in benzene (9), and in studies by the EPR method of radicals formed in the radiolysis of benzene and its derivatives (10), etc. However, these works contain no material on the basis of which it would be possible to obtain a kinetic characteristic of the elementary reaction of formation of the complex radical. The results of the present work make it possible, as a first approximation, to estimate the activation energy of the reaction of a radical with benzene. Experimentally, we determined the values $\frac{k_2}{k_4} = \frac{1}{\gamma_{\text{cr}}}$ at different temperatures:

T, °C	170	145	140
γ_{cr}	0.40	0.69	0.78

From the dependence of $\lg \frac{k_2}{k_4}$ on $\frac{1}{T}$, the difference between the activation energies of the chain-propagation reaction and the reaction of formation of the complex radical was found to be $E_2 - E_4 = 9.0$ kcal/mole. Taking $E_2 = 11.5$ kcal/mole (by analogy with the oxidation reaction of n-decane (11)), we find for E_4 a value equal to approximately 2.5 kcal/mole, i.e., a value quite plausible for reactions of direct addition of radicals to a molecule. Experimental determination of the value of E_2 for the liquid-phase oxidation of butane will enable us subsequently to determine the value of E_4 more accurately.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
26 X 1960

CITED LITERATURE

1. N. M. Emanuel, DAN, **110**, 245 (1950).
2. E. A. Blyumberg, Z. K. Maizus, N. M. Emanuel, Oxidation of hydrocarbons in the liquid phase, 1959, p. 125.
3. H. M. Hutchinson, K. Stevens, U. S. Pat., **2**, 797, 209, June 25 (1957); Ibid. U. S. Pat., **2**, 801, 992, Aug. 6 (1957).
4. M. S. Furman, A. D. Shestakova et al., DAN, **124**, 1083 (1959).
5. G. A. Russell, J. Am. Chem. Soc., **80**, 4987 (1958).

6. R. A. Benkeser, W. Schroeder, J. Am. Chem. Soc., **80**, 3314 (1958).
7. F. K. Mayo, J. Am. Chem. Soc., **75**, 6133 (1953).
8. G. A. Russell, J. Org. Chem., **24**, 300 (1959).
9. G. A. Razuvaev, B. G. Gatev, G. G. Petukhov, DAN, **130**, 336 (1960).
10. Yu. N. Molin, I. I. Chkheidze et al., DAN, **131**, 125 (1960).
11. D. G. Knorre, Z. K. Maizus, N. M. Emanuel, DAN, **112**, 457 (1957).

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

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