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Reactions of Aliphatic Amines over Evaporated Metal Films

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The catalytic reactions of mono-, di-, and trimethylamine, and ethylenimine have been studied in the presence of hydrogen over a variety of evaporated metal films. There was evidence for the incorporation of carbon into the catalyst with Pt, Pd, Ni, W, and Co and for the incorporation of nitrogen with vanadium. Electron diffraction examination showed the presence of separate carbide phases with Ni, Co, and W and a separate nitride phase with V. No separate carbide phases could be detected with Pd and Pt.

Methylamine and dimethylamine each reacted in two distinct ways: (i) simple hydrocracking and (ii) other reactions, of which the most important was a disproportionation involving two amine molecules. Some ethylenimine and acetonitrile were formed during the reaction of methylamine over W, Co, V, and Cu, and during the reaction of dimethylamine over W and Co. Small amounts of hydrocarbons in the range C_2–C_4 were also found in most cases. Under the conditions used, nickel was the metal most to favor hydrocracking, while palladium and platinum favored disproportionation. Over nickel and palladium the rate of hydrocracking of methylamine was close to zero order in amine pressure, while disproportionation was close to second order. Trimethylamine reacted over palladium with hydrocracking as the only primary process and dimethylamine was the most abundant product.

The presence of $C^{13}H_4$ or $N^{15}H_3$ in the methylamine reaction mixture did not result in the incorporation of C^{13} or N^{15} in the disproportionation product, nor was there any exchange with the parent amine. Furthermore, reaction of a mixture containing $C^{13}H_3NH_2$ and $CH_3N^{15}H_2$ did not result in a direct exchange reaction. From these data and from the observed pressure dependence it is concluded that the most likely mechanism for disproportionation is by a surface bimolecular reaction between adsorbed amine residues.

The main reaction of ethylenimine was ring opening by rupture of a carbon–nitrogen bond, the product of this being ethylamine over Pt and Pd, acetonitrile over Co, V, and Cu, and a mixture of both over Ni and W. Appreciable amounts of C_3 and C_4 amines were also produced, particularly over Ni, W, Co, and V.

INTRODUCTION

Anderson and Clark (*1*) recently studied the interaction of hydrogen cyanide plus hydrogen with clean metal surfaces. They noted the appearance in the reaction products of higher amines and hydrocarbons, and some preliminary work was recorded to show that this feature was also found in the reactions with methylamine. It was there concluded that in the interaction with clean metal surfaces, both hydrogen cyanide and methylamine yield surface residues of very similar type. The purpose of the present work has been to study in more detail the reactions of methylamine and dimethylamine plus hydrogen over clean metal surfaces. Reactions of methylamine over some evaporated metal films have been studied previously by Kemball and Moss (*2*).

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EXPERIMENTAL

The general experimental details have been described previously (*1*).

Ammonia-N^{15} was prepared from ammonium chloride-N^{15} (95.3 atom % N^{15}, from Bio-Rad Laboratories), using the method of Clausius and Effenberger (*3*). Purification was by the same method as given previously (*1*) for the aliphatic amines. The recovery of ammonia-N^{15} was quantitative. Methane-C^{13} was prepared by the reduction of methyl iodide-C^{13} (62.4 atom % C^{13}, from Bio-Rad Laboratories) with lithium aluminum hydride in sodium-dried diethyl ether. Reaction occurred readily at room temperature and the product was recovered in quantitative yield after passage through a liquid-air trap, and was then mass-spectrometrically pure.

Methylamine-N^{15} was prepared from potassium phthalimide-N^{15} (96.7 atom % N^{15} from Bio-Rad Laboratories) and excess methyl iodide, using the general method of Cox and Warne (*4*). The amine was purified as described above. An over-all yield of 96% was obtained.

Methylamine-C^{13} was prepared by hydrogenation of potassium cyanide-C^{13} (57.5 atom % C^{13}, from Bio-Rad Laboratories) in acid medium with a platinum oxide catalyst. The amine was purified as described above. An over-all yield of 94% was obtained.

Reactions were followed with an MS10 mass spectrometer in the manner previously described (*1*), using low-energy electrons (nominally 17.5 V).

Where necessary, corrections were made for fragmentation and for naturally occurring C^{13}, N^{15}, and D.

Gas-phase chromatography was used to detect small amounts of minor reaction products and to confirm the presence of compounds indicated in the mass spectrum of the reaction mixture. Three columns were used at various times to analyze for hydrocarbon components: (a) dimethyl sulfolane/Celite [Fredericks and Brooks (*5*)]; (b) squalane/Pelletex [Eggertsen, Knight, and Groennings (*6*)]; (c) paraffin/Celite [Harrison (*7*)]. All gave mutually consistent results. A column of cetyl alcohol supported on alkali-treated firebrick [Yang and Wolf (*8*)] was used to identify nitrogenous products from their retention times. However, with the small amounts of these components present in the sample, strong absorption on the column was always severe (presumably on the support) and quantitative analytical data could not be obtained. Extensive trials of other supports including powdered Teflon were unrewarding. In all cases the columns were used with a flame-ionization detector.

Electron diffraction examination of used catalysts was done in transmission with a Siemens Elmiskop 1 at 100 kV or in reflection at grazing incidence with a Metropolitan-Vickers camera at 50 kV. Film specimens for examination in transmission were stripped from the glass by the method previously described by Anderson, Baker, and Sanders (*9*).

Under standard reaction conditions, the reaction vessel contained 14.1 mm amine and 19.8 mm hydrogen, equivalent to 1.19×10^{20} and 1.67×10^{20} molecules, respectively. The reaction mixture was introduced into the reaction vessel at 273°K and a period of about 10 min was then allowed until a constant mass-spectral response had been reached. The reaction vessel was then raised to the reaction temperature, a period of about 5 min being required to establish constant temperature.

Results

A. Examination of Catalysts Used with Methylamine plus Hydrogen

A mass balance in carbon and nitrogen showed that incorporation of carbon into the catalyst was occurring with all catalysts except copper and vanadium. On vanadium, incorporation of nitrogen occurred. For example, after 25% of the parent methylamine had reacted, the over-all composition of the catalysts, estimated from the mass balance, was as given in Table 1; the nature of the phase has been inferred with the aid of the electron diffraction results.

Electron diffraction examination of the used catalysts gave the following results: Nickel—a diffraction pattern which indexed as $Ni_3C + Ni$; tungsten—$W_2C + W$; vanadium—either (or both) VC and VN + V; cobalt—either (or both) Co_2C and Co_2N

TABLE 1
COMPOSITION OF CATALYSTS AFTER 25% OF METHYLAMINE HAD REACTED

Palladium (10 mg), 16 min at 480°K, one carbon atom per 5 Pd atoms
Platinum (10 mg), 40 min at 480°K, one carbon atom per 15 Pt atoms
Nickel (10 mg), 110 min at 480°K, 83% Ni_3C + 17% Ni
Cobalt (10 mg), 100 min at 560°K, 20% Co_2C + 80% Co
Vanadium (~2 mg), 70 min at 560°K, 25% VN + 75% V
Tungsten (10 mg), 75 min at 560°K, 20% W_2C + 80% W
Copper (10 mg), 560°K, no incorporation

+ Co. Examination of used specimens of palladium and platinum failed to reveal any diffraction features other than those due to the metal.

B. Reactions with Methylamine

Table 2 records the products produced in the early stages of the reaction from methylamine over a variety of metal catalysts. The temperature range used with each metal is included in Table 3. In all cases, standard reaction mixtures were used and the distributions of reaction products were, within experimental error, independent of temperature except for palladium at high temperatures. The behavior in this case is discussed later. The presence of acetonitrile was inferred from a peak at mass 41 which was also used for quantitative estimation. Peaks at masses 42 and 43 were assigned to ethylenimine after gas chromatography showed the presence of a compound with the same retention time as that of ethylenimine.

The over-all rate of reaction was determined from the rate of disappearance of the parent amine, and in general this was measured from the initial rate of disappearance of parent. Reaction rates are represented in Fig. 1 in an Arrhenius plot, and the corresponding kinetic parameters are collected in Table 3. The activation energies and

TABLE 2
PRODUCTS FROM THE REACTION OF $CH_3NH_2 + H_2$ OVER VARIOUS METALS

	Extent of reaction (%)	Composition of reaction product (%)									Carbon/nitrogen imbalance[a]
		NH_3	$(CH_3)_2NH$	$(CH_3)_3N$	CH_3CN	$CH_2—CH_2$ \ / NH	Hydrocarbons C_1	C_2	C_3	C_4	
Pt	12	54	24	1.5	—	—	20	0.5[b]	—	—	7.5% C loss
Pd	20	66	26	5.5	—	—	2	0.5[b]	—	—	27% C loss
Ni	31	92	3.5	—	—	—	3	1.5[c]	trace		86% C loss
W	12	58	16	1	7	11	2	3[d]	1[d]	1[d]	7.5% C loss
Co	30	72	9	1	6	2	1	6[d]	2[b]	1[b]	33% C loss
V	26	48	18	2	16	8	4	2	2	—	12% N loss
Cu	12	52	34	1	2	5	11	4	1	—	—

[a] Due to carbon (or nitrogen) incorporation into catalyst.
[b] Saturate only.
[c] Ratio of olefin to saturate 5:1.
[d] Ratio of olefin to saturate 3:1.

TABLE 3
ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR OVER-ALL REACTION OF METHYLAMINE

	Temperature range (°K)	Activation energy (kcal mole^{-1})	$\log_{10}$ (frequency factor) (molecules sec^{-1} cm^{-2})
Pt	455–515	19.7 (19.9)[a]	22.6 (22.1)
Pd	435–526	21.5 (21.5)	23.9 (23.1)
Ni	445–518	13.3 (16.9)	18.8 (20.2)
W	535–589	15.9 (17.0)	18.4 (18.3)
Co	475–614	9.7	17.1
V	526–643	12.9	18.1
Cu	537–591	18.3	20.5

[a] The bracketed figures are those given by Kemball and Moss (*2*).

frequency factors are subject to estimated uncertainties of ± 1 kcal mole^{-1} and ± 0.5 in the logarithm, respectively. In calculating frequency factors, the same film areas were used as given by Anderson and Clark (*1*).

is linear (Fig. 2). The latter gives an activation energy for methane production of 22 kcal mole^{-1} which is the same, within experimental error, as that listed in Table 3 for the over-all reaction.

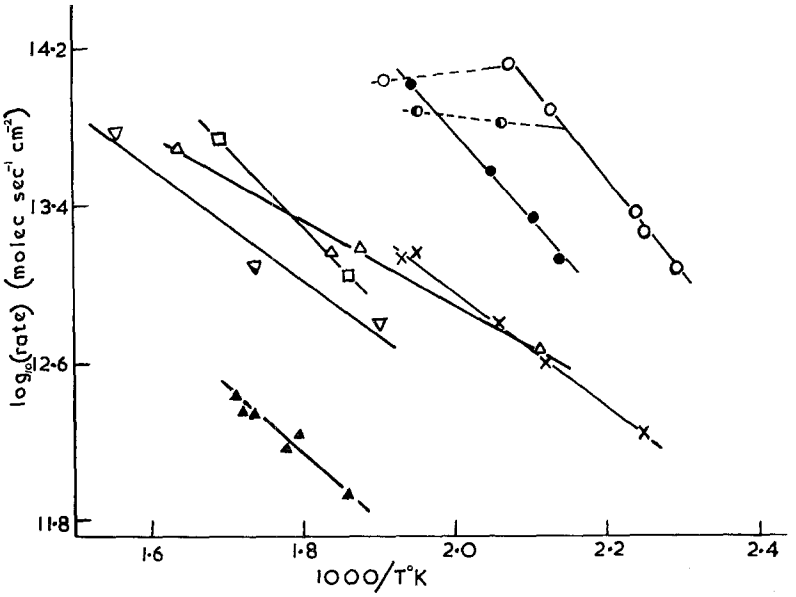


FIG. 1. Variation with temperature of total rate of reaction of methylamine: ×, Ni; ●, Pt; ○, Pd; ◐, Pd with excess NH_3; ▲, W; □, Cu; ▽, V; △, Co.

It is evident from Table 2 that over all metals two reactions occur: (a) simple hydrocracking to give ammonia and, depending on the alternative destination for carbon, some methane; and (b) the synthesis of higher amines and hydrocarbons (or substances closely related to them). For the purpose of the subsequent discussion, these two reactions will be referred to as hydrocracking and synthesis, respectively. The synthesis reaction occurs to a relatively large extent on palladium, yielding mainly dimethylamine, and the reaction was studied in greatest detail over this metal as a typical example.

It is seen in Fig. 1 that at high temperatures over palladium, the over-all rates are abnormally low compared to the Arrhenius plot. This is due to a fall in the rate of the synthesis reaction relative to hydrocracking, since throughout this temperature range the Arrhenius plot for the production of methane

The addition of methane or ammonia to a standard reaction mixture to give a reaction mixture of relative composition CH_4 or NH_3, 0.4: CH_3NH_2, 1.0: H_2, 1.4, gave no significant alteration in either the over-all reaction rate or the product distribution for any metal over most of the temperature range. However, on palladium at high temperatures the addition of ammonia resulted in a depression of the over-all reaction rate; the appropriate points are distinguished in Fig. 1.

The dependence of both hydrocracking and synthesis on gas pressure was determined over palladium and nickel. The results are given in Table 4.

The error in each pressure exponent is estimated at ± 0.2. The data in Table 4 are valid for methylamine pressures up to about a factor of 2 greater than in the standard reaction mixture. Higher methylamine pressure led to irreproducible behavior, possibly due to self-poisoning of the catalyst surface.

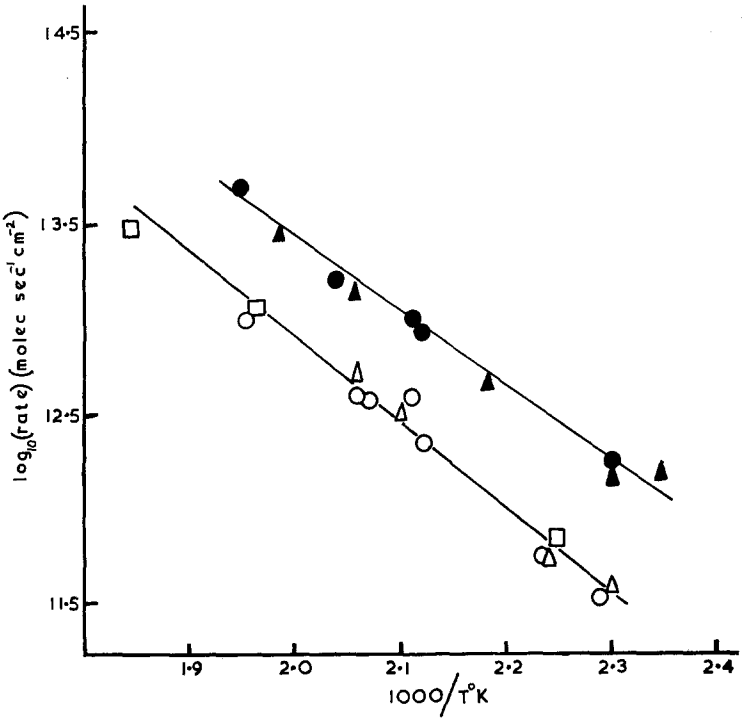


FIG. 2. Variation with temperature of rate of methane production: ○, Pd with methylamine; △, Pd with dimethylamine; ●, Pt with methylamine; ▲, Pt with dimethylamine; □, Pd with trimethylamine.

TABLE 4
PRESSURE-DEPENDENCE EXPONENTS FOR HYDROCRACKING AND SYNTHESIS REACTIONS

	Nickel (483°K)		Palladium (454°K)	
	Exponent for		Exponent for	
	P_{H_2}	$P_{CH_3NH_2}$	P_{H_2}	$P_{CH_3NH_2}$
Hydrocracking	0.4	−0.1	—	0.1
Synthesis	−0.2	1.7	—	2.0

C. Reactions with Isotopic Labeling

Attempts were made to observe a nitrogen atom exchange during the reaction of a $N^{15}H_3/CH_3NH_2/H_2$ mixture and a carbon atom exchange in a $C^{13}H_4/CH_3NH_2/H_2$ reaction mixture. Observation of the mass spectra of mono-, di-, and trimethylamine with natural abundance of heavy isotopes showed that under the present conditions, the sizes of the peaks at the parent-plus-one $(p + 1)$ mass were in the range of 3–5% of the parent peak height and were sensitive to mixture composition and to total pressure. For comparison, the expected contributions at $(p + 1)$ from natural abundances of heavy isotopes in the parent amines are 1.55, 2.68, and 3.83% of the parent peak for mono-, di-, and trimethylamine, respectively. These augmented $(p + 1)$ peaks are attributed to ions of the type $CH_3NH_3^+$, etc., formed in the ion source, and have been observed previously [cf. Beynon (*10*)]. The procedure was therefore adopted of comparing the 32/31, 46/45, and 60/59 peak height ratios from reactions of mixtures containing $N^{15}H_3$ or $C^{13}H_4$ with the ratios measured from similar mixtures, but containing only natural abundances of heavy isotopes. The reproducibility of several $(p + 1)/p$ ratios expressed as percentages varied between ±0.1 and ±0.2%. These reaction mixtures were of the same over-all composition as those, mentioned in the previous section, to which methane or ammonia had been added. The data in Table 5 show that, within experimental error, no nitrogen or carbon atom exchange occurred.

TABLE 5

PEAK HEIGHT RATIOS FROM METHYLAMINE REACTION MIXTURES CONTAINING $N^{15}H_3$ OR NH_3; $C^{13}H_4$ OR CH_4

	Temperature (°K)	Extent of reaction[a] (%)	32/31 (%)		46/45 (%)		60/59 (%)	
			NH_3	$N^{15}H_3$	NH_3	$N^{15}H_3$	NH_3	$N^{15}H_3$
Pt	470	20	4.12	4.00	4.63	4.36	[b]	[b]
Pd	470	40	3.98	3.91	4.70	4.74	4.61	4.54
Ni	520	20	4.26	4.19	4.53	4.48	[b]	[b]
W	540	10	4.83	4.63	4.00	4.32	[b]	[b]
Co	560	40	3.89	3.91	4.10	4.25	[b]	[b]
V	640	16	4.74	4.84	4.98	5.00	[b]	[b]
			CH_4	$C^{13}H_4$	CH_4	$C^{13}H_4$	CH_4	$C^{13}H_4$
Pt	460	10	2.86	2.81	3.28	3.09	[b]	[b]
Pd	460	15	3.02	2.70	3.30	3.35	4.19	4.36
W	583	10	2.75	2.73	3.36	3.36	3.81	3.96

[a] Percentage of methylamine reacted by hydrocracking and synthesis.

[b] Insufficient product for accurate measurements.

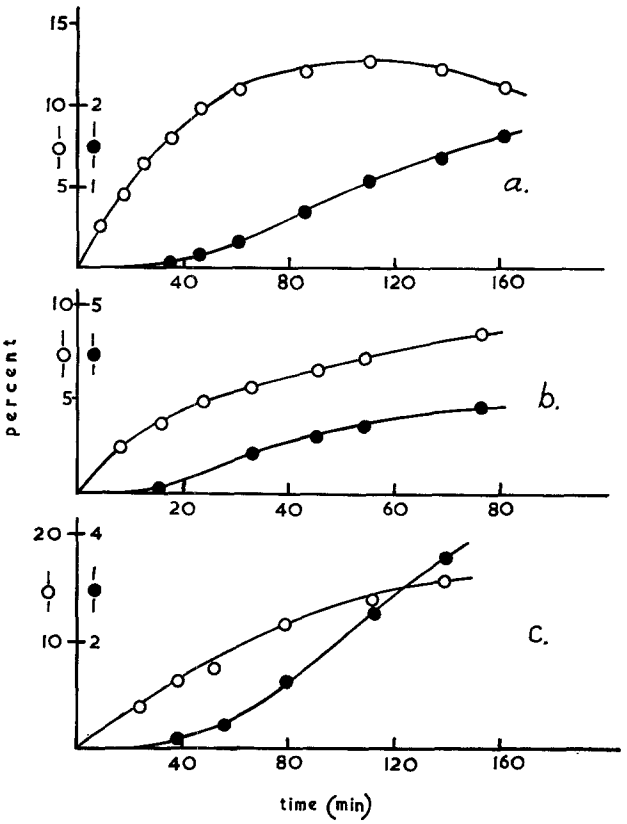


FIG. 3. Production of $C^{13}H_3N^{15}H_2$ (●) and of total dimethylamines (○) from reaction mixture containing $C^{13}H_3NH_2$ plus $CH_3N^{15}H_2$: (a) over 8.4 mg Pt at 488°K; (b) over 8.1 mg Pd at 465°K; (c) over 4.7 mg Ni at 465°K.

The reaction of a mixture containing $C^{13}H_3NH_2 + CH_3N^{15}H_2 + H_2$ was examined for exchange between the methylamines. Were this to occur some $C^{13}H_3N^{15}H_2$ would be produced as an initial reaction product, that is, over and above that which will be produced via the formation of dimethylamine and the subsequent reaction of the latter (see next section). The reactions were studied under the following conditions: platinum, 487°K with $CH_3N^{15}H_2$:$C^{13}H_3NH_2$:CH_3NH_2:H_2 in the ratios 2.26:1.25:1.00:6.31; palladium, 463°K, 1.52:1.28:1.00:5.31; nickel, 513°K, 1.08:1.30:1.00:4.73. In all cases the total methylamine and hydrogen pressures were the same as in a standard mixture.

Figure 3 shows examples of the appearance of the reaction products with increasing time. Of immediate importance is the way in which $C^{13}H_3N^{15}H_2$ clearly appears only as a secondary reaction product, its appearance being dependent upon the previous build-up of an appreciable dimethylamine concentration.

D. Reactions of Dimethylamine and Trimethylamine

The reactions of dimethylamine plus hydrogen were studied most extensively over palladium and platinum. Arrhenius plots for the over-all reaction of dimethylamine are given in Fig. 4 and the corresponding kinetic parameters are contained in Table 6. The compositions of the products from the reaction of dimethylamine are given in Table 7. Reactions of dimethylamine at a single temperature were also studied over nickel, tungsten, and cobalt and these results are also included in Table 7.

TABLE 6
ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR OVER-ALL REACTION OF DIMETHYLAMINE

	Temperature range (°K)	Activation energy (kcal mole^{-1})	$\log_{10}$ (frequency factor) (molecules sec^{-1} cm^{-2})
Pt	425–502°	10.5	18.6
Pd	400–486°	21.4	25.3

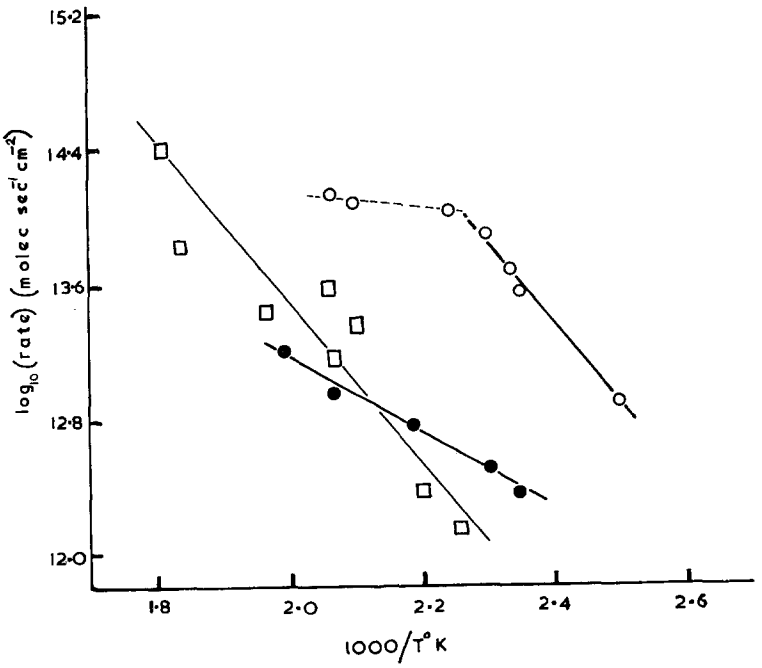


FIG. 4. Variation with temperature of total rate of reaction of dimethylamine: ○, Pd; ●, Pt; □, trimethylamine on Pd.

TABLE 7

PRODUCTS FROM THE REACTION OF $(CH_3)_2NH$ AND H_2 OVER VARIOUS METALS

	Extent of reaction (%)	Composition of reaction products (%)									Over-all reaction rate (molecules sec^{-1} cm^{-2})	Carbon/nitrogen imbalance[a]
		NH_3	CH_3NH_2	$(CH_3)_3N$	CH_3CN	$CH_2—CH_2$ \ / NH	Hydrocarbons C_1	C_2	C_3	C_4		
Pt	20	2.5	45	44	—	—	8.5	—	—	—	[b]	—
Pd	20	3	47	50	—	—	[c]	—	—	—	[b]	~1% C loss
Ni	13	10	53	36	—	—	1	—	—	—	2.0×10^{13} at 493°K	18% C loss
W	10	10	3	10	10	54	5	8[d]	Trace		5.6×10^{11} at 573°K	—
Co	4	20	35	31	6	—	4	4[d]	Trace		6.0×10^{12} at 499°K	17% C loss

[a] Due to carbon incorporation into catalyst.

[b] See Fig. 4.

[c] Small amount about 0.1%.

[d] Ethane only.

Figure 5 shows an example of the time dependence of the composition of the reaction mixture from dimethylamine over palladium. It will be noted that both mono- and trimethylamine are primary reaction products. Over platinum and palladium the distributions of reaction products from dimethylamine were, within experimental error, independent of temperature, except for the high-temperature region with palladium, where the over-all rates are abnormally low compared to the remaining linear portion of the Arrhenius plot (Fig. 4). However, throughout this temperature region the Arrhenius plot for the production of methane is linear (Fig. 2) and the latter gives an activation energy of 22 kcal $mole^{-1}$. The rate of the dimethylamine reaction over palladium was uninfluenced by the addition of ammonia to the reaction mixture.

Pressure dependences for the reaction of dimethylamine were not measured directly, but it was found that on palladium the disappearance of the parent amine closely followed a second order rate law, an example of which is included in Fig. 5. In as much as reaction of dimethylamine on palladium occurs very largely by a synthesis reaction, the latter is concluded to be close to second order in amine pressure, in agreement with the behavior of monomethylamine.

The reaction of trimethylamine was studied over palladium in the range 444–552°K. Hydrocracking was the only primary process and the major product was dimethylamine, together with some methylamine. The results in Fig. 6(a) for the early stages of the reaction show that methylamine was itself a primary product and was not merely formed by reaction of readsorbed dimethylamine. The results in Fig. 6(b) clearly indicate that the rate of reaction of trimethylamine fell to a very low value after only a small proportion of the reactant had been consumed. We ascribe this to poisoning by mono- and dimethylamine or by hydrocarbon residues. The ratio of dimethylamine to methylamine in the reaction product ranged from 10/1 at the bottom of the temperature range to 5/1 at the top. Rates of methane production are included in Fig. 2 and over-all rates of reaction in Fig. 4. The activation energy obtained from the latter is 21 kcal $mole^{-1}$ with $\log_{10}$ (frequency factor) (molecules sec^{-1} cm^{-2}) equal to 22.7. Because of the self-poisoning in this reaction, the rates are known with a lower precision than for other systems, and the error in the activation energy is estimated at ± 2 kcal $mole^{-1}$.

E. Reactions of Ethylenimine

Since with a number of metals ethylenimine was an appreciable product from the reactions of mono- and dimethylamine, the reaction of ethylenimine and hydrogen over metal films was studied. The reaction mixture contained 5.4 mm of ethylenimine and 27 mm of hydrogen. The compositions of the reaction products are given in Table 8. With all the metals listed, product peaks were observed in the mass range 55–59 and 70–73. With all metals gas chromatography

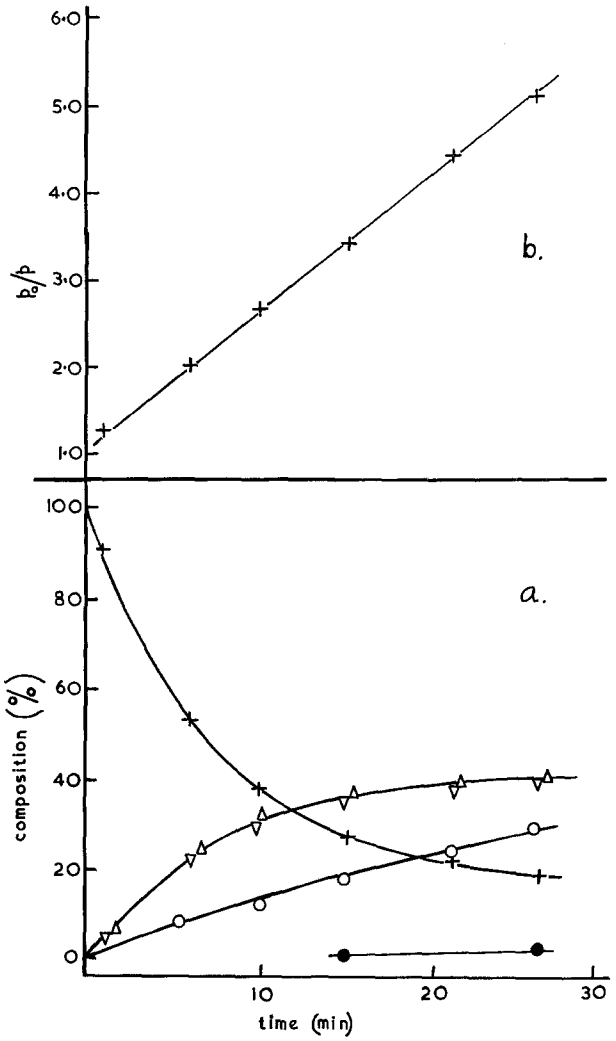


FIG. 5(a). Variation with time of composition of dimethylamine reaction mixture over 9.1 mg Pd at 446°K; +, $(CH_3)_2NH$; ▽, CH_3NH_2; △, $(CH_3)_3N$; ○, NH_3; ●, CH_4. (b) Data from Fig. 5(a) plotted according to second order rate law, where p is the pressure of dimethylamine at time t and p_0 is the initial dimethylamine pressure.

indicated small amounts of C_3 and C_4 hydrocarbons (about 0.5%), together with compounds having retention times comparable to those of C_2 amines. These latter are assumed to be amine in nature, but since their gas chromatogram was complex, with usually four component peaks appearing, detailed identification was not attempted. All of these higher amines have been lumped together in the column in Table 8 called "higher amines." The figures given in this column are subject to a substantial possible error since they were computed using assumed sensitivity calibrations for the unidentified components. In addition to the products listed in Table 8, methane and C_3 and C_4 hydrocarbons were also detected in amounts not exceeding about 0.5%.

DISCUSSION

By comparing over-all reaction rates at about 500°K, the reactivity of the metals towards methylamine is found to fall in the order Pd > Pt > Ni, Co > Cu, V > W.

TABLE 8

PRODUCTS FROM THE REACTION OF ETHYLENIMINE $+H_2$ OVER VARIOUS METALS

	Temperature (°K)	Extent of reaction (%)	Composition of reaction products (%)					
						Higher amines		C_2H_6 and C_2H_4
			NH_3	$C_2H_5NH_2$	CH_3CN	C_3	C_4	
Pt	413	47	9	83	—	Trace		8[a]
Pd	418	42	12	74	—	5	3	6[a]
Ni	443	50	28	5	23	35	7	2[b]
W	484	10	24	15	32	16	6	7[c]
Co	471	35	35	—	23	20	10	12[b]
V	570	20	37	—	29	13	5	16[b]
Cu	421	40	32	—	33	8	17	10[b]

[a] C_2H_6.

[b] C_2H_4.

[c] Approx. equal amounts of C_2H_4 and C_2H_6.

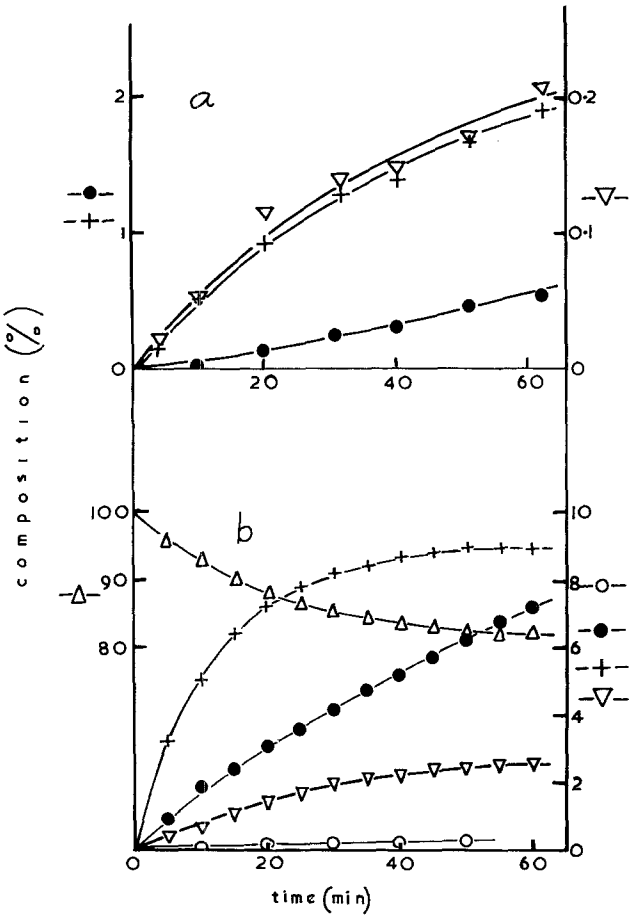


FIG. 6. Variation with time of composition of trimethylamine reaction mixture: (a) over 8.1 mg Pd at 444°K; (b) over 11.3 mg Pd at 509°K; △, $(CH_3)_3N$; +, $(CH_3)_2NH$; ▽, CH_3NH_2; ●, CH_4; ○, NH_3.

In agreement with Kemball and Moss (*12*), the two most generally important reactions of methylamine are

$$CH_3NH_2 + H_2 \rightarrow NH_3 + CH_4 \quad (1)$$

$$2CH_3NH_2 \rightarrow (CH_3)_2NH + NH_3 \quad (2)$$

but with the proviso that other synthesis reactions also occur to an extent that depends on the catalyst, and that a lot of the carbon which would otherwise appear as methane from reaction (1) is incorporated into the catalyst.

In the following discussion, an atom bound directly to the surface is designated by *; the symbol * does not, however, imply the use of any particular number of surface atoms, or any particular number of adsorbate–adsorbent bonds. Often only carbon–nitrogen skeletons, written within square brackets such as

are shown; furthermore, $[C–N]_s$, for instance, is a skeletal surface residue without further specification of its mode of attachment to the surface. In skeletal residues so written, a carbon-to-nitrogen single bond is not necessarily implied.

The hydrocracking reaction may be represented as in Fig. 7.

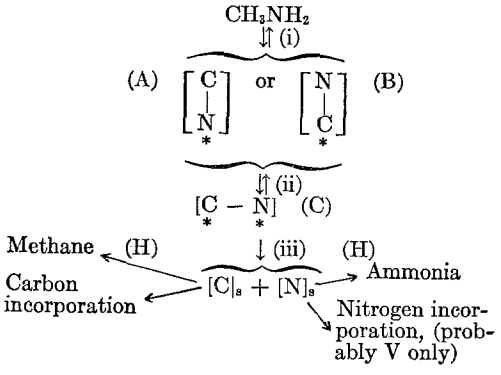
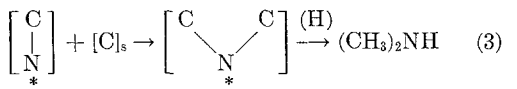


FIG. 7. Fragmentation reactions of methylamine.

Deuterium exchange results with methylamine [Kemball and Wolf (*11*)] suggest that primary adsorption occurs mainly through the nitrogen to give species (A) on palladium and platinum and through the carbon to give species (B) on tungsten and nickel. Arguments have been suggested by Anderson and Clark (*1*) that the immediate precursor to carbon–nitrogen bond rupture (species C) is multiply bonded to the surface at either or both the carbon and nitrogen. This is consistent with the self-poisoning observed by Kemball and Wolf (*11*) at higher temperatures, which indicated the presence of species more strongly adsorbed than those directly involved in the exchange reaction.

Kemball and Moss (*2*, *12*) suggested that a diamine was formed by the process,



Anderson and Clark (*1*) pointed out that if recombination of $[C]_s$ with [C–N*] is possible, recombination of $[C]_s$ with $[N]_s$ should also occur so that step (iii) (Fig. 7) would then be expected to be reversible. The results of Table 5 show that no exchange between methylamine and $N^{15}H_3$ or $C^{13}H_4$ occurs, and the results of Fig. 3 and Table 6 show that no exchange between $C^{13}H_3NH_2$ and $CH_3N^{15}H_2$ occurs. Furthermore no $(C^{13}H_3)(CH_3)NH$ was produced from $CH_3NH_2 + C^{13}H_4$ (cf. Table 5). The negative results with $C^{13}H_4$ could be due to the difficulty of adsorbing methane in competition with strongly adsorbed amine, although it should be noted that the temperatures are generally similar to those at which methane/deuterium exchange occurs [Kemball (*13*)] and on tungsten in particular, methane is adsorbed relatively strongly. Ammonia would be adsorbed with a strength comparable to methylamine, particularly over platinum and palladium and, furthermore, the depression by ammonia of the rate of the synthesis reaction with methylamine at higher temperatures on palladium is evidence that some ammonia adsorption occurred. Moreover, the result with $C^{13}H_3NH_2$ and $CH_3N^{15}H_2$ is unequivocal and we consider there is good evidence that step (iii) (Fig. 7) is irreversible. If the potential similarity of recombination reactions of $[C]_s$ with [C–N*] and $[N]_s$ is accepted, we are led to seek an alternative to reaction (3) for the mechanism

of the synthesis reaction. Furthermore we must seek a mechanism for the production of C_2–C_4 hydrocarbons. It should be noted, however, that if it were in fact the case that $[C]_s$ could recombine with [C–N*] but not with $[N]_s$, the present isotopic results would be consistent with reaction (3). However, reaction (3) does not provide a ready explanation for the observed second order kinetics of the synthesis reaction.

We suggest that the synthesis reactions are constructed from bimolecular surface reactions between adsorbed residues such as $[C–N]_s$. For instance, the formation of dimethylamine follows

$$[C—N]_s + [C—N]_s \rightarrow [C—N—C—N]_s \rightarrow \begin{cases} [C—N—C]_s \xrightarrow{(H)} (CH_3)_2NH \\ + \\ [N]_s \xrightarrow{(H)} NH_3 \end{cases} \quad (4)$$

The entity $[C–N–C–N]_s$ may be a surface intermediate in its own right or it may be a transition complex; in the latter case the formation of the carbon–nitrogen bond occurs almost synchronously with the elimination of the second nitrogen. Reaction (4) is essentially similar to that proposed by Anderson and Clark (*1*) for the formation of dimethylamine during the reaction of hydrogen cyanide with hydrogen over metal films. These authors also suggested an analogous bimolecular surface reaction giving carbon–carbon bond formation and leading to hydrocarbon synthesis products, and we propose that this also occurs in the amine reactions.

The observed isotopic composition of the dimethylamine initially produced in the $C^{13}H_3NH_2 + CH_3N^{15}H_2$ reaction is compared in Table 9 with the distribution predicted for the production of dimethylamine by a bimolecular reaction, and for comparison the table includes the products corresponding to a random distribution of C^{13} and N^{15} in the dimethylamine.

The notation $(CH_3)_2NH$-1, etc., refers to a molecule containing a total of 1, etc., heavy atoms.

The production of trimethylamine and monomethylamine from dimethylamine may be represented as

$$2(CH_3)_2NH \rightarrow (CH_3)_3N + CH_3NH_2 \quad (5)$$

for which the surface process may be considered as analogous to reaction (4), the reacting residues now being of the type $[C_2N]_s$. Comparison of the data in Figs. 1 and 4 shows that on palladium and platinum the over-all reaction rate of dimethylamine is considerably greater than that of methylamine. This is due to the greater reactivity of dimethylamine in the synthesis reaction (almost entirely disproportionation) since it is seen from Fig. 2 that the rate of methane production from methylamine is the same as from dimethylamine.

On nickel and cobalt the synthesis reactions with dimethylamine are seen from Table 7 to be relatively less important than on palladium and platinum, while on tungsten the main reaction is the production of

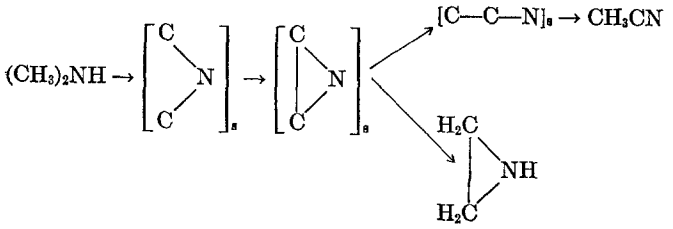
TABLE 9

OBSERVED AND CALCULATED ISOTOPIC DISTRIBUTIONS IN DIMETHYLAMINE PRODUCED FROM REACTION OF $C^{13}H_3NH_2 + CH_3N^{15}H_2$

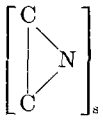
		Distribution (%)			
		$(CH_3)_2NH$-0	$(CH_3)_2NH$-1	$(CH_3)_2NH$-2	$(CH_3)_2NH$-3
Pt	Observed at 10% react.	17.2	60.3	22.5	—
	Calc.[a] Bimolecular	16.1	62.4	21.5	—
	Calc.[a] Random dist.	32.7	45.1	17.3	4.9
Pd	Observed at 13% react.	19.2	55.6	25.2	—
	Calc.[a] Bimolecular	17.4	57.8	24.8	—
	Calc.[a] Random dist.	34.0	39.8	20.3	5.9

[a] The calculated distribution for each metal was computed using the actual isotopic composition appropriate for each mixture.

ethylenimine. In no case was ethylamine detected, but over tungsten the corresponding dehydrogenation product—acetonitrile—was formed. This reaction over tungsten may thus be represented

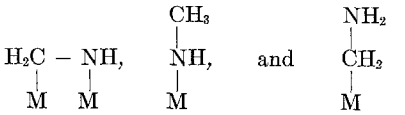


Reaction (6) is in agreement with the behavior of ethylenimine, for which the data in Table 8 show that the main reaction of a



skeleton is carbon–nitrogen bond rupture to give a $[C–C–N]_s$ skeleton, the latter giving on desorption either acetonitrile or ethylamine, or both, depending on the availability of hydrogen on the surface and on the temperature. Some ethane was also produced, possibly by further fragmentation of the $[C–C–N]_s$ skeleton before it could be desorbed. On all metals, ethylenimine reacted at considerably lower temperatures than either mono- or dimethylamine, no doubt reflecting the strain in the three-membered ring. This implies that the slow step in reaction (6) occurs at or prior to the formation of the cyclic intermediate.

Some assessment of the types of residues involved in the rate-controlling steps may be had by comparing the reactions of methylamine and of hydrogen cyanide. As pointed out previously (*1*), the reactions of these two substances with hydrogen over metal films are very similar both with respect to rate and to product distribution, and this strongly suggests that for each of these systems the rate-controlling steps are the same. Now, it was found (*1*) in the reactions of hydrogen cyanide and hydrogen that, over a wide range of metal films, methylamine was not an appreciable reaction product except over platinum where it was still only a minor product. Thus it may be concluded that under the conditions of this reaction the species



are not important, since all of these would, from deuterium exchange data (*11*), be expected to be in rapid equilibrium with gaseous methylamine. We therefore conclude that these residues do not take part in the rate-controlling steps of hydrocracking or synthesis reactions with methylamine. Species (C) of Fig. 7 is probably multiply bonded to the surface at least at one of its points of attachment.

On palladium, the activation energy for hydrocracking (i.e., methane formation) was the same for mono-, di-, and trimethylamines (Fig. 2), and the same is true on platinum for mono- and dimethylamines (Fig. 2) for which data are available. It is likely therefore that the rate-controlling processes for hydrocracking are the same, or at least very similar for each substance. For this, there are two reasonable possibilities: (a) carbon–nitrogen bond rupture in an adsorbed species, or (b) product desorption which regenerates surfaces sites. The evidence for selecting (a) or (b) is not conclusive, but the following argument favors (b), at least for reactions over palladium, platinum, and nickel, a conclusion that agrees with the near zero order dependence of the hydrocracking rate on amine pressure. Previous work on hydrocracking of alkanes (*14*) and amines (*2*, *12*) on metals has assumed that the immediate surface precursor to bond rupture is diadsorbed. If this is so,

the equality of activation energies for methylamine and trimethylamine hydrocracking makes it improbable that carbon–nitrogen bond rupture is rate-controlling, since the molecules cannot give diadsorbed residues of closely similar types. For comparison, in the hydrocracking of saturated hydrocarbons (*15*), ethane, for which diadsorption can only occur in the 1–2 mode, reacts with a much higher activation energy than the higher homologs. This, and a comparison with the rate of methane exchange (*13*), leaves little doubt that the slow step in alkane hydrocracking over platinum and palladium is carbon–carbon bond rupture (*16*, *15*). On the other hand, the rates of methane production from mono-, di-, and trimethylamine on palladium, and from mono- and dimethylamine on platinum and nickel are comparable with the rates of methane exchange (*13*).

Bond formation in a surface reaction such as (4) is the more easily understood if the reacting residue $[C–N]_s$ contains a carbon–nitrogen double bond; it is instructive to compare the polymerization of *adsorbed* acetylene studied by Sheridan (*17*). However, the intermediate

$$\begin{matrix} CH = N \\ | \quad\quad | \\ M \quad\quad M \end{matrix}$$

suggested previously (*1*) cannot accomodate a synthesis reaction from dimethylamine and we suggest that the species active in synthesis reactions are π-bonded to the surface, i.e.,

$$H_2C \overset{\downarrow}{\underset{M}{\mp}} NH \qquad \text{and} \qquad H_2C \overset{\downarrow}{\underset{M}{\mp}} NCH_3$$

from mono- and dimethylamine, respectively. The synthesis reactions on palladium and nickel were found to be approximately second order in amine pressure, and this would suggest that the appropriate surface intermediate S, e.g.,

$$H_2C \overset{\downarrow}{\underset{M}{\mp}} NH$$

is sufficiently weakly adsorbed for its concentration to be approximately proportional to amine pressure.

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