A. I. POROMKOVA, Academician of the Academy of Sciences of the Armenian SSR A. B. NALBANDYAN

1965

SovietRxiv

Abstract

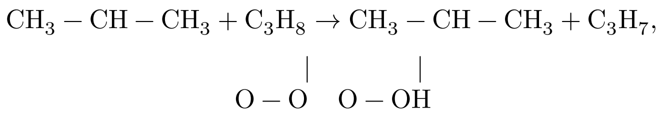
Full Text

Chemistry

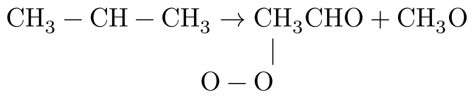
A. I. POROMKOVA, Academician of the Academy of Sciences of the Armenian SSR A. B. NALBANDYAN

FORMATION OF ALCOHOLS IN THE PHOTOCHEMICAL CHLORINE-INITIATED OXIDATION OF PROPANE

More than ten years ago N. N. Semenov (1), on the basis of the data of works (2) and (3), showed that the composition of the products of propane oxidation at temperatures below 300° is determined mainly by the following competing reactions of peroxy radicals:



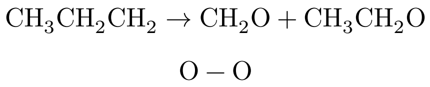
$$CH_3-\underset{\underset{O-O}{|}}{CH}-CH_3+C_3H_8\rightarrow CH_3-\underset{\underset{O-OH}{|}}{CH}-CH_3+C_3H_7, \tag{1}$$



$$CH_3-\underset{\underset{O-O}{|}}{CH}-CH_3\rightarrow CH_3CHO+CH_3O \tag{2}$$

in the case of the isoperoxy radical, and

$$CH_3CH_2CH_2OO+C_3H_8\rightarrow CH_3CH_2CH_2OOH+C_3H_7, \tag{3}$$



$$\underset{O-O}{CH_3CH_2CH_2}\rightarrow CH_2O+CH_3CH_2O \tag{4}$$

in the case of the *n*-peroxy radical.

Indeed, as was shown in works (1,4), at a temperature of 200° comparable amounts of peroxides and aldehydes are formed.

The methoxy radical, stable at 200° (5), then enters into the chain-propagation reaction (5):

$$CH_3O+C_3H_8\longrightarrow CH_3OH+C_3H_7. \tag{5}$$

Such a pathway for the decomposition of the isoperoxy radical, in accordance with reactions (1), (2), and (5), should lead to the formation of acetaldehyde and methyl alcohol in equal amounts.

According to the data of works ([2]) and ([9]), at a temperature of 300° methyl alcohol is present in the reaction products in amounts comparable with CH_3CHO. However, comparison of the amounts of acetaldehyde and methyl alcohol formed under the conditions of these works is made difficult by the subsequent rapid transformation of acetaldehyde ([2]).

During the isomerization and decomposition of the normal peroxy radical, according to reactions (3) and (4), one should expect the formation of formaldehyde and the ethoxy radical in equal amounts. Ethyl alcohol was found in the products of propane oxidation at 285° ([1]). At a higher temperature, ethyl alcohol is absent from the products of thermal ([1]), ([2]) and chlorine-initiated ([9]) oxidation, which is apparently connected with the low stability of the radical CH_3CH_2O, which enters into the competing reactions

$$CH_3CH_2O + C_3H_8 \longrightarrow CH_3CH_2OH + C_3H_7, \tag{6}$$

$$CH_3CH_2O \longrightarrow CH_3 + CH_2O. \tag{7}$$

The activation energy of reaction (6) can be estimated from the data of work ([7]), where the activation energy of the reaction

$$CH_3O + C_3H_8 \longrightarrow CH_3OH + C_3H_7, \tag{8}$$

was determined and was found to be $E_8 = 5.2$ kcal.

To estimate the rates of reactions (6) and (7), N. N. Semenov assumes ([1]) $E_6 = 7$ kcal, the steric factor $f_6 = 0.1$, and $E_7 = 20$ kcal. According to the thermochemical calculations of Gray ([6]), the heat effect of reaction (7) is $Q_7 = 13$ kcal,

and from data on the photolysis of ethyl propionate (12) $E_7 = 13$ kcal. If this latter value is adopted for E_7, which is apparently much too low, then agreement with the data on the formation of ethyl alcohol given in (1) can be obtained only under the condition that $f_6 = 10^{-4}$.

We set ourselves the goal of detecting methyl and ethyl alcohols and comparing their amounts with the amounts of the aldehydes formed, in accordance with scheme (1)–(7), under such conditions that the rates of decomposition and oxidation of the aldehydes can be neglected. From the survey presented it is clear that the greatest yield of ethyl alcohol should be expected at a temperature of 150–250°, when decomposition by reaction (4) proceeds sufficiently rapidly, while reactions (6) and (7) proceed at comparable rates. To carry out the reaction at such low temperatures, we used photochemical initiation of the reaction by additions of Cl_2.

Table 1

Experiment no.	T, °K	C_2H_5OH, %	CH_2O, %	$\gamma = \frac{C_2H_5OH}{CH_2O}$	$\frac{2\gamma}{(1-\gamma)(C_3H_8)} \cdot 10^{19}$, cm^3/molecule	β	$\frac{(2+\beta)\gamma}{(1-\gamma)(C_3H_8)} \cdot 10^{19}$, cm^3/molecule
201,206 – 207211, 212	443	0.011	0.041	0.27	2.18	0.32	2.55
202, 205213, 216	473	0.024	0.145	0.165	1.23	0.51	1.56
203, 204214, 215	493	0.035	0.41	0.085	0.61	0.60	0.80
208218	513	0.039	0.75	0.052	0.376	0.69	0.50
217	549	0.032	–	–	–	–	–

Experimental Part

The procedure for carrying out the process and for analyzing the reaction products will be reported later*. In addition to the products indicated, in the present work the alcohols were analyzed by chromatographic methods. A chromatograph with a flame-ionization detector was used; hydrogen served as the carrier gas. The column was packed with diatomaceous brick; polypropylene glycol adipate was used as the stationary liquid phase (20% by weight of the support). The column was thermostated at 70°. Methyl and ethyl alcohols were analyzed in a solution of *n*-propyl alcohol.

The method used made it possible to analyze alcohol solutions with concentrations down to 0.01 N. The small amounts of C_2H_5OH formed were analyzed with an error of 10–15%. The amounts of methyl alcohol were determined considerably more accurately.

As experiments with artificial mixtures showed, when all of the condensate frozen at a temperature of $-196°$ was dissolved in a small volume of *n*-propyl alcohol, the aldehydes were only partially retained in the solution. In connection with this, in parallel experiments the aldehydes were analyzed in aqueous solutions by the polarographic method.

Propyl alcohols were not found in the reaction products. Taking into account the sensitivity of the method (the analysis for the content of C_3H_7OH was carried out in aqueous solution), it may be considered that the amount of C_3H_7OH is several times smaller than the amount of the main reaction products, n-$C_3H_7OH/CH_2O \leqslant 0.25$.

One of the chromatograms of the condensate dissolved in n-propyl alcohol is shown in Fig. 1.

Figure 2 presents the dependences of the yield of acetaldehyde and methyl alcohol on the contact time at several temperatures. In the range $t_k \leq 2$ sec the yield of acetaldehyde increases linearly with time, which indicates the absence of further conversion of CH_3CHO under the experimental conditions. The detection of equal amounts of CH_3CHO and CH_3OH in the interval $T = 140$–$220°$ is in agreement with the reaction scheme (1)–(5) and the data of work $^{(9)}$.

The yield of formaldehyde at $t_k \leq 2$ sec likewise depends linearly on the contact time*.

Figure 3 shows the dependence of the yield of formaldehyde and ethyl alcohol on temperature (at $t_k = 1.3$ sec). Formaldehyde was detected in amounts considerably greater than C_2H_5OH. The dependence of the yield of ethyl alcohol on temperature has a maximum at $T \simeq 530°K$. From the experimentally found ratio $\gamma = C_2H_5OH/CH_2O$, adopting scheme (1)–(7), one can calculate the ratio of the constants of elementary reactions (6) and (7). In doing so, the following possible reactions of the CH_3 radical formed in reaction (7) must be taken into account:

[Figure 1 and Figure 2]

Fig. 1. Chromatogram of the reaction products (alcohols and aldehydes) in a solution of n-C_3H_7OH (peaks 1, 2 –chlorination products, 3 –acetaldehyde, 4 –acetone, 5 –methyl alcohol, 6 –ethyl alcohol, 7 –solvent-front peak)

Fig. 2. Dependence of the yield (in percent of the propane passed through) of acetaldehyde (a) and methyl alcohol (b) on contact time at various temperatures. Addition of Cl_2 is 3.5%, $p_{\text{tot}} = 350$ mm Hg. 1 –at 140°, 2 –at 170°, 3 –at 200°, 4 –at 220°C

$$CH_3 + C_3H_8 \longrightarrow CH_4 + C_3H_7, \tag{9}$$

$$CH_3 + O_2 \longrightarrow CH_3O_2, \tag{10}$$

$$CH_3O_2 + C_2H_8 \longrightarrow CH_3O_2H + C_3H_7, \tag{11}$$

$$CH_3OO \longrightarrow CH_2O + OH. \tag{12}$$

---

* In press in the journal *Kinetics and Catalysis*.

Fig. 3 and Fig. 4

Figure 1: Fig. 3 and Fig. 4

For calculating (k_6/k_7) it is necessary to know the fraction of CH_2O formed by reaction (12).

From the data of work $^{(10)}$ the following ratio is known:

$$k_{12}/k_{11'} = 2.5 \cdot 10^{22} e^{-8500/RT} \text{ molecules} \cdot \text{cm}^{-3},$$

where $k_{11'}$ is the rate constant of the reaction

$$CH_3O_2 + CH_4 \longrightarrow CH_3O_2H + CH_3. \qquad (11')$$

At temperatures below 250°, reaction (9) proceeds considerably–

* See the communication in the journal *Kinetics and Catalysis*.

slower than reaction (10), since $k_8 \simeq k_9$, $E_8 = 8.2$ kcal (^{11}), $E_9 \ll 1.5$ kcal (^{2}).

If, following N. N. Semenov (^{1}), the Polanyi rule is applied to compare reactions (11) and (11′), then at $T = 250°$ practically all CH_3O_2 radicals form CH_3O_2H, and reaction (12) may be neglected.

In this case

$$\frac{k_6}{k_7} = \frac{2\gamma}{1-\gamma} \cdot \frac{1}{(C_3H_8)}.$$

If reaction (12) is taken into account, assuming $k_{11} \simeq k_{11'}$ and denoting

$$\beta = \frac{w_{12}}{w_{12} + w_{11}} = \frac{1}{1 + k_{11}(C_3H_8)/k_{12}},$$

then

$$\frac{k_6}{k_7} = \frac{(2+\beta)\gamma}{1-\gamma} \cdot \frac{1}{(C_3H_8)}.$$

Table 1 gives the values of the ratio k_6/k_7 with and without allowance for reaction (12).

Fig. 3. Dependence of the yield of formaldehyde (1) and ethyl alcohol (2) at different temperatures. $p_{\text{total}} = 350$ mm Hg, $t_k = 1.3$ sec.

Fig. 4. Determination of the difference in activation energies of reactions (6) and (7). 1 was obtained from the expression $k_6/k_7 = 2\gamma/(1-\gamma) \cdot 1/(C_3H_8)$, 2 from the expression $k_6/k_7 = (2+\beta)\gamma/(1-\gamma) \cdot 1/(C_3H_8)$.

From the graph in Fig. 4 the following values were obtained:

$$\frac{k_6}{k_7} = \frac{2\gamma}{1-\gamma} \cdot \frac{1}{(C_3H_8)} = 10^{-23.3} \cdot e^{11500 \pm 1000/RT} \text{ cm}^3/\text{molecule},$$

$$\frac{k_6}{k_7} = \frac{(2+\beta)\gamma}{1-\gamma} \cdot \frac{1}{(C_3H_8)} = 10^{-22.8} \cdot e^{10000 \pm 1000/RT} \text{ cm}^3/\text{molecule}.$$

The authors express their gratitude to P. I. Valov and E. A. Blyumberg for their help in carrying out alcohol analyses by the chromatographic method.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
17 III 1965

REFERENCES

1. N. N. Semenov, *Uspekhi khimii*, **20**, 708 (1951); *On Certain Problems of Chemical Kinetics and Reactivity*, Moscow, 1958.
2. V. Ya. Shtern, *Mechanism of Oxidation of Hydrocarbons in the Gas Phase*, Moscow, 1960, pp. 227, 235.
3. N. V. Fok, A. B. Nalbandyan, DAN, **85**, 1093 (1952); **89**, 125 (1953); *Problems of Chemical Kinetics, Catalysis, and Reactivity*, 1955, p. 219.
4. A. I. Poroikova, V. V. Voevodskii, A. B. Nalbandyan, ZhFKh, **33**, 1336 (1959).
5. F. F. Rust, F. H. Seubold, W. E. Waughen, *J. Am. Chem. Soc.*, **72**, 338 (1950).
6. P. Gray, *V Symposium on Combustion*, 1955, p. 535.
7. T. Berges, A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1961, 348.
8. M. H. J. Wijnen, *J. Am. Chem. Soc.*, **82**, 3034 (1960).
9. K. E. Kulikova, N. M. Emanuel, *Izv. AN SSSR, OKhN*, 1959, 417.

10. A. B. Nalbandyan, A. A. Mantashyan, *Izv. AN ArmSSR, OKhN*, **14**, No. 3, 185 (1961).
11. E. W. R. Steacie, *Atomic and Free Radical Reactions*, N. Y., 1954, p. 540.

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

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