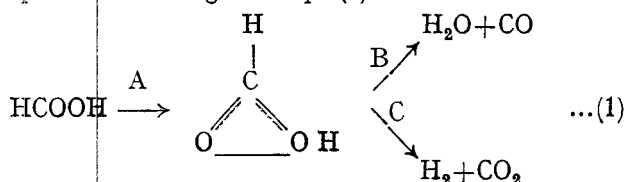# Catalytic Decomposition of Formic Acid on Zinc Molybdate

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Studies on the catalytic decomposition of formic acid on $ZnMoO_4$ showed that the dehydrogenation reaction proceeds through a formate intermediate, identified to be zinc formate. Thermogravimetric, DTA and IR spectroscopic data support this conclusion. X-ray analysis of the catalyst after the reaction with formic acid show that the catalyst breaks down into its component oxides, ZnO and MoO_3, under the reaction conditions.

CATALYTIC decomposition of formic acid, a test reaction for dehydrogenation and dehydration activities, has been shown[1] to proceed through the formation of surface formate species according to Eq. (1).

$$\text{HCOOH} \xrightarrow{A} \underset{O \quad O\,H}{\overset{H}{\underset{}{\overset{|}{C}}}} \begin{array}{l} \overset{B}{\nearrow} H_2O + CO \\ \underset{C}{\searrow} H_2 + CO_2 \end{array} \quad \ldots(1)$$

Depending on the prevailing experimental conditions either step A or B (or C) can be rate-controlling. On acidic oxides like Al_2O_3, SiO_2, TiO_2 the adsorption can be either dissociative or non-dissociative[2-4]. On all other oxides, it has been shown by IR spectroscopic method that the reaction proceeds through the dissociative adsorption of formic acid[1].

The present investigation on the decomposition of formic acid on zinc molybdate ($ZnMoO_4$) has been motivated by the following reasons: (i) $ZnMoO_4$ has been found to be a good dehydrogenation catalyst for the decomposition of isopropyl alcohol[5] and is, therefore, an appropriate system for investigating the parallelism between this reaction and the decomposition of formic acid claimed by Mars et al.[1]. (ii) It is of interest to study the nature of the intermediate surface formate formed on this type of ternary oxides[6].

Materials and Methods

Zinc oxide (prepared from zinc oxalate) was mixed thoroughly with molybdenum oxide (certified ACS quality, Fischer Scientific Co., New Jersey, USA) in 1:1 molar ratio and the mixture heated at 500° for 24 hr. The product thus obtained was confirmed as $ZnMoO_4$ by chemical analysis and IR spectra[7,8].

The decomposition studies were carried out in a flow type steady state reactor at atmospheric pressure in the temperature range 240°-300°. The products collected under steady state conditions were analysed by Orsat analysis and by gas chromatography.

The thermogravimetric analyses of zinc formate and of the same with MoO_3 were carried out isothermally with an automatic recording thermobalance (Stanton model HT-SM).

Differential thermal analyses were made using a recording DTA apparatus, at heating rates of 5°, 10° and 20°/min. Ignited alumina was used as the reference material.

The IR spectra of pure zinc formate and the catalyst after exposure to formic acid vapour were recorded in KBr on a Beckman IR-12 spectrometer.

Results

Catalytic decomposition of formic acid — The catalytic decomposition of formic acid has been carried out on zinc molybdate and zinc oxide in the temperature range 240-300° as a function of contact time. Both these catalysts have been found to promote the dehydrogenation reaction exclusively. The concentration-time plots at various temperatures for the reaction on zinc molybdate are shown in Fig. 1. The values of the activation energy and frequency factor for the decomposition of formic acid on zinc oxide and zinc molybdate catalysts calculated from Arrhenius plots are: E and frequency factor (zinc oxide catalysts) 21·9 kcal/mole and $6·7 \times 10^9$ min^{-1} respectively;
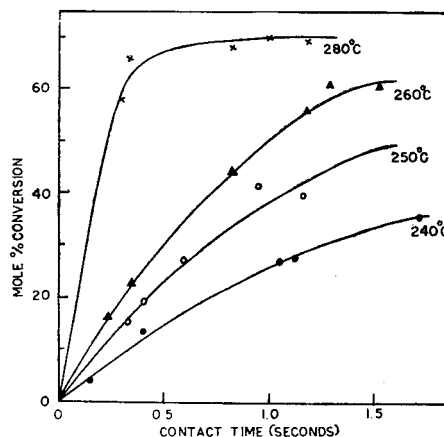

Fig. 1 — Concentration-time plots for the decomposition of formic acid on $ZnMoO_4$

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E and frequency factor (zinc molybdate catalyst) 26·2 kcal/mole and 2.42×10^{11} min^{-1} respectively.

Thermal decomposition of zinc formate: (a) *Thermogravimetric measurements* — The kinetics of isothermal decomposition of zinc formate have been studied in the temperature range 220-300°. The results were analysed through various kinetic equations based on different models and the data have been found to obey (i) the Avrami-Erofeyev Eq. (2)

$$- \log (1-\alpha) = (kt)^n \qquad \ldots(2)$$

where α is the fraction decomposed at time t and (ii) contracting cube Eq. (3)

$$1 - (1-\alpha)^{1/3} = kt \qquad \ldots(3)$$

The corresponding plots are shown in Figs. 2 and 3. The above values of k have been utilized in the construction of Arrhenius type of plots for the evaluation of activation energies, given in Table 1.

(b) *Differential thermal anaylsis* —The differential thermal analysis of zinc formate showed two endothermic peaks around 150° and at 300°. The first peak corresponds to the dehydration process and the second to the decomposition of zinc formate to zinc oxide. The energy of activation as well as the frequency factor have been calculated by the method proposed by Kissinger[9] using Eq. (4)

$$2 \log T_m - \log \frac{dT}{dt} = \frac{E}{2 \cdot 303 \, RT_m} + \log \left(\frac{E}{RA} \right) \quad \ldots(4)$$

where T_m is the temperature at which the peak maximum occurs. This type of analysis has been carried out by Trillo *et al.*[10] for the decomposition of the formates of manganese and iron. The values of E and A obtained from the linear plot of $[2 \log T_m - \log dT/dt]$ versus $1/T_m$ for the decomposition of zinc formate are given in Table 1.

Thermal decomposition of zinc formate in presence of MoO_3 — Molybdenum is known to form dimeric carboxylates only in the oxidation state $+2$. The formation of an analogous formate species under the experimental conditions employed in the present study for the decomposition of HCOOH is highly unlikely. Attempts have been made, therefore, to prepare complex formates of the type $Zn[MoO_3(HCOO)_2].xH_2O$ or $Zn[Mo_2O_5(HCOO)_4].xH_2O$ containing both Z_n^{2+} and Mo^{6+} ions. The corresponding oxalate complexes are known[11]. Our attempts to prepare such formate complexes resulted only in the formation of a mixture of zinc formate and molybdic oxide. The kinetics of decomposition of this mixture was studied for comparison with the kinetics of decomposition of pure zinc formate.

As with the latter, only the Avrami-Erofeyev and the contracting cube equations were found applicable to the kinetic data (Figs. 4 and 5). The values of the kinetic parameters derived are included in Table 1.

Discussion

Catalytic activity of zinc molybdate — Zinc oxide, zinc molybdate and the latter doped with lithium
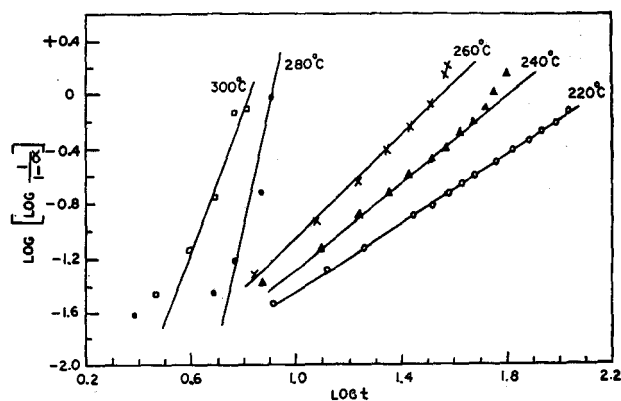

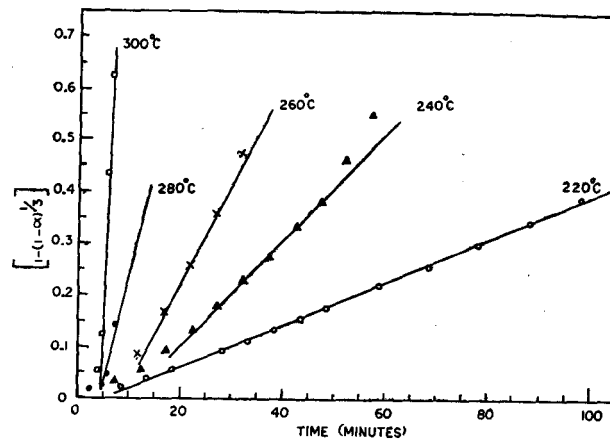Fig. 2 — Zinc formate decomposition kinetics according to Avrami-Erofeyev equation

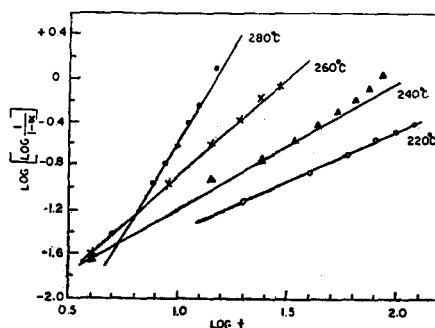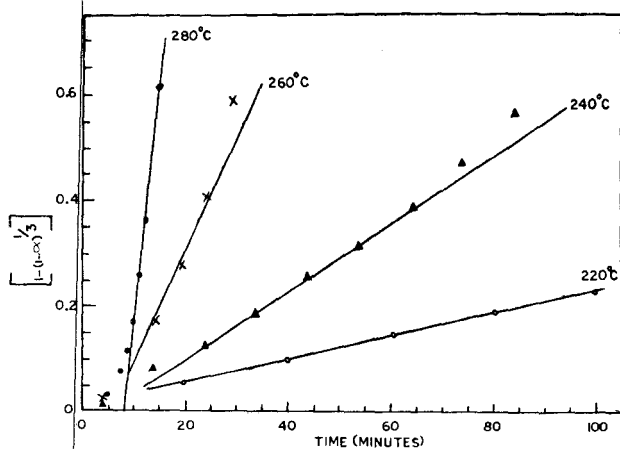Fig. 3 — Zinc formate decomposition kinetics according to contracting cube equation

Fig. 4—Kinetics of zinc formate decomposition in presence of MoO_3 according to Avrami-Erofeyev equation

TABLE 1 — KINETIC PARAMETERS FOR THE DECOMPOSITION OF ZINC FORMATE WITH AND WITHOUT MoO₃

Method	Pure zinc formate		Zinc formate with MoO₃	
	Activation energy (kcal/mole)	Frequency factor (min⁻¹)	Activation energy (kcal/mole)	Frequency factor (min⁻¹)
Contracting cube equation	20·7	$6·2 \times 10^6$	28·3	$8·5 \times 10^9$
Avrami-Erofeyev Equation	21·5	$3·8 \times 10^7$	27·9	$2·3 \times 10^{10}$
Differential thermal analysis	23·8	$3·8 \times 10^8$	30·5	$7·4 \times 10^{11}$

TABLE 2 — X-RAY DIFFRACTION PATTERN

ZnO		MoO₃		ZnMoO₄		ZnMoO₄ after reaction with formic acid	
I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)
m	1·240	w	1·443	w	1·435	w	1·243 (ZnO)
w	1·359	w	1·756	w	1·453	w	1·369 (ZnO)
w	1·379	w	1·982	s	1·513	w	1·441 (MoO₃)
w	1·477	w	2·271	m	1·697	w	1·625 (ZnO)
m	1·626	m	2·655	m	1·725	m	1·757 (MoO₃)
vs	2·476	w	2·702	m	1·933	w	1·973 (MoO₃)
s	2·602	w	3·006	w	2·214	s	2·273 (MoO₃)
s	2·816	vs	3·260	m	2·627	m	2·486 (ZnO)
		s	3·463	m	2·941	m	2·737 (MoO₃)
		s	3·600	vs	3·306	s	2·996 (MoO₃)
		s	3·810	vs	3·354	m	3·213 (MoO₃)
		m	6·930	s	3·627	s	3·471 (MoO₃)
				w	3·842	s	3·619 (MoO₃)
				w	4·487	vs	5·336
						s	7·026 (MoO₃)

Fig. 5 — Kinetics of zinc formate decomposition in presence of MoO₃ according to contracting cube equation

oxide have been found to catalyse the dehydrogenation of formic acid exclusively, yielding carbon dioxide and hydrogen. The fact that doping the zinc molybdate catalyst, with lithium oxide, which lowers its Fermi level, produces no change in the selectivity of the decomposition, shows that the latter does not involve any electron-exchange between the catalyst and the substrate. Further, if the molybdate ions were active in the decomposition of formic acid, as is the case in the decomposition of isopropyl alcohol on the same catalyst[5] the dehydration reaction should also have occurred to some extent. The complete absence of this reaction is a clear indication that the active constituent in zinc molybdate that is responsible for decomposition of formic acid is just zinc oxide which operates through the intermediate formation of zinc formate. The fact that the activation energy for the decomposition of zinc formate in presence of molybdic oxide (~28 kcal/mole) is almost equal to that observed for the decomposition of formic acid on zinc molybdate (~26 kcal/mole) strongly suggests that the dehydrogenation reaction proceeds through the formation of zinc formate as the intermediate on this catalyst. This conclusion receives independent support from the IR spectrum of the

zinc molybdate catalyst taken after exposure to formic acid vapour at 260°. The spectrum [ν_{max} 2910 w (νC-H), 1670 sh (νCO), 1580 br (ν_{as}O-C-O), 1400, 1370, 1360 w (ν_s O-C-O), 760s (τ O-C-O) cm⁻¹] agrees closely with that recorded for pure zinc formate. The νMo-O bands at 910, 950 and 980 cm⁻¹ are not affected in the least, thus confirming the non-involvement of these bonds in the catalytic decomposition.

The X-ray diffraction pattern (Table 2) of the spent zinc molybdate catalyst after being used in several reaction runs showed that the left-over material was a mixture of ZnO and MoO₃. The characteristic lines found in the original ZnMoO₄ were absent in the used catalyst. This again confirms that zinc molybdate is unstable under conditions of catalysis of formic acid decomposition and breaks down into its component oxides. In this respect, it differs from manganese molybdate (MnMoO₄) which remains stable with its spinel structure intact under the same conditions[6].

Acknowledgement

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