

DEHYDROGENATION, DEAMINATION AND DISPROPORTIONATION OF DIETHYLAMINE OVER HETEROPOLY COMPOUNDS

Abdel-Ghaffar A. ALI and Laila I. ALI

*Chemistry Department,
Faculty of Education, Roxy, Cairo, Egypt*Received July 11, 1994
Accepted March 5, 1995

In a continuous flow system, transformation of diethylamine over heteropoly compounds was studied at 250 to 350 °C. It was found that ammonium molybdophosphate and tungstophosphate are the most active catalysts while copper molybdophosphate is the most stable one. 12-Molybdophosphoric acid and its salts were highly selective catalysts for dehydrogenation of diethylamine to ethylenediamine whereas 12-tungstophosphoric acid and its salts directed the reaction selectively to deamination. The role of Lewis acidity of metal cations, Brønsted acidity and basic sites in the reaction mechanism is discussed.

Heteropoly compounds are known to be suitable catalysts for dehydrogenation of O- and N-containing molecules, due to favourable effect of their acidity. 12-Heteropoly acid salts having Mo as the main heteroatom have been frequently used in such oxidations¹. Transformation of diethyl ether over salts of 12-molybdophosphoric acid produced ethylene as the primary product. However, also butenes were formed in small quantities along with acetaldehyde as an oxidation product².

Few studies have been carried out on the reactions of di- and triethylamine over alumina and on alumina treated with boric acid, hydrochloric acid and over silica^{3,4}. It was concluded that ethylene is formed via deamination reaction whereas triethylamine is produced by disproportionation.

The present work deals with the role of the acidity of heteropoly compounds, using diethylamine transformation at 350 °C as a model reaction.

EXPERIMENTAL

Ammonium and copper 12-molybdo- and tungstophosphates were prepared as described by Ono et al.⁵. A total of 100 mg of each catalyst sample was activated at 350 °C in a stream of pure dry nitrogen for 3 h in a differential reactor (length 15 cm, i.d. 1.0 cm). The sample temperature was measured by a digital thermometer. The flow rate of diethylamine was 0.02 mol/h, and the nitrogen to diethylamine molar ratio equaled to 4.

The reaction products (ethylene, butene, ethylamine, ethylenediamine, diethylamine, and triethylamine) were analyzed on Varian 3700 gas-liquid chromatograph equipped with a flame

ionization detector which was connected to Varian 9176 recorder. A stainless steel column (length 4 m, i.d. 3 mm) packed with 10% Squalene on Chromosorb P was used for the analysis of reaction mixtures.

Physicochemical methods such as IR spectroscopy and X-ray diffraction analysis were used to characterize the structure of the samples.

RESULTS AND DISCUSSION

Characterization of Primary and Secondary Structures of Heteropoly Compounds by IR Spectra and X-Ray Diffraction Analysis

It is well known that IR spectra reflect the primary structure (Keggin structure, $\text{PMo}_{12}\text{O}_{40}^{3-}$ and $\text{PW}_{12}\text{O}_{40}^{3-}$) whereas X-ray diffraction pattern reflects the secondary structure of heteropoly compounds (the three-dimensional arrangement of the Keggin anion, H_2O and cations). The IR spectra of the samples showed bands at $1\ 100 - 1\ 600\ \text{cm}^{-1}$ (which are characteristic of the Keggin structure) which were almost the same for all the samples. Two bands in the $1\ 700 - 1\ 600\ \text{cm}^{-1}$ region have been assigned to the bending modes of H_2O and $\text{H}^+(\text{H}_2\text{O})_n$. Both of them appeared for the acid form and disappeared upon heating at low temperatures⁶, $<150\ ^\circ\text{C}$. Broad bands at $3\ 500 - 3\ 200\ \text{cm}^{-1}$ are characteristic of the OH stretching vibrations in the crystalline structure.

X-Ray diffractograms of ammonium molybdo- and tungstophosphates are approximately the same as for the free acids², except for a few changes in the line intensities and positions. This means that the Keggin anion is retained after the salt formation. From the results obtained by IR spectroscopy and X-ray diffraction analysis one can conclude that for the heteropoly compounds, their primary structure is stable whereas the secondary one undergoes changes^{2,6}.

Effect of Residence Time

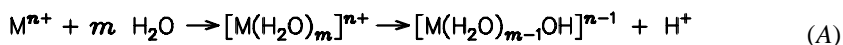
The effect of the residence time W/F on the total conversion (X , %) and the yield (Y , %) for ethylene, ethylamine and triethylamine formation was examined with HPMo at $350\ ^\circ\text{C}$ (Fig. 1). The residence time was varied by changing the total flow rate for a constant catalyst weight. The conversion increased linearly with the residence time, thus indicating that the process is free of external diffusion⁷.

The quantity of ethylene increased linearly with the residence time. This shows that the ethylene formation depends on the partial pressure of diethylamine. The rate of ethylamine and triethylamine formation increased with the pressure of diethylamine till a constant value has been obtained (the saturation partial pressure) at about $W/F = 8\ \text{g}_{\text{cat}}\ \text{h/mol}$. Above this pressure both ethylamine and triethylamine can be transformed into ethylene. The reaction constant k for HPMo catalyst was determined using the equation $\log 1/(1-x) = k(W/F)$, where x is the fractional conversion of diethylamine in the

plug-flow reactor, W is the catalyst weight (g) and F is the volumetric flow rate (ml/min) through the reactor⁸. By plotting $\log 1/(1-x)$ vs W/F , the value of k was found to be $21 \cdot 10^{-3} \text{ ml/g}_{\text{cat}} \text{ min}$.

Effect of Reaction Temperature on Catalyst Activity

The reaction was carried out over the two acids, HPW and HPMo, and the ammonium salt of HPMo at a constant flow rate of diethylamine (0.02 mol/h) and different temperatures from 250 to 350 °C (Fig. 2). Below 250 °C, no products were detected. Above 250 °C, the conversion increased at different rates with increasing reaction temperature. Tungstophosphoric acid is the most active catalyst. At 250 °C, HPW is more active than HPMo and NHPMo. This can be explained by assuming that at high temperatures (>250 °C) strong acidic sites are formed due to interaction of the residual structure water with Lewis acidic sites^{9,10} (Eq. (A), m is the number of moles of H_2O which remains in the pseudo-liquid phase zone).



Due to the flexibility of the secondary structure of heteropoly compounds, polar molecules such as alcohols and amines are readily absorbed into the solid bulk. Based on this pseudo-liquid phase concept, the rate of the amine reaction was found to increase with increasing temperature. This may be caused by the effect of H_2O of crystallization by which the interdistance between polyanions is expanded. The result is the increasing reaction zone in the solid bulk. At temperatures from 250 to 350 °C, the activation energies of HPMo, NHPMo and HPW are 52.3, 58.5 and 54.3 kJ/mol,

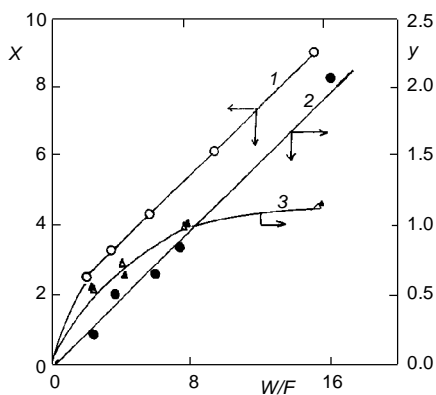


FIG. 1

Total conversion (X , %) of Et_2NH (1) and yield (Y , %) of ethylene (2); EtNH_2 and Et_3N (3) formation as a function of W/F ($\text{g}_{\text{cat}} \text{ h/mol}$)

respectively. This indicates that (i) catalyst pellets have practically the same particle size and (ii) the process is free of the external mass transfer effects¹¹.

Initial Activity and Stability of Catalysts

The initial activity of the catalysts was measured at 350 °C during 4 min. Data obtained are given in Table I. It was found that HPW is more active than HPMo, which can be

TABLE I

Total conversion (X , %), initial activity A_i (mol/h g) after 4 min, final activity A_f (mol/h g) after 180 min, residual activity A_r (%) and product distribution of reaction of diethylamine over heteropoly compounds at 350 °C

Catalyst	X , %	Catalyst activity			Product distribution				
		$A_i \cdot 10^3$	$A_f \cdot 10^3$	A_r	C_2H_4	C_4H_8	$EtNH_2$	EEA	Et_3N
HPMo	28	56	9.9	18	3.9	5.7	6.4	76.4	7.1
NHPMo	58	116	9.0	8	14.5	5.6	25.2	53.0	1.4
CuPMo	35	70	28.8	41	18.0	4.8	5.6	65.0	3.4
HPW	37	74	23.6	32	23.5	3.5	15.8	50.0	6.2
NHPW	51	102	27.8	27	33.6	3.7	7.4	53.3	1.6
CuPW	29	58	18.0	31	23.3	3.4	22.3	43.5	7.5

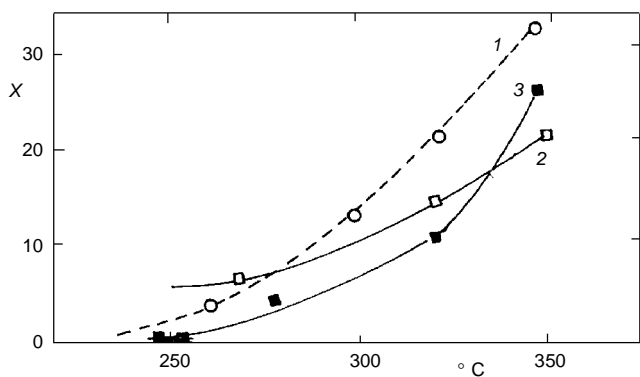


FIG. 2

Total conversion of Et_2NH (X , %) as a function of reaction temperature for 1 HPW, 2 HPMo and 3 NHPMo

due to its higher acid strength. The acidity seems to play an important role in the stabilization of formation of a complex between the polyanion and the reactant and/or reaction intermediate¹². The higher activity of the ammonium salt can result from participation of the surface acidity in addition to the bulk acidity. The ammonium salt has high surface area, which results in increasing initial activity. Hayashi et al.¹³ found that the distribution of the acid strength of the ammonium salts is broader than that of the parent acids. The lower activity of the copper salt is due to both its low surface area (<10 m²/g) and its lower acidity compared to the parent acids and ammonium salts¹⁴.

In order to examine the catalyst stability (Fig. 3), its activity is presented as a function of reaction time. As it is seen, the catalyst activity decreased sharply to a certain value (obtained after 30 min) and then remains approximately constant. This behaviour indicates that the rate of carbon deposit formation is very fast, taking place on the great number of acidic sites present on the fresh catalyst. The stability of the catalyst during the reaction was estimated from the value of the activity (A_r) retained by the catalyst at the end of the experiment. This parameter was expressed as the final activity (in mol/h g) divided by the initial activity, the result obtained was multiplied by a factor of 100. It was found that A_r (after 3 h) decreases in the following order:



This indicates that copper salts are the most stable catalysts. This results likely from formation of new catalytically active sites due to their Lewis acidity. The higher stability of the copper salts may be also due to their lower acidity compared to the free acids and ammonium salts, which leads to a decrease in the rate of coke formation.

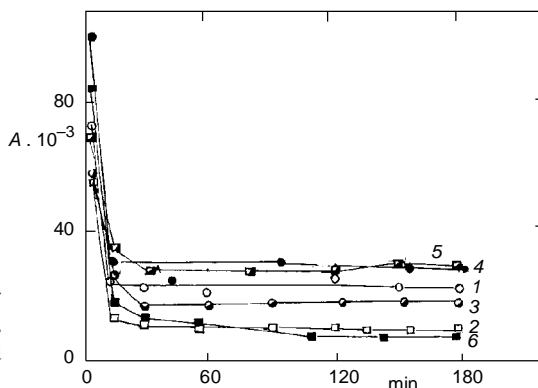


FIG. 3

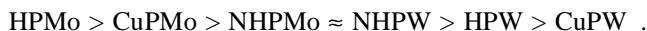
Time dependence of catalyst activity A (mol/h g_{cat}) for 1 HPW, 2 HPMo, 3 CuPW, 4 NHPW, 5 CuPMo, and 6 NHPMo

Catalyst Acidity vs Product Selectivity

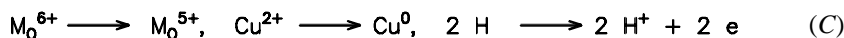
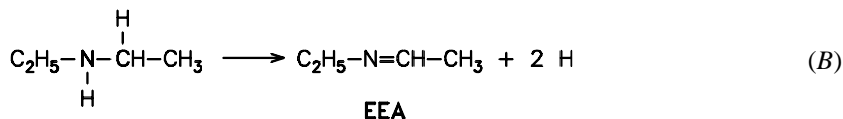
In transformation of diethylamine over heteropoly compounds three reactions competed with each other: dehydrogenation, deamination, and disproportionation. The relative dependance of these process depends on the nature of the catalyst and the strength and number of acid sites. Another important factor is likely the van der Waal's length (nm) of diethylamine molecule. The selectivity of its transformation depends also on the extent to which diethylamine is adsorbed through its nitrogen on the acid site. Very strong alkylamine adsorption is expected to occur when the N atom of the amine group approaches the acid site as close as possible. If not probable for steric reasons, or because all the acid sites were already utilized, the amine sorption should be much weaker¹⁵.

Dehydrogenation Selectivity

It is well known that heteropoly compounds are easily reduced in the solid state to form heteropoly blues. On these catalysts diethylamine is oxidized to ethylidenethylamine via an oxidation-reduction process. The initial relative yield of the dehydrogenation of diethylamine (EEA) is given in Table I. Data show that dehydrogenation selectivity decreases in the following order:



It is evident that HPMo and its salts are the more selective dehydrogenation catalysts. This indicates that molybdenum atom is reduced easier than tungsten atom. The highest selectivity of HPMo for the dehydrogenation is because the rate of reduction equals to the rate of its reoxidation¹⁶. Tsuneki et al.¹ suggested that the central Mo, the countercation and the oxygen atom of Mo–O–Mo are involved in the redox cycle without removal of the oxygen from the polyanion. Based of previous studies and our results, the following mechanism depicted by Eqs (B) and (C) can be proposed (M = Mo, W, Cu). It is clear that Lewis acidity of M and basic sites (O) participate in the dehydrogenation reaction (surface reaction).



The rate of the dehydrogenation decreases during 30 min and then remains constant up to 3 h (Fig. 4). This may be due to the strong adsorption of amine molecules on some Lewis acid sites, leading to the greater dispersion of these sites. At this stage, the rate of the dehydrogenation becomes constant.

Deamination Selectivity

Diethylamine was decomposed into ethylene and ethylamine according to Eq. (D) (ref.¹⁷).



The initial deamination selectivity shown in Table I decreases in the following order:



This sequence is inverse to that obtained for dehydrogenation. The reaction is catalyzed by the acid, which is evidenced by the sequence in which HPW and its salts (which are more acidic than HPMo) are highly selective for the deamination.

Polar molecules such as amines are readily absorbed into the solid bulk (pseudo-liquid phase) to the extent which depends on the absorptivity of the amine on the bulk acid. The protons in the catalyst bulk and those obtained from the dehydrogenation can act as active centers for the reaction (E).

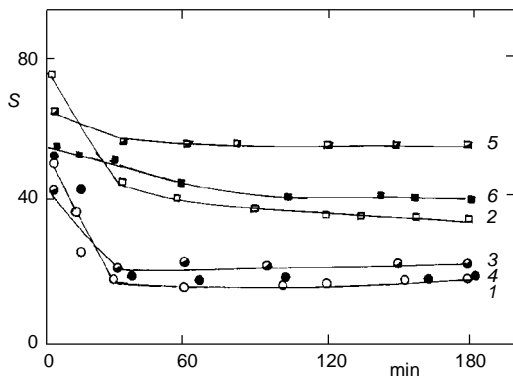
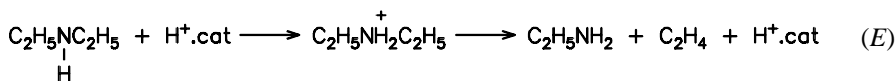


FIG. 4

Selectivity (*S*, %) with respect to the dehydrogenation of Et₂NH as a function of reaction time for 1 HPW, 2 HPM, 3 CuPW, 4 NHPW, 5 CuPMo, and 6 NHPMo

It was found (Fig. 5) that the relative extent of the deamination increases till a maximum reached in 30 min. Then it remains constant up to 3 h. This behaviour indicates the presence of an induction period, during which new and much more catalytically active species are formed. Formation of these species (H^+) improves also the stability of the catalyst in this reaction.

Small amounts of 2-butene are also produced by the reaction of ethylene with strongly adsorbed diethylamine. According to the Zaitsev rule, the more alkylated alkene is the predominant product¹⁸ (Eq. (F)).

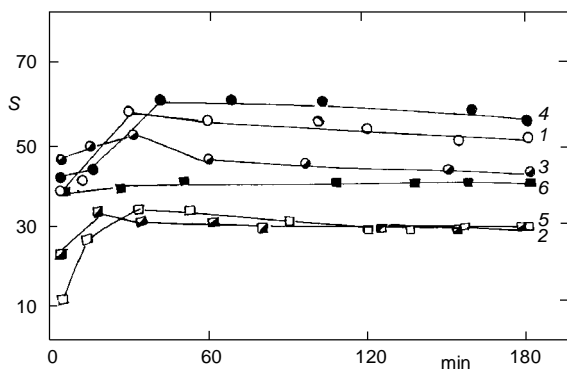
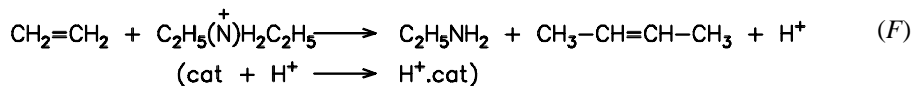


FIG. 5
Selectivity (S , %) with respect to the deamination of Et_2NH as a function of reaction time for 1 HPW, 2 HPMo, 3 CuPW, 4 NHPW, 5 CuPMo, and 6 NHPMo

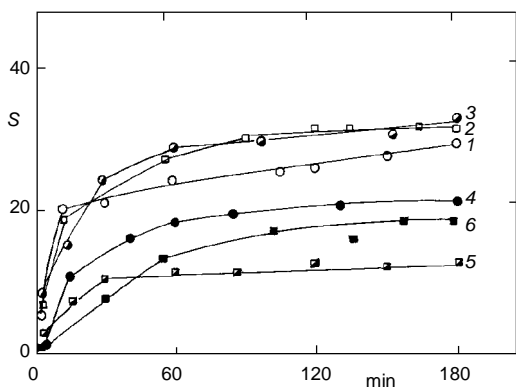


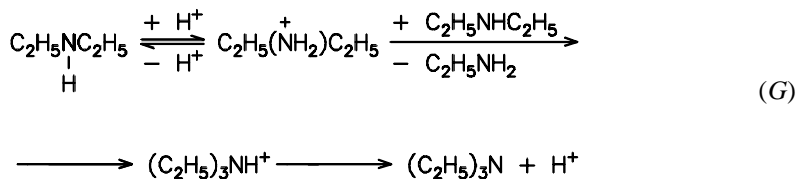
FIG. 6
Selectivity (S , %) of triethylamine formation as a function of reaction time for 1 HPW, 2 HPMo, 3 CuPW, 4 NHPW, 5 CuPMo, and 6 NHPMo

Disproportionation Selectivity

The selectivity is governed by the catalyst pore volume and the presence of adjacent active sites. In this reaction, ethylamine and triethylamine are reaction products. In this case, the selectivity has been measured as a function of triethylamine formation. Ethylamine was produced via deamination and disproportionation reactions. The initial selectivity for triethylamine formation decreases in the following order (see Table I and Fig. 6):



This indicates that the two acids and Cu salts are more selective than the ammonium salts, depending on the number of H^+ present in the catalyst and/or produced during the reaction. The decrease in the rate of triethylamine formation over these catalysts may be due to (i) steric effects which restrict the desorption of triethylamine through catalyst pores and (ii) transformation of triethylamine into ethylamine and ethylene before its desorption (bulk reaction). The disproportionation reaction is depicted schematically in Eq. (G).



In this reaction only one amine molecule adsorbed on the surface takes part in the reaction¹⁹.

CONCLUSIONS

From the results obtained, one can conclude that (i) heteropoly compounds as acidic substances catalyze diethylamine conversion, (ii) molybdophosphoric acid is highly selective for the dehydrogenation of diethylamine due to facile reduction of Mo^{6+} , (iii) the strongly acidic tungstophosphoric acid is selective for the deamination reaction, (iv) copper tungstophosphate shows good stability, being thus of industrial interest and (v) ammonium salts are the most active catalysts for diethylamine transformation.

SYMBOLS

CuPMo	copper molybdophosphate
CuPW	copper tungstophosphate
HPMo	12-molybdophosphoric acid

HPW	12-tungstophosphoric acid
NHPMo	ammonium molybdophosphate
NHPW	ammonium tungstophosphate
EEA	ethylidenethylamine
Et ₂ NH	diethylamine
EtNH ₂	ethylamine
Et ₃ N	triethylamine
A _i	initial catalyst activity (mol/h g _{cat})
A _f	final catalyst activity (mol/h g _{cat})
A _r	percentage residual activity [(A _f /A _i) 100]
H ⁺ . cat	acidic catalyst
M ⁿ⁺	metal ion
m	number of moles
S	selectivity, %
W/F	residence time (g _{cat} h/mol)
X	conversion, wt.%

REFERENCES

1. Tsuneki H., Niiyama H., Echigoya E.: *Chem. Lett.* 1978, 1183.
2. Abdel-Ghaffar A.: *J. Chim. Phys.* 90, 527 (1993).
3. Fikry E. M., Zahra A. M., El-Hilaly A., Laila I.: *Egypt. J. Chem.* 19, 771 (1979).
4. Fikry E. M., Aboul-Gheit A. K., Ezzo E. M., Laila I. A.: *J. Chin. Chem. Soc.* 29, 125 (1982).
5. Ono Y., Baba T., Sakai J., Keii T.: *J. Chem. Soc., Chem. Commun.* 1981, 440.
6. Black J. B., Clayden N. J., Gai P. L., Scott J. D., Serwicka E. M.: *J. Catal.* 106, 1 (1987).
7. Ahmed S., Moffat J. B.: *Appl. Catal.* 40, 101 (1988).
8. Nayak V. S., Moffat J. B.: *Appl. Catal.* 47, 97 (1989).
9. Matsuda T., Sato M., Kanno T., Miura H., Sugiyama K.: *J. Chem. Soc., Faraday Trans.* 77, 3107 (1981).
10. Cynthia T. W., Chang C. D.: *J. Catal.* 86, 297 (1984).
11. Horak J., Pasek J.: *Design of Chemical Reactors from Laboratory Data*, p. 209. Heyden, London 1978.
12. Izumi Y., Matsuo K., Urabe K.: *J. Mol. Catal.* 18, 229 (1983).
13. Hayashi H., Moffat J. B.: *J. Catal.* 83, 192 (1983).
14. Hayakawa N., Okuhara T., Misono M., Yoneda Y.: *Nippon Kagaki Kaishi* 1982, 356.
15. Pope C. G.: *Zeolites* 10, 28 (1990).
16. Misono M., Mizuno N., Komaya T.: *Proc. 8th Int. Cong. on Catalysis Weinheim*, Vol. 5, p. 487. Verlag Chemie, Berlin 1984.
17. Ebeid F. M., Pasek J., Koubek J.: *Egypt. J. Chem.* 19, 1013 (1976).
18. Kaeding W., Butter S.: *J. Catal.* 61, 155 (1980).
19. Ebeid F. M., Pasek J.: *Collect. Czech. Chem. Commun.* 35, 2166 (1970).