

REACTION OF AMINES ON ACID CATALYSTS. IV.*
 KINETICS AND MECHANISM OF OLEFIN FORMATION
 FROM TRIETHYLAMINE AND DIISOPROPYLAMINE ON γ -ALUMINA

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Received September 8th, 1972

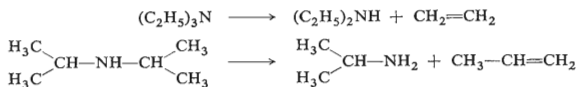
The kinetics of olefin formation from the relatively weakly adsorbed amines, triethylamine and diisopropylamine, on γ -alumina were investigated by means of a differential reactor with one pass. The dependence of initial reaction rate on partial pressure does not correspond to the decomposition of a simply adsorbed molecule on a homogeneous surface. When the feed of diisopropylamine was stopped a marked increase in the rate of propylene formation was almost immediately observed. This effect may be explained by assuming that the reacting molecule is simultaneously adsorbed on two different surface sites. The inhibiting role of water is dependent on the absolute value of water partial pressure.

In the last paper of this series¹ it was found that the decomposition of both monoethylamine and diethylamine to olefin followed zero order kinetics. The reaction rate of the less strongly adsorbed triethylamine was found to be independent of partial pressure only at higher pressures. In another publication² the decomposition of dicyclohexylamine was described by the simple equation

$$r = kK_A p_A / (1 + K_A p_A) \quad (1)$$

In contrast, Catry and Jungers³ claimed that the deamination of even primary amines may be described by Eq. (1). However their experimental technique was not geared to give a complete picture of reaction kinetics.

In this work we had set out to show that the simple monomolecular decomposition, described by Eq. (1), is generally valid for olefin formation from amines and that it is due to the very strong adsorption of certain amines that Eq. (1) reduces to zero order. However, a detailed study of the deamination reactions



showed that the decomposition of amines to olefins is not such a simple process.

* Part III: This Journal 35, 2166 (1970).

EXPERIMENTAL

Apparatus: A differential reactor, with one pass, was used to study the decomposition of triethylamine and diisopropylamine to olefin on γ -alumina in the temperature range 260–300°C and partial pressure range 1–600 Torr. The experimental technique, together with catalyst preparation and properties, is the same as described in previous papers^{1,2,4}; the only innovation is direct connection of reactor and chromatograph. In view of the high activation energy of deamination, the temperature profile of the catalyst bed was read during every measurement. Maximum temperature difference along the catalyst bed was 5°C, but in three-quarters of its length did not exceed 3°C. The average temperature did not vary more than 1°C during measurements.

Chemicals used: γ -Alumina: particle size 0.4–0.63 mm. Amines: less than 0.05% organic impurities. Nitrogen: purged of any trace of oxygen using a copper catalyst. Ethylene and propylene standard: technical grade, 98% purity.

Procedure: The results of differentiability tests are given in Table I. The total feed chosen for our measurements was 0.6 mol/h. The catalyst was regenerated at 430–450°C by air. Reproducibility for triethylamine measurements was good (10%). Diisopropylamine gave less reliable results –15% in the partial pressure range 10–600 Torr and 30% at less than 10 Torr. Chromatographic analysis of the product hydrocarbons showed 99.2% C_3H_6 and 0.8% CH_4 from diisopropylamine; however analysis for hydrogen was not carried out.

RESULTS AND DISCUSSION

Reaction Isotherms

The dependences of the initial rates of decomposition to olefin of triethylamine and diisopropylamine are shown in Fig. 1 and 2 respectively. Evaluation of these results by non-linear regression on the first order rate equation (I) is shown by the broken lines. It can be seen, at pressures greater than 20 Torr, that the experimental results approximately fit Eq. (I); at lower pressures, however, the measured values are consistently higher than the theoretical first order curve. This may be seen more clearly in Fig. 3 and 4. Indeed the reaction rate of neither amine approaches zero as amine pressure approaches zero.

Hence the possibility of two mechanisms operating simultaneously was considered. The rate of one was postulated as being independent of the partial pressure whilst the other was taken to follow the first order rate equation (I). The total rate might then be expressed by the equation

$$r = k_1 + k_2 K'_A p_A / (1 + K'_A p_A) \quad (2)$$

Evaluation of the experimental data by non-linear regression on this equation gave curves, shown by the full lines in Fig. 1–4, which fit the experimental data better. The parameters, calculated by the correlation of experimental data with Eq. (2), are shown in Table II. It is evident that the low accuracy of the calculated adsorption coefficients will also give rise to an error in the calculated rate constants and so activa-

TABLE I
Data Obtained for Reactor Differentiability

Amine	°C	Total feed mol/h	p_A	r	% Conversion
Triethyl-	290	0.25	142	0.073	0.76
		0.46	141	0.069	0.46
		0.75	128	0.070	0.27
		0.77	143	0.075	0.25
Diisopropyl-	300	0.19	22	0.188	16.6
		0.38	21	0.209	9.8
		0.58	22	0.220	6.1
		0.76	22	0.220	4.6
Diisopropyl-	280	0.21	203	0.120	1.07
		0.21	202	0.127	1.13
		0.56	198	0.132	0.45
		0.92	202	0.124	0.25

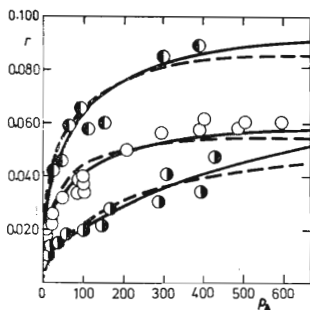


FIG. 1

Dependence of Initial Reaction Rate of Triethylamine Decomposition on Amine Partial Pressure

● 270°C, ○ 280°C, ● 290°C, - - - - Eq. (1), — Eq. (2).

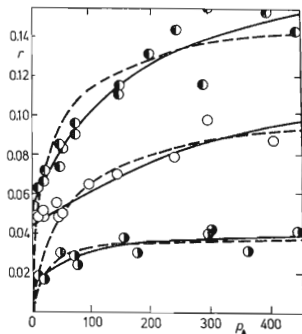


FIG. 2

Dependence of Initial Reaction Rate of Diisopropylamine Decomposition on Amine Partial Pressure

● 260°C, ○ 270°C, ● 280°C, - - - - Eq. (1), — Eq. (2).

tion energy values were calculated directly from the reaction rate values. Values of 34.0 and 37.5 were obtained for triethylamine and diisopropylamine respectively. Within the limits of experimental error these values did not vary with amine partial pressure in the region 50–400 Torr.

TABLE II

Rate Constants and Adsorption Coefficients Computed by Correlation of Experimental Data with Eq. (2)

Constant	Amine	260°C	270°C	280°C	290°C
k_1	triethyl-	—	0.00913	0.0113	0.0203
	diisopropyl-	0.0128	0.0431	0.0523	—
k_2	triethyl-	—	0.0935	0.0509	0.0796
	diisopropyl-	0.0315	0.1190	0.1370	—
K'_A	triethyl-	—	0.00131	0.0135	0.0114
	diisopropyl-	0.0133	0.00191	0.00585	—

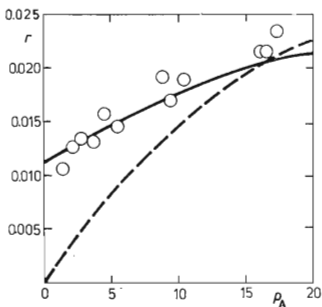


FIG. 3

Dependence of Initial Reaction Rate of Triethylamine Decomposition on Amine Partial Pressure at 280°C at Low Partial Pressure

----- Eq. (1), ——— Eq. (2).

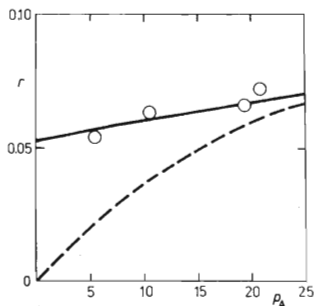


FIG. 4

Dependence of Initial Reaction Rate of Diisopropylamine Decomposition on Amine Partial Pressure at 280°C at Low Partial Pressure

----- Eq. (1), ——— Eq. (2).

Reaction Rate in Non-Steady State

On starting the feed of diisopropylamine, in flow of nitrogen, the rate of production of propylene rapidly increases to a maximum and then slowly decreases to the steady state value. On stopping the amine feed the reaction rate rapidly increases to 2–3 times the steady state value and then quickly decreases. This behaviour is shown in Fig. 5. Triethylamine gave a similar maximum before reaching the steady state. However, on stopping the feed, its rate declines asymptotically to one third of the steady state value after one hour; only at high partial pressures was a slight rate increase noted before this decline.

A possible explanation of both maxima might be that amines have a higher reaction rate at lower partial pressure values. However no such high reaction rate was measured at values as low as 1 Torr. Furthermore, if this were so, the value of the stopped-feed maximum would be independent of the steady state partial pressure and would be obtained at various times after stopping the feed. In reality, however, the value of the maximum is proportional to the steady state partial pressure and is always obtained 2–3 min after stopping the amine feed irrespective of the original partial pressure. It was also shown, by an experiment with diisopropylamine and propylene at 200°C, at which temperature reaction does not proceed, that apparatus' effects, which might cause accumulation of olefin during feed and its sudden libera-

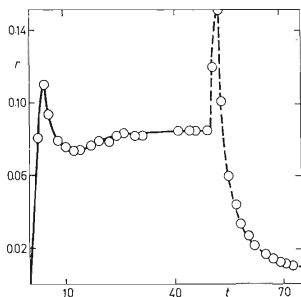


FIG. 5

Reaction Rate of Diisopropylamine Decomposition at 270°C under Non-Steady State Conditions

— Amine feed (10.5 Torr), - - - - no amine feed.

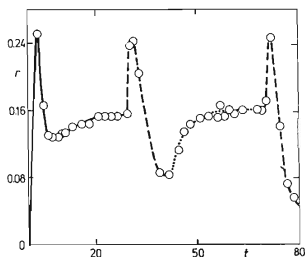


FIG. 6

Reaction Rate of Diisopropylamine Decomposition at 273°C under Non-Steady State Conditions

— Pure amine feed (48 Torr), - - - - no amine feed, amine (48 Torr) + water (0.48 Torr) feed.

tion on stopping feed, do not operate. Furthermore, as may be seen in Fig. 6, the presence of water in the amine feed does not alter the nature or magnitude of the stopped-feed maximum. Hence it may be concluded that the increase in reaction rate, on stopping diisopropylamine feed, is caused only by the non-steady state of adsorption.

Although not directly relevant to our problem, the existence of this phenomenon suggests a method for increasing reactor efficiency (at least for this reaction) utilising a stop-start system as shown in Fig. 7.

Considering the high activation energy of the reaction, the rate maximum, on starting amine feed, may be attributed to the rise in temperature due to adsorption heat. The real temperature rise may be considerably higher than the measured increase of 5°C. This initial maximum may be also caused by the rapid deactivation of some sites of very high activity. Water has been shown to play a decisive role in determining the catalytic activity of γ -alumina. Thus we investigated the effect of the presence of water, in different molar ratios, in the amine feed. The results for water-amine ratio 1 : 100 are given in Fig. 6, for 1 : 10 in Table III and for 1 : 1 in Fig. 8. Fig. 6 shows that, at amine pressure 48 Torr and water-amine ratio 1 : 100 the reaction rate is the same as that of pure amine. Fig. 8 shows that a ten-minute pulse of water, fed in 1 : 1 ratio with amine to the reactor, causes the reaction rate to de-

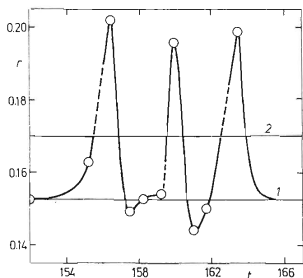


FIG. 7

Reaction Rate of Diisopropylamine Decomposition at 272°C in Stop-Start System

— Diisopropylamine feed (100 Torr),
 ---- no diisopropylamine feed; 2 average reaction rate,
 ——— steady state reaction rate, 1

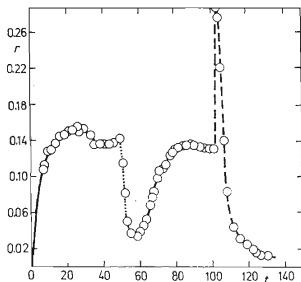


FIG. 8

Reaction Rate of Diisopropylamine Decomposition at 271°C under Non-Steady State Conditions

— Pure amine feed (50 Torr), ---- no amine feed, amine (50 Torr) +
 + water (50 Torr) feed.

TABLE III

Inhibiting Effect of 10 molar% Water on Diisopropylamine Decomposition Rate at Various Partial Pressures at 270°C

p_A Torr	Reaction rate, mol/h l	
	diisopropylamine	diisopropylamine + water
48	0.048	0.048
95	0.063	0.040
438	0.088	0.021

crease sharply. However, water appears to act as a reversible poison as the rate returns to normal 25 minutes after water feeding is stopped. Comparing the inhibiting effect of water, at constant amine pressure (48 Torr), shown in Fig. 6 and Table III (1 : 100 and 1 : 10 respectively) with that shown in Fig. 8 (1 : 1) it may be concluded that rate inhibition depends, not on amine partial pressure, but on water partial pressure.

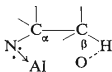
Mechanism

Steric shielding of the nitrogen atom has a marked effect on the form of the kinetic curve. For example, diethylamine follows a zero order curve¹ whereas diisopropylamine, which has bulkier alkyl groups, follows a modified first order curve. Furthermore, it has been found that small amounts of the more basic piperidine poison the condensation reaction of weakly basic aniline⁴. Hence it may be assumed that acid-base aluminium ion-nitrogen dative bonding plays a decisive role in amine reactions on γ -alumina. Indeed, Hirota and coworkers⁵, using IR and NMR techniques, concluded that methylamine adsorption was also *via* such bonding. Otherwise there is little evidence as to the nature of the adsorbed species leading to olefin. In the more thoroughly investigated field of olefin formation from alcohol on alumina, both molecularly adsorbed and alkoxide forms have been proposed. It is clear that olefin formation from the amine analogue to alkoxide, nitride, is highly improbable and so we assume that olefin is formed by the decomposition of molecularly adsorbed amine.

In view of the complex kinetics of these reactions, simple one-point molecular adsorption, on sites of equal acid strength, is ruled out. Since Eq. (2), of all equations tested, best fits our data we divide the spectrum of acid strength between two site regions. This concurs with the findings of Amenomiya and Cvetanovic⁶ with respect to olefin adsorption on alumina. We suppose, therefore, that amine decomposition on the stronger sites, which are limited in number, proceeds with zero order kinetics

(k_1) whereas decomposition on the more numerous weaker sites follows first order kinetics (k_2).

There is conclusive proof in the literature that interaction between basic surface sites and hydrogens on the β -carbon assists olefin formation from alcohols adsorbed on alumina. Vladyko and coworkers⁷, using deuterated 2-propanols, found that these hydrogens have a strong interaction with the surface and Lafer and coworkers⁸, from the IR spectra of 2-propanol on γ -alumina, concluded that there was formation of a quasi-methylene group. Furthermore, Knozinger and Stolz⁹, on the basis of recorded isotope effects, postulated that interaction between basic sites, probably oxide ion, and the β -carbon hydrogens facilitates olefin formation from alcohols. This is supported by the IR findings of Deo and coworkers¹⁰. By analogy, therefore, we might suggest that, for amines, interaction of the following type leads to olefin



i.e. a six-membered cyclic charge-transfer complex. Indeed the findings of Catry and Jungers³, that branching at the β -carbon decreases rate, may thus be explained on steric grounds and that α -carbon branching increases rate on statistical grounds. Furthermore, hydrogen bonding between the N-hydrogen and surface oxide ions, which is possible for diisopropylamine, may tend to limit the number of available oxide ion sites. Such weakly bonded amine is rapidly removed on stopping amine feed, thus many oxide ion sites become vacant and so, for a short time, the concentration of cyclic complex is high. However decomposition of this complex to olefin and desorption of amine, even from the acid sites, cause the reaction rate eventually to decrease. Hence the sharp maximum shown in Fig. 5. It is significant that triethylamine, which has no N-hydrogen, shows no such peak.

Amines, adsorbed only by hydrogen bonding, obviously cannot lead to olefin. However, their nitrogen is more nucleophilic and may act as such in amine disproportionation reactions. This conforms with the first order kinetics for diethylamine disproportionation obtained by Ebeid and Pašek¹ who proposed the participation of some weakly adsorbed form of amine as nucleophile. To their work we might therefore add that this nucleophilic form is hydrogen bonded.

Again, the necessity for having some vacant surface sites for olefin formation from alcohols has been shown by both Nakšunova and coworkers¹¹ and Roy and Bose¹². Thus the proportionately higher rate values, obtained by us at lower amine partial pressures, may also be explained by the higher concentration of vacant basic sites in the neighbourhood of acid-base bonded amine. Therefore the shape of the kinetic curve will be given by, among other factors, a combination of the positive effect of amine pressure on the surface concentration of acid-base bonded amine and its

negative effect on the concentration of vacant sites suitable for β -carbon hydrogen bonding. The generally inhibiting role of water is probably a consequence of its competing with amine for adsorption. Indeed, as shown in Fig. 8, its poisoning effect is reversible indicating that it does not permanently alter the nature of the sites.

LIST OF SYMBOLS

k	reaction rate constant (mol/h l)
K_A	amine adsorption coefficient (Torr ⁻¹)
p_A	amine partial pressure (Torr)
r	reaction rate (mol/h l)
t	time (min)

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