fats. The stabilization of drugs on fat bases containing hydrochloride salts of amines is appreciably enhanced by introducing a mixture of dimethyl-bis(4-phenylaminophenoxy)silane with citric acid as an antioxidant.

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KINETICS OF THE CATALYZED SYNTHESIS OF 2-METHOXYPROPENE IN THE GAS PHASE

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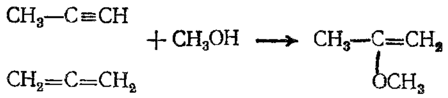
The use of 2-alkoxypropenes, notably 2-methoxypropene (2-MP) in the synthesis of the fat-soluble vitamins A, E, and K_1 has led to increased interest in processes for the preparation of these compounds. We have previously described [2] the kinetics of the catalyzed synthesis of 2-MP in the liquid phase.

It has also been shown to be possible to obtain 2-MP by a more technologically convenient catalyzed process in the gas phase [1], as follows:



$$\begin{matrix} CH_3{-}C{\equiv}CH \\ CH_2{=}C{=}CH_2 \end{matrix} + CH_3OH \longrightarrow \underset{\displaystyle OCH_3}{CH_3{-}\overset{}{C}{=}CH_2}$$

We here describe a study of the kinetics of the gas-phase synthesis of 2-MP. The effects on the course of the reaction of the following factors were studied: catalyst composition, ratio of reactants, reaction temperature, and contact time.

EXPERIMENTAL

The catalyst employed was sodium hydroxide on an activated charcoal (AG-3 grade) as carrier. The choice of carrier was dictated by its relatively large specific surface area (S_{sp} 350 m^2/g), adequately high mechanical strength, and its inertness under the reaction conditions. The reactants used were chemically pure grade methanol and an industrial mixture of methylacetylene and allene in a ratio of 3:1 (known as fraction MAF, C_3H_4 content not less than 98.9%).

The gas-phase synthesis of 2-MP was carried out as follows: methanol was charged by a metering pump to an evaporator, where the vapor was mixed with a stream of gaseous MAF at atmospheric pressure, and thence into an ideal displacement reactor. On emergence from the reactor, the products were condensed in a trap cooled to −5°C. The products were analyzed chromatographically, as described previously [2].

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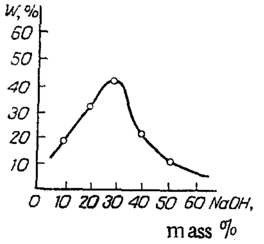


Fig. 1

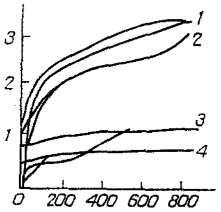


Fig. 2

Fig. 1. Plot of the conversion of MAF against the NaOH content of the catalyst. Horizontal axis, sodium hydroxide content of catalyst (wt. %); vertical axis, conversion of MAF (%).

Fig. 2. Sorption isotherms for MAF on several catalyst samples. Horizontal axis, MAF pressure (Torr); vertical axis, amount of MAF sorbed (mmole per 1 g of catalyst). NaOH content (% of weight of AG-3): 1) 0; 2) 10; 3) 30; 4) 50.

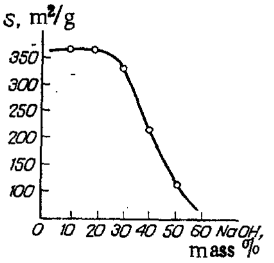


Fig. 3. Plot of specific surface area against the NaOH content of the catalyst (%). Horizontal axis, NaOH content of the catalyst (%); vertical axis, specific surface area of the catalyst (m^2/g).

To determine the optimum catalyst composition, we studied the effects of the concentration of the active component (NaOH) on the carrier, on the rate of formation of 2-MP. The sodium hydroxide concentration was varied from 5 to 60% of the weight of the carrier, the volume flow rate and reactant concentrations being held constant. Figure 1 shows a plot of the conversion of MAF against the active phase in the catalyst. It will be seen that the plot has a maximum, the catalyst showing its highest activity at an NaOH content of 30% of the weight of the carrier. Increase in the NaOH content above this value resulted in a sharp fall in catalytic activity.

To establish the reason for this behavior, we obtained sorption isotherms for MAF at 20°C and pressures of 0-750 Torr on samples of catalyst with a range of sodium hydroxide concentrations (Fig. 2). The isotherms were obtained on a MacBain spring balance as described in [3]. In some experiments, it was found that during the course of sorption of MAF the composition of the gas mixture (allene:methylacetylene ratio) remained unchanged, i.e., the adsorption coefficients of allene and methylacetylene had similar values.

As will be seen from Fig. 2, the sorption isotherm for MAF on the carrier (activated carbon AG-3) is clearly hysteretic at all the pressures examined, whereas the sorption isotherms for MAF on the NaOH/AG-3 catalysts are hysteretic at low pressures only. The sample containing 30% NaOH had approximately the same sorptive capacity for MAF as pure AG-3, and the sorptive capacity of the samples containing 10 and 50% of NaOH was much lower than that of pure AG-3. It is interesting that all the samples showed strong irreversible sorption of substantial amounts of MAF (not removed from the surface by prolonged pumping out *in vacuo*). The amount of firmly bound MAF on the sample containing 30% NaOH (1.05 mmole/g) was greater, and on samples with 10% NaOH less, than on pure AG-3 (0.78 mmole/g).

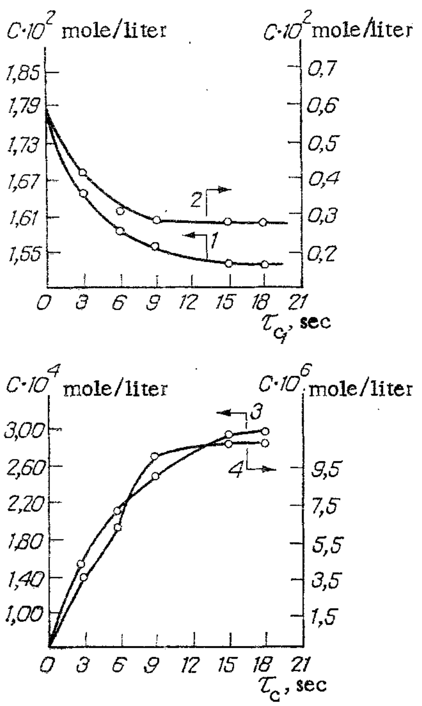


Fig. 4

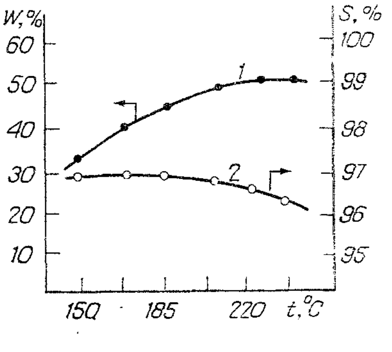


Fig. 5

Fig. 4. Kinetic plots for changes in amounts of products formed in the formation of 2-MP at 185°C, molar ratio MeOH:MAF 0.1:1. Horizontal axis, contact time (sec): vertical axis, product concentrations (mole/liter). 1) Methanol; 2) MAF; 3) 2-MP, 4) acetone.

Fig. 5. Plots of yield and selectivity of formation of 2-MP against temperature at a contact time of 10 sec and an MeOH:MAF ratio of 0.1:1. Horizontal axis, temperature (PC); vertical axis, yield W (%) (plot 1) and selectivity S (%) (plot 2).

Examination of the sorption isotherms leads to the conclusion that there are sites for the irreversible adsorption of MAF on the surface of the AG-3 carrier. These sites are not, however, responsible for the catalytic reaction of NAF with methanol. Application of NaOH to the carrier surface results on the one hand in the blocking of these sites, and on the other hand, to the appearance on the catalyst surface of firm sorption sites of a new type, at which the catalyzed synthesis of 2-MP is brought about. The specific concentration of these sites increases with increasing NaOH content up to 30% of the weight of the carrier, resulting in an increase in the specific activity of the catalyst (Fig. 1). Further increases in the NaOH content of the catalyst lead to a reduction in the amount of firmly adsorbed MAF, perhaps in view of the dependence of the specific surface area of the catalyst on its active component content (Fig. 3). Over the range 0-30%, in fact, the specific surface area of the catalyst changes little, but at concentrations greater than 30% there is a sharp fall in the specific surface area. Consequently, an increase in the concentration of the active component to over 30% of the weight of the carrier does not in any instance decrease the specific surface concentration of active sites therein, but a decrease in the specific surface concentration of active sites therein, but a decrease in the specific surface area of the sample results in a sharp decrease in the specific concentration of these sites, accompanied by a marked reduction in catalyst activity (Fig. 1).

It is noteworthy that the region of pressures over which hysteresis is seen in the sorption isotherms of MAF decreases as the NaOH content of the catalyst is increased up to 30%, following which it remains largely unchanged (Fig. 2). This is apparently due to the phenomenon of capillary condensation of MAF in the narrow pores of the sorbent. The introduction of NaOH in amounts up to 30% blocks the narrowest pores, restricting the region at which hysteresis is seen to values at which only irreversible adsorption of MAF on the catalyst surface occurs (up to $\sim$200 Torr).

TABLE 1. Comparison of Calculated and Experimental Concentrations of Products in the Synthesis of 2-MP

τ_K, sec	Methanol, $C \cdot 10^{-2}$ mole/liter		MAF, $C \cdot 10^{-2}$ mole/liter		2-MP, $C \cdot 10^{-4}$ mole/liter		Acetone, $C \cdot 10^{-6}$ mole/liter	
	1	2	1	2	1	2	1	2
	Methanol : MAF ratio				*6 : 1 (150 °C)*			
1	2,50	2,51	0,40	0,40	0,21	0,17	0,10	0,10
2	2,49	2,50	0,38	0,39	0,42	0,32	0,40	0,38
3	2,47	2,48	0,36	0,37	0,61	0,47	0,71	0,67
4	2,45	2,47	0,35	0,36	0,75	0,62	1,00	0,92
5	2,44	2,45	0,34	0,33	1,84	0,75	1,20	1,18
7,5	2,42	2,42	0,31	1,32	1,12	1,06	1,90	1,93
10	2,41	2,40	0,30	0,29	1,18	1,34	2,20	2,18
15	2,39	2,35	0,29	0,28	1,33	1,80	2,60	2,69
20	2,38	2,34	0,28	0,26	1,42	2,18	2,90	2,90
	Methanol : MAF ratio				*3 : 1 (150 °C)*			
1	2,16	1,18	0,69	0,71	0,51	0,32	0,90	0,72
2	2,14	2,15	0,66	0,68	0,72	0,56	1,30	1,14
3	2,08	2,13	0,61	0,66	1,28	0,81	2,70	2,26
4	2,07	2,10	0,60	0,63	1,36	1,05	3,20	2,97
5	2,06	2,08	0,59	0,61	1,45	1,28	4,20	4,09
7,5	2,05	2,03	0,58	0,56	1,48	1,78	4,60	4,62
10	2,04	1,99	0,58	0,52	1,56	2,22	4,90	5,03
15	2,04	1,91	0,57	0,54	1,63	2,97	5,30	5,38
20	2,03	1,85	0,56	0,53	1,66	3,50	5,70	5,78
	Methanol : MAF ratio				*1 : 0,9 (150 °C)*			
1	1,45	1,50	1,30	1,35	0,94	0,54	1,60	1,03
2	1,41	1,45	1,26	1,30	1,33	1,01	2,70	2,16
3	1,35	1,40	1,20	1,25	1,96	1,45	4,20	3,83
4	1,29	1,37	1,14	1,22	2,55	1,84	6,80	5,71
5	1,22	1,33	1,07	1,18	3,20	2,20	8,30	8,29
7,5	1,16	1,25	1,01	1,10	3,79	2,99	11,10	11,27
10	1,08	1,18	0,93	1,03	4,53	3,66	13,20	13,32
15	1,03	1,08	0,88	0,93	5,08	4,83	14,40	14,48
20	1,01	0,99	0,86	0,84	5,21	5,56	16,00	16,02
	Methanol : MAF ratio				*6 : 1 (185 °C)*			
1	2,25	2,24	0,35	0,34	0,31	0,36	0,30	0,55
2	2,24	2,21	0,34	0,31	0,40	0,65	0,50	0,69
3	2,22	2,19	0,32	0,29	0,63	0,90	0,90	1,19
4	2,20	2,17	0,30	0,27	0,81	1,11	1,30	1,42
5	2,19	2,15	0,29	0,25	0,92	1,30	1,60	1,98
7,5	2,16	2,11	0,26	0,21	1,18	1,68	2,30	2,36
10	2,15	2,08	0,25	0,18	1,31	1,98	2,60	2,79
15	2,14	2,03	0,24	0,14	1,38	2,42	3,00	3,27
20	2,13	2,00	0,23	0,11	1,40	2,56	3,30	3,42
	Methanol : MAF ratio				*3 : 1 (185 °C)*			
1	1,95	1,94	0,61	0,61	0,51	0,59	1,30	1,38
2	1,88	1,89	0,54	0,56	1,14	1,05	2,40	2,59
3	1,85	1,86	0,51	0,52	1,51	1,41	3,40	3,67
4	1,81	1,82	0,47	0,49	1,86	1,72	4,60	4,92
5	1,78	1,80	0,44	0,46	2,15	1,92	5,50	5,79
7,5	1,72	1,74	0,38	0,41	2,75	2,54	7,60	7,96
10	1,69	1,69	0,35	0,36	3,06	2,97	9,20	10,13
15	1,68	1,63	0,34	0,29	3,08	3,62	10,10	11,27
20	1,67	1,58	0,33	0,24	3,10	4,10	11,00	11,86
	Methanol : MAF ratio				*1 : 0,9 (185 °C)*			
1	1,27	1,30	1,13	1,16	1,24	0,97	2,60	2,73
2	1,22	1,24	1,08	1,10	1,78	1,61	5,00	5,38
3	1,16	1,18	1,02	1,04	2,30	2,10	6,30	6,79
4	1,10	1,14	0,96	1,00	2,96	2,50	7,20	7,92
5	1,02	1,11	0,88	0,97	3,65	2,84	10,20	10,87
7,5	0,94	1,03	0,80	0,89	4,45	3,53	13,10	13,90
10	0,90	0,97	0,76	0,83	4,87	4,08	14,30	15,07
15	0,88	0,89	0,74	0,75	5,04	4,92	16,80	17,13
20	0,87	0,82	0,73	0,68	5,11	5,56	21,00	21,67
	Methanol : MAF ratio				*6 : 1 (220 °C)*			
1	2,09	2,04	0,32	0,28	0,25	0,76	0,30	0,26
2	2,07	2,01	0,30	0,24	0,45	1,09	0,70	0,59
3	2,05	1,99	0,28	0,22	0,68	1,20	1,20	0.93
4	2,03	1,97	0,26	0,20	0,83	1,31	1,50	1,27
5	2,02	1,95	0,25	0,19	0,99	1,49	2,00	1,62
7,5	2,00	1,92	0,23	0,16	1,19	1,64	2,60	2,49
10	1,99	1,90	0,22	0,14	1,28	1,92	3,00	3,36
15	1,98	1,87	0,21	0,10	1,32	2,13	3,10	5,12
20	1,97	1,85	0,20	0,09	1,34	2,22	3,80	6,86

TABLE 1 (Continued)

Methanol:MAF ratio *3 : 1 (220 °C)*								
1	1,76	1,75	0,53	0,52	0,91	1,01	1,60	1,66
2	1,71	1,71	0,48	0,47	1,36	1,43	3,10	3,43
3	1,66	1,67	0,43	0,44	1,81	1,73	4,50	4,72
4	1,63	1,65	0,40	0,42	2,12	1,96	5,50	5,94
5	1,62	1,63	0,39	0,40	2,15	2,16	6,70	6,82
7,5	1,56	1,59	0,32	0,36	2,88	2,56	8,70	8,96
10	1,55	1,56	0,31	0,32	2,96	2,86	10,20	10,47
15	1,54	1,51	0,30	0,28	2,98	3,30	10,80	10,06
20	1,53	1,47	0,29	0,24	2,99	3,63	11,40	11,87
Methanol:MAF ratio *1 : 0,9 (220 °C)*								
1	1,16	1,17	1,02	1,04	1,42	1,24	3,00	3,46
2	1,12	1,12	0,99	0,99	1,78	1,73	5,20	5,83
3	1,06	1,09	0,93	0,96	2,38	2,09	7,00	7,56
4	0,98	1,06	0,85	0,93	3,14	2,38	2,90	9,75
5	0,92	1,03	0,79	0,90	3,65	2,63	10,30	10,49
7,5	0,85	0,98	0,72	0,85	4,40	3,11	14,10	15,02
10	0,84	0,94	0,71	0,81	4,43	3,49	16,40	16,38
15	0,83	0,87	0,70	0,74	4,45	4,07	18,00	18,69
20	0,82	0,83	0,69	0,70	4,46	4,50	21,10	21,84

Note. 1) Experimental, 2) calculated values.

Thus, in the gas-phase synthesis of 2-MP, the catalyst displays its maximum activity at a caustic alkali concentration of 30% of the weight of the carrier. For this reason all subsequent kinetic studies were carried out using this catalyst sample.

In the kinetic studies, the concentration of MAF was varied over the range $0.21 \cdot 10^{-2}$ to $1.31 \cdot 10^{-2}$ mole/liter, and that of methanol from $0.83 \cdot 10^{-2}$ to $2.51 \cdot 10^{-2}$ mole/liter. The initial methanol:MAF ratios were varied from 1:6 to 0.9:1, the contact time from one to 20 sec, and the reaction temperature from 150 to 220°C.

Table 1 shows the experimental results for the changes in composition of the reactants and the formation of products at several temperatures, methanol:MAF ratios, and contact times.

Figure 4 presents typical plots of changes in reactant and product concentrations against the contact time τ_c (analysis was carried out on emergence from the reactor). As will be seen from Fig. 4, plots 1 and 2, as τ_c increases, conversion of the reactants (methanol and MAF) increases. With contact times up to 10 sec, the concentration of 2-MP in the products increases rapidly, but over 10 sec there was little change (Fig. 4, plot 3). However, when τ_c lay between 7.5 and 10 sec, the yield of acetone was substantially increases (Fig. 4, plot 4).

Figure 5 presents typical plots for 2-MP yield and selectivity with respect to 2-MP against temperature. It will be seen that the greatest yield of 2-MP is obtained at temperatures of 180-200°C. The selectivity of the reaction is high, and is weakly dependent on temperature, the maximum selectivity being obtained at 185°C.

Examination of the experimental results shown in Table 1, reveals the optimum conditions for the reaction, namely, temperature 185°C, contact time 10 sec, and methanol:MAF ratio 1:0.9.

It is noteworthy that the sigmoid shape of the plot for acetone formation (Fig. 4, plot 4) suggests that the formation of this product is consecutive in nature, as follows:

$$C_3H_4 + CH_3OH \xrightarrow{k_1} CH_3C(OCH_3){=}CH_2 \xrightarrow{k_2} (CH_3)_2CO.$$

Separate experiments using 2-MP as reactant confirmed this hypothesis.

The experimental results were evaluated on an ES-1033 computer using the 'Kinetics' suite of programs developed by the VNIIOS, as on a previous occasion [2]. Calculations were carried out on the assumption that acetone was formed in a consecutive reaction, together with other alternatives. The results led to a mathematical model which also confirmed the consecutive nature of the reaction:

$$r_1 = \frac{k_1 p_1 p_2}{1 + b_1 p_2 + b_2 p_3},$$

$$r_2 = \frac{k_2 p_3}{1 + b_1 p_2 + b_2 p_3},$$

where r_1 and r_2 are the rates of formation of 2-MP and acetone, k_1 and k_2 the rate constants for the formation of 2-MP and acetone, b_1 and b_2 the adsorption coefficients for methanol and 2-MP, and p_1, p_2, and p_3 are the partial pressures of MAF, methanol, and 2-MP.

Table 1 compares the experimental and calculated values of the concentrations of reactants and products under different experimental conditions. It will be seen that in all cases there is good agreement between the calculated and experimental values.

The mean square deviations S_1 (2.18% for the first and 1.06% for the second stage) indicate the validity of the proposed model for the actual reaction.

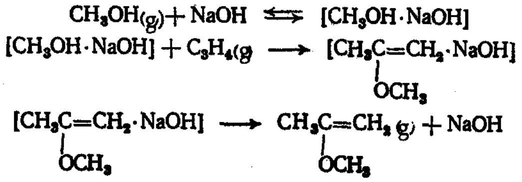
During the treatment of the experimental kinetic data, the values for the rate constants of the first (formation of 2-MP) and second (formation of acetone) stages were obtained:

$$k_1 = 7{,}86 \cdot 10^4 \text{ liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}; \quad k_2 = 2{,}43 \cdot 10^3 \text{ sec}^{-1} \text{ (150 °C)};$$
$$k_1 = 2{,}40 \cdot 10^5 \text{ liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}; \quad k_2 = 1{,}01 \cdot 10^5 \cdot \text{sec}^{-1} \text{ (220 °C)}$$

and the activation energies for the two stages of the reaction were E_1 = 6.61 Kcal/mole and E_2 = 22.04 Kcal/mole.

Mathematical treatment of the kinetic data showed that gaseous MAF most likely reacts with adsorbed molecules of methanol. Calculations based on another possibility (reaction of gaseous methanol with adsorbed allene and methylacetylene) resulted in a more than tenfold increase in the mean square deviation of the calculated model from the experimental results.

These findings suggest the following reaction sequence for the formation of 2-MP in the gas phase:



$$\begin{aligned}
&CH_3OH_{(g)} + NaOH \rightleftarrows [CH_3OH \cdot NaOH] \\
&[CH_3OH \cdot NaOH] + C_3H_{4(g)} \longrightarrow [CH_3\underset{\displaystyle OCH_3}{\underset{|}{C}}{=}CH_2 \cdot NaOH] \\
&[CH_3\underset{\displaystyle OCH_3}{\underset{|}{C}}{=}CH_2 \cdot NaOH] \longrightarrow CH_3\underset{\displaystyle OCH_3}{\underset{|}{C}}{=}CH_{2(g)} + NaOH
\end{aligned}$$

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