INFLUENCE OF ANILINE ON DECOMPOSITION
AND DISPROPORTIONATION REACTIONS OVER γ-ALUMINA*

P.Hogan and J.Pašek

Department of Organic Technology,
Institute of Chemical Technology, 166 28 Prague 6

The effect of aniline on the decomposition to olefin of diethylamine and diisopropylamine and on the disproportionation of diethylamine was studied over γ-alumina in a differential reactor with one pass. Olefin formation was inhibited by aniline both in the steady and non-steady states; the rate of diethylamine disproportionation to triethylamine and monoethylamine was also decreased. In addition, the kinetics of N-ethylaniline formation were investigated under various conditions. Mechanisms are proposed involving the participation of both acidic and basic surface sites in the decomposition and disproportionation reactions. Mathematical modeling of the reactions met with some success.

In a previous paper[1], the decomposition and disproportionation reactions of di-ethylamine over γ-alumina were discussed. Reaction (A) and also monoethylamine

$$(C_2H_5)_2NH \longrightarrow C_2H_5NH_2 + CH_2{=}CH_2 \qquad (A)$$

$$2(C_2H_5)_2NH \rightleftharpoons C_2H_5NH_2 + (C_2H_5)_3N \qquad (B)$$

decomposition were found to follow zero order kinetics. Earlier[2] it was found that cyclohexylamine decomposition to olefin also followed zero order kinetics whereas dicyclohexylamine decomposition followed first order kinetics. However the theory, based on these results, that amines in general decompose over γ-alumina in accordance with the equation

$$r = kK_Ap_A/(1 + K_Ap_A) \qquad (1)$$

was confounded by the results, obtained for triethylamine and diisopropylamine decompositions to olefin, given in the last paper[3] of this series; obviously the decomposition could no longer be taken to occur *via* the simple amine adsorption on a single site of homogeneous surface presupposed by Eq. (1). In addition it was found that the rate of diisopropylamine decomposition increases to a maximum, 2−3 times its steady state rate, when its feed is stopped in continued flow of nitrogen.

These results were best explained by proposing the following transition state leading to olefin involving the participation of both surface acidic (aluminium ion) and basic (oxide ion) sites in a six-membered cyclic charge-transfer complex. In this work we investigate the effect of more weakly basic aniline on the decomposition reaction.

$$C_\alpha - C_\beta$$
$$N \qquad H$$
$$Al \qquad O$$

The disproportionation of diethylamine over γ-alumina (reaction (B)) was found[1] to follow the first order rate equation (1). It was proposed that this reaction occurred by interaction between amine species, strongly adsorbed on acidic sites, and some weakly adsorbed amine species. In the analogous field of ether formation from alcohols over γ-alumina the simultaneous participation of both acidic and basic sites has been suggested[4]; this reaction is thought to proceed by interaction of electrophilic surface species with the nucleophilic oxygen of hydrogen-bonded species[5,6].
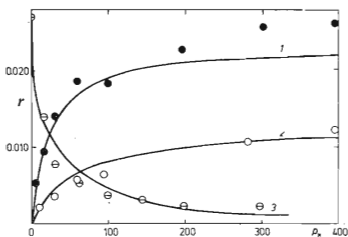

FIG. 1

Dependence of Initial Rate of Ethylene Formation on Partial Pressures of Diethylamine (1), (2) and aniline (3) at 310°C

   ● X = diethylamine, $p_{AN} = 15$ (constant); ○ X = diethylamine, $p_{AN} = 100$ (constant); ⊖ X = aniline, $p_{DA} = 30$ (constant); —— Eq. (2).
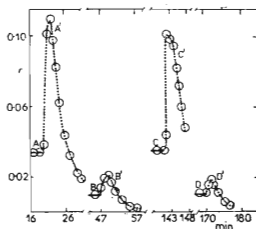

FIG. 2

Stopped-Feed Maxima of Diisopropylamine in the Presence and in the Absence of Aniline at 270°C

   A, C — Pure diisopropylamine (50 Torr); A′C′... no amine feed; B — diisopropylamine (50 Torr) + aniline (50 Torr), B′... aniline (50 Torr) only; D — diisopropylamine (46 Torr) + + aniline (96 Torr), D′... aniline (96 Torr) only.

We hoped to throw more light on the mechanism of amine disproportionation by investigating reaction (B) in the presence of aniline. In addition, the reaction

$$(C_2H_5)_2NH \ + \ C_6H_5NH_2 \ \rightleftharpoons \ C_2H_5NHC_6H_5 \ + \ C_2H_5NH_2 \qquad (C)$$
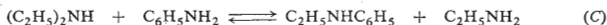
which occurs simultaneously with (A) and (B) in the diethylamine–aniline system over γ-alumina and which is essentially of the same type as the disproportionation (B), was also studied.

EXPERIMENTAL

A differential reactor with one pass was used in our investigations. Preparation of catalyst is described in a previous paper[7]; the particle size used was $0.40-0.63$ mm. The amines contained less than 0.05% organic impurities. Nitrogen, which was used as inert, was purged of any trace of oxygen by means of a copper catalyst. The experimental technique was the same as described in previous papers[1-3,7] except that the amine outflow from the reactor was frozen at $-60°C$. The average temperature in the catalyst bed did not vary by more than $1°C$ during measurements. A qualitative analysis of all the possible sources of error revealed[8] that the maximum possible error is $\pm 35\%$; however the error obtained in any one measurement could be taken to be not more than $\pm 15\%$.

RESULTS AND DISCUSSION

Decomposition to Olefin

The dependences of the initial rate of olefin formation (reaction (A)) in the diethylamine–aniline system over γ-alumina at $310°C$ are shown in Fig. 1. It is evident that in the presence of aniline the rate is no longer independent of the diethylamine partial pressure. However, at constant aniline partial pressure 15 Torr *1* and higher diethylamine pressures, the rate approaches that of pure diethylamine (0.027). Also the rate decreases sharply with the aniline partial pressure up to 100 Torr but does not decrease by much thereafter *3*. It was also found that, where the aniline feed was stopped and the diethylamine feed continued, the rate soon increased to the value for pure diethylamine.

The effect of aniline on the rate of diisopropylamine decomposition was briefly investigated. It was found that it shows approximately the same sensitivity to aniline as does diethylamine[8]. As shown in Fig. 2 the large rate increase already observed[3] on stopping the diisopropylamine feed was considerably reduced (but not completely eliminated) in the presence of aniline. The rate of diethylamine decomposition, which decreases slowly with time after stopping the amine feed[1], decreased more rapidly in the presence of aniline[8].

We now confront these results with the mechanism proposed in the previous paper[3]. Clearly the strong inhibition of the decomposition rates of both diethylamine

and diisopropylamine by aniline is further evidence for the participation of basic (oxide ion) sites; if the reaction occurred only on acidic (aluminium ion) sites, the weakly basic aniline would hardly have such a marked effect on the rate. It may then be suggested that the major part of the inhibition is due to aniline competing with the β-hydrogen of aliphatic amine for the basic sites. The reversible nature of this inhibition suggests that aniline interaction with these sites is by hydrogen bonding. The fact that the stopped-feed maximum obtained for diisopropylamine, attributed in the last paper[3] to an increase in the concentration of vacant basic sites for β-hydrogen abstraction, was considerably lessened in the presence of aniline may be explained by competition between aniline and β-hydrogen for the vacant basic sites liberated by the desorption of hydrogen-bonded aliphatic amine. The fact that the rate of di-ethylamine decomposition after its feed is stopped decreases more rapidly in the presence of aniline may also be explained in this way. The rate of decomposition in accordance with the proposed mechanism may be expressed as follows

$$r = k\Theta_A^{AS}\Theta_{vacant}^{BS}$$

which for the diethylamine–aniline system may be written

$$r = k\,\frac{K_{DA}^{AS}p_{DA}}{(1 + K_{DA}^{AS}p_{DA} + K_{AN}^{AS}p_{AN})(1 + K_{DA}^{BS}p_{DA} + K_{AN}^{BS}p_{AN})}. \tag{2}$$

This equation assumes Langmuir dependence of adsorption of both amines on acidic and basic sites. The correlation of the experimental data with Eq. (2), by a non-linear regression method, shown by the full lines in Fig. 1 indicates satisfactory agreement

TABLE I

Rate Constants and Adsorption Coefficients Computed by Correlation of Measured Formation Rates, in the Diethylamine–Aniline System at 310°C, of Ethylene, Triethylamine and N-Ethylaniline with Eqs (2), (3) and (4), Respectively

Parameter	Ethylene formation	Triethylamine formation	N-Ethylaniline formation
k	0·0277	0·177	0·157
K_{DA}^{AS}	0·0551	3·036	0·154
K_{AN}^{AS}	0·0189	2·303	0·149
K_{DA}^{BS}	0·00001	0·00414	0·0161
K_{AN}^{BS}	0·0117	0·0236	0·890

between the model and the measured data. The expectation that diethylamine is preferentially adsorbed on acidic sites and aniline on basic sites is borne out in the values of the calculated adsorption coefficients given in Table I. It should however be pointed out that we do not judge the validity of the proposed mechanism solely on the basis of the quantitative correlatability of the experimental data with Eq. (2). Such an approach is in our case ruled out by the large number of constants coupled with the simplifications of Langmuir adsorption.

Disproportionation

The main products of disproportionation reactions in the diethylamine–aniline system at 310°C over γ-alumina were triethylamine and monoethylamine (reaction (B)) and N-ethylaniline and monoethylamine (reaction (C)). The initial rate of tri-ethylamine formation is seen in Fig. 3 to increase with increasing diethylamine partial pressure and to decrease with increasing aniline partial pressure. The initial rate of N-ethylaniline formation (Fig. 4), at constant diethylamine partial pressure 30 Torr, also decreases with increasing aniline partial pressure in the range of aniline pressure 15 – 300 Torr. At constant aniline pressure 100 Torr the rate increases with increasing
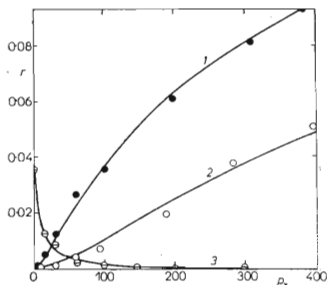
FIG. 3

Dependence of Initial Rate of Triethylamine Formation on Partial Pressures of Diethyl-amine *1, 2* and Aniline *3* at 310°C

● X = diethylamine, $p_{AN} = 15$ (constant); ○ X = diethylamine, $p_{AN} = 100$ (constant); ⊖ X = aniline, $p_{DA} = 30$ (constant); —— Eq. (*3*).
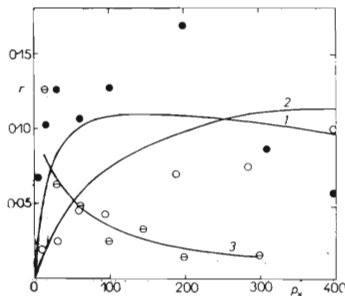
FIG. 4

Dependence of Initial Rate of N-Ethylaniline Formation on Partial Pressures of Diethyl-amine (*1*), (*2*) and Aniline (*3*) at 310°C

● X = diethylamine, $p_{AN} = 15$ (constant); ○ X = diethylamine, $p_{AN} = 100$ (constant); ⊖ X = aniline, $p_{DA} = 30$ (constant); —— Eq. (*4*).

diethylamine partial pressure in the measured pressure range; however where the aniline pressure is constant at 15 Torr the rate dependence on diethylamine partial pressure goes through a maximum in the region 100—200 Torr.

These results provide further evidence towards the exclusion of mechanism involving reaction between adsorbed molecule and molecule from the gas phase (Rideal–Eley type mechanism): in the diethylamine–aniline system, if diethylamine were the adsorbed species, the rate of N-ethylaniline formation would never decrease with increasing diethylamine partial pressure at constant aniline pressure and, if aniline were the adsorbed species, the rate would not decrease with increasing
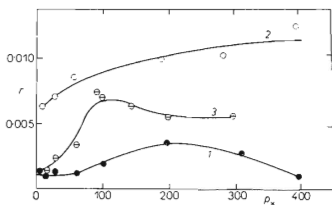

Fig. 5

Dependence of Initial Rate of N,N-Diethylaniline Formation on Partial Pressures of Diethylamine *1*, *2* and Aniline *3* at 310°C

● X = diethylamine, p_{AN} = 15 (constant);   ○ X = diethylamine, p_{AN} = 100 (constant); ⊖ X = aniline, p_{DA} = 30 (constant).
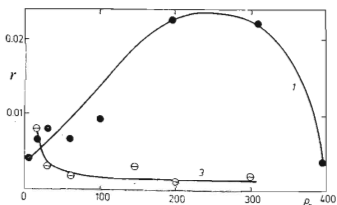

Fig. 6

Dependence of Initial Rate of Triethylaniline Formation on Partial Pressures of Diethylamine *1* and Aniline *3* at 310°C

● X = diethylamine, p_{AN} = 15 (constant); ⊖ X = aniline, p_{DA} = 30 (constant).

aniline pressure at constant diethylamine partial pressure. We therefore go on to consider the Langmuir–Hinshelwood type mechanism (reaction between two adsorbed molecules). That weak base aniline inhibits the disproportionation reaction of stronger base diethylamine whereas stronger bases (*e.g.* pyridine) inhibit the disproportionation (condensation) reaction of aniline[7] indicates that the two surface sites involved are not of the same type but that one is acidic and the other basic. That the kinetics of diethylamine disproportionation have been found to be first and not second order has been taken as evidence that one of the adsorbed molecules (electrophilic species) is strongly adsorbed on acidic site[1]. We therefore propose that the other is nucleophilic species less strongly adsorbed by hydrogen-bonding to basic (oxide ion) site. The following transition state may then be suggested for the disproportionation reaction
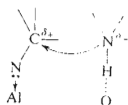
This mechanism may be described mathematically by the following equations assuming that both amines may be adsorbed on both types of sites. For triethylamine formation

$$r = k\Theta_{DA}^{AS}\Theta_{DA}^{BS},$$

$$r = k \frac{K_{DA}^{AS}p_{DA}}{1 + K_{DA}^{AS}p_{DA} + K_{AN}^{AS}p_{AN}} \frac{K_{DA}^{BS}p_{DA}}{1 + K_{DA}^{BS}p_{DA} + K_{AN}^{BS}p_{AN}} \qquad (3)$$

and for N-ethylaniline formation assuming that the nucleophilic species is aniline

$$r = k\Theta_{DA}^{AS}\Theta_{AN}^{BS},$$

$$r = k \frac{K_{DA}^{AS}p_{DA}}{1 + K_{DA}^{AS}p_{DA} + K_{AN}^{AS}p_{AN}} \frac{K_{AN}^{BS}p_{AN}}{1 + K_{DA}^{BS}p_{DA} + K_{AN}^{BS}p_{AN}} \qquad (4)$$

Correlation of Eqs (*3*) and (*4*) against the experimental data by non-linear regression is shown by the full lines in Figs 3 and 4 respectively. The values of the calculated constants are given in Table I. The regression method is such that, whilst the absolute value of these constants need not be very reasonable, the relations between them may be considered significant. It is clear that these relations are similar for all three reactions. However, as in the case of olefin formation, we cannot judge the validity of the proposed disproportionation mechanism solely on the basis of the quantitative correlatability of the experimental data with Eqs (*3*) and (*4*). More fruitful is the

qualitative interpretation of our experimental results in the light of the mechanism proposed.

It may be expected that the surface coverages of diethylamine on both sites (Θ_{DA}^{AS} and Θ_{DA}^{BS}) will decrease with increasing aniline partial pressure and increase with increasing diethylamine partial pressure. This fits in with the observed behaviour of the rate of triethylamine formation (Fig. 3). Where the rate of N-ethylaniline formation (Fig. 4) increases with increasing diethylamine partial pressure at constant aniline pressure it may be asserted that the increase in the concentration of the electrophilic species (Θ_{DA}^{AS}) is more important than the decrease in Θ_{AN}^{BS}. This evidently no longer holds at higher diethylamine pressures at constant aniline partial pressure 15 Torr (Fig. 4, 1) where the rate begins to decrease. Under these conditions the displacement of aniline by diethylamine from the basic sites clearly becomes decisive. This may be because the strongly acidic sites are now approaching saturation; indeed the rate of olefin formation, which has been proposed to occur on these sites, becomes almost constant under these conditions (Fig. 1, 1). The rate decrease, at constant diethylamine partial pressure 30 Torr, with increasing aniline pressure 15 − 300 Torr (Fig. 4, 3) means that here the displacement of diethylamine from acidic sites is more important than the increase in the concentration of aniline on basic sites.

The initial rates of formation of minor disproportionation products N,N-diethylaniline and triethylaniline are shown in Figs 5 and 6. It is of interest that the rate of N,N-diethylaniline formation is about 10% that of N-ethylaniline. The formation of N,N-diethylaniline, in a differential reactor with aniline conversion 0·05 − 9·9%, by the consecutive reaction

$$C_6H_5NHC_2H_5 + (C_2H_5)_2NH \rightleftharpoons C_6H_5N(C_2H_5)_2 + C_2H_5NH_2$$
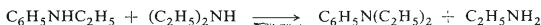
is acceptable only if it may be assumed that N-ethylaniline either is adsorbed on the basic sites much more strongly than aniline, or that it is a much stronger nucleophile than aniline. However, N,N-diethylaniline formation directly from aniline acting as electrophile and diethylamine as nucleophile cannot be excluded *a priori*. It was calculated, from experimental data for diphenylamine formation from aniline[7], that at 310°C the N—C bond in aniline is cleaved at a rate comparable to the rate of N,N-diethylaniline formation; against this however is the fact that diphenylamine itself was not found to be present in the reaction mixture. Attempts to determine the exact structure of triethylaniline using mass spectroscopy were not successful.

LIST OF SYMBOLS

r	initial reaction rate	(mol/h l)
k	reaction constant	(mol/h l)
K	adsorption coefficient	(Torr^{-1})

p partial pressure   (Torr)
Θ surface coverage
A   amine in general
X   variable amine
DA   diethylamine
AN   aniline
AS   acidic site
BS   basic site

REFERENCES

1. Fikry Ebeid M., Pašek J.: This Journal *35*, 2166 (1970).
2. Pašek J., Tyrpekl J., Machová M.: This Journal *31*, 4108 (1966).
3. Hogan P., Pašek J.: This Journal *38*, 1513 (1973).
4. Figueras F., Nohl A., de Mourgues L., Trambouze Y.: Trans. Faraday Soc. *67*, 1155 (1971).
5. Jain J. R., Pillai C. N.: J. Catal. *9*, 322 (1967).
6. Knozinger H., Scheglila A., Watson A. M.: J. Phys. Chem. *72*, 2770 (1968).
7. Pašek J.: This Journal *28*, 1007 (1963).
8. Hogan P.: *Thesis*. Institute of Chemical Technology, Prague 1973.