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## ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

# Kinetic Relationships in Synthesis of Dimethoxymethane

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**Abstract**—The kinetics of formation of dimethoxymethane by acetalization of formaldehyde with methanol, catalyzed by silicotungstic heteropoly acid, were studied.

Dimethoxymethane (DMM) is a colorless solvent with a low boiling point, low viscosity, and an excellent dissolving power. It finds application in organic and pharmaceutical syntheses, paint and varnish industry, as a washing solvent, as component of cleaning and degreasing solvents, in production of adhesives and plastics, as a fuel additive, and as a component of in technical aerosols and in household chemistry articles.

The starting reagents for preparation of DMM are formaldehyde (FA) and methanol (M). These are readily accessible and cheap chemicals, which, combined with their acceptable production costs, affords a cheap commercial DMM. The overall reaction of DMM formation can be represented schematically as

$$2CH_3OH + HCHO \overset{\text{Cat.}}{\rightleftarrows} CH_2(OCH_3)_2 + H_2O.$$

Since recently, commercial plants have been using as catalysts ion-exchange resins, which afford DMM in high yields but degrade during the reaction into small particles clogging the column, lose their activity under exploitation, and need either regeneration or replacement [1]. Also, inorganic acids such as sulfuric acid have been tested as catalysts, but they cause many nuisances like corrosion activity, environmental pollution, the need for neutralization of wastewater, and irreversible loss of the acid [2].

We believe that tungstic heteropoly acids and, in particular, silicotungstic heteropoly acid $H_4SiW_{12}O_{40}$ (STA), are suitable as catalysts. The trials on laboratory batch and continuous-operation units showed that tungstic heteropoly acids can be successfully applied as catalysts in synthesis of DMM.

In the context of development of the optimal procedure for isolation and purification of DMM, it is necessary to analyze the kinetic aspects of its synthesis, which constituted the aim of this study.

## EXPERIMENTAL

In experiments, we used a water-methanol solution of formalin containing 37 wt % FA; the amount of FA was determined by the sodium sulfate technique, and that of M, by gas chromatography. We used M purified by distillation; gas chromatographic analysis showed that it contained residual water only. Analytically pure silicotungstic heteroply acid was dried by calcination at 250°C for 3 h.

The kinetic relationships were experimentally studied in a glass reactor ($V$ = 100 ml) equipped with a water jacket, two ground-glass joints connecting the reactor with a reflux condenser and a thermometer, and a sampler. To exclude hot spots, the reaction mixture was stirred with a magnetic stirrer. A constant temperature in the reactor was maintained by water circulating between the thermostat and the reactor jacket, with the temperature monitored within the latter. A water thermostat connected to the reactor case was operated in the forced-circulation mode.

The reaction mixture was prepared by mixing M, FA, and water to achieve the desired ratio of the reactants, whereupon the required amount of the resulting mixture was sampled, weighed on an analytical balance, and placed in the reactor. When the desired temperature was established in the reactor, the required amount of STA was added, from which moment the time of the process was measured. Samples (0.2 ml) were taken at regular intervals; a sample was added to 5 ml of aqueous NaOH of the concentration required for neutralizing the acid contained in the taken volume of the reaction mixture, and the mixture contained in the test tube was thoroughly stirred.

All the samples were analyzed chromatographically on a Tsvet 500 gas chromatograph with a flame-

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ionization detector and a 2000 × 3 mm steel column packed with Polysorb (0.16–0.2 mm grains). The carrier gas was nitrogen; the flow rate of nitrogen and hydrogen was 30, and that of air, 300 $\mathrm{cm^3\,min^{-1}}$. The temperatures of the column, detector, and vaporizer were 150°C. The relative error of analysis was 3%.

As mentioned above, DMM is formed by a two-stage reaction between M and FA:

$$\mathrm{HCHO} + \mathrm{CH_3OH} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{HOCH_2OCH_3}, \qquad (1)$$

$$\mathrm{HOCH_2OCH_3} + \mathrm{CH_3OH} \underset{k_{-2}}{\overset{k_1}{\rightleftarrows}} \mathrm{CH_2(OCH_3)_2} + \mathrm{H_2O}. \qquad (2)$$

The rate of formation of hemiacetal (HA) is very high [3], with the equilibrium strongly shifted toward its formation [4]. Since M was taken in excess in all the experiments, we assumed that the whole amount of FA was in the form of HA. Thus, we developed a kinetic model taking into account reaction (2) only. We described the DMM formation rate of by the differential equation

$$\mathrm{d}c_{\mathrm{DMM}}/\mathrm{d}\tau = k_2' c_{\mathrm{PA}} c_{\mathrm{M}} - k_{-2}' c_{\mathrm{DMM}} c_{\mathrm{H_2O}},$$

where $k_2'$ and $k_{-2}'$ are the effective rate constants, $\mathrm{l\,min^{-1}\,mol^{-1}}$; $c_{\mathrm{PA}}$, $c_{\mathrm{M}}$, $c_{\mathrm{DMM}}$, and $c_{\mathrm{H_2O}}$, concentrations (M) of PA, M, DMM, and water, respectively.

This equation was solved by the Runge-Kutta method. The rate constants were calculated by the least-squares method. Figure 1 shows the typical kinetic curves of DMM formation.

The dependence of the effective rate constants $k_2'$ and $k_{-2}'$ on the catalyst concentration was described by the equation

$$k_2' = k_2 c_{\mathrm{cat}}^n, \quad k_{-2}' = k_{-2} c_{\mathrm{cat}}^m,$$

where $k_2$ and $k_{-2}$ are true rate constants, $\mathrm{l^2\,min^{-1}\,mol^{-2}}$; $c_{\mathrm{cat}}$, catalyst concentration, M; and $n$ and $m$, reaction orders with respect to the catalyst.

Figure 2 shows that the logarithm of the effective rate constants linearly varies with the logarithm of the catalyst concentration. The orders with respect to the catalyst are identical for the constants $k_2'$ and $k_{-2}'$, namely, 1.43.

The constants $k_2$ and $k_{-2}$ were calculated by the equations

$$k_2 = k_2'/c_{\mathrm{cat}}^{1.43}, \quad k_{-2} = k_{-2}'/c_{\mathrm{cat}}^{1.43}.$$

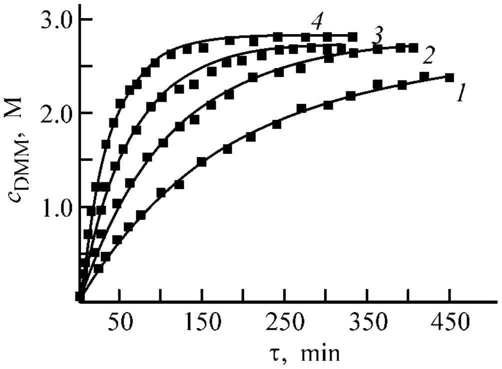

**Fig. 1.** Kinetic curves of DMM formation at (*1*) 303, (*2*) 308.3, (*3*) 313.3, and (*4*) 318.3 K. M : FA molar ratio 2 : 1. ($c_{\mathrm{DMM}}$) DMM concentration, and (τ) time. (*Solid line*) Calculated values and (*black squares*) experimental values at $c_{\mathrm{cat}}$ = 0.1298 M.

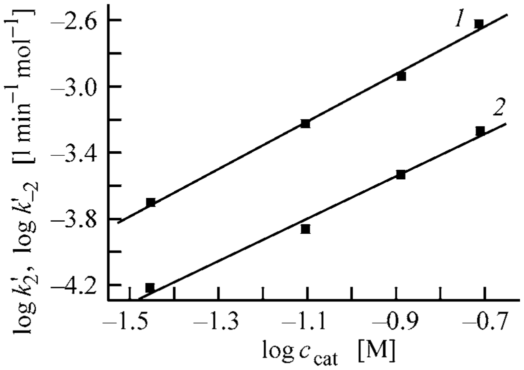

**Fig. 2.** Variation of the effective rate constants (*1*) $k_2'$ and (*2*) $k_{-2}'$, of DMM formation with the catalyst concentration $c_{\mathrm{cat}}$ at 313.3 K.

The temperature dependence of the rate constant is described by the Arrhenius equation (see table), and it was used for determining the expressions for $k_2 = f(T)$ and $k_{-2} = f(T)$ (activation energy, $\mathrm{J\,mol^{-1}}$; temperature, K):

$$k_2 = 1.478 \times 10^{13} e^{-88\,800/RT},$$

$$k_{-2} = 6.798 \times 10^{11} e^{-84\,690/RT}.$$

Rate constants $k_2$ and $k_{-2}$ at different temperatures

| $T$, K | $k_2$ | $k_{-2}$ |
|---|---|---|
| | $\mathrm{l^2\,min^{-1}\,mol^{-2}}$ | |
| 303 | 0.007421 | 0.001855 |
| 308.3 | 0.01318 | 0.002784 |
| 313.3 | 0.02226 | 0.005566 |
| 318.3 | 0.03897 | 0.008165 |
| 323.1 | 0.06679 | 0.01484 |

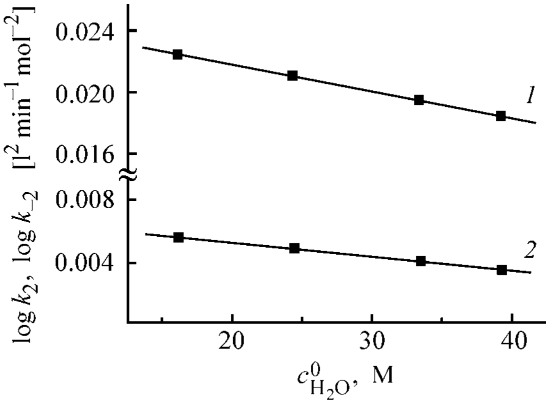

**Fig. 3.** Variation of the rate constants (*1*) $k'_2$ and (*2*) $k'_{-2}$, of DMM formation with the initial water concentration $c^0_{H_2O}$ at 313.3 K.

Using the dependences of $k_2$ and $k_{-2}$ ($T$ = 313.3 K) on the initial concentration of water in the system (Fig. 3), we derived the expressions

$$k_2 = 0.02493 - 0.000161c^0_{H_2O},$$
$$k_{-2} = 0.0069 - 0.00008454c^0_{H_2O}.$$

These dependences suggest that the rate constants $k_2$ and $k_{-2}$ are weakly dependent both on the initial water concentration in the system and, evidently, on the composition of the reaction mixture as a whole.

## CONCLUSION

A kinetic model was developed for synthesis of dimethoxymethane from methanol and formaldehyde, catalyzed by silicotungstic heteropoly acid $H_4SiW_{12}O_{40}$. The dependences of the rate constants of the process on the temperature and composition of the medium were obtained.

## REFERENCES

1. Chinese Patent 688 041.
2. UK Patent 1 379 444.
3. Walker, J.F., *Formaldehyde*, 2-nd ed., New York: American Chem. Soc., 1953. Translated under the title *Formal'degid*, Moscow: Goskhimizdat, 1957.
4. Zhenghun Shan, Yanru Wang, Shouchang Qiu, *et al.*, *Fluid Phase Equil.*, 1995, vol. 111, no. 1, pp. 113–126.